



**The use of spectroscopic, electrochemical and
spectroelectrochemical techniques in the development of improved
organic and inorganic photocatalysts for the production of solar
fuels.**

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A thesis presented to Dublin City University for the degree of PhD

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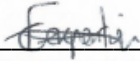
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Declaration

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Research Output

Publications

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Thesis outline

Chapter 1

This chapter introduces the concept of solar fuels, in particular hydrogen and CO. The need for renewable solar fuels as well as the challenges in the production of these fuels is summarized. Both inter- and intramolecular photocatalytic systems are introduced, and a typical catalytic pathway is described. A brief overview of ruthenium systems applied for photocatalytic hydrogen evolution or CO₂ reduction is given. Finally, an overview of the various techniques used to investigate these complexes is presented, with a particular focus on the application of spectroelectrochemistry.

Chapter 2

This chapter describes the investigation of (μ -alkyne)Co₂(CO)₆ complexes in the light assisted Pauson-Khand reaction. In particular, the role of the ligands on the mechanistic pathway following photolysis was studied using ultrafast spectroscopic techniques, spectroelectrochemistry and density function techniques. Previously, it was assumed that CO dissociation is the first step in the catalytic mechanism following photolysis with visible light. However, the most active ferrocenyl complex only showed limited CO dissociation following laser pulse photolysis at 400 nm. Instead, Co-Co bond cleavage may occur forming a high-spin diradical species.

Chapter 3

This chapter describes the synthesis of two novel ruthenium complexes for visible light driven CO₂ reduction and hydrogen evolution. A triazole bridging ligand was used to attach the ruthenium photosensitizer to either a ruthenium or platinum catalytic centre. The peripheral ligands contained ester moieties as anchoring groups to connect the catalytic assemblies to semiconductor surfaces. The complexes were fully characterized and their electrical and photophysical properties were investigated using a combination of techniques. The photocatalytic activity in solution and on a NiO surface was investigated. Undesired electron transfer towards the peripheral ligands, as observed in the time-resolved infrared studies and the spectroelectrochemical experiments, may explain the lack of activity of this catalyst in solution.

Chapter 4

This chapter describes the synthesis of a novel tris-heteroleptic ruthenium complex and its use in ruthenium-rhenium and ruthenium-palladium supramolecular assemblies for the photoelectrochemical reduction of CO₂ and the photoelectrochemical production of hydrogen. The supramolecular assemblies contain a peripheral ligand functionalised with carboxylic acid groups which were used to chemically immobilise the assemblies onto a NiO semiconductor. The photoelectrochemical efficiencies were tested for both assemblies under different pH values and at different electrode potentials. While the ruthenium-palladium assembly only showed low activity, the ruthenium-rhenium assembly showed promising results in the photoelectrocatalytic conversion of CO₂ to carbon monoxide.

Chapter 5

This chapter describes the synthesis and study of a novel rhenium complex containing a modified naphthalene-diimide ligand. The extended aromatic system of the novel ligand results in strong absorption in the visible region for both the ligand and the complex. The ligand and complex were studied using a suite of steady state spectroscopical, electrochemical, spectroelectrochemical and ultrafast spectroscopic techniques. The spectroelectrochemical studies showed that the first two reductions take place on the ligand, and intraligand charge transfer dominates the photophysical processes following excitation into the lowest energy absorption band. The complex was tested for photocatalytic CO₂ reduction in solution. Only traces of CO were observed. However, 36 turnovers of hydrogen were achieved following 24 hours of irradiation.

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Abbreviations

¹H-NMR: Proton nuclear magnetic resonance

¹³C-NMR: Carbon nuclear magnetic resonance

ACN: Acetonitrile

BIH: 1,3-dimethyl-2-phenylbenzimidazoline

Bpy: 2,2'-bipyridine

Bpt: 3,5-di(pyridine-2-yl)-1,2,4-triazolate)

CV: Cyclic voltammetry

Dceb: diethyl[2,2'-bipyridine]-4,4'-dicarboxylate

DCM: dichloromethane

DMF: N,N-dimethylformamide

DPV: Differential pulse voltammetry

fs: femtosecond

HER: Hydrogen evolution reaction

IL: Interligand

IR: infrared

ISC: Intersystem crossing

LF: Ligand field

MC: Metal centred

MLCT: Metal-to-ligand charge transfer

ns: nanosecond

PEC: Photoelectrochemical cell

ps: picosecond

PS: Photosensitiser

SA: Sacrificial agent

TA: Transient absorption

TEA: Triethyl amine

TEOA: Triethanol amine

TOF: Turnover frequency

TON: Turnover number

Tpphz: tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine

Tpy: 2,2':50,2''-terpyridine

TRIR: Time resolved infrared

UV-Vis: Ultraviolet-visible

Thesis abstract

Title: The use of spectroscopical, electrochemical and spectroelectrochemical techniques in the development of improved organic and inorganic photocatalysts for the production of solar fuels.

Name: Florian Cerpentier

The use of fossil fuels is resulting in a significant rise in global temperature. To mitigate further detrimental effects to the environment and the climate, a transition from fossil fuels to renewable energy resources is urgently required. To enable this transition, efficient storage of renewable energy is required. Hydrogen and carbon-based fuels using CO₂ as feedstock are interesting options, if they can be produced photocatalytically using sunlight as the energy source. Organometallic complexes are promising photocatalysts, with desirable properties such as strong visible light absorption, good photostability and good catalytic activity and selectivity. For these systems to succeed, a better understanding of the working of these systems is required. This research focussed on developing and studying new organometallic complexes using either ruthenium or rhenium metal centres and their application in photocatalytic systems for hydrogen evolution and CO₂ reduction. New catalysts were synthesised and analysed using NMR-, UV-Vis-, emission and IR spectroscopy. Electrical properties of these complexes such as their reduction potentials were determined using cyclic voltammetry. The complexes were probed using various ultrafast spectroscopic techniques including transient absorption (TA) and time-resolved infrared spectroscopy (TRIR). These techniques can provide a better understanding of the interaction of these catalysts with light, which is the important first step in the photocatalytic cycle. In addition, the catalysts were studied with a variety of spectroelectrochemical techniques. In this approach, reduced intermediate species were electrochemically produced and studied using steady state spectroscopic. The study of these reduced intermediates is underappreciated in photocatalytic research, even though these species play an important role in the photocatalytic cycle. This thesis provides insights in how reduced intermediate species may influence the photocatalytic process. In addition, this thesis shows that immobilisation of these systems onto a semiconductor surface greatly influences the excited state properties and activity of these photocatalytic assemblies.

Appendices

A: Supporting information for chapter 2

B: Supporting information for chapter 3

C: supporting information for chapter 4

D: supporting information for chapter 5

Chapter 1: Introduction to the production of hydrogen and the reduction of CO₂ using photocatalytic systems.

Chapter 1 describes the need for a transition from an energy economy based on fossil fuels towards one based on renewable energy. The challenges associated with renewable energy production are explained, in particular the intermittency of renewable sources and the difficulties associated with the storage of renewable energy sources. The basic concepts of photocatalytic hydrogen evolution and photocatalytic CO₂ reduction are described. A short summary centring on intermolecular and intramolecular approaches for hydrogen evolution based on ruthenium complexes is given. Rhenium based (photo)catalysts for CO₂ reduction are also included. An overview is given of standard techniques in the field of photocatalysis with a focus on spectroelectrochemistry.

1.1. Solar fuels

The increasing use of fossil fuels has led to an unprecedented level of CO₂ and other greenhouse gasses in the earth's atmosphere (Figure 1-1). These greenhouse gasses cause an increase of temperature, an effect commonly known as global warming (Figure 1-1).¹

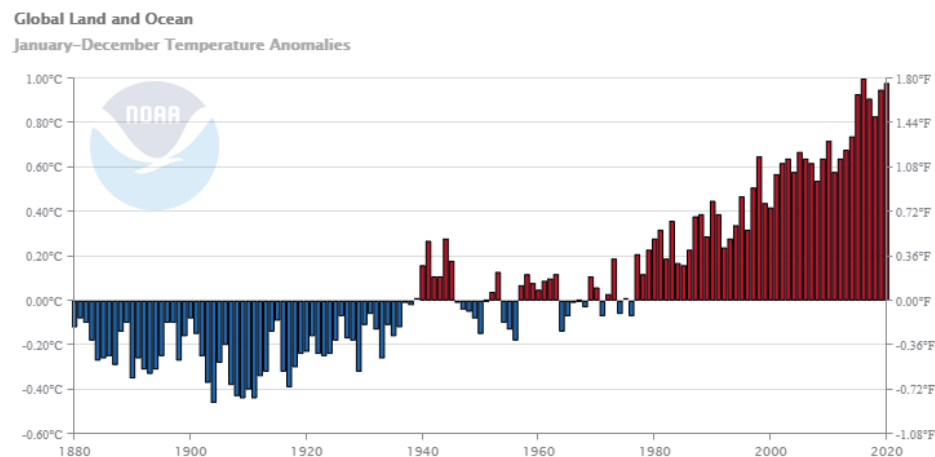


Figure 1-1. Average annual global temperature compared to the average temperature of the 20th century. Image reproduced from the National Oceanic and Atmospheric Administration.²

If the current consumption of fossil fuels and emission of greenhouse gasses continues, an unsustainable situation will be created in which global warming will cause long-lasting or permanent damage to the environment, as well as to the human population.¹ International agreements such as the Paris agreement and the Glasgow climate pact have put in place frameworks to contain the average increase in global temperature to 1.5 °C, and the United Nations have set out policies to achieve net-zero carbon dioxide emission by 2050.³⁻⁵ In 2020, only 13.3% of the total energy consumption in Ireland was generated from renewable resources, while the remaining energy was obtained from fossil fuels, in particular oil (45%) and natural gas (34.1%).⁶

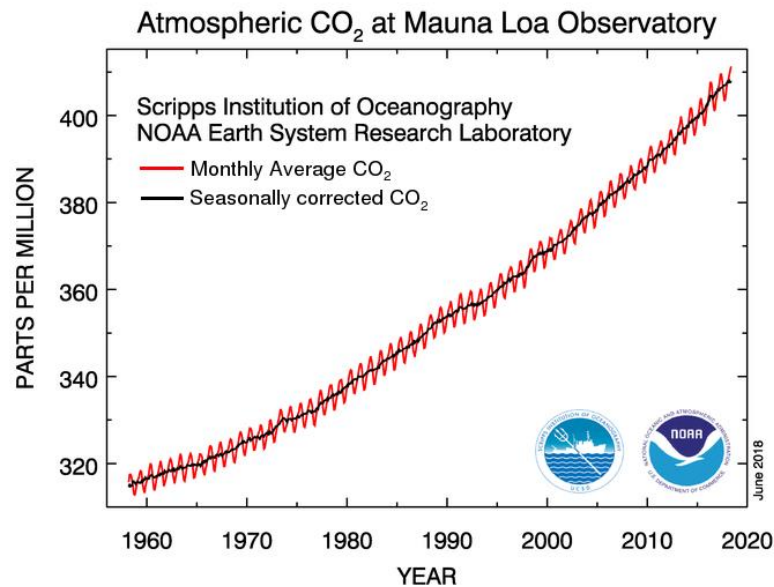


Figure 1-2. Monthly mean atmospheric CO₂ at the Mauna Loa Observatory in Hawaii. Image reproduced from the National Oceanic and Atmospheric Administration.⁷

Apart from the detrimental effects from the use of fossil fuels, there are also larger political implications to the usage of these resources due to their uneven distribution globally. A good example of this is the current situation between Europe and Russia, in which Europe is heavily dependent on Russia for fossil fuels and thus energy security, resulting in political tensions. For these reasons, a shift towards renewable energy is highly desired. A wide range of renewable alternatives are available, including wind, solar, biomass, hydro and tidal energy. Following European guidelines, Ireland aims to obtain 32.5% of all energy from renewable sources by 2030.⁸ However, due to the nature of these energy sources, the amount of energy provided may vary as the day progresses. For solar energy, one of the prime candidates for renewable energy, the delivered energy peaks in the middle of the day.⁹ However, the demand for energy peaks in the morning and in the evening.¹⁰ To ensure a stable supply of energy, forms of storage are necessary. Preferentially, storage takes place in the form of a fuel. Fuels are a more desirable energy source compared to electricity in for example transport, which constitutes a large amount of the current energy uptake (34.5%).

1.1.1. Hydrogen

One of the most prominent potential solar fuels is hydrogen gas.¹¹ This highly combustible gas can be made using electrical current via electrolysis of water^{12–14} or using sunlight through heterogeneous^{15,16} or homogeneous photocatalysts.^{17,18} Water is an ideal starting material for fuel production as it is widely available. Furthermore, hydrogen has a high energy density and can be transported through the current infrastructure in place for natural gas.¹⁹ The only

product of the combustion or electrochemical oxidation of hydrogen is water. Therefore, the hydrogen economy, in which hydrogen gas is the main energy carrier, has gained increased attention over the past years.²⁰

While direct splitting of water is desired, this process is still difficult, and limited systems are known that can directly split water into hydrogen and oxygen, most of which are heterogeneous catalysts.^{16,18,21–23} To optimize this process, it is beneficial to separate the two half reactions involved, i.e. the oxidation of water to oxygen, protons and electrons, and the reduction of protons to hydrogen (Scheme 1-1). To achieve this, a photoelectrochemical cell (PEC) can be constructed (Figure 1-3).^{24–26}

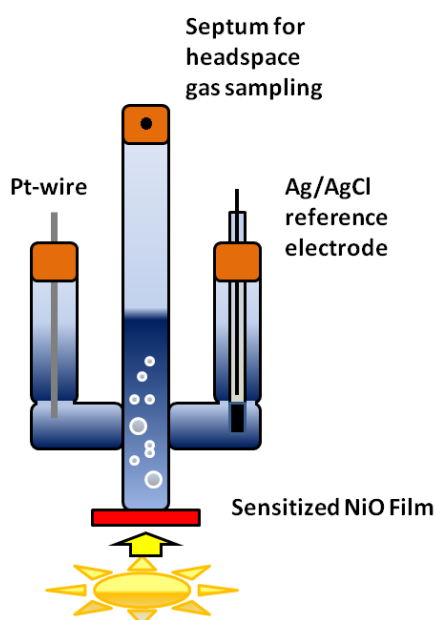


Figure 1-3. Schematic of a photoelectrochemical cell (PEC) used for CO₂ reduction experiments. Adapted with permission from reference 51.

In a PEC, a water oxidation occurs at the anode, often by covalently binding the photocatalyst to the electrode surface, while a proton reduction catalyst is placed at the cathode. The electrons generated at the cathode in the water oxidation process are transferred to the anode, while the protons generated at the cathode by the water oxidation process can be transferred to the anode through a selective membrane. In this way, both processes can be optimized separately, which can greatly increase the efficiency of the overall process. In this thesis, the attention is focussed on the hydrogen evolution reaction (HER) which takes place at the cathode. A schematic overview of the key steps of the cathode of a PEC sensitised with the

$\text{Ru}(\text{dceb})_2(\text{bpt})\text{PtI}_2$ complex (dceb = diethyl[2,2'-bipyridine]-4,4'-dicarboxylate, bpt = 3,5-di(pyridine-2-yl)-1,2,4-triazolate) is shown in Figure 1-4.²⁷

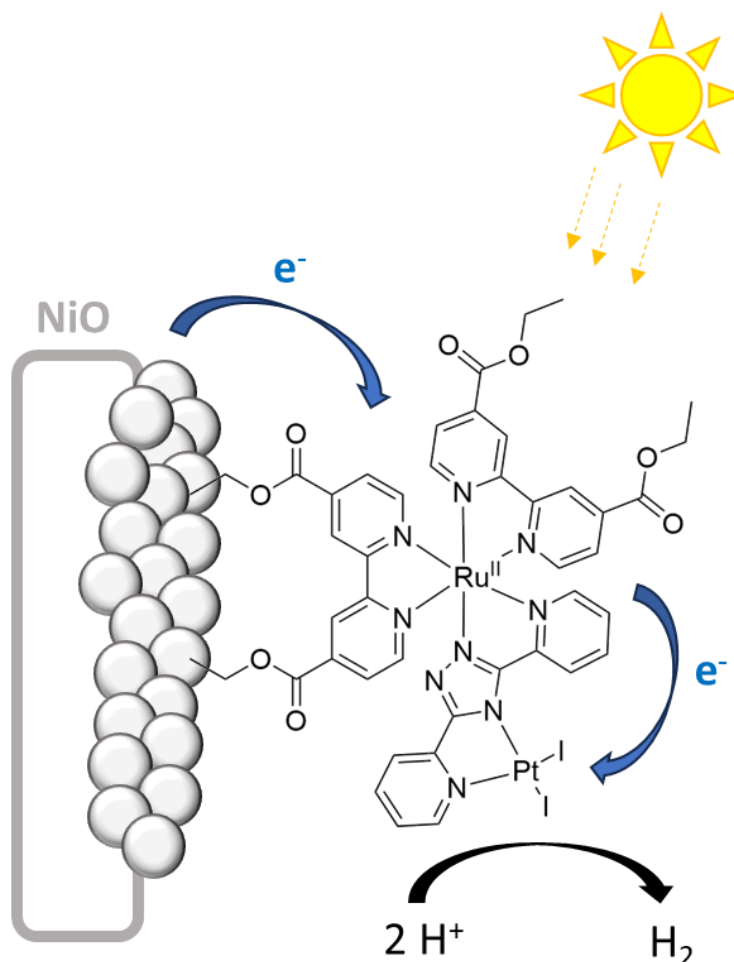
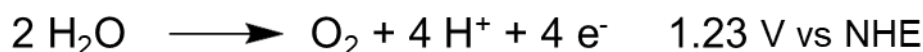


Figure 1-4. Schematic overview of the processes occurring for a dye-sensitised cathode for hydrogen evolution utilising the $\text{Ru}(\text{dceb})_2(\text{bpt})\text{PtI}_2$ photocatalyst.

In general, four steps occur for an immobilised photocatalyst in the process of photocatalytically reducing protons to hydrogen. In the first step, the photocatalyst is irradiated with light resulting in charge separation on the photosensitiser (in this case the ruthenium centre). In the second step, an electron is injected from the NiO film to occupy the hole that was created on the photosensitiser. In the third step, the additional electron localised on the photosensitiser moves to the catalytic metal where the electron is used in step four to reduce protons to hydrogen.



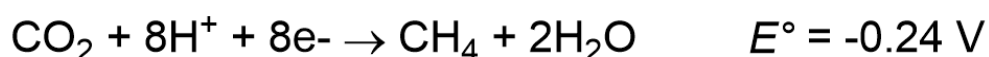
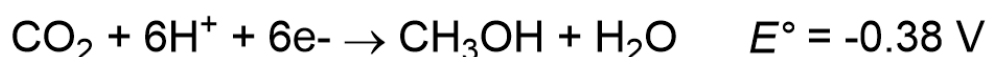
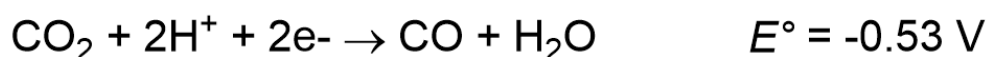
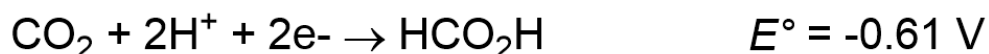
Scheme 1-1. The two half reactions involved in the splitting of water into oxygen and hydrogen and the corresponding potentials vs the normal hydrogen electrode.

1.1.2. Carbon dioxide reduction

A second option for renewable fuels is the conversion of atmospheric CO₂ into carbon-based fuels such as carbon monoxide, methanol, methane, and longer alkane chains in a process called artificial photosynthesis. This approach is based on natural photosynthesis, in which plants capture the energy from sunlight to convert water and CO₂ to produce carbohydrates.^{28–}

³⁰ Apart from providing fuels based on renewable energy through electrocatalysis or photocatalysis, artificial photosynthesis can also help to solve the current problems with global warming as the greenhouse gas CO₂ is actively removed from the atmosphere.

Unlike the hydrogen evolution reaction, various products can be formed following the reduction of CO₂. As the one electron reduction of CO₂ to the CO₂^{•-} radical species is highly unfavourable (-1.9 V vs the normal hydrogen electrode), proton-assisted multielectron reduction processes are preferred.³¹ The products CO (two electron reduced product), formic acid (two electron reduced product), formaldehyde (four electron reduced product), methanol (six electron reduced product) and methane (eight electron reduced product) are the most common (Scheme 1-2).³¹



Scheme 1-2. Overview of the potential products following reduction of CO₂ and the corresponding reduction potentials vs the normal hydrogen electrode.

As seen in Scheme 1-2, the formation of all these proton-assisted multielectron products is energetically more favourable than the one-electron reduction of CO₂. Furthermore, all the

products that are formed are stable and can be used in follow up reactions. From these products, CO is an important chemical feedstock that is currently used in various industrial processes, including Fischer-Tropsch synthesis of carbohydrates,³² aldehyde formation through hydroformylation³³ and acetic acid synthesis.³⁴

Various catalysts have been reported for the reduction of CO₂. The group of Lehn were among the first to report direct photocatalytic CO₂ reduction. They reported the use of Re(bpy)(CO)₃Cl (bpy = 2,2'-bipyridine) for the photocatalytic conversion of CO₂ to CO in 1983.³⁵ Ever since, various complexes of manganese and rhenium have been extensively studied for photocatalytic CO₂ reduction.^{36–39} In particular, much attention has been given to the catalytic mechanism for these photocatalysts.^{40–45}

1.1.3. Two component systems

To successfully convert sunlight into a chemical fuel, a photocatalyst needs to perform two key functions:

- 1) Absorb light and harness the energy in a charge-separated excited state,
- 2) Chemically reduce the substrate, (protons or CO₂), to the desired product, for example hydrogen or CO.

The efficiency of these photocatalysts can be improved by incorporating specific components for each of the functions mentioned above. These so-called two component systems comprise of two parts: 1) the photosensitiser, which is designed to efficiently absorb light and form a long lived-charge separated state, and 2) the catalyst, which often consists of a metal complex capable of reducing the substrate (protons, CO₂) to the desired product using the electrons provided by the photosensitiser (Figure 1-5). Both components can be optimized separately through targeted design. Some examples of these systems will be given later in this chapter.

1.1.3.1. Intermolecular and intramolecular systems

Two component systems can exist in two forms (Figure 1-5). In an intermolecular system, the photosensitiser and catalyst are both present in solution and interact through diffusion-controlled collisions. For these intermolecular systems, the rate of charge transfer is largely dictated by the rate of diffusion of the photosensitiser to the catalytic centre.⁴⁶ In general, rate constants for diffusion-controlled reactions are on the order of 10⁸-10⁹ s⁻¹.⁴⁶

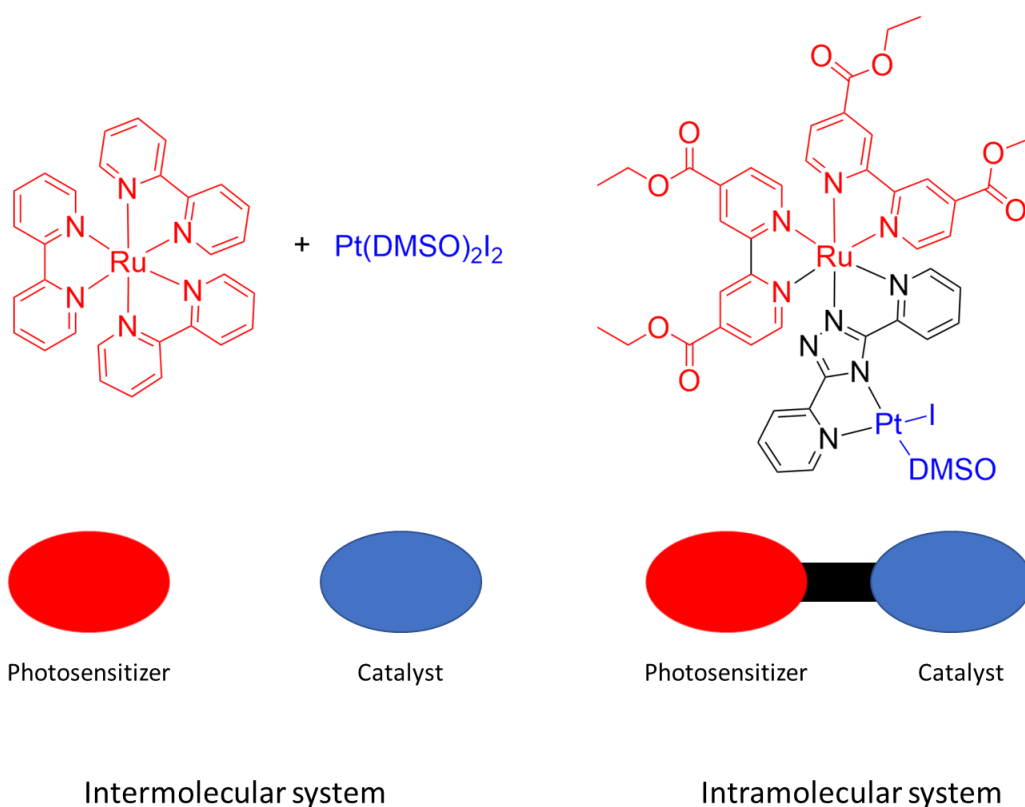


Figure 1-5. An example of an intermolecular (left, $\text{Ru}(\text{bpy})_3$) and an intramolecular (right, $\text{Ru}(\text{dceb})_2(\text{bpt})\text{PtI}(\text{dmsO})$) photocatalytic system consisting of a photosensitiser (red), catalyst (blue) and bridge (black).

In intramolecular systems, the photosensitiser and catalyst are covalently bonded to each other. In this way, diffusion is no longer a limiting factor for successful electron transfer from the photosensitiser to the catalyst. Furthermore, the bridging moieties are often extended conjugated systems, improving electron transfer between the photosensitiser and the catalyst.^{47,48} However, this may also result in increased undesired back electron transfer from the catalytic centre to the photosensitiser.⁴⁹ Additionally, these supramolecular systems can be anchored to semiconductor surfaces. When these semiconductor surfaces are placed under an electrical potential, they can act as the electron source for the desired photocatalytical reactions to occur.^{50,51} The immobilisation of photocatalysts on semiconductor surfaces will be discussed in more detail later in this chapter.

1.1.3.2. A standard reaction cycle and reductive and oxidative quenching

Several steps are required for successful catalysis to occur (Figure 1-6). First, the photosensitiser must be irradiated to form a long-lived charge separated state. This excited state can then undergo two different pathways. In the reductive quenching pathway, an electron from a sacrificial agent provides an electron to “fill” the positive charge or hole that is formed on the photosensitiser. The now negatively charged photosensitiser can transfer an electron to the

catalyst. In the oxidative pathway, an electron from the excited photosensitiser is transferred to the catalyst, leaving the photosensitiser oxidized. The neutral photosensitiser is then regenerated upon electron transfer from a sacrificial agent. Two cycles are required to reduce two protons to one molecule of hydrogen or a molecule of CO_2 to a molecule of CO . In general, a large excess of sacrificial agent is present in the solution. As the rate of the reductive quenching pathway is dependent on the concentration of sacrificial agent, this pathway is often dominant in photocatalytic experiments.^{46,52,53}

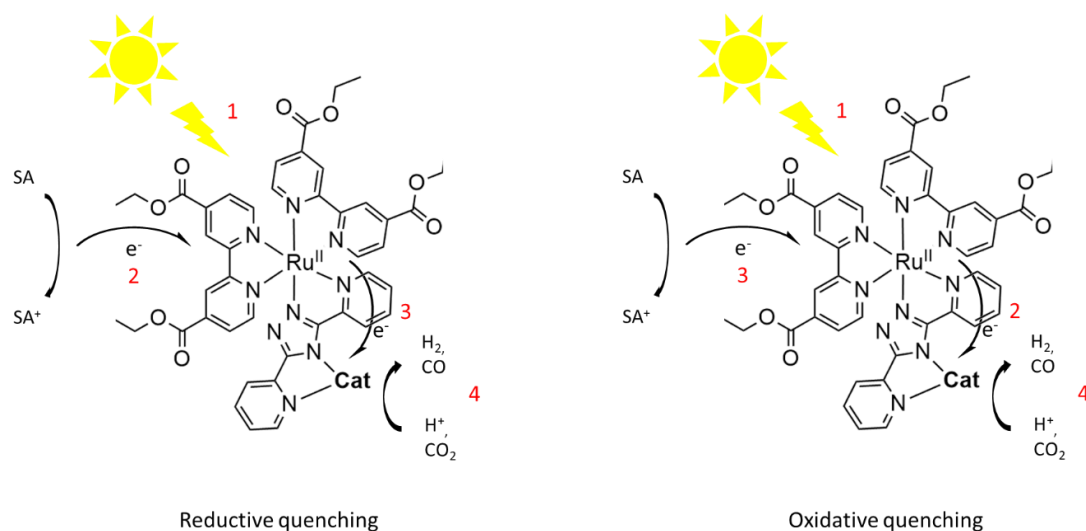


Figure 1-6. Overview of both oxidative and reductive mechanisms for an intramolecular ruthenium photocatalyst. Left: the reductive quenching mechanism. The photosensitiser is excited (step 1), after which the photosensitiser is reduced by a sacrificial electron donor (step 2). The excited electron on the photosensitiser is transferred to the catalyst (step 3). These steps are repeated once more to allow the two-electron reduction of two protons to hydrogen or the reduction of CO_2 to CO (step 4). Right: the oxidative quenching mechanism. The photosensitiser is excited (step 1), after which an electron is transferred to the hydrogen evolution or CO_2 reduction catalyst (step 2). The now oxidized photosensitiser is reduced by a sacrificial electron donor (step 3). These steps are repeated once more to allow the two-electron reduction of two protons to hydrogen or the reduction of CO_2 to CO (step 4).

1.1.4. Influence of reaction conditions and quantification techniques.

A wide range of factors plays a role in how efficient photocatalysis is. In addition to the type of catalyst or photosensitiser other experimental factors such as solvent,⁵⁴ pH,⁵⁵ catalyst or photosensitiser concentration,⁵⁶ sacrificial agent,⁵⁷ (presence of a) proton source,⁵⁸ irradiation wavelength and irradiation intensity,⁵⁹ all play a role in the overall efficiency of a photocatalytic system. It is difficult to standardise all these factors, and therefore comparing various systems is qualitatively very difficult. To standardise the quantification, some key reporting parameters that are used in the field to compare the amount of hydrogen generated are reported. These parameters can help to fairly compare the efficiency of different photocatalytic systems.

1.1.4.1. Turnover number and turnover frequency

To compare the performance of various photocatalytic systems, turnover number (TON) or turnover frequency (TOF) is often used. In TON, the amount of product molecules produced per molecule of catalyst (or molecule of photosensitiser) is determined. The TON is generally given in moles of product produced *per* mole of catalyst used (Equation 1-1). While useful, some important precautions must be taken when using the TON to compare catalysts. Generally, the TON is calculated for the catalytic centre. If the catalyst and the photosensitiser are present in a 1:1 ratio, the TON is the same for the catalyst and the photosensitiser and can give a good idea on the efficiency of one or both components. However, if one of the components is in excess, the TON can give a wrongful impression of the efficiency of a system if not represented for both the photosensitiser and the catalyst. For the prototypical $[\text{Ru}(\text{tbbpy})_2(\text{tpphz})\text{PdI}_2](\text{PF}_6)_2$ (tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, tpphz = tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine) a TON of 276 was obtained following 470 nm excitation.⁶⁰

$$\text{Turnover number (TON)} = \frac{\text{moles of product produced}}{\text{moles of catalyst in solution}}$$

Equation 1-1. Formula to determine the turnover number.

While the TON can give a good indication of the efficiency of the catalyst, it does not provide any indication about the rate of catalysis or stability of the catalyst. Therefore, the turnover frequency (TOF) is often reported. The TOF is calculated by dividing the TON by the time (Equation 1-2). The TOF provides information about the stability of the catalyst over the course of the experiment. For the $[\text{Ru}(\text{tbbpy})_2(\text{tpphz})\text{PdI}_2](\text{PF}_6)_2$ complex, a turnover frequency of 6 per hour was observed.⁶⁰

$$\text{Turnover frequency (TOF)} = \frac{\text{turnover number}}{\text{time in hours}}$$

Equation 1-2. Formula to determine the turnover frequency.

1.1.4.2. Quantum yield

A second indicator of the efficiency of a photocatalytic system is the fraction of (sun)light that is efficiently captured. After the photosensitiser absorbs a photon and reaches an excited state, various pathways are available for this excited state to return to the ground state. While some of these pathways are productive for catalysis, such as energy or electron transfer towards the catalytic centre, other pathways are non-productive such as emission, non-radiative relaxation, or charge recombination. The distribution in which these various processes occur can be determined using irradiation studies and are called quantum yields.⁴⁶ A quantum yield is defined

as the fraction of excited photosensitisers that follows a specific pathway following excitation, and thus every pathway has its own quantum yield. The values of all pathways combined result in a quantum yield of 1 to account for all photons absorbed.

$$\phi_n = \frac{\text{Number of molecules that undergo process } n}{\text{Total number of photons of light absorbed}}$$

Equation 1-3. Formula for determination of the quantum yield of a specific process n. The sum of all process equals 1.

1.1.5. Sacrificial agents

Ideally, systems are created in which the electrons required for catalysis are provided by a cathode by tethering the catalytic systems to the electrode surface. However, in solution studies sacrificial agents are a necessary evil. A wide range of SAs, mostly based on biological electron carriers, are known and used depending on the type of reaction and the catalyst. The efficiency of a sacrificial agent depends on various properties, such as the solubility in the system used, the pKa of the sacrificial agent in the solvent and the reductive strength of the sacrificial agent. Furthermore, most of the effective sacrificial agents undergo rapid degradation following electron transfer, thereby actively inhibiting the reverse electron transfer from the photosensitiser to the sacrificial agent, so called back-electron transfer (BET). It is important that these degradations do not lead to reactive species, as these can interact with, or result in degradation of the photocatalyst, or influence the experiment. Finally, one must consider the environment in which this electron transfer occurs. Both sacrificial agent and photocatalyst are surrounded by solvent molecules. Following electron transfer, the oxidized sacrificial agent must diffuse away from the photocatalyst to avoid back-electron transfer.⁶¹ This rate of diffusion, and thus the rate of undesired BET, depend on the solvent conditions.⁶¹ As stated before, in PEC systems the electrons are instead provided by an electrode, removing the need of a sacrificial agent.^{24–26} PEC systems will be described in more detail later in this chapter.

1.1.5.1. Triethylamine (TEA) and triethanolamine (TEOA)

Various sacrificial agents are used for photocatalytic hydrogen evolution or CO₂ reduction experiments, but the most commonly used are the tertiary amines, triethylamine (TEA) and triethanolamine (TEOA). Both compounds work in a similar way; the central nitrogen atom contains a free electron pair which can be oxidized relatively easily (TEA = 0.69 V vs SCE, TEOA = 0.57-0.82 V vs SCE),^{62,63} providing one electron that can be used for catalytic purposes and forming a radical species. An additional advantage of these sacrificial agents is their well-known degradation pathway.⁶⁴ TEOA and TEA showcase very similar mechanisms, which are shown in

Figure 1-7. One electron oxidation of the amine results in the formation of a radical species. This radical species is reactive and would normally be available for back-electron transfer, in which the electron that was transferred to the photocatalyst is transferred back to the amine resulting in no overall reaction occurring. However, deprotonation of the radical species rapidly occurs by a second molecule of TEA/TEOA. This deprotonation leads to a carbon centred radical, which itself is a strong reducing agent. This radical acts as a second molecule of sacrificial agent to dispose of the negative charge and form a stable iminium species, which can be hydrolysed in the presence of water to release a secondary amine and ethanal.

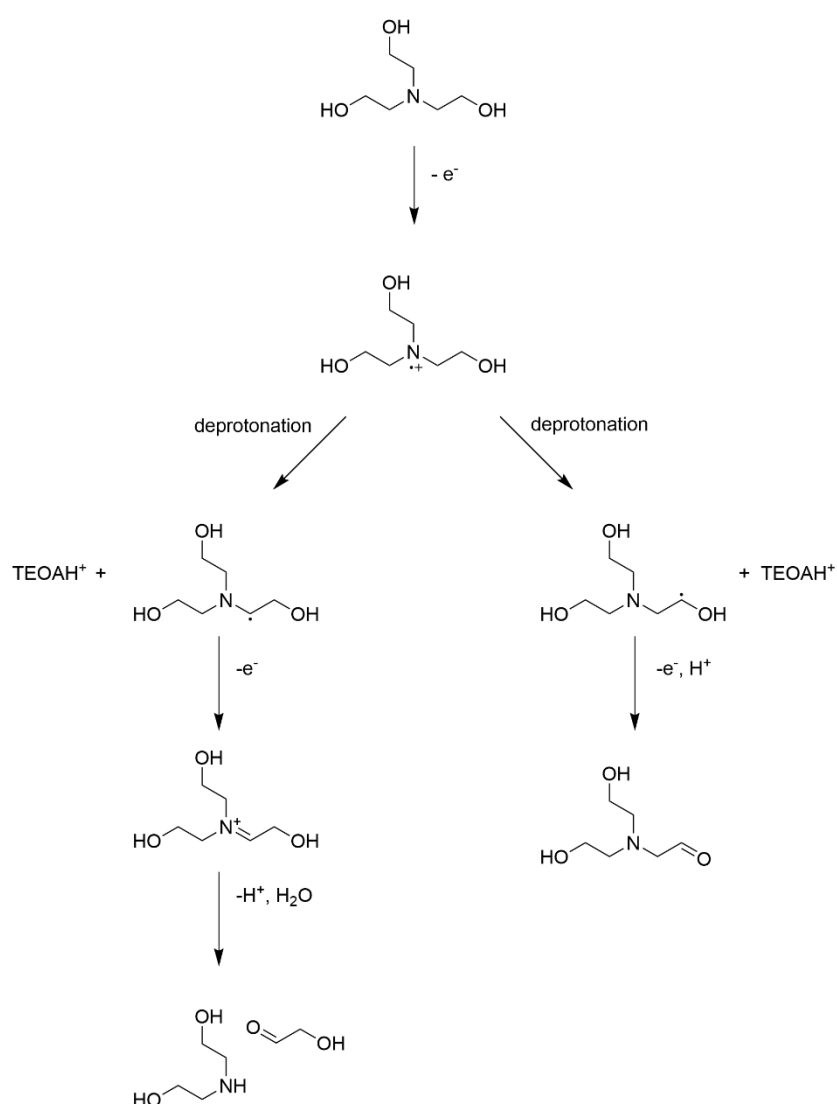


Figure 1-7. Degradation pathway of TEOA monoelectronic oxidation. The mechanism for TEA is the same and therefore not shown separately.

1.1.5.2. 1,3-dimethyl-2-phenylbenzimidazoline (BIH)

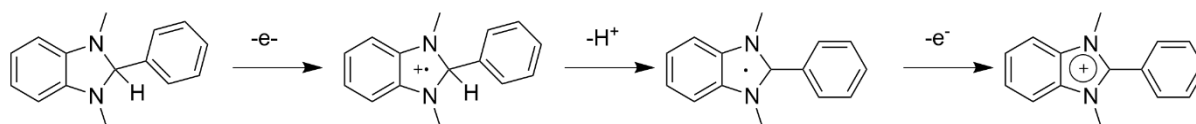


Figure 1-8. Degradation pathway of BIH following monoelectronic oxidation.

1,3-dimethyl-2-phenylbenzimidazoline (BIH) is another sacrificial agent, and is often used for the photocatalytic reduction of CO₂ using rhenium catalysts.⁶⁵ Technically, BIH acts as a hydride donor, as two electrons and one proton are released following oxidation (Figure 1-8).⁶⁶ Deprotonation following the first one-electron oxidation is extremely fast, driving the formation of the BI[•] radical species and inhibiting back-electron transfer.⁶⁷ The BI[•] species is itself a strong reducing agent and can transfer a second electron to form the stable BI⁺ molecule.

1.1.6. Ruthenium compounds as photosensitiser in intermolecular and intramolecular systems

1.1.6.1. Introduction

Ruthenium complexes have been studied as potential photosensitisers for decades due to their stability, good visible light absorption, long lifetime emissions and highly efficient conversion to the triplet state.^{60,62,68,69} The properties of these complexes are easily fine-tuned through modification of the ligands. The traditional benchmark complex is Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine), as the bipyridine ligand provides a stable bond to the ruthenium via the two nitrogen atoms with a desirable bond angle, resulting in a highly stable octahedral complex.⁶⁰

1.1.6.2. Photophysics

A good understanding of the photophysics of ruthenium complexes is essential to enable optimization of these systems for photocatalysis. Various factors must be considered when optimizing photosensitisers for photocatalytic applications, including lifetime, excited state localisation, decay pathways and stability, as well as reactivity of the excited molecule with a catalyst or electron donor.

1.1.6.2.1. Excited states and Jablonski diagram

The general photophysical properties of ruthenium tris(α -diimine) complexes are well understood.^{51,70–72} Like other octahedral metal complexes, the UV-vis spectrum is dominated by three main transitions. (Figure 1-9). The highest energy transition can be observed in the UV region of the spectrum and is assigned to an interligand (IL), (blue arrow in Figure 1-9) transition. For the benchmark complex [Ru(bpy)₃](PF₆)₂ this absorption is observed at 285 nm. Weak signals in the region from 300-350 nm are observed for the ligand field transition (LF), (green arrow in

Figure 1-9). A metal-to-ligand charge transfer transition (MLCT), red arrow in Figure 1-9) is observed in the visible region from 400 and 500 nm, (red arrow in Figure 1-9). For $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ this band has a λ_{max} at 455 nm in acetonitrile.⁷³

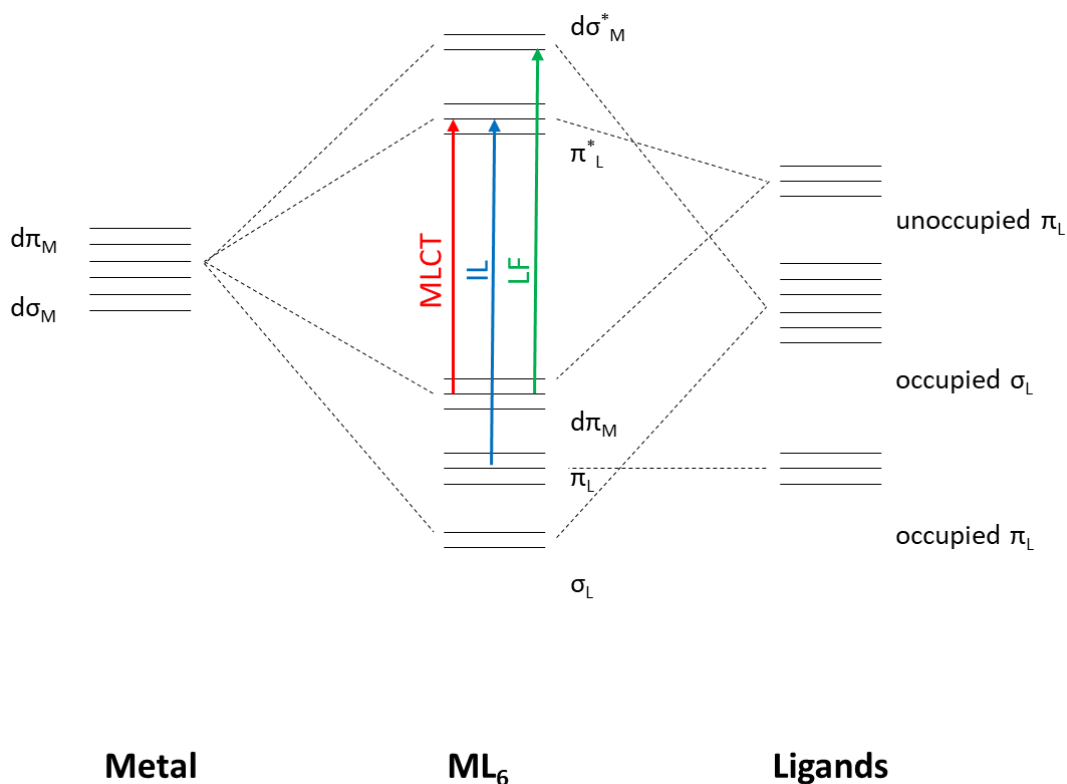


Figure 1-9. Molecular orbital diagram and most common transitions for an octahedral complex with π -accepting ligands.⁷⁰

When these complexes are excited into their MLCT band, charge transfer occurs from the ruthenium metal centre to the surrounding ligands, forming a singlet metal-to-ligand charge transfer state ($^1\text{MLCT}$) (Figure 1-10). This state is vibrationally hot and loses a small amount of energy in the form of heat in the first few femtoseconds after excitation. The cooled down $^1\text{MLCT}$ state then undergoes rapid intersystem crossing (ISC) on the femtosecond timescale (within 200 fs) to the $^3\text{MLCT}$ state with quantum yields reaching unity.⁷⁴ The femtosecond time-window of intersystem crossing makes it hard to observe even with ultrafast techniques.⁷⁴ The $^3\text{MLCT}$ state relaxes back to the ground state, often through the emission of a photon *via* phosphorescence. As this transition is spin-forbidden, this relaxation is relatively slow, with lifetimes in the range of a few hundred nanoseconds up to several microseconds in anaerobic conditions (860 ns for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in deaerated acetonitrile).^{46,70,75} In particular the long lived triplet state is of interest in photocatalysis, as the lifetime of this species is sufficiently long for further reactions or electron transfer to occur.

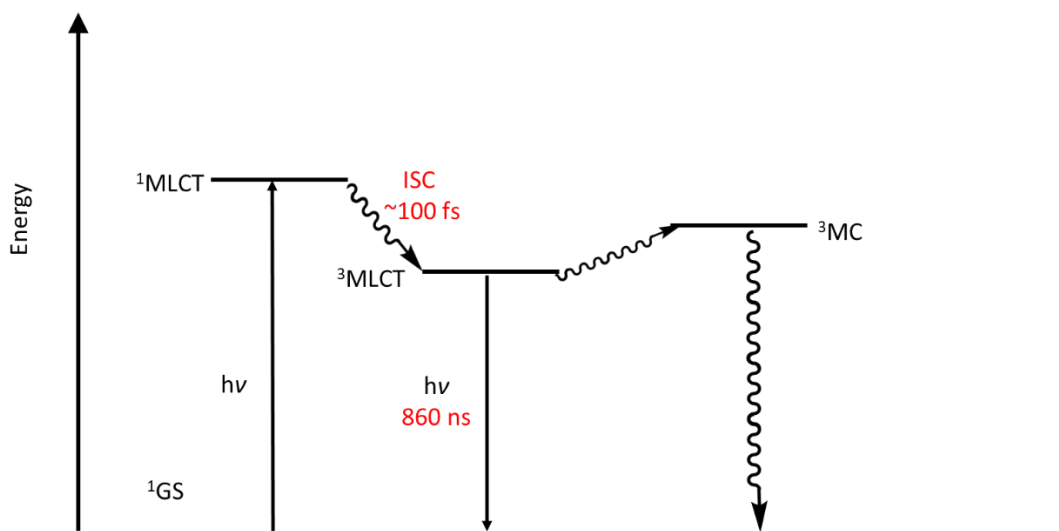


Figure 1-10. Simplified Jablonski diagram for the octahedral $[Ru(bpy)_3](PF_6)_2$ complex.. Straight arrows indicating radiative processes. Wavy lines indicate non-radiative processes.

1.1.6.2.2. Decay pathways and stability

Depending on the ligands attached to the ruthenium centre, a second excited state that is energetically near to the ^3MLCT state can be populated. This metal centred (^3MC) state is localized on the ruthenium centre, with the electron populating an antibonding d-orbital (Figure 1-9, green arrow).^{70,76} While this state can relax back to the ground state via emission or non-radiative decay, it can also lead to ligand dissociation and thus decomposition of the complex.^{75,77–81} Therefore, it is important to design a complex in which the ^3MLCT state is lower in energy than the ^3MC state, to prevent photodecomposition of the complex.

1.1.6.3. Role of the ligands

1.1.6.3.1. The bridging ligand

For intramolecular systems, charge transfer from the ruthenium centre *via* the bridging ligand to the catalytic centre is required to perform catalysis. As such, modification of the bridging ligand can greatly influence the efficiency of the photocatalyst. Generally, it is suggested that catalytic efficiency is improved when charge transfer from the ruthenium metal centre to the bridging ligand is maximised, as this brings the electron in closer proximity to the catalytic centre.^{82,83} Further charge transfer from the bridging ligand to the catalytic centre can then occur. Tschierlei et al have previously reported wavelength dependent studies for the $[Ru(tbbpy)_2(dppz)PdCl_2](PF_6)_2$ ($tbbpy=4,4'$ -di-*tert*-butyl-2,2'-bipyridine, $tpphz=tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]$ phenazine, **Ru1**, Figure 1-11) supramolecular assembly. The photon-to-hydrogen yield was found to increase when the irradiation wavelength was increased, improving from 0.01 molecules of hydrogen per photon at 410 nm irradiation to approximately

0.04 molecules of hydrogen per photon at 525 nm excitation. Resonance Raman studies showed that irradiation at 514 nm resulted in efficient population of the unoccupied molecular orbital localised on the tpphz bridging ligand, while mixed population of both the tpphz bridging ligand and the tbbpy peripheral ligands was observed following 458 nm excitation. However, the Pryce group has reported that electron transfer away from the bridging ligand can improve catalytic activity of ruthenium-palladium supramolecular assemblies (see section 1.2.6.3.2).^{84,85}

Functionalisation of the bridging ligand has been applied to improve catalysis. For example, Karnahl et al.⁸³ functionalised a tpphz (tpphz = tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine) bridging ligand with bromine atoms (Figure 1-11).

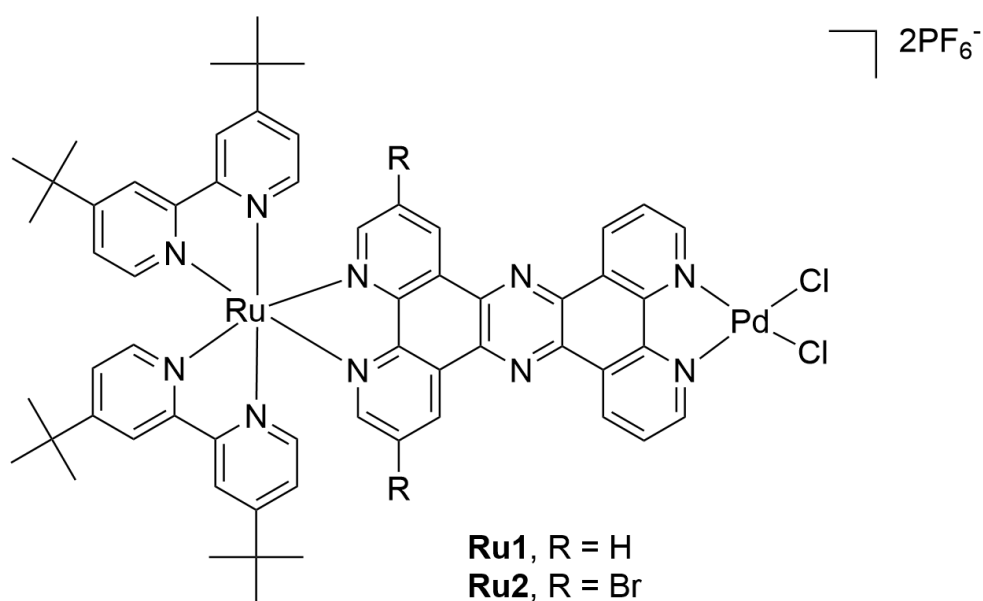


Figure 1-11. The chemical structures of the complexes reported by Karnahl et al.⁸³

Inclusion of bromine at the bridging ligand (**Ru2**) resulted in a blue shift of the maximum absorbance when compared to the unsubstituted analogue (**Ru1**). When both complexes were assessed for photocatalytic hydrogen evolution, **Ru2** was less active **Ru1**, most likely due to the electron withdrawing effect from the bromine slowing down photoelectron transfer from the ruthenium centre to the palladium catalyst.

Previous work done by Singh Bindra et al showed how a change in the shape of a terpyridine bridging ligand can result in a large change in photocatalytic activity.⁸⁶ Two ruthenium-palladium supramolecular complexes **Ru3** and **Ru4** were studied for photocatalytic hydrogen evolution (**Ru3** = [Ru(bpy)₂((2,5-bpp)Pd(CH₃CN)Cl)](PF₆)₂, **Ru4** = [Ru(bpy)₂((2,6-bpp)Pd(CH₃CN)Cl)](PF₆)₂, 2,5-bpp = 2,2':5',2''-terpyridine, 2,6-bpp = 2,2':6',2''-terpyridine, Figure 1-12). Both supramolecular complexes contained two bpy peripheral ligands but contained different

bridging ligands. **Ru3** utilised the straight 2,5-bpp bridging ligand while **Ru4** utilised the bend 2,6-bpp bridging ligand. The variation from the straight bridging ligand to the bend bridging ligand results in a TON of 130 for **Ru3** while no hydrogen was observed for **Ru4** in a 60:30:10 acetonitrile:TEA:water mixture following 470 nm irradiation.

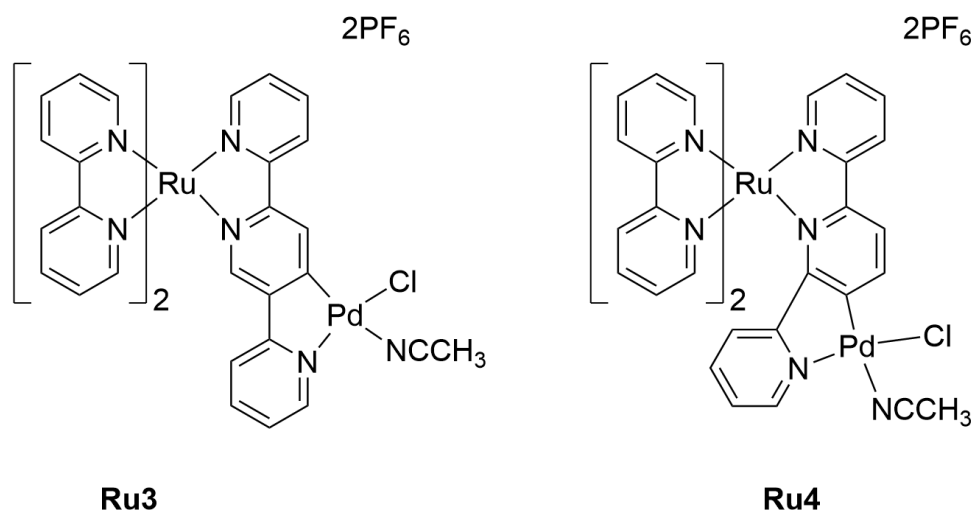


Figure 1-12. The structures studied by Singh Bindra et al.⁸⁶

Ru3 and **Ru4** showed similar UV-Vis spectra and electrochemical properties. However, while **Ru3** showed a long-lived emission at 630 nm with a lifetime of 105 ns, **Ru4** did not show emission longer lived than the instrument response time of 1 ns. Computation studies combined with Raman studies suggest the difference in activity is due to a difference in localisation of the LUMO for both complexes. For **Ru3**, the LUMO was found to be localised on the bridging ligand, whereas the LUMO for **Ru4** was localised mainly on the bpy ligands and the Ru metal centre. As mentioned before, charge transfer towards the bridging ligand is important to drive successful reduction of the catalytic Pd moiety, which may explain the inactivity of **Ru4** to produce hydrogen.

In the two-electron catalytic process for both hydrogen evolution and CO₂ reduction, the bridging ligand can act as an electron storage reservoir.⁸⁷ However, previous reports have suggested that efficient catalysis can occur even when the bridging ligand does not contain the LUMO. Work done in the Pryce group has shown that the peripheral ligands can act as electron storage reservoir to facilitate the two-electron catalytic process.⁸⁴ In these cases, the peripheral ligands act as reservoirs for the first electron following excitation and quenching. This enables more facile transfer of the second electron following the second excitation.

1.1.6.3.2. Peripheral ligands

The ligands on the ruthenium complex that are not used to connect the photosensitiser to the catalytic moiety are called peripheral ligands. The standard peripheral ligand for many ruthenium systems is bpy, due to the facile synthesis and stable nature of these complexes. However, modifying these ligands can have a significant influence on the supramolecular system.⁸⁵ Firstly, the ligand, as well as any functional groups present on the ligand, will influence the electronic structure of the complex. For systems in which the LUMO is located on the bridging ligand, electron donating moieties, such as methyl groups or amines, red shift the MLCT absorbance further towards the visible area by increasing the electron density on the ruthenium centre.⁵² Electron withdrawing groups such as carboxylic acids or esters moieties remove electron density from the ruthenium centre, resulting in a blue shift in the absorbance spectrum.⁸⁵ In terms of solar energy harvesters, electron donating groups on the peripheral ligands such as methyl or tert-butyl groups have been preferred.^{88,89} These electron donating moieties also raise the energy levels of the ³MLCT states located on the peripheral ligands, resulting in localisation of the LUMO on the bridging ligand and improving electron transfer to the bridging ligand following excitation. However, the desire to immobilise these supramolecular systems has resulted in the requirement of functional groups on these peripheral ligands that can interact with surfaces. For this, groups containing oxygen moieties such as carboxylic acids, phosphoric acids and ester moieties are typically used.^{51,71,90,91} These moieties are in general electron withdrawing and as such lower the energy of the unoccupied molecular orbital on the peripheral ligand. While this may lead to a desired red shift of the absorption spectrum due to a decrease of the HOMO-LUMO gap, it may also lead to charge transfer towards the peripheral ligands following excitation. Charge transfer towards the peripheral ligands has been considered undesirable, as charge transfer *via* the bridging ligand towards the catalytic metal centre is considered necessary for catalysis to occur. While one would expect charge transfer towards the peripheral ligand to decrease efficiency of the system in general, it has been shown that localisation of the excited state and thus the electron following photo-reduction on the peripheral ligands can be beneficial for these systems as well, as the peripheral ligands can aid the system to carry the negative charge while a second photo-reduction takes place. This phenomenon was reported for the [Ru(dceb)₂(tpy)PtI(H₂O)](PF₆)₂ complex (dceb = diethyl[2,2'-bipyridine]-4,4'-dicarboxylate, tpy = 2,2':5',2''-terpyridine) (**Ru5**, Figure 1-13), where localisation of the first electron on the peripheral dceb ligand was preferred over localisation on the bridging tpy ligand.^{84,85,92} The first electron was shown to aid electron transfer of the second electron upon a second cycle of excitation and quenching by a sacrificial

agent, and the photocatalytic results for this complex were found better than the bpy analogue $[(Ru(bpy)_2(tpy)PtI(H_2O))](PF_6)_2$ (**Ru6**).

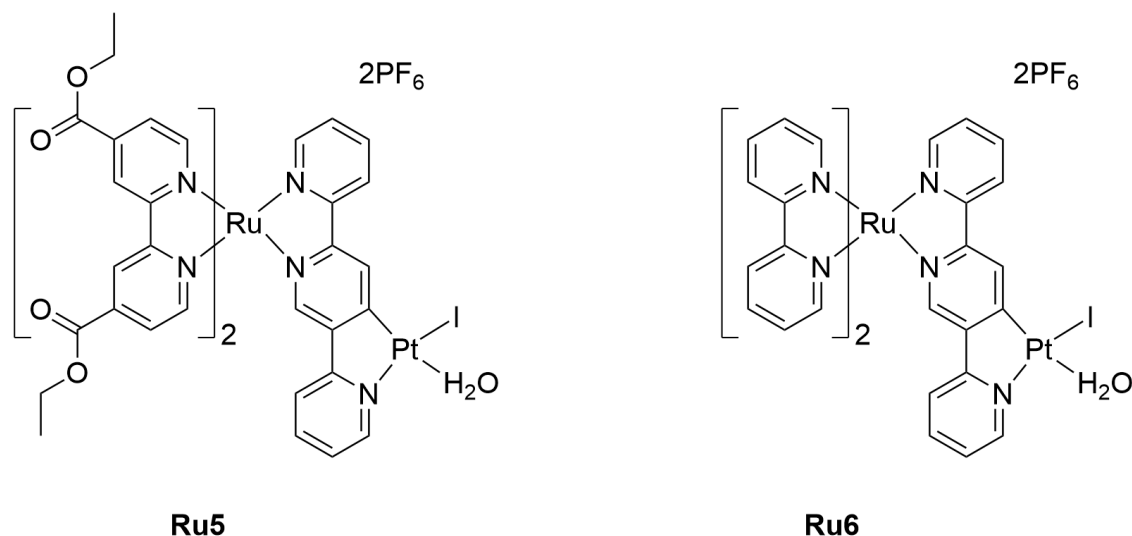


Figure 1-13. The $[Ru(dceb)_2(tpy)PtI(H_2O)](PF_6)_2$ (**Ru5**) and $[(Ru(bpy)_2(tpy)PtI(H_2O))](PF_6)_2$ (**Ru6**) complexes.⁸⁴

1.1.7. Immobilising system on semiconductor surfaces

While systems using sacrificial agents are useful to study the dynamics and mechanisms of photocatalytic systems, they are not sustainable for larger scale applications. Therefore, systems were designed in which the catalytic system is attached to a semiconductor or electrode surface.^{71,93,94} Instead of using sacrificial agents to provide the required electrons, these electrons are delivered by the electrodes using an electric current. Generally, intramolecular systems are mostly used for this purpose as they prove more efficient than their intermolecular counterparts. However, new challenges arise in the form of stability, electron transfer towards the electrode and charge recombination. Furthermore, the immobilisation at the electrode can influence the electronic properties of the photosensitiser. For example, Pöldme et al have reported the influence of immobilising ruthenium-palladium supramolecular systems on a NiO semiconductor surface.⁷¹ $[Ru(dceb)_2(bpt)PdCl(H_2O)](PF_6)_2$ (bpt = 3,5-bis(2-pyridyl)-1,2,4-triazole, **Ru7**) and $[Ru(dceb)_2(2,5-bpp)PtI(CH_3CN)](PF_6)_2$ (**Ru8**) were studied in solution and when immobilised on a NiO semiconductor surface using UV-Vis spectroscopy and ultrafast transient absorption among others.

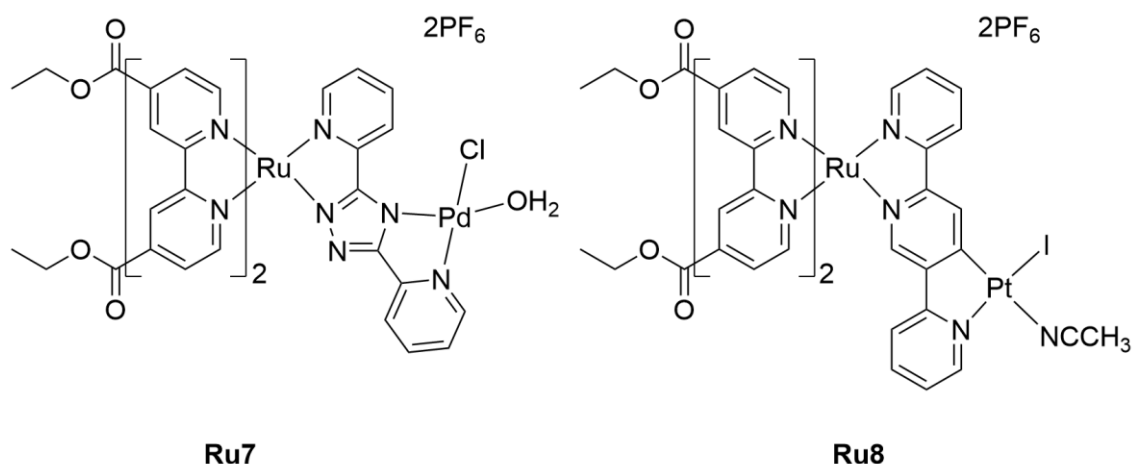


Figure 1-14 The $[Ru(dceb)_2(bpt)PdCl(H_2O)](PF_6)_2$ (**Ru7**) and $[(Ru(bpy)_2(tpy)PtI(MeCN))](PF_6)_2$ (**Ru8**) complexes

Immobilisation of the complexes onto NiO resulted in a blue shift of the λ_{max} of the MLCT transition of 10 nm for both complexes (490 to 480 nm for **Ru7**, 480 to 470 nm for **Ru8**), due to an interaction between the semiconductor surface and the ground state of the dye. Transient absorption spectroscopy was performed using 470 nm excitation. Both **Ru7** and **Ru8** showed formation of a nanosecond lived ^3MLCT state with lifetimes of 1.8 ns and >3 ns for **Ru7** and **Ru8**, respectively. Immobilisation of the complexes on NiO resulted in a shortening of the lifetimes observed for these ^3MLCT states in the TA experiments, to 1 ns for **Ru7** and ~4 ns for **Ru8**. In addition, following global analysis additional time constants were observed for the complexes on the NiO solution. For **Ru7**, a time constant of 20 ps was observed, which was assigned to the formation of the reduced complex following hole injection into the NiO surface. Two additional time constants were observed for **Ru8** with $\tau_1 = 2$ ps and $\tau_2 = 80$ ps. The 2 ps component is once again assigned to hole injection into the NiO semiconductor forming the negatively charged complex, while the 80 ps component is assigned to formation of a ruthenium-to-terpyridine ^3MLCT state. This $Ru \rightarrow tpy$ ^3MLCT state is formed in equilibrium with the ruthenium-to-dceb ^3MLCT state. The 4 ns component is assigned to this latter $Ru \rightarrow dceb$ ^3MLCT state. Both systems were tested for photoelectrochemical hydrogen evolution. The electrode was tested in pH 3 buffer containing 0.1 M potassium hydrogen phthalate under either -0.2, -0.4 or -0.6 V vs Ag/AgCl under chopped visible light irradiation. **Ru7** performed best at an applied potential of -0.2 V, with 46 TON after 1 hour, while **Ru8** performed best at an applied potential of -0.6 V with 147 turnovers.

1.1.8. Rhenium photocatalysts for CO₂ reduction

1.1.8.1. Introduction

Rhenium diimine tricarbonyl complexes of the form Re(NN)(CO)₃X (NN = diimine ligand, X = ancillary ligand) have been studied as CO₂ reduction catalysts since the early 1980s.^{35,95} These complexes have seen significant interest due to their high photostability, good efficiencies and high selectivity for the reduction of carbon dioxide.^{96–100} The activity of these complexes in photocatalytic CO₂ reduction is dependent on various factors, including the nucleophilic strength of the rhenium centre,^{101,102} wavelength of irradiation¹⁰³ and the catalytic pathway.^{104,105} These factors can be influenced by modifying the ligand or the rhenium complex, enabling tuning of the electronic and excited state properties of the complex as well as the reactivity of reduced intermediate species.

1.1.8.2. Excited state properties

As for the ruthenium systems described above, the lowest excited states of rhenium complexes are generally singlet metal-to-ligand (¹MLCT) transitions from the rhenium metal centre to the diimine ligand.^{106,107} For simple diimine ligands such as bipyridine or phenanthroline these transitions generally take place close to the UV region, with λ_{max} values of 372 nm for Re(bpy)(CO)₃Cl¹⁰⁸ and 386 nm for Re(phen)(CO)₃Cl¹⁰⁹. Due to the significant mixing of rhenium orbitals in the ¹MLCT excited state, these complexes undergo rapid intersystem crossing to the triplet surface, with the formation of the ³MLCT occurring within a few hundred femtoseconds.¹¹⁰ However, depending on the diimine and ancillary ligands, other transitions such as ligand-to-ligand charge transfer or (LLCT),¹¹¹ sigma-bond-to-ligand charge transfer (SBLCT),¹¹² π - π^* intraligand (IL)¹¹³ or intraligand charge transfer (ILCT)¹¹⁴ can also become relevant for the lowest lying excited state orbitals.

1.1.8.3. Functionalisation of the diimine ligand

1.1.8.3.1. Substituting on the aromatic system

The easiest and most popular approach to modify the properties of rhenium complexes is through modification of the diimine ligand. These modifications are generally synthetically facile and the relative effect of the modification can be modulated through both the functional group as well as the location of the substituent. Koike et al studied various [Re(4,4-X₂bpy)(CO)₃PR₃]⁺ (X = CH₃, H, CF₃, PR₃ = phosphorous ligands) complexes (**Re1-Re7**) for photocatalytic CO₂ reduction (Figure 1-15).¹¹⁵ They found that the inclusion of electron withdrawing moieties such as CF₃ resulted in a significant decrease in photocatalytic ability. The best performing complexes **Re3**, **Re4**, **Re5** and **Re6** showcased TON ranging from 4.1 (**Re6**) to 6.2 (**Re3**) in 5:1 v/v DMF-TEOA

solution. It is not entirely clear why the electron withdrawing CF_3 moieties in **Re7** reduces photocatalytic activity. However, the second-order rate constant for the reaction of the complex with CO_2 was significantly smaller for **Re7** ($5.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) compared to those found for the better performing complexes **Re3** ($94.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), **Re4** ($56.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), **Re5** ($60 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) and **Re6** ($186 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), suggesting that the reduced intermediate species is not a strong enough nucleophile to react with CO_2 .

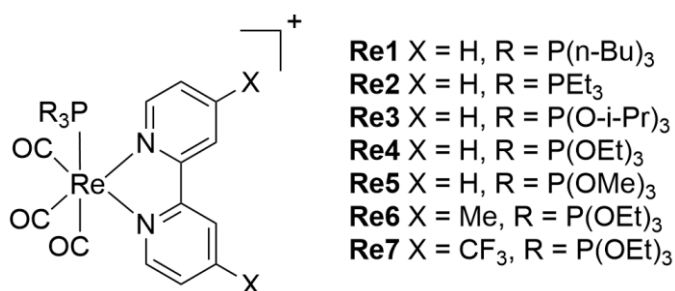


Figure 1-15. The substituted $\text{Re}(\text{X}_2\text{bpy})(\text{CO})_3\text{PR}_3$ Complexes studied by Koike et al.¹¹⁵

Ono et al reported the effect of substituents on the 4,4' position of the bipyridine ligand.¹¹⁶ They compared systems with H, CH_3 , COOH or CN as substituents on the ring for their ability to photocatalytically reduce CO_2 . They reported that the inclusion of the CN group decreased activity compared to the benchmark $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$, while the compounds with either a CH_3 or COOH group performed better. For the latter, it was suggested that the higher extinction coefficient (approximately 1.2 times that of the H and CH_3 substituted complexes) of this complex may have resulted in this complex achieving higher CO_2 production rates. Inclusion of CH_3 and COOH groups on the bpy ring also reduced the degradation rates of the photocatalyst under 365 nm irradiation.

1.1.8.3.2. Extending the aromatic system

An alternative approach to modifying the properties of the diimine ligand is by extending the conjugation in the light harvesting unit. This approach provides two main advantages over smaller molecules. First, increasing the conjugation generally lowers the reduction potential,^{117,118} which makes formation of the one-electron reduced intermediate species easier. For example, the potential for the first reversible one-electron reduction increases when extending the conjugated system from perylene (-1.1 V vs SCE) to terrylene (-0.73 V vs SCE) and quarterrylene (-0.62 V vs SCE).¹¹⁶ Secondly, extending the conjugation results in a lowering of ligand-centred excited states such as the $\pi\text{-}\pi^*$ interligand (IL) or interligand charge transfer states (ILCT) states.^{113,119,120} These transitions can give rise to long lived triplet state species which are desirable for photocatalytic applications.^{109,113,119–122} Waterland et al reported unsubstituted

and substituted $\text{Re}(\text{dppz})(\text{CO})_3\text{Cl}$ complexes (dppz = dipyrdo[3,2,-a:2',3'-c]phenazine) that utilise extended conjugation on the dppz ligand to access a long-lived $^3\text{ILCT}$ excited state (**Re8-Re11**) (Figure 1-16). Resonance-Raman studies show that for the unsubstituted system (**Re8**), the lowest lying excited state is mainly $^3\text{ILCT}$ in nature, while the complex containing an electron-withdrawing nitro group (**Re11**) has a $^3\text{MLCT}$ state as lowest excited state. These Raman studies show that the energies of the ILCT and MLCT states are in close proximity for these systems utilising dppz ligands. This proximity in energy enables access to long lived $^3\text{ILCT}$ states either *via* the $^1\text{ILCT}$ state or through $^3\text{MLCT}$ excited states.

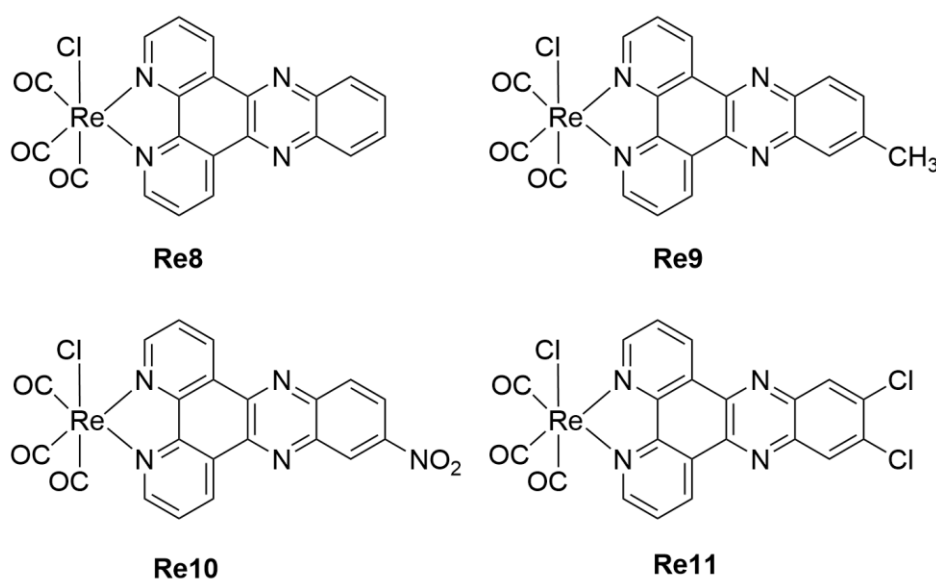


Figure 1-16. Unsubstituted and substituted $\text{Re}(\text{dppz})(\text{CO})_3\text{Cl}$ complexes reported by Waterland et al.¹¹⁹

Yarnell et al reported a rhenium-phenanthroline complex extended with a naphthalene-monoimide moiety (**Re12**) (Figure 1-17).¹⁰⁹ This complex provides an elegant example of the interaction between the MLCT and ILCT states accessible for Re complexes with extended conjugation.

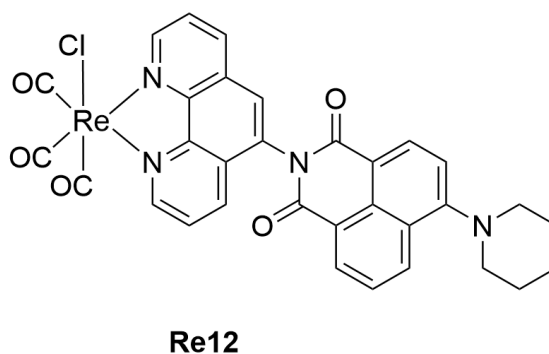


Figure 1-17. The $\text{Re}(\text{phen-NDI})(\text{CO})_3\text{Cl}$ (**Re12**) complex studied by Yarnell et al.¹⁰⁹

Re12 was studied with time-resolved infrared spectroscopy due to the presence of various carbonyl reporter groups on both the Re metal centre as well as the naphthalene monoimide ligand (Figure 1-18). Following 400 nm excitation, bleaches for the parent complex were formed within the laser pulse at 2019, 1918, 1893, 1714 and 1673 cm^{-1} . The first three bleaches can be assigned to the metal carbonyl moieties on the rhenium centre for the parent complex, while the latter two are assigned to the naphthalene monoimide ligand. Within 1 ps, a shift to higher wavenumbers is observed for the metal carbonyl species with new bands at 1945 and ~ 2060 cm^{-1} , while for the organic carbonyl stretches a shift to lower wavenumbers is observed with new signals at ~ 1600 and 1645 cm^{-1} . The shift to higher wavenumbers for the metal carbonyl stretches suggests a decrease in electron density on the Re centre, and the relative shift of ~ 40 cm^{-1} matches well the assignment of a MLCT state. The shift to lower wavenumbers for the organic carbonyls further supports this assignment, as an increase in electron density on the ligand is expected for a MLCT transition. The signals increase in intensity over the first 100 ps. ns time-resolved infrared spectroscopy was performed to study the behaviour of the complex on the ns timescale. Within 60 ns of the excitation at 410 nm, the signals for the metal carbonyl stretches at 1945 and 2060 cm^{-1} deplete and new stretches are observed at slightly lower wavenumbers than the parent bleaches. This suggest a species is formed in which the metal centre is not significantly involved in the excited state transition. The obtained pattern matched well with previously reported triplet ligand centred (^3LC) species, in which the excited state is fully localised on the ligand.

This $^3\text{ILCT}$ state localised on the naphthalene moiety was found to be non-emissive and relaxed to the ground state via nonradiative decay pathways. However, the $^3\text{MLCT}$ state was close enough in energy for thermal population from the $^3\text{ILCT}$ state, resulting in an equilibrium of both the $^3\text{ILCT}$ and $^3\text{MLCT}$ states. The $^3\text{MLCT}$ state was emissive and the equilibrium with the $^3\text{ILCT}$ state resulted in a 3000-fold increase in $^3\text{MLCT}$ emission lifetime for $\text{Re}(\text{phen-NDI})(\text{CO})_3\text{Cl}$ (651 μs) compared to the $\text{Re}(\text{phen})(\text{CO})_3\text{Cl}$ benchmark (197 ns).

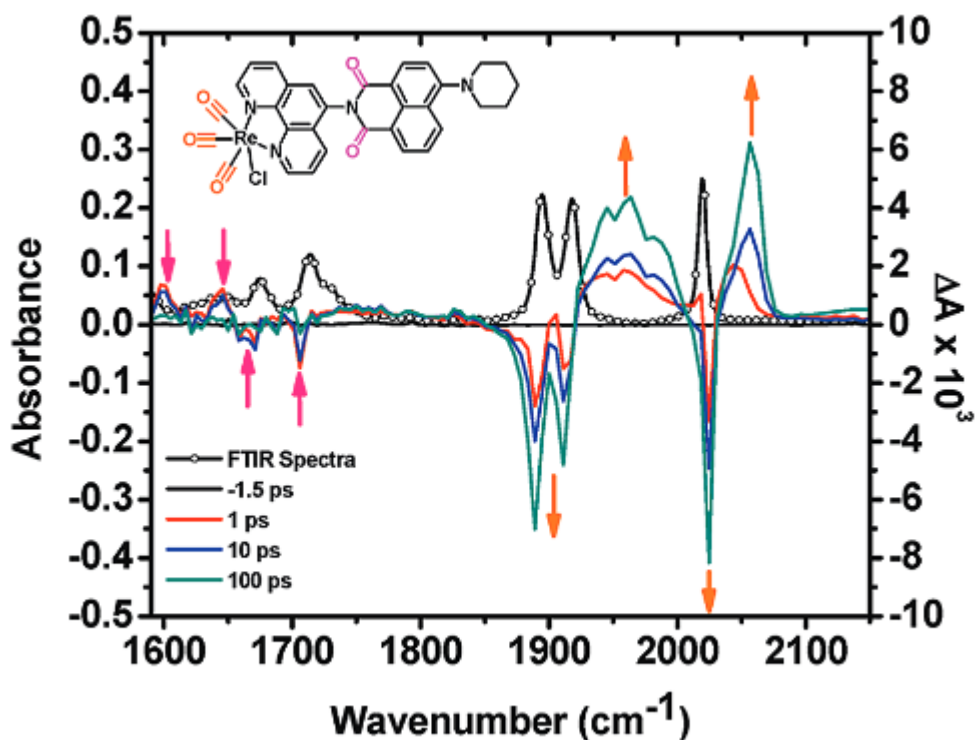


Figure 1-18. Picosecond time-resolved infrared study following 400 nm excitation of **Re12** in THF studied by Yarnell et al.¹⁰⁹

1.1.8.3.3. N-Heterocyclic carbenes (NHC)

Bpy and phen and their functionalised derivatives are a popular choice as ligands for rhenium complexes due to their high stability and desirable binding angle to the metal.

Another family of ligands for rhenium complexes are N-heterocyclic carbenes (NHC) due to their strong sigma-donating and π -accepting properties.^{123–126} Examples have been reported in which rhenium-NHC-tricarbonyl systems were studied as photocatalysts for CO₂ reduction. Huckaba et al reported a series of rhenium complexes with substituted N'-pyridyl-N''-R-imidazole N-heterocyclic carbene ligands (**Re13X-Re17X**, X = Cl, Br, Figure 1-19).¹²⁷

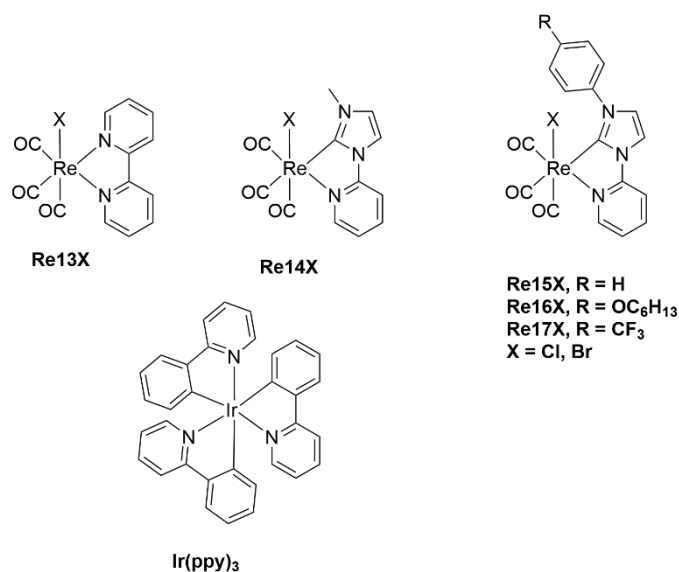


Figure 1-19. The rhenium catalysts and the iridium photosensitiser Ir(ppy)₃ studied by Huckaba et al.¹²⁷

The substituent on one nitrogen of the imidazole ring was kept constant in the form of a pyridyl ring, which also provided a second nitrogen atom to coordinate the rhenium metal centre, while the second nitrogen bore a phenyl ring with either a proton, OC₆H₁₃ or CF₃ group on the para position. The systems were assessed as photocatalysts for CO₂ reduction in the presence of the iridium photosensitiser Ir(ppy)₃ (ppy = 2-phenylpyridine) and compared to Re(bpy)(CO)₃Cl and Re(bpy)(CO)₃Br (**Re13Cl** and **Re13Br**, respectively) as benchmark catalysts. The substituent on the phenyl moiety was found to influence the efficiency of catalysis. The rhenium complex with the electron withdrawing CF₃ group (**Re17X**) performed slightly better than the benchmark catalysts, while the unsubstituted phenyl (**Re15X**) and hexyl-ether substituted (**Re16X**) analogues produces similar turnovers as the benchmark catalysts (Figure 1-20).

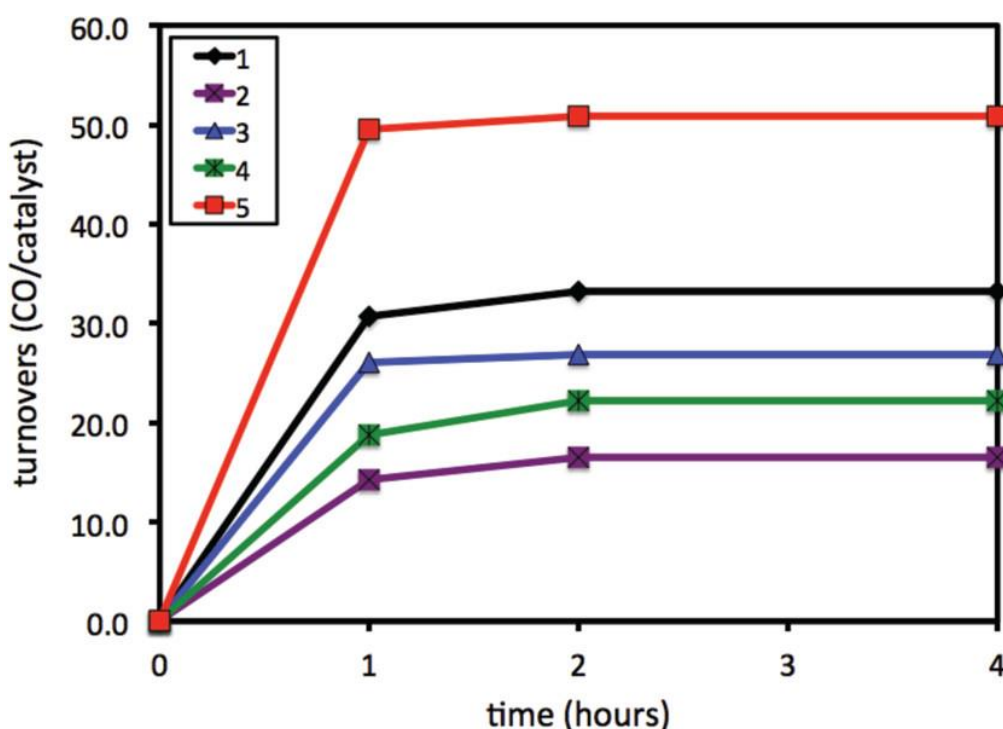


Figure 1-20. Turnover numbers for photocatalytic CO₂ reduction for **Re13Br** (black), **Re14Br** (purple), **Re15Br** (blue), **Re16Br** (green) and **Re17Br** with 1 equivalent of Ir(ppy)₃ (photosensitiser) and 100 equivalents of BIH as a sacrificial agent in 5% TEA/MeCN solution.¹²⁷

Carpenter et al further studied the most active compounds **Re17**.¹²⁸ A significant decrease in excited state lifetime was observed for the NHC complexes (4.2 ns for **Re17Br**) compared to Re(bpy)(CO)₃X (X = Cl, Br) benchmarks (150 ns for Re(bpy)(CO)₃Br). However, this decrease in lifetime did not seem to negatively affect the catalytic properties of the system. **Re17Cl** was tested as a stand-alone photocatalyst without the presence of a photosensitiser and reported similar activities to that of the benchmark Re(bpy)(CO)₃Cl photocatalyst. A 0.2 mM solution of the photocatalyst in acetonitrile with 0.02 mM BIH sacrificial agent and 5% v/v were irradiated with simulated solar light (AM1.5 filter). Under anhydrous conditions, **Re17Cl** achieved approximately 17 turnovers after 2 hours, while Re(bpy)(CO)₃Cl achieved approximately 21 turnovers in the same time window. Catalytic studies were also performed in the presence of water (0.05 to 3.2% v/v) and air (0 to 40 % v/v of the headspace). The **Re17Cl** appeared less affected by the presence of water or air than the benchmark Re(bpy)(CO)₃Cl catalyst. Addition of 3.2% v/v only resulted in a 43% decrease in TON for **Re17Cl**, while the TON for the benchmark Re(bpy)(CO)₃Cl dropped by ~90% under the same conditions. In addition, **Re17Cl** appeared relatively robust under oxygenated conditions (40% air v/v in the headspace), maintaining up to 40% of the activity observed in deaerated conditions. With 40% air present in the headspace, **Re17Cl** was found to outperform the Re(bpy)(CO)₃Cl benchmark catalyst. The authors suggest

that the higher resistance of **Re17Cl** against water and air in the reaction is most likely due to a difference in the catalytic cycle for **Re17Cl** and the $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ benchmark.

1.1.9. The ancillary ligand

A second site often targeted for rhenium-tricarbonyl complex modification is the ancillary ligand. The ancillary ligand is a pendant atom or molecule that is coordinated to the rhenium centre. Most commonly, anionic (X) ancillary ligands are used in rhenium-tricarbonyl complexes, as the anionic ligand in combination with the positively charged Re^I metal centre results in a neutral complex. Most popular choices are halides, in particular Cl and Br, and these complexes are generally also used as synthetic precursors for systems with other ancillary ligands, as $\text{Re}(\text{CO})_5\text{Cl}$ and $\text{Re}(\text{CO})_5\text{Br}$ are the most common rhenium precursors currently available. Substitution of the ancillary ligand directly influences the orbitals on the metal centre.¹²⁹ Therefore, transitions involving the metal centre such as MLCT transition, or the ancillary ligand such as XLCT transitions are significantly affected by changes to the ancillary ligand.^{111,112,130} In particular the MLCT transitions play a significant role in accessing the triplet state,^{114,131} and as such are important for efficient photocatalysis.

1.1.10. Catalytic mechanism

While many research groups focus on studying the mechanism leading to CO_2 reduction, there are still many unanswered questions regarding the catalytic mechanism for rhenium photocatalysts. While the exact cycle is unclear, some examples of catalytic pathways have been reported. Lang et al have reported one photocatalytic pathway for $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ (**1**)¹⁰³ as shown in Figure 1-21. Following one-electron reduction of the catalyst, the ancillary ligand dissociates resulting in the formation of a neutral $[\text{Re}(\text{bpy})(\text{CO})_3]$ species (**2**). Alternatively, one-electron reduction can form the anionic $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^-$ species (**2Cl**), which following a second one-electron reduction undergoes chloride dissociation to form the anionic $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ species (**3**). Complex **2** can undergo three different pathways. In pathway 1, CO_2 is bound in between two rhenium complexes forming a CO_2 bridged species (**10**). A second CO_2 molecule can be inserted into the Re-O bond (**11**). Loss of carbon monoxide results in a carboxylate bridged dimer (**12**), which can be reduced in the presence of protons to release carbonate and recover the $[\text{Re}(\text{bpy})(\text{CO})_3]$ complex.

In pathway 2, the neutral $[\text{Re}(\text{bpy})(\text{CO})_3]$ species is reduced by a second electron to form the anionic $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ species (**3**). This complex can bind CO_2 to form the anionic $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CO}_2)]^-$ carboxylic intermediate species (**4**). Protonation of this species results in the hydroxylcarbonyl intermediate $[\text{Re}(\text{bpy})(\text{CO})_3(\text{COOH})]$ (**5**). A second protonation step of this

complex results in the loss of water and formation of the cationic tetracarbonyl species $[\text{Re}(\text{bpy})(\text{CO})_4]^+$ (**6**). This species undergoes two consecutive reductions. The first reduction results in the formation of the neutral tetracarbonyl species $[\text{Re}(\text{bpy})(\text{CO})_4]$ (**7**). The second reduction causes dissociation of one of the carbon monoxide ligands to regenerate the $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ complex.

In pathway 3, the neutral $[\text{Re}(\text{bpy})(\text{CO})_3]$ complex undergoes dimerization with a second molecule of $[\text{Re}(\text{bpy})(\text{CO})_3]$ forming a Re-Re dimeric species (**9**). This dimeric species is expected to be inactive in catalysis and requires two further electron reductions to cleave the Re-Re bond forming two $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ anions (**3**). These species can then undergo CO_2 reduction following pathway 2.

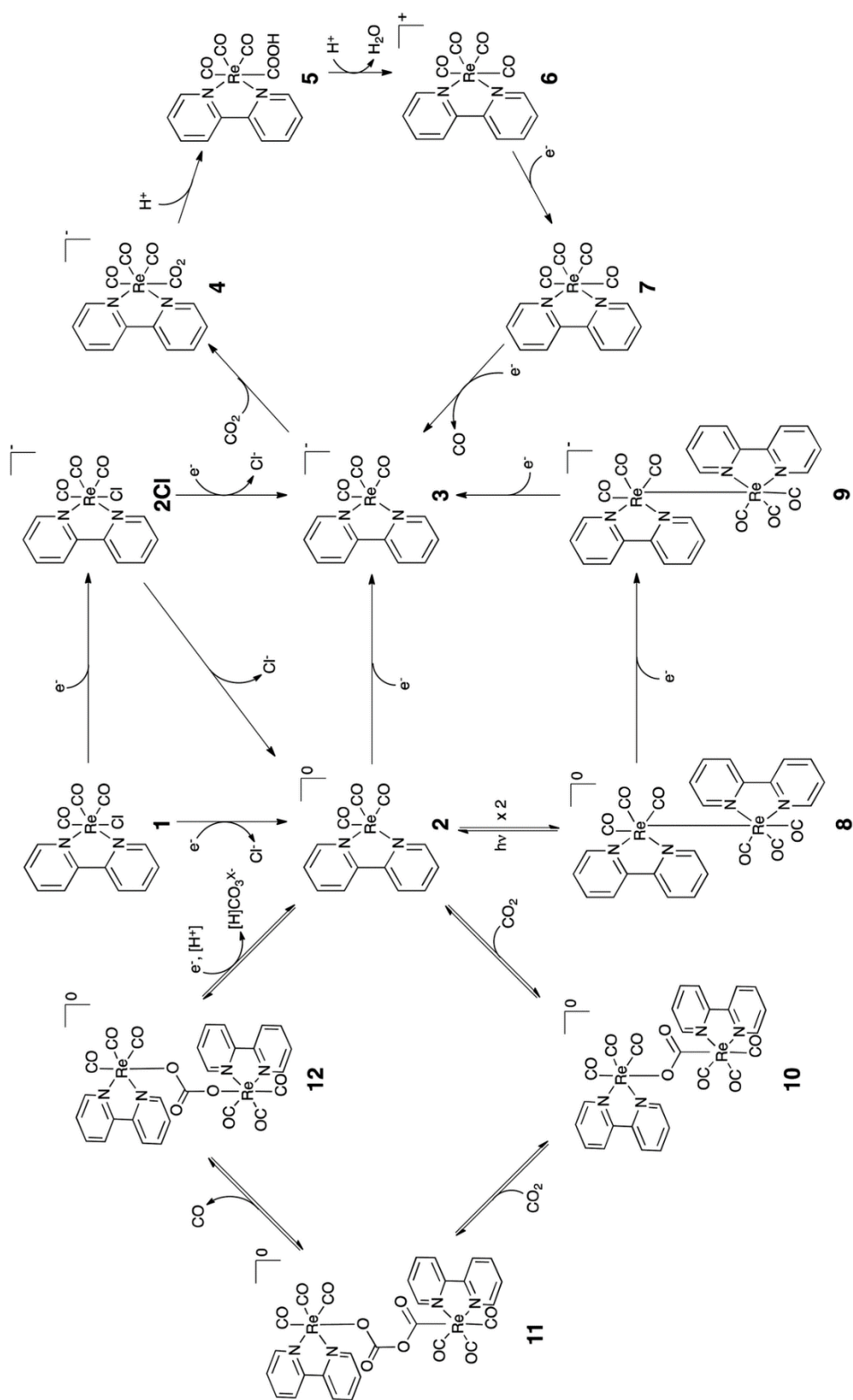


Figure 1-21. Proposed CO₂ reduction catalytic cycle for the Re(bpy)(CO)₃Cl catalyst.¹⁰³

1.2. Commonly used techniques

1.2.1. *Steady state spectroscopy*

Techniques such as UV-Vis spectroscopy, emission spectroscopy and IR spectroscopy are unmissable tools in characterising the photocatalysts. UV-Vis spectroscopy can be used to determine the energies of the various transitions that occur for the photocatalyst. Emission spectroscopy can provide information on the lowest energy excited state. Through a combination of UV-Vis and emission spectroscopy, the HOMO-LUMO gap for the photocatalyst can be determined. IR-spectroscopy can be used to characterise the complex through the unique signals for functional groups such as double and triple carbon-carbon bonds, carbonyl moieties, amides or alcohols.

1.2.2. *Electrochemistry*

Electrochemistry is a powerful but underused technique in the field of solar fuels. Techniques like cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are easy to perform and can provide valuable information on the reductive strength of the reduced intermediates of the catalyst, as well as enable the calculation of thermodynamic driving force for the desired reaction.¹³² More recently, electrochemical techniques have been applied in the field of solar fuels to help determine the energy levels of the ground state complex and the one-electron reduced complex, which is generally considered an intermediate in catalysis.^{104,132} Together with the values obtained in the UV-Vis and emission experiments, energy diagrams can be constructed which give an idea of the thermodynamics of the various electron transfers involved in photocatalysis.

1.2.2.1. *Ultrafast spectroscopy*

Ultrafast spectroscopy, in particular transient absorption (TA, for short time scale UV-Vis spectra), time-resolved infrared spectroscopy (TRIR, for short time scale infrared spectra), time resolved emission spectroscopy and time-resolved Raman spectroscopy have been widely applied to analyse the properties of photocatalytic systems.^{51,133–135} As all these techniques have their unique advantages and disadvantages, a combination is often used to create a complete picture of the excited state properties of the photocatalyst. An understanding of the excited states of these systems is very important for photo driven hydrogen evolution or CO₂ reduction, as they are a key intermediate in the catalytic cycle. Ultrafast techniques can be used to determine various characteristics of the excited state such as lifetime, localisation of the excited state in the catalytic system, deactivation pathways and issues for stability. The lifetime of the excited state is of importance for the efficiency of the catalyst. The rate of electron transfer

from the sacrificial agent to the photocatalyst is diffusion dependent and generally takes place on the nanosecond timescale.¹³⁶ Therefore, for efficient electron transfer to occur lifetimes on the ns timescale or longer are required, and extended lifetimes increase the chance for electron transfer to occur. The localisation of the excited state is important to ensure electron transfer is occurring in the right direction, hence from the photosensitiser moiety towards the catalytic metal.^{71,137} Furthermore, the formation of other excited state species following the initial excitation may result in decomposition of the system and other undesired side reactions or may result in electron transfer in the wrong direction or relaxation to the ground state without electron transfer to the catalytic metal.

1.2.2.1.1. Time-resolved infrared spectroscopy (TRIR)

TRIR spectroscopy is amongst one of the most important techniques used in this thesis. TRIR is, like other ultrafast spectroscopical techniques, a highly useful tool in determining excited state properties of the compound of interest.¹⁰⁷ In essence, TRIR spectroscopy is a technique in which an infrared spectrum is recorded of the excited state species. In order to obtain this spectrum, the compound is first excited with an ultrashort (fs to ps timescale) laser at the desired excitation wavelength.¹³³ Following excitation, the sample is then irradiated with an infrared probe beam to obtain an infrared absorbance spectrum. To determine how the excited state species changes over time, spectra are recorded at different time intervals after the compound is excited. In the field of photocatalysis, an understanding of the exact processes that occur following light excitation are invaluable for catalyst design and optimisation.⁵¹ For this thesis, TRIR is preferred over other ultrafast techniques such as transient absorption or time-resolved Raman spectroscopy. The main reason that TRIR is favoured is due to the increased detail that this technique offers for the study of the complexes reported in this work. All complexes study herein contain functional groups with strong and unique IR stretching vibrations that can be readily observed in TRIR spectroscopy.¹³⁸ In particular, all studied complexes contain either organic and/or metal-carbonyl groups which provide strong stretching vibrations in the 1500-2100 cm⁻¹ region of the infrared spectrum. For some complexes, carbonyl groups are present at various locations of the molecule, enabling us to pinpoint excited state localisation by comparing relative shifts of the various carbonyl moieties.

1.2.2.2. Spectroelectrochemistry

1.2.2.2.1. Introduction

Spectroelectrochemistry is one of the main themes of this thesis. In spectroelectrochemical experiments, steady state or ultrafast spectroscopical techniques are combined with electrochemistry.^{139–141} Generally, the substrate of interest is electrochemically reduced or

oxidized and subsequently studied with a spectroscopical technique of choice. In the field of solar fuels, this technique is very useful to study the reduced species that are suspected intermediates in the photocatalytic cycle.¹⁰³ While these intermediates can also be produced in situ using chemical reductants¹⁴² or via solvent pulse radiolysis¹⁴³, the spectroelectrochemical approach generally provides a better control over the products that are formed and prevents the need to introduce additional chemicals that might hinder or influence the spectroscopical study.

1.2.2.2.2. Spectroelectrochemical studies for ruthenium complexes

Spectroelectrochemical approaches can provide valuable insights about the excited state species. This insight is mainly obtained by mimicking the HOMO and LUMO species of the complex through electrochemical oxidation or reduction of the compound of interest.¹⁴⁴ After all, for the lowest energy transition, an electron is removed from the HOMO and added to the LUMO. Therefore, studying the first reduction and first oxidation of a compound can provide an estimated picture of the expected lowest lying excited state and can aid in the analysis of ultrafast spectroscopical results.

The complementary use of steady state spectroelectrochemistry and ultrafast techniques is common in the literature. For example, Zhang et al have studied various ruthenium complexes (**Ru9-Ru11**, Figure 1-22) using both UV-Vis and Resonance Raman spectroelectrochemistry, as well as steady state and ultrafast spectroscopic techniques and time-dependent DFT calculations.¹⁴⁴

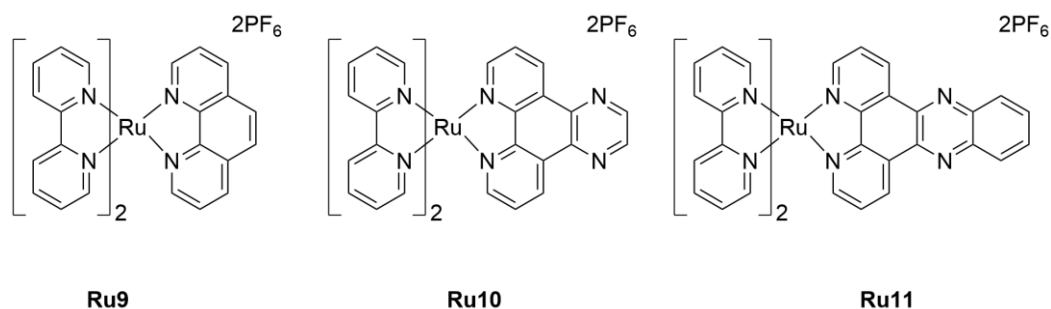


Figure 1-22. The ruthenium complexes studied by Zhang et al.¹⁴⁴

Spectroelectrochemistry was employed to mimic the charge transfer process that can occur following light excitation (Figure 1-23). Similar to other octahedral ruthenium complexes, the UV-Vis spectra of **Ru9-Ru11** showcase a broad MLCT transition ranging from 400-500 nm. Following one-electron reduction, these MLCT bands undergo a slight red shift (446 to 455 for **Ru9**) due to a slight increase in electron density on the ruthenium centre. In addition, new bands

appeared for the complexes at ~600 nm. To determine the nature of the reduced species, resonance Raman spectroscopy was applied. The reduced complex **Ru9⁻** was studied with resonance-Raman spectroscopy following both 405 and 473 nm excitation. Following 405 nm excitation, the bands assigned to the bpy ligand increase in intensity. In addition, some of the bands undergo slight shifts. These observations suggest that the bpy ligand is involved in the transition following 405 nm excitation. The authors assign this transition as an MLCT from the ruthenium centre to the bpy ligands. Signals associated with the phenanthroline moiety of the dppz ligand were absent, suggesting MLCT towards the dppz ligand no longer occurs for **Ru9⁻**. Secondly, the new band between 500 and 800 nm was studied through resonance Raman spectroscopy using 643 nm irradiation. Excitation at 643 nm resulted in resonance Raman bands that were assigned to the dppz ligand, while signals for the bpy ligand were absent in this experiment. The results following 405 and 643 nm excitation suggest that the first reduction of **Ru9⁻** takes place on the dppz ligand. Reduction of the dppz ligand disfavours further MLCT to the dppz ligand, and MLCT transitions to the bpy ligands become more favourable instead.

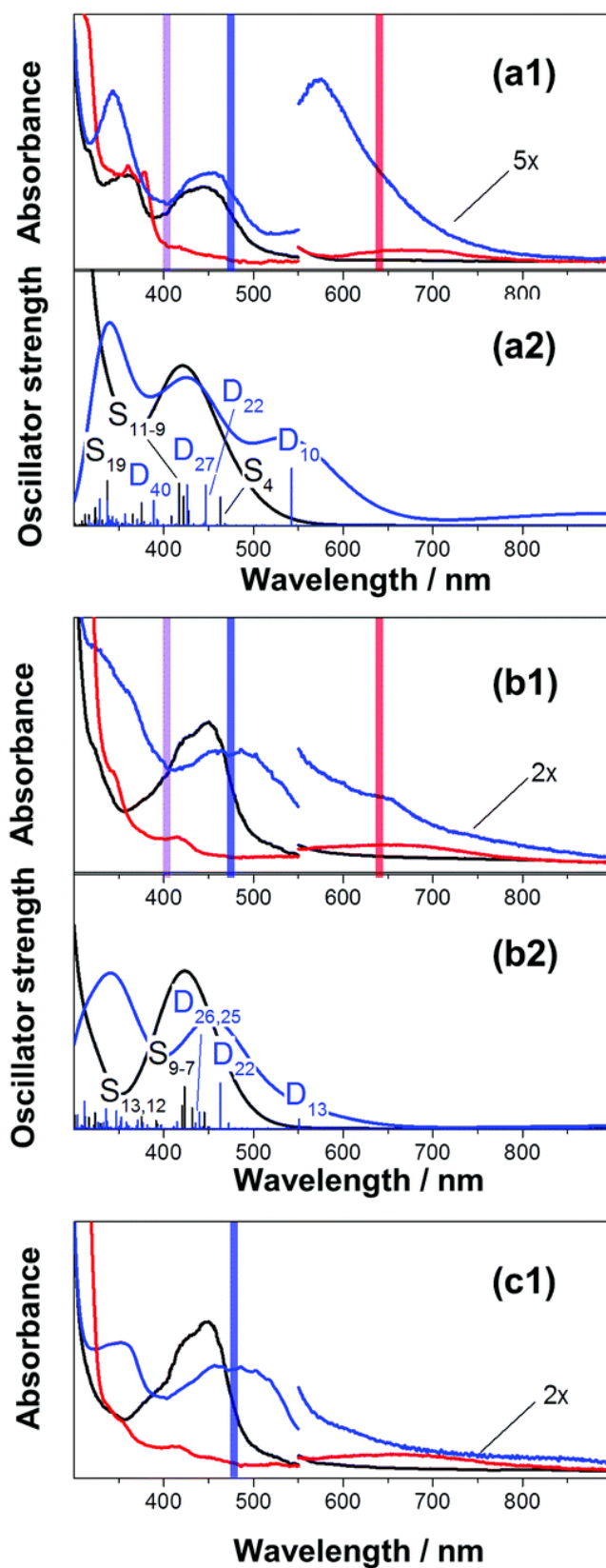


Figure 1-23. UV-Vis spectra of the neutral (black), one-electron oxidised (red) and one-electron reduced (blue) for $[Ru(bpy)_2(dppz)]$ (**Ru9**) (a1), $[Ru(bpy)_2(dpq)]$ (**Ru10**) (a2) and $[Ru(bpy)_2(phen)]$ (**Ru11**) (a3) (left). Calculated charge density shifts (blue to red) for the corresponding transitions.¹⁴⁴

Zedler et al reported the application of UV-Vis- Raman- transient absorption spectroelectrochemistry to further determine the photocatalytic pathway of a ruthenium-rhodium hydrogen evolution catalyst (**Ru12** & **Ru13**, Figure 1-24).¹³⁷

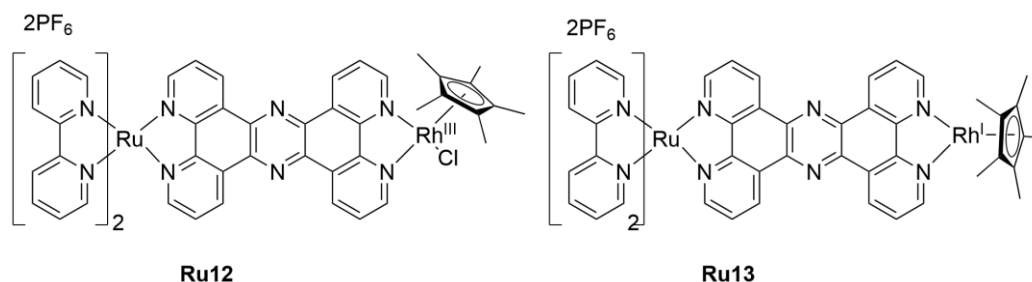


Figure 1-24. The ruthenium-rhodium assembly studied by Zedler et al.¹³⁷ The unreduced pre-catalyst (**Ru12**) and the two-electron reduced "fully charged" catalytic species (**Ru13**).

The first reduction of **Ru12** was found to be a two-electron process centred on the rhodium metal centre. Dissociation of the halide resulted in a change in orientation between the cyclopentadienyl ligand and the tpphz bridging ligand. This species was considered the "fully charged" molecular photocatalyst (**Ru13**). Transient absorption experiments on the unreduced species (**Ru12**) suggested that charge transfer from the ruthenium metal centre to the rhodium centre resulted in the formation of a similar species. Transient absorption spectra were then recorded for the two-electron reduced species (**Ru13**) to determine the further photophysical processes (Figure 1-25). A MLCT transition from the reduced rhodium centre to the nearby phenanthroline end of the tpphz ligand was observed at 600 nm excitation, while MLCT transitions involving the ruthenium centre were observed following 403 nm excitation. Following 600 nm excitation, the Rh centred MLCT state was shown to undergo intra-ligand charge transfer towards the centre of the tpphz ligand within 485 ps. This ILCT state persisted beyond the time window of the experiment. Following 403 nm, MLCT transitions from the ruthenium centre to the tpphz and tbbpy ligands are observed. These MLCT states underwent electron hole transfer towards the rhodium metal centre within the experimental time resolution. Rapid vibrational cooling (2 ps) and inter-ligand charge transfer (43 ps), followed by slower intra-ligand charge transfer (600 ps) result in formation of the same ns lived ILCT state which persisted outside the time window of the experiment. This study presents one of the first examples of combining electrochemical techniques with ultrafast spectroscopy and showcases how these techniques can be used to study the behaviour of active intermediates in the photocatalytic cycle.

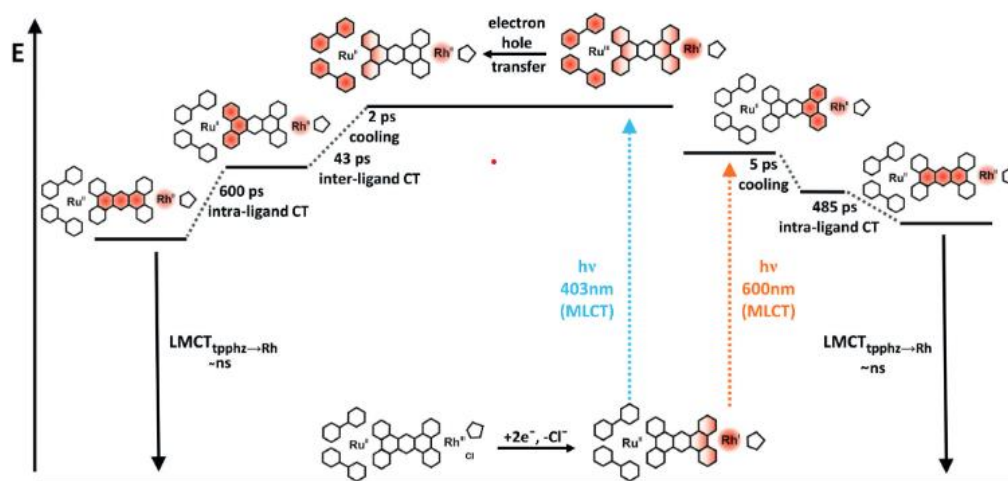


Figure 1-25. Proposed photophysical pathways for the electrochemically reduced $\text{Ru}(\text{tpphz})\text{RhCp}$ complex.

1.2.2.2.3. Spectroelectrochemical studies for rhenium catalysts

In the field of CO_2 reduction, a large volume of work has been reported on the various intermediates in the CO_2 reduction catalysed by group 5 and 6 metals. Rhenium has been particularly well studied as the metal carbonyls act as useful reporter groups in IR-spectroelectrochemistry.^{145–148} Giereth et al reported the use of UV-Vis and IR-spectroelectrochemistry to help elucidate the catalytic mechanism of a xanthene-bridged bimetallic rhenium complex (**Re18**, Figure 1-26).¹⁰⁴

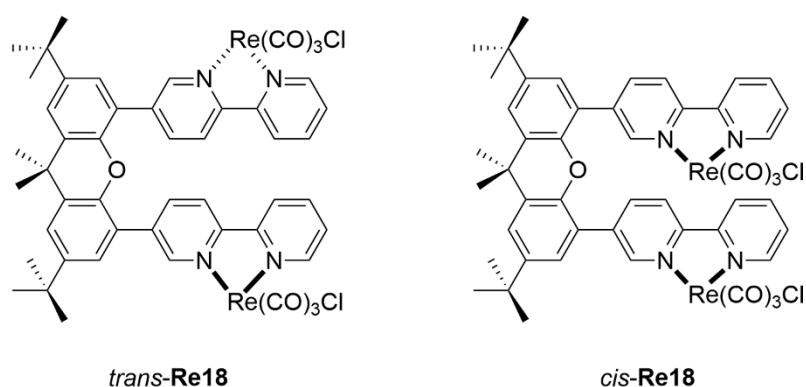


Figure 1-26. The *trans* and *cis* dinuclear rhenium complexes studied by Giereth et al.¹⁰⁴

Due to the rigid structure of the bridging ligand, the *trans* and *cis* isomeric species of **Re18** could be isolated after synthesis. UV-Vis and IR spectroelectrochemistry were used to elucidate the reaction mechanism in the *trans* system. For the *trans* isomer, signals for a Re-Re dimer species were observed in the spectroelectrochemical experiments, even though this species could not be isolated as the complex was found to be kinetically unstable. The strength of the Re-Re bond was weakened due to the significant strain imposed by the rigid Xanthene ligand backbone, and

breaking of the Re-Re bond in this intramolecular dimeric compound was found to occur at less negative potentials than observed for other intermolecularly formed Re-Re dimer species. This may be beneficial in reducing the required potential to form the catalytically active anionic species for systems where deactivation through dimer formation is a problem.

Stanton et al utilised IR-spectroelectrochemistry to elucidate the various intermediate species following reduction of pyridyl (Bi-Py) or pyrimidyl (bi-pyrm) substituted rhenium benzimidazole NHC complexes (**Re19** & **Re20**, Figure 1-27).¹⁴⁵

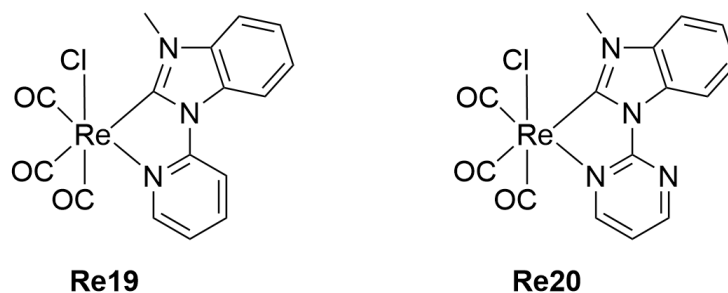


Figure 1-27. The Rhenium complexes studied by Stanton et al.¹⁴⁵

Both complexes were studied using infrared spectroelectrochemistry under reductive conditions (Figure 1-28). Upon the first one-electron reduction, **Re19** underwent facile chloride dissociation, and signals were observed in the IR spectrum for both the neutral radical $[\text{Re}(\text{Bi-Py})(\text{CO})_3]^{\bullet}$ and dimeric $\text{Re}(\text{Bi-Py})(\text{CO})_3)_2$ species. The authors suggest that dimer formation occurs rapidly through Re-Re bond formation between two radical species. Once the potential was moved to more negative potential reduction of the dimer takes place, resulting in the formation of the anionic $\text{Re}(\text{Bi-Py})(\text{CO})_3]^{-}$ species. These observations match well with mechanistic pathways described for $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ (*vide supra*). A cleaner conversion to the radical species was observed for the pyrimidyl species **Re20**. Further reduction converted the radical species directly to the anionic species, and no signals for the dimeric species was observed. It remains unclear why no dimer was formed for **Re20**.

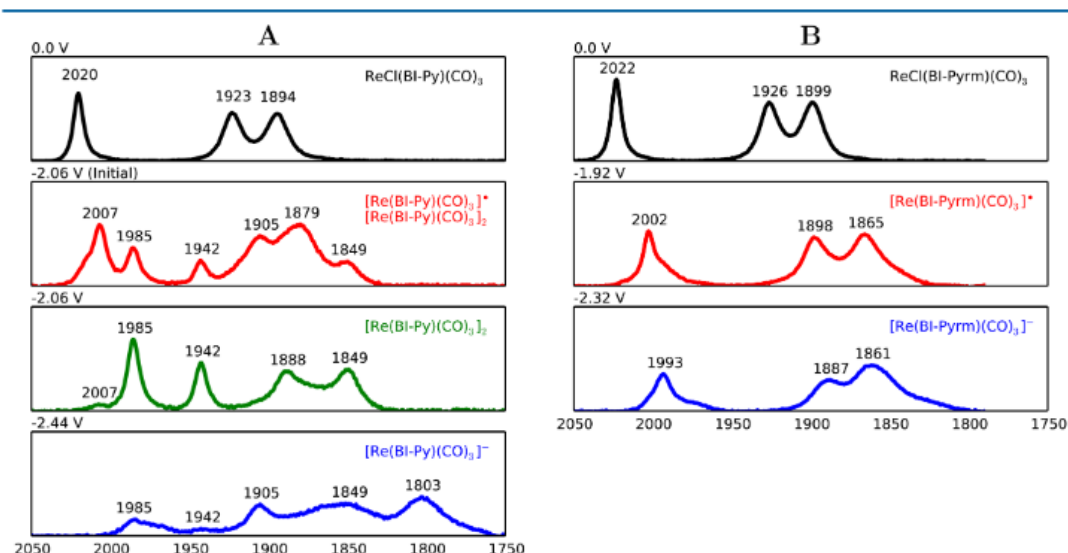


Figure 1-28. IR spectroelectrochemical study of $\text{ReCl}(\text{Bi-Py})(\text{CO})_3$ (A) and $\text{ReCl}(\text{Bi-Pyrm})(\text{CO})_3$ (B). The radical species (red), dimer (green) and anionic species (blue) are shown for both complexes.¹⁴⁵

1.3. Conclusion and outlook

This chapter briefly introduced the need for and challenges for the production of solar fuels, in particular hydrogen evolution and CO_2 reduction. A general overview of the various parameters used for quantification of the production of solar fuels was given. The use of some important sacrificial agents as electron source for photocatalytic hydrogen production and CO_2 reduction was explained and their mechanisms were summarized. Finally, a brief overview was given of the use of ruthenium complexes for the photocatalytic generation of hydrogen or CO_2 reduction with a focus on intramolecular systems. An introduction was provided on the use of rhenium complexes for photocatalytic CO_2 reduction. Some strategies to functionalise these complexes for improved catalytic properties were also described. Finally, the most important techniques in studying photocatalytic systems were described. These include among others ultrafast spectroscopic techniques such as time-resolved infrared spectroscopy, which are essential in investigating the photophysical processes that occur following light irradiation of a photocatalyst. In addition, spectroelectrochemical techniques were discussed, and some examples for both ruthenium and rhenium complexes were given in which spectroelectrochemistry was used to complement ultrafast techniques in elucidating photocatalytic pathways.

This thesis has a large focus on furthering the understanding in the photocatalytic pathways that exist for various metal complexes, in particular those systems that were developed for small molecule activation such as the hydrogen evolution reaction and CO_2 reduction. Chapter 2

describes the study of cobalt-cobalt dimer complexes that act as catalysts in the Pauson-Khand reaction. A combined approach of ultrafast spectroscopy, spectroelectrochemistry and computational methods has provided an improved understanding of the catalytic mechanism following photolysis of the complex. Chapter 3 reports the development of novel ruthenium-rhenium and ruthenium-platinum supramolecular assemblies for hydrogen evolution and CO₂ reduction. A combination of time-resolved spectroscopy and spectroelectrochemistry was used to determine part of the photocatalytic cycle for these catalysts. Chapter 4 describes the synthesis of related ruthenium-supramolecular assemblies and focusses on the ultrafast photophysical processes when these systems are anchored to a nickel oxide semiconductor surface. Finally, chapter 5 reports the development and study of a novel rhenium centre with an extended ligand backbone. The increased conjugated systems have a significant influence on the excited state properties of the complex, and wavelength dependence behaviour was observed suggesting that the desired photophysical processes only take place at higher energy radiation. UV-Vis and IR-spectroelectrochemistry further aid the assignments made in the ultrafast spectroscopic experiments.

1.4. References

- 1 Z. Z. I. (Malaysia) Hans-O. Pörtner (Germany), Debra C. Roberts (South Africa), Helen Adams (United Kingdom), Carolina Adler (Switzerland/Chile/Australia), Paulina Aldunce (Chile), Elham Ali (Egypt), Rawshan Ara Begum (Malaysia/Australia/Bangladesh), Richard Betts (United Ki, *Climate Change 2022 - Impacts, Adaptation and Vulnerability - Summary for Policymakers*, 2022.
- 2 National Oceanic and Atmospheric Administration, Global Climate Report - Annual 2020, <https://www.ncei.noaa.gov/access/monitoring/monthly-report/global/202013>.
- 3 United Nations, Sustainable Development Goals, <https://www.un.org/sustainabledevelopment/climate-change/> .
- 4 United Nations, Glasgow Climate pact, <https://unfccc.int/process-and-meetings/the-paris-agreement/the-glasgow-climate-pact-key-outcomes-from-cop26> .
- 5 United Nations, The Paris Agreement, <https://unfccc.int/process-and-meetings/the-paris-agreement>.
- 6 SEAI 2020 energy consumption in Ireland, <https://www.seai.ie/data-and-insights/seai-statistics/key-statistics/energy-use-overview/>.
- 7 National Oceanic and Atmospheric Administration, carbon dioxide levels breach another threshold at mauna loa, <https://www.noaa.gov/news/carbon-dioxide-levels-breach-another-threshold-at-mauna-loa>.

- 8 European Commision 2030 renewable energy goals,
https://energy.ec.europa.eu/topics/renewable-energy/renewable-energy-directive-targets-and-rules/renewable-energy-targets_nl.
- 9 IEA solar panel performance, <https://www.iea.org/data-and-statistics/charts/example-of-daily-load-profile-for-solar-pv-production-relative-to-electricity-demand-in-2050>.
- 10 I. Khan, M. W. Jack and J. Stephenson, *Energy and Buildings*, 2019, **194**, 232–246.
- 11 R. Gao, J. Zhu and D. Yan, *Nanoscale*, 2021, **13**, 13593–13603.
- 12 X. Xiao, L. Yang, W. Sun, Y. Chen, H. Yu, K. Li, B. Jia, L. Zhang and T. Ma, *Small*, 2022, **18**, 1–16.
- 13 S. Li, E. Li, X. An, X. Hao, Z. Jiang and G. Guan, *Nanoscale*, 2021, **13**, 12788–12817.
- 14 S. Zhang, J. Li and E. Wang, *ChemElectroChem*, 2020, **7**, 4526–4534.
- 15 W. H. Chen, J. E. Lee, S. H. Jang, S. S. Lam, G. H. Rhee, K. J. Jeon, M. Hussain and Y. K. Park, *International Journal of Energy Research*, 2022, **46**, 5467–5477.
- 16 R. Marschall, *European Journal of Inorganic Chemistry*, 2021, **2021**, 2435–2441.
- 17 A. Mazzeo, S. Santalla, C. Gaviglio, F. Doctorovich and J. Pellegrino, *Inorganica Chimica Acta*, 2020, **517**, 119950.
- 18 Y. H. Hong, Y. M. Lee, W. Nam and S. Fukuzumi, *Journal of the American Chemical Society*, 2022, **144**, 695–700.
- 19 F. J. Beck, *ACS Applied Energy Materials*, 2019, **2**, 6395–6403.
- 20 J. D. Hunt, A. Nascimento, N. Nascimento, L. W. Vieira and O. J. Romero, *Renewable and Sustainable Energy Reviews*, 2022, **160**, 112291.
- 21 T. Kawawaki, M. Kawachi, D. Yazaki, Y. Akinaga, D. Hirayama and Y. Negishi, *Nanomaterials*, 2022, **12**, 344.
- 22 C. Zhong, M. Song, Q. Zhou and X. Li, *Nano Futures*, DOI:10.1088/2399-1984/ac1db9.
- 23 P. Verma, J. J. M. Le Brocq and R. Raja, *Molecules*, DOI:10.3390/molecules26144181.
- 24 N. Manfredi, L. Boldrini and A. Abboto, 2018, 2395–2402.
- 25 C. D. Windle, H. Kumagai, M. Higashi, R. Brisse, S. Bold, B. Jusselme, M. Chavarot-kerlidou, K. Maeda, R. Abe, O. Ishitani and V. Artero, *Journal of the American Chemical Society*, 2019, **141**, 9593–9602.
- 26 F. Li, K. Fan, B. Xu, E. Gabrielsson, Q. Daniel, L. Li and L. Sun, *Journal of the American Chemical Society*, 2015, **137**, 9153–9159.
- 27 E. Giannoudis, S. Bold, C. Müller, A. Schwab, J. Bruhnke, N. Queyriaux, C. Gablin, D. Leonard, C. Saint-Pierre, D. Gasparutto, D. Aldakov, S. Kupfer, V. Artero, B. Dietzek and M. Chavarot-Kerlidou, *ACS Appl. Mater. Interfaces*, 2021, **13**, 49802–49815.

- 28 S. Kim, K. H. Kim, C. Oh, K. Zhang and J. H. Park, *Carbon Energy*, 2022, **4**, 21–44.
- 29 S. Fukuzumi, Y. M. Lee and W. Nam, *Tetrahedron*, , DOI:10.1016/j.tet.2020.131024.
- 30 S. Yoshino, T. Takayama, Y. Yamaguchi, A. Iwase and A. Kudo, *Accounts of Chemical Research*, 2022, **55**, 966–977.
- 31 E. Fujita, *Coordination Chemistry Reviews*, 1999, **185–186**, 373–384.
- 32 H. Jahangiri, J. Bennett, P. Mahjoubi, K. Wilson and S. Gu, *Catalysis Science and Technology*, 2014, **4**, 2210–2229.
- 33 R. Franke, D. Selent and A. Börner, *Chemical Reviews*, 2012, **112**, 5675–5732.
- 34 J. H. Jones, *Platinum Metals Review*, 2000, **44**, 94–105.
- 35 J. Hawecker, J.-M. Lehn and R. Ziessel, *Chemical Communications*, 1983, 536–538.
- 36 M. Bourrez, F. Molton, S. Chardon-Noblat and A. Deronzier, *Angewandte Chemie - International Edition*, 2011, **50**, 9903–9906.
- 37 C. D. Windle and R. N. Perutz, *Coordination Chemistry Reviews*, 2012, **256**, 2562–2570.
- 38 S. A. Chabolla, E. A. Dellamary, C. W. Machan, F. A. Tezcan and C. P. Kubiak, *Inorganica Chimica Acta*, 2014, **422**, 109–113.
- 39 H. Hori, F. P. A. Johnson, K. Koike, O. Ishitani and T. Ibusuki, *Journal of Photochemistry and Photobiology A: Chemistry*, 1996, **96**, 171–174.
- 40 A. J. Huckaba, E. A. Sharpe and J. H. Delcamp, *Inorganic Chemistry*, 2016, **55**, 682–690.
- 41 E. E. Benson, K. A. Grice, J. M. Smieja and C. P. Kubiak, *Polyhedron*, 2013, **58**, 229–234.
- 42 G. J. Stor, F. Hartl, J. W. M. Van Outersterp and D. J. Stufkens, *Organometallics*, 1995, **14**, 1115–1131.
- 43 E. E. Benson and C. P. Kubiak, *Chemical Communications*, 2012, **48**, 7374–7376.
- 44 J. Agarwal, T. W. Shaw, C. J. Stanton, G. F. Majetich, A. B. Bocarsly and H. F. Schaefer, *Angewandte Chemie - International Edition*, 2014, **53**, 5152–5155.
- 45 J. Bonin, M. Robert and M. Routier, *Journal of the American Chemical Society*, 2014, **136**, 16768–16771.
- 46 E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*, 2006.
- 47 S. C. Marguet, M. J. Stevenson and H. S. Shafaat, *Journal of Physical Chemistry B*, 2019, **123**, 9792–9800.
- 48 Y. Yang, J. Brückmann, W. Frey, S. Rau, M. Karnahl and S. Tschierlei, *Chemistry - A European Journal*, 2020, **26**, 17027–17034.
- 49 N. T. La Porte, J. F. Martinez, S. Chaudhuri, S. Hedström, V. S. Batista and M. R. Wasielewski, *Coordination Chemistry Reviews*, 2018, **361**, 98–119.

- 50 N. Pöldme, L. O'Reilly, I. Fletcher, J. Portoles, I. V. Sazanovich, M. Towrie, C. Long, J. G. Vos, M. T. Pryce and E. A. Gibson, *Chem. Sci.*, 2019, **10**, 99–112.
- 51 F. J. R. Cerpentier, J. Karlsson, R. Lalrempuia, M. P. Brandon, I. V. Sazanovich, G. M. Greetham, E. A. Gibson and M. T. Pryce, *Frontiers in Chemistry*, 2021, **9**, 1–13.
- 52 E. Deponti and M. Natali, *Dalton Transactions*, 2016, **45**, 9136–9147.
- 53 K. Koike, D. C. Grills, Y. Tamaki, E. Fujita, K. Okubo, Y. Yamazaki, M. Saigo, T. Mukuta, K. Onda and O. Ishitani, *Chemical Science*, 2018, **9**, 2961–2974.
- 54 R. R. Rodrigues, C. M. Boudreaux, E. T. Papish and J. H. Delcamp, *ACS Applied Energy Materials*, 2019, **2**, 37–46.
- 55 B. B. Beyene and C. H. Hung, *Sustainable Energy and Fuels*, 2018, **2**, 2036–2043.
- 56 K. Yamamoto, A. Call and K. Sakai, *Chemistry - A European Journal*, 2018, **24**, 16620–16629.
- 57 A. J. Huckaba, H. Shirley, R. W. Lamb, S. Guertin, S. Autry, H. Cheema, K. Talukdar, T. Jones, J. W. Jurss, A. Dass, N. I. Hammer, R. H. Schmehl, C. E. Webster and J. H. Delcamp, *ACS Catalysis*, 2018, **8**, 4838–4847.
- 58 N. P. Liyanage, H. A. Dulaney, A. J. Huckaba, J. W. Jurss and J. H. Delcamp, *Inorganic Chemistry*, 2016, **55**, 6085–6094.
- 59 P. Lang, R. Giereth, S. Tschierlei and M. Schwalbe, *Chemical Communications*, 2019, **55**, 600–603.
- 60 M. G. Pfeffer, T. Kowacs, M. Wächtler, J. Guthmuller, B. Dietzek, J. G. Vos and S. Rau, *Angewandte Chemie - International Edition*, 2015, **54**, 6627–6631.
- 61 Y. Pellegrin and F. Odobel, *Comptes Rendus Chimie*, 2017, **20**, 283–295.
- 62 K. Kalyanasundaram, J. Kiwi and M. Grätzel, *Helvetica Chimica Acta*, 1978, **61**, 2720–2730.
- 63 E. D. Cline, S. E. Adamson and S. Bernhard, *Inorganic Chemistry*, 2008, **47**, 10378–10388.
- 64 P. J. DeLaive, T. K. Foreman, D. G. Whitten and C. Giannotti, *Journal of the American Chemical Society*, 1980, **102**, 5627–5631.
- 65 Y. Ueda, H. Takeda, T. Yui, K. Koike, Y. Goto, S. Inagaki and O. Ishitani, *ChemSusChem*, 2015, **8**, 439–442.
- 66 X. Q. Zhu, M. T. Zhang, A. Yu, C. H. Wang and J. P. Cheng, *Journal of the American Chemical Society*, 2008, **130**, 2501–2516.
- 67 Y. Tamaki, K. Koike, T. Morimoto and O. Ishitani, *Journal of Catalysis*, 2013, **304**, 22–28.
- 68 Y. Kuramochi, O. Ishitani and H. Ishida, *Coordination Chemistry Reviews*, 2018, **373**, 333–356.

- 69 S. Kaufhold, D. Imanbaew, C. Riehn and S. Rau, *Sustainable Energy and Fuels*, 2017, **1**, 2066–2070.
- 70 D. M. Arias-Rotondo and J. K. McCusker, *Chemical Society Reviews*, 2016, **45**, 5803–5820.
- 71 N. Pöldme, L. O'Reilly, I. Fletcher, J. Portoles, I. V. Sazanovich, M. Towrie, C. Long, J. G. Vos, M. T. Pryce and E. A. Gibson, *Chemical Science*, 2019, **10**, 99–112.
- 72 D. Isakov, R. Giereth, D. Nauroozi, S. Tschierlei and S. Rau, *Inorganic Chemistry*, 2019, **58**, 12646–12653.
- 73 A. Ghosh, A. Mandoli, D. K. Kumar, N. S. Yadav, T. Ghosh, B. Jha, J. A. Thomas and A. Das, *Dalton Trans.*, 2009, 9312.
- 74 N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank and J. K. McCusker, *Science*, 1997, 275, 54–57.
- 75 B. Durham, J. V. Caspar, J. K. Nagle and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4803–4810.
- 76 V. Balzani, P. Ceroni, A. Credi and M. Venturi, *Coordination Chemistry Reviews*, 2021, **433**, 213758.
- 77 B. Durham, J. L. Walsh, C. L. Carter and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 860–865.
- 78 K. Eastham, P. A. Scattergood, D. Chu, R. Z. Boota, A. Soupart, F. Alary, I. M. Dixon, C. R. Rice, S. J. O. Hardman and P. I. P. Elliott, *Inorg. Chem.*, 2022, **61**, 19907–19924.
- 79 B. S. Howerton, D. K. Heidary and E. C. Glazer, *J. Am. Chem. Soc.*, 2012, **134**, 8324–8327.
- 80 J. Van Houten and R. J. Watts, *Inorg. Chem.*, 1978, **17**, 3381–3385.
- 81 R. Wang, J. G. Vos, R. H. Schmehl and R. Hage, *J. Am. Chem. Soc.*, 1992, **114**, 1964–1970.
- 82 M. Schulz, M. Karnahl, M. Schwalbe and J. G. Vos, *Coordination Chemistry Reviews*, 2012, **256**, 1682–1705.
- 83 M. Karnahl, C. Kuhnt, F. Ma, A. Yartsev, M. Schmitt, B. Dietzek, S. Rau and J. Popp, *ChemPhysChem*, 2011, **12**, 2101–2109.
- 84 T. Kowacs, A. Huijser, S. Rau, M. T. Pryce, D. Schlettwein, Q. Pan, L. Freitag, L. González, J. G. Vos, J. C. Falgenhauer, W. R. Browne and J. P. Korterik, *Chemical Communications*, 2016, **52**, 9371–9374.
- 85 Q. Pan, J. G. Vos, P. Lang, A. Huijser, T. Kowacs, L. O'Reilly, M. T. Pryce, S. Rau and W. R. Browne, *Inorganic Chemistry*, 2016, **55**, 2685–2690.
- 86 G. Singh Bindra, M. Schulz, A. Paul, R. Groarke, S. Soman, J. L. Inglis, W. R. Browne, M. G. Pfeffer, S. Rau, B. J. MacLean, M. T. Pryce and J. G. Vos, *Dalton Transactions*, 2012, **41**, 13050–13059.

- 87 Y. Yang, J. Brückmann, W. Frey, S. Rau, M. Karnahl and S. Tschierlei, *Chemistry - A European Journal*, 2020, **26**, 17027–17034.
- 88 A. K. Mengele, S. Kaufhold, C. Streb and S. Rau, *Dalton Transactions*, 2016, **45**, 6612–6618.
- 89 S. Rau, D. Dini, Y. Halpin, J. G. Vos and M. T. Pryce, *Dalton Transactions*, 2013, **42**, 16243.
- 90 Y. Pellegrin, L. Le Pleux, E. Blart, A. Renaud, B. Chavillon, N. Szuwarski, M. Boujtita, L. Cario, S. Jobic, D. Jacquemin and F. Odobel, *Journal of Photochemistry and Photobiology A: Chemistry*, 2011, **219**, 235–242.
- 91 R. A. Wahyuono, S. Amthor, C. Müller, S. Rau and B. Dietzek, *ChemPhotoChem*, 2020, **4**, 618–629.
- 92 N. Das, S. Bindra, A. Paul, J. G. Vos, M. Schulz and M. T. Pryce, 2017, 5330–5337.
- 93 K. Muraoka, H. Kumagai, M. Eguchi, O. Ishitani and K. Maeda, *Chemical Communications*, 2016, **52**, 7886–7889.
- 94 G. Sahara, R. Abe, M. Higashi, T. Morikawa, K. Maeda, Y. Ueda and O. Ishitani, *Chemical Communications*, 2015, **51**, 10722–10725.
- 95 J.-M. Lehn and R. Ziessel, *Proc. Natl. Acad. Sci. U.S.A.*, 1982, **79**, 701–704.
- 96 H. Takeda, K. Koike, H. Inoue and O. Ishitani, *J. Am. Chem. Soc.*, 2008, **130**, 2023–2031.
- 97 H. Takeda and O. Ishitani, *Coordination Chemistry Reviews*, 2010, **254**, 346–354.
- 98 Y. Kou, Y. Nabetani, D. Masui, T. Shimada, S. Takagi, H. Tachibana and H. Inoue, *J. Am. Chem. Soc.*, 2014, **136**, 6021–6030.
- 99 M. Schreier, P. Gao, M. T. Mayer, J. Luo, T. Moehl, M. K. Nazeeruddin, S. D. Tilley and M. Grätzel, *Energy Environ. Sci.*, 2015, **8**, 855–861.
- 100 T. W. Schneider, M. Z. Ertem, J. T. Muckerman and A. M. Angeles-Boza, *ACS Catal.*, 2016, **6**, 5473–5481.
- 101 E. E. Benson, K. A. Grice, J. M. Smieja and C. P. Kubiak, *Polyhedron*, 2013, **58**, 229–234.
- 102 M. L. Clark, P. L. Cheung, M. Lessio, E. A. Carter and C. P. Kubiak, *ACS Catal.*, 2018, **8**, 2021–2029.
- 103 P. Lang, R. Giereth, S. Tschierlei and M. Schwalbe, *Chem. Commun.*, 2019, **55**, 600–603.
- 104 R. Giereth, P. Lang, E. McQueen, X. Meißner, B. Braun-Cula, C. Marchfelder, M. Obermeier, M. Schwalbe and S. Tschierlei, *ACS Catal.*, 2021, **11**, 390–403.
- 105 R. Giereth, M. Obermeier, L. Forschner, M. Karnahl, M. Schwalbe and S. Tschierlei, *ChemPhotoChem*, 2021, **5**, 644–653.
- 106 Del Guerzo, S. Leroy, F. Fages and R. H. Schmehl, *Inorg. Chem.*, 2002, **41**, 359–366.
- 107 M. George, *Coordination Chemistry Reviews*, 1998, **177**, 201–217.

- 108 Y. F. Lee, J.R. Kirchhoff, R. M Berter, D. Gosztola, *J. Chem. Soc. Dalton. Trans.*, 1995, 3677-3682.
- 109 J. E. Yarnell, J. C. Deaton, C. E. McCusker and F. N. Castellano, *Inorg. Chem.*, 2011, **50**, 7820–7830.
- 110 A. Cannizzo, A. M. Blanco-Rodríguez, A. El Nahhas, J. Šebera, S. Záliš, A. Vlček and M. Chergui, *J. Am. Chem. Soc.*, 2008, **130**, 8967–8974.
- 111 A. Gabrielsson, M. Busby, P. Matousek, M. Towrie, E. Hevia, L. Cuesta, J. Perez, S. Záliš and A. Vlček, *Inorg. Chem.*, 2006, **45**, 9789–9797.
- 112 B. D. Rossenaar, D. J. Stufkens and A. Vlc, .
- 113 A. M. Blanco-Rodríguez, H. Kvapilová, J. Sýkora, M. Towrie, C. Nervi, G. Volpi, S. Záliš and A. Vlček, *J. Am. Chem. Soc.*, 2014, **136**, 5963–5973.
- 114 G. E. Shillito, D. Preston, P. Traber, J. Steinmetzer, C. J. McAdam, J. D. Crowley, P. Wagner, S. Kupfer and K. C. Gordon, *Inorg. Chem.*, 2020, **59**, 6736–6746.
- 115 K. Koike, H. Hori, M. Ishizuka, J. R. Westwell, K. Takeuchi, T. Ibusuki, K. Enjouji, H. Konno, K. Sakamoto and O. Ishitani, *Organometallics*, 1997, **16**, 5724–5729.
- 116 Y. Ono, *AJAC*, 2014, **2**, 74.
- 117 R. J. Fernández-Terán, E. Sucre-Rosales, L. Echevarria and F. E. Hernández, *Phys. Chem. Chem. Phys.*, 2022, **24**, 28069–28079.
- 118 S. K. Lee, Y. Zu, A. Herrmann, Y. Geerts, K. Müllen and A. J. Bard, *J. Am. Chem. Soc.*, 1999, **121**, 3513–3520.
- 119 M. R. Waterland, K. C. Gordon, J. J. McGarvey and P. M. Jayaweera, .
- 120 M. K. Kuimova, W. Z. Alsindi, A. J. Blake, E. S. Davies, D. J. Lampus, P. Matousek, J. McMaster, A. W. Parker, M. Towrie, X.-Z. Sun, C. Wilson and M. W. George, *Inorg. Chem.*, 2008, **47**, 9857–9869.
- 121 C. B. Larsen, H. van der Salm, C. A. Clark, A. B. S. Elliott, M. G. Fraser, R. Horvath, N. T. Lucas, X.-Z. Sun, M. W. George and K. C. Gordon, *Inorg. Chem.*, 2014, **53**, 1339–1354.
- 122 R. Fernández-Terán and L. Sévery, *Inorg. Chem.*, 2021, **60**, 1334–1343.
- 123 O. Hiltner, F. J. Boch, L. Brewitz, P. Härter, M. Drees, E. Herdtweck, W. A. Herrmann and F. E. Kühn, *Eur. J. Inorg. Chem.*, 2010, **2010**, 5284–5293.
- 124 A. Maurin, C.-O. Ng, L. Chen, T.-C. Lau, M. Robert and C.-C. Ko, *Dalton Trans.*, 2016, **45**, 14524–14529.
- 125 E. L. Rosen, C. D. Varnado, A. G. Tennyson, D. M. Khramov, J. W. Kamplain, D. H. Sung, P. T. Cresswell, V. M. Lynch and C. W. Bielawski, *Organometallics*, 2009, **28**, 6695–6706.

- 126 C. J. Stanton, C. W. Machan, J. E. Vandezande, T. Jin, G. F. Majetich, H. F. Schaefer, C. P. Kubiak, G. Li and J. Agarwal, *Inorg. Chem.*, 2016, **55**, 3136–3144.
- 127 A. J. Huckaba, E. A. Sharpe and J. H. Delcamp, *Inorg. Chem.*, 2016, **55**, 682–690.
- 128 C. Carpenter, P. Brogdon, L. McNamara, G. Tschumper, N. Hammer and J. Delcamp, *Inorganics*, 2018, **6**, 22.
- 129 D. A. Kurtz, K. R. Brereton, K. P. Ruoff, H. M. Tang, G. A. N. Felton, A. J. M. Miller and J. L. Dempsey, *Inorg. Chem.*, 2018, **57**, 5389–5399.
- 130 D. Stufkens, *Coordination Chemistry Reviews*, 1998, **177**, 127–179.
- 131 G. E. Shillito, T. B. J. Hall, D. Preston, P. Traber, L. Wu, K. E. A. Reynolds, R. Horvath, X. Z. Sun, N. T. Lucas, J. D. Crowley, M. W. George, S. Kupfer and K. C. Gordon, *J. Am. Chem. Soc.*, 2018, **140**, 4534–4542.
- 132 J. S. O'Neill, L. Kearney, M. P. Brandon and M. T. Pryce, *Coordination Chemistry Reviews*, 2022, **467**, 214599.
- 133 G. M. Greetham, P. Burgos, C. Qian, I. P. Clark, P. S. Codd, R. C. Farrow, M. W. George, M. Kogimtzis, P. Matousek, A. W. Parker, M. R. Pollard, D. A. Robinson, X. Zhi-Jun and M. Towrie, *Applied Spectroscopy*, 2010, **64**, 1311–1319.
- 134 M. Wächtler, J. Guthmüller, L. González and B. Dietzek, *Coordination Chemistry Reviews*, 2012, **256**, 1479–1508.
- 135 S. Tschierlei, M. Presselt, C. Kuhnt, A. Yartsev, T. Pascher, V. Sundström, M. Karnahl, M. Schwalbe, B. Schäfer, S. Rau, M. Schmitt, B. Dietzek and J. Popp, *Chemistry - A European Journal*, 2009, **15**, 7678–7688.
- 136 G. Singh Bindra, M. Schulz, A. Paul, R. Groarke, S. Soman, J. L. Inglis, W. R. Browne, M. G. Pfeffer, S. Rau, B. J. MacLean, M. T. Pryce and J. G. Vos, *Dalton Transactions*, 2012, **41**, 13050–13059.
- 137 L. Zedler, A. K. Mengele, K. M. Ziems, Y. Zhang, M. Wächtler, S. Gräfe, T. Pascher, S. Rau, S. Kupfer and B. Dietzek, *Angewandte Chemie International Edition*, 2019, **58**, 13140–13148.
- 138 J. M. Butler, M. W. George, J. R. Schoonover, D. M. Dattelbaum and T. J. Meyer, *Coordination Chemistry Reviews*, 2007, **251**, 492–514.
- 139 J. Tory, G. Gobaille-Shaw, A. M. Chippindale and F. Hartl, *Journal of Organometallic Chemistry*, 2014, **760**, 30–41.
- 140 Y. Zhang, S. Kupfer, L. Zedler, J. Schindler, T. Bocklitz, J. Guthmüller, S. Rau and B. Dietzek, *Physical Chemistry Chemical Physics*, 2015, **17**, 29637–29646.
- 141 Y. Zhang, L. Zedler, M. Karnahl and B. Dietzek, *Physical Chemistry Chemical Physics*, 2019, **21**, 10716–10725.

- 142 F. W. Vergeer, C. J. Kleverlaan, P. Matousek, M. Towrie, D. J. Stufkens and F. Hartl, *Inorg. Chem.*, 2005, **44**, 1319–1331.
- 143 D. C. Grills, J. A. Farrington, B. H. Layne, S. V. Lyman, B. A. Mello, J. M. Preses and J. F. Wishart, *J. Am. Chem. Soc.*, 2014, **136**, 5563–5566.
- 144 Y. Zhang, P. Traber, L. Zedler, S. Kupfer, S. Gräfe, M. Schulz, W. Frey, M. Karnahl and B. Dietzek, *Phys. Chem. Chem. Phys.*, 2018, **20**, 24843–24857.
- 145 C. J. Stanton, C. W. Machan, J. E. Vandezande, T. Jin, G. F. Majetich, H. F. Schaefer, C. P. Kubiak, G. Li and J. Agarwal, *Inorganic Chemistry*, 2016, **55**, 3136–3144.
- 146 J. O. Taylor, R. D. Leavey and F. Hartl, *ChemElectroChem*, 2018, **5**, 3155–3161.
- 147 F. P. A. Johnson, M. W. George, F. Hartl and J. J. Turner, *Organometallics*, 1996, **15**, 3374–3387.
- 148 F. Hartl and A. Vlček, *Inorganic Chemistry*, 1992, **31**, 2869–2876.

Chapter 2: Photochemical or Electrochemical Bond Breaking – Exploring the Chemistry of $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ Complexes using Time-Resolved Infrared Spectroscopy, Spectro- electrochemical and Density Functional Methods

In Chapter 2, the photochemistry of $(\mu_2\text{-CRCR}')\text{Co}_2(\text{CO})_6$ complexes ($R=\text{pyrenyl}$, $R'=\text{H}$; $R=\text{pyrenyl}$, $R'=\text{ferrocenyl}$; $R=\text{ferrocenyl}$, $R'=\text{H}$) was investigated by ps-time-resolved infrared spectroscopy at room temperature in dichloromethane solution. The main focus of these studies was to determine the primary photoprocess relevant to the light assisted Pauson-Khand reaction. These studies were supported by spectro-electrochemical investigations and density functional calculations which suggest that the primary process to initiate the Pauson-Khand reaction involves a homolytic cleavage of the Co-Co bond forming a high-spin diradical species and not CO-loss as previously thought. This chapter introduces spectroelectrochemistry and time-resolved infrared spectroscopy, two techniques that are widely applied within this thesis.

J. P. Manton, F. J. R. Cerpentier, E. C. Harvey, I. P. Clark, G. M. Greetham, C. Long, M. T. Pryce.
Dalton Trans., **2019**, 48, 14642-14652.

2.1. Introduction

Soon after the emergence of organometallic chemistry as a discrete topic in chemistry, photochemical methods were used to probe the unique properties of this molecular class.^{1,2} In particular the photoinduced heterolytic cleavage of metal-ligand bonds, for example a metal carbonyl bond, where the bonding electrons leave with the ligand, provides the opportunity to investigate the chemistry of highly electron deficient and reactive metal complex fragments. The newly developed time-resolved (flash photolysis)³ and low-temperature techniques such as matrix isolation⁴ were ideally suited to study these systems. Homolytic cleavage, of a bond to produce radical species, is also an important process in many catalytic systems including polymerisations.^{5,6}

The Group 6 metal hexacarbonyl complexes, and in particular $\text{Cr}(\text{CO})_6$, emerged as a prototypical system, mainly because of the exceptionally high quantum yield (Φ_{CO}) for CO loss, and also the fact that the photochemical reaction was observed even at very low temperatures (10 K). In addition, the spectroscopic properties of the photoproducts $\text{Cr}(\text{CO})_5$ and molecular CO are quite distinct from those of the starting complex, making detection and identification of the photoproduct relatively unambiguous. The pioneering work of Turner and Perutz⁷⁻¹⁴ who investigated the low-temperature matrix photochemistry of $\text{Cr}(\text{CO})_6$ in a variety of matrix media revealed two important features: firstly the photochemical reaction occurred under conditions where the thermal energy is scarce, suggesting that the photo-expulsion occurs from an excited state which presents an accelerating potential with respect to CO-loss. Secondly the resulting 16-electron $\text{Cr}(\text{CO})_5$ fragment interacts with the isolating medium, indicating exceptional reactivity.¹² These two features were subsequently confirmed by time-resolved spectroscopic techniques which showed that photoinduced CO-loss from $\text{Cr}(\text{CO})_6$ occurs very rapidly, on the timescale of molecular vibrations, a so-called ultrafast process.¹⁵⁻¹⁸ The $\text{Cr}(\text{CO})_5$ photofragment is also very reactive interacting even with alkanes, hitherto considered chemically inert.¹⁹ Thus a general consensus developed that photoinduced CO-loss from all *homoleptic* metal carbonyl complexes are ultrafast.

More recently the development of *ab initio* quantum chemical methods provided a theoretical basis to explain the ultrafast nature of CO-loss from homoleptic metal carbonyl complexes. Both wavefunctional^{20,21} and Density Functional Theory (DFT)^{22,23} were used to model the development of the lowest energy singlet excited state of $\text{Cr}(\text{CO})_6$ along productive vibrational modes, which explained both the high quantum yield and the time-scale of the CO-loss

processes. Of these methods, DFT is the more computationally reasonable for most organometallic systems. The application of Time-Dependent Density Functional Theory (TDDFT) to heteroleptic metal carbonyl complexes such as (η^6 -benzene)Cr(CO)₃, revealed “bound” excited states on the singlet surface.^{24,25} These excited states can be detected using Time-Resolved InfraRed spectroscopy with pico-second time-resolution (ps-TRIR) as they exist for many tens of pico-seconds. CO-loss is achieved by traversing a small thermal barrier, a process called “arrested” CO-loss. The timescale of CO-loss can therefore range from tens of femto-seconds to hundreds of pico-seconds depending on the electronic structure of accessible excited states, and CO-loss can also compete with the formation of electronic excited states.²⁶

There are many organometallic systems where the role of light in promoting chemical process remains poorly understood. One of these is the Pauson-Khand Reaction (PKR) which involves a [2+2+1] cycloaddition of an alkene, an alkyne and CO to form a cyclopentenone.²⁷ It is generally accepted that the reaction mechanism involves the initial reaction of the reagent alkyne with Co₂(CO)₈, to form (μ_2 -alkyne)Co₂(CO)₆. The Co₂(CO)₆ fragment supplies the CO required in the subsequent cyclisation reaction. Typically, the PKR is initiated thermally,²⁸ however some examples of visible light/thermal or light-assisted reactions are known in which the reaction mixture is irradiated with little regard to which step in the overall reaction is promoted by photon absorption. There are few reports of purely light-driven PKR.²⁹ An intriguing feature of these investigations, is the fact that experiments have revealed little about the chemical or indeed photochemical behaviour of (μ_2 -alkyne)Co₂(CO)₆ complexes. Once the (μ_2 -alkyne)Co₂(CO)₆ complex is formed it proceeds to product without trace of observable intermediates apart from one example where a pendant alkene is present on the alkyne ligand.^{30,31} Matrix isolation experiments indicated that CO-loss occurs upon photolysis but at photon energies far in excess of those used in the light-assisted PKR.^{32,33} Light activation of the PKR can be useful as it facilitates the synthesis of thermally sensitive cyclopentenones.³⁴ Consequently a better understanding of the electronic structure of the (μ_2 -alkyne)Co₂(CO)₆ complexes and accessible excited states is important.

Simple wave functional methods such as Hartree-Fock calculations cannot accurately model the ground state electronic structure of (μ_2 -alkyne)Co₂(CO)₆ complexes.^{35,36} Multi-configuration methods suggest that the ground state of (μ_2 -alkyne)Co₂(CO)₆ complexes are best described as singlet (or low-spin) diradical species with less than optimal overlap of the cobalt d orbitals involved in the Co-Co bond. This results in a so-called “bent” Co-Co bond where the volume of maximum electron density does not lie on the vector joining the two cobalt nuclei. However multi-configuration calculations are computationally expensive, and their use quickly becomes

unrealistic when many calculations are required to model excited state behaviour along specific reaction coordinates. Consequently, both Density Functional (BLYP)^{37,38} or Hybrid Density Functional (B3LYP)³⁹ methods can be used to provide reasonable models for the bonding in this complex at moderate computational cost. These methods when coupled with Time Dependent (TD)⁴⁰⁻⁴⁶ calculations can then model the dynamic behaviour of the ground and excited states along chosen reaction coordinates. Energy profiles which steadily reduce are described as “unbound” states with respect to the chosen reaction coordinate, while those exhibiting a local minimum are dubbed “bound” states.

In addition to quantum chemical calculations, we have used time-resolved spectroscopic techniques to gain a fuller understanding of the mechanism of light-assisted PKR. Three alkyne-substituted complexes were synthesized as represented in Figure 2-1. In addition, spectro-electrochemical methods have been used to determine the stability of the oxidized and reduced complexes.

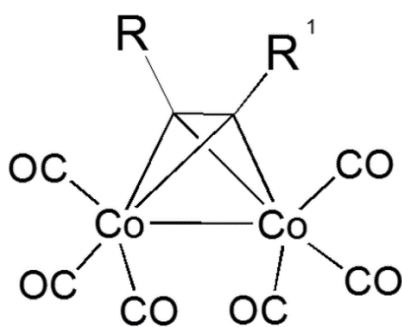


Figure 2-1. The $(\mu_2\text{-}R,R'\text{-alkyne})\text{Co}_2(\text{CO})_6$ complexes in this investigation, **1** $R=\text{pyrenyl}, R'=\text{H}$; **2** $R=\text{pyrenyl}, R'=\text{ferrocenyl}$; **3** $R=\text{ferrocenyl}, R'=\text{H}$

2.2. Results

As a starting point, the UV/visible characteristics of the unsubstituted $(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6$ complex were modelled using DFT and TDDFT methods. Dichloromethane (DCM) was selected as solvent for most calculations.⁴⁷ The lowest energy, and very weak transition centred at 500 nm, consists mainly of a cobalt-centred σ to σ^* transition of the Co-Co bond with minor contributions from a Co to CO(axial) charge-transfer, forming the lowest energy singlet Excited State (ES1).^{33,48} By following this excited state along the axial CO-loss reaction coordinate it is clear that ES1 is bound with respect to this reaction (see supporting information Figure SA1). The second singlet excited state (ES2) is mainly ligand-field in character and is unbound with respect to axial CO loss, but this excited state cannot be directly populated from the ground-state as the transition is formally symmetry forbidden. The more intense absorption at 350 nm (ES8) is also mainly Co-based but with greater contributions from a Co to alkyne charge-transfer transition which has

the effect of increasing the oscillator strength. This excited state is bound with respect to axial CO loss but offers the possibility of crossing to the lower ligand field state in a non-adiabatic description which can result in axial CO-loss. This process will be ultrafast as it is achieved by population of an excited state which presents an accelerating energy profile towards CO-loss but the efficiency of the process is low because of crossing to lower energy bound excited states in particular ES1. Examination of the energetics of equatorial CO-loss confirmed that no optically accessible excited states lead to this reaction. This conclusion is consistent with published results where only axial CO loss was observed following photolysis.^{32,33}

The effect of varying the Co-Co distance on the excited state energies of $(\mu_2\text{-HCCH})\text{Co}_2(\text{CO})_6$ was then calculated to determine if population of the accessible singlet excited states result in a lengthening of the Co-Co bond. The results of these calculations are presented in Figure 2-2 and show that population of the lowest energy singlet state will tend to lengthen the Cobalt-Cobalt distance to 2.56397 Å (downward arrow in Figure 2-2(a)).

The experimental and simulated UV/visible spectra of the alkyne-substituted complexes which are the subject of this study were then investigated. The UV/visible spectra of **1**, **2**, and **3** complexes are presented as Figure SA2 with extinction parameters in Table SI1 of the supporting information.

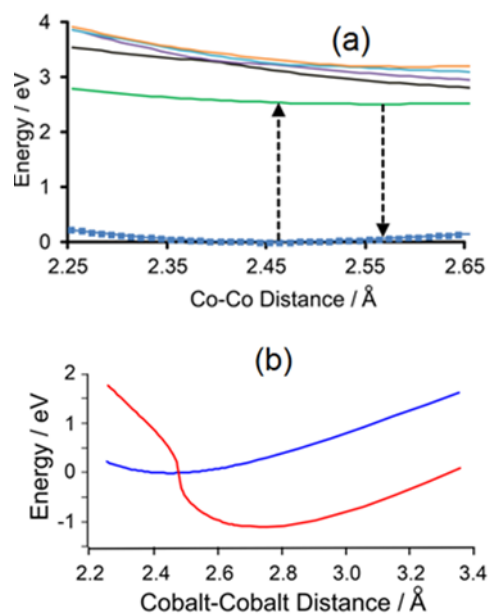


Figure 2-2. (a) The adiabatic behaviour of the five lowest energy singlet excited states relative to the singlet ground-state energy (blue) as the Co-Co distance is varied in $(\mu_2\text{-HCCH})\text{Co}_2(\text{CO})_6$. The data interval is indicated by the data markers on the singlet ground-state profile but are omitted from the excited state profiles for clarity, (b) The adiabatic behaviour of the lowest energy triplet excited state (red) and the singlet ground state (blue) indicating the accelerating profile of the lowest energy triplet excited state towards a high spin di-radical species (red plot).

Both pyrenyl-substituted complexes (**1** and **2**) exhibit an absorbance maximum close to 400 nm, the excitation wavelength used in the ps-TRIR experiments. In the case of **1** there is excellent agreement between the simulated and experimental spectrum (Figure 2-3) particularly in terms of the lowest energy absorption maximum.

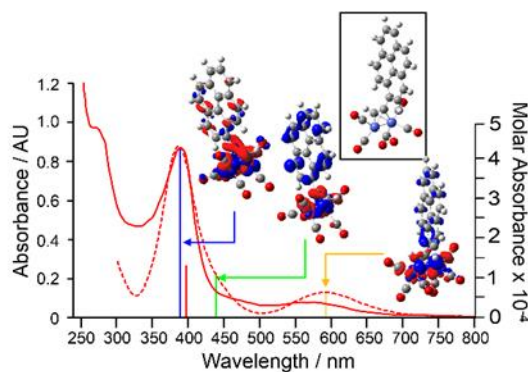


Figure 2-3. The simulated (dashed) and experimental (solid line) spectra of **1** in dichloromethane (1.2×10^{-2} M) with the principal vertical transition energies and associated electron density difference maps for the resulting excited states, blue volumes indicating regions where the electron density is lower in the excited state compared to the ground-state, and red volumes regions where the electron density is greater in the excited state compared to the ground state, the inset is a ball-and-stick diagram for **1** showing the orientation of the molecule.

This is reassuring, as it confirms that the constituent transitions, derived from the TDDFT calculations, are realistic descriptions of the optically accessible excited states.

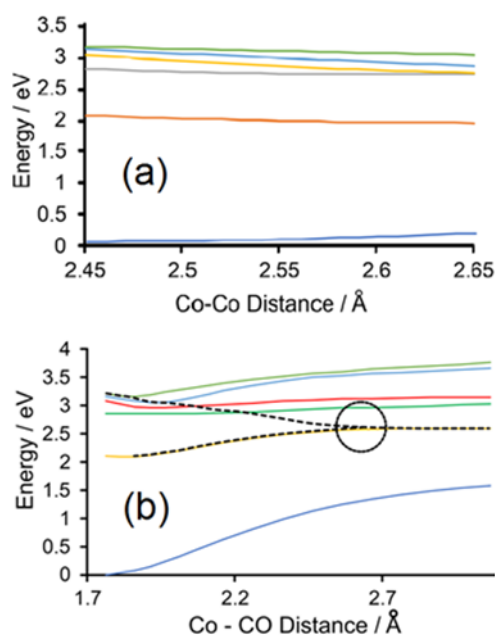


Figure 2-4. (a) The behaviour of ES1 to ES5 for $(\mu_2\text{-1-pyrenylethyne})\text{Co}_2(\text{CO})_6$ (**1**) along the Cobalt-Cobalt stretch reaction coordinate showing the non-bonding character of all low-lying singlet excited states; (b) the behaviour of the five lowest energy singlet excited states with respect to the axial Co-CO bond length, the dashed curve represents the non-adiabatic description showing the crossing to lower states, with the branching region highlighted with a circle.

The lowest energy absorption at approximately 590 nm is predominantly pyrene to cobalt charge-transfer in character with some electron density moving to the carbonyl ligands but also with substantial σ to σ^* character. A similar description applies to the absorption at 433 nm.

The intense feature at 387 nm is mainly a ligand-field transition which is non-bonding with respect to the Co-Co interaction (Figure 2-4(a)), but ES3, ES4 and ES5 singlet excited states present an accelerating profile towards axial CO loss (Figure 4(b)). This process must compete with crossings to lower energy bound states reducing the efficiency of the CO-loss process (see dashed curve in Figure 2-4(b)). These calculations suggest that population of, for example, ES5 will result in ultrafast axial CO-loss but will also populate lower energy excited states.

Turning to the ferrocenyl-substituted derivative (**3**), the simulated UV/vis spectrum is compared to the experimental spectrum in Figure 2-5. Again, the simulated spectrum agrees well with the experimental one despite the weakness of the features in the visible region. The lowest energy transitions can be classified as ferrocenyl to cobalt carbonyl charge-transfer in nature and have small oscillator strengths, i.e. they are very weak. Plotting the behaviour of these states along the Co-CO (axial) reaction coordinate, (supporting information Figure SA3) confirmed that these states are bound with respect to axial CO-loss. It is only when the 10th excited state is reached that an accelerating profile towards CO-loss is predicted. This state must cross nine lower energy states in progressing to CO-loss and each of these lower energy states are bound with respect to CO-loss. Consequently, the ferrocenyl derivative is not a good candidate for ultrafast CO loss and this reaction is likely to be very inefficient. This is very surprising given the observation of high yielding visible light induced PKR when **3** is irradiated in the presence of excess norbornene. This calls into question whether the proposal that photoinduced CO-loss is the primary step in the PKR is correct.²⁹

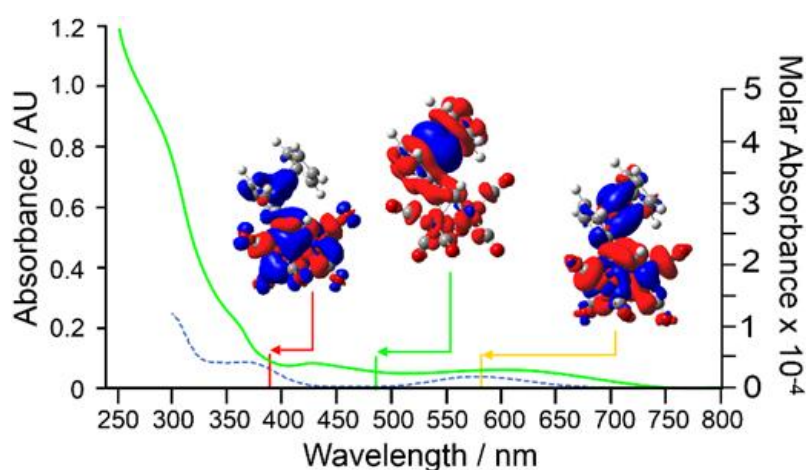


Figure 2-5. A comparison of the simulated and experimental UV/vis spectrum of (μ_2 -1-ferrocenylethyne) $\text{Co}_2(\text{CO})_6$ (**3**) (1.6×10^{-2} M) showing the weak visible absorptions at 580 (yellow transition) and 480 nm (green transition) which are mainly iron to $\text{Co}_2(\text{CO})_6$ charge transfer in character and a mainly Cobalt-based ligand field transition at 380 nm (red transition) corresponding to population of ES10.

2.2.1. ps-TRIR studies

Quantum chemical calculations described above indicated that the most likely system to observe photoinduced CO loss was the pyrene substituted complex **1**. This complex absorbs strongly at excitation wavelength used in the ps-TRIR apparatus ($\lambda_{\text{exc.}} = 400 \text{ nm}$) and progression of the accessible excited states (Figure 2-4(b)) would lead, at least in part, to ultrafast CO loss. The spectral changes observed in the ν_{CO} region following pulsed photolysis of **1** in hexane solution at 19°C are presented in Figure 2-6 (IR spectral features are presented in the supporting information Table SA2). These are presented as difference spectra (Δ absorbance) where the negative absorbances indicate bleaching of the parent hexacarbonyl absorptions following excitation. Product bands are evident as positive absorbances, and the spectrum measured within 7.64 ps of the excitation pulse exhibits three broad features, each approximately 10 cm^{-1} to the low energy side of each parent band. Their broadness, relative to the width of the parent bands, suggesting excess vibrational energy which is dissipated in approximately 10 ps. The features decay over the subsequent 40 ps with concomitant recovery of the parent absorptions, as indicated by the arrows in Figure 6. It is reasonable to assign the three broad product features to a “hot” species but whether this species is electronically excited or in the ground-state will be discussed later. A residual bleach of the parent features persists for over 1 ns, and the largest residual bleach is observed for the 2053 cm^{-1} feature at approximately 14% of the initial bleach. In addition, persistent ($> 500 \text{ ps}$) features are evident at 1975, 2005, and 2071 cm^{-1} and a further band at 2028 cm^{-1} is implied because the intensities of the bleach signals do not correspond to the ν_{CO} band intensities of the parent. These new features are indicated by asterisks in the inset in Figure 2-6, and agree well with the calculated ν_{CO} positions (B3LYP/6-31G(d)) of the CO-loss species, $(\mu_2\text{-pyrenylethyne})\text{Co}_2(\text{CO})_5$ (the red spectrum) and the band positions observed in matrix isolation studies for the initially produced axial CO-loss species in related systems.^{32,33} The ps-TRIR data were analysed using a global analysis approach, and this confirmed the presence of the CO-loss features in the early timescale data (blue spectrum in the insert of Figure 2-6). Excitation of **1** at 400 nm produces both a hot ground-state species with a lifetime of 40 ps and a CO-loss species formed in an ultrafast process.

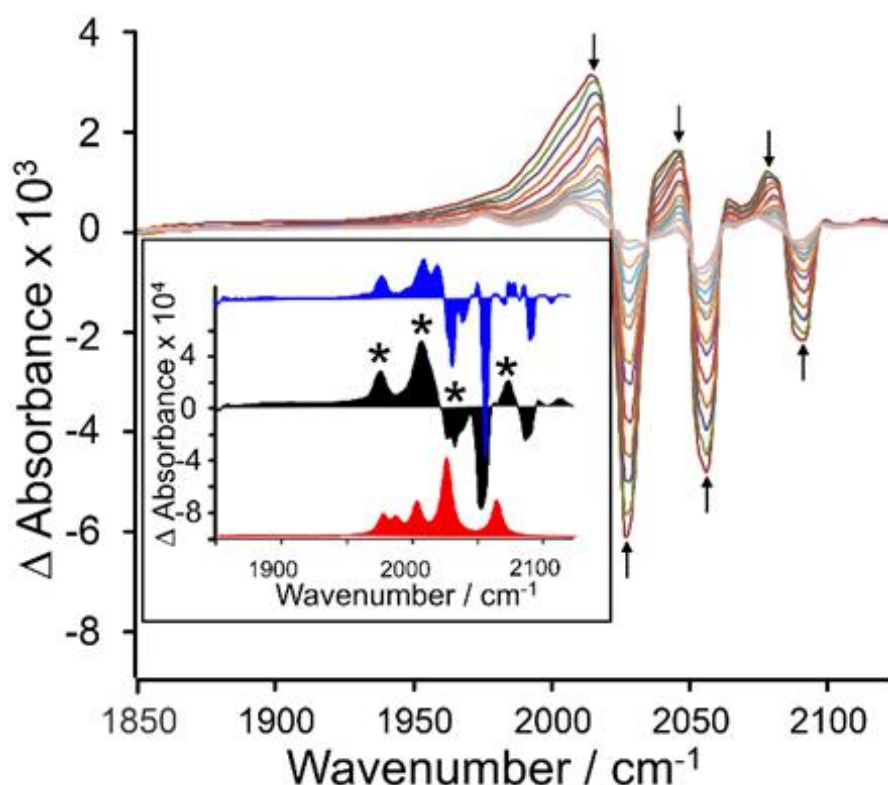


Figure 2-6. The ps-TRIR spectra recorded following pulsed photolysis of **1** ($\lambda_{\text{exc.}} = 400$ nm) in hexane solution at 19 °C, spectra were recorded at delay times of 7.64, 11.8, 16.22, 25.98, 37.34, 50.9, 67.72, 89.94, 104.42, 122.68, 147.46, 186.16, 280.0 and 500.0 ps after the excitation pulse with arrows indicating the time-dependent behaviour of the features, and the insert shows the spectrum obtained at 500 ps with an expanded Δ absorbance scale with persistent features marked with asterisks at 1975, 2005, ca 2028, and 2071 cm^{-1} (black spectrum in insert), the lower red spectrum, in both the main plot and in the inset is the calculated spectrum at the B3LYP/6-31g(d) level of **1** and the CO-loss species (μ_2 -pyrenylethyne) $\text{Co}_2(\text{CO})_5$ respectively, while the blue spectrum was extracted by global analysis of the time-dependent data (see text).

A ps-TRIR study of the spectral changes observed following 400 nm excitation of **3** showed similar features to those obtained for **1**, however features which could be associated with the CO-loss product are considerably weaker (Figure 2-7). The residual depletion of the 2050 cm^{-1} band, measured 500 ps after the excitation pulse, is approximately 5% of the initial depletion. This represents the maximum yield of any CO-loss species. It is clear therefore that photoinduced CO-loss from **3** is less efficient than in the case of **1**. Global analysis of the spectral data revealed a long-lived species which is formed within the excitation pulse (blue spectrum in the inset in Figure 2-7) which has characteristics like the CO-loss species obtained following photolysis of **1**, for example the band indicated with an asterisk. However, the global

analysis indicated that the lifetime of this species was considerably shorter than the lifetime of the CO-loss species obtained from species **1** (220 ps vs 1200 ps supporting information Figure SA3). In addition, the calculated IR spectrum of the CO-loss species at its optimum geometry (red spectrum in the inset in Figure 2-7) shows the presence of a bridging carbonyl band just below 1900 cm^{-1} which is not observed in the ps-TRIR data. The green spectrum in the inset in Figure 2-7 shows the calculated spectrum of the CO-loss species at a local minimum on the potential energy hypersurface close to the initially produced CO-loss species, and this spectrum correlates well with both the final spectrum obtained in the ps-TRIR experiment (500 ps after excitation, black spectrum) and the initially produced component extracted from the global analysis treatment of the ps-TRIR data (blue spectrum). The features indicated with asterisks are common to all three spectra. This suggests that the initially produced CO-loss species may then isomerise over the subsequent 200 ps but it is not clear from the ps-TRIR data what is the ultimate product of this isomerisation.

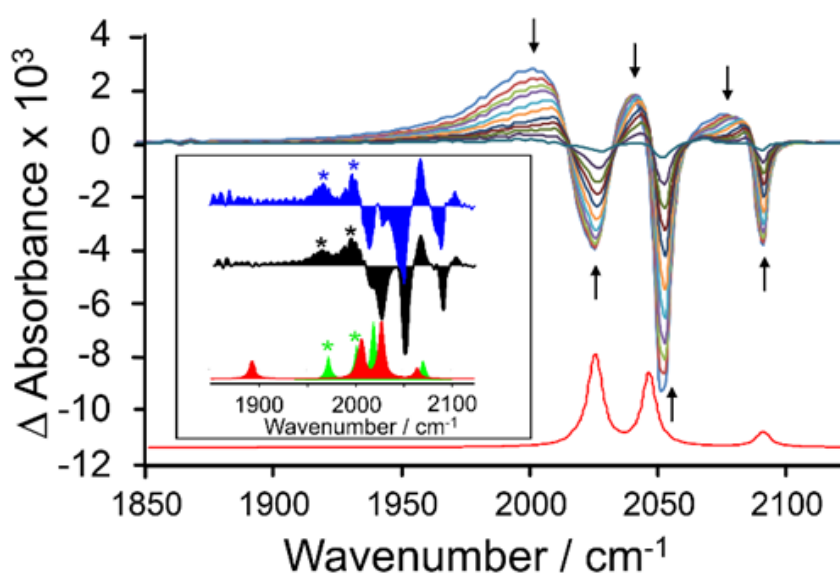


Figure 2-7. The ps-TRIR spectra recorded following pulsed photolysis of **3** ($\lambda_{\text{exc.}} = 400 \text{ nm}$) in hexane solution at 19°C , spectra were recorded at delay times of 7.64, 11.8, 16.22, 20.92, 31.42, 43.78, 67.72, 89.94, 122.68, 186.16, and 500 ps after the excitation pulse with arrows indicating the time-dependent behaviour of the features, the insert shows the final spectrum obtained 500 ps after the excitation pulse (black) the decay adjusted spectrum of the long-lived species (blue) and the calculated spectrum (red) of the optimized CO-loss species and (green) the calculated spectrum of the initially produced CO-loss species.

The calculated structure indicates an asymmetric coordination of the alkyne ligand to the two Co centres. Bitterwolf and co-workers suggested a structural rearrangement of the carbonyl ligands from the initially produced axial CO-loss species to the equatorial CO-loss to explain the spectroscopic changes observed upon annealing a Nujol matrix to 140 K.³³ It is clear from the

global analysis data that the axial CO-loss species produced from **1** and especially **3** are labile (Figure SA4). However, in no case did the calculations indicate the formation of a CO-loss photoproduct in which the vacant coordination site is in the equatorial position. The dominant product following 400 nm photolysis of **3** is a vibrationally excited species and that the very low yield of the CO-loss species could only have a minor role in promoting the PKR.

2.2.2. Spectro-electrochemical Studies

Spectro electrochemistry with monitoring in both the IR and UV-Vis regions was used to detect products that may form following either reduction or oxidation of the complexes. These studies were undertaken to gauge the stability of these complexes with respect to a one electron change to the overall configuration. The studies were performed at applied potentials of -1.5 V (vs Ag/Ag⁺) for complexes **1**, **2**, and **3** where the radical anion is formed. Two oxidising potentials were applied, a 1 V potential for complexes **2** and **3** to observe the oxidation of the ferrocenyl substituent, and at 1.7 V for **1**, **2**, and **3** where the radical cations based on the cobalt centres are formed.

2.2.2.1. IR Spectro-electrochemistry

When a potential of -1.5 V was applied to solutions of complexes **1**, **2**, or **3**, a decrease in the absorbance of all cobalt-carbonyl ν_{CO} bands (down arrows in Figure 2-8(a)) was observed. A broad feature at 1900 cm^{-1} is produced indicating the formation of $\text{Co}(\text{CO})_4^-$ as the only observable metal carbonyl fragment.⁴⁹ Evidence for the release of the alkyne ligand was obtained by monitoring in the UV/vis region (Figure 2-8(b)) where the structured features of the free ligand are produced (up arrows).

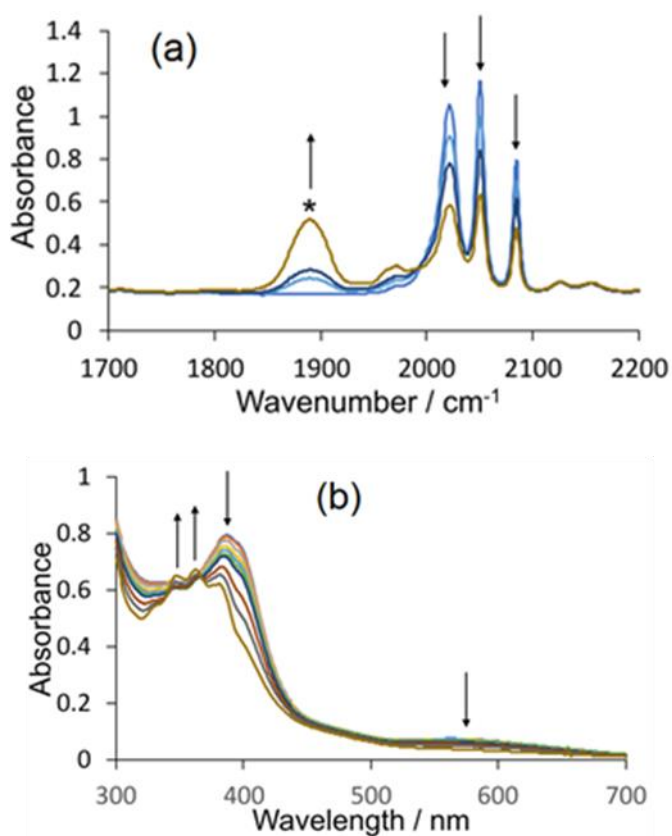


Figure 2-8. (a) the spectral changes observed in the IR region following reduction (-1.5 V) of **2** in DCM showing the loss of metal carbonyl features (down arrows) and formation of $\text{Co}(\text{CO})_4^-$ (* up arrow); (b) The UV/vis absorption changes observed following reduction (-1.5 V) of **2** in DCM showing the decay of **2** (down arrows) and the liberation of uncoordinated pyrene ligand (up arrows).

At an applied potential of 1 V, **1** appeared to be stable because this potential was insufficient to form the cobalt-centred radical cation. In the case of complexes **2** or **3**, both of which contain a ferrocene moiety, a decrease in the parent bands in the carbonyl region was observed with concomitant formation of new bands at 2097, 2065, and circa 2040 cm^{-1} for **2** and 2033 and 2002 cm^{-1} for **3** (Figure 2-9) The product bands appear at slightly higher wavenumbers to those of the parent cobalt-carbonyl complexes and these new stretching vibrations result from the oxidation of the ferrocenyl substituent ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$).

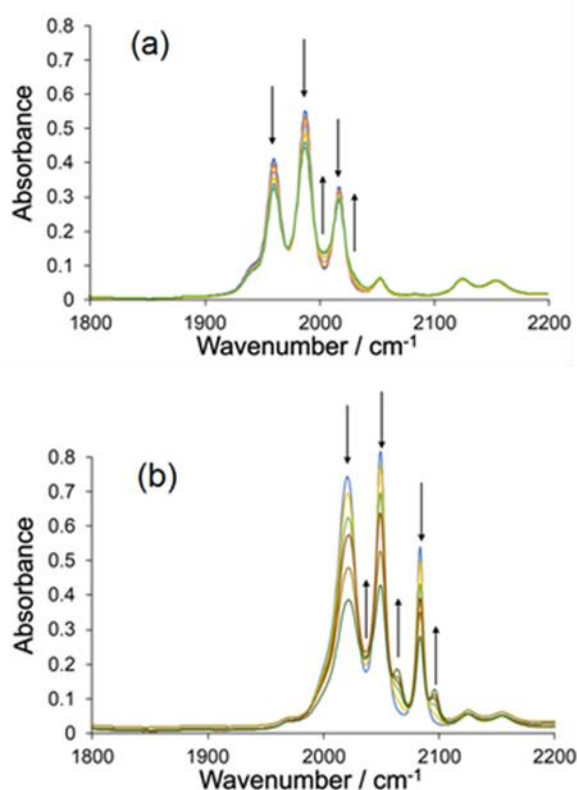


Figure 2-9. The IR spectral changes following electrolysis at 1 V for (a) **1** and (b) **2** in DCM solution.

It would appear, at least qualitatively, that these complexes are more stable with respect to oxidation than reduction. Reduction of all complexes results in ligand loss and the formation of inorganic cobalt species and free alkyne ligand. The structure and reactivity of the singly reduced **1** (i.e. **1**^{•-}) were modelled. In the reduced species the Co-Co bond length is greater than in the parent (2.755 and 2.442 Å respectively). There is also evidence for a slight asymmetric binding of the alkyne ligand to the Co, Co-C1 2.01617 compared to Co-C2 1.99427 Å. Several possible reaction coordinates were selected to model decomposition routes for this complex and the energy changes along these reaction coordinates are presented in the supporting information Figure SA5. The Co-Co bond stretching is the lowest energy pathway which perhaps explains the formation of the Co(CO)₄⁻ decomposition fragment.

2.3. Discussion

The ps-TRIR studies supported by TDDFT calculations on **1** or **2** showed that axial CO-loss occurs upon photolysis at 400 nm. This process is ultrafast but very inefficient. In addition, global analysis of the ps-TRIR data suggests that the CO-loss species are themselves labile. Photolysis of **3** at 400 nm also produced the axial CO-loss product but with a greatly reduced efficiency even compared to **1** or **2**. This contrasts with the observation that **3**, in particular, catalyses the

PKR when irradiated with visible light.²⁹ This would suggest, contrary to the common belief, that CO-loss is not the primary process in the photo-assisted PKR. The spectro-electrochemical studies indicate that a single electron reduction of all complexes in this study is sufficient to decompose the di-cobalt complexes, producing uncoordinated alkyne ligand and a rupture of the Co-Co bond. Clearly a relatively minor change to the electron configuration can have a dramatic effect on the overall stability of these complexes particularly with respect to weakening of the Co-Co bond. The ps-TRIR studies indicate that the dominant photochemical pathway following photolysis of **1** at 400 nm is the formation of a vibrationally hot species as indicated by the broadness of the ν_{CO} bands (30 cm^{-1} Full Width at Half Maximum) when compared to the parent (7 cm^{-1} FWHM). The nature of this species is worthy of discussion, in particular whether it is an electronically excited or a ground state species. Time-resolved investigations by Harris and co-workers,⁵⁰ using both IR pump;IR probe and UV pump;IR probe methods on a related diiron system, $(\mu_2\text{-benzene-1,2-dithiolate})\text{Fe}_2(\text{CO})_6$, produced similar transient features to those observed here. It was concluded that the transient IR features were the result of processes on the electronic ground state. In common with our results, the initially produced broad IR features relaxed to the parent in two stages, the first a cooling process where excess energy is dissipated to the solvent quickly, within 20 ps. A second slower process involving the vibrational relaxation of the isolated metal carbonyl modes takes place over 80 to 300 ps. With our systems, and using only UV-pump;IR-probe, we also observed two relaxation processes that occur on similar, if slightly shorter, timescales of 10 ps and 57 ps. We propose a similar explanation for the faster decay process, i.e. vibrational cooling by dissipation of thermal energy to the solvent. However, we can offer an alternative explanation for the slower process namely the formation of a ground-state species in which the Co-Co bond distance is longer than in the parent, possibly a high-spin diradical species (Figure 2(b)). Such a proposal is not without precedent; a transient lengthening of the Fe-Fe bond in $(\mu_2\text{-S}_2\text{C}_3\text{H}_6)\text{Fe}_2(\text{CO})_6$ was proposed following visible light excitation.⁵¹

The fundamental problem remains, how does visible light absorption promote the PKR? By populating the lowest energy excited state either directly or through internal conversion from higher optically accessible excited states, the Co-Co bond length increases. This provides a pathway to move from the initially formed low-spin diradical excited state to a high-spin diradical such as that described in Figure 2(b). This would have a lifetime sufficiently long to engage in bimolecular reactions with alkene substrates.^{52,53} To confirm that a high spin diradical is consistent with the spectral changes in the IR, the ps-TRIR spectrum was obtained 90 ps after 532 nm excitation of **1** in hexane solution. This spectrum is presented in Figure 2-10 which

compares the experimental spectrum to the calculated difference spectrum obtained by subtracting the simulated spectrum of the parent complex from that of the high spin diradical. Despite the significant overlap of features, particularly the middle feature, the 90 ps difference spectrum is an excellent fit to the simulated spectrum. It is worth noting also, that the broadness of the low energy feature is the result of the overlap of four fundamental modes and not an indication of vibrational relaxation. The symmetry of the high-spin diradical is reduced to C_1 which exhibits in six ν_{CO} bands only two of which (the two high energy bands) are fully resolved.

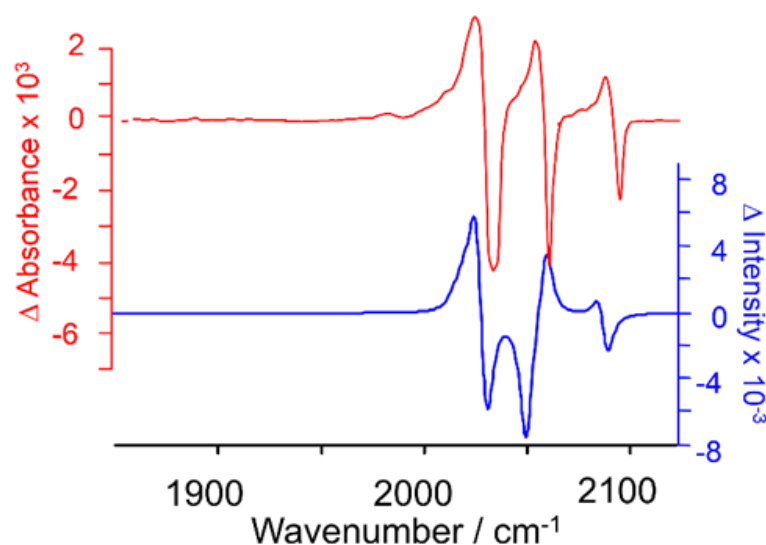
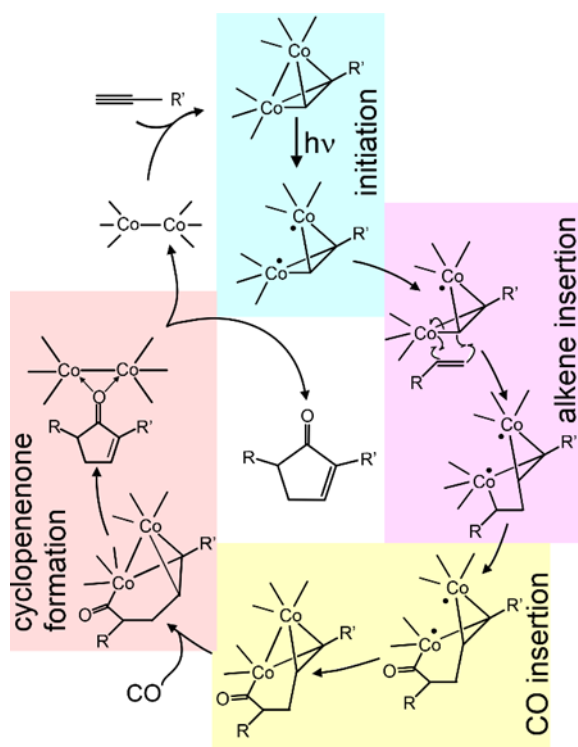


Figure 2-10. The experimental difference spectrum obtained 78 ps after 532 nm excitation of **1** in hexane (red) and the simulated difference spectrum obtained by subtracting the parent spectrum from that of the high-spin diradical species (assuming 90% conversion) (blue).

We can propose a slight modification to the accepted catalytic cycle for the thermal PKR to explain the visible light promoted PKR.^{30,54} This scheme does not involve photoinduced CO-loss as the primary step (Scheme 2-1).

The initial photochemical step involving cleavage of the Co-Co bond forming the high-spin diradical. This is followed by an insertion of the alkene into one Co-alkyne bond. The reaction then proceeds in the conventional manner involving CO insertion uptake of CO, release of the product cyclopentenone and regeneration of the di-cobalt alkyne complex. It is noteworthy that this scheme involves insertion of CO into a CO-alkyl bond from a coordinatively saturated cobalt centre. The inserted CO originates on the original $\text{Co}_2(\text{CO})_6$ fragment. This is consistent with mass spectrometry experiments using ^{13}CO enrichment which confirmed that the carbonyl unit in the resulting cyclopentenone originated in the $\text{Co}_2(\text{CO})_6$ unit.⁵⁵ Notwithstanding the primary focus of this work to elucidate the photochemical initiation of the PKR, at the suggestion of a

reviewer, the proposed catalytic cycle in the Scheme was modelled using B3LYP/6-31G(d) in acetonitrile. The species modelled were the alkene insertion, CO-insertion, and cyclopentenone formation when bound to a $\text{Co}_2(\text{CO})_6$ fragment starting with complex **1** in the presence of prop-1-ene and CO. Both high-spin and low-spin configurations were examined, and their energies expressed relative to the energy of the starting mixture defined at zero kJ mol^{-1} . These results are presented in Figure 2-11.



Scheme 2-1. The proposed reaction scheme for the light assisted Pauson-Khand reaction (metal carbonyl ligands are represented as simple lines for clarity), the Co to Co interaction indicated with a single bond for low-spin and two radicals high-spin configurations, the shading indicates the principal intermediate species in the catalytic cycle.

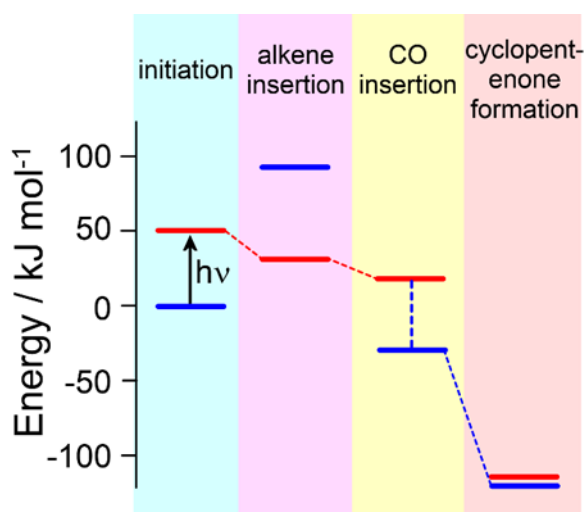


Figure 2-11. The energies of **1** (low-spin blue; high-spin red) and the alkene-insertion, CO-insertion and cyclopentenone species as indicated in the Scheme, showing an energy cascade from the high-spin starting complex through to the cyclopentanone product species, the shading colour indicates the corresponding intermediate steps in the Scheme.

These calculations indicate that once the high-spin species is produced in the initiation step, the insertion reactions and the product formation occur in a cascade of energetically favourable intermediates. No activation parameters were calculated for these steps, as these will be the subject of future work. These results also suggest that the displacement of the cyclopentenone from the coordination sphere of the cobalt is likely to be the rate determining step in the catalytic cycle, and that the relaxation from the high-spin to low-spin surface happens at the CO-insertion step. A full description of the structures and energies of these intermediates is available in the supporting information as .mol files.

2.4. Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Mobile phases for column chromatography were dried over MgSO_4 before use. All solutions were deoxygenated by purging with nitrogen for ~10 min. Column chromatography was carried out using neutral silica gel. Silica Gel (Merck) was used as received. 1-bromopyrene, 1-ethynylferrocene, TMS acetylene, and cobaltcarbonyl ($\text{Co}_2(\text{CO})_8$) were obtained from Sigma-Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer (2 cm^{-1} resolution) in a 0.1 mm pathlength cell with NaCl plates using spectrophotometric grade DCM.⁵⁶⁻⁵⁸ ^1H NMR spectra were recorded using a Brüker AC 400 spectrophotometer in CDCl_3 and were calibrated by the residual proton resonances of the solvent peak. UV spectra were measured using an Agilent 8453 UV-Vis spectrophotometer in a 1 cm quartz cell using spectrophotometric grade DCM. ps-TRIR photolysis was carried out with

λ_{exc} 400 nm, and $\tau_{\text{FWHM}} = 150$ fs using the ULTRA facility at the Rutherford Appleton Laboratory. Details of the experimental setup have been presented elsewhere.⁵⁹ Spectrophotometric grade DCM or *n*-hexane were used for these experiments. The photochemical quantum yields for CO-loss were determined using potassium ferrioxalate actinometry at irradiation wavelengths of 313, 365, 405 or 546 nm in spectrophotometric grade *n*-heptane (see supporting information Table SA3). Triphenylphosphine, present in excess, was used as the trapping ligand for the pentacarbonyl photoproduct.

All spectro-electrochemical measurements were performed at room temperature. Solutions were prepared under a nitrogen flow with a freshly prepared 0.1 M tetrabutylammonium hexafluorophosphate solution in either dichloromethane or acetonitrile. A 1 mm omni-cell (Specac) was used equipped with a platinum mesh working electrode, platinum mesh counter electrode and silver wire quasi-reference electrode. All spectroelectric experiments were conducted on a CHI 600E (CH Instruments) potentiostat. IR measurements used a Spectrum 65 FT-IR spectrometer (Perkin Elmer), while UV-Vis experiments measurements used an Agilent 8453 UV-Visible spectrometer.

2.4.1. Computational Studies

All quantum calculations were conducted using the Gaussian 16 suite of programmes (Revision B.01).⁶⁰ The computational studies initially focussed on the simplest alkyne complex ($\mu_2\text{-C}_2\text{H}_2$)Co₂(CO)₆ before attempting to model the larger pyrenyl and ferrocenyl substituted derivatives. Our initial calculations on ($\mu_2\text{-C}_2\text{H}_2$)Co₂(CO)₆ were centred on obtaining an accurate molecular geometry at a convenient model chemistry (in terms of computational cost) in order to simulate the infrared absorptions particularly in the ν_{CO} region. In these calculations the ground state structure was optimized to tight convergence limits using a pruned (99,590) grid. Both the BLYP and B3LYP functionals were used with a 6-311G basis set,^{61,62} augmented with diffuse and polarisation functions (6-311++G(3df,3pd)).^{63,64} Geometry optimizations using unrestricted BLYP or B3LYP functionals yielded ground state singlet species with no evidence for significant spin contamination. For both functionals, the lowest energy triplet state occurs at higher energy than the singlet at the optimized geometry of the lowest energy singlet state (1.82 eV for BLYP and 1.58 eV for B3LYP). Both values are smaller than the singlet-triplet energy gap of 2.284 eV obtained from the computationally more expensive complete active space calculations using a molecular geometry derived from X-ray diffraction data. The optimized Co-Co distance was 2.551 Å for BLYP and 2.488 Å for B3LYP (a value of 2.442 Å was obtained using the B3LYP functional and the smaller 6-31G(d) basis set). These compare to the Co-Co distance

of 2.463 Å in $(\mu_2\text{-HCCCC}_6\text{H}_{10}\text{OH})\text{Co}_2(\text{CO})_6$ ^{65,36} or 2.476 Å in $(\mu_2\text{-C}_6\text{H}_5\text{CCC}_6\text{H}_5)\text{Co}_2(\text{CO})_6$ both values were obtained by single crystal X-ray diffraction methods. Because of the respectable performance of the B3LYP functional in modelling the Co-Co distance coupled with the smaller 6-31G(d) basis set this model chemistry was selected to probe the ground and excited-state behaviour of all the complexes in this study. Complete descriptions of the optimised structures are available as .mol files in the supporting information.

2.4.2. Syntheses.

All the ligands used in this study were prepared using the Sonogashira coupling reaction,⁶⁷ using the following method. A 25 cm³ aliquot of di-isopropylamine was purged with nitrogen for 10 minutes, following which 1.77 mmol of the appropriate bromoalkane was added and the solution was purged with nitrogen for a further 10 minutes. Pd(PPh₃)₂Cl₂ 0.071 mmol (4%), CuI 0.071 mmol (4%) and PPh₃ 0.142 mmol (8%) and the required terminal alkyne 2.66 mmol were then added and the solution was brought to its reflux temperature (88°C) for 8 hours under a nitrogen atmosphere. The solvent was then removed under reduced pressure. The product was extracted into a mixture of DCM:hexane (1 : 5 v/v). The resulting solution was dried over anhydrous MgSO₄, filtered, and the solvent removed under reduced pressure. The product was purified using column chromatography on silica using *n*-hexane:DCM, 25:75 (v/v) as the mobile phase.

Pyrene-ethynylferrocene. Yield: 96%. ¹H NMR: (400 MHz, CDCl₃) 8.62 ppm (d, *J* = 9.2 Hz, 1H), 7.9 ppm (m, 8H), 4.665 ppm (dd, *J*_a = 1.6 Hz, *J*_b = 1.6 Hz, 2H), 4.33 ppm (s, 7H).⁶⁸

Removal of the TMS protection groups. 20 cm³ of freshly distilled methanol was purged with nitrogen for 10 min and 1.3 mmol of 1-trimethylsilylacetylene was then added followed by 0.17 mmol of K₂CO₃. The solution was stirred under nitrogen for 4 hr and the solvent was then removed under reduced pressure. The residue was dissolved in 100 cm³ of dichloromethane and washed with 4 × 25 cm³ of 5% (w/v) aqueous NaHCO₃. The organic phase was dried over anhydrous MgSO₄. The solvent was removed. The product was purified by chromatography using silica and hexane: DCM, 25:75 (v/v) as the mobile phase.⁶⁹

1-ethynylpyrene. Yield: 70%. ¹H NMR: (400 MHz, CDCl₃), 8.5 ppm (d, *J* = 8.8 Hz, 1H), 8.15 ppm (m, 8H), 3.6 ppm (s, 1H).

Synthesis of $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ complexes. 25 cm³ of hexane was purged with N₂ for 10 min and 0.45 mmol of the alkyne ligand was then added and solution was purged with N₂ for a further 10 min. 0.9 mmol of cobaltcarbonyl was added to the reaction mixture and the vessel

was sealed. The reaction mixture was allowed to stir for 8 hr under N₂. The solvent was removed and the pure product was obtained by column chromatography using a silica solid phase and DCM: hexane, 1:1 as the solvent.

(μ_2 -1-ethynylpyrene)Co₂(CO)₆ (**1**). Yield: 78%. ¹H NMR: (400 MHz, CDCl₃), 8.55 ppm (d, J= 9.2 Hz 1H), 8.15 ppm (m, 8H), 6.95 ppm (s, 1H). UV-Vis: (DCM) 274 nm (20.5 x 10³ M⁻¹ cm⁻¹), 392 nm (19.1 x 10³ M⁻¹ cm⁻¹), 577 nm (1.1 x 10³ M⁻¹ cm⁻¹). IR: (DCM) 2092, 2056, 2030 cm⁻¹.

(μ_2 -Pyrene-ethynylferrocene)Co₂(CO)₆ (**2**). Yield: 59%. ¹H NMR: (400 MHz, CDCl₃), 8.7 ppm (d, J= 8.08 Hz, 1H), 8.24 ppm (m, 8H), 4.6 ppm (dd, J_a= 1.84 Hz, J_b= 1.84 Hz, 2H), 4.48 ppm (dd, J_a= 1.84 Hz, J_b= 1.84 Hz 2H), 4.32 ppm (s, 5H). UV-Vis: (DCM) 279 nm (18.7 x 10³ M⁻¹ cm⁻¹), 389 nm (11.7 x 10³ M⁻¹ cm⁻¹), 574 nm (1.3 x 10³ M⁻¹ cm⁻¹). IR: (DCM) 2085, 2048, 2023 cm⁻¹.

(μ_2 -1-ethynylferrocene)Co₂(CO)₆ (**3**). Yield: 98%, ¹H NMR: (400 MHz, CDCl₃), 6.28 ppm (s, 1H), 4.33 ppm (d, J_a= 1.84 Hz, J_b= 1.84 Hz 4H), 4.15 ppm (s, 5H). UV-Vis: (DCM) 290 nm (17.1 x 10³ M⁻¹ cm⁻¹), 361 nm (4.4 x 10³ M⁻¹ cm⁻¹), 430 nm (1.8 x 10³ M⁻¹ cm⁻¹), 614 nm (1.1 x 10³ M⁻¹ cm⁻¹). IR: (DCM) 2090, 2051, 2023 cm⁻¹. Complexes **1**, **2** and **3** have been synthesised previously and all spectroscopic data obtained is in agreement with previous reports.^{29,71}

2.5. Supporting Information.

Supporting information includes details of actinometric quantum yield experiment, TRIR spectra of **1b**, **2b** and **3b**, electrochemical data and details of quantum chemical calculations including atomic coordinates of all optimised structures in the form of embedded .mol files.

2.6. Conclusions

Contrary to previous proposals that photoinduced CO-loss from (μ_2 -alkyne)Co₂(CO)₆ complexes was the primary photochemical step in the visible light assisted Pauson-Khand reaction, our investigations implicate a high-spin diradical species formed by homolytic cleavage of the Co-Co bond. Attempts to maximise the quantum efficiency of CO-loss by tuning the absorption profile of a series of alkyne-substituted complexes to the excitation wavelength in time-resolved spectroscopic studies failed to significantly increase the CO-loss efficiency. This, despite the increased efficiency of the visible light assisted Pauson-Khand reaction for the ferrocenyl substituted derivative, led to the conclusion that CO-loss was not required to promote the reaction.

2.7. References

- 1 P. L. Pauson, *J. Am. Chem. Soc.*, 1954, **76**, 2187-2191.

- 2 T. E. Bitterwolf, *J. Organomet. Chem.*, 2004, **689**, 3939-3952.
- 3 R. G. W. Norrish and G. Porter, *Nature*, 1949, **164**, 658-658.
- 4 E. Whittle, D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, 1954, **22**, 1943-1943.
- 5 L. E. N. Allan, M. R. Perry and M. P. Shaver, *Prog. Polym. Sci.*, 2012, **37**, 127-156.
- 6 M. Hurtgen, C. Detrembleur, C. Jerome and A. Debuigne, *Polymer Reviews*, 2011, **51**, 188-213.
- 7 J. K. Burdett, J. M. Grzybowski, R. N. Perutz, M. Poliakoff, J. J. Turner and R. F. Turner, *Inorg. Chem.*, 1978, **17**, 147-154.
- 8 J. J. Turner, J. K. Burdett, R. N. Perutz and M. Poliakoff, *Pure Appl. Chem.*, 1977, **49**, 271-285.
- 9 J. K. Burdett, R. N. Perutz, M. Poliakoff and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 1975, 157-159.
- 10 J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner and R. F. Turner, *J. Am. Chem. Soc.*, 1975, **97**, 4805-4808.
- 11 J. K. Burdett, R. N. Perutz, M. Poliakoff and J. J. Turner, *Inorg. Chem.*, 1976, **15**, 1245-1245.
- 12 R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, 1975, **97**, 4791-4800.
- 13 R. N. Perutz and J. J. Turner, *J. Chem. Soc., Faraday Trans.*, 1973, 452-461.
- 14 M. A. Graham, J. J. Turner, Poliakof.M and R. N. Perutz, *J. Organomet. Chem.*, 1972, **34**, C34-&.
- 15 X. L. Xie and J. D. Simon, *J. Phys. Chem.*, 1989, **93**, 4401-4404.
- 16 J. D. Simon and X. L. Xie, *J. Phys. Chem.*, 1989, **93**, 291-293.
- 17 J. D. Simon and X. L. Xie, *J. Phys. Chem.*, 1987, **91**, 5538-5540.
- 18 J. D. Simon and X. L. Xie, *J. Phys. Chem.*, 1986, **90**, 6751-6753.
- 19 J. M. Kelly, C. Long and R. Bonneau, *J. Phys. Chem.*, 1983, **87**, 3344-3349.
- 20 S. Villaume, A. Strich, C. Daniel, S. A. Perera and R. J. Bartlett, *PCCP*, 2007, **9**, 6115-6122.
- 21 N. Ben Arnor, S. Villaume, D. Maynau and C. Daniel, *Chem. Phys. Lett.*, 2006, **421**, 378-382.
- 22 A. Rosa, E. J. Baerends, S. J. A. van Gisbergen, E. van Lenthe, J. A. Groeneveld and J. G. Snijders, *J. Am. Chem. Soc.*, 1999, **121**, 10356-10365.
- 23 C. Pollak, A. Rosa and E. J. Baerends, *J. Am. Chem. Soc.*, 1997, **119**, 7324-7329.
- 24 C. Long, in *Photophysics of Organometallics*, ed. A. J. Lees, Springer, Berlin/Heidelberg, 2010, vol. 29, ch. 2, pp. 37-71.

- 25 I. P. Clark, M. W. George, G. M. Greetham, E. C. Harvey, C. Long, J. C. Manton and M. T. Pryce, *J. Phys. Chem. A*, 2010, **114**, 11425 - 11431.
- 26 B. J. Aucott, A. K. Duhme-Klair, B. E. Moulton, I. P. Clark, I. V. Sazanovich, M. Towrie, L. A. Hammarback, I. J. S. Fairlamb and J. M. Lynam, *Organometallics*, 2019, **38**, 2391-2401.
- 27 P. L. Pauson and I. U. Khand, *Ann. N.Y. Acad. Sci.*, 1977, **295**, 2-14.
- 28 B. L. Pagenkopf and T. Livinghouse, *J. Am. Chem. Soc.*, 1996, **118**, 2285-2286.
- 29 A. C. Coleman, C. Long, A. Meetsma, B. L. Feringa, W. R. Browne and M. T. Pryce, *J. Chem. Soc., Dalton Trans.*, 2009, 7885-7887.
- 30 M. Yamanaka and E. Nakamura, *J. Am. Chem. Soc.*, 2001, **123**, 1703-1708.
- 31 S. A. Brusey, E. V. Banide, S. Dörrich, P. O'Donohue, Y. Ortin, H. Müller-Bunz, C. Long, P. Paul Evans and M. J. McGlinchey, *Organometallics*, 2009, **28**, 6308-6319.
- 32 C. M. Gordon, M. Kiszka, I. R. Dunkin, W. J. Kerr, J. S. Scott and J. Gebicki, *J. Organomet. Chem.*, 1998, **554**, 147-154.
- 33 T. E. Bitterwolf, W. B. Scallorn and C. A. Weiss, *J. Organomet. Chem.*, 2000, **605**, 7-14.
- 34 K. Asano, Y. Uesugi and J. Yoshida, *Org. Lett.*, 2013, **15**, 2398-2401.
- 35 J. Overaard, H. F. Clausen, J. A. Platts and B. B. Iversen, *J. Am. Chem. Soc.*, 2008, **130**, 3834-3843.
- 36 J. A. Platts, G. J. S. Evans, M. P. Coogan and J. Overgaard, *Inorg. Chem.*, 2007, **46**, 6291-6298.
- 37 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
- 38 C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
- 39 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
- 40 R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454-464.
- 41 M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439-4449.
- 42 R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218-8224.
- 43 C. Van Caillie and R. D. Amos, *Chem. Phys. Lett.*, 2000, **317**, 159-164.
- 44 C. Van Caillie and R. D. Amos, *Chem. Phys. Lett.*, 1999, **308**, 249-255.
- 45 F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2002, **117**, 7433-7447.
- 46 G. Scalmani, J. Frisch, B. Mennucci, J. Tomasi, R. Cammi and V. Barone, *J. Chem. Phys.*, 2006, **124**, 094107-094104.
- 47 M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327-335.
- 48 J. Marhenke, S. M. Massick and P. C. Ford, *Inorg. Chim. Acta*, 2007, **360**, 825-836.

- 49 R. L. Hollingsworth, J. W. Beattie, A. Grass, P. D. Martin, S. Groysman and R. L. Lord, *J. Chem. Soc., Dalton Trans.*, 2018, **47**, 15353-15363.
- 50 B. W. Caplins, J. P. Lomont, S. C. Nguyen and C. B. Harris, *J. Phys. Chem. A*, 2014, **118**, 11529–11540.
- 51 J. L. Bingaman, C. L. Kohnhorst, G. A. Van Meter, B. A. McElroy, E. A. Rakowski, B. W. Caplins, T. A. Gutowski, C. J. Stromberg, C. E. Webster and E. J. Heilweil, *J. Phys. Chem. A*, 2012, **116**, 7261-7271.
- 52 J. Mattay, *Angew. Chem. Int. Ed.*, 2007, **46**, 663-665.
- 53 L. Bertini, P. Fantucci and L. De Gioia, *Organometallics*, 2011, **30**, 487-498.
- 54 P. Magnus and L. M. Principe, *Tetrahedron Lett.*, 1985, **26**, 4851-4854.
- 55 D. Lesage, A. Milet, A. Memboeuf, J. Blu, A. E. Greene, J. C. Tabet and Y. Gimbert, *Angew. Chem. Int. Ed.*, 2014, **53**, 1939-1942.
- 56 I. P. Clark, M. W. George, G. M. Greetham, E. C. Harvey, C. Long, J. C. Manton and M. T. Pryce, *J. Phys. Chem. A*, 2010, **114**, 11425-11431.
- 57 I. P. Clark, M. W. George, G. M. Greetham, E. C. Harvey, C. Long, J. C. Manton and M. T. Pryce, *J. Phys. Chem. A*, 2011, **115**, 2985-2993.
- 58 I. P. Clark, M. W. George, G. M. Greetham, E. C. Harvey, C. Long, J. C. Manton, H. McArdle and M. T. Pryce, *J. Phys. Chem. A*, 2012, **116**, 962-969.
- 59 G. M. Greetham, Q. Cao, I. P. Clark, P. S. Codd, M. W. George, R. C. Farrow, T. Matousek, A. W. Parker, M. Pollard, D. A. Robinson, Z. J. Xin and M. Towrie, *Appl. Spectrosc.*, 2010, **64**, 1311-1319.
- 60 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16*, 2016.
- 61 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639-5648.

- 62 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.
- 63 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294-301.
- 64 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265-3269.
- 65 J. Overgaard, H. F. Clausen, J. A. Platts and B. B. Iversen, *J. Am. Chem. Soc.*, 2008, **130**, 3834-3843.
- 66 D. Gregson and J. A. K. Howard, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1983, **39**, 1024-1027.
- 67 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467-4470.
- 68 L. Cuffe, R. D. A. Hudson, J. F. Gallagher, S. Jennings, C. J. McAdam, R. B. T. Connelly, A. R. Manning, B. H. Robinson and J. Simpson, *Organometallics*, 2005, **24**, 2051-2060.
- 69 W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280-2286.
- 70 N. M. Boyle, A. C. Coleman, C. Long, K. L. Ronayne, W. R. Browne, B. L. Feringa and M. T. Pryce, *Inorg. Chem.*, 2010, **49**, 10214-10216.
- 71 A. Coleman, Ph.D. Thesis, Dublin City University, 2007.

Chapter 3: Ruthenium Assemblies for CO₂ Reduction and H₂ Generation: Time Resolved Infrared Spectroscopy, Spectroelectrochemistry and a Photocatalysis Study in Solution and on NiO

*In Chapter 3, two novel supramolecular complexes **RuRe** ([Ru(dceb)₂(bpt)Re(CO)₃Cl](PF₆)₃) and **RuPt** ([Ru(dceb)₂(bpt)Pt(H₂O)](PF₆)₂) (dceb = diethyl[2,2'-bipyridine]-4,4'-dicarboxylate, bpt = 3,5-di(pyridine-2-yl)-1,2,4-triazolate) were synthesized as new catalysts for photocatalytic CO₂ reduction and H₂ evolution, respectively. The influence of the catalytic metal for successful catalysis in solution and on a NiO semiconductor was examined. IR-active handles in the form of carbonyl groups on the peripheral ligand on the photosensitiser were used to study the excited states populated, as well as the one-electron reduced intermediate species using infrared and UV-Vis spectroelectrochemistry, and time resolved infrared spectroscopy. Inclusion of ethyl-ester moieties led to a reduction in the LUMO energies on the peripheral bipyridine ligand, resulting in localization of the ³MLCT excited state on these peripheral ligands following excitation. **RuPt** generated hydrogen in solution and when immobilized on NiO in a photoelectrochemical (PEC) cell. **RuRe** was inactive as a CO₂ reduction catalyst in solution, and produced only trace amounts of CO when the photocatalyst was immobilized on NiO in a PEC cell saturated with CO₂. The time-resolved infrared studies were performed in the ULTRA laser facility at the Rutherford Appleton Laboratories (RAL) in the U.K. in collaboration with Elizabeth Gibson's Research Group, from Newcastle University, U.K.*

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3.1. Introduction

The transition to renewable energy has become a key global objective due to the dwindling supply of fossil fuels, as well as the detrimental effect they have on the environment. While sufficient renewable energy is available in the form of sunlight and wind, the intermittency of these sources remains a problem. Storage of excess energy captured from these sources into chemical bonds can potentially provide a viable solution.¹ Nature captures sunlight by photosynthesis, and much effort has been made in our research group and others to mimic this process and create efficient systems for artificial photosynthesis.^{2–7}

A typical catalytic system consists of two components: a photosensitiser (**PS**) which captures (visible) light and a catalyst capable of converting a low energy substrate, such as CO₂ or water, into a higher energy vector, for example carbon fuels or hydrogen gas.^{8,9} Classical intermolecular systems have been reported, where both components are present in solution and interact with each other upon collision in a bimolecular process.¹⁰ However, in order to improve the interaction between the **PS** and catalyst, and thus the rate of forward electron transfer, the two functionalities can be covalently bonded to each other.^{11–15} These intramolecular systems show that electron transfer from the **PS** to the catalyst is improved,^{12,16,17} but these systems may suffer from rapid charge recombination. Ruthenium polypyridyl complexes have played a major role in the development of supramolecular systems, both for hydrogen evolution and CO₂ reduction. For the former, the groups of Rau and Dietzek^{18–20} and the group of Sakai^{12,17,21,22}, as well as our own,^{13,23–25} have reported a large range of dinuclear complexes in which the catalytic metals, as well as bridging ligand and peripheral ligands, were varied and the effects investigated.

We and others have shown the importance of the energy levels of the peripheral and bridging ligand,²⁰ as directional electron transfer from the ruthenium centre via the bridging ligand to the catalytic centre is required to facilitate catalysis.^{20,26–28} For CO₂ reduction, the group of Ishitani has reported various suitable systems, showcasing the influence of the bridging ligand in particular on the catalysis.^{29–32} In their systems, it was apparent that catalysis was enhanced if the bridging ligand was not conjugated, minimizing the electronic interaction between the ruthenium and the rhenium centres.^{33–36} They reported that stronger conjugation led to a weaker reduction potential of the rhenium unit, and decreased the efficiency of the catalyst to reduce CO₂.³⁶ For large scale application, photoelectrochemical cells where the reductive reactions are coupled with a suitable oxidative reaction which can provide electrons are required.^{37–39} A preferred way to do so is by attaching the system for proton reduction to a semiconductor cathode, while a water oxidation system is coupled to a semiconductor anode, facilitating the electron flow.⁴⁰ For this, the **PS** requires suitable anchoring groups to be attached

to a semiconductor surface.^{30,41,42} We have previously shown that these anchoring groups affect the energy levels of the peripheral ligands.²³ In the case of the ester anchoring groups employed by us, they lower the triplet metal to ligand charge transfer (³MLCT) excited state localized on the peripheral ligand resulting in increased electron density on the peripheral ligands in the excited state. While this reduces electron transfer to the metal centre via the bridging ligand,^{20,26–28} it might also aid in storing the two reductive equivalents required for catalysis^{7,43}. As previously reported by our groups,⁷ the interaction with the semiconductor drastically influences the properties of these supramolecular systems. In our case, the ruthenium-palladium system **RuPd** was inactive in solution but was active for hydrogen production when immobilized on a NiO semiconductor surface through a shift in the energy levels of the peripheral and bridging ligands. Transient absorption spectroscopy (TAS) indicated that when the **RuPd** sample was integrated on the NiO semiconductor, rapid hole injection occurred following excitation, however the reduced species undergoes charge recombination within 30 ps. Furthermore, surface based TAS studies indicated that the electron density is localized on the bridging ligand. This is in contrast to the studies in solution, where the excited state was mainly localised on the peripheral ligands. Previous reports have shown that supramolecular systems with either palladium or platinum as the hydrogen evolution catalyst perform catalysis via different mechanisms.⁴⁴ For systems using palladium, partial decomposition of the supramolecular assembly has been observed, resulting in the release of palladium from the supramolecular assemblies to form palladium colloids which are thought to act as catalysts.^{44–46} In the case of platinum, it remained coordinated to the bridging ligand during photocatalysis. For catalysis to occur, efficient electron transfer towards the metal centre via the bridging ligand is required.^{20,26–28,44} We synthesized **RuRe** and **RuPt** complexes as the rhenium and platinum analogues of **RuPd**, to investigate the influence of the catalytic metal on the excited state properties and the catalytic properties of these systems, not only in solution but when integrated onto NiO (Figure 3-1).

Infrared and UV-Vis spectroelectrochemistry, as well as steady state photophysical methods, time-resolved infrared spectroscopy and time-resolved emission spectroscopy were used to probe and compare the properties of these complexes. The mononuclear photosensitiser **Ru** was used as a benchmark in these studies. Spectroelectrochemistry has been a valuable tool in the analysis of ruthenium complexes and their bimetallic supramolecular systems. Specifically, UV-Vis and Raman spectroelectrochemistry have been widely applied to study the localization of the electron in the one electron reduced species.^{18,47,48} This species is considered an intermediate in the catalytic cycle to produce hydrogen and thus a better understanding of its

properties is of interest.¹⁸ UV-Vis spectroelectrochemistry can indicate the electronic transitions involved in the localization of the first light-induced electron transfer and the transition involved in the second excitation. However, various states often overlap making their assignment difficult, generally requiring complementary computational chemistry to interpret the spectra.¹⁸ Raman spectroelectrochemistry shows more detail and can use the various electronic transitions to focus on different aspects of the molecule. In order to analyse the various signals and assign them to the various, often very similar parts of the complexes, benchmarks or additional computational studies are required.^{18,47,49} Infrared spectroelectrochemistry can complement these techniques. The presence of IR-active functional groups, such as carboxyl moieties, can make interpretation of the changes occurring following reduction of the complex easier, as these functional groups have unique signals in the IR spectrum. In our complex, we use the organic carbonyl groups on the peripheral ligands, as well as the metal-carbonyl groups on the rhenium catalyst to investigate the localization of the electron after the first reduction. Finally, time-resolved infrared spectroscopy (TRIR) on the picosecond and nanosecond timescale was used to study the excited state of the complexes. TRIR has been a widely applied tool to study ruthenium based supramolecular systems, in particular for systems containing metal-carbonyl moieties such as $\text{Re}(\text{CO})_3\text{X}$ (X= halide), as the metal carbonyls at the catalytic site are valuable handles in the IR spectrum.^{7,33,34,42,50} The metal-carbonyl moieties are mostly influenced through effects on the bridging ligand, while the organic carbonyls are mostly influenced by effects on the peripheral ligands. This helped us to assign the localization of the excited states following excitation.

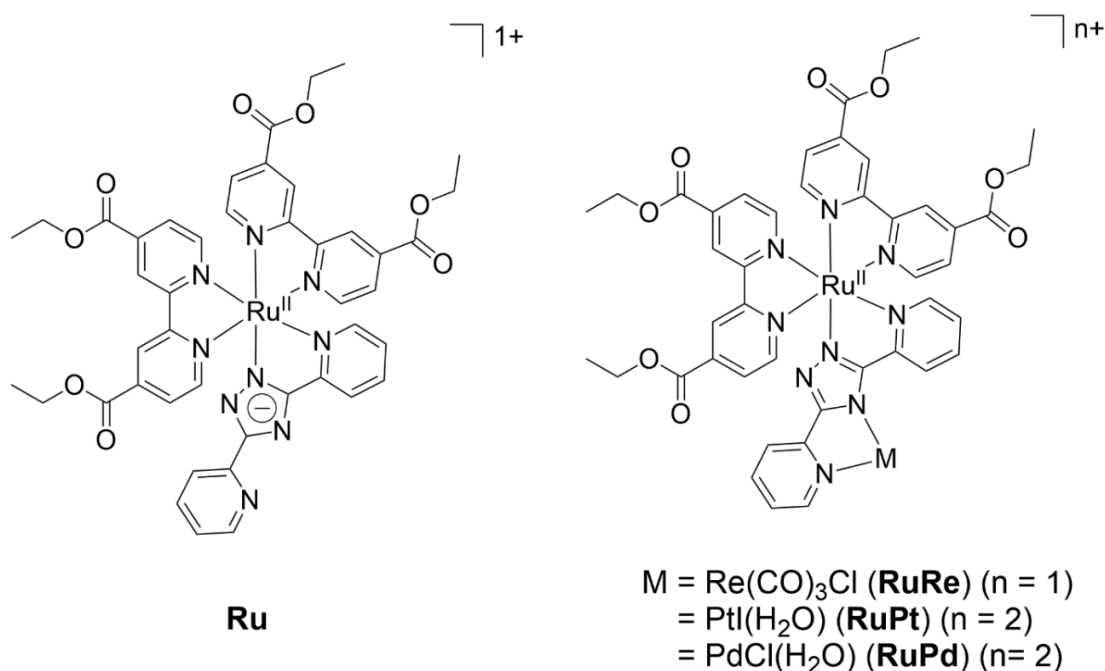


Figure 3-1. The complexes studied in this paper and the previously reported⁷ RuPd complex.

3.2. Results and discussion

3.2.1. UV-Vis spectroscopy and emission spectra

The UV-vis absorption and emission spectra for **Ru**, **RuRe** and **RuPt** are shown in Figure 3-2 and summarized in Table 3-1. Absorption bands are observed at 312 and 381 nm for **Ru** and are assigned to ligand centred (LC) $\pi\text{-}\pi^*$ transitions on the bridging and peripheral ligands.⁵¹ The broad absorption with a λ_{max} at 505 nm as well as the slight shoulder at 455 nm are assigned to metal-to-ligand charge transfer (MLCT) transitions from the Ru metal centre to the ligands.^{7,51} The absorption spectra of both **RuRe** and **RuPt** resemble that of **Ru**, showing two similar LC $\pi\text{-}\pi^*$ transitions in the UV region of the spectrum. A slight blue shift is observed for the MLCT transition for both dinuclear species following complexation with the second metal (Re or Pt) when compared to the **Ru** precursor, with a shift of the λ_{max} from 505 nm for **Ru** to 492 and 486 nm for **RuRe** and **RuPt**, respectively. This indicates some electronic coupling via the bridging ligand between the ruthenium centre and the second metal centre.

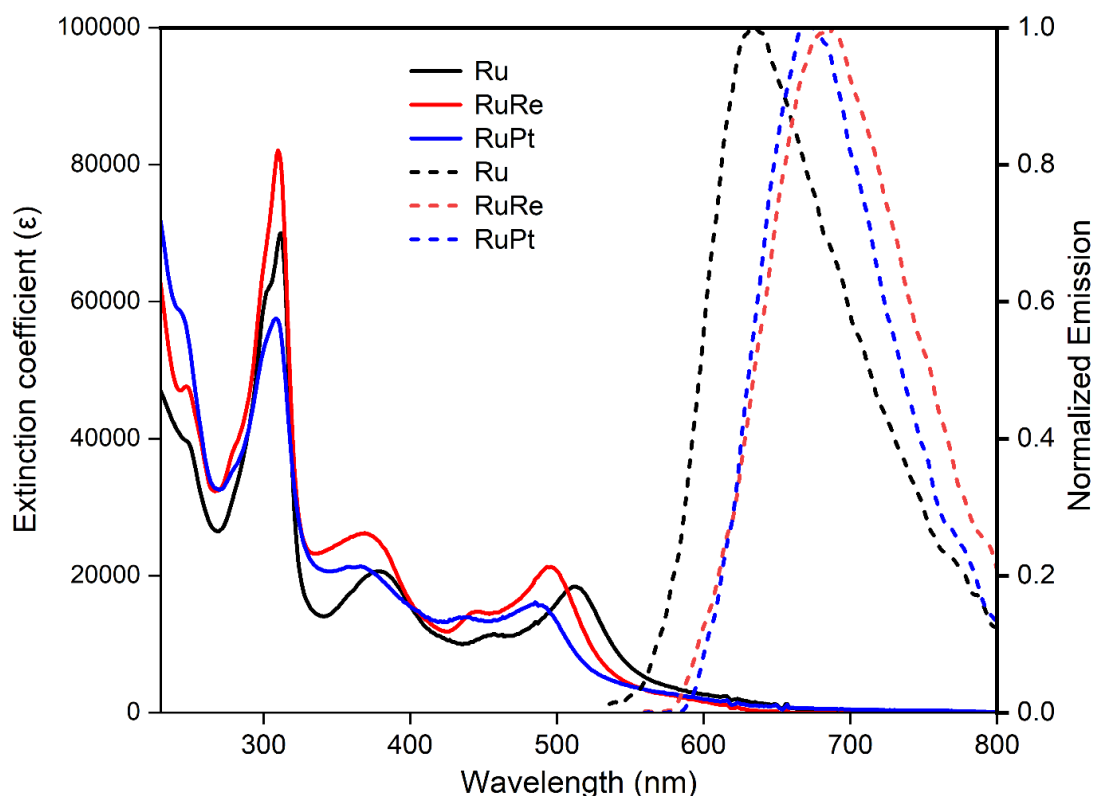


Figure 3-2. UV-Vis absorption of **Ru** (black), **RuRe** (red) **RuPt** (blue) and normalized emission spectra of **Ru** (dashed black), **RuRe** (dashed red), **RuPt** (dashed blue). UV-Vis spectra were collected using a 0.025 mM solution of the complexes in aerated acetonitrile in a 1 cm path length cell. Emission spectra were collected in a 1 cm pathlength cell at 490 nm excitation with all complexes having an absorbance of 0.1 at 490 nm.

The emission spectra further demonstrate the influence of the additional metal centres. The emission maximum for Ru was observed at 639 nm, which is in good agreement with values reported for related compounds.^{43,50} Complexation with the second metal results in a red shift in emission, with maxima at 697 and 682 nm for **RuRe** and **RuPt**, respectively. A similar red shift in emission properties was previously observed for analogous complexes.⁵² A significant change is observed in the Stokes shift which increases from 3871 cm⁻¹ for Ru to 5727 and 5914 cm⁻¹ for **RuRe** and **RuPt**, respectively. This large increase indicates that the energy of the excited states is influenced upon coordination of a second metal.

Table 3-1. Summarized absorption and emission maxima and emission lifetimes in aerated acetonitrile. ^aExtinction coefficient at λ_{max} for the MLCT band. ^bEmission spectra were collected following excitation at 490 nm and all samples

were isoabsorptive (0.1 A). ^cThe UV-Vis spectra for these species can be found in the (Figure 2). ^dLifetimes were determined at 690 nm following excitation at 355 nm.

Compound	λ_{max} (nm)	$\epsilon \times 10^4$ (M ⁻¹ cm ⁻¹) ^a	λ_{em} (nm) ^b	Stokes shift (cm ⁻¹)	τ (ns) ^d
Ru	312, 381, 455, 505	1.38	639	3871	94, 1294
RuRe	310, 374, 441, 492	2.06	697	5727	557
RuPt	309, 376, 439, 486	1.57	682	5914	14, 517

3.2.2. Electrochemistry

All complexes were studied using standard cyclic voltammetry techniques in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The potentials are quoted versus the ferrocene/ferrocenium redox couple unless otherwise noted. **Ru** is studied as a benchmark for the dinuclear species **RuPt** and **RuRe**, as well as providing a comparison to other ruthenium photosensitisers in literature. As with other heteroleptic ruthenium polypyridine complexes, three reversible reductions are observed, which can be assigned to the individual reductions of each of the three polypyridyl ligands^{50,53} (Figure SB 1). Using infrared spectroelectrochemistry (*vide infra*) the reductions are assigned as follows: the first two waves, with closely spaced $E_{1/2}$ potentials at -1.41 and -1.54 V are assigned to reductions on the dceb ligands. The third reduction, with a characteristic $E_{1/2}$ value of -2.12 V, is assigned to the reduction of the triazole bridging ligand. This value matches well with that previously observed for a similar ruthenium complex bearing the same triazole ligand studied by Mulhern et al., who reported a reduction on the triazole ligand at -2.16 V.⁵⁴ One reversible oxidation was observed at 0.68 V which is assigned to the reversible Ru^{II/III} oxidation. A second shouldering oxidation feature was observed at 0.81 V which was confirmed with differential pulse voltammetry (Figure SB 2). In previous work reported on the analogues [Ru(bpy)₂(bpt)]⁺ complex (bpy = 2,2'-bipyridine) by Browne et al.,⁵⁵ a positive shift of the oxidation potential was observed upon protonation of the triazole ligand, prompting us to investigate if these two oxidations could be assigned to the protonated and deprotonated species in solution. CV experiments in the presence of 0.02 M NaOH resulted in the disappearance of the oxidation band at 0.81 V,

confirming that this oxidation is indeed that for the protonated species (Figure SB 3). The reductive processes were not affected by the addition of base to the solution, suggesting that these signals should be assigned to the deprotonated species.

Table 3-2. Reduction and oxidation potentials of the reported ruthenium complexes in nitrogen purged acetonitrile with 0.1 M TBAPF₆ as supporting electrolyte. All potentials are versus the Fc/Fc⁺ reference. i = irreversible process.

Compound	E _{1/2} (V)	E _{1/2} (V)	E _{1/2} (V)	E _{1/2} (V)	E (V)
Ru	-1.41	-1.54	-2.12	0.68 (Ru)	-
RuRe	-1.39	-1.61	-2.11	0.87 (Ru)	1.12 (i) (Re)
RuPt	-1.38	-1.62	-2.16 (i)	0.98 (i) (Ru)	1.22 (i)

RuRe showcased electrochemical properties very similar to those observed for **Ru** (Figure 3-3). Three reversible reductions were evident with E_{1/2} potentials at -1.39, -1.61 and -2.11 V. A reversible oxidation was observed with an E_{1/2} potential of 0.87 V which was assigned to the Ru^{II/III} oxidation. This oxidation has shifted to a more positive potential (0.87 V vs 0.68 V for **Ru**). As previously discussed for **Ru**, protonation of the triazole unit has been shown to effect such an anodic shift in the Ru^{II} oxidation potential. It is therefore not unreasonable to postulate that the observed increase in potential for Ru^{II/III} couple arises due to the coordination of the Re centre to the triazole bridge, which helps to neutralize negative charge on this ligand. A second irreversible oxidation is observed at 1.12 V which is assigned to the Re^{I/II} oxidation. This value matches well with the Ru-Re quaterpyridine analogue Ru(dceb)₂(L)Re(CO)₃Cl (L = 2,2',5',3'',6'',2'''-quaterpyridine) previously reported by Frayne et al.,⁵⁰ who observed an irreversible oxidation assigned to the Re^{I/II} couple at 1.07 V. The profile of this peak is reminiscent of a coupled electrochemical-chemical process in which the oxidation product is consumed by an irreversible chemical (decomposition) reaction. When the experiment was conducted at a scan rate of 0.1 V.s⁻¹, a small inflection was observed at 1.00 V on the return scan following the oxidation at 1.12 V. This inflection is assigned to the re-reduction of a residual amount of the 1.12 V oxidation product that has not decomposed. When the time-scale of the experiment was increased by changing the scan rate to 0.01 V.s⁻¹ (Figure SB 4), more complete chemical decomposition of the oxidation product occurs and consequently the inflection feature becomes less prominent. This observation coincides with the results of oxidative spectroelectrochemistry experiments (*vide infra*) where a significant loss of signal for the metal carbonyls was noted following oxidation, suggesting that decomposition may follow directly upon the oxidation of the Re moiety.

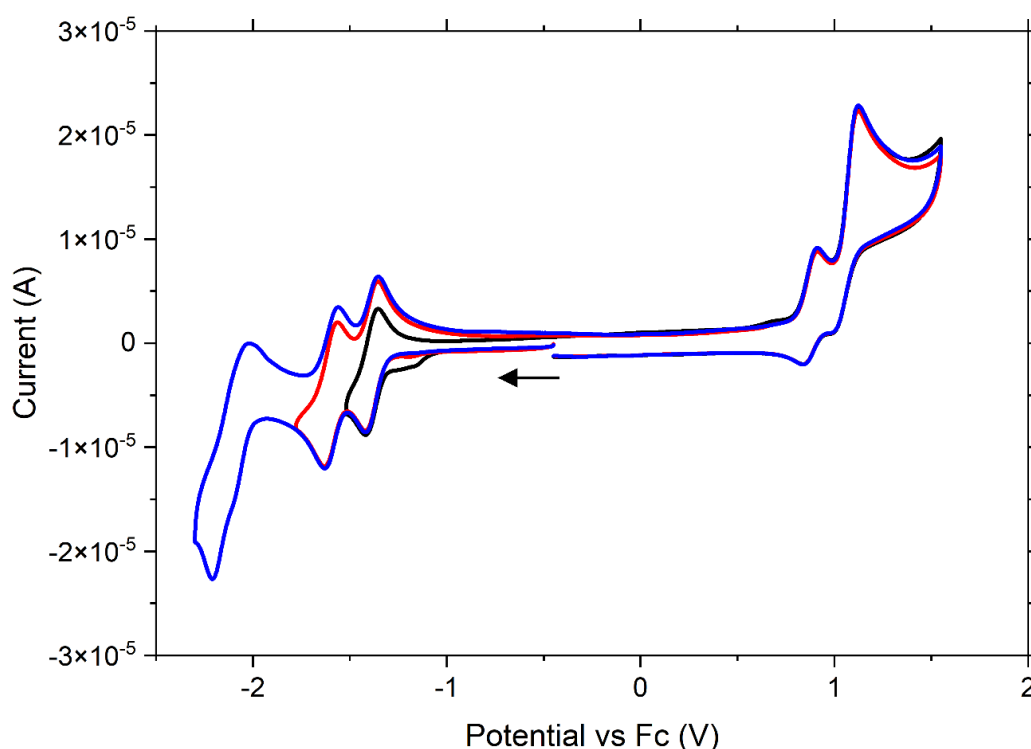


Figure 3-3. Cyclic voltammogram of **RuRe** vs ferrocene. Experiments were run with 1 mM **RuRe** in nitrogen purged acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A glassy carbon electrode, platinum wire and Ag/AgNO₃ electrode were used as working, counter and reference electrodes, respectively. Scans were taken at 0.1 V/s.

For **RuPt** slightly different behaviour was observed (Figure SB 5). Three reductions were observed at -1.38, -1.62 and -2.16 V, similar to those reported for **Ru** and **RuRe**. However, reversibility was partially lost for the first two reductions and completely lost for the third reduction. By analogy to the potentials observed for **Ru** and **RuRe**, these reductions are assigned to take place on the peripheral ligands and bridging ligand, respectively. However, a possible Pt centred reduction overlapping with the ligand centred reduction at -1.62 V cannot be ruled out. Two irreversible oxidations were observed at 0.98 and 1.22 V. The first oxidation at 0.98 V is tentatively assigned to the Ru^{II/III} oxidation. This oxidation has shifted anodically 300 mV when compared to **Ru**. We are currently unclear about the origin of the rather broad anodic current peak at 1.22 V, as similar oxidative features have not been observed for other Ru-Pt dinuclear species reported in the literature.^{56–58}

3.2.3. Spectroelectrochemistry

Infrared and UV-Vis spectroelectrochemistry were used to gain a better understanding of the potential intermediates generated during photocatalysis. IR-SEC can help to determine

localization of the electrons during photocatalysis and aid in determining the mechanisms, as well as optimizing ligand and complex design. In the case of the **RuRe** complex, the metal-carbonyls on the rhenium centre provide an extra handle to monitor changes in electron density at the metal centre.

3.2.3.1. *Infrared spectroelectrochemistry*

Initially, the **RuRe** complex was studied and carbonyls of the ester functional groups, as well as the metal carbonyls on the rhenium centre are used as a handle to determine the localization of the electrons during electrochemical reduction.

The IR spectrum of **RuRe** has metal carbonyl stretches at 2022, 1913 and 1899 cm^{-1} , as expected for a *fac*-tris carbonyl rhenium species, together with the organic carbonyl band at 1730 cm^{-1} (Figure 3-4, black trace). Upon the first 1-electron reduction starting at -1.2 V vs the Ag/Ag^+ pseudo-electrode (Figure 3-4, red trace), bleaching of the organic carbonyl at 1730 cm^{-1} occurs, with the formation of a broad absorption ranging from 1712 to 1656 cm^{-1} . This suggests localization of the electron on the peripheral ligand resulting in weakening of the C-O bond, with shifting of the stretching vibration to lower energy by approximately 40 cm^{-1} . The Re-carbonyl stretching vibrations also shift slightly to lower energy from 2022, 1913 and 1899 to 2018, 1905 and 1885 cm^{-1} . This shift is smaller than that observed for the organic carbonyls, suggesting that the reduction takes place on the peripheral ligands and not on the bridging ligand.

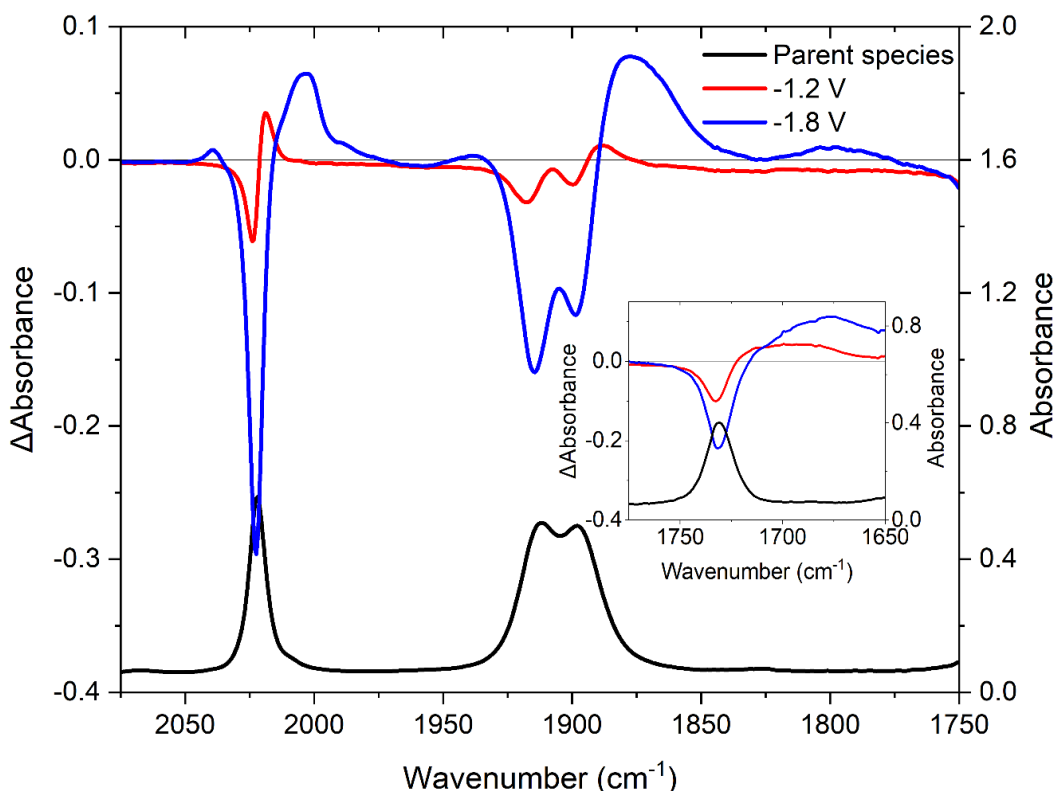


Figure 3-4. IR-SEC spectra for **RuRe** in acetonitrile with 0.1 M TBAPF₆ as supporting electrolyte. The IR (black) and difference spectra at -1.2 V (red) and -1.8 V (blue) vs silver wire pseudo-reference.

As the reduction potential was slowly decreased, the second reduction was reached at -1.4 V vs the Ag/Ag⁺ couple and the intensity of the new signals for the organic carbonyl between 1712 and 1656 cm⁻¹ increased, while the signals in the metal carbonyl region at 2018, 1905 and 1885 further depleted. This indicates that the reduction of the second peripheral ligand occurs prior to the reduction of the bridging ligand as suggested by the electrochemical data (*vide supra*). A third reduction occurs at -1.8 V vs the Ag/Ag⁺ couple, leading to the changes shown in Figure 3-4, (blue trace). Initially, the bleach at 2022 cm⁻¹ increases and the new signal at 2018 cm⁻¹ disappears with a new broad band at ~2000 cm⁻¹. The bleaches at 1913 and 1899 deplete further, together with the formation of a new broad band at 1880 cm⁻¹. The similarity of the new signals to the neutral complex suggest that the reduction takes place on the bridging ligand and not at the rhenium centre, as reduction of the rhenium metal would result in the dissociation of the halide and subsequent reactions.⁵⁹⁻⁶¹

Oxidation of **RuRe** at 2 V vs the Ag/Ag⁺ couple leads to bleaching of the metal carbonyl signals at 2022, 1913 and 1899 cm⁻¹ (Figure SB 9) together with bleaching of the organic carbonyl signal at 1730 cm⁻¹. New Re-CO carbonyl stretching vibrations were observed at higher energy, at 2031 and 1932 cm⁻¹ (albeit very weak in intensity). This may suggest possible loss of the metal

carbonyl moieties under oxidative conditions. A stronger new signal is observed for the organic carbonyl at 1740 cm^{-1} indicating a decrease of electron density on the peripheral ligand. Oxidation on the ruthenium centre induces an electron withdrawing effect on the peripheral ligands leading to a lowering in electron density on the ligand and a shift in the carbonyl bands to higher energy. A similar but weaker effect is observed for the metal carbonyls.

3.2.3.2. *UV-Vis spectroelectrochemistry*

Reductive UV-SEC was also carried out using **RuRe** with the changes observed depicted in Figure 3-5. Upon the first one electron reduction at -1.2 V vs the Ag/Ag^+ couple, the ligand centred transitions at 310 nm and the MLCT bands at 441 nm and 492 nm are bleached. New ligand centred transitions appear at 276 nm and 352 nm , in addition to new absorptions in the visible region at 444 nm and 548 nm . The new band at 444 nm is assigned to a ligand-to-metal charge transfer (LMCT) based on the literature.^{7,62} The new band at 548 nm is assigned to a ligand centred $\pi\text{-}\pi^*$ transition.^{7,13,18} Changing the potential to include the second reversible reduction at -1.4 V resulted in a further increase of intensity for the signals observed after the first reduction (Figure 3-5, blue trace), further supporting the assignment of this reduction on the second peripheral ligand. Probing of the third irreversible reduction was attempted. However, interference from solvent loss prevented us from studying the changes in the absorbance spectra following the third electron reduction.

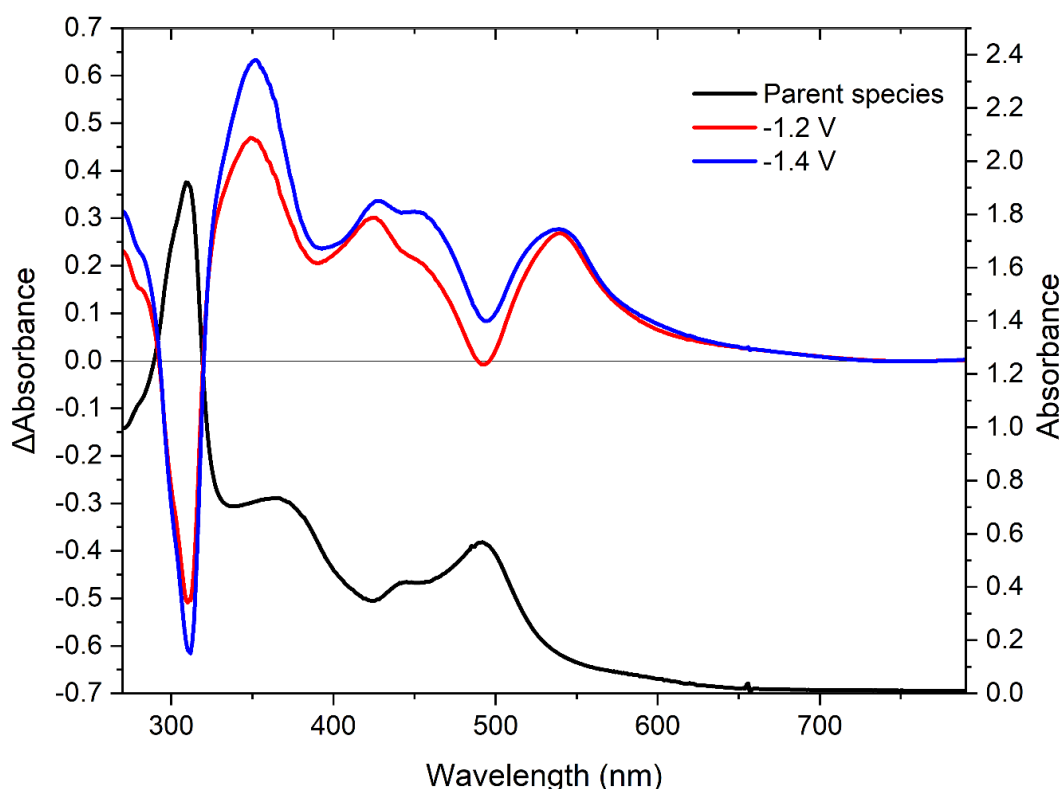


Figure 3-5. UV-Vis SEC spectra of **RuRe** in acetonitrile with 0.1 M TBAPF₆. The UV-Vis spectrum (black) and difference spectra at -1.2 V (red) and -1.4 V (blue) vs the silver wire pseudo-reference.

The oxidative UV-Vis spectroelectrochemistry of **RuRe** is presented in the ESI in Figure SB 17. At the onset of the first reversible oxidation of the ruthenium centre at 1.4 V vs the Ag/Ag⁺ couple, the ligand-centred transition at 310 nm redshifts slightly to 332 nm, through an inductive effect of the more positively charged ruthenium metal centre. The bands at 441 and 492 nm are bleached. As an electron is removed from the ruthenium centre, insufficient electron density is present on the metal centre to facilitate a MLCT. A broad but weak absorption between 650 and 1080 nm is observed. This absorption is assigned to a new LMCT from the polypyridyl ligands to the ruthenium centre.⁴⁸

3.2.4. Time-resolved infrared spectroscopy

Time-resolved infrared spectroscopy (TRIR) was used to investigate the excited state properties of the dinuclear complexes. Insight into the localization and lifetimes of the excited states is important to further improve materials for either hydrogen generation or CO₂ reduction.^{34,63,64} The TRIR spectra for **RuRe** following excitation at 510 nm are shown in Figure 3-6.

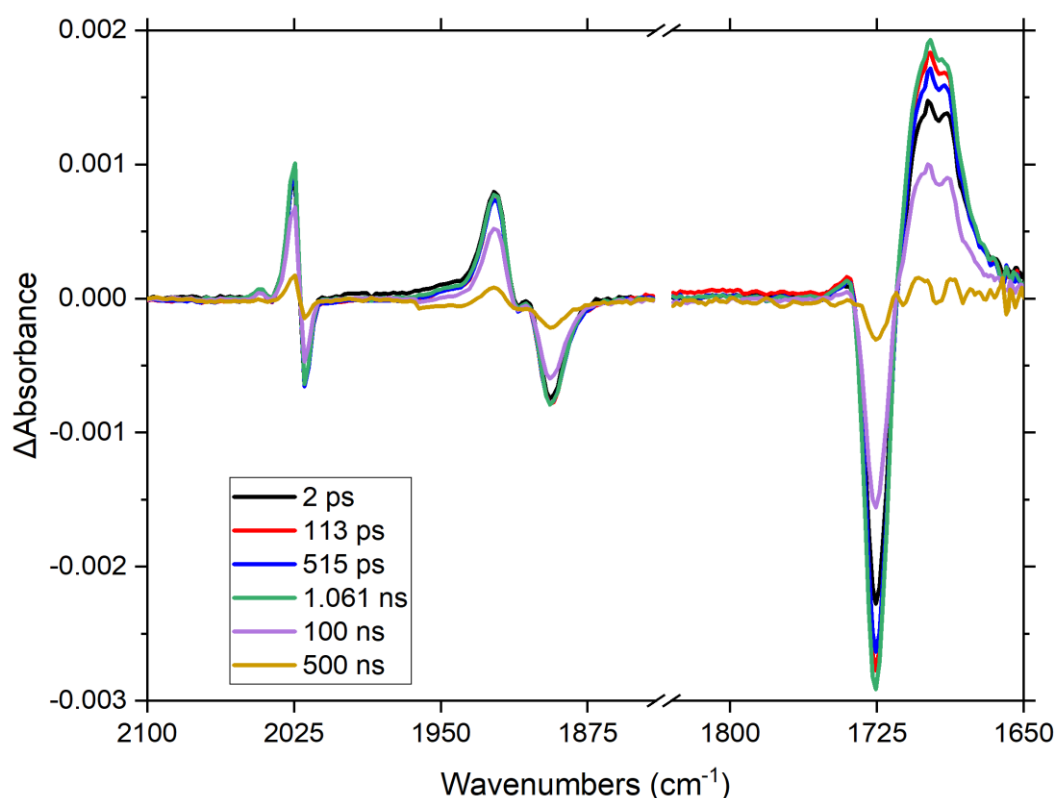


Figure 3-6. Time-resolved infrared spectrum following excitation of **RuRe** in $\text{CH}_3\text{CN-d}_3$ at 510 nm (1 mJ). Note- the spectra were collected using two separate solutions, indicated by the dash in the axis.

Upon excitation at 510 nm, the Re-CO stretching vibrations at 1892, 1911 and 2019 cm^{-1} deplete (Figure 3-6), together with the organic carbonyl (1730 cm^{-1}) on the peripheral ligands. Four new absorptions in this region are observed within the pulse; a broad signal at 1708 cm^{-1} and three sharper signals at 1904, 1922 (overlaps with parent depletion) and 2024 cm^{-1} (there is another feature to the high energy side of this latter band, the origin of which is unclear). These signals decay within 500 ns with concomitant recovery of the parent species, in non-degassed acetonitrile. The shift of the organic carbonyl to lower energy suggests that charge transfer takes place from the ruthenium centre towards the peripheral ligands. The shift of the metal-carbonyl signals to higher energy suggests that electron density decreases on the rhenium centre, thus ruling out electron transfer occurring from the ruthenium centre via the bridging ligand towards the rhenium metal centre, following excitation at 510 nm. These spectral changes agree with the previous observations in the electrochemical and spectroelectrochemical results (*vide supra*), where the LUMO was assigned to be localized on the peripheral dceb ligand with reduction on the bridging ligand only occurring at much lower potentials.

The TRIR data for **RuPt** is shown in the ESI (Figure SB 21). As for **RuRe**, the organic carbonyl from the ester moiety on the peripheral ligands in **RuPt** bleaches at 1729 cm^{-1} following excitation at 510 nm. A new absorption at approximately 1700 cm^{-1} is observed, again indicating an increase in electron density on the peripheral ligands, as was similarly observed for **RuRe**. This signal decays over 500 ns with concomitant recovery of the parent species.

3.2.5. Emission lifetimes

Emission lifetimes were determined at 690 nm following excitation at 355 nm (Figure SB 22-29). The three complexes were studied in deoxygenated acetonitrile solutions. For the mononuclear **Ru** species, a biexponential decay with lifetimes of 94 and 1284 ns was observed. The longer lifetime corresponds well to those found for similar ruthenium complexes.⁵³ The origin of the shorter lifetime is currently unclear. For the **RuRe** dinuclear complex a single lifetime of 557 ns was observed which was assigned to the $^3\text{MLCT}$ state and is significantly shorter than that of the mononuclear analogue. For the **RuPt** complex a biexponential decay with lifetimes of 14 and 517 ns was observed. In other dinuclear species, electron transfer towards the second metal resulted in a decrease of the lifetimes.^{13,24,52,65} However, the TRIR data did not indicate any electron transfer from the ruthenium centre towards the second metal centre for **RuRe**. Instead, the coordination of the Re and Pt metal centres alters the energy levels of the ground and excited states, as observed in the shift in the UV-Vis spectra and emission spectra between the mononuclear **Ru** and the dinuclear **RuRe** and **RuPt** (*vide supra*).

3.2.6. Photocatalysis in solution

RuPt was assessed for photocatalytic hydrogen evolution in an acetonitrile:triethylamine:water (60:30:10) mixture, using a 470 nm LED. A time dependent study over 24 hours showed no induction period for hydrogen generation (Figure SB 25) with a TON of 81 at 24 hours. In addition, TOFs of up to 20 h^{-1} were observed in the early stage of the catalytic reaction, which decreased notably within 10 hours. Absorption spectra obtained before and after photocatalysis experiments (Figure SB 26) indicates decomposition which correlated with the TONs observed for **RuPt**. The formation of a black precipitate after 10 hours further supports this assignment. Under identical conditions no hydrogen was detected for the previously reported palladium analogue (**RuPd**). However, other Ru-Pt dinuclear systems, for example $\text{Ru}(\text{tbbpy})_2(\text{tpphz})\text{PtI}_2$ (tbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine, tpphz = tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine) reported by Pfeffer et al. reported TONs of up to 238 under similar experimental conditions.⁶⁶ Another ruthenium complex, $\text{Ru}(\text{dceb})_2(2,5\text{-dpp})\text{PtCl}(\text{H}_2\text{O})$ (dpp = 2,2';5',2''-terpyridine) which contains the same peripheral ligands but a terpyridine bridging ligand also

yielded much higher TONs of up to 400 after 6 hours of irradiation.⁴³ This indicates that the bpt bridging ligand limits electron transfer towards the platinum centre following excitation and reductive quenching.

RuRe was assessed for photocatalytic CO₂ reduction in a 5:1 DMF:TEOA solution (purged with CO₂) with 1000 equivalents (vs catalyst) of BIH as a sacrificial agent, and 470 nm irradiation. However, no CO was detected in solution after 24 hours of irradiation.

3.2.7. Photoelectrocatalysis on NiO

RuPt and **RuRe** were also tested for photoelectrocatalytic water-splitting and CO₂ reduction respectively when immobilized on a p-type semiconductor (NiO) in a small-scale photoelectrochemical (PEC) test device. Photoelectrochemical experiments were performed in a gas-tight three electrode glass cell with the photocatalyst immobilized on a thin film of mesoporous NiO. In this setup the counter electrode was a platinum wire and the reference Ag/AgCl (3 M KCl). Mesoporous NiO thin films of approximately 1.5 micron thickness were produced by doctor blading NiO precursor solution onto conductive glass substrates (Pilkington TEC 15 fluorine doped tin oxide glass), followed by annealing at 450 °C for 30 minutes with a ramp time of 30 mins. Full details of the method for preparing a NiO precursor solution can be found in the experimental section. The assembled PEC cell was filled with the desired aqueous electrolyte and purged for 20 minutes with research grade CO₂ (BOC) or argon before an experiment. The electrodes were connected to a potentiostat (Palmsens EmStat3 Blue) and illumination was provided by a 300 W Xe arc lamp. The distance from the lamp to the face of the photocathode was adjusted so that illumination intensity was equivalent to 1 sun (100 mW cm⁻²). An AM 1.5 filter was used with the light source to simulate the solar spectrum.

We and others showed previously⁷ that the ethyl ester group is an effective means of adsorption of the photocatalyst to the NiO surface, as it facilitates photoinduced charge transfer at the interface and has an impact on tuning the energy and dynamics of the excited states.

With the photocatalysts immobilized on the NiO following dye bath (3 mM concentration of dye in dry acetonitrile) deposition for 12 hours, the NiO was visibly coloured. UV-vis spectroscopy revealed that the absorption maxima for **RuPt** and **RuRe** had red-shifted, the absorption maximum for the MLCT band now residing at 575 for **Ru**, 520 for **RuPt** and 537 nm for **RuRe** (Figure SB 28). Similar broadening and red-shifting of the spectra is consistent with previous studies with similar photocatalysts on NiO.⁷

Dye adsorption was quantified by UV-vis absorption measurements of solutions following dye desorption from the sensitized NiO films after soaking in 0.5 M NaOH solution. Using this

method the approximate dye loading of the systems on NiO was 9 nmol cm⁻² for **Ru**, 7 nmol cm⁻² for **RuRe** and 4 nmol cm⁻² for **RuPt**. Poldme et al. found 9 nmol nmol cm⁻² for **RuPd**. These values are similar in magnitude to other systems with typical anchoring groups such as phosphonic acid and carboxylic acid.^{67,68}

Photoelectrocatalysis was performed in various aqueous buffer solutions for **RuRe**, at pH 5, 8 and 9.2. The aim was to optimize device operating conditions such as the maximum and most stable photocurrent, as well as the detection of gaseous products. Tables 3 and 4 provides a summary of electrochemical measurements in our PEC cell. In the case of **RuRe** photocurrent densities were consistently 1 mA cm⁻² in pH 5 acetate buffer with an applied bias of -0.2 V, but this was improved in more alkaline conditions, with an average current density of 5.0 mA cm⁻² in pH 9.2 carbonate buffer. Linear sweep voltammetry was used to determine an appropriate bias to be applied to the system without degrading the photocatalyst. Optimum performance was seen with an applied bias of -0.2 V in the carbonate buffer, where minimal surface charging of the NiO was observed. The systems were also irradiated with an applied bias of -0.5 V (see supporting information).

Control experiments consisted of measuring blank NiO films and a NiO film with the compound lacking the catalytic centre (**Ru**). For a bare NiO film in pH 5 buffer with an applied bias of -0.2 V, light response was far less than with any of the dyed films, with an average photocurrent density of approx. 0.3 mA cm⁻² recorded. Under the same conditions we recorded a photocurrent density of 1.3 mA cm⁻² for **RuRe**. The experiments confirm that in general the performance of these photocatalysts is quite poor in acidic media, but there is evidence to suggest that more alkali conditions improve the performance. Gas chromatography measurement by head space sampling showed trace amounts of carbon monoxide being produced during photocatalysis of **RuRe** in pH 5 acetate buffer. After 1 hour irradiation, ca. 25 nmols CO was recorded (see Figure SB 48 for GC trace) which is equivalent to a TON of 4.5. For **RuPt** we could not detect more than very small trace amounts of evolved hydrogen from the NiO surface. After 1 hour, approximately 0.3 μmol H₂ was recorded by GC. Photocurrent densities were similar to those of **RuRe** under similar conditions, but rapid dye desorption prevented measurements at higher pH.

Table 3-3. Photoelectrochemical measurement of mesoporous NiO films containing the photocatalyst RuRe. Values are an average photocurrent across a measurement spanning 15 minutes.

RuRe photocurrent density (mA cm ⁻²)	pH 5 acetate buffer	pH 8 phosphate buffer	pH 9.2 carbonate buffer
-0.2 V	1.3	1.0	4.5
-0.5 V	1.1	2.5	5.0

Table 3-4. Photoelectrochemical measurement of mesoporous NiO films containing the photocatalyst RuPt. Values are an average photocurrent across a measurement spanning 15 minutes.

RuPt photocurrent density (mA cm ⁻²)	pH 5 acetate buffer	pH 8 phosphate buffer
-0.2 V	2.2	1.3
-0.5 V	7.9	7.4

3.3. Conclusion

Two novel supramolecular photocatalysts **RuRe** and **RuPt** were synthesized for CO₂ reduction and H₂ evolution, respectively. The complexes showed comparable photophysical properties and also similar electrochemical properties were observed for the **RuRe** and the mononuclear benchmark **Ru** complex. Three reversible reductions were observed for **Ru** and **RuRe**, while for the **RuPt** analogue the reversibility of the third reduction was lost. The three reductions could be assigned to the various ligands using the spectroelectrochemical results. The first two reductions were found to take place on the peripheral ligands, while the third reduction takes place on the bridging ligand. Upon one electron reduction, the organic carbonyl stretch of the ester moiety on the peripheral ligand moves to lower energy, suggesting an increase in electron density on the peripheral ligand. A smaller shift of the metal carbonyls for **RuRe** was assigned to an inductive effect due to the overall increase in electron density. Time-resolved infrared spectroscopy on the picosecond to nanosecond timescale was used to probe the nature of the excited state. A shift to lower energy for the organic carbonyl with a concomitant shift of the metal-carbonyls to higher energy suggest a MLCT excited state that predominantly localizes on the peripheral ligands. **RuRe** was found to be inactive for photocatalytic CO₂ reduction in DMF solution with BIH as sacrificial agent using 470 nm irradiation. The directionality of electron

transfer towards the peripheral ligand, as observed in the TRIR experiment, may explain the inactivity of the photocatalyst. Additionally, the significantly more negative reduction potential of the bridging ligand at -2.11 V vs $\text{Fc}^{0/+}$, compared to the reduction potentials of the peripheral ligands at -1.39 and -1.61 V vs $\text{Fc}^{0/+}$, suggest a clear preference of the complex to store any photo accumulated electrons on the peripheral ligand, from where electron transfer to the rhenium centre does not occur. In contrast, **RuPt** showed activity for the generation of H_2 , with TONs of 81 after 24 h. This was quite surprising as the previously reported palladium analogue, **RuPd** did not show any activity in solution. The difference in mechanism between palladium and platinum complexes may account for this variation in results. When immobilized on a NiO surface and assembled in a photoelectrocatalysis cell, **RuPt** showed very little activity, unlike the previously reported **RuPd** analogue. This was surprising and suggests that the mechanism taking place in solution is different compared to the immobilized system. The photocurrent density was disappointing for both **RuRe** under CO_2 and **RuPt** under Ar. It is likely that electron transfer to the peripheral ligand rather than the bridge favours charge-recombination at the interface between the NiO and the **Ru** photosensitiser rather than charge-transfer to the Re or Pt catalyst. Further work is necessary to optimize the relative energy of the components in the photocatalyst in order to improve the performance both in solution and in photocathodes.

3.4. Experimental

3.4.1. Materials

All chemicals and solvents were supplied by Aldrich Chemicals Co. and anhydrous solvents containing sure/seal were used under the flow of nitrogen.

3.4.2. UV-Vis and emission spectroscopy

All UV spectra were recorded on an Agilent 8453 UV-vis spectrophotometer equipped with Agilent ChemStation software. Emission and excitation spectra were obtained on a Perkin Elmer LS 50B at 20 ± 1 °C. UV-Vis spectra were taken at 0.025 mM concentration in aerated acetonitrile in a 1 cm pathlength cell. Emission spectra were measured at ~0.01 mM with all complexes being iso-absorptive at 490 nm in a 1 cm pathlength fluorescence cuvette. All three complexes were excited at 490 nm.

3.4.3. Fourier transform Infrared spectroscopy

FTIR measurements were carried out on Perkin-Elmer 2000 FTIR spectrophotometer in a liquid solution cell using spectrophotometric grade acetonitrile.

3.4.4. Electrochemistry

All experiments were conducted with 1 mM solutions of the complex in spectroscopic grade acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. All solutions were purged for at least 10 minutes with N₂. A glassy carbon electrode, platinum wire and Ag/AgNO₃ electrode were used as working, counter and reference electrode, respectively. Ferrocene was added as internal reference. Scans were taken at 0.1 V/s.

3.4.5. Spectroelectrochemistry

All experiments were conducted in A custom OTTE cell supplied by Spectroelectrochemistry Reading with a platinum mesh working electrode, platinum mesh counter electrode and silver wire pseudo reference electrode. Fresh solutions of the complexes at 1.5 mM (UV-Vis) or 10 mM (IR) in spectroscopic grade acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte were used. All solutions were purged for at least 10 minutes with N₂.

3.4.6. NMR spectroscopy

All NMR spectra were recorded on either a Bruker 400 or 600 MHz spectrometer and were referenced to the deuterated solvent peak as an internal reference.

3.4.7. Ps-time resolved infrared spectroscopy

ps-TRIR spectra were recorded using the ULTRA instrument at the Central Laser Facility in the Rutherford Appleton Laboratory in the U.K. and has been described elsewhere.⁶⁹ Spectra were collected using 510 nm excitation with 1 microjoule power in a 0.1 mm pathlength Harrick cell.

3.4.8. Time resolved emission spectroscopy

Time-resolved photoluminescence was recorded using an Edinburgh Instruments LP980 Transient Absorption Spectrometer. The samples were prepared in anhydrous acetonitrile (Sigma-Aldrich, purity>99.9%) and degassed by 3 cycles of freeze- pump-thaw. The samples had a typical absorbance (in optical density OD) at the excitation wavelength (355 nm) equal to 0.1-0.15.

3.4.9. Photocatalytic homogeneous H₂ evolution and CO₂ reduction experiments

For photocatalytic hydrogen evolution, each sample was prepared in a 23 mL glass Schlenk tube stoppered with an air-tight rubber septum. 0.01 mM catalyst was dissolved in a 6:3:1 mixture of acetonitrile:triethylamine:water. The solution was degassed using three freeze-pump-thaw cycles and placed under an N₂ atmosphere prior to irradiation. An array with 470 nm LEDs with

20 mW output power was used to irradiate the sample. At selected timepoints, 1 mL of the headspace was withdrawn and injected into a GC to quantify the amount of hydrogen.

For photocatalytic CO₂ reduction, each sample was prepared in a 23 mL glass Schlenk tube stoppered with an air-tight rubber septum. 0.01 mM catalyst was dissolved in a 5:1 N,N-dimethyl formamide:triethanolamine mixture with 0.01 M BIH (dimethylphenylbenzimidazoline) as sacrificial agent. The solution was degassed using three freeze-pump-thaw cycles prior to irradiation and subsequently purged with CO₂ for 5 minutes. An array with 470 nm LEDs with 20 mW output power was used to irradiate the sample. At selected timepoints, 1 mL of the headspace was withdrawn and injected into a GC to quantify the amount of carbon monoxide.

3.4.10. Photoelectrochemical Measurements on NiO

Photoelectrochemical measurements on dye-sensitized mesoporous NiO thin films were performed using the device illustrated in the supporting information, connected to a PalmSens EMStat3 Blue USB potentiostat. NiO sol-gel precursor solution was prepared by adding anhydrous NiCl₂ (1 g, Sigma) and tri-block co-polymer F108 (poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)) (1g, Sigma) to ethanol (6 ml) and ultrapure water (5 ml). The solution was left to age in a vial for two weeks and subsequently centrifuged to remove any large aggregated polymer.

The thin films were then prepared by doctor blading onto cleaned conductive fluorine doped tin oxide glass (TEC™ 15, Pilkington), cut into 2x2 cm squares. The area of the NiO was 0.79 cm², punched through Scotch Magic Tape. After doctor blading, the film was allowed to dry for 5 minutes before annealing in a furnace for 30 minutes at 450 °C (in air), with a ramp time of 30 minutes. The doctor blading was repeated two more times at which point the “three-layer” mesoporous films have an approximate thickness of 1.5 microns (measured with a Dektak³ST surface profiler).

Steady-state UV-vis absorption measurements were performed using an Ocean Optics USB-2000+ spectrophotometer connected to a light source with deuterium and tungsten iodide lamps via a fibre optic coupling. The following aqueous buffer solutions were used for photoelectrocatalysis experiments: 0.1 M pH 5 acetate buffer, 0.1 M pH 8 phosphate buffer. 0.1 M pH 9.2 carbonate buffer.

3.4.11. Synthesis

Ru(dceb)₂Cl₂

Ru(dceb)₂Cl₂ was synthesized using a procedure developed in our lab. 0.42 g (2.05 mmol) *RuCl₃·3 H₂O* was dissolved in 45 mL of ethanol. The mixture was brought to reflux and 1 g (4.1 mmol) 4,4'-dicarboxylic acid-2,2'-bipyridine was slowly added over 30 minutes. The reaction was refluxed for 24 hours, after which the ethanol was removed under reduced pressure. The residue was washed with 10 mL diethyl ether and air dried yielding the product as a dark red solid (1.31 g, 1.7 mmol, 83%). ¹H-NMR (DMSO-*d*₆): 1.309 (t, 4 H), 1.4495 (t, 4H), 4.36 (q, 3H), 4.5322 (q, 3H), 7.494 (m, 2H), 7.761 (m, 2H), 8.258 (m, 2H), 8.931 (m, 2H), 9.117 (m, 2H), 10.105 (m, 2H).

[Ru(dceb)₂(bpt)](PF₆) (Ru)

0.42 g 3,5-di(pyridin-2-yl)-4H-1,2,4-triazole (HBpt) (1.88 mmol 1.4 equivalents) was dissolved in 300 mL of a 2:1 ethanol /water mixture. The solution was refluxed for 20 minutes. 1 g (1.30 mmol) of *Ru(dceb)₂Cl₂* was dissolved in 200 mL ethanol and added to the reaction mixture over 30 minutes. The reaction was refluxed for 6 hours, after which the ethanol was removed under reduced pressure. 200 mL of water was added, the mixture was filtered and 0.4 g (2.45 mmol, 1.9 equivalents) of *NH₄PF₆* was added. The product precipitated out of solution as a red solid which was further purified by column chromatography using SiO₂ as stationary phase and 10:1:0.1 acetonitrile/water/10% *KNO₃* solution in water as the eluent yielding **Ru** as a dark red solid (0.33 g, 0.26 mmol, 20%). 600 MHz ¹H-NMR (DMSO-*d*₆): 1.346 ppm (12H, m), 4.426 ppm (8H, m), 7.271 (1H, td), 7.304 (1H, td), 7.538 (1H, d), 7.775 (2H, m), 7.860 (1H, dd), 7.917 (2H, d), 7.968 (1H, dd), 8.020 (1H, dd), 8.043-8.086 (2H, m), 8.098 (1H, d), 8.119 (1H, d), 8.257 (1H, d), 8.467 (1H, d), 9.225 (2H, dd), 9.250 (2H, dd). ESI mass spectroscopy: 924.205 (calc.), 924.2046 (found).

[Ru(dceb)₂(bpt)Re(CO)₃Cl](PF₆) (RuRe)

0.1 g (0.082 mmol) of **Ru** was dissolved in 5 mL of methanol. 0.046 g (0.124 mmol, 1.5 equivalents) of *Re(CO)₅Cl* was added. The flask was wrapped in tin foil to avoid any contact with light. The reaction was refluxed for two hours, after which the solvent was removed under reduced pressure. 5 mL of ether was added and the formed suspension was stirred for an additional 30 minutes to remove unreacted *Re(CO)₅Cl*. The mixture was filtered and air dried to yield **RuRe** as a purple-red solid (0.098 g, 0.07 mmol, 87%). ¹H-NMR (DMSO-*d*₆): 1.361 (12H, m), 4.443 (8H, m), 7.562 (1H, td), 7.62 (1H, d), 7.641 (1H, td), 7.748 (1H, dd), 7.797 (1H, dd), 7.886

(2H, d), 7.995 (1H, dd), 8.037 (1H, d), 8.073-8.152 (m, 4H), 8.346 (1H, td), 8.604 (1H, d), 8.989 (1H, d), 9.248-9.299 (4H, m). ESI mass spectroscopy: 1230.115 (calc.), 1230.113 (found).

[Ru(dceb)₂(bpt)Pt(I)H₂O)](PF₆)₂ (RuPt)

0.1 g Ru (0.082 mmol) and 0.075 g (0.124 mmol, 1.5 eq.) Pt(I)₂(DMSO)₂ were dissolved in 10 mL acetonitrile. The solution was refluxed overnight. The solvent was removed under reduced pressure and 10 mL diethyl ether was added. The suspension was stirred for 30 minutes to remove unwanted Pt(I)₂(DMSO)₂. The suspension was filtered and air dried to yield **RuPt** as a dark-red solid (0.106 g, 0.07 mmol, 85%). 600 MHz ¹H-NMR (dmso-d₆): 1.358 ppm (12H, m), 4.426 (8H, m), 7.386 (1H, t), 7.447 (1H, t), 7.576 (1H, d), 7.784-7.863 (3H, m), 7.931, (1H, t), 7.986 (2H, m), 8.021 (1H, d), 8.162, (1H, t), 8.238 (1H, d), 8.356 (2 H, s, br), 8.623 (1H, br), 8.722 (1H, br), 9.128 (1H, s), 9.221 (3H, m) ESI-mass spectroscopy: 1372.980 (calc.), found 1372.977(found).

3.5. References

- 1 E. D. Cline and S. Bernhard, *CHIMIA International Journal for Chemistry*, 2009, **63**, 709–713.
- 2 K. E. Dalle, J. Warnan, J. J. Leung, B. Reuillard, I. S. Karmel and E. Reisner, *Chemical Reviews*, 2019, **119**, 2752–2875.
- 3 M. Dokić and H. Sen Soo, *Chemical Communications*, 2018, **54**, 6554–6572.
- 4 Y. Tamaki, D. Imori, T. Morimoto, K. Koike and O. Ishitani, *Dalton Transactions*, 2016, **45**, 14668–14677.
- 5 T. Toupance, M. Chavarot-Kerlidou and V. Artero, , DOI:10.1021/acsaem.9b00652.
- 6 S. Kaufhold, D. Imanbaew, C. Riehn and S. Rau, *Sustainable Energy and Fuels*, 2017, **1**, 2066–2070.
- 7 N. Pöldme, L. O'Reilly, I. Fletcher, J. Portoles, I. V. Sazanovich, M. Towrie, C. Long, J. G. Vos, M. T. Pryce and E. A. Gibson, *Chemical Science*, 2019, **10**, 99–112.
- 8 E. Deponti and M. Natali, *Dalton Transactions*, 2016, **45**, 9136–9147.
- 9 A. M. Cancelliere, F. Puntoriero, S. Serroni, S. Campagna, Y. Tamaki, D. Saito and O. Ishitani, *Chemical Science*, 2020, **11**, 1556–1563.
- 10 S. Hansen, M. Klahn, T. Beweries and U. Rosenthal, *ChemSusChem*, 2012, **5**, 656–660.
- 11 M. Ogawa, B. Balan, G. Ajayakumar, S. Masaoka, H. B. Kraatz, M. Muramatsu, S. Ito, Y. Nagasawa, H. Miyasaka and K. Sakai, *Dalton Transactions*, 2010, **39**, 4421–4434.
- 12 H. Ozawa, M. Kobayashi, B. Balan, S. Masaoka and K. Sakai, *Chemistry - An Asian Journal*, 2010, **5**, 1860–1869.
- 13 L. O'Reilly, Q. Pan, N. Das, K. Wenderich, J. P. Korterik, J. G. Vos, M. T. Pryce and A. Huijser, *ChemPhysChem*, 2018, **19**, 3084–3091.

- 14 N. Kaeffer, J. Massin, C. Lebrun, O. Renault, M. Chavarot-Kerlidou and V. Artero, *Journal of the American Chemical Society*, 2016, **138**, 12308–12311.
- 15 T. Kowacs, Q. Pan, P. Lang, L. O'Reilly, S. Rau, W. R. Browne, M. T. Pryce, A. Huijser and J. G. Vos, *Faraday Discussions*, 2015, **185**, 143–170.
- 16 C. Li, M. Wang, J. Pan, P. Zhang, R. Zhang and L. Sun, *Journal of Organometallic Chemistry*, 2009, **694**, 2814–2819.
- 17 H. Ozawa, M. A. Haga and K. Sakai, *Journal of the American Chemical Society*, 2006, **128**, 4926–4927.
- 18 L. Zedler, J. Guthmuller, R. de M. Inês, S. Kupfer, S. Kriek, M. Schmitt, J. Popp, S. Rau and B. Dietzek, *Chemical Communications*, 2014, **50**, 5227–5229.
- 19 A. K. Mengele, S. Kaufhold, C. Streb and S. Rau, *Dalton Transactions*, 2016, **45**, 6612–6618.
- 20 S. Tschierlei, M. Karnahl, M. Presselt, B. Dietzek, J. Guthmuller, L. González, M. Schmitt, S. Rau and J. Popp, *Angewandte Chemie - International Edition*, 2010, **49**, 3981–3984.
- 21 K. Yamauchi, S. Masaoka and K. Sakai, *Journal of the American Chemical Society*, 2009, **131**, 8404–8406.
- 22 H. Ozawa and K. Sakai, *Chemical Communications*, 2011, **47**, 2227–2242.
- 23 T. Kowacs, A. Huijser, S. Rau, M. T. Pryce, D. Schlettwein, Q. Pan, L. Freitag, L. González, J. G. Vos, J. C. Falgenhauer, W. R. Browne and J. P. Korterik, *Chemical Communications*, 2016, **52**, 9371–9374.
- 24 S. Rau, D. Dini, Y. Halpin, J. G. Vos and M. T. Pryce, *Dalton Transactions*, 2013, **42**, 16243.
- 25 G. Singh Bindra, M. Schulz, A. Paul, S. Soman, R. Groarke, J. Inglis, M. T. Pryce, W. R. Browne, S. Rau, B. J. MacLean and J. G. Vos, *Dalton Transactions*, 2011, **40**, 10812–10814.
- 26 G. Singh Bindra, M. Schulz, A. Paul, R. Groarke, S. Soman, J. L. Inglis, W. R. Browne, M. G. Pfeffer, S. Rau, B. J. MacLean, M. T. Pryce and J. G. Vos, *Dalton Transactions*, 2012, **41**, 13050–13059.
- 27 M. Karnahl, C. Kuhnt, F. Ma, A. Yartsev, M. Schmitt, B. Dietzek, S. Rau and J. Popp, *ChemPhysChem*, 2011, **12**, 2101–2109.
- 28 L. Zedler, A. K. Mengele, K. M. Ziems, Y. Zhang, M. Wächtler, S. Gräfe, T. Pascher, S. Rau, S. Kupfer and B. Dietzek, *Angewandte Chemie International Edition*, 2019, **58**, 13140–13148.
- 29 A. Nakada, K. Koike, T. Nakashima, T. Morimoto and O. Ishitani, *Inorganic Chemistry*, 2015, **54**, 1800–1807.
- 30 Y. Tamaki and O. Ishitani, *ACS Catalysis*, 2017, **7**, 3394–3409.
- 31 S. Sato, K. Koike, H. Inoue and O. Ishitani, *Photochemical and Photobiological Sciences*, 2007, **6**, 454–461.

- 32 Y. Ueda, H. Takeda, T. Yui, K. Koike, Y. Goto, S. Inagaki and O. Ishitani, *ChemSusChem*, 2015, **8**, 439–442.
- 33 Z. Y. Bian, K. Sumi, M. Furue, S. Sato, K. Koike and O. Ishitani, *Journal of the Chemical Society. Dalton Transactions*, 2009, 983–993.
- 34 Y. Yamazaki, K. Ohkubo, D. Saito, T. Yatsu, Y. Tamaki, S. Tanaka, K. Koike, K. Onda and O. Ishitani, *Inorganic Chemistry*, 2019, **58**, 11480–11492.
- 35 Z. Bian, K. Sumi, M. Furue, S. Sato, K. Koike and O. Ishitani, *Inorganic Chemistry*, 2008, **47**, 10801–10803.
- 36 B. Gholamkhass, H. Mametsuka, K. Koike, T. Tanabe, M. Furue and O. Ishitani, *Inorganic Chemistry*, 2005, **44**, 2326–2336.
- 37 K. Morita, K. Takijiri, K. Sakai and H. Ozawa, *Dalton Transactions*, 2017, **46**, 15181–15185.
- 38 D. A. Hoogeveen, M. Fournier, S. A. Bonke, X. Y. Fang, A. J. Mozer, A. Mishra, P. Bäuerle, A. N. Simonov and L. Spiccia, *Electrochimica Acta*, 2016, **219**, 773–780.
- 39 Z. Yu, F. Li and L. Sun, *Energy and Environmental Science*, 2015, **8**, 760–775.
- 40 R. Kamata, H. Kumagai, Y. Yamazaki, M. Higashi, R. Abe and O. Ishitani, *Journal of Materials Chemistry A*, , DOI:10.1039/d0ta07351b.
- 41 K. L. Materna, N. Lalaoui, J. A. Laureanti, A. P. Walsh, B. P. Rimgard, R. Lomoth, A. Thapper, S. Ott, W. J. Shaw, H. Tian and L. Hammarström, *ACS Applied Materials and Interfaces*, 2020, **12**, 4501–4509.
- 42 R. Kamata, H. Kumagai, Y. Yamazaki, G. Sahara and O. Ishitani, *ACS Applied Materials and Interfaces*, 2019, **11**, 5632–5641.
- 43 Q. Pan, J. G. Vos, P. Lang, A. Huijser, T. Kowacs, L. O'Reilly, M. T. Pryce, S. Rau and W. R. Browne, *Inorganic Chemistry*, 2016, **55**, 2685–2690.
- 44 M. G. Pfeffer, B. Schäfer, G. Smolentsev, J. Uhlig, E. Nazarenko, J. Guthmuller, C. Kuhnt, M. Wächtler, B. Dietzek, V. Sundström and S. Rau, *Angewandte Chemie - International Edition*, 2015, **54**, 5044–5048.
- 45 M. Staniszewska, S. Kupfer and J. Guthmuller, *Journal of Physical Chemistry C*, 2019, **123**, 16003–16013.
- 46 P. Lei, M. Hedlund, R. Lomoth, H. Rensmo, O. Johansson and L. Hammarström, *Journal of the American Chemical Society*, 2008, **130**, 26–27.
- 47 Y. Zhang, S. Kupfer, L. Zedler, J. Schindler, T. Bocklitz, J. Guthmuller, S. Rau and B. Dietzek, *Physical Chemistry Chemical Physics*, 2015, **17**, 29637–29646.
- 48 Y. Zhang, P. Traber, L. Zedler, S. Kupfer, S. Gräfe, M. Schulz, W. Frey, M. Karnahl and B. Dietzek, *Physical Chemistry Chemical Physics*, 2018, **20**, 24843–24857.

- 49 C. Kranz and M. Wächtler, *Chemical Society Reviews*, 2021, **50**, 1407–1437.
- 50 L. Frayne, N. Das, A. Paul, S. Amirjalayer, W. J. Buma, S. Woutersen, C. Long, J. G. Vos and M. T. Pryce, *ChemPhotoChem*, 2018, **2**, 323–331.
- 51 D. Isakov, R. Giereth, D. Nauroozi, S. Tschierlei and S. Rau, *Inorganic Chemistry*, 2019, **58**, 12646–12653.
- 52 N. Das, S. Bindra, A. Paul, J. G. Vos, M. Schulz and M. T. Pryce, 2017, 5330–5337.
- 53 R. Hage, J. G. Haasnoot, J. Reedijk, R. Wang and J. G. Vos, *Inorganic Chemistry*, 1991, **30**, 3263–3269.
- 54 D. Mulhern, S. Brooker, H. Görls, S. Rau and J. G. Vos, *Dalton Transactions*, 2006, 51–57.
- 55 W. R. Browne, C. M. O'Connor, H. P. Hughes, R. Hage, O. Walter, M. Doering, J. F. Gallagher and J. G. Vos, *Journal of the Chemical Society, Dalton Transactions*, 2002, 4048–4054.
- 56 M. Miyaji, K. Kitamoto, H. Ozawa and K. Sakai, *European Journal of Inorganic Chemistry*, 2017, **2017**, 1237–1244.
- 57 M. Kobayashi, S. Masaoka and K. Sakai, *Molecules*, 2010, **15**, 4908–4923.
- 58 M. Ogawa, G. Ajayakumar, S. Masaoka, H. B. Kraatz and K. Sakai, *Chemistry - A European Journal*, 2011, **17**, 1148–1162.
- 59 G. J. Stor, F. Hartl, J. W. M. Van Outersterp and D. J. Stufkens, *Organometallics*, 1995, **14**, 1115–1131.
- 60 S. Zálíš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl and A. Vlček, *Inorganica Chimica Acta*, 2011, **374**, 578–585.
- 61 S. Frantz, J. Fiedler, I. Hartenbach, T. Schleid and W. Kaim, *Journal of Organometallic Chemistry*, 2004, **689**, 3031–3039.
- 62 M. Rupp, T. Auvray, E. Rousset, G. M. Mercier, V. Marvaud, D. G. Kurth and G. S. Hanan, *Inorganic Chemistry*, 2019, **58**, 9127–9134.
- 63 K. Koike, D. C. Grills, Y. Tamaki, E. Fujita, K. Okubo, Y. Yamazaki, M. Saigo, T. Mukuta, K. Onda and O. Ishitani, *Chemical Science*, 2018, **9**, 2961–2974.
- 64 S. Tschierlei, M. Presselt, C. Kuhnt, A. Yartsev, T. Pascher, V. Sundström, M. Karnahl, M. Schwalbe, B. Schäfer, S. Rau, M. Schmitt, B. Dietzek and J. Popp, *Chemistry - A European Journal*, 2009, **15**, 7678–7688.
- 65 Q. Pan, F. Mecozzi, J. P. Korterik, D. Sharma, J. L. Herek, J. G. Vos, W. R. Browne and A. Huijser, *Journal of Physical Chemistry C*, 2014, **118**, 20799–20806.
- 66 M. G. Pfeffer, T. Kowacs, M. Wächtler, J. Guthmüller, B. Dietzek, J. G. Vos and S. Rau, *Angewandte Chemie - International Edition*, 2015, **54**, 6627–6631.

- 67 R. A. Wahyuono, S. Amthor, C. Müller, S. Rau and B. Dietzek, *ChemPhotoChem*, 2020, **4**, 618–629.
- 68 Y. Pellegrin, L. Le Pleux, E. Blart, A. Renaud, B. Chavillon, N. Szuwarski, M. Boujtita, L. Cario, S. Jobic, D. Jacquemin and F. Odobel, *Journal of Photochemistry and Photobiology A: Chemistry*, 2011, **219**, 235–242.
- 69 G. M. Greetham, P. Burgos, C. Qian, I. P. Clark, P. S. Codd, R. C. Farrow, M. W. George, M. Kogimtzis, P. Matousek, A. W. Parker, M. R. Pollard, D. A. Robinson, X. Zhi-Jun and M. Towrie, *Applied Spectroscopy*, 2010, **64**, 1311–1319.

Chapter 4: Ruthenium-Rhenium and Ruthenium-Palladium Supramolecular Photocatalysts for Photoelectrocatalytic CO₂ and H⁺ Reduction

Chapter 4 describes the synthesis of novel tris-heteroleptic ruthenium photosensitisers bearing a 2,2-bipyridine peripheral ligand, a 2,2'-bipyridine-4,4'-carboxylic acid peripheral ligand and a 3,5-di(pyridin-2-yl)-1,2,4-triazole bridging ligand. Re(CO)₃Cl and PdCl₂ metal centres were attached to the triazole bridging ligand to create novel supramolecular assemblies for photocatalytic CO₂ reduction and photocatalytical hydrogen evolution. The excited state properties of the complexes were tested in solution and on a NiO semiconductor surface. Finally, the photocatalytical properties of these complexes were tested when immobilized on a NiO semiconductor surface under visible light irradiation.

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4.1. Abstract

Photoelectrocatalysis offers the opportunity to close the carbon loop and convert captured CO₂ back into useful fuels and feedstocks, mitigating against anthropogenic climate change. However, since CO₂ is inherently stable and sunlight is a diffuse and intermittent energy source, there are considerable scientific challenges to overcome. In this paper we present the integration of two new metal-organic photocatalysts into photocathodes for the reduction of CO₂ using ambient light. The two molecular dyads contained a rhenium carbonyl or Pd-based catalytic centre bridged to a ruthenium bipyridyl photosensitiser functionalised with carboxylic acid groups to enable adsorption onto the surface of mesoporous NiO cathodes. The photocathodes were evaluated for photoelectrochemical reduction of CO₂ to CO or H⁺ to H₂ and the performances were compared directly with a control compound lacking the catalytic site. A suite of electrochemical, UV-visible steady-state/time-resolved spectroscopy, X-ray photoelectron spectroscopy and gas chromatography measurements were employed to gain kinetic and mechanistic insight to primary electron transfer processes and relate the structure to the photoelectrocatalytic performance under various conditions in aqueous media. A change in behaviour when the photocatalysts were immobilized on NiO was observed. Importantly, the transfer of electron density towards the Re-CO catalytic centre was observed, using time resolved infrared spectroscopy, only when the photocatalyst was immobilized on NiO and not in MeCN solution. We observed that photocurrent and gaseous photoproduct yields are limited by a relatively low yield of the required charge-separated state across the NiO|Photocatalyst interface. Nonetheless, the high Faradaic Efficiency (94%) and selectivity (99%) of the Re system towards CO evolution are very promising.

4.2. Introduction

For many decades, chemists have been trying to create molecular systems that mimic photosynthesis in order to capture the energy available in sunlight in chemical bonds. There are now an abundance of chromophores and catalysts,^{1–3} and various colloidal semiconductors that can drive the water splitting reaction or reduce CO₂ to produce energy dense fuels such as H₂, CO, HCO₂H and hydrocarbons.^{4–8} These systems offer opportunities to tune the products with high selectivity and atom efficiency. Pioneering work into artificial photosynthesis and molecular photophysics from the 1970s and 1980s provided a wealth of information on the photophysics of such systems.^{9,10} The challenges of light-driven water-splitting and CO₂ reduction using molecular systems in solution are well documented.^{11–14} These include the difficulty of driving multi-electron chemistry when each photon absorbed only provides a single pair of an electron and hole. Storing charges on the appropriate timescale to drive the

chemistry, while avoiding decomposition pathways, is a major focus of current research. As more elaborate chromophores have been developed to resolve these challenges, detailed mechanistic insight has been gained from investigations into primary photo-induced electron transfer and energy transfer. These processes are highly sensitive to minor structural changes and modification of the local environment, adding another layer of complexity.¹⁵ At this point, for systems in solution, the thermodynamic and kinetic requirements for developing effective assemblies to separate redox pairs from light harvesting arrays are well-understood, nonetheless. Some headway has also been made towards developing catalysts from earth-abundant metals.^{16–20} A key issue still remains for molecular and colloidal artificial photosynthetic systems. That is, that the charge required to drive the oxidation or reduction reactions, which are usually performed with two separate photocatalysts, is usually provided by a sacrificial reagent. This requirement limits the sustainability of the process as well as generating reactive waste products.

An alternative approach is to use a photoelectrochemical system where electrons liberated by the water oxidation reaction at the photoanode can then be consumed at the fuel forming reaction at the photocathode.^{21–26} Such systems perform with promising light-to-fuel efficiency but in aqueous solutions, CO₂ reduction competes with the kinetically more favourable hydrogen evolution reaction and selectivity is difficult to control.^{27–30} A challenge is finding a p-type semiconductor that is stable to corrosion and has an appropriate electronic band alignment with the desired electrochemical reactions to deliver a high photovoltage and photocurrent density.³¹ Photocathodes have been reported based on metal phosphides, chalcogenides, oxides, III-V, p-Si and metal free semiconductors.^{7,23,28,32} For example, Kang et al. demonstrated that photocathodes based on CuFeO₂ and CuO binary films selectively produced formate from aqueous CO₂ at ~1% efficiency over 24 h, under AM 1.5G; 100 mW cm⁻² simulated sunlight. However, the photocathode gradually degraded over 17 days.³¹ Zhang et al. reported a Cu₂O-SnO_x nanowire-based photocathode that produced syngas (CO and H₂ with a ratio that could be adjusted with composition and applied bias) with a 11.61 mA cm⁻² at -0.55 V versus RHE, and a total Faradaic efficiency of 90.32% at -0.35 V versus RHE.³³ p-Si decorated with catalytic metal nanoparticles (e.g. Cu, Ag, Au) has been used to convert CO₂ to CO with Faradaic efficiencies >80%, but parasitic light absorption can limit the overall solar to fuel efficiency. Gong et al. reported an amorphous silicon photocathode, protected by a thin layer of TiO₂ and decorated with Au of variable thickness that enabled photocurrent densities of up to 6 mA m⁻² and CO/H₂ ratios that could be tuned between 1 : 2 and 1 : 3.1 by changing the applied bias between -0.1 V_{RHE} to 0.4 V_{RHE}.³⁴ Lewis et al. optimized a microstructured p-Si photocathode decorated with Cu

and attained a photocurrent density of 30 mA cm^{-2} in $0.1 \text{ M KHCO}_3(\text{aq})$ at -0.62 V vs RHE under AM 1.5 simulated solar illumination. CO , CH_4 , and C_2H_4 , were detected but the major product was hydrogen, with only 10% faradaic efficiency for carbon products.²⁸

A higher selectivity and lower parasitic absorption can be reached with molecular catalysts immobilized on semiconductor photocathodes.⁷ For example, Kumar et al. reported a p-type silicon photocathode coated with $[\text{Re}(\text{bipy-}^t\text{Bu})(\text{CO})_3\text{Cl}]$ that reduced CO_2 to CO under non-aqueous conditions with a faradaic efficiency of 97%.³⁵ $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ was immobilised via phosphonate linkers on the surface of a photocathode assembled from a nanostructured TiO scaffold deposited on TiO_2 -protected Cu_2O photocathodes.³⁶ Under non-aqueous conditions, the photocathode produced an initial photocurrent density of 2.5 mA cm^{-2} and Faradaic yields for CO between 80 and 95%. The catalyst molecules exceed 70 turnovers during a 1.5 h test at -2.05 V vs Fc^+/Fc , but there was a loss of activity. There are few reports of such high selectivity for CO under aqueous conditions, however.

In recent years, the wealth of knowledge gained from decades of research into dye-sensitized solar cells (DSSC) has been applied to optimizing photoelectrochemical (PEC) systems for both water-splitting and CO_2 reduction.^{37–41} Photoelectrochemical systems based on dye-sensitized electrodes (DS-PEC)^{42–44} can be used to generate solar fuels, circumventing one of the main obstacles encountered by molecular photocatalytic systems in solution, namely the frequent need for a sacrificial electron and proton source other than water.^{45,46} Instead, the molecular chromophore and catalyst are immobilized on the surface of a transparent electrode and excitation of the chromophore drives a cascade of electron transfer reactions between the electrode and the catalyst.^{47,48} TiO_2 is the optimum material for the photoanode. While a number of mesoporous materials were used for the photocathode, NiO is the most common choice due to its good transparency, p-type character, and stability under the conditions of the experiments.^{49–57} NiO is a well-understood p-type material with a valence band edge that lies sufficiently positive in energy to donate an electron to an excited molecular photosensitizer. It is typically chosen as the cathode material in photoelectrochemical systems due to its relatively good stability under a moderate pH range used and its optical band gap (3.6 eV) is sufficiently large that it does not compete for light absorption with the dyes and photocatalysts.^{58–61}

While these systems are fairly straightforward to assemble, and they maintain the high atom efficiency of the catalyst while benefitting from the robust semiconductor scaffold, the mechanism is complicated and optimization of the system is not so simple. The dynamics of the light-driven processes determined via studies of analogous chromophores in dilute solution do

not directly transfer to the equivalent DS-PEC device.^{62,63} Electron transfer from a dye/catalyst anchored to a semiconductor surface by the traditional strategy of an acid or phosphonate anchoring group leads to multiple competing recombination pathways, many similar to those seen with DSSCs.^{57,64–67} It is also now known that the chromophore's anchoring group itself can have a significant impact on charge-recombination.⁶⁸ Recent work has begun to recognise the challenges in engineering suitable catalysts and sensitizers for DS-PEC, which involves a combination of device engineering, optimizing reaction conditions and dye/catalyst design.^{48,69–77} A key design feature in DS-PEC systems is the spatial separation of the catalytic centre from the semiconductor surface to slow down charge-recombination and maximise catalytic turnover. Mastering all these facets simultaneously and scaling up devices presents a major challenge.

CO₂ reduction with DS-PEC has been investigated previously with devices incorporating a Ru(II)-Re(I) molecular photocatalyst. Ishitani and co-workers successfully demonstrated such a model system utilizing a phosphonic acid anchor for the Ru-Re catalyst on NiO where CO₂ was reduced predominantly to CO with a MeCN electrolyte at an applied potential of -1.2 V vs Ag/AgCl.⁷⁸ To function effectively over 15 hours in an aqueous environment, a polymer layer was added on top of the catalyst sensitized NiO to prevent desorption.^{43,44} Optimization of this system led to remarkable stability over 100 hours and the total TON of the photocatalytic CO₂ reduction exceeded 1200 (TON_{CO} = 576, TON_{HCOOH} = 695, TON_{H₂} = 172).⁷⁷

Previously we have shown that supramolecular photocatalysts containing ruthenium bipyridyl photosensitisers linked through a conjugated bridging ligand to a rhenium carbonyl or Pd catalytic centre drive photoelectrocatalytic reduction of CO₂ to CO or H⁺ to H₂ when integrated in NiO-based photocathodes. The Ru component enables the photocatalyst to absorb further into the red (towards 600 nm or beyond) than the Re complex alone (~ 450 nm).⁷⁹ A second advantage is that the absorption coefficient of the bimetallic system is higher than the Ru system alone, which means the NiO film can be quite thin to overcome the slow hole-transport.⁸⁰ Co-immobilization of the photosensitiser and catalyst would lead to competition for binding sites at the surface and so the thickness of the NiO would need to be even thicker to immobilize the equivalent number of chromophores as the supramolecular system. The third advantage of the structure is to improve the photophysics. The supramolecular structure is intended to provide conjugation from the NiO through to the catalytic centre so that excitation of the photocatalyst leads directly to reduction. In other systems the catalyst has been electronically decoupled from the photosensitiser and so sequential electron transfer steps are

required to reduce the catalyst. These processes compete with charge-recombination, which is prominent in NiO photoelectrodes, and so could limit the efficiency.⁸¹

In our previous work, the photocatalysts were adsorbed on the NiO surface through ester groups, but only trace amounts of CO were produced and it was noted that carboxylic acids may be preferable for anchoring to metal oxide surfaces.^{80–82} In this paper, we consider two photoelectrocatalysts, one for CO₂ reduction (PC1), one for H₂ evolution (PC2), with carboxylic acid groups for NiO photocathodes. PC3 was included as a catalyst-free compound to benchmark the activity. We also tested a Pt analogue of PC2, but this gave negligible photocurrent, so we have not included it here. This paper describes the optimization of reaction conditions, analysis of the electrochemical and photophysical properties in addition to chromatography measurements of gaseous products. Some of the major bottlenecks that we found in designing DS-PEC systems where the chromophore and catalyst are integrated in one molecule are discussed.

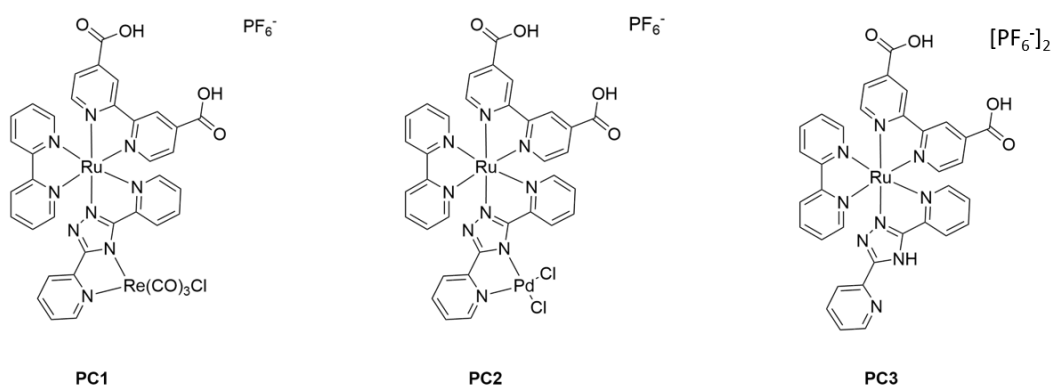


Figure 4-1. Molecular structures of the photocatalysts used in the present study. [Ru(bpy)(dcb)(bpt)Re(CO)₃Cl](PF₆)⁻ [PC1], [Ru(bpy)(dcb)(bpt)PdCl₂](PF₆)₂ [PC2], [Ru(bpy)(dcb)(bpt)](PF₆)₂ [PC3], (bpy = 2,2'-bipyridine, bpt = 3,5-di(pyridin-2-yl)-triazole, dcb = 2,2'-bipyridine-4,4'-dicarboxylic acid. PC1 is designed for CO₂ reduction, PC2 is designed for H₂ evolution and PC3 is a catalyst-free control.

4.3. Results and Discussion

4.3.1. Optical, electronic and electrocatalytic properties of the photocatalysts.

The photocatalysts were synthesized according to the procedures provided in the Supporting Information (SI) and were characterized by NMR, mass spectrometry and FTIR spectroscopy. Steady-state absorption and emission properties of the photocatalysts PC1-PC3 in solution, are summarized in Figure 2 and Table 1. The FTIR spectra of the ruthenium complexes in the 1650-2100 cm⁻¹ region are shown in Figure SC 28. All complexes show a signal at 1735 cm⁻¹ which is assigned to the CO stretch in the acid moiety on the dcb peripheral ligand. The IR spectrum for

[Ru(dcb)(bpy)(bpt)Re(CO)₃Cl](PF₆) contains stretching vibration at 1735 (COOH), 1896, 1908, 1930, 2020 and 2036 cm⁻¹. Based on the relative shapes of these stretches we assign these signals to a mixture of two different fac-Re(CO)₃Cl complexes. Similar observations have been observed by other groups for Ru-Re assemblies, and attributed to isomers.^{83–85}

Table 4-1 Summary of basic optical parameters for the photocatalysts used in this study. The molar absorption coefficient ϵ was determined at the absorption maximum, in acetonitrile.

Compound	λ_{max}^{abs} (MeCN) /nm	λ_{max}^{fluor} (MeCN) / nm	λ_{max}^{abs} (NiO) / nm	E ₀₀ /eV (MeCN)	ϵ / M ⁻¹ cm ⁻¹	Dye loading / mol cm ⁻²
PC1	470	671	470	2.05	9400	4.33 x10 ⁻⁸
PC2	474	665	467	1.98	12300	2.50 x10 ⁻⁸
PC3	490	720	480	1.99	2700	3.70 x10 ⁻⁸

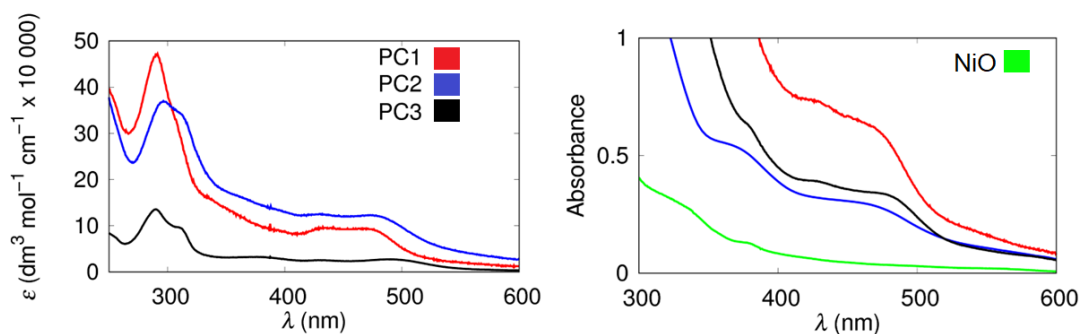


Figure 4-2 Left panel: steady-state absorption spectra of the photocatalysts in acetonitrile. Right panel: absorption spectra of the same systems when adhered to NiO electrodes following dye-bath deposition.

The chromophores developed in this study have absorption and emission properties analogous to other molecular systems developed around a ruthenium trisbipyridyl sensitizer, with metal-to-ligand charge transfer bands observed between 400-500 nm.^{62,86} As can be observed from Figure SC 29, the Re(Hbpt)(CO)₃Cl catalyst has very limited absorbance in the visible region of the solar spectrum. The RuRe supramolecular assembly PC1, however, has a significantly extended absorbance range, which should enable this assembly to deliver an improved photoelectrocatalytic activity compared to the Re(Hbpt)(CO)₃Cl complex by itself.

The dyes were adsorbed on the NiO surface by immersing the electrodes in an acetonitrile solution containing 3 mM photocatalyst overnight. A 10-20 nm blue shift in the absorption spectra was observed for each photocatalyst, which is consistent with the behaviour of the ester equivalents.⁶² The loading of the photocatalyst on the freshly prepared surface of the NiO was

quantified by desorbing the photocatalyst using 1 M NaOH solution and recording the UV-visible absorption spectrum. The loading was approximately 25-50 nmol cm⁻², which is much higher than the ester analogues (4-7 nmol cm⁻²).^{27,28, 61,87} This means that the light harvesting efficiency is sufficient with a thin NiO film (1.5 μm). Weak fluorescence was readily observed in solution (see SI), but this was very hard to detect reliably from the NiO surface. Therefore, fluorescence quenching could not be used effectively to characterise charge-transfer at the NiO|PC interface. Instead, transient absorption spectroscopy was employed (see below).

For charge-transfer to occur from the NiO to the photocatalyst following light absorption, the HOMO of the dye needs to be at more positive potential than the potential of the valence band edge, which is E_{VB} = c.a. -0.12 V vs. Fc for NiO in MeCN.⁸⁸ To estimate the ample driving force for charge transfer at the NiO|PC interface, cyclic voltammetry (CV) for PC1-3 was performed and the data acquired is provided in the SI. The CVs were not as straightforward as for the ester moieties, which show three reversible reductions and a reversible oxidation, due to the non-innocent behaviour of the acid moieties,⁷⁶ as the acids can undergo deprotonation following electrochemical reduction forming the carboxylates, causing irreversibility of the reduction process.

The CV for PC3 contains three reduction processes at -1.7, -2.0 and -2.2 V vs. Fc, which can be assigned to reduction of the three ligands. Based on previous reports, the reduction takes place in the order dcb > bpy > bpt.^{80,89,90} The first reduction appears to be irreversible while the second and third reduction have some reversible character. A fourth irreversible reduction at -2.8 V vs. Fc, may be assigned to a second reduction taking place on the bpt bridging ligand, as previously reported by Vos *et al.* for the Ru(bpy)₂(bpt) complex. A reversible oxidation at ca. 0.75 V vs. Fc is assigned to the Ru^{II/III} oxidation. A small shouldering irreversible oxidation at 0.44 V was also observed for the Ru-ester analogue (Ru(dceb)₂(bpt)) and can be assigned to residual Ru(dcb)(bpy)(Hbpt) in which the triazole moiety on the ruthenium complex is still protonated.⁹¹ No reductive signals were observed for this protonated species as the proton is lost under slight reductive conditions forming the deprotonated species which is consequently observed in the reductive region of the CV.

The CV for PC2 was more complicated than that of the Ru mononuclear species, PC3. The separate reduction processes observed between -1.7 and -2.2 V for PC3 were less resolved for PC2 and became fully irreversible. The reversible oxidation for the Ru centre was also shifted anodically to 0.85 V vs Fc. A second irreversible oxidation was observed at 1.4 V vs. Fc, which relates to oxidation of the Pd centre. As for PC2, the CV for the RuRe analogue PC1 contained

additional reductive and oxidative features compared to PC3. The reduction processes on the three ligands of the Ru complex also became irreversible and were observed at -1.8, -2.0 and -2.1 V. Reversibility was also partially lost for the $\text{Ru}^{\text{II/III}}$ oxidation which is observed at 0.9 V vs. Fc. A second oxidation at 1.1 V is likely to be associated with the $\text{Re}^{\text{I/II}}$ oxidation.⁹²

To determine the feasibility of CO_2 reduction by the supramolecular assembly, PC1 and the corresponding $\text{Re}(\text{Hbpt})(\text{CO})_3\text{Cl}$ fragment were tested for electrocatalytic reduction of CO_2 . First, both catalysts were tested in a homogeneous system using DMF as the solvent bubbled either with N_2 (blank test) or CO_2 (catalytic test) respectively. Both PC1 and the $\text{Re}(\text{bpt})(\text{CO})_3\text{Cl}$ complex showed a similar increase in current under a CO_2 atmosphere with an $\frac{I_{\text{cat}}}{I_0}$ of 3.31 for the PC1 assembly and 3.04 for the $\text{Re}(\text{Hbpt})(\text{CO})_3\text{Cl}$ complex (Figures S40 & S41). The observed current increase for the $\text{Re}(\text{Hbpt})(\text{CO})_3\text{Cl}$ matches well with the value observed for the similar $\text{Re}(\text{Hph})(\text{CO})_3\text{Cl}$ (3.58) which was previously reported for electrocatalytic CO_2 reduction by Nguyen et al.⁹³ The fairly small difference in catalytic activity between the $\text{Re}(\text{bpt})(\text{CO})_3\text{Cl}$ fragment and the supramolecular assembly PC1 is consistent with the limited influence of the Ru fragment on the Re catalytic centre as observed for the analogous supramolecular assembly utilising the bpt bridging ligand but with ester rather than acid groups on the peripheral bpy ligands.⁸⁰

4.3.2. Kinetic experiments

Ultrafast UV-visible transient absorption spectroscopy (TA) and time-resolved infrared spectroscopy (TRIR) measurements were used to explore the excited state dynamics of PC1-3 in solution and when adsorbed on the NiO substrates. The spectra at selected time delays after excitation at 500 nm are shown in Figure 3 and the results from global analysis of the data are provided in the SI. The spectra are consistent with rapid intersystem crossing from the singlet excited state to form the triplet metal-to-ligand charge (MLCT) transfer states.⁹⁴ For PC3, there was a positive differential absorption < 430 nm, a bleach corresponding to the ground state absorption below 560 nm, and a broad transient absorption above 560 nm. The spectral features changed little within the timescale of the experiment (6 ns). The excited state absorption > 500 nm for $\text{Ru}(\text{bpy})_3^{2+}$ is normally weak, but a fairly intense absorption was observed for PC3*, which suggests that electron density on the bridging ligand plays a role in the excited states, even though the dcb ligand lies at lower energy than the bpt (see above). Global analysis of the data revealed two components, $\tau_1 \sim 200$ ps, and $\tau_2 \gg 1$ ns. The transient absorption < 380 nm was consistent with the bipyridyl-centred ligand $\pi\text{-}\pi^*$ transition, and the broad absorption > 550 nm was consistent with ILCT. The point where $\Delta A = 0$ was slightly

different for the two components, with τ_2 slightly red shifted > 500 nm and τ_3 slightly blue shifted < 400 nm compared to τ_1 . It is likely that there is a mixture of excited states where the electron density is more localised on the different ligands (bpy, dcb or bridge) and each relaxes to the ground state with different lifetimes.

TA measurements of NiO|PC3 films revealed very different dynamics and global analysis revealed characteristically heterogeneous behaviour for dyes adsorbed on mesoporous semiconductor surfaces, which can be described by a minimum of three components. The two short-lived components were similar in shape and lifetime compared to PC3* in solution, $\tau_1 = 13$ ps, and $\tau_2 = 260$, and these are likely to be associated with relaxation of the excited states and charge-transfer from the NiO to PC3* to form NiO⁺|PC3⁻. $\tau_3 \gg 1$ ns, is assigned to the reduced photocatalyst (PC3⁻), with a weak transient absorption < 400 nm and > 510 nm. Dietzek et al. showed that MLCT states localized on the carboxylic acid-functionalised bipyridine are unfavourable for charge-separation.⁹⁵ In our previous work, we observed the presence of both charge-separated (NiO⁺|PC⁻) and excited states (NiO|PC*) for photocatalysts with diester-functionalised bipyridine ligands.^{62,63} In this case, for PC3, although most of the signal decays within 1 ns, there is evidence for successful charge-separation with the formation of NiO⁺|PC3.

The transient absorption spectra for PC1 in MeCN and PC1|NiO followed the same trend as PC3 and PC3|NiO, which suggests that the Re-centre has little impact on the photophysics of the ruthenium complex. However, PC2 behaved differently. The excited states for PC2 in MeCN decayed mostly within 6 ns window of the experiment. RuPd complexes typically have a low-lying triplet state which quenches the ³MLCT states. PC2|NiO contained spectral features and dynamics that were consistent with PC1|NiO and PC3|NiO, suggesting that charge-transfer from NiO to PC2* takes place, but the yield of the charge-separated state, NiO⁺|PC2⁻ could be lower than that of the other systems because of the shorter lifetime of the excited state of the photocatalyst.

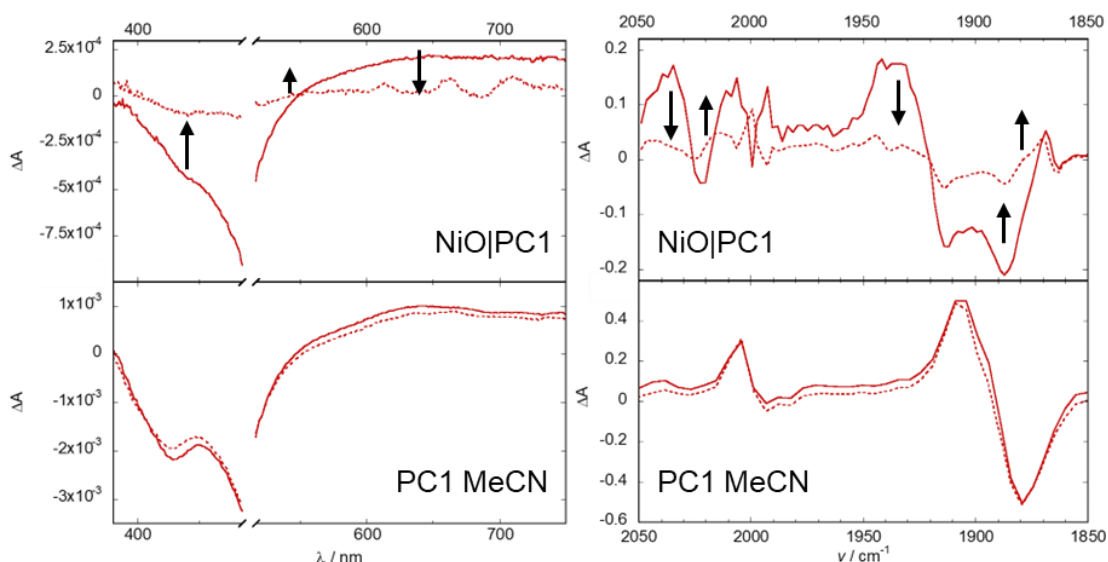


Figure 4-3 UV-visible transient absorption spectra (left) and time resolved infrared spectra (right) for PC1, 1 ps (solid line) and 1 ns (dotted line) following excitation at 500 nm in acetonitrile (bottom) and on a NiO thin film (top).

TRIR measurements of the metal carbonyl region provided information regarding the distribution of electron density in the excited state. The TRIR spectra for PC1 in MeCN are shown in Figure 3. Strong depletion of the parent bands at 1735, 1880 and 1993 cm^{-1} , and transient absorption bands at 1706, 1909 and 2004 cm^{-1} were observed to form within the laser pulse. The signals decayed beyond the 5 ns duration of the experiment, which is consistent with the ester analogue.²⁸ Global fitting (SI) of the TRIR data gave two components but very little spectral change between species, with $\tau_1 = 130$ ps, and $\tau_2 \gg 1$ ns, consistent with the TA spectra. The transient absorption bands for the Re-CO were positioned at the higher frequency side of the ground state bleach. This indicates that electron density moves away from the Re centre, resulting in a decrease in π -back bonding to the CO ligands. The transient absorption bands for the bpy-C(O)OH were positioned at the lower frequency side of the ground state bleach. This indicates that electron density moves towards the dcb ligands in the excited state rather than towards the catalytic centre. The TRIR spectra for PC2 and PC3 in MeCN are shown in the SI. The spectra were similar to PC1, containing bleaching of the parent bands at 1735 cm^{-1} and a transient absorption at 1700 cm^{-1} , consistent with $^3\text{MLCT}$ states with the electron density moving towards the bipyridine dicarboxylic acid ligand following excitation. The lifetime of the excited PC2 (major component $\tau_2 = 1.2$ ns) was short compared to PC3 in MeCN (major component $\tau_2 \gg 1$ ns). It would be possible, but less likely than PC3 and PC1, that electron transfer from NiO to the excited photocatalyst PC2 would be able to compete with the decay of this excited state, and the charge-injection efficiency is probably limited by this fast decay. The results from the solution studies were consistent with our prior results for the ester derivatives.

We repeated the TRIR experiments for the immobilised photocatalysts, NiO|PC. The data were affected by typical scattering from dye-sensitized films, but the key features were observed. For NiO|PC3 and NiO|PC2, there was no observable signal in the carbonyl region. It was expected that the C=O stretch for the acid anchoring group would be absent in the IR spectra of photocatalysts adsorbed onto NiO.⁹⁶ Instead, we observed a broad absorption across the fingerprint region corresponding to changes in electron density in the aromatic ligands following excitation. These features decayed on timescales broadly consistent with the transient absorption spectra. For NiO|PC1, we were able to observe the characteristic bleach and corresponding absorption for the CO ligands on the Re centre. Interestingly, the spectral shape changed during the duration of the experiment, unlike in the solution TRIR. The transient absorption shifts to lower wavenumber at increasing delay time after excitation and this is consistent with an increase in electron density on the Re centre, leading to increased π -back bonding to the CO ligands, lengthening the CO bond. This is consistent with the reduction of the photocatalyst and the shift in electron density towards the Re centre would favour catalysis. We attribute this difference to a change in the relative energy of the ligands when the photocatalysts are immobilised on NiO. An increase in the LUMO energy on binding to NiO would be consistent with the blue shift in the absorption spectrum observed (above).

Table 4-2 Summary of lifetimes estimated by fitting the evolution of the TA and TRIR spectra using global analysis.

	PC1	PC2	PC3
TAS in MeCN	$\tau_1 = 160$ ps, and $\tau_2 = >>1$ ns	$\tau_1 = 35$ ps, and $\tau_2 = 980$ ps, $\tau_3 >>1$ ns	$\tau_1 = 200$ ps, and $\tau_2 = >>1$ ns
TAS on NiO	$\tau_1 = 4.6$ ps, $\tau_2 = 110$ ps, and $\tau_3 \sim 5.1$ ns	$\tau_1 = 6.0$ ps, $\tau_2 = 120$ ps, and $\tau_3 >> 1$ ns	$\tau_1 = 13$ ps, and $\tau_2 = 260$, $\tau_3 >>1$ ns
TRIR in MeCN	$\tau_1 = 130$ ps, and $\tau_2 = >>1$ ns	$\tau_1 = 22$ ps, and $\tau_2 = 1.2$ ns, $\tau_3 >>1$ ns	$\tau_1 = 14$ ps, and $\tau_2 = >>1$ ns
TRIR Film	$\tau_1 = 2.4$ ps, $\tau_2 = 150$ ps, and $\tau_3 >>1$ ns	$\tau_1 = 7.0$ ps, $\tau_2 = 120$ ps, and $\tau_3 >> 1$ ns	$\tau_1 = 7$ ps, and $\tau_2 = 81$, $\tau_3 >>1$ ns

4.3.3. Photoelectrocatalysis

The photocurrent for NiO|PC1 was recorded under chopped light illumination in the presence of an electron acceptor in solution (10 mM tris(ethylenediamine)cobalt(III)) (see SI). This provides an idealized case to test the photocathodic response where electrons are extracted from the photocathode. The observed current density of approx. $20 \mu\text{A cm}^{-2}$ confirmed that PC1

transfers charge from the NiO electrode to the electron acceptor in solution in the presence of light.

Photoelectrochemical experiments were then performed with PC1|NiO without the electron acceptor but, instead, bubbling with CO₂ or Ar to evaluate whether PC1 could drive photoelectrocatalysis. The photocurrents and evolved gasses were evaluated under a range of pH between 5 to 9.2. An ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, was also tested due to its CO₂-solvation ability.^{97,98} A summary of results for the evaluated systems is provided in Table 3. Similar current densities were recorded for each, under simulated 100 mW cm⁻² intensity AM1.5 irradiation. Figures 4-4 and SC65-73 illustrate the photocurrent observed in the devices tested.

At the beginning of each experiment a characteristic spike in the dark current was recorded which has been associated with charging of the electrode surface.⁹⁹ Results from PEC experiments under two different applied bias, -0.2 and -0.5 V vs Ag/AgCl, are presented in the SI (Figures SC65-73). -0.5 V was initially chosen to mimic the potential applied by a TiO₂ photoanode in a tandem device. Control experiments with unsensitized NiO films confirmed that the majority of photocurrent generated arose from light absorption by the chromophore. Typical photocurrent densities were approximately 2-5 $\mu\text{A cm}^{-2}$ for all systems in aqueous electrolytes where the applied bias was -0.5 V vs Ag/AgCl. At a lower applied bias of -0.2 V vs. Ag/AgCl, the dark current for all systems was smaller and surface charging was less pronounced. The photocurrent density for PC2|NiO was remarkably lower than that attained with the ester analogue (ca. 40 $\mu\text{A cm}^{-2}$).⁶² However, the photocurrent density for PC1|NiO was ca. 6 times higher than the ester analogue (1.3 $\mu\text{A cm}^{-2}$).⁸⁰ Both were higher than the catalyst-free control, PC3|NiO.

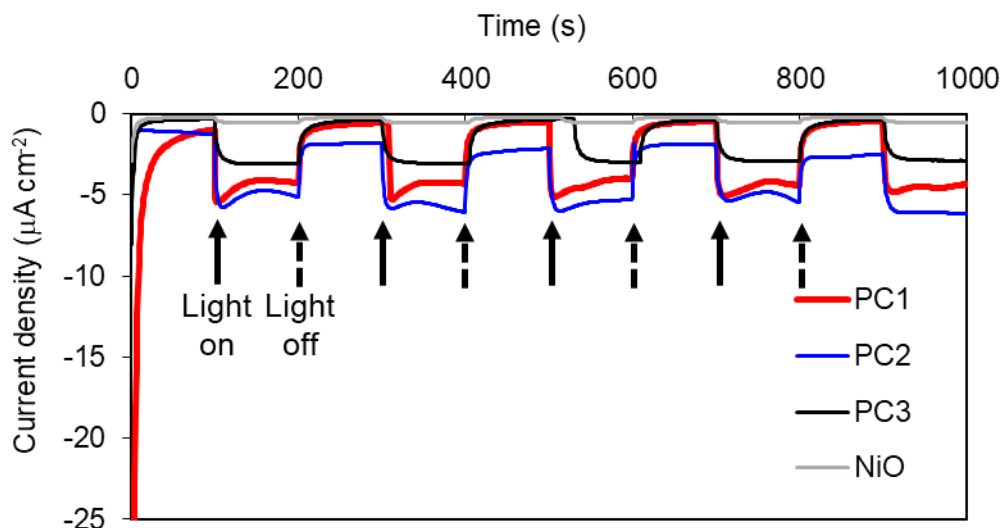


Figure 4-4. Representative example of photocurrent in 0.1 M pH 5 acetate buffer under chopped light illumination for photoelectrocatalysis experiments of NiO films sensitized with photocatalysts. The applied bias was -0.2 V vs. Ag/AgCl. NiO, PC1/NiO and PC3/NiO are saturated with CO₂, PC2/NiO is saturated with Ar.

Bubbles were observed to form on the electrode surface during extended periods of irradiation (AM1.5, 100 mW cm⁻²). Care was taken with gas sampling experiments to compare rigorously with appropriate control experiments so that any decomposition of the photocatalyst could be accounted for. Evolved gases from NiO|PC1, NiO|PC2 and NiO|PC3 and the NiO control were tested over a three-hour irradiation experiment in the three aqueous electrolytes. The headspace was periodically sampled, and the products were quantified by gas chromatography. This required occasional shaking of the cell to promote mixing. The electrolyte was tested for liquid products using ion chromatography, but no formate was detected. The results are provided in Table 3 and the SI. A very small amount of H₂ was evolved from NiO|PC2. CO was the main product from NiO|PC1 and in pH 5 acetate buffer and -0.5 V vs Ag/AgCl, CO was produced with a Faradaic efficiency of approx. 91% and a turnover per catalytic centre of 5.4 in 3 hours. The turnover frequency for this system was equal to that reported by Ishitani et al. for a Ru-Re catalyst with a protective polymer layer.⁶⁹ Hydrogen was also detected, but in very small amounts. To confirm the origin of the CO was the gas rather than decomposition of the photocatalyst, the electrolyte was purged with ¹³CO₂, and gaseous products were analysed by mass spectrometry. The major product under both -0.5V and -0.2 V vs Ag/AgCl in pH 5 acetate buffer was ¹³CO (see SI).

To further optimise the system, the electrolyte was replaced with pH 6.6 NaHCO₃ solution. At -0.2V, the average photocurrent density was 2.9 μA cm⁻², the faradaic efficiency for CO was 94%, and a turnover of 4.88 per catalyst over 3 hours was attained. To our knowledge, this is the

highest selectivity for CO production with a dye-sensitized photocathode. The summary of results for NiO|PC1 in different buffers is shown in Figure 4-5.

Table 4-3. Average current density (J), Faradaic efficiencies (η_{Far}) and turnover frequency per hour (TOF) averaged over 3 hours for CO and H₂ production during photoelectrocatalysis for NiO|PC1 under AM1.5 illumination (100 mW cm⁻²). The applied bias to these systems was -0.2 V vs Ag/AgCl.

PC1 NiO @ -0.2 V vs Ag/AgCl	pH 5 acetate (under CO ₂)	pH 6.6 50 mM NaHCO ₃ (under CO ₂)	pH 8 phosphate buffer (under CO ₂)	pH 9.2 carbonate buffer (under CO ₂)
$J / \mu\text{A cm}^{-2}$	4.6	2.9	3.8	3.1
$\eta_{\text{Far}}/\% (\text{CO})$	54.3	94.0	61.8	20.2
$\eta_{\text{Far}}/\% (\text{H}_2)$	0.46	0.33	0.32	0.1
$[\text{CO}]/\mu\text{mol h}^{-1} \text{ cm}^{-2}$	0.12 (± 0.014)	0.27 (± 0.022)	0.11 (± 0.015)	0.09 (± 0.016)
$[\text{H}_2]/\text{nmol h}^{-1} \text{ cm}^{-2}$	1.06 (± 0.13)	0.93 (± 0.074)	0.54 (± 0.076)	0.40 (± 0.072)
TOF (CO) h ⁻¹	0.75	1.63	0.63	0.52
TOF (H ₂) h ⁻¹	0.007	0.007	0.003	0.003

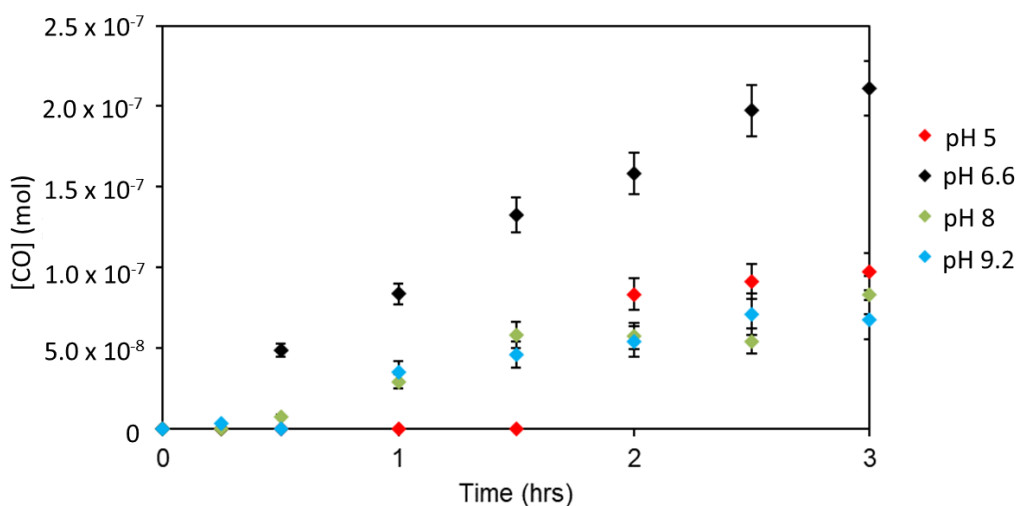


Figure 4-5. Evolved CO detected by gas chromatography for PC1|NiO thin films with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation in various pH buffer solutions as described earlier. Note the pH 6.6 is 50 mM NaHCO₃ solution.

4.3.4. Surface analysis

After the photoelectrocatalysis experiments, the UV-visible absorption spectra were re-recorded. There was an approx. 20% reduction in the absorption maxima for the three photocatalysts on average according to UV-vis absorption difference spectra. Some of this may be accounted for by the reduction of surface Ni^{3+} states during the reduction (see comment on current spikes above), but it appears that some of the photocatalyst was lost during the reaction. To further characterize the surface of the photocathode before and after the experiments, X-ray photoelectron spectroscopy was used.

The results from the X-ray photoelectron spectroscopy provided evidence the photocatalysts were indeed deposited on the NiO surface and enabled us to determine changes/losses of chromophore after a standard photocatalysis reaction. No noticeable change in the oxidation state of the key elements was determined for our experiments, but there was a slight decrease in signal intensity following photocatalysis for 15 minutes (note these were different samples from the same batch). PC2 was observed to be less stable than PC1, with some loss of ruthenium after the photoelectrocatalysis experiments (Figure SC108 Supporting Information). This is consistent with the relatively poor Faradaic efficiency for PC2 as compared to PC1 (Table 3).

4.4. Conclusions

In summary, we have evaluated the photoelectrocatalytic performance of two supramolecular photocatalysts with carboxylic acid anchoring groups, integrated in NiO photocathodes for CO_2 reduction and hydrogen evolution. The Ru-Re compound PC1, performed better than the ester analogue previously reported.²⁸ In contrast, the Ru-Pd compound PC2 was significantly less active for hydrogen generation than the ester analogue.²⁷ The main reason for the change in behaviour is attributed to the difference in lifetime of the excited state. This is much shorter in the case of PC2, which could limit light-induced charge transfer at the NiO|PC2 interface. The NiO|PC1 system is, however, a promising, highly selective system for dye-sensitized NiO photocathodes for CO_2 reduction. Further tuning of PC2 could improve the photocurrent and TON. For example, modifying the bridging ligand to promote charge transfer towards the catalytic metal and away from NiO. The absorption coefficients of the photocatalysts are quite low compared to state-of-the-art photosensitisers in NiO-based DSSCs, which are typically organic systems rather than coordination complexes. A hybrid system with an organic chromophore may lead to much higher light harvesting efficiency and, consequently, better performance. Finally, the solubility of CO_2 in the solvent should be greater to support the higher photocurrent densities and further work on alternatives to MeCN are necessary.

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4.6. Supporting information

Supplementary information containing experimental details and data for electrochemical measurements (linear sweeps, chronoamperometry and cyclic voltammetry), characterization data for the photocatalyst materials, XPS data, information on gas chromatography experiments and detailed transient infrared absorption spectroscopy results can be found in Appendix C.

References

- 1 S. Berardi, S. Drouet, L. Francàs, C. Gimbert-Suriñach, M. Guttentag, C. Richmond, T. Stoll and A. Llobet, *Chem. Soc. Rev.*, 2014, **43**, 7501–7519.
- 2 D. Gust, T. A. Moore and A. L. Moore, *Acc Chem Res*, 2009, **42**, 1890–1898.
- 3 T. S. Teets and D. G. Nocera, *Chemical Communications*, 2011, **47**, 9268.
- 4 W. J. Youngblood, S.-H. A. Lee, K. Maeda and T. E. Mallouk, *Acc Chem Res*, 2009, **42**, 1966–1973.
- 5 R. Abe, K. Shinmei, K. Hara and B. Ohtani, *Chemical Communications*, 2009, 3577.
- 6 A. Harriman, I. J. Pickering, J. M. Thomas and P. A. Christensen, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1988, **84**, 2795.
- 7 Y. Yang, S. Ajmal, X. Zheng and L. Zhang, *Sustain Energy Fuels*, 2018, **2**, 510–537.
- 8 Y. Liu, F. Wang, Z. Jiao, · Shengjie Bai, H. Qiu and · Liejin Guo, *Electrochemical Energy Reviews*, 2018, **5**, 5.

- 9 J. R. Darwent, P. Douglas, A. Harriman, G. Porter and M.-C. Richoux, *Coord Chem Rev*, 1982, **44**, 83–126.
- 10 M. R. Wasielewski, *Chem Rev*, 1992, **92**, 435–461.
- 11 J. L. White, M. F. Baruch, J. E. Pander, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev and A. B. Bocarsly, *Chem Rev*, 2015, **115**, 12888–12935.
- 12 G. Sahara and O. Ishitani, *Inorg Chem*, 2015, **54**, 5096–5104.
- 13 M. F. Kuehnelt, K. L. Orchard, K. E. Dalle and E. Reisner, *J Am Chem Soc*, 2017, **139**, 7217–7223.
- 14 T. Kowacs, L. O'Reilly, Q. Pan, A. Huijser, P. Lang, S. Rau, W. R. Browne, M. T. Pryce and J. G. Vos, *Inorg Chem*, 2016, **55**, 2685–2690.
- 15 Y. Yamazaki, K. Ohkubo, D. Saito, T. Yatsu, Y. Tamaki, S. Tanaka, K. Koike, K. Onda and O. Ishitani, *Inorg Chem*, 2019, **58**, 11480–11492.
- 16 N. Queyriaux, D. Sun, J. Fize, J. Pécaut, M. J. Field, M. Chavarot-Kerlidou and V. Artero, *J. Am. Chem. Soc.*, 2020, **142**, 274–282.
- 17 B. C. M. Martindale, G. A. M. Hutton, C. A. Caputo and E. Reisner, *J. Am. Chem. Soc.*, 2015, **137**, 6018–6025.
- 18 V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angewandte Chemie International Edition*, 2011, **50**, 7238–7266.
- 19 H. Takeda, Y. Monma and O. Ishitani, *ACS Catal*, 2021, **11**, 11973–11984.
- 20 G. Segev, J. Kibsgaard, C. Hahn, Z. J. Xu, W.-H. (Sophia) Cheng, T. G. Deutsch, C. Xiang, J. Z. Zhang, L. Hammarström, D. G. Nocera, A. Z. Weber, P. Agbo, T. Hisatomi, F. E. Osterloh, K. Domen, F. F. Abdi, S. Haussener, D. J. Miller, S. Ardo, P. C. McIntyre, T. Hannappel, S. Hu, H. Atwater, J. M. Gregoire, M. Z. Ertem, I. D. Sharp, K.-S. Choi, J. S. Lee, O. Ishitani, J. W. Ager, R. R. Prabhakar, A. T. Bell, S. W. Boettcher, K. Vincent, K. Takanabe, V. Artero, R. Napier, B. R. Cuenya, M. T. M. Koper, R. van de Krol and F. Houle, *J Phys D Appl Phys*, 2022, **55**, 323003.
- 21 D. H. Nam, J. Z. Zhang, V. Andrei, N. Kornienko, N. Heidary, A. Wagner, K. Nakanishi, K. P. Sokol, B. Slater, I. Zebger, S. Hofmann, J. C. Fontecilla-Camps, C. B. Park and E. Reisner, *Angewandte Chemie International Edition*, 2018, **57**, 10595–10599.
- 22 M. S. Prévot and K. Sivula, *The Journal of Physical Chemistry C*, 2013, **117**, 17879–17893.
- 23 H. Pang, T. Masuda and J. Ye, *Chem Asian J*, 2018, **13**, 127–142.
- 24 S. Mandal, D. Ghosh and P. Kumar, *J Mater Chem A Mater*, 2022, **10**, 20667–20706.

- 25 P. Ding, T. Jiang, N. Han and Y. Li, *Mater Today Nano*, 2020, **10**, 100077.
- 26 E. Kalamaras, M. M. Maroto-Valer, M. Shao, J. Xuan and H. Wang, *Catal Today*, 2018, **317**, 56–75.
- 27 J. L. White, M. F. Baruch, J. E. Pander, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev and A. B. Bocarsly, *Chem Rev*, 2015, **115**, 12888–12935.
- 28 Y. Liu, S. Bai, F. Wang and Y. Chen, *Environ Chem Lett*, 2022, **20**, 1169–1192.
- 29 X. Li, J. Yu, M. Jaroniec and X. Chen, *Chem Rev*, 2019, **119**, 3962–4179.
- 30 P. Wen, H. Li, X. Ma, R. Lei, X. Wang, S. M. Geyer and Y. Qiu, *J Mater Chem A Mater*, 2021, **9**, 3589–3596.
- 31 U. Kang and H. Park, *J Mater Chem A Mater*, 2017, **5**, 2123–2131.
- 32 J. H. Kim, H. E. Kim, J. H. Kim and J. S. Lee, *J Mater Chem A Mater*, 2020, **8**, 9447–9482.
- 33 Y. Zhang, D. Pan, Y. Tao, H. Shang, D. Zhang, G. Li and H. Li, *Adv Funct Mater*, 2022, **32**, 2109600.
- 34 U. Kang, S. K. Choi, D. J. Ham, S. M. Ji, W. Choi, D. S. Han, A. Abdel-Wahab and H. Park, *Energy Environ Sci*, 2015, **8**, 2638–2643.
- 35 B. Kumar, J. M. Smieja and C. P. Kubiak, *The Journal of Physical Chemistry C*, 2010, **114**, 14220–14223.
- 36 M. Schreier, J. Luo, P. Gao, T. Moehl, M. T. Mayer and M. Grätzel, *J Am Chem Soc*, 2016, **138**, 1938–1946.
- 37 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740.
- 38 M. Grätzel, in *Materials for Sustainable Energy*, Co-Published with Macmillan Publishers Ltd, UK, 2010, pp. 26–32.
- 39 A. B. Muñoz-García, I. Benesperi, G. Boschloo, J. J. Concepcion, J. H. Delcamp, E. A. Gibson, G. J. Meyer, M. Pavone, H. Pettersson, A. Hagfeldt and M. Freitag, *Chem Soc Rev*, 2021, **50**, 12450–12550.
- 40 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem Rev*, 2010, **110**, 6595–6663.
- 41 A. Listorti, B. O'Regan and J. R. Durrant, *Chemistry of Materials*, 2011, **23**, 3381–3399.
- 42 J. R. Swierk and T. E. Mallouk, *Chem. Soc. Rev.*, 2013, **42**, 2357–2387.
- 43 K. Fan, F. Li, L. Wang, Q. Daniel, E. Gabrielsson and L. Sun, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25234–25240.

- 44 M. K. Brennaman, R. J. Dillon, L. Alibabaei, M. K. Gish, C. J. Dares, D. L. Ashford, R. L. House, G. J. Meyer, J. M. Papanikolas and T. J. Meyer, *J Am Chem Soc*, 2016, **138**, 13085–13102.
- 45 B. Zhang and L. Sun, *Chem Soc Rev*, 2019, **48**, 2216–2264.
- 46 M. D. Kärkäs, O. Verho, E. v. Johnston and B. Åkermark, *Chem Rev*, 2014, **114**, 11863–12001.
- 47 D. L. Ashford, M. K. Gish, A. K. Vannucci, M. K. Brennaman, J. L. Templeton, J. M. Papanikolas and T. J. Meyer, *Chem Rev*, 2015, **115**, 13006–13049.
- 48 E. A. Gibson, *Chem Soc Rev*, 2017, **46**, 6194–6209.
- 49 A. Charisiadis, E. Giannoudis, Z. Pournara, A. Kosma, V. Nikolaou, G. Charalambidis, V. Artero, M. Chavarot-Kerlidou and A. G. Coutsolelos, *Eur J Inorg Chem*, 2021, **2021**, 1122–1129.
- 50 S. Sumikura, S. Mori, S. Shimizu, H. Usami and E. Suzuki, *J Photochem Photobiol A Chem*, 2008, **199**, 1–7.
- 51 D. Saito, Y. Yamazaki, Y. Tamaki and O. Ishitani, *J Am Chem Soc*, 2020, **142**, 19249–19258.
- 52 G. Sahara, H. Kumagai, K. Maeda, N. Kaeffer, V. Artero, M. Higashi, R. Abe and O. Ishitani, *J Am Chem Soc*, 2016, **138**, 14152–14158.
- 53 H. Kumagai, G. Sahara, K. Maeda, M. Higashi, R. Abe and O. Ishitani, *Chem Sci*, 2017, **8**, 4242–4249.
- 54 M. Shizuno, K. Kato, S. Nishioka, T. Kanazawa, D. Saito, S. Nozawa, A. Yamakata, O. Ishitani and K. Maeda, *ACS Appl Energy Mater*, 2022, **5**, 9479–9486.
- 55 Y. Kou, S. Nakatani, G. Sunagawa, Y. Tachikawa, D. Masui, T. Shimada, S. Takagi, D. A. Tryk, Y. Nabetani, H. Tachibana and H. Inoue, *J Catal*, 2014, **310**, 57–66.
- 56 F. Kuttassery, H. Kumagai, R. Kamata, Y. Ebato, M. Higashi, H. Suzuki, R. Abe and O. Ishitani, *Chem Sci*, 2021, **12**, 13216–13232.
- 57 Y. Ueda, H. Takeda, T. Yui, K. Koike, Y. Goto, S. Inagaki and O. Ishitani, *ChemSusChem*, 2015, **8**, 439–442.
- 58 J. He, H. Lindström, A. Hagfeldt and S.-E. Lindquist, *Solar Energy Materials and Solar Cells*, 2000, **62**, 265–273.
- 59 D. Dini, Y. Halpin, J. G. Vos and E. A. Gibson, *Coord Chem Rev*, 2015, **304–305**, 179–201.
- 60 G. Boschloo and A. Hagfeldt, *J Phys Chem B*, 2001, **105**, 3039–3044.
- 61 C. J. Wood, G. H. Summers, C. A. Clark, N. Kaeffer, M. Braeutigam, L. R. Carbone, L. D’Amario, K. Fan, Y. Farré, S. Narbey, F. Oswald, L. A. Stevens, C. Parmenter, M. W.

- Fay, A. la Torre, C. E. Snape, B. Dietzek, D. Dini, L. Hammarström, Y. Pellegrin, F. Odobel, L. Sun, V. Artero, E. A. Gibson, *Phys. Chem. Chem. Phys.*, 2016, **18**, 10727–10738.
- 62 N. Pöldme, L. O'Reilly, I. Fletcher, J. Portoles, I. v. Sazanovich, M. Towrie, C. Long, J. G. Vos, M. T. Pryce and E. A. Gibson, *Chem Sci*, 2019, **10**, 99–112.
- 63 A. A. Cullen, K. Heintz, L. O'Reilly, C. Long, A. Heise, R. Murphy, J. Karlsson, E. Gibson, G. M. Greetham, M. Towrie and M. T. Pryce, *Front Chem*, , DOI:10.3389/fchem.2020.584060.
- 64 T. Daeneke, A. J. Mozer, Y. Uemura, S. Makuta, M. Fekete, Y. Tachibana, N. Koumura, U. Bach and L. Spiccia, *J Am Chem Soc*, 2012, **134**, 16925–16928.
- 65 U. B. Cappel, S. M. Feldt, J. Schöneboom, A. Hagfeldt and G. Boschloo, *J Am Chem Soc*, 2010, **132**, 9096–9101.
- 66 J. Wiberg, T. Marinado, D. P. Hagberg, L. Sun, A. Hagfeldt and B. Albinsson, *The Journal of Physical Chemistry C*, 2009, **113**, 3881–3886.
- 67 M. Braumüller, M. Schulz, M. Stanisiewska, D. Sorsche, M. Wunderlin, J. Popp, J. Guthmüller, B. Dietzek and S. Rau, *Dalton Transactions*, 2016, **45**, 9216–9228.
- 68 L. Zhang, X. Yang, S. Li, Z. Yu, A. Hagfeldt and L. Sun, *Solar RRL*, 2020, **4**, 1900436.
- 69 R. Kamata, H. Kumagai, Y. Yamazaki, G. Sahara and O. Ishitani, *ACS Appl Mater Interfaces*, 2019, **11**, 5632–5641.
- 70 K. L. Materna, A. M. Beiler, A. Thapper, S. Ott, H. Tian and L. Hammarström, *ACS Appl Mater Interfaces*, 2020, **12**, 31372–31381.
- 71 T.-T. Li, B. Shan and T. J. Meyer, *ACS Energy Lett*, 2019, **4**, 629–636.
- 72 A. Charisiadis, E. Glymenaki, A. Planchat, S. Margiola, A.-C. Lavergne-Bril, E. Nikoloudakis, V. Nikolaou, G. Charalambidis, A. G. Coutsolelos and F. Odobel, *Dyes and Pigments*, 2021, **185**, 108908.
- 73 J. Huang, B. Xu, L. Tian, P. B. Pati, A. S. Etman, J. Sun, L. Hammarström and H. Tian, *Chemical Communications*, 2019, **55**, 7918–7921.
- 74 D. Wang, Y. Wang, M. D. Brady, M. V. Sheridan, B. D. Sherman, B. H. Farnum, Y. Liu, S. L. Marquard, G. J. Meyer, C. J. Dares and T. J. Meyer, *Chem Sci*, 2019, **10**, 4436–4444.
- 75 S. Bold, J. Massin, E. Giannoudis, M. Koepf, V. Artero, B. Dietzek and M. Chavarot-Kerlidou, *ACS Catal*, 2021, **11**, 3662–3678.
- 76 J.-S. Lee, D.-I. Won, W.-J. Jung, H.-J. Son, C. Pac and S. O. Kang, *Angewandte Chemie International Edition*, 2017, **56**, 976–980.

- 77 R. Kamata, H. Kumagai, Y. Yamazaki, M. Higashi, R. Abe and O. Ishitani, *J Mater Chem A Mater*, 2021, **9**, 1517–1529.
- 78 G. Sahara, R. Abe, M. Higashi, T. Morikawa, K. Maeda, Y. Ueda and O. Ishitani, *Chemical Communications*, 2015, **51**, 10722–10725.
- 79 G. Li, D. Zhu, X. Wang, Z. Su and M. R. Bryce, *Chem. Soc. Rev*, 2020, **49**, 765.
- 80 F. J. R. Cerpentier, J. Karlsson, R. Lalrempuia, M. P. Brandon, I. V. Sazanovich, G. M. Greetham, E. A. Gibson and M. T. Pryce, *Front Chem*, , DOI:10.3389/fchem.2021.795877.
- 81 N. Pöldme, L. O'Reilly, I. Fletcher, J. Portoles, I. V. Sazanovich, M. Towrie, C. Long, J. G. Vos, M. T. Pryce and E. A. Gibson, *Chem Sci*, 2019, **10**, 99–112.
- 82 A. A. Seddon, J. K. G. Karlsson, E. A. Gibson, L. O'Reilly, M. Kaufmann, J. G. Vos and M. T. Pryce, *Johnson Matthey Technology Review*, 2022, **66**, 21–31.
- 83 Z.-Y. Bian, K. Sumi, M. Furue, S. Sato, K. Koike and O. Ishitani, *Dalton Trans.*, 2009, 983–993.
- 84 R. Sahai, D. P. Rillema, R. Shaver, S. Van Wallendael, D. C. Jackman and M. Boldaji, *Inorganic Chemistry*, 1989, **28**, 1022–1028.
- 85 S. Van Wallendael, R. J. Shaver, D. P. Rillema, B. J. Yoblinski, M. Stathis and T. F. Guarr, *Inorganic Chemistry*, 1990, **29**, 1761–1767.
- 86 J. V. Caspar and T. J. Meyer, *J Am Chem Soc*, 1983, **105**, 5583–5590.
- 87 L. Li, E. A. Gibson, P. Qin, G. Boschloo, M. Gorlov, A. Hagfeldt and L. Sun, *Advanced Materials*, 2010, **22**, 1759–1762.
- 88 E. A. Gibson, L. le Pleux, J. Fortage, Y. Pellegrin, E. Blart, F. Odobel, A. Hagfeldt and G. Boschloo, *Langmuir*, 2012, **28**, 6485–6493.
- 89 D. Mulhern, S. Brooker, H. Görls, S. Rau and J. G. Vos, *Dalton Trans.*, 2006, 51–57.
- 90 W. R. Browne, C. M. O'Connor, H. P. Hughes, R. Hage, O. Walter, M. Doering, J. F. Gallagher and J. G. Vos, *Dalton Trans.*, 2002, 4048–4054.
- 91 R. Hage, A. H. J. Dijkhuis, J. G. Haasnoot, R. Prins, J. Reedijk, B. E. Buchanan and J. G. Vos, *Inorg Chem*, 1988, **27**, 2185–2189.
- 92 B. Gholamkhass, H. Mametsuka, K. Koike, T. Tanabe, M. Furue and O. Ishitani, *Inorg Chem*, 2005, **44**, 2326–2336.
- 93 P. N. Nguyen, T.-B.-N. Dao, T. T. Tran, N.-A. T. Tran, T. A. Nguyen, T.-D. L. Phan, L. P. Nguyen, V. Q. Dang, T. M. Nguyen and N. N. Dang, *ACS Omega*, 2022, **7**, 34089–34097.
- 94 J. K. McCusker, *Acc Chem Res*, 2003, **36**, 876–887.

- 95 M. Bräutigam, J. Kübel, M. Schulz, J. G. Vos and B. Dietzek, *Physical Chemistry Chemical Physics*, 2015, **17**, 7823–7830.
- 96 P. Qin, J. Wiberg, E. A. Gibson, M. Linder, L. Li, T. Brinck, A. Hagfeldt, B. Albinsson and L. Sun, *The Journal of Physical Chemistry C*, 2010, **114**, 4738–4748.
- 97 T. C. Lourenço, M. F. C. Coelho, T. C. Ramalho, D. van der Spoel and L. T. Costa, *Environ Sci Technol*, 2013, **47**, 7421–7429.
- 98 A. M. Schilderman, S. Raeissi and C. J. Peters, *Fluid Phase Equilib*, 2007, **260**, 19–22.
- 99 A. D. Taggart, J. M. Evans, L. Li, K. J. Lee, J. L. Dempsey, Y. Kanai and J. F. Cahoon, *ACS Appl Energy Mater*, 2020, **3**, 10702–10713.

Chapter 5: A novel naphthalene-diimide rhenium carbonyl compound; a spectroscopic, electrochemical and CO₂ reduction study

Chapter 5 describes the synthesis of a novel extended conjugated ligand and the corresponding Re complex. The ligand and complex were studied with a suite of spectroscopic, electrochemical and spectroelectrochemical techniques and assessed for its activity as a photocatalyst for CO₂ reduction.

5.1. Abstract

The novel ligand 2-octylbenzo[10',1'] [3,8]phenanthrolino[3',2':1,2]imidazo[4,5-f][1,10]phenanthroline-1,3,6(2H)-trione (oppt) and the corresponding $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex were synthesised. The oppt ligand and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex showcase red shifted intraligand charge transfer (ILCT) transitions with high extinction coefficients, makes this an interesting candidate for CO_2 photocatalysis. The ligand and the Re complex were studied using a range of spectroscopic and electrochemical techniques and the Re complex was assessed as photocatalyst for CO_2 reduction. Electrochemical and spectroelectrochemical studies indicate that the LUMO for the $\text{Re}(\text{oppt})(\text{CO})\text{Cl}$ complex is located on the ligand, with ligand-centred excited states expected to dominate the photophysical processes. Time-resolved infrared spectroscopy experiments following excitation at either 400 or 510 nm point to wavelength dependent behaviour. Following 400 nm excitation, a $^1\pi\text{-}\pi^*$ excited state is initially populated, which undergoes charge transfer to the phenanthroline component of the ligand with a time constant of 1.2 ps leading to population of a $^1\text{ILCT}_{\text{phen}}$ state. The $^1\text{ILCT}_{\text{phen}}$ state subsequently undergoes a second charge transfer step from the phenanthroline unit to the naphthalene-dicarboximide unit of the ligand with a time constant of 16.6 ps forming the $^1\text{ILCT}_{\text{NDI}}$ state, which recovers to the ground state on the nanosecond timescale. Following 510 nm excitation, a $^1\pi\text{-}\pi^*$ state is also populated, which undergoes charge transfer to the naphthalene-dicarboximide unit of the ligand with a time constant of 550 fs forming a hot $^1\text{ILCT}_{\text{NDI}}$ state. After vibrational cooling (within 18 ps) this $^1\text{ILCT}_{\text{NDI}}$ state relaxes back to the ground state on the ns timescale. Weak signals assigned to metal-to-ligand charge transfer (MLCT) states were observed following both 400 and 510 nm excitation. Steady state emission and transient absorption studies show formation of a long-lived $^3\text{ILCT}$ state, however the exact formation of this $^3\text{ILCT}$ state is not fully clear. The TRIR results point to two potential pathways: either intersystem crossing from the $^1\text{ILCT}$ states, or internal conversion from the $^3\text{MLCT}$ states.

5.2. Introduction

Rhenium-diimine tricarbonyl complexes such as $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ (bpy = 2,2'-bipyridine) have received considerable attention as photocatalysts for the reduction of CO_2 since the initial studies of Lehn and co-workers.¹ These compounds have been applied as photocatalysts for CO_2 conversion due to their intrinsic efficiency, high photostability and selectivity for desired products such as carbon monoxide.¹⁻⁷ Following excitation, a singlet metal-to-ligand-charge transfer ($^1\text{MLCT}$) state is populated,⁸⁻¹¹ which rapidly undergoes intersystem crossing (ISC) to the $^3\text{MLCT}$ state within the femtosecond time window (85 fs for $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$), driven by the

rhodium centre through the heavy atom effect.¹² The ³MLCT state populated is generally emissive in nature, and persists on the nanosecond time scale.

To improve the activity of these complexes, photocatalysts that absorb in the visible region of the spectrum are required to optimise absorption of solar energy.^{13,14} For systems in which the ¹MLCT is the lowest excited state, the HOMO level of the complex can be altered by varying the ancillary ligand (for example by replacing the chloride ligand by an acetonitrile ligand) at the Re centre to decrease the HOMO-LUMO gap, together with a red shift in the absorption spectrum.¹⁰ However, this approach is less desirable for photocatalytic applications, as the ancillary ligand dissociates during the photocatalytic cycle.¹⁵

Another route to extending the absorbance in the visible region of the spectrum is to attach a light harvesting antenna to the peripheral diimine ligand, leading to supramolecular assemblies. A range of inorganic^{16–22} or organic^{23–28} light harvesting antennae have been tethered to a rhodium centre for CO₂ reduction.

A red shift in the absorbance spectra of Re-diimine complexes also occurs by incorporating electron-withdrawing groups onto the diimine ligand.²⁹ This approach leads to a lowering of the LUMO on the diimine ligand and a lowering in the energy for the MLCT transition. While these approaches can result in a red shift in the absorbance bands, they also indirectly influence the electron density on the rhodium centre. This has been observed in electrocatalytic studies in which substitution on the ring affects the reduction potentials of these complexes.^{30–33} Re(bpy-COOH)(CO)₃Cl (bpy-COOH = 4,4'-dicarboxy-2,2'-bipyridine) showcased a reduction potential 400 mV more positive than Re(bpy)(CO)₃Cl, while Re(bpy-tBu)(CO)₃Cl (bpy-tBu = 4,4'-tert-butyl-2,2'-bipyridine) resulted in a shift of 145 mV more negative compared to Re(bpy)(CO)₃Cl.³⁴ In addition, Re(bpy-tBu)(CO)₃Cl showed a 3.5 fold increase in catalytic performance compared to Re(bpy)(CO)₃Cl.³⁴ while the inclusion of strong electron-withdrawing CF₃ groups on the bpy ring completely inhibited catalysis.³³

Another possibility to increase visible light absorption is by utilising non-MLCT excited states. In particular, ligand centred states such as intraligand charge transfer (ILCT) can be targeted as ³ILCT states are generally long-lived, which is desirable for photocatalyst applications.^{13,35–37} In addition, the energy of these states can easily be modified by changing the conjugation or by including donor-acceptor moieties. For example, Gordon, George and coworkers have reported various studies on rhodium complexes utilizing unsubstituted and substituted dppz (dppz = dipyrido[3,2-a:2',3'-c]phenazine) as the diimine ligand.^{38–44} For Re(dppz)(CO)₃Cl, two MLCT states and an ILCT state are close in energy and dominate the lower lying transitions.⁴⁰ The MLCT

states are assigned to charge transfer from the rhenium centre onto the nearby phenanthroline moiety ($\text{MLCT}_{\text{phen}}$) or to charge transfer from the rhenium centre onto the phenazine part of the ligand (MLCT_{phz}),⁴³ and these MLCT states can be identified with time-resolved infrared spectroscopy through the relative shift of the metal carbonyl stretches. For $\text{Re}(\text{dppz})(\text{CO})_3\text{Cl}$, the $\text{MLCT}_{\text{phen}}$ state is populated and shifts of $\sim +40 \text{ cm}^{-1}$ were observed for the metal carbonyl stretches, while for $\text{Re}(\text{dppzCl}_2)(\text{CO})_3\text{Cl}$ ($\text{dppzCl}_2 = 11,12\text{-Dichlorodipyrido}[3,2\text{-}a:2',3'\text{-}c]\text{phenazine}$) the MLCT_{phz} state is populated, with shifts of $\sim +60 \text{ cm}^{-1}$ for the metal carbonyl signals.⁴³ For $\text{Re}(\text{dppzBr}_2)(\text{CO})_3\text{Cl}$ ($\text{dppzBr}_2 = 11,12\text{-Dibromodipyrido}[3,2\text{-}a:2',3'\text{-}c]\text{phenazine}$), internal conversion from what appears to be the $\text{MLCT}_{\text{phen}}$ state to the MLCT_{phz} state has been observed within 20 picoseconds evident by a shift of a broad feature at 2060 cm^{-1} assigned to the $\text{MLCT}_{\text{phen}}$ state, to a sharper feature at 2080 cm^{-1} assigned to the MLCT_{phz} state. However, the authors suggest that this shift may also be assigned to vibrational cooling of the MLCT_{phz} state.³⁸ While a mixture of MLCT and ILCT states was observed for $\text{Re}(\text{dppz})(\text{CO})_3\text{Cl}$, no ILCT states were observed in time-resolved infrared spectroscopy for the systems with electron withdrawing groups (Cl, Br, NO_2) on the dppz ligand, as these electron withdrawing groups lower the energy of the MLCT states.⁴³ In contrast, inclusion of electron donating groups at the end of the dppz resulted in a stabilisation of the ILCT state.⁴² Larsen et al studied the $\text{Re}(\text{dppz-PhNPh}_2)(\text{CO})_3\text{X}$ and $\text{Re}(\text{dppz-PhNMe}_2)(\text{CO})_3\text{X}$ ($\text{dppz-PhNPh}_2 = 11\text{-(4-diphenylaminophenyl)dipyrido}[3,2\text{-}a:2',3'\text{-}c]\text{phenazine}$, $\text{dppz-PhNMe}_2 = 11\text{-(4-dimethylaminophenyl)dipyrido}[3,2\text{-}a:2',3'\text{-}c]\text{phenazine}$, $\text{X} = \text{Cl, py, 4-dimethylaminopyridine}$) complexes, in which electron donating dimethylaminophenyl or diphenylaminophenyl functional groups were appended to the end of the dppz ligand furthest from the metal centre. The lowest energy transitions for these complexes were calculated to take place on the ligand with intraligand charge transfer from the electron donating group to the dppz ligand as the lowest energy transition. Following 400 nm excitation, only ILCT states were observed in the ps-TRIR experiments with a shift of $\sim -20 \text{ cm}^{-1}$ of the metal carbonyl signals. Three processes were observed with time constants of 20 ps, 300 ps and 2.8 ns. The first process was tentatively assigned to vibrational cooling, while the second process is most likely interconversion of two ILCT states. No signals were observed with positive shifts of the carbonyl features, ruling out formation of MLCT states. A dark triplet ILCT state on the phenazine part of the dppz ligand ($^3\text{ILCT}_{\text{phz}}$) was observed in transient absorbance experiments, with lifetimes of 2.2 and 3.8 μs for the $\text{Re}(\text{dppz-PhNMe}_2)(\text{CO})_3\text{Cl}$ and $\text{Re}(\text{dppz-PhNPh}_2)(\text{CO})_3\text{Cl}$ complexes, respectively. The lifetimes for these $^3\text{ILCT}$ states are significantly longer than those observed for $\text{Re}(\text{dppz})(\text{CO})_3\text{Cl}$ (160 ns) where a $^3\text{MLCT}$ state is populated instead.

While population of the long-lived $^3\text{ILCT}$ state occurs for these complexes, the exact photophysical pathway to this $^3\text{ILCT}$ state remains debated. In an attempt to elucidate the photophysical pathway to this excited state, Shillito et al studied a set of $\text{Re}(\text{phen-TPA-R})(\text{CO})_3\text{Cl}$ complexes ($\text{phen-TPA-R} = 5\text{-}\{4\text{-}[\text{N,N-(4-R-phenyl)aminophenyl}]\text{-1,10-phenanthroline}$, $\text{R} = \text{H, CN, OMe}$).⁴⁵ The nature of the R substituent enabled further finetuning of the energy levels of the ILCT transitions. The systems with either a proton or a methoxy substitute further lowered the ILCT energy state, and excited state processes were dominated by ligand-based transitions, while inclusion of the electron withdrawing cyano functionality resulted in a system in which the lowest lying ILCT and MLCT states were nearly identical in energy. Surprisingly, emission was observed from a $^3\text{MLCT}$ state for all three rhenium complexes, suggesting that higher lying excited states can be involved in the photophysical processes for these complexes. Population of a MLCT state was further supported by resonance Raman and time-resolved resonance Raman experiments. The lowest lying excited state for all three complexes was found to be a dark $^3\text{ILCT}$ state which was observed through time-resolved resonance Raman experiments. Time-dependent DFT calculations suggest that intersystem crossing from the $^1\text{ILCT}$ to the $^3\text{ILCT}$ state is unlikely, as no spin-orbit coupling was predicted for this transition. However, large spin-orbit coupling values were obtained for ISC from $^1\text{MLCT}$ to $^3\text{MLCT}$ states. Based on the observation of $^3\text{MLCT}$ states in the emission and Raman experiments, in combination with time-dependant DFT calculations, the authors suggest that intersystem crossing from the $^1\text{ILCT}$ state to the $^3\text{ILCT}$ state does not occur, and that the triplet surface is only accessed through the MLCT excited states.

In contrast, Blanco-Rodriguez et al reported intersystem crossing to occur from the $^1\text{ILCT}$ state to the $^3\text{ILCT}$ for $\text{Re(3-R-1-(2-pyridyl)-imidazo[1,5-}\alpha\text{]pyridine)}(\text{CO})_3\text{Cl}$ ($\text{R} = \text{CH}_3, \text{Ph, PHBu}^t, \text{PhCF}_3, \text{PhNO}_2, \text{PhNMe}_2$) complexes.³⁶ They observed long-lived $^3\text{ILCT}$ states ($\tau = 29\text{-}37 \mu\text{s}$) in μs -TRIR experiments. Contrary to the dppz and phen-TPA systems, ps-TRIR experiments and time-dependent DFT (TD-DFT) calculations suggested that all excited state processes were ligand based, with remarkably slow (20-80 ps) intersystem crossing from the $^1\text{ILCT}$ to the $^3\text{ILCT}$ state. No excited state absorptions at higher wavenumbers were observed in the ps-TRIR experiments, ruling out formation of a $^3\text{MLCT}$ state.

Fernandez-Terran and Sévery reported the $\text{Re(4-(4-R-phenyl)terpyridine)}(\text{CO})_3\text{Cl}$ ($\text{R} = \text{CN, CF}_3, \text{Br, H, OMe, NMe}_2$) complexes.³⁵ Depending on the nature of the pendant group, signals for a lowest lying $^3\text{MLCT}$ or $^3\text{ILCT}$ state were observed in time-resolved experiments. As was observed

for previous systems, inclusion of electron withdrawing groups (CN, CF₃, Br) on the end of the ligand furthest from the metal centre resulted in stabilisation of the MLCT transitions, while addition of electron donating groups (OMe, NMe₂) in this position resulted in stabilisation of the ILCT transitions. The system with NMe₂ as pendant group was most capable of populating the long-lived ³ILCT state and showcased up to 9000 turnover numbers as a photosensitiser to produce hydrogen using a cobaloxime catalyst in an intermolecular approach.

Recently, there has been an increase in interest in utilising naphthalene derivatives including naphthalene monoimides and diimides in extended ligand systems.^{13,37,46} Naphthalene derivatives gained popularity due to their high photostability, large extinction coefficients and desirable electron acceptor properties.^{13,26,27,37,46–51} In addition, these systems have been shown to access μ s lived ³ILCT excited states.^{13,36,37,48} Yarnell et al reported the study of the Re(PNI-phen)(CO)₃Cl (PNI-phen = N-(1,10-phenanthroline)-4-(1-piperidinyl)naphthalene-1, 8-dicarboximide) complex comprising a ligand consisting of 5-amino-phenanthroline coupled to a naphthalene monoamide (NMI) moiety.³⁷ Following 400 nm excitation, formation of the initial ¹ILCT state on the naphthalene moiety was observed, which converted to a ³MLCT state on the phenanthroline moiety within 45 picoseconds. The emissive ³MLCT state was in equilibrium with a long-lived non-emissive ³ILCT state, and this equilibrium resulted in a 3000-fold increase in the lifetime for the ³MLCT emission from 197 ns to 651 μ s. Recently, Wells et al reported two Re(NBI-phen)(CO)₃X (NBI-phen = 16H-Benzo[4',5']isoquinolino[2',1':1,2]imidazo[4,5-f][1,10]phenanthroline-16-one, X = acetonitrile, PPh₃) complexes.¹³ While structurally similar to dppz, this ligand incorporates a slightly larger aromatic system from the fused naphthalene moiety. Like the publications by Blanco-Rodriguez et al on similar compounds,³⁶ transient absorption experiments supported by TD-DFT calculations indicated that the only excited states populated were based on the ligand and similar slow ISC from the singlet to triplet manifold occurred with time constants of 39 and 74 ps for the Re(NBI-phen)(CO)₃(MeCN) and Re(NBI-phen)(CO)₃(PPh₃) complexes, respectively.

Based on the previous reports on complexes incorporating naphthalene mono-imide functionalities,^{13,37} we were interested in the effect of further extending the conjugated system by appending the naphthalene moiety with a second dicarboximide moiety (Figure 5-1). Similar organic systems reported in the literature showcased a red shift in ILCT transitions compared to the naphthalene mono-imide counterparts,⁴⁹ which would be desirable for photocatalysis applications. The additional carboxamide moiety also provides additional reporter groups which can be utilised in TRIR spectroscopy, to further help identify the excited states populated. In this manuscript, the effect of extending the ligand with an additional dicarboximide moiety on the

photophysical and electrochemical properties were probed using a wide array of steady state and ultrafast spectroscopic, electrochemical and spectroelectrochemical techniques. Finally, the rhenium complex was assessed as a photocatalyst for CO₂ reduction as a proof of concept of utilising these systems in photocatalytic applications.

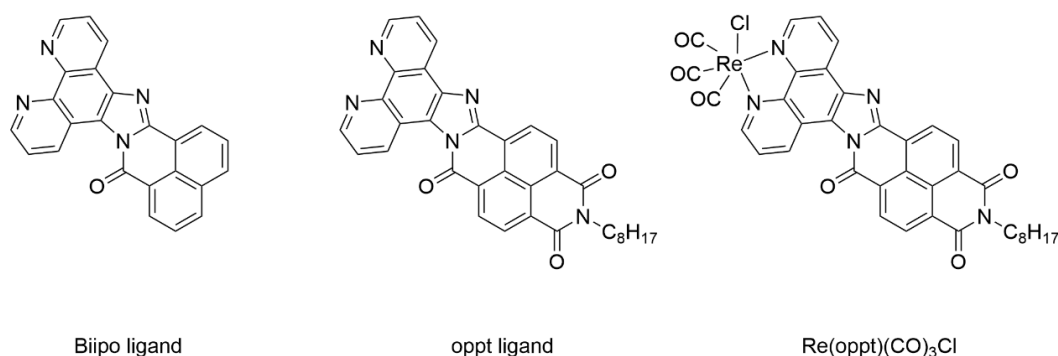


Figure 5-1. The previously reported biipo ligand⁴⁶ and the novel oppt ligand and Re(oppt)(CO)₃Cl complex studied in this manuscript.

5.3. Experimental

5.3.1. Methods and equipment

5.3.1.1. Synthesis

Isochromeno[6,5,4-def]isochromene-1,3,6,8-tetraone and 1,10-phenanthroline-5,6-dione were purchased from Fluorochem and used as received. 1-octylamine was purchased from TCI chemicals and used as received. 7-octyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone⁵² and 1,10-phenanthroline-5,6-diamine⁴⁶ were prepared following literature procedures.

2-octylbenzo[10',1']-[3,8]phenanthrolino[3',2':1,2]imidazo[4,5-f][1,10]phenanthroline-1,3,6(2H)-trione (oppt)

The following procedure was adapted from the similar 16Hbenzo[4',5']isoquinolino[2',1':1,2]imidazo[4,5-f]-[1,10]-phenanthroline-16-one(biipo) ligand previously reported.⁴⁶ 0.25 g (1.18 mmol) 7-octyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone and 0.42 g (1.1 mmol, 0.93 eq.) 1,10-phenanthroline-5,6-diamine were dissolved in 5 mL of glacial acetic acid. The mixture was heated at 140 °C for 24 h resulting in the formation of a bright red precipitate. The mixture was slowly added to 20 mL of saturated Na₂CO₃. The bright red precipitate was filtered over a glass frit, washed with water, ethanol and diethyl ether and air dried to yield **oppt** as a bright red powder (0.342 g, 0.618 mmol, 52%) Small amounts of the mono-substituted 7-octyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (5%) and bis-substituted 2,7-dioctylbenzo[Imn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (3%) were present which were removed following complexation.

^1H -NMR (600 MHz, CDCl_3): 0.89 (t, 3H), 1.30 (m, 8H, the bis-octyl precursor), 1.40 (m, 3H, contains bis octyl impurity), 1.47 (m, 2H), 1.78 (m, 3H), 4.20 (t, 2H), 7.77 (m, 2H), 8.65 (d, 1H), 8.70 (d, 1H), 8.73-8.78 (mono- and bis octyldicarboximide byproducts), 8.80 (d, 1H), 8.82 (d, 1H), 8.92 (dd, 1H), 9.16 (dd, 1H), 9.20 (dd, 1H), 9.86 (dd, 1H).

^{13}C -NMR (151 MHz, CDCl_3): 14.3, 22.8, 27.3, 28.3, 29.4, 29.5, 32.0, 41.2, 120.3, 122.6, 122.9, 123.9, 124.3, 124.8, 125.4, 125.9, 126.6, 127.0, 127.2, 128.1, 130.8, 131.4, 131.8, 132.3, 135.4, 145.7, 145.9, 145.6, 149.5, 151.0, 159.7, 162.6, 162.8.

Positive mode mass spectrometry: $[\text{oppt}+\text{H}^+]$ calculated $m/z = 554.2187$, found = 554.2191.

$\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$

0.07 g (0.126 mmol) of oppt and 0.05 g (0.139 mmol, 1.1 eq.) of $\text{Re}(\text{CO})_5\text{Cl}$ were dissolved in 10 mL of ethanol and heated at reflux overnight. A red precipitate formed upon cooling and was collected by vacuum filtration, washed with ethanol and diethyl ether and airdried to yield $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ as a red powder (0.084 g, 0.098 mmol, 78%). ^1H -NMR (600 MHz, CDCl_3): 0.088 (dd, 3H), 1.23-1.36 (m, 8H, solvent impurity), 1.39 (quintet, 2H), 1.47 (quintet, 2H), 1.79 (quintet, 2H), 4.24 (t, 2H), 8.02 (dd, 1H), 8.05 (dd, 1H), 8.91 (dd, 2H), 9.10 (d, 1H), 9.17 (d, 1H), 9.43 (d, 1H), 9.48 (d, 1H), 9.50 (d, 1H), 10.41 (d, 1H). ^{13}C -NMR (151 MHz, CDCl_3): 14.1, 22.7, 27.1, 28.2, 29.2, 29.3, 31.8, 41.2, 123.0, 125.2, 125.3, 125.4, 125.6, 126.5, 126.6, 127.2, 127.8, 128.8, 131.1, 132.0, 133.3, 133.9, 138.0, 139.9, 146.4, 146.6, 146.7, 147.0, 150.6, 152.2, 153.3, 159.9, 162.1, 162.4, 162.6.

Positive mode mass spectrometry: $[\text{Re}(\text{oppt})(\text{CO})_3\text{Cl} + \text{Na}^+]$ calculated $m/z = 882.1100$, found = 882.1081.

5.3.1.2. Physical Measurements

NMR spectra were recorded on either a Bruker 400 or 600 MHz spectrometer and were referenced to the deuterated solvent peak as an internal reference. Mass spectra were measured on a waters Q-TOF 6200 series. All UV spectra were recorded on either an Agilent 8453 UV-vis spectrophotometer equipped with Agilent ChemStation software or a Horiba Duetta Spectrometer. Emission spectra were recorded on a Horiba Duetta or a FLS1000 photoluminescence spectrometer (Edinburgh instruments), equipped with a Xe Arc lamp for steady-state measurements and a visible PMT-900 detector. For Time-correlated single photon counting (TCSPC) experiments, either a 375 nm or 510 nm variable pulse length (VPL) diode laser (VPL 375 or VPL-510) was utilised to excite the samples. FTIR measurements were carried out

on Perkin-Elmer 2000 FTIR spectrophotometer in solution cells using spectrophotometric grade dichloromethane.

5.3.1.3. Electrochemistry

All experiments were carried out using 1 mM solutions of the complex in spectroscopic grade dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. All solutions were purged for at least 10 min with N₂. A glassy carbon electrode, platinum wire and a Ag/AgNO₃ electrode were used as the working, counter and reference electrodes, respectively. Ferrocene was used as internal reference. Cyclic voltammetry scans were run at 0.1 V/s. Scan-rate dependent studies were performed at 0.02, 0.05, 0.1, 0.2 and 0.5 V/s.

5.3.1.4. Spectroelectrochemistry

All experiments were conducted in a custom-made OTTE cell supplied by Spectroelectrochemistry Reading with a platinum mesh working electrode, platinum mesh counter electrode and silver wire pseudo reference electrode. Fresh solutions of the complexes were prepared in dry spectroscopic grade dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte and purged for at least 10 min with N₂.

5.3.1.5. Transient absorption spectroscopy

Transient absorption spectra were recorded using an Edinburgh Instruments LP980 Transient Absorption Spectrometer. The samples were prepared in anhydrous dichloromethane and degassed by three cycles of freeze-pump-thaw. The optical density (OD) of the samples at the excitation wavelength (355 nm or 532 nm) was in the range of 0.1–0.15.

5.3.1.6. ps-Time Resolved Infrared Spectroscopy

ps-TRIR spectra were recorded using the ULTRA instrument at the Central Laser Facility in the Rutherford Appleton Laboratory in the United Kingdom and has been described elsewhere.⁵³ Spectra were collected using 400 or 510 nm excitation with 1 μ J power in a 0.1 mm pathlength Harrick cell.

5.3.1.7. Photocatalytic CO₂ Reduction Experiments

For photocatalytic CO₂ reduction experiments, each sample was prepared in a 23 ml glass Schlenk tube stoppered with an air-tight rubber septum. 0.01 mM catalyst was dissolved in a 5:1 N,N-dimethyl formamide:triethanolamine mixture with 0.05 M dimethylphenylbenzimidazole (BIH) as sacrificial agent. The solution was degassed using three freeze-pump-thaw cycles prior to irradiation and subsequently purged with CO₂ for 5 min. A 470 nm LED array with 20 mW output power was used to irradiate the samples. At selected

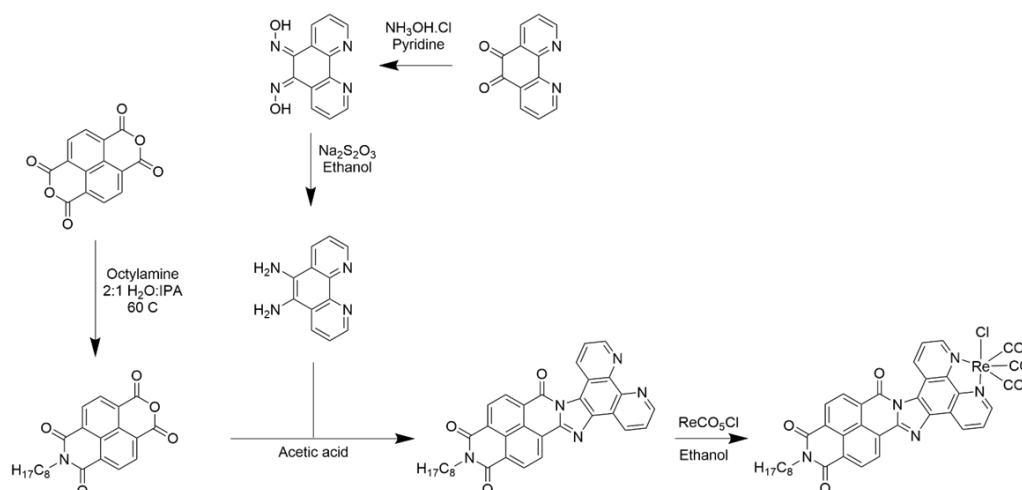
timepoints, 1 ml of the headspace was withdrawn, and injected into a GC to quantify the amount of carbon monoxide in the headspace.

5.4. Results and discussion

5.4.1. Synthesis

The oppt ligand was synthesised following a procedure reported for the similar biipo ligand (biipo = 16H-Benzo[4',5']isoquinolino[2',1':1,2]imidazo[4,5-f][1,10]phenanthroline-16-one) as shown in Scheme 5-1.⁵⁴

The ligand was fully characterised by NMR, IR, UV-Vis and mass spectrometry. ¹H-NMR spectra suggest that the ligand is asymmetric as found by the slight shift of the protons on the phenanthroline and naphthalene moieties (Figure SD 14).



Scheme 5-1 the synthetic pathway for the synthesis of the oppt ligand and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$.

$\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ was synthesised by refluxing the oppt ligand and the $\text{Re}(\text{CO})_5\text{Cl}$ precursor in ethanol overnight. The $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex showed similar asymmetry as the oppt ligand, as well as a significant downfield shift of the aromatic proton signals (Figure SD 19). Based on the coupling constants, the protons on the 2 and 9 positions of the oppt ligand are assigned to the signals at 9.16 and 9.19 ppm. For $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$, these signals undergo a significant downfield shift to 9.48 and 9.50 ppm. Even more significant is the shift of the proton in the 3 position. For the oppt ligand, this proton is assigned to the signal at 9.85 ppm. This signal shifts downfield by 0.55 ppm to 10.40 ppm for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$. This significant shift is attributed to the good electronic communication between the nitrogen and the proton in the para position of the pyridine ring. Complexation with the $\text{Re}(\text{CO})_3\text{Cl}$ moiety has a greater influence on the proton in the 3 position compared to the other protons on the oppt ligand. The proton on the

opposite side of the phenanthroline moiety in position 8 undergoes a shift of 0.51 ppm from 8.92 to 9.43 ppm. A slight shift between the protons in positions 5 and 6 and the protons in the positions 4 and 7 results in the formation of four doublets between 8.9 and 9.2 ppm.

5.4.2. UV-Vis spectroscopy

The UV-Vis spectrum for the oppt ligand in aerated dichloromethane shows various transitions that extend to 600 nm (Figure 5-2). Two overlapping bands are observed at 311 and 324 nm which are assigned to π -to- π^* transitions on the phenanthroline and naphthalene moieties. Two weaker bands are observed at 374 and 392 nm which based on their shape likely involve the naphthalene moiety.⁵³ Finally, a broad band is observed between 415 and 587 nm with a λ_{max} at 489 nm, is assigned to a π -to- π^* transition with significant charge-transfer character.^{13,49} This assignment is in line with similar systems reported by Wells et al, in which the naphthalene building block is fused with either a benzene or a naphthalene diamine, whereas in this work a phenanthroline diamine is used. TD DFT calculations for the benzene and naphthalene ligands reported by Wells et al suggested significant charge transfer from the imidazole moiety towards the dicarboximide takes place following population of the $^1\pi$ - π^* state, resulting in broad absorption features.

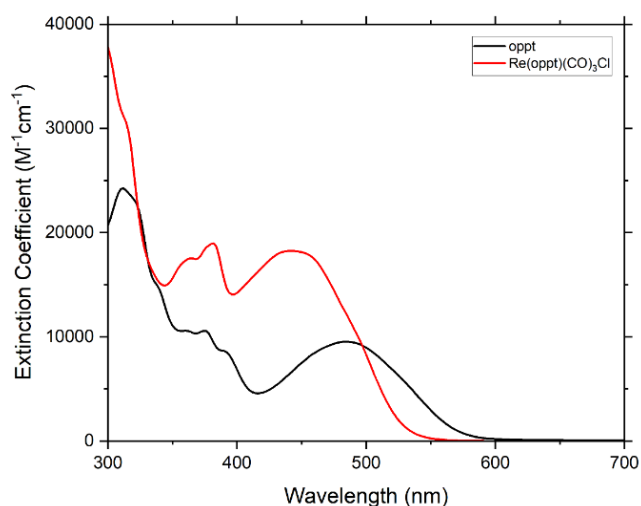


Figure 5-2. UV-Vis in aerated dichloromethane of oppt (black, solid line) and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ (red, solid line). Low solubility of the oppt ligand may have resulted in a slight error in the determination of the extinction coefficient.

Table 5-1. UV-Vis, emission and lifetime data for oppt and Re(oppt)(CO)₃Cl. ^a450 nm excitation. ^bMeasured in aerated dichloromethane. ^cMeasured in deaerated dichloromethane. ^d 510 nm excitation. ^e375 nm excitation.

Compound	$\lambda_{\text{max abs}} (\epsilon [\text{M}^{-1}\text{cm}^{-1}])$	$\lambda_{\text{em}}^a (\text{nm})$	Emission lifetime (ns)	Emission quantum yield ^e (%)	Stokes shift (cm^{-1})
Oppt	312 (24243), 375 (10576), 390 (8645), 487 (9534)	651	1.50 ^b 1.16 ^c	1	5173
Re(oppt)(CO) ₃ Cl	316 (29664), 381 (18968), 441 (18245)	585, 651, 721	1.5, 7.85 1.2 7.01 ^c	<<1	5434

Coordination of the [Re(CO)₃Cl] moiety to the phenanthroline unit of the oppt ligand results in a significant blueshift of the lowest energy feature in the UV-Vis absorption spectrum, together with an increase in the molar extinction coefficient. For Re(oppt)(CO)₃Cl, a broad absorption is observed from 397 to 550 nm with a λ_{max} at 450 nm. Based on the electrochemical data (*vide infra*) we assign this shift to higher energy for the complex to a change in the HOMO level. Furthermore, the band observed at 375 nm for the oppt ligand has shifted marginally to 381 nm, with an enhancement in intensity for the complex. The overall profile for the UV-Vis spectrum of Re(oppt)(CO)₃Cl is in agreement with similar Re(NDI-phen)(X) complexes (NDI-phen = biipo = 16H-Benzo[4',5']isoquinolino[2',1':1,2]imidazo[4,5-f][1,10]phenanthrolin-16-one, X = PPh₃, MeCN) reported by Wells et al.¹³ TD-DFT calculations performed by Wells et al for similar Re(NDI-phen)(X) complexes showed that the two lowest energy transitions are ligand-centred in nature. MLCT character was only reported for the S₀→S₃ transition with significantly weaker oscillator strengths compared to the first two transitions. In contrast, MLCT transitions were reported to be involved in the lowest energy transitions for Re(dppz)(CO)₃Cl and Re(phen-TPA)(CO)₃Cl.^{38,42,45,55} For Re(oppt)(CO)₃Cl, both LC and MLCT states appear to contribute to the lowest absorbance band based on the time-resolved infrared spectroscopy experiments (*vide infra*).

5.4.3. FT-IR spectroscopy

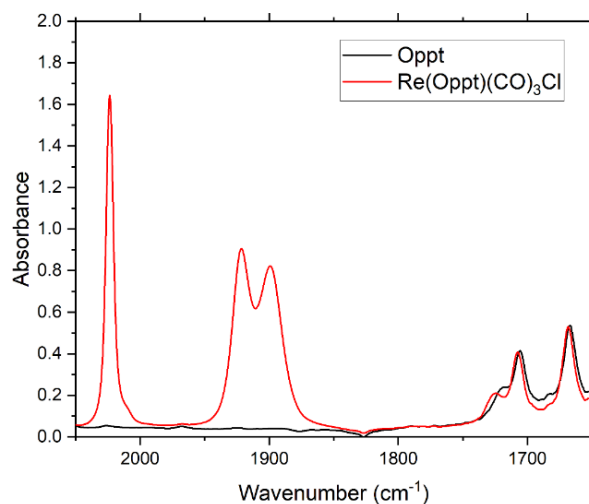


Figure 5-3. FTIR spectra of the oppt ligand (black) and Re(oppt)(CO)₃Cl complex (red).

The FTIR spectrum of the oppt ligand showcases three organic carbonyl signals at 1668, 1706 and 1718 cm⁻¹ (Figure 5-3). Based on the literature^{37,46} and the octylamine 7-octyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone precursor (Figure SD 1), the signals at 1668 and 1724 cm⁻¹ are assigned to the octyl-dicarboximide moiety of the ligand, while the signal at 1706 cm⁻¹ is assigned to the carbonyl moiety located next to the imidazole ring. As expected, the Re(oppt)(CO)₃Cl complex has similar stretches in the organic carbonyl region at 1669, 1708 and 1725 cm⁻¹. In addition, three metal carbonyl stretching vibrations are evident at 1899, 1922 and 2023 cm⁻¹ confirming the formation of a *fac*-tricarbonyl complex.

5.4.4. Cyclic voltammetry

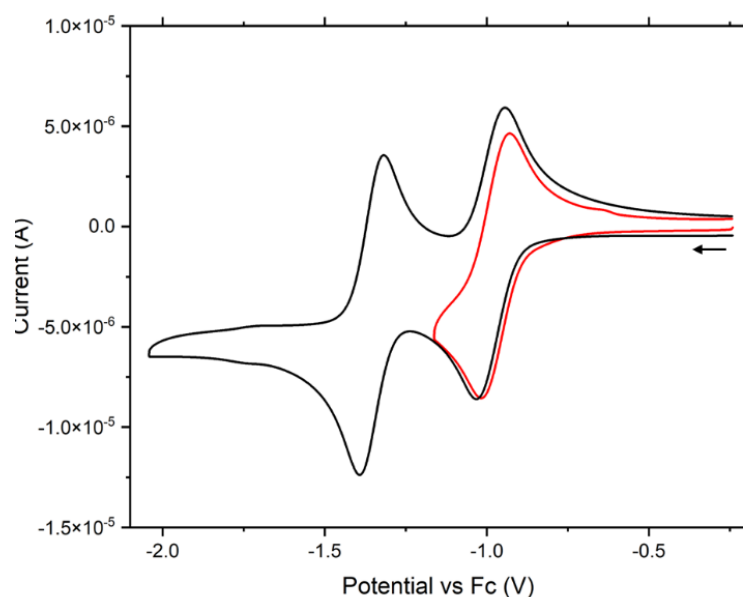


Figure 5-4. Cyclic voltammogram of the oppt ligand in deaerated dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Fc/Fc⁺ was used as internal standard. The red trace shows the reversibility of the first reduction. The black trace shows reversibility of the second reduction.

The electrochemical properties of the oppt ligand, were studied by cyclic voltammetry (Figure 5-4). Two reversible reductions were observed at -0.99 and -1.36 V vs the Ferrocene/ferrocenium couple. Reversibility of these reductions was confirmed by scan rate dependent studies (Figure SD 2). When dichloromethane was used in the electrochemistry experiments, and no evidence for oxidation processes were observed within the solvent window (up to approximately 0.65 V vs ferrocene). For the analogous biipo ligand similar redox behaviour was reported with two reductions at -1.59 and -2.29 V vs the ferrocene/ferrocenium couple in acetonitrile, with no evidence for oxidations up to 1.1 V vs ferrocene.⁴⁶ The significant shift observed for the oppt ligand versus the reported biipo ligand is assigned to the presence of the electron accepting dicarboximide moiety in the oppt ligand, which is not present in the biipo ligand. Indeed, for the similar 2-octylbenzo[Imn]perimidino[2,1-b][3,8]phenanthroline-1,3,6(2H)-trione compound reported by Wells et al a reduction was observed at -1.00 V vs the ferrocene/ferrocenium couple in acetonitrile.⁴⁹ Wells et al did not report a second reduction but instead reported an oxidation at 0.74 V. The solvent used in our CV studies for the oppt ligand did not permit oxidation studies beyond 0.65 V because of the solvent window.

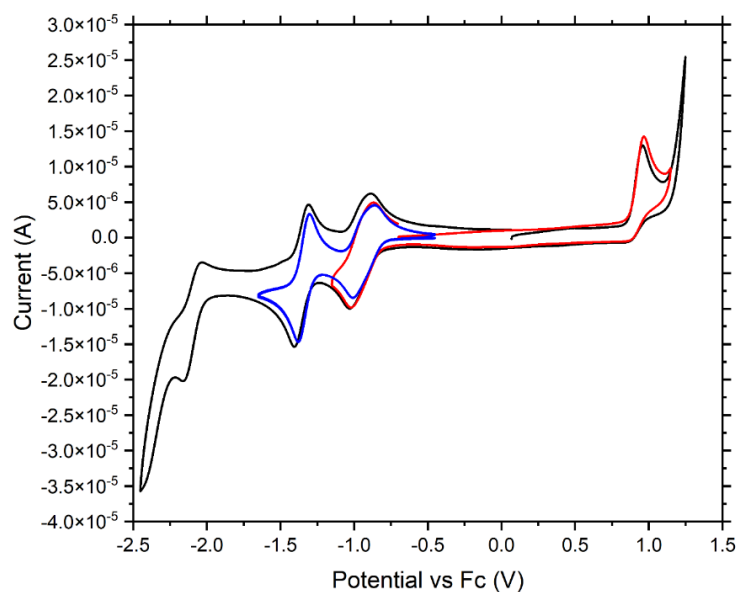


Figure 5-5. Cyclic voltammogram for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in deaerated dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Fc/Fc^+ was used as internal standard.

The cyclic voltammograms for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ are shown in Figure 5-5. The two ligand centred reductions previously observed for the free ligand were also observed in the cyclic voltammograms for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ at -0.96 and -1.36 V respectively. The similarity in the 1st and 2nd reduction potential indicates that coordination of the metal centre to the ligand does not significantly influence the electrochemical properties of the ligand. However, in the case of the complex a third reduction is observed at -2.1 V, and scan-rate dependent studies indicate that this reduction is at most semi-reversible (Figure SD 3). Partial reversible character is also observed at a slower scan rate (0.02 V/s, Figure SD 4) and in cyclic voltammetry experiments conducted in DMF (Figure SD 5). This reduction is assigned to the $\text{Re}^{\text{I}/0}$ reduction and the potential matches well with those reported in the literature for $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ (-2.085 V vs Fc)⁵⁶ and $\text{Re}(\text{phen})(\text{CO})_3\text{Cl}$ (-2.1 vs Fc)⁵⁷. The semi-reversible nature of this reduction is similar to what is observed for $\text{Re}(\text{phen})(\text{CO})_3\text{Cl}$, for which the $\text{Re}^{\text{I}/0}$ reduction was observed as an irreversible wave in DMF.⁵⁷ Infrared-spectroelectrochemistry (SEC) studies (*vide infra*) suggest formation of a dimer species following the $\text{Re}^{\text{I}/0}$ reduction, which explain the semi-reversible behaviour observed in the CV experiments.

In addition, an irreversible oxidation is observed for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ at 0.96 V which is assigned to the Re^{II} oxidation. This potential matches well with that observed for the related $\text{Re}(\text{phen})(\text{CO})_3\text{Cl}$ compound (0.99 V).⁵⁷

Table 5-2. Reduction and oxidation potentials for oppt and Re(oppt)(CO)₃Cl (1mM) in deaerated dichloromethane with 0.1 M TBAPF₆ as supporting electrolyte. Glassy carbon working electrode, platinum wire counter electrode and Ag/AgCl pseudo-reference electrode. 100 mV/s scanrate. Redox potentials vs E_{1/2}(Fc/Fc⁺). ^aIrreversible process. ^bSemi-reversible process.

Compound	E _{1/2} (V) 1 st reduction	E _{1/2} (V) 2 nd reduction	E _{1/2} (V) 3 rd reduction	E _{1/2} (V) 1 st oxidation
oppt	-0.99	-1.36	-	-
Re(oppt)(CO) ₃ Cl	-0.96	-1.36	-2.1 ^b	0.96 ^a

5.4.5. Spectroelectrochemistry

5.4.5.1. UV-Vis spectroelectrochemistry

UV-Vis spectroelectrochemical studies were performed on the oppt ligand and the Re(oppt)(CO)₃Cl to study the various reduced species, which may form in the photocatalytic process. Additionally, the generation of such species can provide us with an idea of the LUMO in the Re(oppt)(CO)₃Cl complex. The first reversible reduction for oppt (Figure 5-6) at -0.7 V vs the Ag/Ag⁺ pseudo-reference results in a decrease of the bands at 375, 390 and 487 nm, with concomitant formation of new bands at 283 and 351 nm, as well as a broad new band with maxima at 561, 694 and 745 nm, assigned [oppt]⁻. Upon the second reversible reduction (Figure 6) at -1.1 V vs Ag/Ag⁺, the signals for [oppt]⁻ at 351, 561, 694 and 745 nm decrease, with the appearance of new bands at 429 and 622 nm assigned to the [oppt]²⁻. These changes match well with those observed following one- and two-electron reduction of other naphthalene-monoimide compounds such as N-(2,5-Di-tert-butylphenyl)-3,4-perylenedicarboximide and naphthalene-diimide compounds such as N,N'-dioctyl-1,8:4,5-naphthalenetetracarboxydiimide.^{58,59}

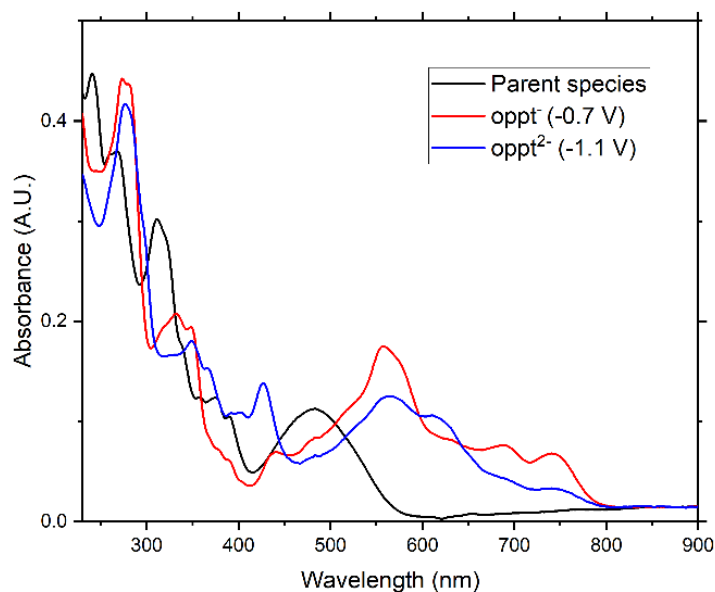


Figure 5-6. UV-Vis spectroelectrochemical study of *oppt* in dichloromethane with 0.1 M TBAPF₆ as supporting electrolyte. The *oppt* ligand (black), *oppt*⁻ (red) and *oppt*²⁻ (blue). The increase in absorbance from 600 to 900 nm is due to imperfect baselining in the spectroelectrochemical cell.

For the $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex the first reversible reduction at -0.7 V vs Ag/Ag^+ leads to a depletion of the parent bands at 316, 381 and 441 nm (Figure 5-7). New absorbance features formed at 261 and 350 nm, as well as a broad band with maxima at 506, 610 and 701 nm, the latter band tailing to 880 nm. Based on the similarity of these changes to those observed for the *oppt* ligand, these changes are attributed to formation of the reduced species $[\text{Re}^{\text{I}}(\text{oppt})^-(\text{CO})_3\text{Cl}]$, where reduction of the ligand occurs. As was discussed above for the *oppt* ligand, the second reduction at -1.1 V vs Ag/Ag^+ leads to a depletion of these bands, however the decrease this time is less apparent, as that observed for the *oppt* ligand. The bands at 506 and 610 nm decrease in absorbance while the shoulder at 701 nm disappears, and these changes are attributed to formation of $[\text{Re}^{\text{I}}(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$. New bands are also observed at 278, 365 and 441 nm for this dianionic $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ species. In addition, the absorbance between 640-930nm persists. The third reduction at -1.7 V vs Ag/Ag^+ only leads to minor changes in the UV-Vis spectrum. The signal at 278 nm and the broad tailing absorption between 640 and 930 nm decrease while an increase in signal is observed at 535 nm, and this final species is assigned as $[\text{Re}^0(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$.

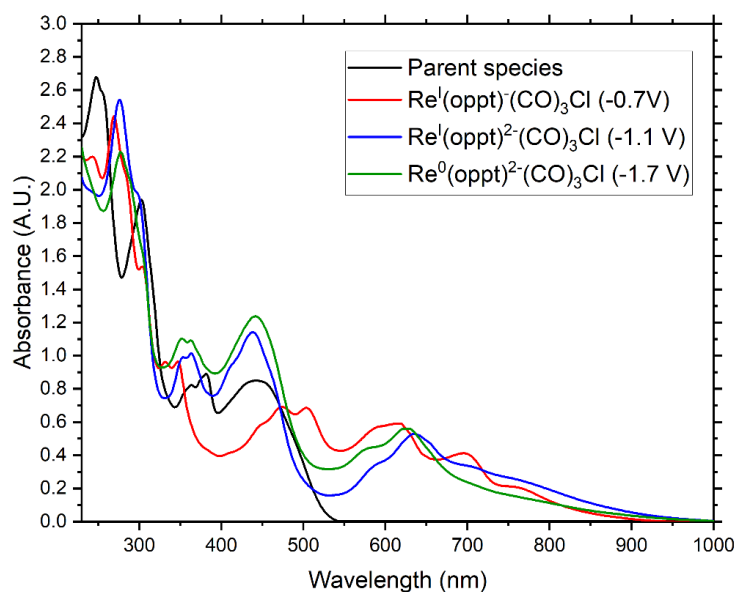


Figure 5-7. UV-Vis spectroelectrochemical study of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in dichloromethane with 0.1 M TBAPF_6 as supporting electrolyte. The $[\text{Re}^I(\text{oppt})(\text{CO})_3\text{Cl}]$ parent species (black), $[\text{Re}^I(\text{oppt})(\text{CO})_3\text{Cl}]$ (red), $[\text{Re}^I(\text{oppt})^2(\text{CO})_3\text{Cl}]$ (blue) and $[\text{Re}^0(\text{oppt})^2(\text{CO})_3\text{Cl}]$ (green).

5.4.5.2 Infrared spectroelectrochemistry

Infrared spectroelectrochemistry experiments were performed to confirm the assignments made in the UV-Vis spectroelectrochemistry experiments as the carbonyl units on the complex can be used as reporter groups for electron density (Figure 5-8, Table 5-3). Due to low solubility infrared spectroelectrochemical data of sufficient quality for the oppt ligand could not be obtained, and data for the oppt ligand is therefore not included.

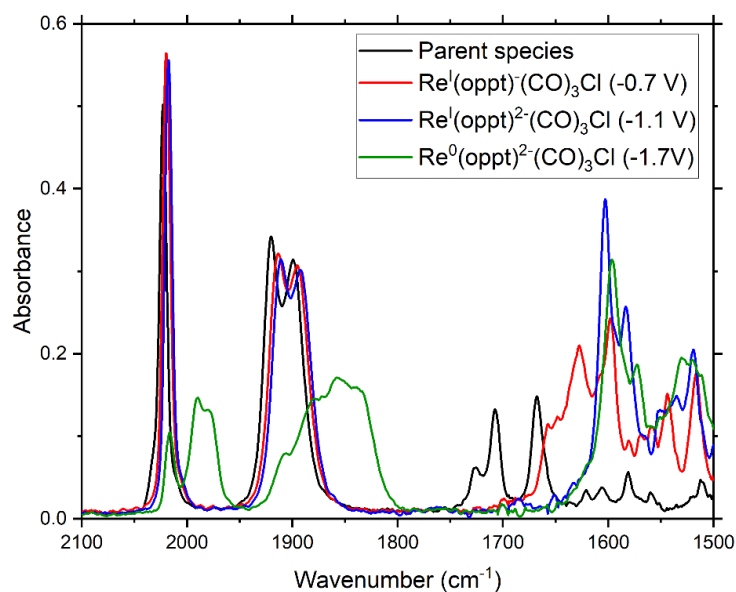


Figure 5-8. IR-SEC data for the three reductions of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$. The experiments were performed in deaerated dichloromethane with 0.1 M TBAPF_6 as supporting electrolyte in a thin-layer OTTE cell. The $[\text{Re}^{\text{I}}(\text{oppt})(\text{CO})_3\text{Cl}]$ parent species (black), $[\text{Re}^{\text{I}}(\text{oppt})^-(\text{CO})_3\text{Cl}]$ (red), $[\text{Re}^{\text{I}}(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$ (blue) and $[\text{Re}^0(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$ (green).

Upon the first reduction at $-0.5 \text{ V vs Ag/Ag}^+$, the signals for the parent species at 1668, 1706 and 1718 cm^{-1} depleted together with the formation of new stretching vibrations at 1596, 1626 and 1650 cm^{-1} , assigned to $[\text{Re}^{\text{I}}(\text{oppt})^-(\text{CO})_3\text{Cl}]$. This significant shift further supports the assignment of a fully ligand-based reduction, as it demonstrates a large increase in electron-density in the π^* orbitals of the organic carbonyls. The shifts for the dicarboximide carbonyls (to lower frequency by 72 and 74 cm^{-1}) and the carbonyl on the imidazole ring (also to lower frequency by 80 cm^{-1}) are similar, suggesting that the additional charge is distributed relatively evenly over the delocalised π -system of the naphthalene and imidazole moieties. The changes at the metal-carbonyl centre upon reduction are not as significant. As shown in Figure 5-8, following the first reduction at -0.5 V , the stretching vibrations at 1899, 1922 and 2023 cm^{-1} undergo only a marginal shift to 1894, 1911 and 2019 cm^{-1} , indicating that the first reduction is ligand based. The second reduction at $-0.9 \text{ V vs Ag/Ag}^+$, also takes place on the ligand, which results in depletion of the signals for $[\text{Re}^{\text{I}}(\text{oppt})^-(\text{CO})_3\text{Cl}]$, with the appearance of new organic carbonyl bands 1603 and 1581 cm^{-1} . As for the first ligand-based reduction only a small shift was observed for the metal-carbonyl stretching vibrations with the new bands for $[\text{Re}^{\text{I}}(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$ observed at 1892, 1910 and 2018 cm^{-1} . For the third reduction at -1.7 V , there was a switch from the location of the reduction from a ligand to metal-based reduction and this reduction is assigned to the $\text{Re}^{\text{I/0}}$ redox couple. Following this reduction, only a small shift was observed for the organic carbonyls from 1581 and 1603 cm^{-1} ($[\text{Re}^{\text{I}}(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$) to 1571 and 1595 cm^{-1} for $[\text{Re}^0(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$. This time a notable shift was observed for the metal-carbonyl stretching

vibrations, with the bands at 1892, 1910 and 2018 decaying with concomitant formation of four new bands 1835, 1856, 1976 and 1989 cm^{-1} . The pattern of this species matches well with those observed for the Re-Re dimer $[\text{Re}(\text{bpy})(\text{CO})_3]_2$ at 1859, 1887, 1951 and 1988 cm^{-1} .⁶⁰ This pattern along with the semi-reversible behaviour observed in the cyclic voltammetry experiment (*vide supra*) suggest formation of a Re-Re dimer species.^{60,61} The limited solvent window up to -2 V vs Ag/Ag^+ prevented us from obtaining full conversion to the dimer species at the third reduction. The higher concentration employed in the spectroelectrochemical experiments (5 mM vs 0.5 mM for the CV experiments) may increase the rate of dimerization following the third reduction in the spectroelectrochemical experiment resulting in formation of the dimer under these conditions while partial reversibility is still observed in the CV experiments.

Table 5-3. Selected infrared stretches in the organic and metal-carbonyl region following reduction of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in the IR-SEC experiments. All experiments were conducted in deaerated dichloromethane with 0.1 M TBPAF_6 as supporting electrolyte.

Species	Organic carbonyl stretches (cm^{-1})	Metal carbonyl stretches (cm^{-1})
$[\text{Re}^{\text{I}}(\text{oppt})(\text{CO})_3\text{Cl}]$	1668, 1706, 1724	1899, 1922, 2023
$[\text{Re}^{\text{I}}(\text{oppt})^-(\text{CO})_3\text{Cl}]$ (anion)	1596, 1626, 1650	1894, 1911, 2019
$[\text{Re}^{\text{I}}(\text{oppt})^{2-}(\text{CO})_3\text{Cl}]$ (dianion)	1581, 1603	1892, 1910, 2018
$[(\text{Re}(\text{oppt})^{2-}(\text{CO})_3)]_2$ (dimer)	1530, 1571, 1595	1835, 1856, 1976, 1989

5.4.6. Steady state emission studies

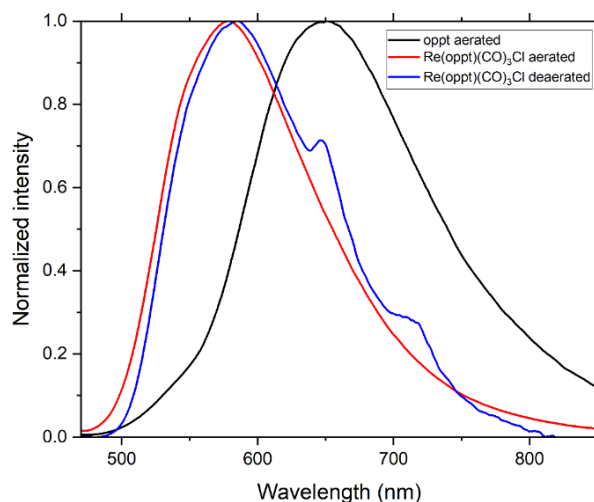


Figure 5-9. Emission spectra for oppt (black) and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ (red) in aerated dichloromethane and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in deaerated dichloromethane (blue) following 400 nm excitation.

Emission spectra were obtained for the oppt ligand and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in aerated and deaerated dichloromethane (Figure 5-9). As expected, the free ligand only showcased fluorescence from the singlet excited state with an emission maximum at 651 nm under both aerated and deaerated conditions. The Stokes shift of this emission ($5,173\text{ cm}^{-1}$) is significantly smaller than that observed for the smaller biipo ligand ($5,931\text{ cm}^{-1}$).⁴⁶ A fluorescence quantum yield of 1% was determined for the fluorescence emission in aerated dichloromethane. In aerated dichloromethane, the emission spectrum for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ has a maximum at 585 nm, significantly blue-shifted from the free ligand. The Stokes shift ($5,434\text{ cm}^{-1}$) determined for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ is larger than that of the free ligand ($5,173\text{ cm}^{-1}$). Under deaerated conditions, two additional weak signals were observed at 651 and 721 nm following 400 nm irradiation, which were assigned to phosphorescence originating from a $^3\text{ILCT}$ state of the oppt ligand on the $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex.^{13,48} These wavelengths match well with $^3\text{ILCT}$ emission from rhenium complexes with a similar ligand such as $\text{Re}(\text{NDI-phen})(\text{CO})_3\text{MeCN}$ (624 and 688 nm).¹³ We attempted to verify whether the phosphorescence bands at 651 and 721 nm were also observed following population of the lowest lying excited state. Unfortunately, excitation at $>500\text{ nm}$ resulted in very weak signals in the emission experiments making a definitive conclusion difficult.

5.4.7. Photophysical studies

Lifetimes for both oppt and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ were obtained in both aerated and deaerated dichloromethane following excitation at both 375 and 510 nm (Table 5-1, Figures SD 6-7).

Following excitation of oppt in aerated dichloromethane, at 375 nm an exponential decay with a lifetime of 1.58 ns was observed. This value matches reasonably well with that observed by Wells et al, who reported a lifetime of 3.23 ns for a similar system. Following 510 nm excitation, a similar lifetime of 1.50 ns was also observed. Under deaerated conditions, the lifetimes decreased to 1.20 and 1.16 ns for the oppt ligand following 375 and 510 nm excitation, respectively. In the case of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$, in aerated dichloromethane, a lifetime of 7.5 ns was observed following 375 nm excitation and 6.3 ns following 510 nm excitation. For the deaerated samples, lifetimes of 7.1 ns and 6.8 ns were observed following 375 and 510 nm excitation respectively.

No significant change in lifetime was observed upon purging the samples, suggesting the observed emission arises from a singlet state as previously observed for similar complexes.¹³ The extended lifetime of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ (7.5 ns) compared to the lifetime obtained for oppt (1.5 ns) is in good agreement with the increase in Stokes shift and the energy-gap law.^{8,62}

Unfortunately, the signals of the phosphorescence (651 and 721 nm) were very weak and it was not possible to determine lifetimes using TCSPC.

Instead, laser flash photolysis was used (Figure SD 8). Based on the report by Wells et al,¹³ in addition to the UV-Vis spectroelectrochemical data discussed previously, we expected long-lived transient signals spanning the visible spectrum following excitation. A weak signal for a triplet state species was observed in our laser flash photolysis experiment. Based on the reports on similar complexes, we assign this excited state species to a $^3\text{ILCT}$ excited state. While formation of a long lived $^3\text{MLCT}$ state for these complexes is possible, no evidence for a long lived $^3\text{MLCT}$ state was observed in the TRIR experiments (*vide infra*). The best signal-to-noise ratio was obtained at 460 nm, and the trace could be fit with a mono-exponential function with $\tau_1 = 252$ ns. This lifetime is in line with $^3\text{ILCT}$ states previously reported for other rhenium complexes with extended conjugated ligands.^{43,63} We attempted to obtain transient absorbance spectra following 532 nm excitation. However, the weak absorbance of the complex at this wavelength resulted in a poor signal-to-noise ratio for this experiment which prevented us from collection data of sufficient quality.

5.4.8. ps-Time-resolved infrared spectroscopy

Time resolved infrared spectroscopy (TRIR) spanning the femto- and picosecond timescales was employed to probe the excited state processes for both the oppt ligand and the $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex. We studied the organic and metal carbonyl region (following 400 and 510 nm

excitation), as the oppt ligand and $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex have various unique organic and metal carbonyl moieties that can function as useful reporter groups.

5.4.8.1. Oppt ligand

400 nm irradiation

Following excitation of oppt at 400 nm in dichloromethane, the parent bands at 1672, 1712 and 1730 cm^{-1} depleted within the laser pulse (200 fs) with the formation of new bands at 1553, 1618, 1625 and 1645 cm^{-1} (Figure SD 9). The organic carbonyls shift to lower energy suggesting an increase in electron density in the π^* orbitals of these carbonyl moieties. Based on calculations reported by Wells et al, in addition to our spectroelectrochemistry data for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ (*vide infra*) we assign these bands to population of the $^1\text{ILCT}$ state on the NDI chromophore.⁴⁹ Rapid picosecond charge transfer (1-10 ps) has been observed for other organic chromophores,^{28,64} and is also expected for these systems.⁴⁹ While we were able to observe this charge transfer process more clearly for the $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex (*vide infra*), some changes in the early picosecond time-window for the oppt system point towards a charge transfer process. Analysis of the signal at 1625 cm^{-1} resulted in a biexponential decay with $\tau_1 = 2.42$ ps and $\tau_3 = > 1$ ns (Figure SD 10). We label the longer lifetime as τ_3 as we observed a further picosecond feature when analysing other parts of the spectrum. The τ_1 component matches well with time constants observed for intraligand charge transfer in other organic systems^{28,64} as well as with the time constant observed for intraligand charge transfer in the $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex (*vide infra*). While the fits for the other ESAs were noisy, reasonable biexponential fits were obtained for the bleaches at 1672, 1712 and 1730 cm^{-1} with $\tau_2 = \sim 14$ ps and $\tau_3 = > 1$ ns. (Figure SD 10) Closer inspection of the spectra within the first 20 ps indicate that the ESA signals at 1623 and 1645 cm^{-1} narrow and undergo a slight shift to higher wavenumbers with new maxima at 1620 and 1648 cm^{-1} . Based on the literature, we assign the τ_2 component to vibrational cooling.^{36,65,66} It was not possible to obtain the time constant for τ_3 time in the TRIR studies, and this lifetime was obtained using TCSPC studies and is assigned to fluorescence from the $^1\text{ILCT}$ state to the ground state over 1.5 ns.

510 nm irradiation

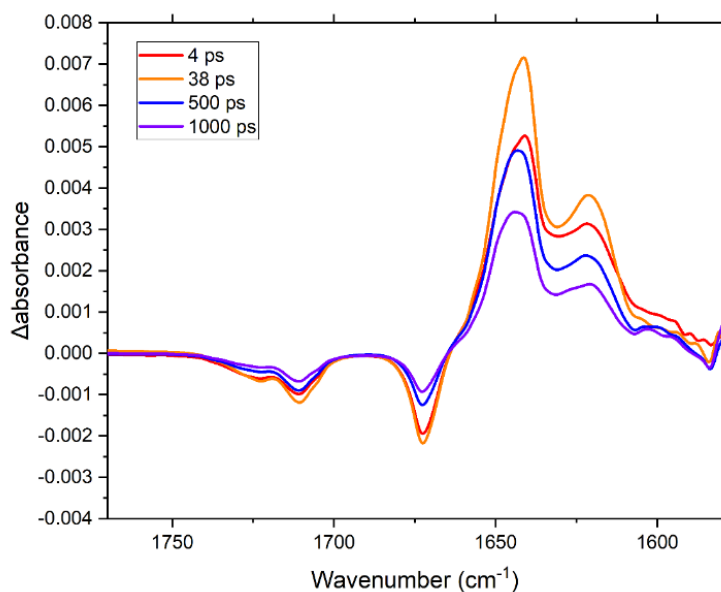


Figure 5-10. Time-resolved infrared spectroscopy of the oppt ligand in aerated dichloromethane following 510 nm irradiation (left) and selected kinetic traces (right). Times in picoseconds.

510 nm excitation of the oppt ligand allows for selective population of the lowest lying excited state (Figure 5-10). Following 510 nm excitation, bleaching of the ground state occurs within the laser pulse evidenced by a depletion of the bands at 1673, 1709 and 1722 cm^{-1} . Concomitantly, new bands are observed at 1622 and 1640 cm^{-1} . The intensity of these bands following excitation reaches a maximum after 38 ps. Based on the similarity to the spectra obtained following 400 nm excitation discussed above, in combination with results reported by Wells et al,⁴⁹ we assign this initial excited state to a S_1 $^1\text{ILCT}$ state. Changes in the shape of the ESA at 1640 cm^{-1} are observed with a shift of the peak maximum to slightly higher wavenumbers, suggesting vibrational cooling, and the band at 1640 cm^{-1} was successfully fitted with a biexponential function with $\tau_1 = 15$ ps and a $\tau_2 = > 1$ ns.

5.4.8.2. $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$

400 nm excitation

Following 400 nm excitation of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in dichloromethane solution, the parent bands at 1670, 1708, 1725, 1899, 1918 and 2023 cm^{-1} depleted within the laser pulse (Figure 5-11). Within the first 10 ps, new infrared stretching vibrations for two species are observed. The first excited state species has bands at 1623, 1656, 1910 and 2014 cm^{-1} , and is assigned to the S_2 $^1\pi$ -to- π^* state based on the literature.^{13,49} Global analysis of the bleach at 2023 cm^{-1} resulted in a triexponential fit with resulting time constants $\tau_1 = 1.19$ ps, $\tau_2 = 16.56$ ps and $\tau_3 = > 1$ ns (Figure SD 11). Within 2 ps after excitation, the bleaches at 1670, 1899, 1918 and 2023 decreased in

intensity, while a new band appeared at 1882 cm^{-1} , together with a shift to lower energy. The marginal shift in the stretching vibrations for the rhenium carbonyl fragment indicates that this excited state is not fully localised on the naphthalene dicarboximide moiety but is also partially spread out over the phenanthroline component of the complex. This behaviour matches well with the calculated excited states for the similar $\text{Re}(\text{NDI-phen})(\text{CO})_3(\text{X})$ ($\text{X} = \text{MeCN}, \text{PPh}_3$) complexes reported by Wells et al.¹³ For the $\text{Re}(\text{NDI-phen})(\text{CO})_3(\text{X})$ complexes the LUMO+1 state was calculated to be localised on the phenanthroline moiety. Thus, we assign the τ_1 component to intraligand charge transfer towards the phenanthroline moiety of the ligand forming the $^1\text{ILCT}_{\text{phen}}$ state. Within 20 picoseconds, the metal carbonyl absorptions at 1882 and 2019 cm^{-1} decay, together with the formation of new signals at 1907 , 1928 and 2021 cm^{-1} . The signals in the organic carbonyl region remain relatively unchanged, other than a slight recovery of the bleach at 1670 cm^{-1} . The metal carbonyl stretching vibrations for this new species shift slightly to higher wavenumbers signifying a decrease in population of the π^* orbitals of the CO groups and thus a decrease in electron density on the metal. These changes in the TRIR spectra suggest population of a ligand-centred excited state, with no evidence for formation of a MLCT. In rhenium complexes where MLCT transitions are observed, the infrared stretching vibrations usually move to higher energy than that the parent bands (by $\sim 60\text{ cm}^{-1}$). Therefore, we assign the τ_2 component to charge transfer from the phenanthroline moiety towards the naphthalene-dicarboximide moiety resulting in a $^1\text{ILCT}_{\text{NDI}}$ excited state. Narrowing of the signals in the organic region, together with the signal at 2023 cm^{-1} was also observed within the first 20 picosecond timeframe, suggesting that phen to NDI charge transfer (τ_2) is coupled with vibrational cooling of the complex.^{66–71} This assignment is further supported by the studies performed at 510 nm excitation (*vide infra*). While we tentatively assign these bands to a ligand-centred excited state on the singlet surface, intersystem crossing of a $^1\text{ILCT}$ species to a $^3\text{ILCT}$ species combined with vibrational cooling has been reported on a similar timescale by others.³⁶ Further studies are required to confirm our interpretation. The $^1\text{ILCT}_{\text{NDI}}$ state persists beyond the time-window of the experiment (i.e. $> 1\text{ ns}$), the final τ_3 component was assigned to recovery of the ground state species.

In addition, upon 400 nm excitation weak broad signals (highlighted with asterisks at 1966 and 2081 cm^{-1}) are observed within the first 10 ps . The position and weak profile of these signals matches well with previous studies using similar rhenium compounds and were assigned to a $^3\text{MLCT}$ state.^{45,55,65} While fitting of these signals is difficult due to the poor signal to noise ratio, the shape of the band at 2081 cm^{-1} changes over the first 2 picoseconds after excitation resulting in a sharper signal at 2096 cm^{-1} . Similar changes have been assigned for the interconversion of

a phenanthroline centred $^3\text{MLCT}$ band to a phenazine based $^3\text{MLCT}$ in the analogues $\text{Re}(\text{dppz})(\text{CO})_3\text{Cl}$ complexes, as well as to vibrational cooling of a phenazine-localised MLCT state.^{45,55} We therefore suggest that a similar process takes place for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$, in which the phenanthroline centred $^3\text{MLCT}$ ($^3\text{MLCT}_{\text{phen}}$) observed at $X \text{ cm}^{-1}$ state interconverts to a naphthalene-centred $^3\text{MLCT}$ state ($^3\text{MLCT}_{\text{NDI}}$) observed at 2096 cm^{-1} within 2 ps. The signal at 2096 cm^{-1} for the $^3\text{MLCT}_{\text{NDI}}$ decays over 10 ps. Potentially, internal conversion to a lower lying $^3\text{ILCT}$ state occurs on this timescale, as internal conversion from a $^3\text{MLCT}$ state to a $^3\text{ILCT}$ state has been observed to occur within 20 ps for similar rhenium complexes.⁴³

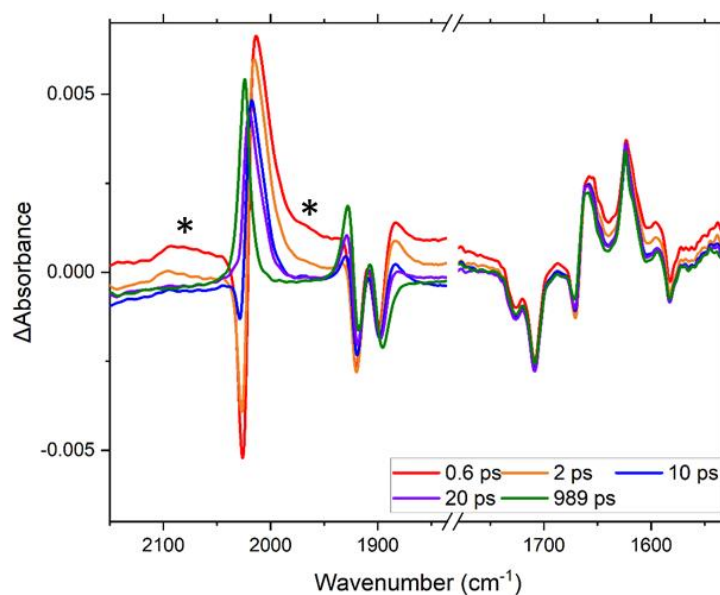


Figure 5-11. Time-resolved infrared spectra for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ following 400 nm excitation in aerated dichloromethane. The metal-carbonyl and organic carbonyl were recorded on separate detectors and the relative intensities for the signals on both detectors were not normalised. (*) indicate the signals observed for the $^3\text{MLCT}$ excited state.

510 nm excitation

Following excitation of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ at 510 nm excitation (Figure 5-1), bleaching of the parent bands at 1668, 1706, 1724, 1899, 1922 and 2023 occurred within the laser pulse. As was observed in the experiments following 400 nm excitation, infrared stretching vibrations for two distinct species were observed. The first excited state species has bands at 1626, 1651, 1914, 1940 and 2013 cm^{-1} . Based on the results obtained for the free ligand and the experiment following excitation at 400 nm, these bands are assigned to population of the $S_1 \pi$ -to- π^* excited state. Global analysis of the spectra resulted in three time components with $\tau_1 = 550 \text{ fs}$, $\tau_2 = 17.83 \text{ ps}$ and $\tau_3 = > 1 \text{ ns}$. Contrary to the experiment following 400 nm excitation, no metal carbonyl signal at 1882 cm^{-1} is observed in the first 2 picoseconds following

excitation at 510 nm. (Figure 5-12). Instead, new metal carbonyl stretching vibrations appeared within the first few ps at 1914, 1934 and 2016 cm^{-1} . These bands match well with those observed for the $^1\text{ILCT}_{\text{NDI}}$ following 400 nm experiments. Fitting of the ESAs at 1668 and 2020 cm^{-1} as well as the bleach at 2023 cm^{-1} result in a significantly shorter time constant for this charge transfer process, with $\tau_1 \approx 550$ fs. Similar to the experiment at 400 nm excitation, vibrational cooling with $\tau_2 = 17.83$ ps is observed for this $^1\text{ILCT}_{\text{NDI}}$ species, evidenced by narrowing of the metal-carbonyl bands, as well as a further shift of the stretches at 1914, 1934 and 2016 cm^{-1} to 1911, 1931 and 2020, respectively (Figure 5-12, left). These observations match well with vibrational cooling observed for other tricarbonyl complexes.^{66–71} The $^1\text{ILCT}_{\text{NDI}}$ state persists beyond the time-window of the experiment (1 ns) and decays to the ground state.

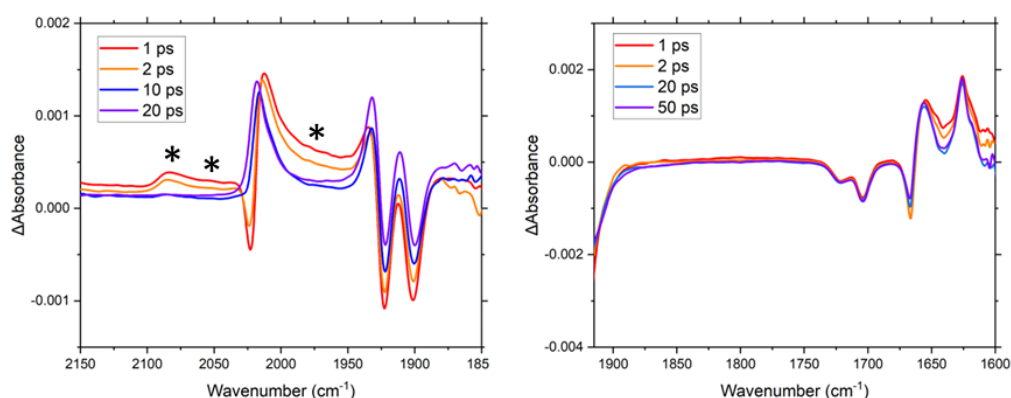


Figure 5-12. Time-resolved infrared spectra for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ following 510 nm excitation in aerated dichloromethane. The metal carbonyl (left) and organic carbonyl (right) regions were recorded on separate detectors and the relative intensities for the signals on both detectors were not normalised. The organic carbonyl region showcases the end of the lowest energy bleach of the metal carbonyl at 1900 cm^{-1} . (*) indicate the signals observed for the $^3\text{MLCT}$ excited state.

As for the experiment following 400 nm excitation, the second species showcases weak broad signals indicated by asterisks at 1978, 2051 and 2082 cm^{-1} which are assigned to a combination of the $^3\text{MLCT}_{\text{phen}}$ (2051 cm^{-1} band) and $^3\text{MLCT}_{\text{NDI}}$ (2082 cm^{-1} band) species. Within 5 ps, the signal at 2051 cm^{-1} decays, indicating internal conversion of the $^3\text{MLCT}_{\text{phen}}$ species to the $^3\text{MLCT}_{\text{NDI}}$ species. The band for the $^3\text{MLCT}_{\text{NDI}}$ at 2082 cm^{-1} species depletes within 10 ps as observed 400 nm excitation, and this process is again assigned to internal conversion to a $^3\text{ILCT}$ state.

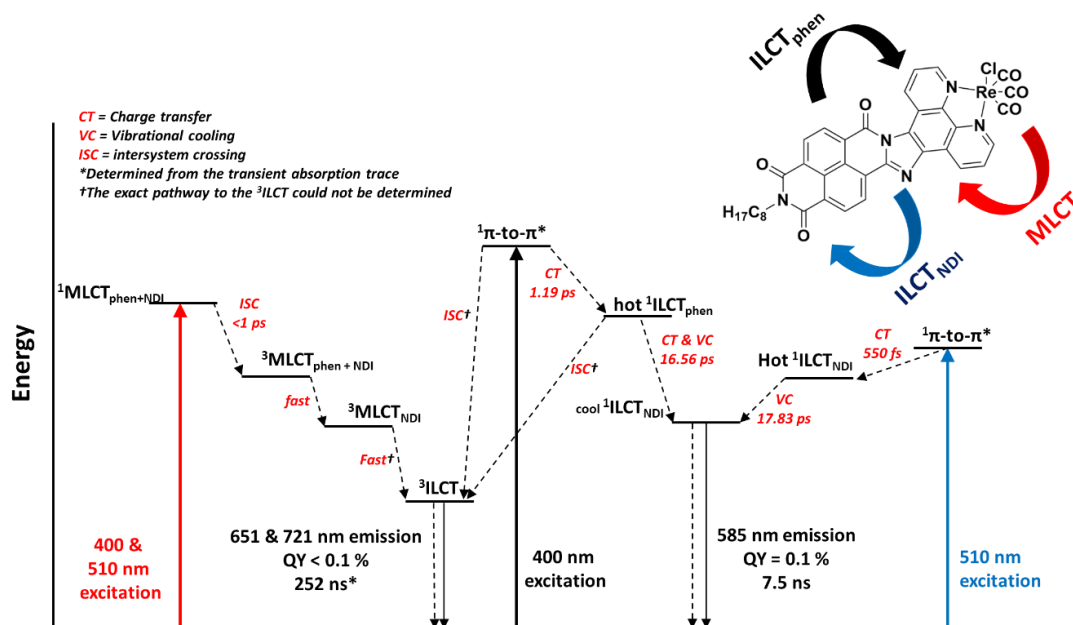


Figure 5-13. Jablonski diagram showcasing the possible transitions for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ following 510 and 400 nm excitation.

The proposed excited state processes are shown in the Jablonski diagram (Figure 5-13). Steady-state emission, time-correlated single-photon counting, transient absorption and ps-time-resolved infrared spectroscopy were combined to elucidate the excited state processes spanning the picosecond to nanosecond timescale. ps-TRIR experiments following 510 nm excitation suggest that the LUMO consists of a $^1\pi\text{-to-}\pi^*$ state which rapidly undergoes charge transfer ($\tau_1 \approx 550$ fs) towards the naphthalene-dicarboximide moiety of the ligand. This finding matches well with the excited states observed and calculated for similar Re complexes.^{13,49} Vibrational cooling with a time constant of 17.83 ps results in the vibrationally cool $^1\text{ILCT}_{\text{NDI}}$ excited state. In addition, signals for the formation of $^3\text{MLCT}_{\text{phen}}$ and $^3\text{MLCT}_{\text{NDI}}$ states are observed in the early picosecond timescale of the experiment. Steady-state emission studies following excitation at 510 nm showcase only weak fluorescence (QY < 1%) with a lifetime of approximately 7 ns. No evidence for phosphorescence from a $^3\text{ILCT}$ state was observed in these experiments. Consistent with the findings in the (spectro)electrochemical experiments, the $^1\text{ILCT}_{\text{NDI}}$ state is located fully on the ligand and does not contain enough mixing of metal orbitals to undergo sufficient intersystem crossing to the triplet surface, even with partial formation of the $^3\text{MLCT}$ state. Alternatively, there was no evidence to support population of the $^1\text{ILCT}_{\text{phen}}$ state following 510 nm excitation, and this also explain why the $^3\text{ILCT}$ state is not populated.

Irradiation at 400 nm enables population of a higher lying $\pi\text{-to-}\pi^*$ state. This state undergoes rapid charge transfer ($\tau_1 = 1.19$ ps) to the phenanthroline moiety of the ligand. Charge transfer

towards the naphthalene-dicarboximide moiety of the ligand combined with vibrational cooling occurs with a time constant of 16.56 ps to generate the $^1\text{ILCT}_{\text{NDI}}$ state, which is also observed following 510 nm excitation. Signals of the $^3\text{MLCT}_{\text{phen}}$ and $^3\text{MLCT}_{\text{NDI}}$ species are also observed in the first picoseconds following excitation. Steady-state emission, TCSPC and TA studies suggest more efficient formation of the $^3\text{ILCT}$ states following 400 nm excitation compared to the experiments at 510 nm excitation. The reason for the increase in population of these states following 400 nm excitation will require further studies. Potentially, inefficient ISC occurs from the S_2 π -to- π^* state or the intermediate $^1\text{ILCT}_{\text{phen}}$ state. Particularly the $^1\text{ILCT}_{\text{phen}}$ state may be sufficiently close to the metal centre to promote ISC via the heavy-atom effect, and others have reported that intersystem crossing occurs for similar complexes leading to the population of $^3\text{ILCT}$ states.^{13,36} However, no additional time constant for ISC crossing is observed in the ps-TRIR experiments at 400 nm. Alternatively, population of the $^1\text{MLCT}$ state may be more efficient at 400 nm excitation compared to 510 nm excitation. Calculations for the similar $\text{Re}(\text{NDI-phen})(\text{CO})_3\text{L}$ complexes suggest that the $^1\text{MLCT}$ is close in energy to the S_2 π -to- π^* excited state, albeit with significantly weaker oscillator strength than the ligand centred transitions.¹³ The weak oscillator strength for this transition may explain the low efficiency of ISC for these systems. Further in-depth photophysical studies as well as computational approaches are required to fully elucidate the exact origin of this triplet species and will be the subject of further work.

5.4.9. Photocatalysis

$\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ was studied as a photocatalyst for CO_2 reduction in dimethyl formamide (DMF) using 0.5 M 1,3-Dimethyl-2-phenylbenzimidazoline (BIH, 5000 equivalents) as a sacrificial agent and triethanolamine as a base similar to conditions previously reported for photocatalytic CO_2 reduction.^{20,72} Solutions of 0.01 mM of the photocatalyst in a 5:1 DMF:TEOA solution containing 0.5 M (5000 eq.) BIH were prepared and degassed using three freeze-pump-thaw cycles and subsequently bubbled for 2 minutes with CO_2 . The solutions were irradiated with a 470 nm LED and sampled at set intervals, with the results shown in Figure 5-14. After two hours of radiation, only trace amounts of CO was observed (turnover number (TON) of ~ 0.7). The amount of CO slowly increased to approximately 2 turnovers after 24 hours. A steady decrease in TOF from 0.35 after two hours to 0.07 after 24 hours suggests deactivation of the photocatalyst. UV-Vis spectra taken before and after photocatalysis (Figure SD12) suggest partial photobleaching of the complex under these conditions. However, deactivation through hydrogenation of the free nitrogen in the ligand as observed for hydrogen photocatalytic systems utilizing dppz type ligands cannot be ruled out.⁷³ Hydrogen was observed over the course of the experiment,

reaching 79 turnovers after 24 hours of irradiation. Traces of methane (< 1 TON) were also detected after 24 hours.

The poor activity of the system may be due to a poor quantum yield for the formation of the long-lived triplet state at the excitation wavelength (470 nm). The observed singlet state with a lifetime of approximately 7 ns may not be sufficiently long lived for successful electron transfer from the sacrificial agent to occur. Alternatively, formation of the active catalyst, in which the ancillary ligand dissociates, was only observed at significantly more negative reduction potentials in the spectroelectrochemical studies. Formation of this species may be inefficient under the reported conditions.

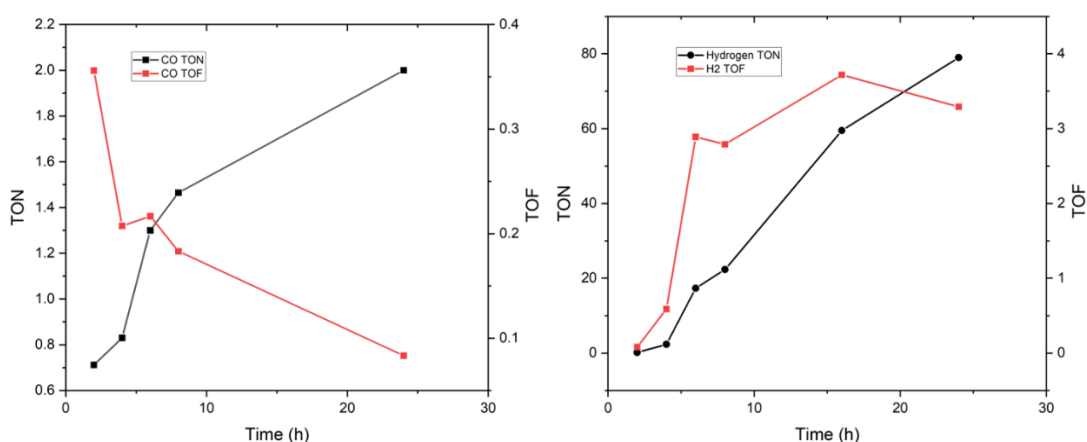


Figure 5-14. Overview of the turnover numbers and turnover frequencies achieved by the $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ catalyst for both hydrogen and carbon monoxide.

5.5. Conclusion

We have reported the successful synthesis and analysis of the novel oppt ligand and the $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ complex. We applied a wide range of spectroscopical, electrochemical and ultrafast spectroscopical techniques to analyse the properties of the ligand and the complex. The extended conjugated system in combination with the electron accepting dicarboximide group results in extending the absorbance into the visible region. The electrochemistry experiments show that the ligand undergoes two reversible reductions. For the complex, three reductions were observed. The initial two reductions are ligand-centred based on the spectroelectrochemical experiments, and the reduction potentials were not significantly influenced by the introduction of the metal centre. The third reduction takes place on the Re centre and results in dissociation of the ancillary Cl ligand and dimer formation. The results further suggest that the lowest lying excited state for the complex is localised on the extended conjugated system of the ligand, like analogue systems that have been previously reported.

Weak fluorescence was observed for the ligand regardless of excitation wavelength. For the rhenium complex, wavelength dependence was observed in the emission studies. Only fluorescence from the $^1\text{ILCT}$ state was observed when the lowest lying excited state was populated, while a combination of fluorescence and phosphorescence from the $^1\text{ILCT}$ and $^3\text{ILCT}$ states was observed when exciting at wavelengths <420 nm. Picosecond time-resolved infrared spectroscopy, nanosecond transient absorption and nanosecond time-correlated single-photon counting experiments all confirm that a considerable amount of the excited state species remains on the singlet surface following excitation regardless of the excitation wavelength. Only a small portion of the excited state species undergoes intersystem crossing to the triplet surface. ps-TRIR experiments suggest that both MLCT and ILCT states are populated following both 400 and 510 nm excitation, similar to the highly analogous $\text{Re}(\text{dppz})(\text{CO})_3\text{X}$ and $\text{Re}(\text{phen-TPA})(\text{CO})_3\text{X}$ complexes. At 355 nm excitation, a long-lived $^3\text{ILCT}$ state is observed in the transient absorption experiments with a lifetime of 252 ns. However, no signals for this long-lived state were observed in the TA experiments when excited at 532 nm. Thus, the exact pathway to the triplet surface remains partly unclear. Two potential pathways are suggested: in pathway 1, partial intersystem crossing takes place from the $^1\pi\text{-to-}\pi^*$ (S_2) or $^1\text{ILCT}_{\text{phen}}$ states, which are located on the phenanthroline moiety of the ligand and thus could undergo ISC driven by the heavy atom effect. In pathway 2, ISC occurs from a $^1\text{MLCT}$ state. Internal conversion of the $^3\text{MLCT}$ results in the formation of the $^3\text{ILCT}$ which is observed in the TA and emission experiments. The population of the MLCT states may be more efficient when excited at higher energy which could explain why the $^3\text{ILCT}$ state was not observed following 510 nm excitation. Evidence for both pathways has been reported for systems similar to ours.^{13,36,45} Further experiments in which the energy levels of the ILCT and MLCT are further modified in combination with computational approaches may provide further insight into the photophysical processes and are currently underway in our laboratory. Finally, we assessed $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ as a photocatalyst for CO_2 reduction using 470 nm light. Only small amounts of CO and hydrogen were observed, suggesting that the $^1\text{ILCT}$ state that is predominantly formed cannot facilitate efficient photocatalysis.

5.6. References

- 1 J.-M. Lehn and R. Ziessel, *Proc. Natl. Acad. Sci. U.S.A.*, 1982, **79**, 701–704.
- 2 H. Takeda, K. Koike, H. Inoue and O. Ishitani, *J. Am. Chem. Soc.*, 2008, **130**, 2023–2031.
- 3 H. Takeda and O. Ishitani, *Coordination Chemistry Reviews*, 2010, **254**, 346–354.
- 4 Y. Kou, Y. Nabetani, D. Masui, T. Shimada, S. Takagi, H. Tachibana and H. Inoue, *J. Am. Chem. Soc.*, 2014, **136**, 6021–6030.

- 5 M. Schreier, P. Gao, M. T. Mayer, J. Luo, T. Moehl, M. K. Nazeeruddin, S. D. Tilley and M. Grätzel, *Energy Environ. Sci.*, 2015, **8**, 855–861.
- 6 T. W. Schneider, M. Z. Ertem, J. T. Muckerman and A. M. Angeles-Boza, *ACS Catal.*, 2016, **6**, 5473–5481.
- 7 B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum and C. P. Kubiak, *Annu. Rev. Phys. Chem.*, 2012, **63**, 541–569.
- 8 J. V. Caspar and T. J. Meyer, *J. Phys. Chem.*, 1983, **87**, 952–957.
- 9 M. George, *Coordination Chemistry Reviews*, 1998, **177**, 201–217.
- 10 J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 2444–2453.
- 11 Del Guerzo, S. Leroy, F. Fages and R. H. Schmehl, *Inorg. Chem.*, 2002, **41**, 359–366.
- 12 A. Cannizzo, A. M. Blanco-Rodríguez, A. El Nahhas, J. Šebera, S. Zálíš, A. Vlček and M. Chergui, *J. Am. Chem. Soc.*, 2008, **130**, 8967–8974.
- 13 K. A. Wells, J. E. Yarnell, S. Sheykhi, J. R. Palmer, D. T. Yonemoto, R. Joyce, S. Garakyaraghi and F. N. Castellano, *Dalton Trans.*, 2021, **50**, 13086–13095.
- 14 V. Balzani, S. Campagna, A. Barbieri and I. Ebrary, *Photochemistry and Photophysics of Coordination Compounds II*, Springer-Verlag, Berlin, Germany, 2007.
- 15 P. Lang, R. Giereth, S. Tschierlei and M. Schwalbe, *Chem. Commun.*, 2019, **55**, 600–603.
- 16 Z.-Y. Bian, K. Sumi, M. Furue, S. Sato, K. Koike and O. Ishitani, *Inorg. Chem.*, 2008, **47**, 10801–10803.
- 17 Z.-Y. Bian, K. Sumi, M. Furue, S. Sato, K. Koike and O. Ishitani, *Dalton Trans.*, 2009, 983–993.
- 18 A. M. Cancelliere, F. Puntoriero, S. Serroni, S. Campagna, Y. Tamaki, D. Saito and O. Ishitani, *Chem. Sci.*, 2020, **11**, 1556–1563.
- 19 L. Frayne, N. Das, A. Paul, S. Amirjalayer, W. J. Buma, S. Woutersen, C. Long, J. G. Vos and M. T. Pryce, *ChemPhotoChem*, 2018, **2**, 323–331.
- 20 K. Koike, D. C. Grills, Y. Tamaki, E. Fujita, K. Okubo, Y. Yamazaki, M. Saigo, T. Mukuta, K. Onda and O. Ishitani, *Chem. Sci.*, 2018, **9**, 2961–2974.
- 21 Y. Kuramochi and O. Ishitani, *Inorg. Chem.*, 2016, **55**, 5702–5709.
- 22 S. Sato, T. Morikawa, T. Kajino and O. Ishitani, *Angew. Chem. Int. Ed.*, 2013, **52**, 988–992.
- 23 G. A. Andrade, A. J. Pistner, G. P. A. Yap, D. A. Lutterman and J. Rosenthal, *ACS Catal.*, 2013, **3**, 1685–1692.
- 24 J. D. B. Koenig, Z. S. Dubrawski, K. R. Rao, J. Willkomm, B. S. Gelfand, C. Risko, W. E. Piers and G. C. Welch, *J. Am. Chem. Soc.*, 2021, **143**, 16849–16864.
- 25 Y. Kuramochi, Y. Fujisawa and A. Satake, *J. Am. Chem. Soc.*, 2020, **142**, 705–709.

- 26 J. F. Martinez, N. T. La Porte, S. Chaudhuri, A. Sinopoli, Y. J. Bae, M. Sohail, V. S. Batista and M. R. Wasielewski, *J. Phys. Chem. C*, 2019, **123**, 10178–10190.
- 27 J. F. Martinez, N. T. La Porte and M. R. Wasielewski, *J. Phys. Chem. C*, 2018, **122**, 2608–2617.
- 28 C. D. Windle, M. W. George, R. N. Perutz, P. A. Summers, X. Z. Sun and A. C. Whitwood, *Chem. Sci.*, 2015, **6**, 6847–6864.
- 29 K. A. Walters, Y.-J. Kim and J. T. Hupp, *Inorg. Chem.*, 2002, **41**, 2909–2919.
- 30 E. E. Benson, K. A. Grice, J. M. Smieja and C. P. Kubiak, *Polyhedron*, 2013, **58**, 229–234.
- 31 M. L. Clark, P. L. Cheung, M. Lessio, E. A. Carter and C. P. Kubiak, *ACS Catal.*, 2018, **8**, 2021–2029.
- 32 K. Koike, N. Okoshi, H. Hori, K. Takeuchi, O. Ishitani, H. Tsubaki, I. P. Clark, M. W. George, F. P. A. Johnson and J. J. Turner, *J. Am. Chem. Soc.*, 2002, **124**, 11448–11455.
- 33 L. Rotundo, E. Azzi, A. Deagostino, C. Garino, L. Nencini, E. Priola, P. Quagliotto, R. Rocca, R. Gobetto and C. Nervi, *Front. Chem.*, 2019, **7**, 417.
- 34 J. M. Smieja and C. P. Kubiak, *Inorg. Chem.*, 2010, **49**, 9283–9289.
- 35 R. Fernández-Terán and L. Sévery, *Inorg. Chem.*, 2021, **60**, 1334–1343.
- 36 A. M. Blanco-Rodríguez, H. Kvapilová, J. Sýkora, M. Towrie, C. Nervi, G. Volpi, S. Zális and A. Vlček, *J. Am. Chem. Soc.*, 2014, **136**, 5963–5973.
- 37 J. E. Yarnell, J. C. Deaton, C. E. McCusker and F. N. Castellano, *Inorg. Chem.*, 2011, **50**, 7820–7830.
- 38 H. van der Salm, M. G. Fraser, R. Horvath, S. A. Cameron, J. E. Barnsley, X.-Z. Sun, M. W. George and K. C. Gordon, *Inorg. Chem.*, 2014, **53**, 3126–3140.
- 39 H. van der Salm, C. B. Larsen, J. R. W. McLay, G. S. Huff and K. C. Gordon, *Inorganica Chimica Acta*, 2015, **428**, 1–7.
- 40 M. R. Waterland, K. C. Gordon, J. J. McGarvey and P. M. Jayaweera, .
- 41 C. B. Larsen, H. van der Salm, G. E. Shillito, N. T. Lucas and K. C. Gordon, *Inorg. Chem.*, 2016, **55**, 8446–8458.
- 42 C. B. Larsen, H. van der Salm, C. A. Clark, A. B. S. Elliott, M. G. Fraser, R. Horvath, N. T. Lucas, X.-Z. Sun, M. W. George and K. C. Gordon, *Inorg. Chem.*, 2014, **53**, 1339–1354.
- 43 M. K. Kuimova, W. Z. Alsindi, A. J. Blake, E. S. Davies, D. J. Lampus, P. Matousek, J. McMaster, A. W. Parker, M. Towrie, X.-Z. Sun, C. Wilson and M. W. George, *Inorg. Chem.*, 2008, **47**, 9857–9869.
- 44 B. S. Adams, G. E. Shillito, H. van der Salm, R. Horvath, C. B. Larsen, X.-Z. Sun, N. T. Lucas, M. W. George and K. C. Gordon, *Inorg. Chem.*, 2017, **56**, 12967–12977.

- 45 G. E. Shillito, D. Preston, P. Traber, J. Steinmetzer, C. J. McAdam, J. D. Crowley, P. Wagner, S. Kupfer and K. C. Gordon, *Inorg. Chem.*, 2020, **59**, 6736–6746.
- 46 Y. Yang, J. Brückmann, W. Frey, S. Rau, M. Karnahl and S. Tschierlei, *Chem. Eur. J.*, 2020, **26**, 17027–17034.
- 47 J. E. Yarnell, C. E. McCusker, A. J. Leeds, J. M. Breaux and F. N. Castellano, *Eur. J. Inorg. Chem.*, 2016, **2016**, 1808–1818.
- 48 J. E. Yarnell, P. De La Torre and F. N. Castellano, *Eur. J. Inorg. Chem.*, 2017, **2017**, 5238–5245.
- 49 K. A. Wells, J. R. Palmer, J. E. Yarnell, S. Garakyaraghi, B. C. Pemberton, J. M. Favale, M. K. Valchar, A. Chakraborty and F. N. Castellano, *Phys. Chem. Chem. Phys.*, 2021, **23**, 24200–24210.
- 50 F. N. Castellano, *Dalton Trans.*, 2012, **41**, 8493.
- 51 F. N. Castellano, *Acc. Chem. Res.*, 2015, **48**, 828–839.
- 52 S. Neumann and O. S. Wenger, *Inorg. Chem.*, 2019, **58**, 855–860.
- 53 G. M. Greetham, P. Burgos, Q. Cao, I. P. Clark, P. S. Codd, R. C. Farrow, M. W. George, M. Kogimtzis, P. Matousek, A. W. Parker, M. R. Pollard, D. A. Robinson, Z.-J. Xin and M. Towrie, *Appl Spectrosc*, 2010, **64**, 1311–1319.
- 54 Y. Yang, J. Brückmann, W. Frey, S. Rau, M. Karnahl and S. Tschierlei, *Chemistry - A European Journal*, 2020, **26**, 17027–17034.
- 55 G. E. Shillito, T. B. J. Hall, D. Preston, P. Traber, L. Wu, K. E. A. Reynolds, R. Horvath, X. Z. Sun, N. T. Lucas, J. D. Crowley, M. W. George, S. Kupfer and K. C. Gordon, *J. Am. Chem. Soc.*, 2018, **140**, 4534–4542.
- 56 J. M. Smieja and C. P. Kubiak, *Inorganic Chemistry*, 2010, **49**, 9283–9289.
- 57 B. J. Neyhouse and T. A. White, *Inorganica Chimica Acta*, 2018, **479**, 49–57.
- 58 D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas and M. R. Wasielewski, *J. Phys. Chem. A*, 2000, **104**, 6545–6551.
- 59 N. T. La Porte, J. F. Martinez, S. Chaudhuri, S. Hedström, V. S. Batista and M. R. Wasielewski, *Coordination Chemistry Reviews*, 2018, **361**, 98–119.
- 60 G. J. Stor, F. Hartl, J. W. M. van Outersterp and D. J. Stufkens, *Organometallics*, 1995, **14**, 1115–1131.
- 61 F. P. A. Johnson, M. W. George, F. Hartl and J. J. Turner, *Organometallics*, 1996, **15**, 3374–3387.
- 62 J. V. Caspar, E. M. Kober, B. P. Sullivan and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 630–632.

- 63 J. E. Barnsley, G. E. Shillito, C. B. Larsen, H. van der Salm, R. Horvath, X. Z. Sun, X. Wu, M. W. George, N. T. Lucas and K. C. Gordon, *Inorg. Chem.*, 2019, **58**, 9785–9795.
- 64 A. Gabrielsson, F. Hartl, H. Zhang, J. R. Lindsay Smith, M. Towrie, A. Vlček, and R. N. Perutz, *J. Am. Chem. Soc.*, 2006, **128**, 4253–4266.
- 65 A. B. S. Elliott, R. Horvath, X.-Z. Sun, M. G. Gardiner, K. Müllen, N. T. Lucas, M. W. George and K. C. Gordon, *Inorg. Chem.*, 2016, **55**, 4710–4719.
- 66 A. A. Cullen, K. Heintz, L. O'Reilly, C. Long, A. Heise, R. Murphy, J. Karlsson, E. Gibson, G. M. Greetham, M. Towrie and M. T. Pryce, *Front. Chem.*, 2020, **8**, 584060.
- 67 A. M. Blanco-Rodríguez, M. Busby, C. Grădinaru, B. R. Crane, A. J. Di Bilio, P. Matousek, M. Towrie, B. S. Leigh, J. H. Richards, A. Vlček and H. B. Gray, *J. Am. Chem. Soc.*, 2006, **128**, 4365–4370.
- 68 M. Busby, A. Gabrielsson, P. Matousek, M. Towrie, A. J. Di Bilio, H. B. Gray and A. Vlček, *Inorg. Chem.*, 2004, **43**, 4994–5002.
- 69 B. W. Caplins, J. P. Lomont, S. C. Nguyen and C. B. Harris, *J. Phys. Chem. A*, 2014, **118**, 11529–11540.
- 70 A. Gabrielsson, M. Busby, P. Matousek, M. Towrie, E. Hevia, L. Cuesta, J. Perez, S. Zálaiš and A. Vlček, *Inorg. Chem.*, 2006, **45**, 9789–9797.
- 71 D. J. Liard, M. Busby, P. Matousek, M. Towrie and A. Vlček, *J. Phys. Chem. A*, 2004, **108**, 2363–2369.
- 72 F. J. R. Cerpentier, J. Karlsson, R. Lalrempuia, M. P. Brandon, I. V. Sazanovich, G. M. Greetham, E. A. Gibson and M. T. Pryce, *Front. Chem.*, 2021, **9**, 795877.
- 73 M. G. Pfeffer, C. Müller, E. T. E. Kastl, A. K. Mengele, B. Bagemihl, S. S. Fauth, J. Habermehl, L. Petermann, M. Wächtler, M. Schulz, D. Chartrand, F. Laverdière, P. Seeber, S. Kupfer, S. Gräfe, G. S. Hanan, J. G. Vos, B. Dietzek-Ivanšić and S. Rau, *Nat. Chem.*, 2022, **14**, 500–506.

Chapter 6: Conclusions and future work

This thesis described the development and study of new photocatalytic systems for various applications.

Chapter 2 discussed three cobalt-cobalt dimer compounds and their application in the photo-assisted Pauson-Khand reaction. Through a combination of spectroelectrochemical, ultrafast spectroscopy and computational techniques we propose an alternative mechanism for the photo-assisted Pauson-Khand. This study aided in elucidating the first step in the catalytic cycle, which was found not to be loss of a CO ligand but instead Co-Co bond breaking forming a high-spin diradical species. Spectroelectrochemistry was found to be very useful in determining the nature of the HOMO and LUMO by one-electron oxidation or reduction. Future work could include temperature-dependent spectroelectrochemical studies in particular at low temperature to attempt to isolate these reactive intermediates.

In **chapter 3**, two new ruthenium supramolecular assemblies were synthesised and studied for photocatalytic hydrogen evolution and CO₂ reduction. These assemblies contained peripheral ligands with pendant ethyl-ester groups which were used to immobilise the assemblies onto a NiO semiconductor surface. IR-spectroelectrochemistry indicated that the peripheral ligands with the ester moieties were reduced first, at significantly less negative potential than the bridging ligand. These findings suggested that the LUMO for these systems would also be located on the peripheral ligand. This hypothesis was confirmed with time-resolved infrared spectroscopy in charge transfer from the ruthenium metal centre to the peripheral ligands was observed while no charge transfer occurred to the bridging ligand or the catalytic metal. While the assembly with a PtI₂ fragment as catalytic metal produced hydrogen in solution, the assembly with a Re(CO)₃Cl fragment did not reduce CO₂ to carbon monoxide in solution. However, immobilisation of the assemblies onto a NiO semiconductor resulted in a change of activity, with both assemblies showing catalytic activity under 470 nm irradiation. Future studies could include the application of transient absorption or time-resolved infrared spectroscopy to

determine how the semiconductor surface influences the photophysical properties of these systems. In addition, spectroelectrochemical studies can be performed for these systems on the NiO surface to determine the nature of the reduced intermediate species for these systems when immobilised.

Chapter 4 described the synthesis and study of three tris-heteroleptic supramolecular assemblies for hydrogen evolution (containing either a PdCl_2 or PtI_2 catalytic fragment) or CO_2 reduction (containing a $\text{Re}(\text{CO})_3\text{Cl}$ catalytic fragment). These assemblies also contained pendant carboxylic acid groups which were used to immobilise the assemblies onto a NiO semiconductor surface. While the Ru-Pd assembly was found inactive on the surface, both the Ru-Pt and Ru-Re assemblies showcased catalytic activity when immobilised on NiO. Transient absorption and time-resolved infrared spectroscopy were performed in solution and on the NiO surface. It was found that immobilisation greatly affects the energy level of the peripheral ligand. In solution, only charge transfer from ruthenium to the peripheral ligand with the carboxylic acid moiety was observed, while on the surface, charge transfer to the catalytic fragment via the bridging ligand was observed instead. This chapter helps to showcase the impact of immobilising photocatalytic assemblies on their activity. Future studies for these systems could involve variation of the second peripheral ligand. For example, by changing the substituents on this second peripheral ligand the reduction potential can be changed to be the lowest, middle or highest of the three ligands, and the effect of this on the catalytic activity can be studied.

Chapter 5 described the synthesis and study of a rhenium complex with an extended organic ligand. The ligand is based on a naphthalene-diimide core which was fused with a phenanthroline moiety to create an extended conjugated system. Both the ligand and the complex showcased a charge transfer band in the visible region of the UV-Vis spectrum. Both ligand and complex showcased weak emission with short lifetimes of 1.5 ns for the ligand and 7.5 ns for the complex, which were assigned to fluorescence from a singlet intraligand charge

transfer ($^1\text{ILCT}$) excited state. Transient absorption experiments confirmed that the rhenium complex also populated a long lived $^3\text{ILCT}$ state with a lifetime of several hundred nanoseconds. Time resolved infrared studies highlighted wavelength dependant behaviour for both the ligand and the complex. Following excitation into the lowest energy absorption band at 510 nm, both the ligand and complex a $^1\text{ILCT}$ state localised on the dicarboximide moiety of the ligand was populated, while excitation at 400 nm resulted in formation of an ILCT state localised on the phenanthroline moiety. The ILCT localised on the phenanthroline moiety was short lived ($\tau < 20$ ps) and quickly underwent internal conversion to the ILCT localised on the dicarboximide end of the ligand. For the rhenium complex, weak signals which could be assigned to $^3\text{MLCT}$ states were observed following both 510 and 400 nm excitation. These signals were only observed on the early picosecond timescale. Currently, the origin of the long-lived $^3\text{ILCT}$ state for the rhenium complex is unsure. This state may be populated via heavy atom assisted intersystem crossing from the initial $^1\text{ILCT}$ state localised on the phenanthroline ligand or from the $^1\text{ILCT}$ state localised on the dicarboximide end of the ligand. However, population of this $^3\text{ILCT}$ state may also occur via internal conversion from the $^3\text{MLCT}$ states. Finally, the rhenium complex was assessed for photocatalytic CO_2 reduction. While only traces (2 TON) amounts of carbon monoxide were observed, 81 turnovers of hydrogen were obtained following 24 hours of 470 nm light irradiation. Future work could include studying the origin of the $^3\text{ILCT}$ state. For example, the ancillary ligand on the rhenium centre can be varied to change the energy of the MLCT states and therefore change the distribution of population of the excited states, thus determining if the $^3\text{ILCT}$ state originates from a MLCT state. In addition, the quantum yield for formation of triplet states populated should be determined.

Appendix A: Photochemical or Electrochemical Bond
Breaking – Exploring the Chemistry of $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$
complexes, using Time-Resolved Infrared Spectroscopy, Cyclic
Voltammetry, Spectroelectrochemistry and Density Functional
Methods. – Supporting information

Jennifer C. Manton,[†] Florian J.R. Cerpentier,[†] Emma C. Harvey[†], Ian P. Clark[‡], Gregory
M. Greetham[‡], Conor Long,[†] and Mary T. Pryce^{†*}

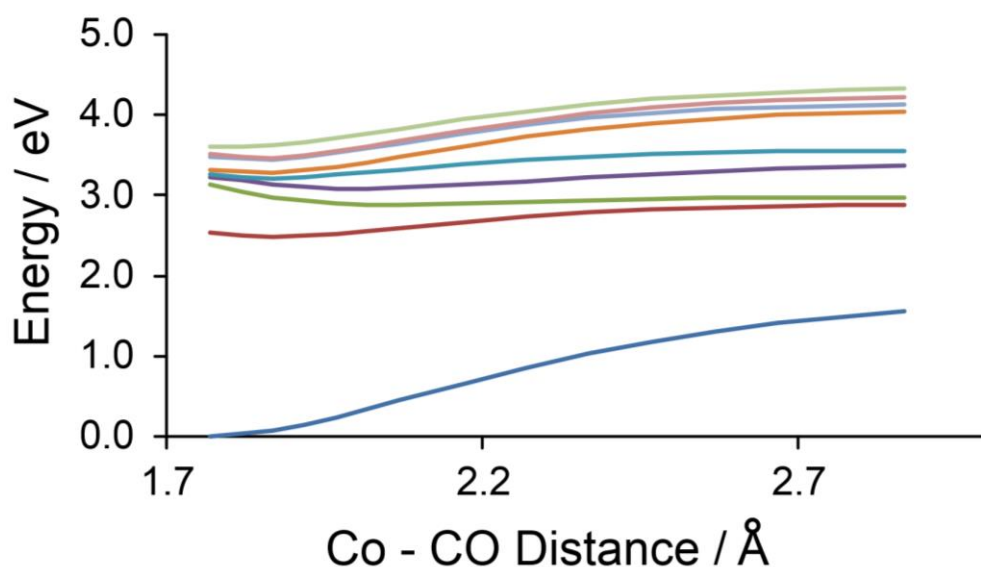


Figure SA 1. The behavior of the ground-state and eight lowest energy singlet excited states of $(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6$ along the axial CO-loss reaction coordinate

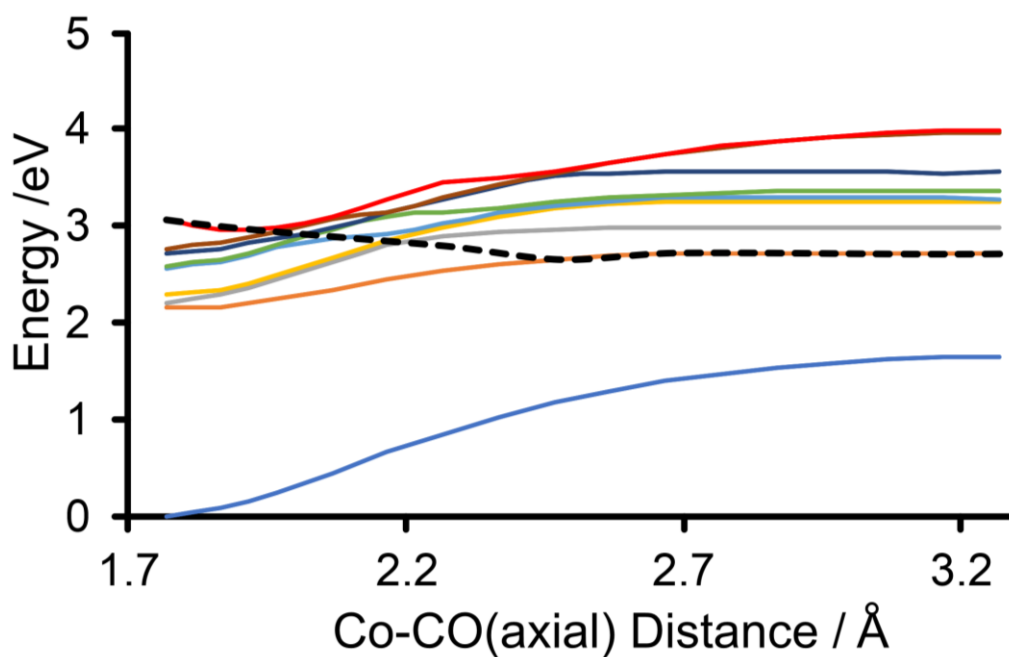


Figure SA 2. The behaviour of the 10 lowest energy singlet excited states along the Co-CO (axial) reaction coordinate for 3a, the dashed curve represents the non-adiabatic path to CO-loss.

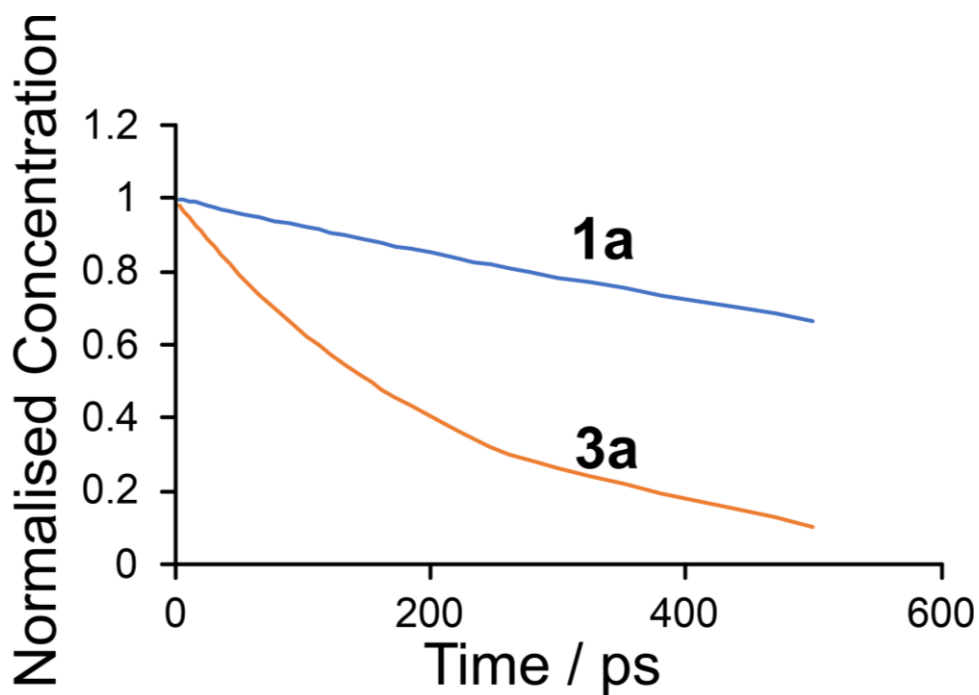


Figure SA 3. The time-dependent behavior of the normalized concentration of the initially produced CO-loss species obtained by global analysis of the ps-TRIR data following excitation of 1a and 3a at 400 nm.

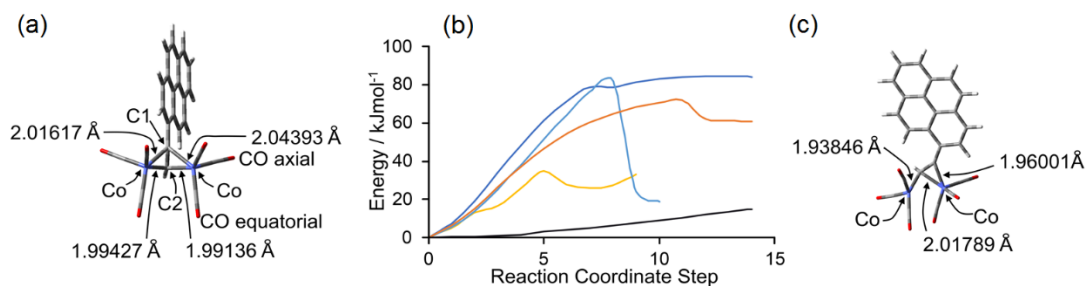


Figure SA 4. (a) The optimized structure of **1a**•⁻ with the atoms involved in the reaction coordinates indicated (atomic coordinates are provided in the supporting information); (b) the energy changes calculated along the Co-Co stretch reaction coordinate (grey), the Co-C1(alkyne) (yellow), the Co-C2(alkyne) (light blue), Co-CO(axial) (red) and Co-CO(equatorial) (dark blue); (c) the optimized structure at the local minimum, step 7 on the Co-C1 stretch reaction coordinate (yellow plot)

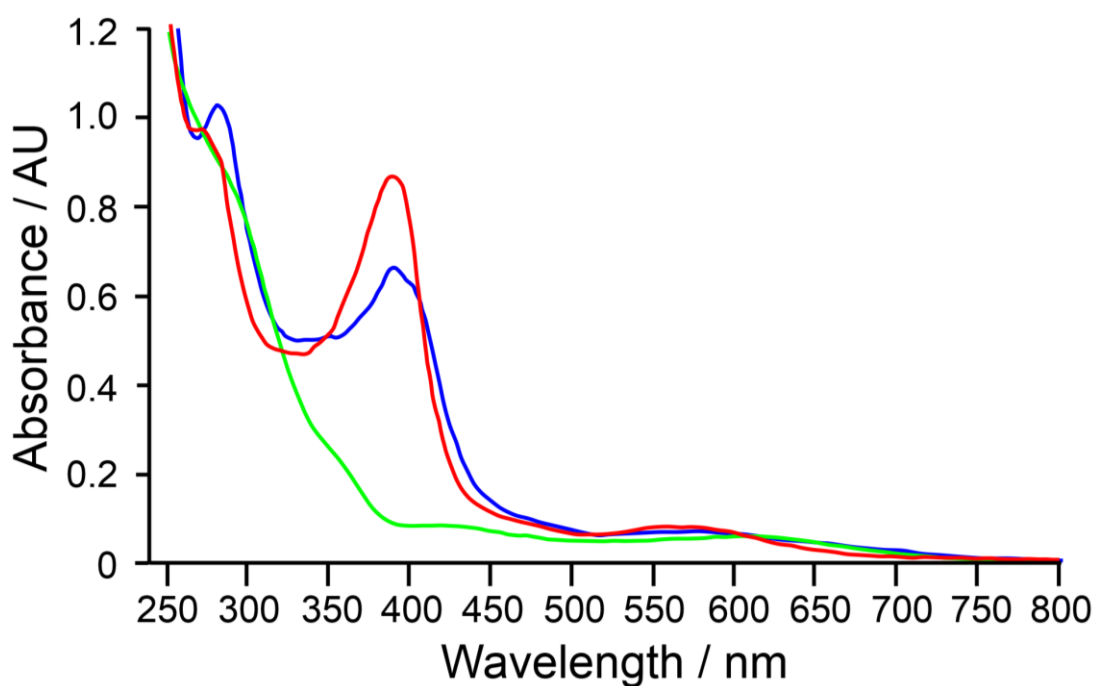


Figure SA 5. Overlay of electronic absorbance spectra of $(\mu_2\text{-R,R'-alkyne})\text{-Co}_2(\text{CO})_6$ complexes in DCM. **1a** (red line, 1.2×10^{-2} M), **2a** (blue line, 1.5×10^{-2} M) and **3a** (green line, 1.6×10^{-2} M).

Table SA 1. UV-vis absorption data for complexes in this study. All spectra were recorded in spectroscopic grade CH_2Cl_2 .

Complex	λ max (nm), ϵ ($\times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)
1a	274 (20.5), 392 (19.1), 577 (1.1)
2a	279 (18.7), 389 (11.7), 574 (1.3)
3a	290 (17.1), 361 (4.4), 430 (1.8), 614 (1.14)

Table SA 2. *ps*-TRIR spectral data for all complexes in this study. *ps*-TRIR for $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ complexes were carried out in spectroscopic grade *n*-heptane

Complex	Parent Spectrum (cm^{-1})	Vibrationally "hot" species (cm^{-1})	Diradical species (cm^{-1})	CO loss photoproduct (cm^{-1})
1a	2092, 2056, 2030	2078, 2046, 2012	2081, 2048, 2016	2074, 2034, 2007, 1977
2a	2085, 2048, 2023	2067, 2034, 2003	2076, 2041, 2012	2064, 2004, 1970
3a	2090, 2051, 2023	2069, 2039, 1999	2081, 2041, 2007	N/A

Quantum yield measurements for the CO-loss process.

The UV-vis absorbance spectra of both hexacarbonyl complexes show intense absorbances in the UV region up to 400 nm with broad but weak absorbances in the visible region extending to 700 nm (Fig. 2). The triphenylphosphine pentacarbonyl derivatives of **1a** and **2a**; exhibit strong absorbances around 430 nm. Thus monitoring the absorbance change at 430 nm provides a convenient method for measuring the yield of photoinduced CO-loss species (see ESI 1).

The conversion to photoproduct was limited to 10%, to minimize the effect of photoproduct absorbance at the excitation wavelengths (546 to 313 nm). See Table SI2 for quantum yields obtained. These results demonstrate that the quantum yield of CO-loss (Φ_{CO}) is strongly dependent on both the excitation wavelength and the nature of the alkyne substituent. Table 2 shows that the quantum yield for CO loss (Φ_{CO}) from **1a** increases from 4% to 25% when the excitation wavelength is reduced from 546 nm to 313 nm. In the case of **2a**, however, the largest Φ_{CO} was obtained for 365 nm irradiation. All Φ_{CO} values are low compared to organometallic compounds such as $\text{Cr}(\text{CO})_6$ or $(\eta^6\text{-$

benzene)Cr(CO)₃, where $\Phi_{\text{CO}} > 60\%$ have been reported. It should be noted that the Φ_{CO} values obtained at 405 nm are similar to those estimated using the ps-TRIR technique (400 nm excitation), based on the recovery of the parent ν_{CO} bands following excitation.

Table SA 3. Quantum yields of CO loss for 1a and 2a using potassium ferrioxalate actinometry and that estimated from recovery of parent bands during ps-TRIR experiments. Results recorded in spectroscopic grade n-heptane.

λ_{exc} (nm)	From ferrioxalate actinometry		Estimated from TRIR	
	1a	2a	1a	2a
313	25 %	8 %	-	-
365	10 %	19 %	-	-
405	9 %	13 %	10 %	15 %
546	4 %	10 %	-	-

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4 Co4 -2.2085 1.0232 -0.7734 Co

5 C5 -2.4461 0.0778 -2.2882 C

6 C6 -3.7654 1.8933 -0.5081 C

7 C7 -1.2012 2.3473 -1.3783 C

8 C8 -2.9824 -2.0718 -0.2157 C

9 C9 -4.0415 -0.2112 1.6651 C

10 C10 -1.7753 -1.6752 2.2186 C

11 O11 -3.3070 -2.9121 -0.9314 O

12 O12 -5.0038 0.1544 2.1758 O

13 O13 -1.2929 -2.2730 3.0733 O

14 O14 -4.7533 2.4493 -0.3168 O

15 O15 -2.5894 -0.5288 -3.2542 O
 16 O16 -0.5518 3.2134 -1.7649 O
 17 H17 -1.2887 1.5897 1.8112 H
 18 C18 0.4837 -0.5255 -0.1497 C
 19 C19 1.7039 0.1196 0.2068 C
 20 C20 0.5421 -1.7238 -0.8852 C
 21 C21 2.9483 -0.4769 -0.1812 C
 22 C22 1.7522 1.3573 0.9349 C
 23 C23 1.7438 -2.3021 -1.2601 C
 24 H24 -0.3890 -2.2083 -1.1613 H
 25 C25 4.1863 0.1481 0.1669 C
 26 C26 2.9668 -1.7009 -0.9178 C
 27 C27 2.9332 1.9539 1.2623 C
 28 H28 0.8229 1.8283 1.2269 H
 29 H29 1.7461 -3.2318 -1.8226 H
 30 C30 4.1930 1.3749 0.8967 C
 31 C31 5.4278 -0.4501 -0.2149 C
 32 C32 4.2271 -2.2793 -1.2879 C
 33 H33 2.9345 2.8910 1.8133 H
 34 C34 5.4203 1.9734 1.2288 C
 35 C35 6.6308 0.1834 0.1397 C
 36 C36 5.4048 -1.6827 -0.9517 C
 37 H37 4.2211 -3.2113 -1.8472 H
 38 C38 6.6249 1.3813 0.8534 C
 39 H39 5.4201 2.9079 1.7840 H
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4 Co4 0.8481 -1.5443 1.5245 Co

5 C5 0.3830 -3.2603 1.8076 C

6 C6 2.4960 -1.3743 2.2369 C

7 C7 -0.1143 -0.7784 2.8001 C

8 C8 1.0282 -3.5108 -1.1350 C

9 C9 3.2127 -1.8830 -0.6417 C

10 C10 1.2955 -1.1172 -2.4727 C

11 O11 0.8045 -4.6215 -1.3319 O

12 O12 4.3486 -2.0100 -0.5110 O

13 O13 1.2049 -0.6877 -3.5358 O

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15 O15 0.0897 -4.3600 1.9706 O

16 O16 -0.7116 -0.3068 3.6618 O

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18 C18 -2.5261 -0.0002 -0.0440 C

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20 C20 -3.9032 -0.1088 -0.4286 C

21 C21 -2.1383 1.1488 0.7266 C

22 C22 -3.4381 -2.2372 -1.5161 C

23 H23 -1.4247 -2.9280 -1.4112 H

24 C24 -4.8377 0.9113 -0.0651 C

25 C25 -4.3608 -1.2356 -1.1785 C

26 C26 -3.0317 2.1170 1.0779 C

27 H27 -1.1076 1.2525 1.0347 H
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 33 C33 -5.3436 3.0332 1.0425 C
 34 C34 -7.1072 1.8215 -0.0867 C
 35 C35 -6.6279 -0.3396 -1.2152 C
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Mol File for 3

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5 C5 2.5788 1.1894 1.5263 C
6 C6 3.7288 0.7196 -1.0690 C
7 C7 1.7870 2.6341 -0.6528 C
8 C8 1.0579 -1.4742 1.8397 C
9 C9 2.8898 -2.0691 -0.2506 C
10 C10 0.2455 -2.5777 -0.5738 C
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13 O13 -0.4098 -3.4217 -1.0009 O
14 O14 4.7010 0.5897 -1.6687 O
15 O15 2.8520 1.3100 2.6377 O
16 O16 1.5356 3.7165 -0.9485 O
17 H17 0.8587 -0.1108 -2.4445 H
18 C18 -0.9672 0.9472 0.1200 C
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20 C20 -1.5824 0.9218 1.4174 C
21 C21 -2.7997 2.3749 0.0988 C
22 H22 -1.5396 2.0831 -1.7331 H
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31 H31 -5.7317 0.5559 -0.2555 H
32 C32 -3.1202 -1.2892 -1.2724 C
33 H33 -4.2714 0.1923 -2.4976 H
34 C34 -3.2683 -1.6968 0.0895 C
35 H35 -4.7266 -1.0525 1.6652 H
36 H36 -2.3657 -1.6399 -1.9636 H
37 H37 -2.6490 -2.4136 0.6120 H
@<TRIPOS>BOND

1 1 2 2
2 1 3 1
3 1 4 1
4 1 18 1
5 2 3 1
6 2 4 1
7 2 17 1
8 3 4 1
9 3 8 1
10 3 9 1
11 3 10 1
12 4 5 1
13 4 6 1
14 4 7 1
15 5 15 3
16 6 14 3
17 7 16 3
18 8 11 3
19 9 12 3
20 10 13 3
21 18 19 Ar
22 18 20 Ar
23 19 21 Ar
24 19 22 1
25 19 27 1
26 20 23 Ar
27 20 24 1
28 21 23 Ar
29 21 25 1
30 23 26 1
31 28 29 Ar
32 28 30 Ar
33 28 31 1
34 29 32 Ar
35 29 33 1
36 30 34 Ar
37 30 35 1
38 32 34 Ar

39 32 36 1

40 34 37 1

Mol File for Reduced **1**

@<TRIPOS>MOLECULE

Reduced 1a

42 47

SMALL

NO_CHARGES

@<TRIPOS>ATOM

1 C1 -0.8675 -0.0538 0.2163 C

2 C2 -1.5066 0.7042 1.1007 C

3 Co3 -2.5491 -0.9757 0.8387 Co

4 Co4 -2.1262 1.2659 -0.7065 Co

5 C5 -2.3629 0.4926 -2.2864 C

6 C6 -3.6604 2.0455 -0.2772 C

7 C7 -1.0289 2.6418 -1.0612 C

8 C8 -2.9969 -2.0190 -0.5264 C

9 C9 -4.0632 -0.4562 1.6043 C

10 C10 -1.8272 -2.1062 2.0313 C

11 O11 -3.2995 -2.7262 -1.3960 O

12 O12 -5.0394 -0.1109 2.1268 O

13 O13 -1.3476 -2.8404 2.7895 O

14 O14 -4.6559 2.5693 0.0078 O

15 O15 -2.5125 0.0081 -3.3300 O

16 O16 -0.3612 3.5561 -1.3116 O

17 H17 -1.3321 1.2710 2.0041 H

18 C18 0.4382 -0.5515 -0.1921 C

19 C19 1.6614 0.0595 0.2193 C

20 C20 0.5119 -1.6759 -1.0387 C

21 C21 2.9110 -0.4887 -0.2189 C

22 C22 1.7003 1.2196 1.0655 C

23 C23 1.7184 -2.2044 -1.4689 C

24 H24 -0.4178 -2.1349 -1.3589 H

25 C25 4.1450 0.1057 0.1948 C
26 C26 2.9399 -1.6348 -1.0710 C
27 C27 2.8755 1.7892 1.4568 C
28 H28 0.7621 1.6498 1.3918 H
29 H29 1.7265 -3.0758 -2.1195 H
30 C30 4.1412 1.2552 1.0434 C
31 C31 5.3928 -0.4455 -0.2386 C
32 C32 4.2047 -2.1657 -1.4908 C
33 H33 2.8695 2.6691 2.0960 H
34 C34 5.3643 1.8237 1.4392 C
35 C35 6.5908 0.1569 0.1834 C
36 C36 5.3793 -1.5996 -1.0941 C
37 H37 4.2057 -3.0389 -2.1391 H
38 C38 6.5739 1.2778 1.0126 C
39 H39 5.3562 2.6987 2.0847 H
40 H40 7.5376 -0.2636 -0.1467 H
41 H41 6.3304 -2.0133 -1.4206 H
42 H42 7.5109 1.7293 1.3279 H

@<TRIPOS>BOND

1 1 2 2

2 1 3 1

3 1 4 1

4 1 18 1

5 2 3 1

6 2 4 1

7 2 17 1

8 3 8 1

9 3 9 1

10 3 10 1

11 4 5 1

12 4 6 1

13 4 7 1

14 5 15 2

15 6 14 2

16 7 16 2

17 8 11 2

18 9 12 2

19 10 13 2

20 18 19 Ar
21 18 20 Ar
22 19 21 Ar
23 19 22 Ar
24 20 23 2
25 20 24 1
26 21 25 Ar
27 21 26 Ar
28 22 27 2
29 22 28 1
30 23 26 Ar
31 23 29 1
32 25 30 Ar
33 25 31 Ar
34 26 32 Ar
35 27 30 Ar
36 27 33 1
37 30 34 Ar
38 31 35 Ar
39 31 36 Ar
40 32 36 2
41 32 37 1
42 34 38 Ar
43 34 39 1
44 35 38 Ar
45 35 40 1
46 36 41 1
47 38 42 1

Mol File for High-Spin Diradical of 1

@<TRIPOS>MOLECULE

Molecule Name

42 47

SMALL

NO_CHARGES

@<TRIPOS>ATOM

1 C1 0.9290 -0.0294 -0.1588 C
2 C2 1.5970 0.6192 -1.1220 C
3 Co3 2.4162 -1.1626 -0.8558 Co
4 Co4 2.1333 1.4137 0.5931 Co
5 C5 2.2065 0.9156 2.3311 C
6 C6 3.7251 2.1470 0.1242 C
7 C7 1.0969 2.9577 0.7271 C
8 C8 3.6392 -1.5258 0.4921 C
9 C9 3.4722 -1.1246 -2.3173 C
10 C10 1.5910 -2.8007 -0.8571 C
11 O11 4.3766 -1.7314 1.3477 O
12 O12 4.1162 -1.0876 -3.2684 O
13 O13 1.0242 -3.7965 -0.9185 O
14 O14 4.7501 2.5495 -0.2047 O
15 O15 2.2536 0.5813 3.4296 O
16 O16 0.3724 3.8459 0.6973 O
17 H17 1.4806 1.1107 -2.0776 H
18 C18 -0.3882 -0.4341 0.3396 C
19 C19 -1.6035 0.0417 -0.2286 C
20 C20 -0.4510 -1.3127 1.4357 C
21 C21 -2.8513 -0.3962 0.3252 C
22 C22 -1.6454 0.9462 -1.3445 C
23 C23 -1.6560 -1.7345 1.9736 C
24 H24 0.4803 -1.6643 1.8699 H
25 C25 -4.0857 0.0618 -0.2316 C
26 C26 -2.8761 -1.2932 1.4361 C
27 C27 -2.8232 1.3830 -1.8722 C
28 H28 -0.7124 1.2886 -1.7734 H
29 H29 -1.6622 -2.4157 2.8206 H
30 C30 -4.0860 0.9598 -1.3413 C
31 C31 -5.3307 -0.3754 0.3196 C
32 C32 -4.1397 -1.7154 1.9692 C
33 H33 -2.8204 2.0691 -2.7157 H

34 C34 -5.3099 1.3982 -1.8733 C
35 C35 -6.5299 0.0896 -0.2453 C
36 C36 -5.3140 -1.2779 1.4364 C
37 H37 -4.1386 -2.3985 2.8150 H
38 C38 -6.5176 0.9660 -1.3290 C
39 H39 -5.3047 2.0822 -2.7183 H
40 H40 -7.4752 -0.2437 0.1756 H
41 H41 -6.2641 -1.6064 1.8505 H
42 H42 -7.4559 1.3145 -1.7517 H

@<TRIPOS>BOND

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2 1 3 1

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17

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11 4 5 1

12 4 6 1

13 4 7 1

14 5 15 3

15 6 14 3

16 7 16 3

17 8 11 3

18 9 12 3

19 10 13 3

20 18 19 Ar

21 18 20 Ar

22 19 21 Ar

23 19 22 Ar
 24 20 23 2
 25 20 24 1
 26 21 25 Ar
 27 21 26 Ar
 28 22 27 2
 29 22 28 1
 30 23 26 Ar
 31 23 29 1
 32 25 30 Ar
 33 25 31 Ar
 34 26 32 Ar
 35 27 30 Ar
 36 27 33 1
 37 30 34 Ar
 38 31 35 Ar
 39 31 36 Ar
 40 32 36 2
 41 32 37 1
 42 34 38 Ar
 43 34 39 1
 44 35 38 Ar
 45 35 40 1
 46 36 41 1

Summary of Calculated Electronic Transitions for **1**

nm 1000 cm⁻¹ eV f Assignment (excitations with contrib. greater than 10.0%)
 1 589.2 16.97 2.104 0.0866 128->129(60.9%) 127->129(15.9%) 125->129(10.2%)
 2 433.4 23.07 2.861 0.1116 127->129(31.4%) 128->129(29.4%) 125->129(16.6%)
 3 401.9 24.88 3.085 0.0267 123->129(52.9%)
 4 391.4 25.55 3.168 0.0041 121->129(38.2%) 119->129(20.4%) 122->129(15.0%)
 5 387.0 25.84 3.204 0.4234 128->130(56.2%) 119->129(10.3%)

6 385.2 25.96 3.219 0.1094 119->129(25.7%) 128->130(18.8%) 121->129(13.1%) 118->129(12.7%)

7 378.5 26.42 3.276 0.0017 122->129(39.6%) 127->129(16.4%) 121->129(10.0%)

8 364.6 27.43 3.400 0.0338 117->129(28.7%) 127->129(12.3%) 118->129(10.7%) 126->129(10.6%)

9 359.4 27.82 3.450 0.0934 126->129(38.3%) 120->129(16.6%)

10 356.1 28.08 3.482 0.0171 120->129(48.4%) 118->129(10.4%)

11 348.1 28.73 3.562 0.0012 125->129(26.0%) 128->133(14.9%) 117->129(14.8%) 128->131(13.6%)

12 342.6 29.19 3.619 0.0111 128->131(55.2%)

13 338.8 29.51 3.659 0.0300 128->132(64.3%)

14 325.8 30.69 3.805 0.0070 127->130(31.2%) 125->129(26.7%) 128->133(25.5%)

15 317.0 31.55 3.912 0.0016 128->134(69.4%)

16 310.3 32.23 3.996 0.0091 126->130(39.9%) 128->135(15.6%)

17 307.5 32.52 4.032 0.0087 128->135(39.9%) 126->130(18.3%) 128->136(17.8%)

18 305.3 32.76 4.061 0.0630 127->130(27.9%) 128->133(17.2%)

19 302.6 33.04 4.097 0.0105 124->129(46.5%) 125->130(12.6%)

20 301.6 33.15 4.110 0.0055 128->137(51.5%) 128->136(13.2%)

21 300.5 33.28 4.126 0.0088 128->136(42.7%) 128->135(20.5%) 128->137(20.4%)

22 297.5 33.61 4.168 0.0091 128->139(32.4%) 128->138(13.3%) 125->130(10.3%)

23 294.6 33.95 4.209 0.0016 128->138(45.9%) 128->139(23.9%)

24 287.4 34.80 4.315 0.0186 126->131(23.0%) 126->132(19.1%) 128->140(12.8%)

25 287.0 34.84 4.320 0.0047 126->132(48.3%)

26 286.4 34.91 4.329 0.0496 128->140(38.2%) 128->141(25.0%)

27 284.5 35.14 4.357 0.0386 128->141(46.8%) 126->131(13.9%)

28 283.1 35.32 4.379 0.0408 127->131(16.4%) 127->132(10.1%)

29 280.8 35.61 4.415 0.0202 127->132(20.6%)

30 279.4 35.79 4.437 0.0718 127->131(18.1%) 125->130(10.5%) 126->131(10.4%)

31 277.5 36.03 4.467 0.1032 125->130(21.7%) 122->130(16.4%)

32 274.5 36.43 4.516 0.0076 123->130(34.6%)

33 273.2 36.60 4.538 0.0223 123->130(12.7%)

34 271.1 36.89 4.574 0.0029 126->134(59.0%)

35 269.1 37.16 4.608 0.0011 121->130(23.3%)

36 268.7 37.22 4.614 0.0094 128->144(10.5%)

37 267.6 37.37 4.633 0.0244 128->142(22.7%) 128->143(14.9%) 124->130(10.6%)
 38 267.0 37.46 4.644 0.0075 128->143(32.0%)
 39 266.6 37.51 4.651 0.0031 128->142(45.6%) 124->130(24.6%)
 40 265.4 37.68 4.672 0.0063 128->144(24.1%) 128->145(11.8%)
 41 264.8 37.76 4.682 0.0087 124->130(22.8%) 123->130(10.3%)
 42 263.7 37.92 4.702 0.0038 128->143(12.4%) 128->144(12.3%) 122->131(11.6%)
 43 263.5 37.96 4.706 0.0014 128->145(10.7%)
 44 261.7 38.21 4.738 0.0037
 45 260.3 38.41 4.762 0.0167
 46 259.8 38.50 4.773 0.0439 121->130(10.9%) 122->132(10.4%)
 47 258.5 38.68 4.796 0.0210 127->136(17.3%) 126->135(12.7%)
 48 258.3 38.71 4.800 0.0421 122->132(13.2%) 121->132(10.1%)
 49 256.8 38.94 4.828 0.1205 127->133(24.3%) 126->135(10.9%)
 50 255.5 39.13 4.852 0.0039 128->145(20.7%) 127->133(11.6%)
 51 255.2 39.19 4.859 0.0055 126->136(31.3%) 126->135(14.0%)
 52 254.2 39.34 4.878 0.0100
 53 253.7 39.42 4.887 0.0071 126->137(18.7%) 120->132(13.8%)
 54 253.0 39.52 4.900 0.0153 127->136(11.0%)
 55 251.9 39.69 4.921 0.0282 127->137(11.9%)
 56 251.4 39.78 4.932 0.0004 126->137(25.9%)
 57 250.9 39.86 4.942 0.0137
 58 250.3 39.95 4.953 0.0004 120->130(15.2%) 125->131(13.4%)
 59 248.7 40.21 4.986 0.0021 125->131(10.8%)
 60 248.5 40.24 4.989 0.0612 123->134(13.3%)
 61 247.8 40.36 5.004 0.0053 125->131(16.0%)
 62 246.9 40.49 5.021 0.0042 128->146(15.9%) 121->132(10.9%)
 63 246.8 40.52 5.024 0.1242 127->138(14.1%)
 64 245.8 40.68 5.044 0.0194 121->134(10.5%) 128->146(10.1%)
 65 245.3 40.76 5.054 0.0202 128->146(27.3%)
 66 244.9 40.83 5.062 0.0357
 67 244.1 40.96 5.079 0.0065 125->132(24.4%) 127->139(12.7%)
 68 242.7 41.21 5.109 0.0243 126->133(15.5%) 126->138(11.2%)
 69 242.0 41.32 5.122 0.0066
 70 241.4 41.43 5.136 0.0110 126->133(13.6%)

71 240.5 41.58 5.155 0.0019 121->131(11.5%)
 72 240.1 41.65 5.164 0.0196 121->137(11.6%)
 73 239.7 41.72 5.173 0.0061
 74 239.5 41.75 5.176 0.0061
 75 238.6 41.92 5.197 0.0132 127->141(28.9%) 124->133(12.5%)
 76 237.8 42.05 5.213 0.0093 127->140(11.3%)
 77 236.3 42.31 5.246 0.0263
 78 235.7 42.42 5.259 0.0670
 79 234.5 42.64 5.287 0.0829 116->129(24.2%)
 80 234.1 42.71 5.296 0.0492 118->130(12.6%)

Summary of Calculated Electronic Transitions for 2

nm 1000 cm⁻¹ eV f Assignment (excitations with contrib. greater than 10.0%)

1 615.1 16.26 2.016 0.0478 175->176(54.5%) 172->176(14.1%)
 2 556.0 17.99 2.230 0.0002 173->176(20.2%) 174->193(12.2%)
 3 550.7 18.16 2.251 0.0067 174->176(18.9%)
 4 509.4 19.63 2.434 0.0026 173->176(37.5%) 175->176(17.8%) 174->193(15.0%)
 5 505.8 19.77 2.451 0.0112 174->176(64.4%)
 6 472.8 21.15 2.623 0.0006 174->193(13.5%) 171->194(10.1%)
 7 462.6 21.61 2.680 0.0100 171->193(17.8%)
 8 454.0 22.03 2.731 0.0750 172->176(24.1%) 173->176(17.8%) 169->176(16.0%) 175->176(13.0%)
 9 420.0 23.81 2.952 0.0134 170->176(23.4%) 172->176(17.2%) 169->176(17.1%) 168->176(10.2%)
 10 406.8 24.58 3.048 0.1198 175->177(83.7%)
 11 395.1 25.31 3.138 0.0219 174->177(87.9%)
 12 390.9 25.58 3.172 0.1260 163->176(23.2%) 173->177(16.1%)
 13 387.1 25.83 3.203 0.0170 171->176(24.4%) 159->176(24.2%)
 14 385.6 25.93 3.215 0.0978 159->176(29.5%) 173->177(24.9%)
 15 384.2 26.03 3.227 0.0776 173->177(20.7%) 166->176(13.8%) 160->176(11.3%) 171->176(10.6%)
 16 376.0 26.60 3.298 0.0075 163->176(40.8%) 170->176(11.4%)
 17 369.4 27.07 3.356 0.0304 158->176(25.6%) 168->176(13.4%)

18 360.0 27.78 3.445 0.0174 175->178(29.2%) 161->176(23.6%)
 19 357.7 27.96 3.467 0.0075 175->179(19.3%) 158->176(13.0%) 161->176(10.7%)
 20 355.6 28.12 3.486 0.0555 168->176(21.9%) 158->176(18.4%)
 21 354.0 28.25 3.502 0.0064 171->193(16.8%) 175->179(11.6%)
 22 351.7 28.43 3.525 0.0023 175->178(28.9%) 161->176(12.0%)
 23 350.6 28.52 3.537 0.0167 175->179(22.5%) 173->179(13.6%)
 24 349.1 28.64 3.551 0.0099 170->176(16.3%) 169->176(10.6%)
 25 337.1 29.66 3.678 0.0011 174->178(78.6%)
 26 335.3 29.82 3.698 0.0014 173->178(70.5%)
 27 332.8 30.05 3.726 0.0039 175->180(47.9%) 175->181(23.9%)
 28 331.5 30.17 3.740 0.0153 172->177(49.6%)
 29 327.3 30.55 3.788 0.0069 173->179(37.7%) 174->179(22.7%)
 30 325.9 30.69 3.804 0.0042 174->179(45.8%) 173->179(13.2%)
 31 324.6 30.81 3.820 0.0308 170->177(22.7%) 175->181(13.3%)
 32 316.4 31.60 3.918 0.0001 174->180(15.6%)
 33 315.6 31.68 3.928 0.0004 174->180(32.1%) 174->181(17.7%) 173->180(17.1%)
 34 314.5 31.80 3.942 0.0105 175->183(19.4%)
 35 313.9 31.86 3.950 0.0006 167->176(84.9%)
 36 313.6 31.89 3.954 0.0058 175->184(26.8%) 175->182(19.3%) 175->183(10.5%)
 37 311.6 32.10 3.979 0.0053 175->183(27.0%) 173->180(15.0%) 173->181(11.4%)
 38 310.0 32.26 3.999 0.0061 171->177(37.2%)
 39 309.7 32.29 4.003 0.0056 175->182(21.6%) 169->177(16.6%)
 40 308.4 32.42 4.020 0.0011 171->177(25.9%) 175->185(17.2%)
 41 306.0 32.68 4.052 0.0204 169->177(19.9%) 175->182(12.4%) 175->185(10.8%)
 42 305.3 32.76 4.062 0.0033 173->181(14.3%) 175->185(13.2%) 175->181(10.9%)
 43 302.7 33.04 4.096 0.0002 174->181(33.8%) 174->180(14.3%) 165->176(14.0%) 166->176(10.6%)
 44 302.0 33.11 4.106 0.0010 165->176(24.0%) 166->176(17.5%) 173->181(15.4%)
 45 300.4 33.29 4.127 0.0003 175->186(22.5%)
 46 299.5 33.39 4.140 0.0025 174->184(23.6%) 173->183(18.0%) 173->182(10.6%) 172->178(10.5%)
 47 299.3 33.41 4.143 0.0022 174->184(32.7%) 174->183(24.7%)
 48 299.1 33.43 4.145 0.0015 174->183(24.1%) 174->184(22.9%) 174->182(19.9%)
 49 298.0 33.55 4.160 0.0017 173->184(43.9%) 174->182(14.4%)

50 296.7 33.70 4.179 0.0012 173->182(27.7%) 175->185(11.9%)
 51 296.5 33.72 4.181 0.0058 174->183(24.5%) 174->182(15.0%)
 52 296.0 33.79 4.189 0.0063 173->183(18.6%)
 53 295.0 33.90 4.203 0.0137 168->177(19.8%) 173->183(16.7%)
 54 294.0 34.01 4.217 0.0070 168->177(14.3%) 173->182(13.1%) 173->184(10.2%)
 55 292.9 34.14 4.233 0.0194 174->185(35.0%)
 56 292.0 34.25 4.247 0.0023 173->185(43.6%) 174->185(22.8%)
 57 290.8 34.39 4.264 0.0268 173->185(15.2%) 174->185(10.2%)
 58 289.0 34.60 4.290 0.0129 169->178(14.8%) 164->176(10.0%)
 59 288.6 34.65 4.296 0.0028 175->188(15.3%) 164->176(11.7%)
 60 287.6 34.77 4.310 0.0074 174->187(20.9%)
 61 286.9 34.85 4.322 0.0097 164->176(27.8%)
 62 286.0 34.97 4.336 0.0019 174->187(36.1%) 174->186(13.4%)
 63 284.8 35.11 4.353 0.0419 174->186(36.7%)
 64 283.8 35.24 4.369 0.0804 173->186(24.3%) 174->186(21.0%)
 65 283.4 35.28 4.374 0.0145 173->187(41.8%)
 66 282.7 35.37 4.385 0.0207 172->180(24.1%) 172->181(13.4%)
 67 282.0 35.46 4.396 0.1308 173->186(17.1%)
 68 279.2 35.81 4.440 0.0314 162->176(41.9%)
 69 278.8 35.87 4.447 0.0123 175->189(54.4%) 175->188(10.7%)
 70 277.9 35.99 4.462 0.0147 162->176(37.4%)
 71 275.7 36.28 4.498 0.0013 171->178(28.1%) 168->178(14.7%)
 72 275.1 36.35 4.507 0.0009 169->180(17.6%) 170->180(14.3%) 169->181(10.5%)
 73 273.4 36.57 4.535 0.0105 171->178(18.6%)
 74 272.1 36.74 4.556 0.0134
 75 271.5 36.83 4.567 0.0013 175->190(28.7%)
 76 271.0 36.90 4.575 0.0037
 77 270.1 37.02 4.590 0.0079 174->189(36.1%)
 78 269.9 37.04 4.593 0.0162 166->177(17.4%) 167->177(11.6%)
 79 269.7 37.08 4.598 0.0038 175->190(12.5%) 175->192(10.1%)
 80 268.6 37.22 4.615 0.0069 173->189(35.9%) 173->188(15.8%)

Summary of Calculated Electronic Transitions for 3

nm 1000 cm⁻¹ eV f Assignment (excitations with contrib. greater than 10.0%)

1 579.1 17.27 2.141 0.0285 123->124(46.7%) 121->124(27.6%)

2 558.7 17.90 2.219 0.0002 122->124(34.2%) 122->134(16.4%) 122->128(10.8%)

3 538.7 18.56 2.302 0.0008 121->124(31.4%) 123->134(13.5%)

4 481.6 20.76 2.574 0.0013 122->124(12.0%) 122->138(11.3%)

5 476.4 20.99 2.603 0.0014 122->124(23.4%) 123->138(11.1%) 123->136(10.9%)

6 454.9 21.98 2.726 0.0009 123->124(34.2%) 121->124(13.1%)

7 446.4 22.40 2.777 0.0009 122->124(24.4%) 120->138(13.2%)

8 404.2 24.74 3.067 0.0036 118->124(45.2%) 116->124(15.3%)

9 397.6 25.15 3.118 0.0029 116->124(41.9%) 111->124(14.5%) 114->124(11.8%)

10 384.2 26.03 3.227 0.0195 111->124(50.9%) 119->124(20.3%)

11 374.2 26.72 3.313 0.0068 114->124(46.4%)

12 369.8 27.04 3.352 0.0061 120->124(25.1%) 111->124(11.3%)

13 367.3 27.23 3.376 0.0268 119->124(21.0%) 116->124(19.5%) 114->124(12.5%)

14 356.9 28.02 3.474 0.0035 113->124(28.8%) 112->124(23.9%) 110->124(11.0%)

15 348.2 28.72 3.560 0.0004 120->138(18.9%) 120->136(14.1%) 123->136(11.0%) 122->128(10.3%)

16 342.9 29.17 3.616 0.0121 110->124(33.9%) 123->126(18.8%) 109->124(10.6%)

17 341.0 29.32 3.636 0.0037 120->124(30.4%) 120->134(11.4%)

18 335.6 29.79 3.694 0.0243 123->126(45.6%) 121->126(13.2%)

19 333.9 29.95 3.713 0.0098 123->125(56.2%) 121->125(23.1%)

20 321.6 31.09 3.855 0.0017 122->126(84.5%)

21 316.9 31.56 3.913 0.0000 122->125(78.2%) 122->126(10.5%)

22 313.9 31.85 3.950 0.0027 123->127(63.6%) 121->127(16.0%)

23 311.2 32.14 3.985 0.0049 121->126(42.9%) 123->126(21.1%)

24 308.3 32.44 4.022 0.0333 121->125(30.8%) 123->125(15.3%) 123->130(10.4%)

25 304.5 32.84 4.071 0.0452 123->128(31.4%) 123->129(17.7%)

26 304.4 32.86 4.074 0.0025 117->124(85.4%)

27 303.1 32.99 4.090 0.0017 123->129(15.6%) 123->130(14.3%)

28 301.4 33.18 4.114 0.0144 122->128(44.0%)

29 300.0 33.34 4.133 0.0064 122->127(49.4%)

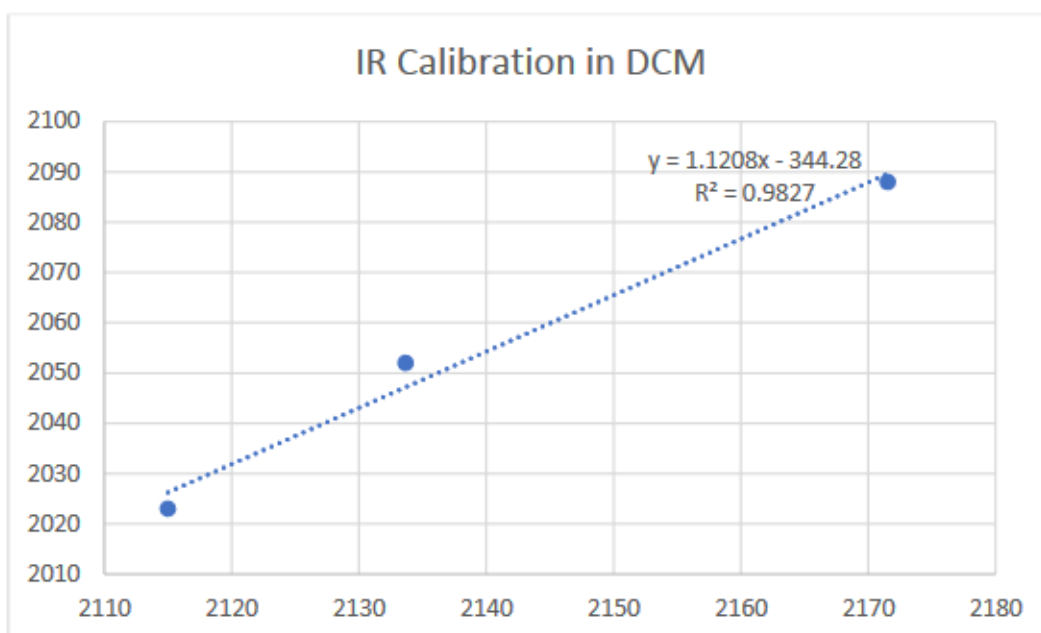
30 299.5 33.38 4.139 0.0013 123->130(29.3%) 122->127(17.6%)

31 298.6 33.49 4.153 0.0395 115->124(16.1%) 122->127(14.7%) 109->124(11.1%) 118->124(11.0%)

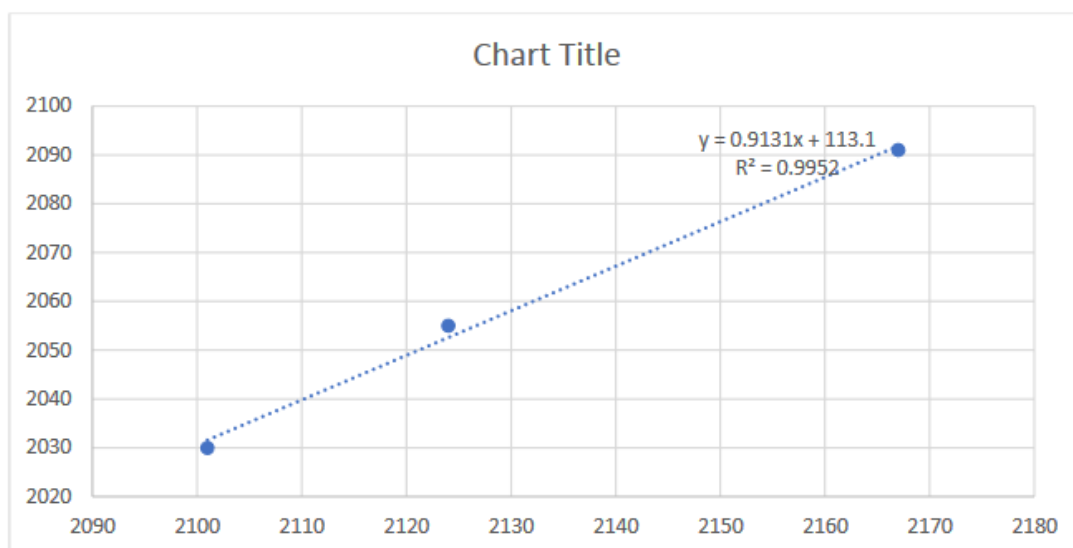
32 295.7 33.81 4.192 0.0132 123->131(38.8%) 123->130(17.3%)
 33 290.8 34.39 4.264 0.0007 122->130(83.7%)
 34 289.2 34.58 4.287 0.0025 123->132(32.5%) 121->127(14.5%)
 35 288.3 34.68 4.300 0.0026 122->129(28.8%) 121->127(15.6%) 123->132(12.8%)
 36 288.0 34.72 4.305 0.0007 122->129(33.0%) 123->132(11.1%)
 37 287.9 34.73 4.306 0.0032 123->133(27.1%) 119->126(13.3%) 121->127(13.3%)
 38 286.8 34.86 4.323 0.0029 119->126(57.7%)
 39 283.4 35.29 4.375 0.0363 121->128(17.7%) 123->129(12.4%) 121->129(10.1%)
 40 282.6 35.38 4.387 0.0007 122->131(72.1%) 122->129(13.1%)
 41 281.2 35.57 4.410 0.0471 123->133(20.9%) 119->125(20.0%)
 42 279.7 35.75 4.433 0.0141 119->125(40.3%) 121->130(15.2%)
 43 279.0 35.85 4.445 0.0009 122->132(66.7%) 122->133(16.8%)
 44 277.8 35.99 4.463 0.0009 119->128(17.3%) 121->131(13.3%) 123->131(11.1%)
 45 275.3 36.32 4.503 0.0016 122->133(61.8%) 122->132(17.1%)
 46 274.3 36.46 4.521 0.0024 121->129(14.1%) 113->124(13.3%)
 47 273.7 36.53 4.529 0.0077 115->124(22.1%) 119->127(15.3%)
 48 273.3 36.60 4.537 0.0047 121->129(21.8%) 112->124(15.2%) 113->124(12.0%)
 49 271.9 36.77 4.559 0.0106 121->131(14.1%) 119->128(11.0%)
 50 270.6 36.95 4.581 0.0031 112->124(20.1%) 121->132(11.6%) 113->124(10.7%)

IR calibration in the metal carbonyl region.

The following plot of calculated vs experimental metal carbonyl stretching bands was used to correct all calculated bands in DCM.



The following plot of calculated vs experimental metal carbonyl stretching bands was used to correct all calculated bands in heptane.



Appendix B: Ruthenium assemblies for CO₂ reduction and H₂ generation: time resolved infrared spectroscopy, spectroelectrochemistry and a photocatalysis study in solution and on NiO – supporting information.

Electrochemistry

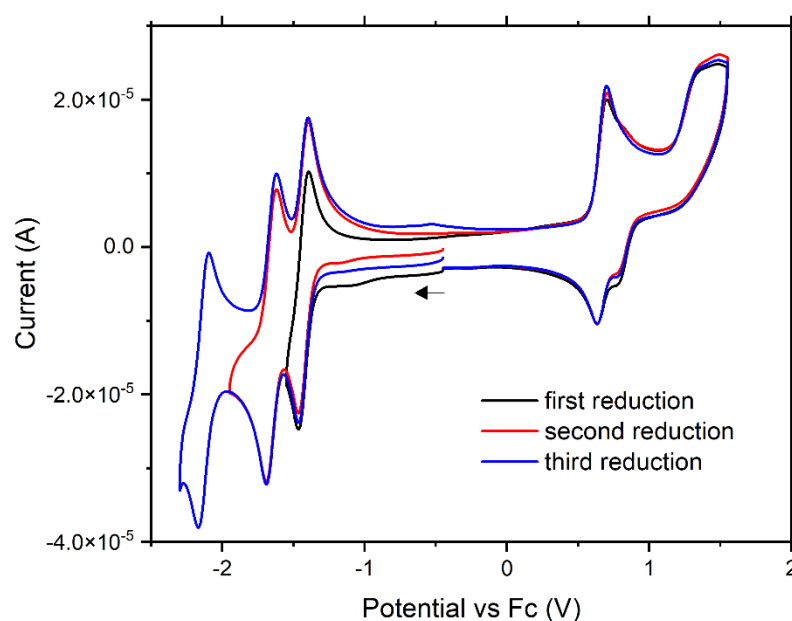


Figure SB 1. Cyclic voltammogram of **Ru**. Experiments were run with 1 mM **Ru** in nitrogen purged acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The reversibility of the three reductions was probed by returning the scan at various potentials. A glassy carbon electrode, platinum wire and Ag/AgNO₃ electrode were used as working, counter and reference electrode, respectively. Ferrocene was added as internal reference. Scans were taken at 0.1 V/s.

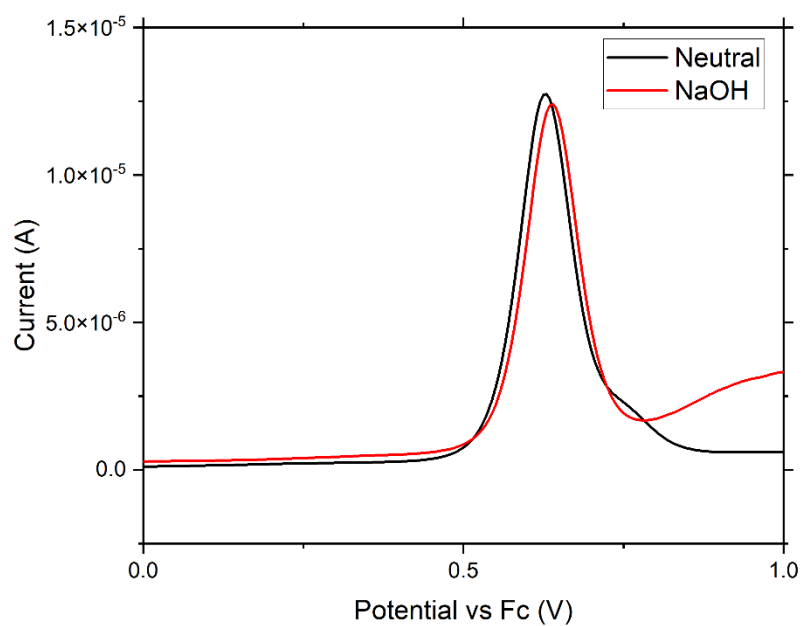


Figure SB 2. DPV study of the oxidation for **Ru** in the absence (black) and presence (red) of 0.02 M NaOH. Experiments were run with 1 mM **Ru** in nitrogen purged acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A glassy carbon electrode, platinum wire and Ag/AgNO₃ electrode were used as working, counter and reference electrode, respectively. Ferrocene was added as internal reference. Scans were taken with an increment of 0.005 V, amplitude of 0.025 V, pulse width of 0.05 s, sample width of 0.02 s and pulse period of 1 s.

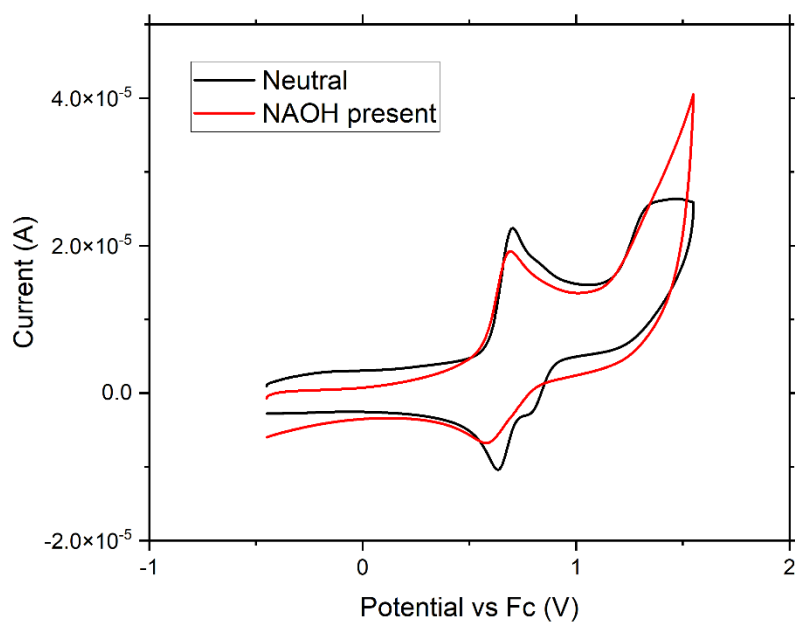


Figure SB 3. CV study of the oxidation for **Ru** in the absence (black) and presence (red) of 0.02 M NaOH. Experiments were run with 1 mM **Ru** in nitrogen purged acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as

supporting electrolyte. A glassy carbon electrode, platinum wire and Ag/AgNO₃ electrode were used as working, counter and reference electrode, respectively. Ferrocene was added as internal reference. Scans were taken at 0.1 V/s.

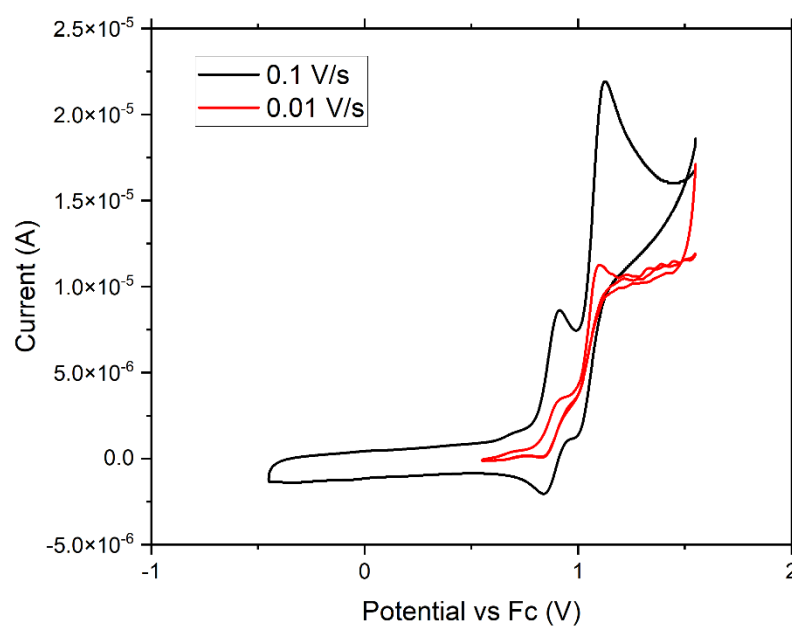


Figure SB 4. Scan rate study of the oxidations for **RuRe**. Cyclic voltammograms between -0.45 V and 1.55 V at 0.1 V/s (black) and 0.01 V/s (red). Experiments were run with 1 mM **RuRe** in nitrogen purged acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A glassy carbon electrode, platinum wire and Ag/AgNO₃ electrode were used as working, counter and reference electrode, respectively. Ferrocene was added as internal reference.

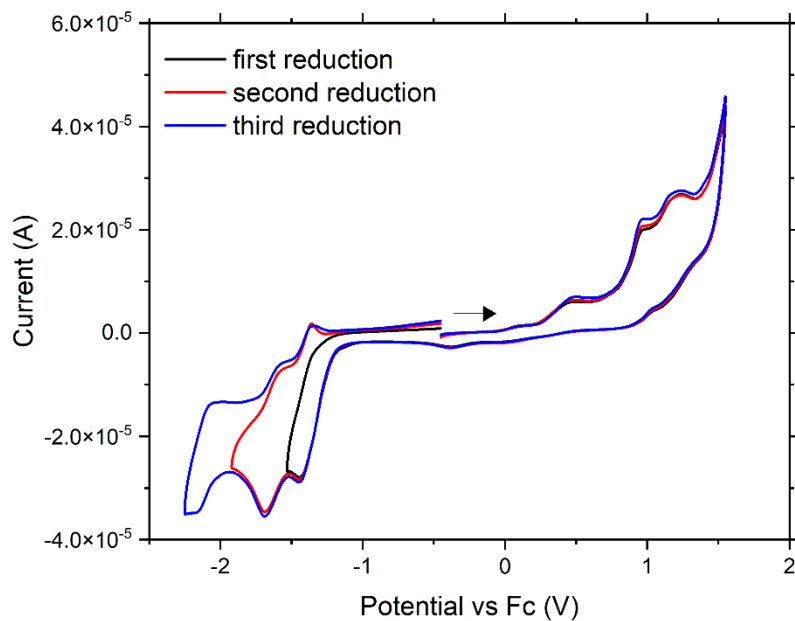


Figure SB 5. Cyclic voltammogram of **RuPt**. Experiments were run with 1 mM **RuPt** in nitrogen purged acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The reversibility of the three reductions was probed by returning the scan at various potentials. A glassy carbon electrode, platinum wire and Ag/AgNO₃ electrode were used as working, counter and reference electrode, respectively. Ferrocene was added as internal reference. Scans were taken at 0.1 V/s.

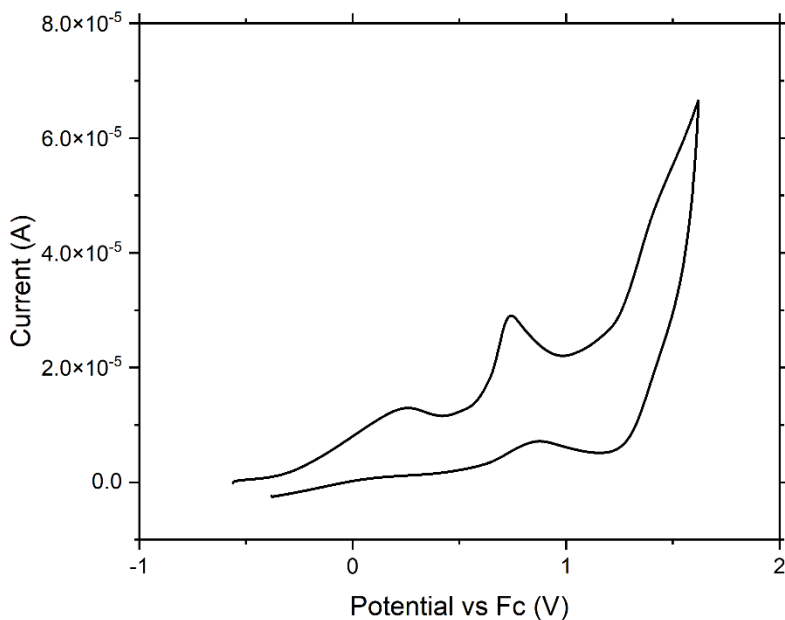


Figure SB 6. Cyclic voltammogram of the Nabpt ligand. Experiment was conducted with 1 mM of the Hbpt ligand in dry nitrogen purged acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. 0.1 M NaOH was added to deprotonate the ligand and form the Nabpt complex to enable the ligand to dissolve in the solution.

FTIR spectroelectrochemistry

[Ru(dceb)₂(bpt)](PF₆) (**Ru**)

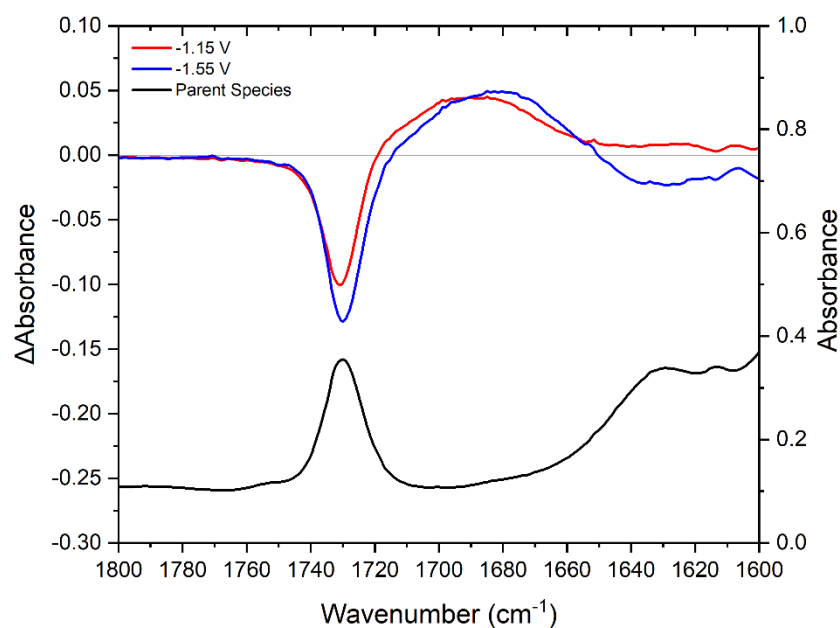


Figure SB 7. 2.5 mM **Ru** in 0.1 M TBPAF₆/ACN. The IR spectrum (black) and difference spectra at -1.15 (red) and -1.55 V (blue) are shown. All potentials vs the silver wire pseudo-reference. The signal at 1632 cm⁻¹ is a residual signal from solvent.

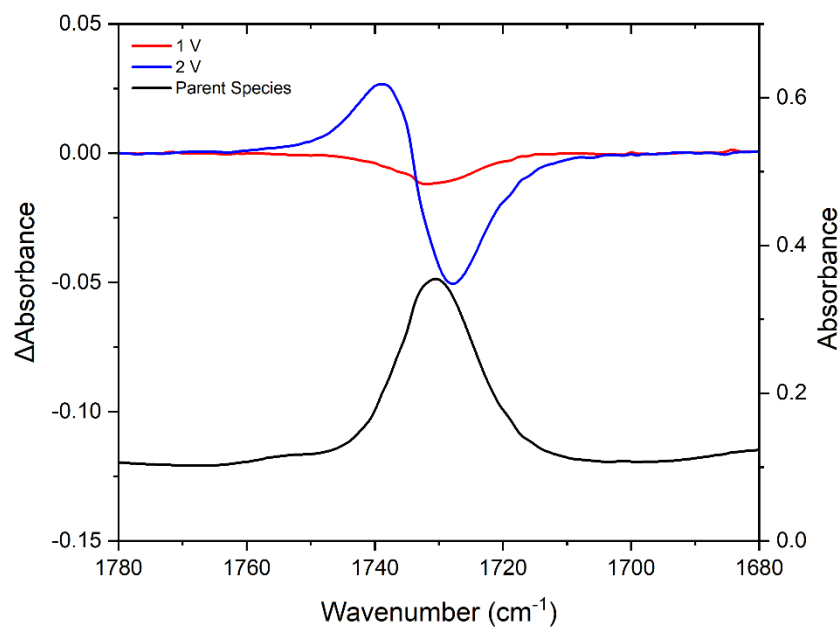


Figure SB 8. 2.5 mM **Ru** in 0.1 M TBPAF₆/ACN. IR spectrum (black) and difference spectra at 1 V (red) and 2 V (blue) vs silver wire pseudo-reference.

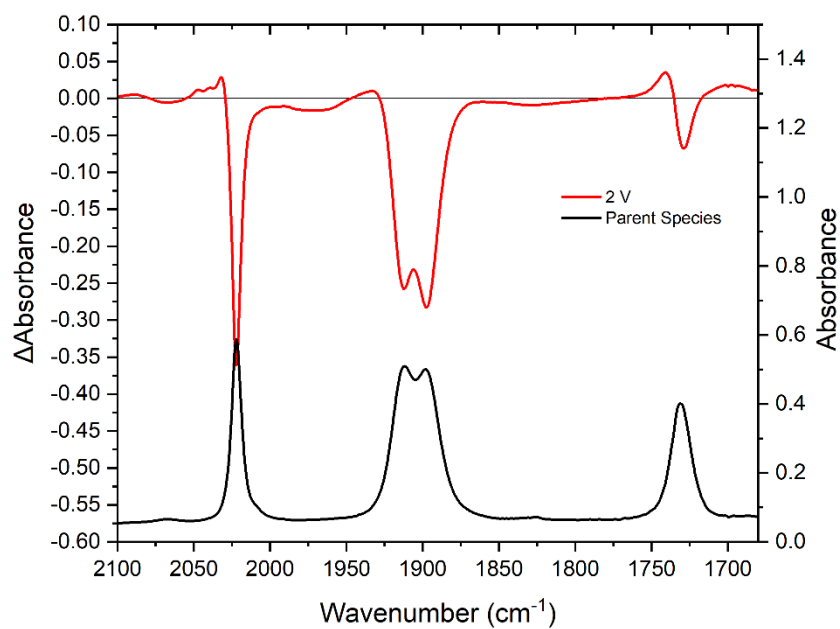
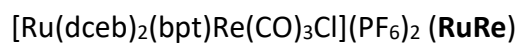


Figure SB 9. 2.5 mM **RuRe** in 0.1 M $\text{TBPAF}_6/\text{ACN}$. The IR spectrum (black) and difference spectra at 2 V (red) vs silver wire pseudo-reference.

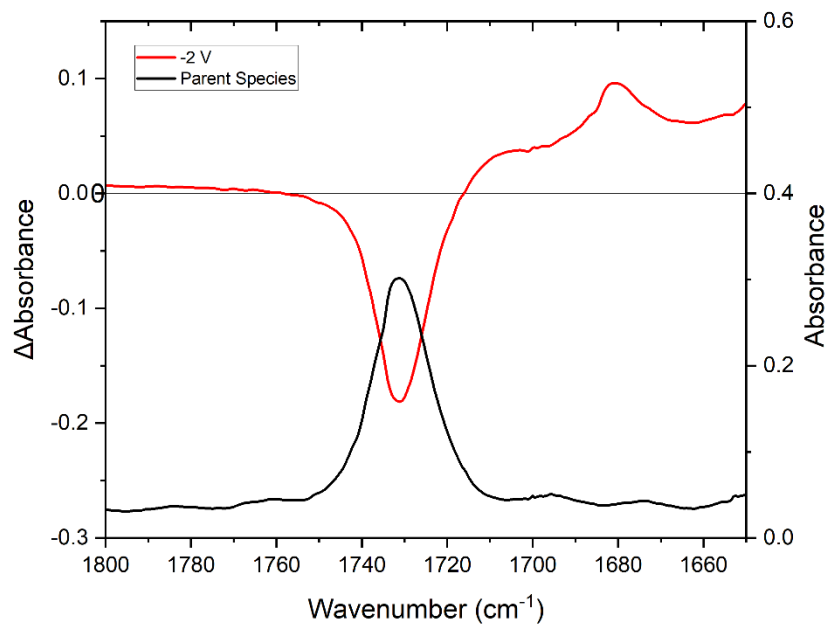
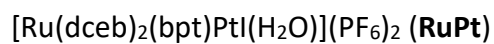


Figure SB 10. 2.5 mM **RuPt** in 0.1 M $\text{TBPAF}_6/\text{ACN}$. The IR spectrum (black) and difference spectra at -2 V (red) vs silver wire pseudo-reference.

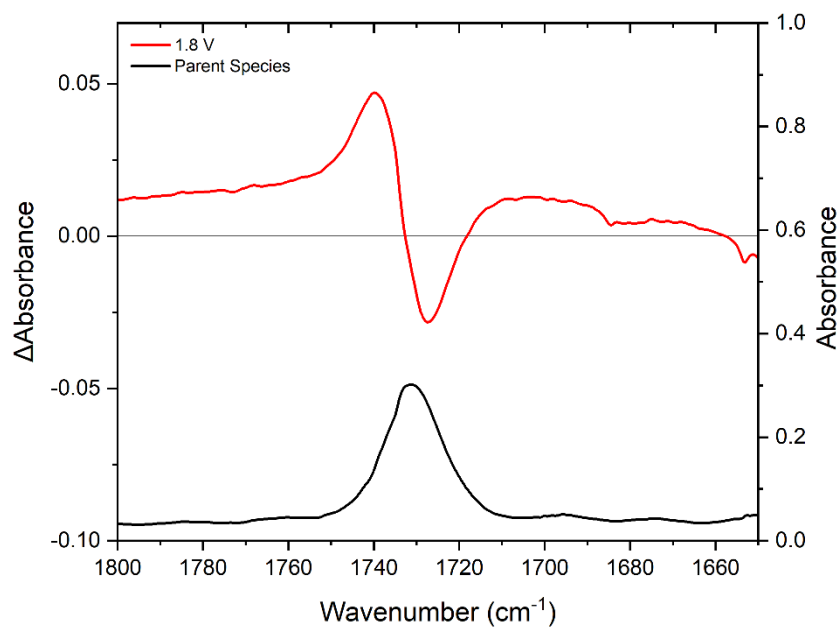


Figure SB 11. 2.5 mM **RuPt** in 0.1 M $\text{TBPAF}_6/\text{ACN}$. The IR spectrum (black) and difference spectra at 1.8 V (red) vs silver wire pseudo-reference.

UV-Vis spectroelectrochemistry

[Ru(dceb)₂(bpt)](PF₆) (**Ru**)

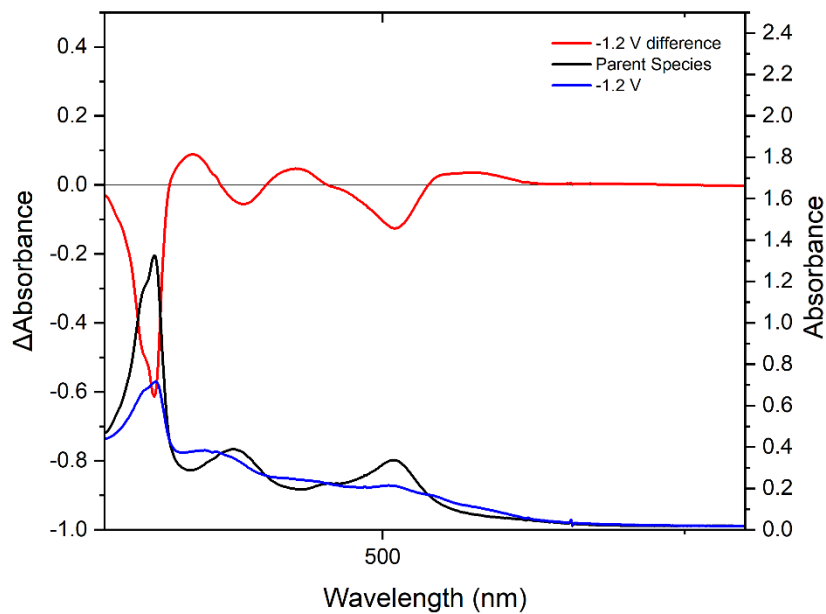


Figure SB 12. **Ru** reductive UV-Vis spectroelectrochemistry. The UV-Vis spectrum at open circuit potential (black), and at -1.2 V (blue) as well as the difference spectrum at -1.2 V (red) vs silver wire pseudo-reference.

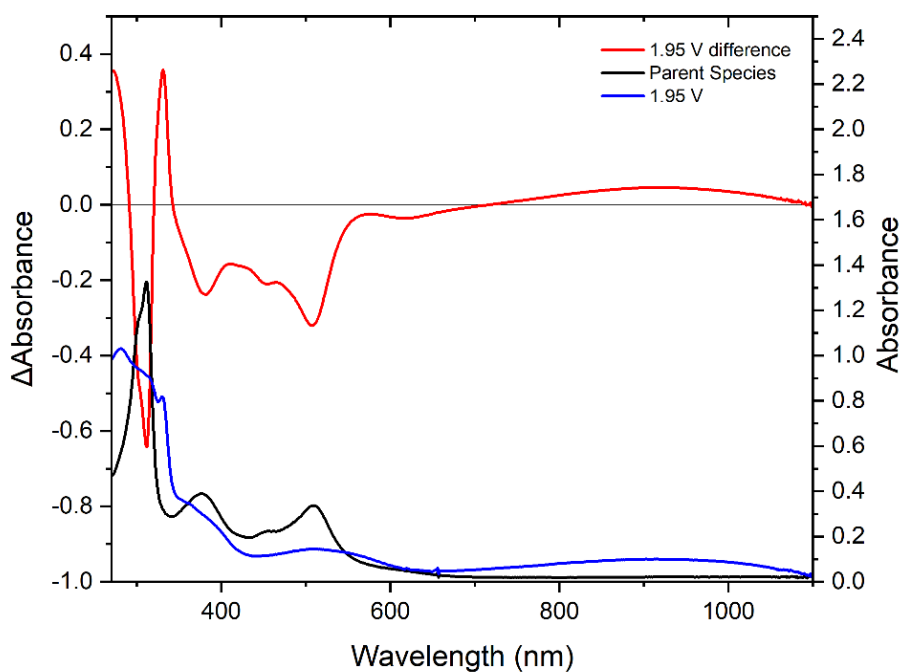


Figure SB 13. **Ru** oxidative UV-Vis spectroelectrochemistry. The UV-Vis spectrum at open circuit potential (black) and at 1.95 V (blue) as well as the difference spectrum at 1.95 V (red) vs silver wire pseudo-reference.

[Ru(dceb)₂(bpt)PtI₂](PF₆) (RuPt**)**

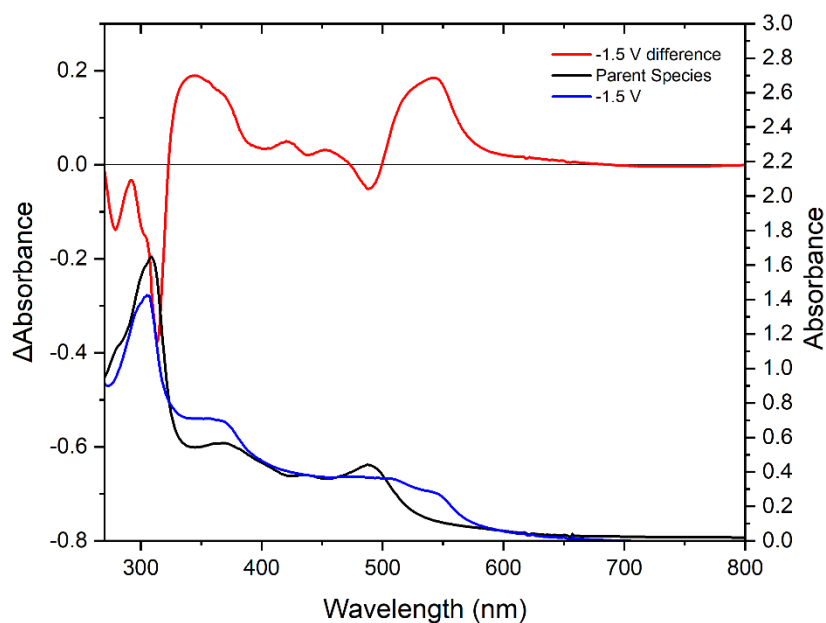


Figure SB 14. **RuPt** reductive UV-Vis spectroelectrochemistry. The UV-Vis spectrum at open circuit potential (black) and at -1.5 V (blue), as well as the difference spectrum at -1.5 V (red) vs silver wire pseudo-reference.

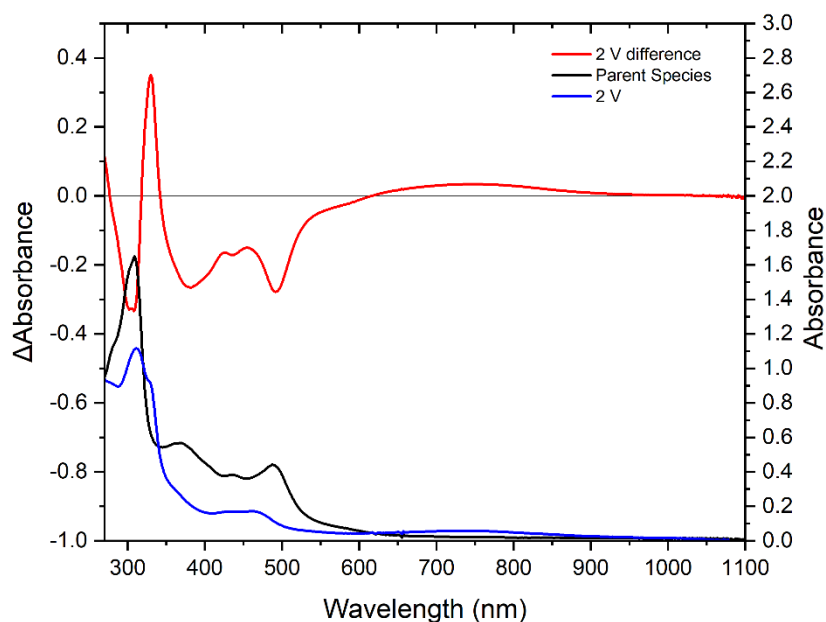


Figure SB 15. **RuPt** oxidative spectroelectrochemistry. The UV-Vis spectrum at open circuit potential (black) and at 2 V (blue), as well as the difference spectrum at 2 V (red) vs silver wire pseudo-reference.

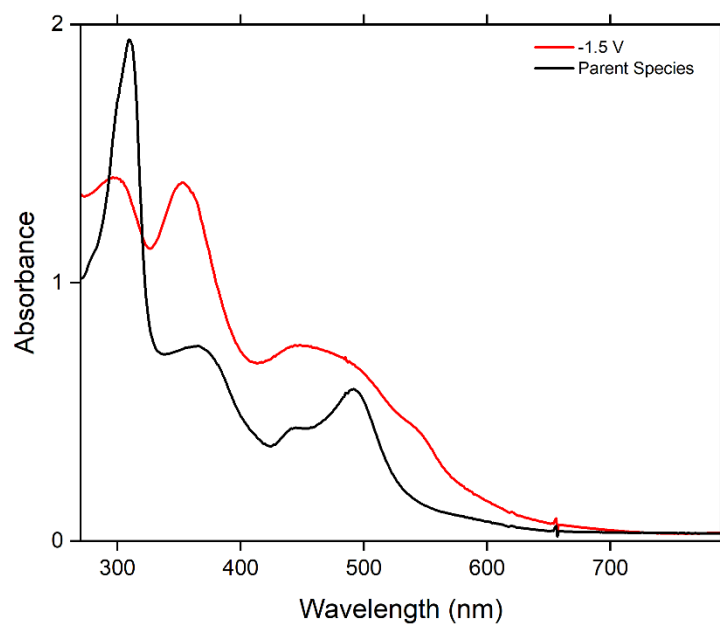
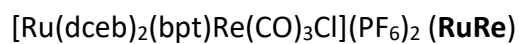


Figure SB 16. **RuRe** reductive UV-Vis spectroelectrochemistry. The UV-Vis spectrum at open circuit potential (black) and at -1.5 V (red) vs silver wire pseudo-reference.

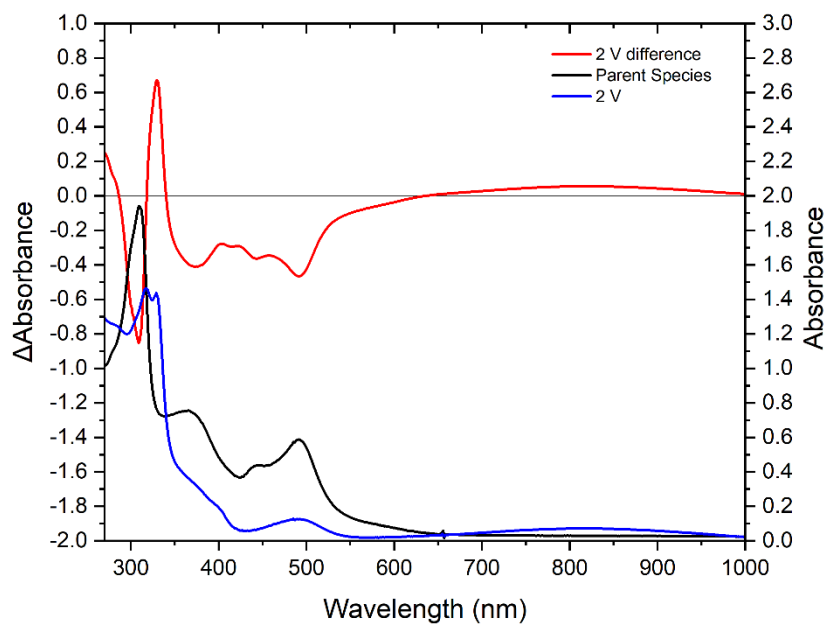


Figure SB 17. **RuRe** oxidative UV-Vis spectroelectrochemistry. The UV-Vis spectrum at open circuit potential (black) and at 2 V (blue), as well as the difference spectrum at 2 V (red) vs silver wire pseudo-reference.

Time resolved infrared spectroscopy

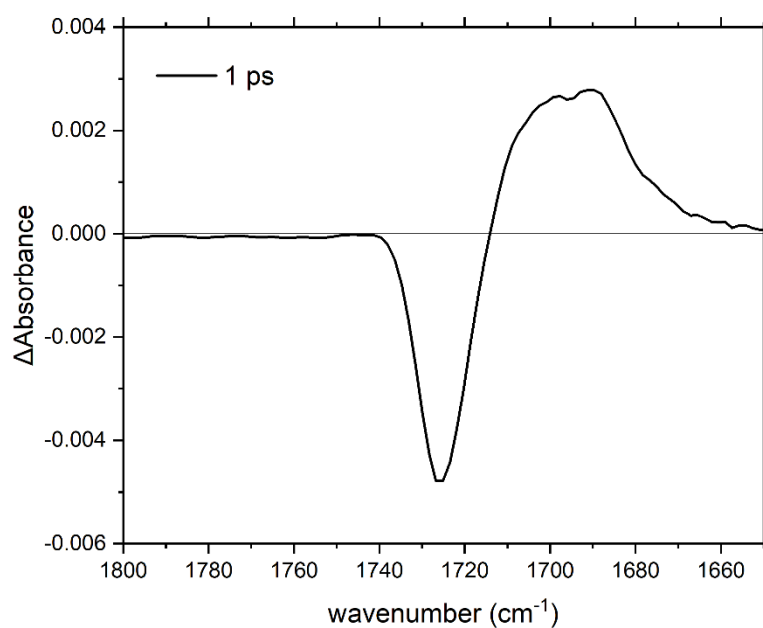


Figure SB 18. TRIR spectrum of **Ru** in d_3 -acetonitrile at 1 picosecond. Excited at 510 nm with 1 microjoule energy.

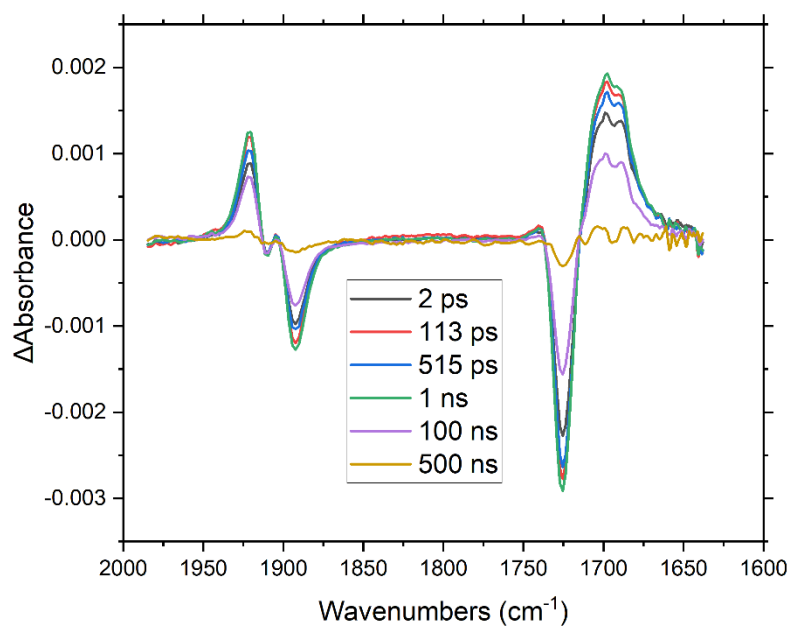
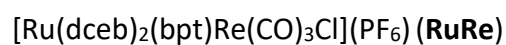


Figure SB 19. TRIR spectrum of **RuRe** in d_3 -acetonitrile. Excited at 510 nm with 1 microjoule power. Spectra at 2 ps (black), 113 ps (red), 515 ps (blue), 1 ns (green), 100 ns (purple) and 500 ns (yellow). 1650-2000 cm^{-1} range.

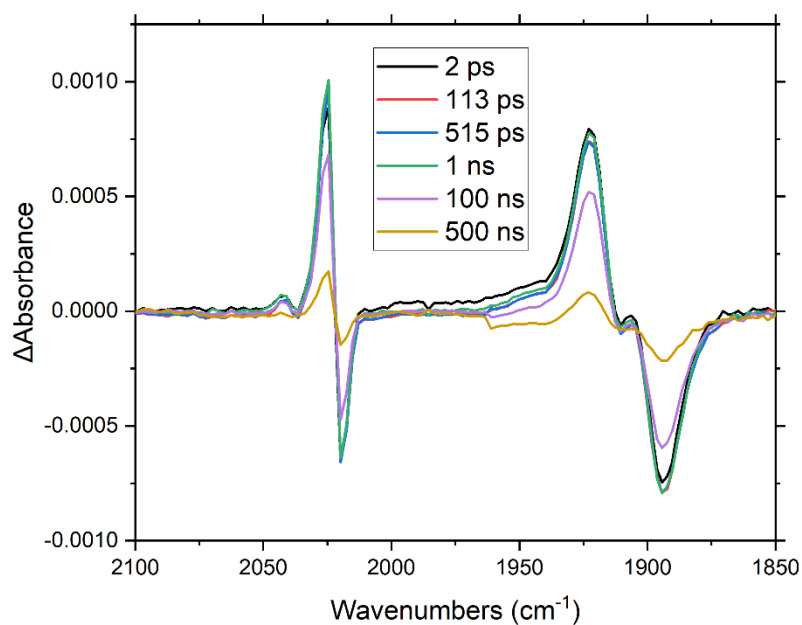


Figure SB 20. **RuRe** in d_3 -acetonitrile, excited at 510 nm with 1 microjoule power. Spectra at 2 ps (black), 113 ps (red), 515 ps (blue), 1 ns (green), 100 ns (purple) and 500 ns (yellow).. 1750-2150 cm^{-1} range.

Ru(dceb)₂(bpt)Pt(l)₂ (RuPt)

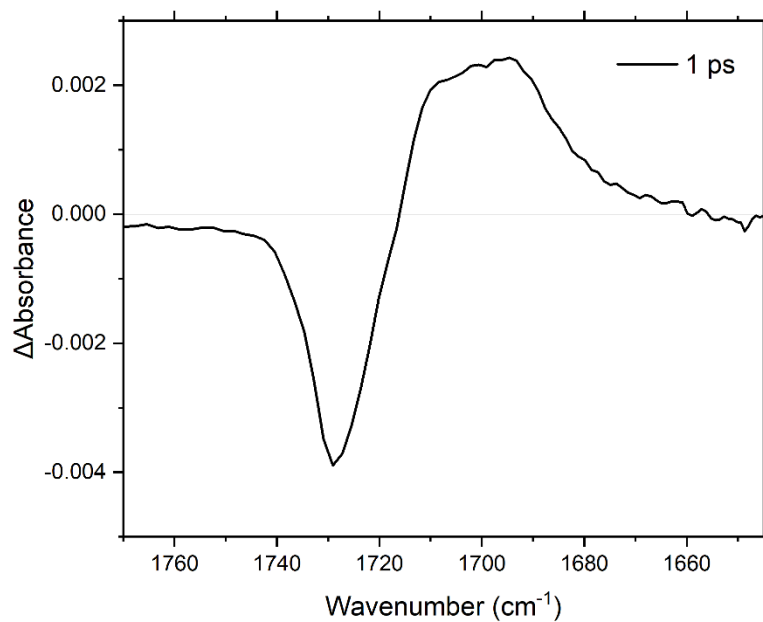


Figure SB 21 TRIR spectrum of **RuPt** in ACN- d_3 at 510 nm excitation with 1 microjoule power. Spectrum at 1 ps.

Time-Resolved emission spectroscopy

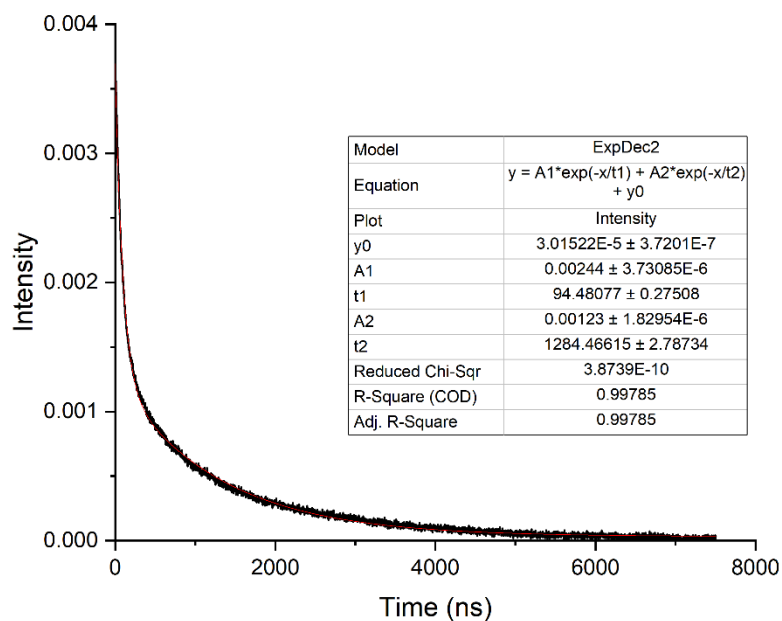


Figure SB 22. 690 nm emission lifetime of **Ru**. Experiments were run in deaerated acetonitrile at 0.01 mM concentration with 355 nm excitation.

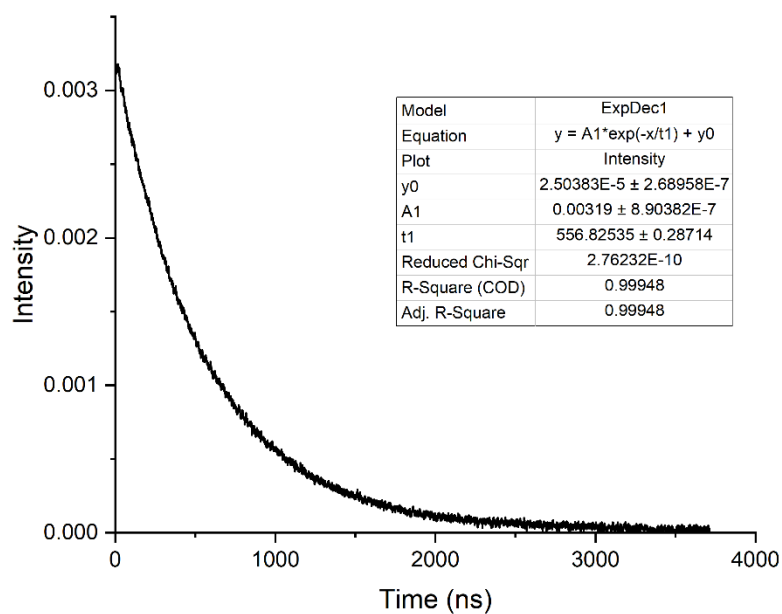


Figure SB 23. 690 nm emission lifetime of **RuRe**. Experiments were run in deaerated acetonitrile at 0.01 mM concentration with 355 nm excitation.

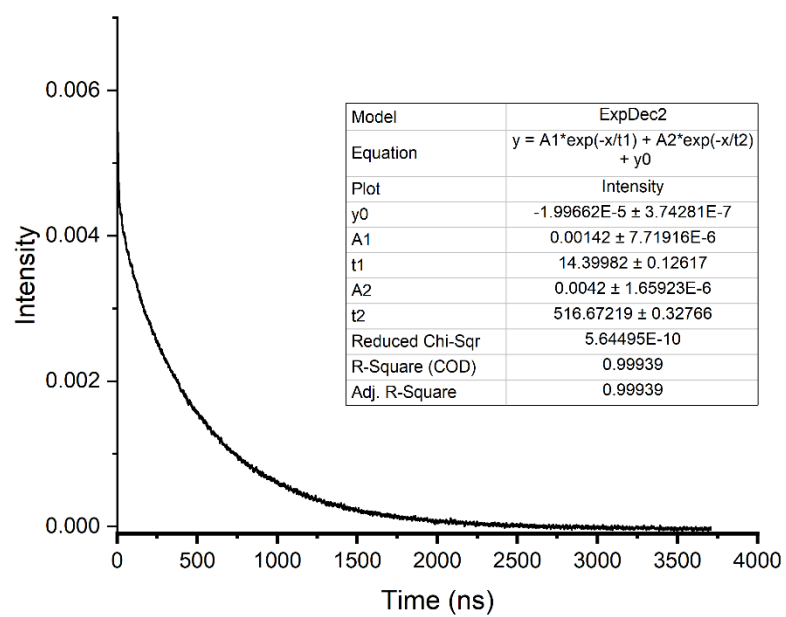


Figure SB 24. 690 nm emission lifetime of **RuPt**. Experiments were run in deaerated acetonitrile at 0.01 mM concentration with 355 nm excitation.

Photocatalysis

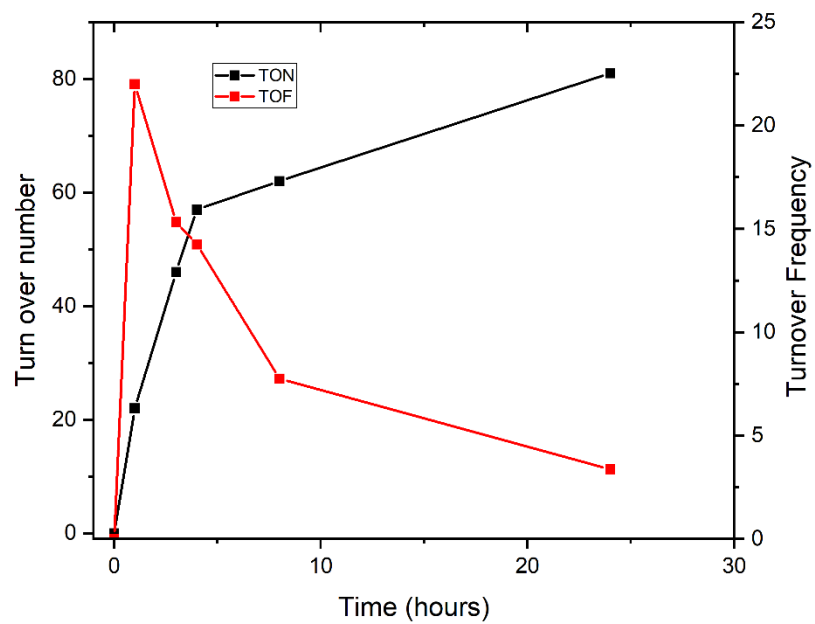


Figure SB 25. Time dependent photocatalysis for **RuPt**. The turnover numbers at various time intervals (black) and TOF (red).

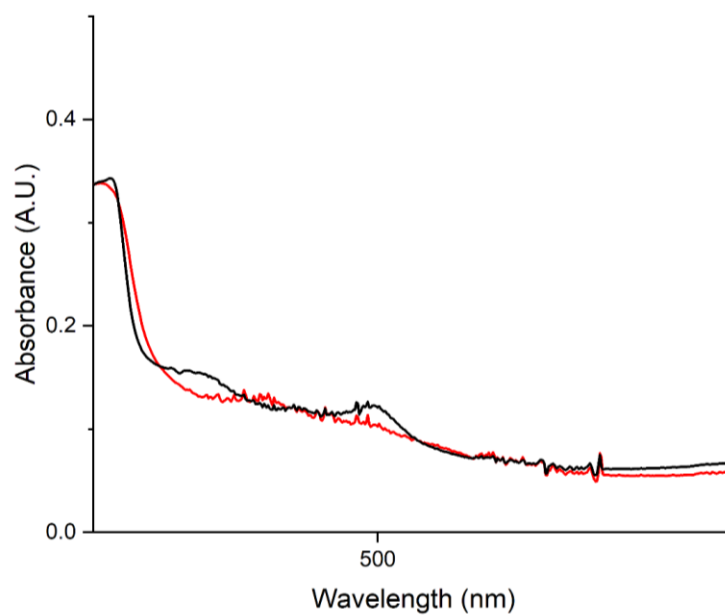


Figure SB 26 UV-Vis spectrum of **RuPt** in 60:30:10 acetonitrile:triethylamine:water before (black) and after (red) 24 hour of 470 nm irradiation.

Surface studies

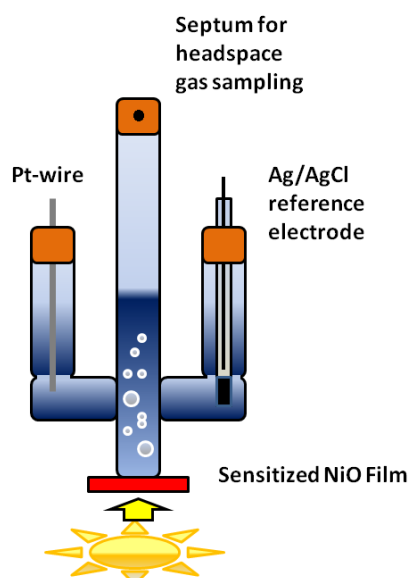


Figure SB 27. Schematic of photoelectrochemical cell used for CO_2 reduction experiments.

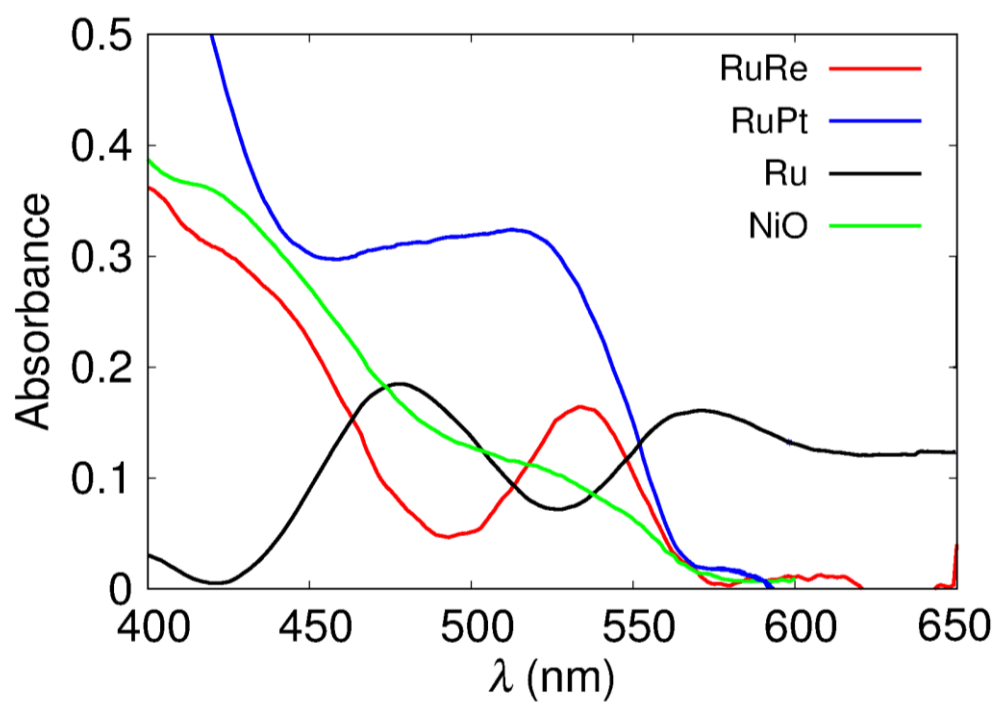


Figure SB 28. UV-visible absorption spectra of chromophores used in this study on mesoporous NiO thin films. Note the spectrum for NiO has been subtracted from Ru, **RuPt** and **RuRe** for clarity and have been normalized.

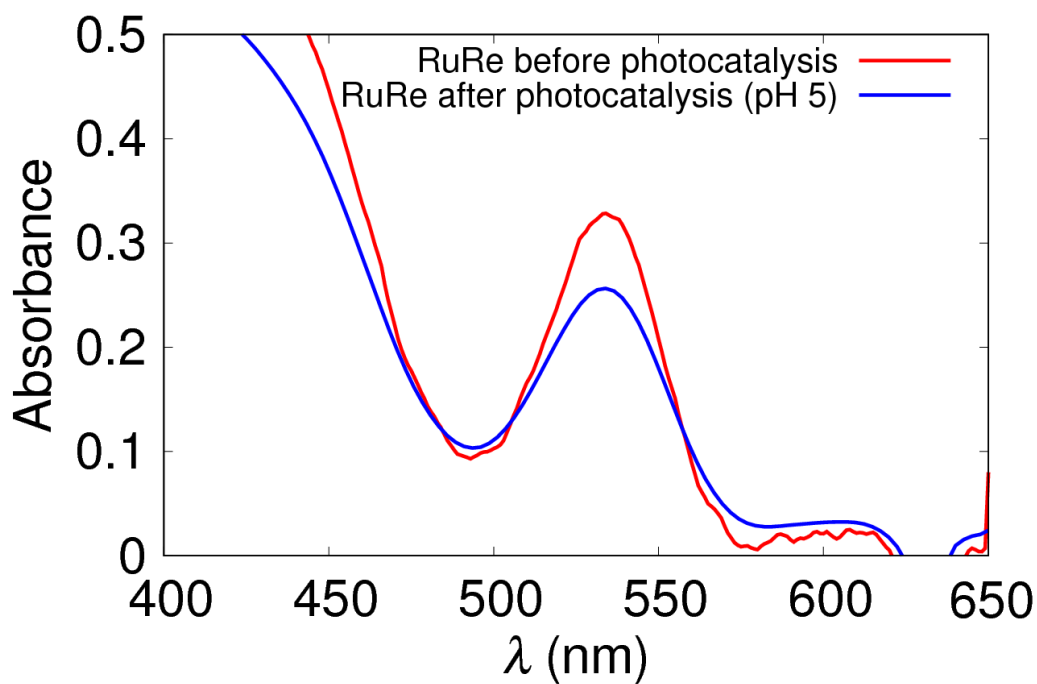


Figure SB 29. UV-visible absorption spectra of **RuRe** on mesoporous NiO thin films before (red) and after (blue) photocatalysis in pH 5 acetate buffer. For the raw data, please reference <https://doi.org/10.25405/data.ncl.c.5696935.v1>.

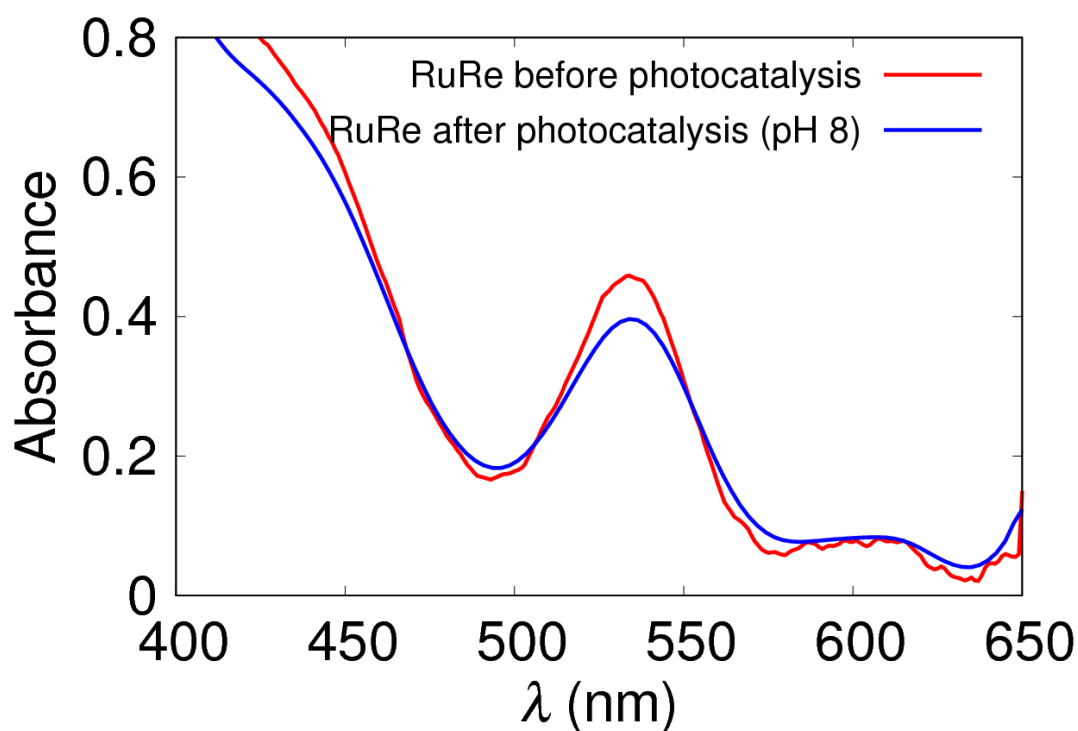


Figure SB 30. UV-visible absorption spectra of **RuRe** on mesoporous NiO thin films before (red) and after (blue) photocatalysis in pH 8 acetate buffer. For the raw data, please reference <https://doi.org/10.25405/data.ncl.c.5696935.v1>.

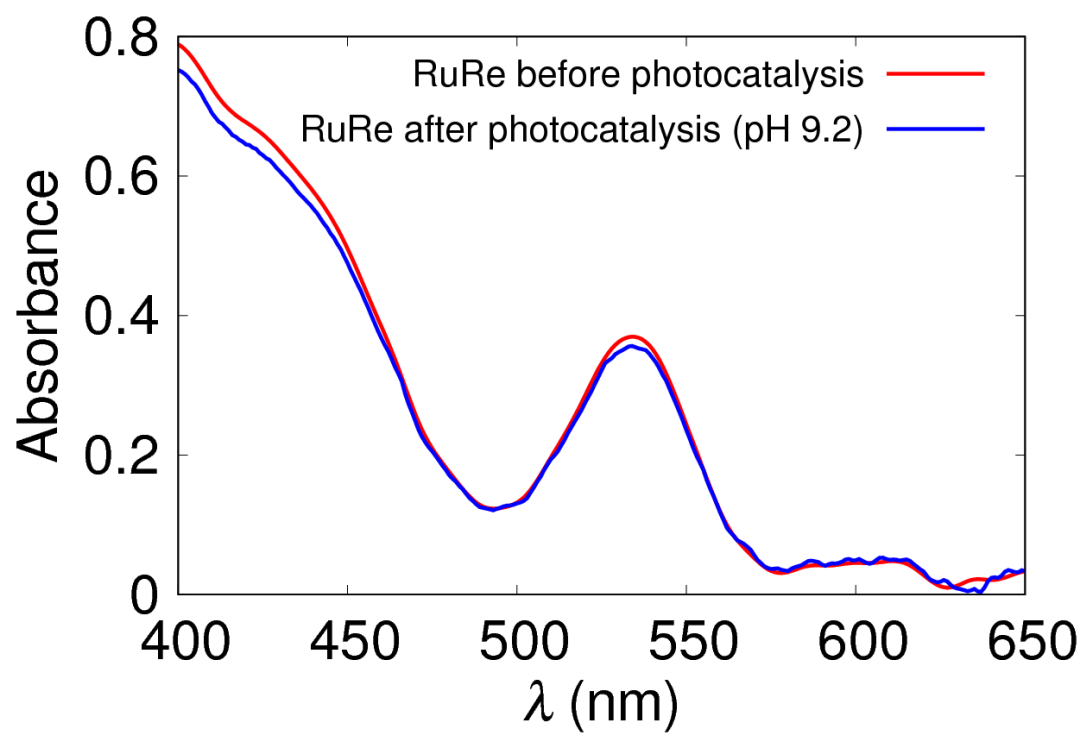


Figure SB 31. UV-visible absorption spectra of **RuRe** on mesoporous NiO thin films before (red) and after (blue) photocatalysis in pH 9.2 acetate buffer. For the raw data, please reference <https://doi.org/10.25405/data.ncl.c.5696935.v1>.

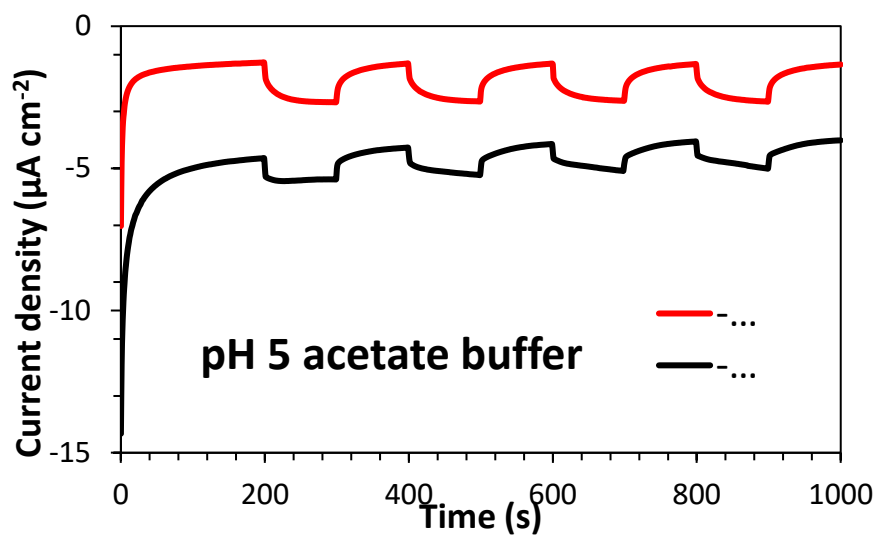


Figure SB 32. Chronoamperometry measurement for **RuRe** on NiO in pH 5 acetate buffer at different applied bias, under chopped 1 sun illumination. The solution was saturated with CO_2 before starting the experiment.

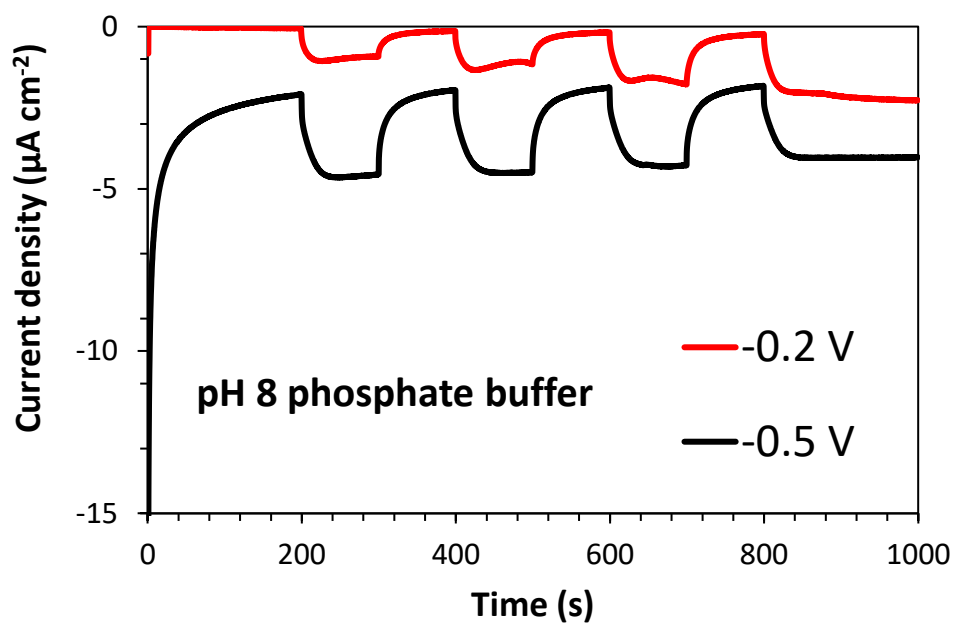


Figure SB 33. Chronoamperometry measurement for **RuRe** on NiO in pH 8 phosphate buffer at different applied bias, under chopped 1 sun illumination. The solution was saturated with CO_2 before starting the experiment.

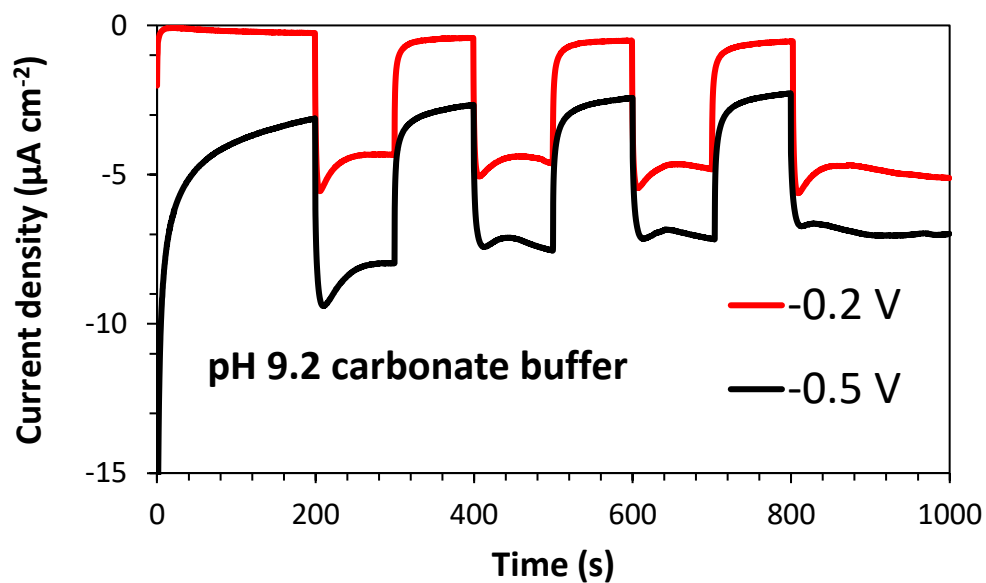


Figure SB 34. Chronoamperometry measurement for **RuRe** on NiO in pH 9.2 carbonate buffer at different applied bias, under chopped 1 sun illumination. The solution was saturated with CO_2 before starting the experiment.

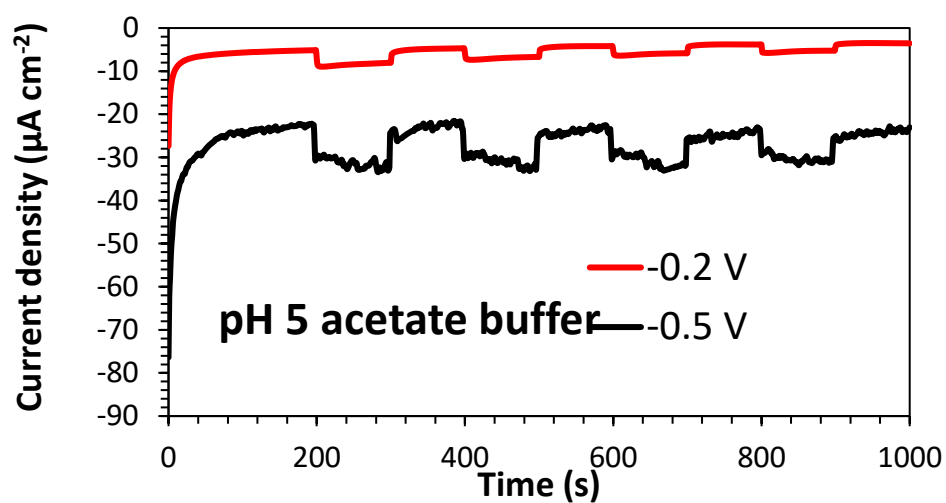


Figure SB 35. Chronoamperometry measurement for **RuPt** on NiO in pH 5 acetate buffer at different applied bias, under chopped 1 sun illumination. The solution was saturated with argon before starting the experiment.

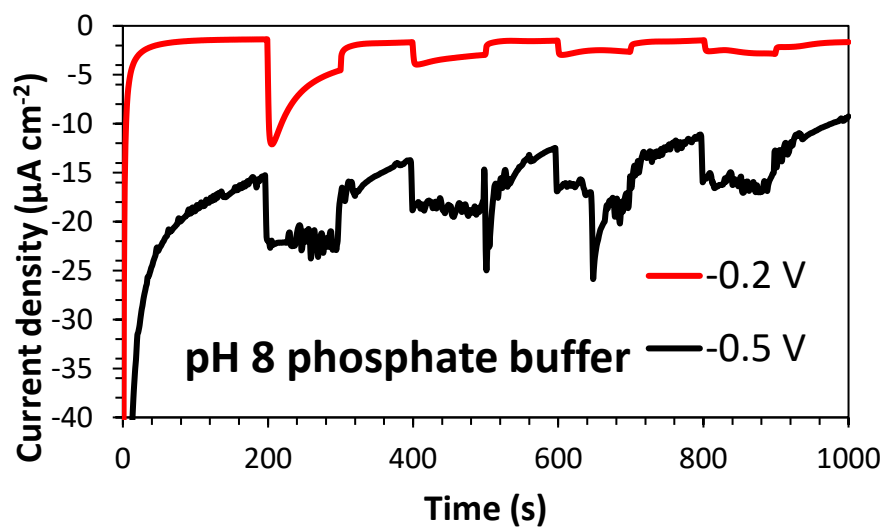


Figure SB 36. Chronoamperometry measurement for **RuPt** on NiO in pH 8 phosphate buffer at different applied bias, under chopped 1 sun illumination. The solution was saturated with argon before starting the experiment.

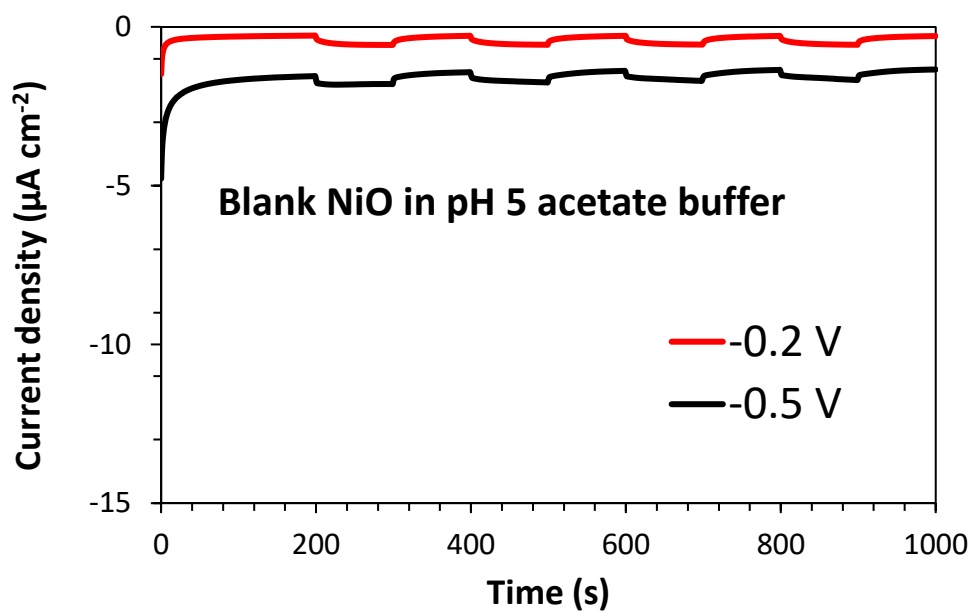


Figure SB 37. Chronoamperometry measurement for an unsensitized NiO film in pH 5 acetate buffer at different applied bias, under chopped 1 sun illumination. The solution was saturated with argon before starting the experiment.

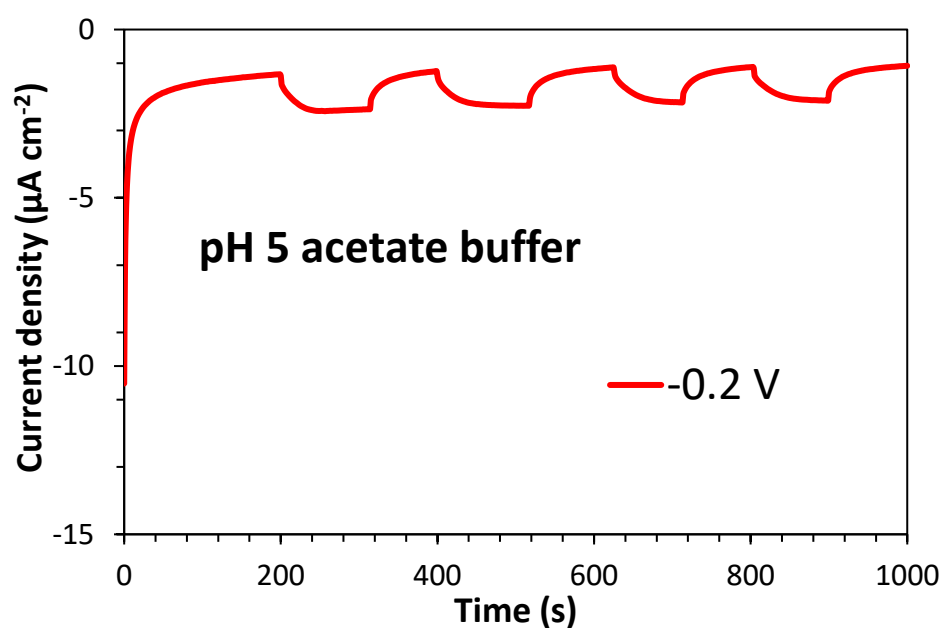


Figure SB 38. Chronoamperometry measurement for **Ru** on NiO in pH 5 acetate buffer at under a bias of -0.2 V, under chopped 1 sun illumination. Note that at higher applied bias the sample became unstable. The solution was saturated with argon before starting the experiment.

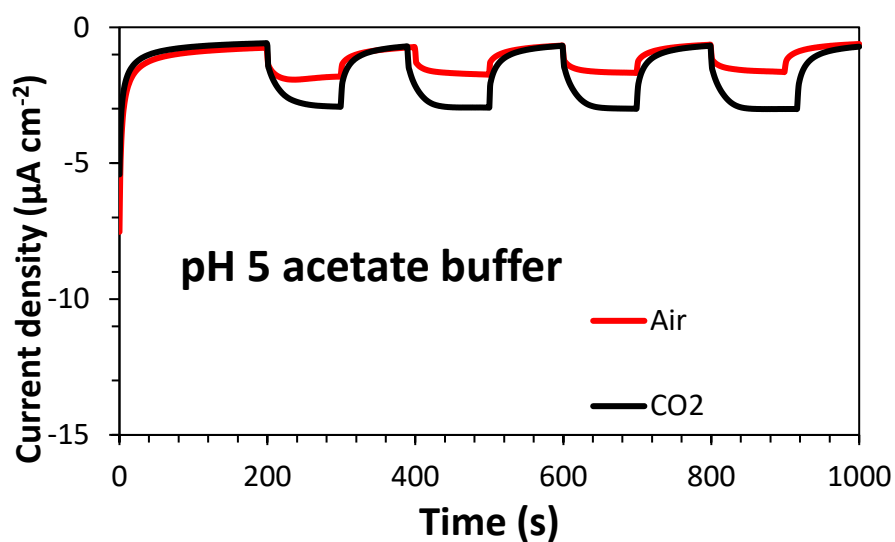


Figure SB 39. Chronoamperometry measurement for **RuRe** on NiO in pH 5 acetate buffer under chopped 1 sun illumination, both in the presence of air and in saturated with CO_2 .

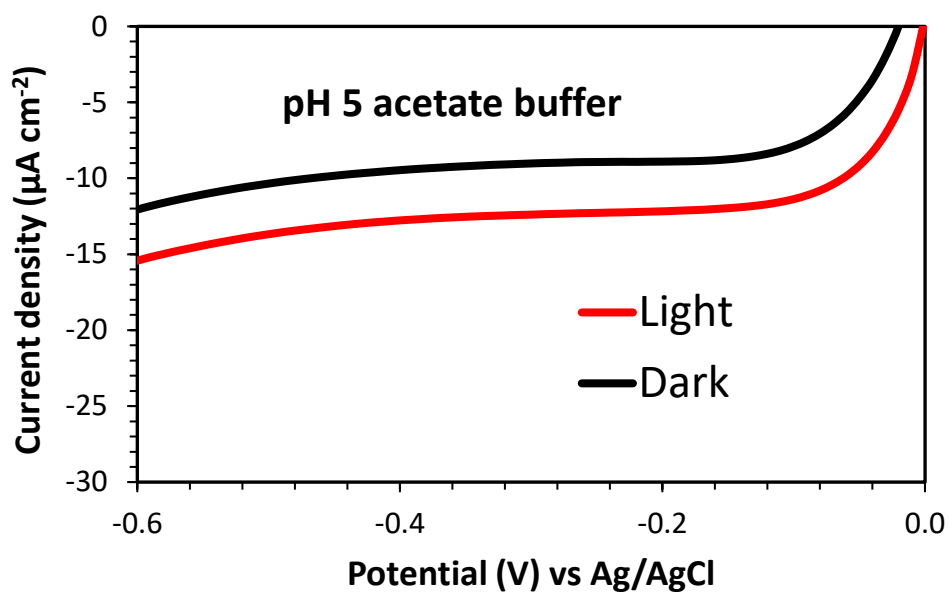


Figure SB 40. Linear sweep scan for **RuRe** on NiO in pH 5 acetate buffer both under simulated 1 sun illumination and in the dark. The scan speed is 0.1 Vs-1. The solution was saturated with CO_2 before starting the experiment.

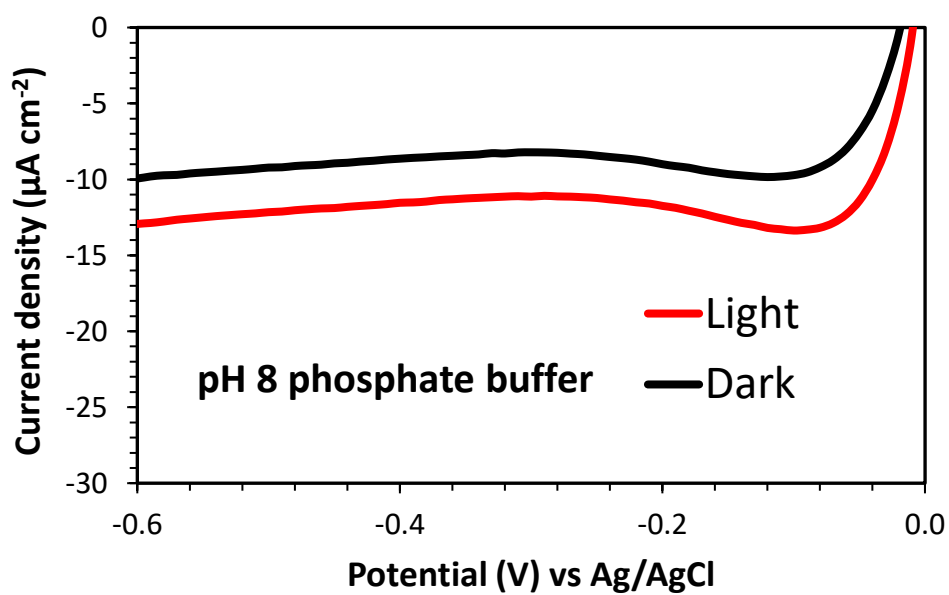


Figure SB 41. Linear sweep scan for **RuRe** on NiO in pH 8 phosphate buffer both under simulated 1 sun illumination and in the dark. The scan speed is 0.1 Vs-1. The solution was saturated with CO_2 before starting the experiment.

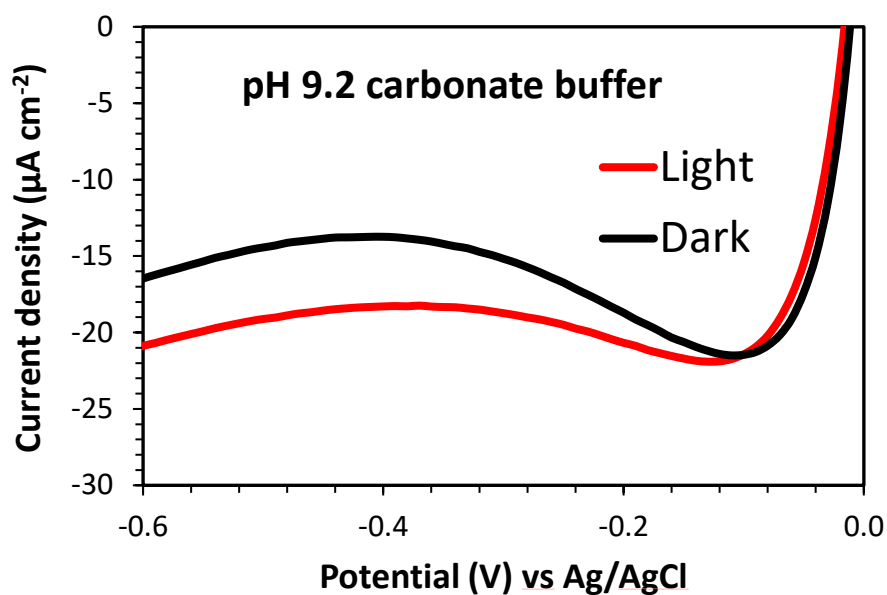


Figure SB 42. Linear sweep scan for **RuRe** on NiO in pH 9.2 carbonate buffer both under simulated 1 sun illumination and in the dark. The scan speed is 0.1 Vs⁻¹. The solution was saturated with CO₂ before starting the experiment.

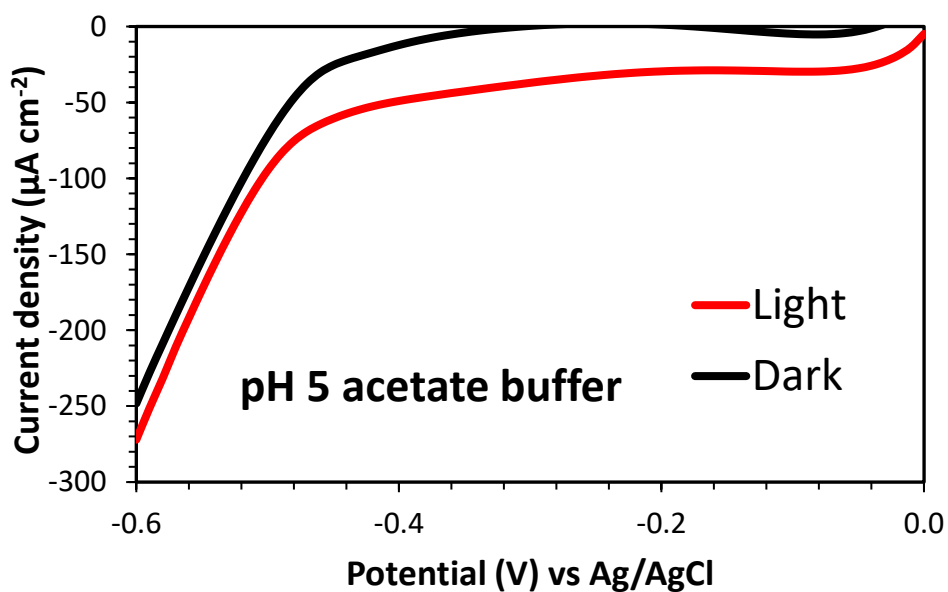


Figure SB 43. Linear sweep scan for **RuPt** on NiO in pH 5 acetate buffer both under simulated 1 sun illumination and in the dark. The scan speed is 0.1 Vs⁻¹. The solution was saturated with argon before starting the experiment.

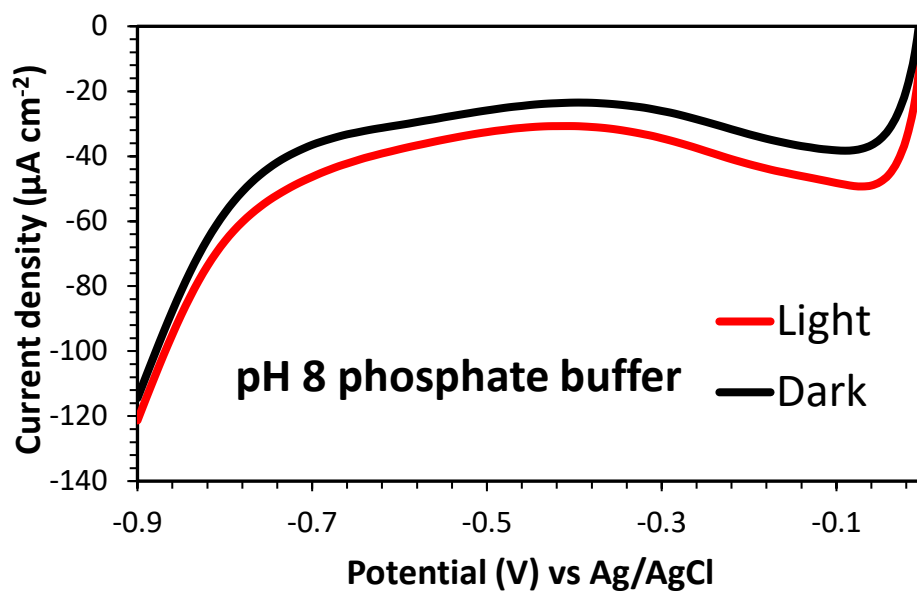


Figure SB 44. Linear sweep scan for **RuPt** on NiO in pH 8 phosphate buffer both under simulated 1 sun illumination and in the dark. The scan speed is 0.1 Vs^{-1} . The solution was saturated with argon before starting the experiment.

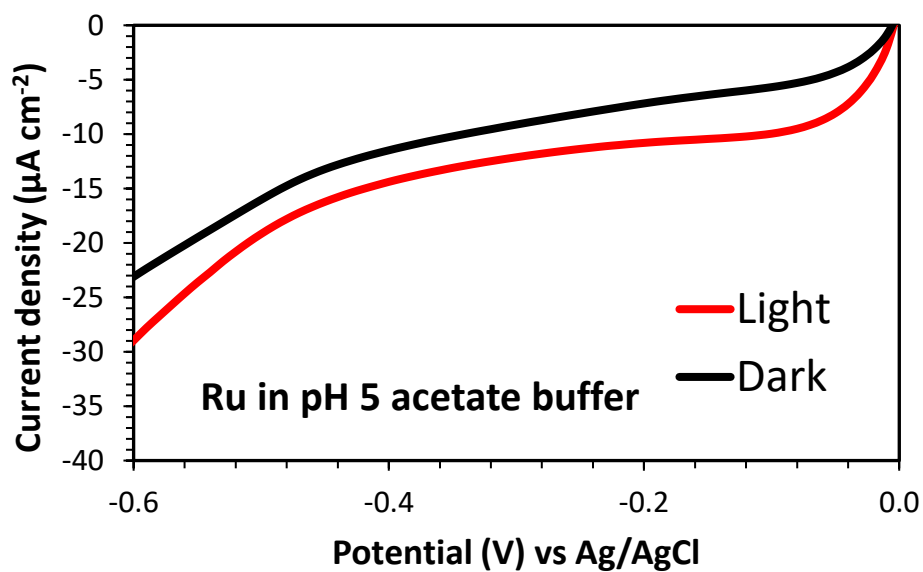
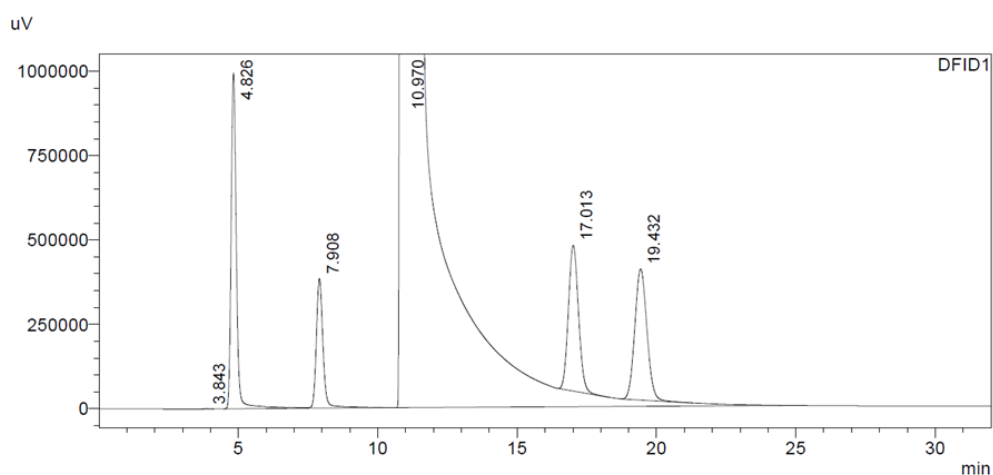


Figure SB 45. Linear sweep scan for **Ru** on NiO in pH 5 acetate buffer both under simulated 1 sun illumination and in the dark. The scan speed is 0.1 Vs^{-1} . The solution was saturated with argon before starting the experiment.

Gas Chromatography Measurements

Gas chromatography measurements were performed with a Shimadzu GC-2014 instrument where a thermal conductivity detector at 80 °C (TCD) and flame-ionisation detector (FID) at 150 °C operated in tandem. A Restek ShinCarbon ST packed column (2 metre, 2 mm ID) was used where argon was used as the carrier gas, and the oven temperature was 50 °C. For determining locations of key product peaks and for calibration purposes a standard gas mixture containing 5000 ppm propylene, 5000 ppm ethane, 5000 ppm ethylene, 5000 ppm methane, 1% carbon monoxide, 1 % carbon dioxide, and the balance carbon dioxide (BOC).



Peak#	Ret. Time	Area	Height
1	3.843	9244	762
2	4.826	13006030	994363
3	7.908	6459451	384652
4	10.970	#####	47222205
5	17.013	10927461	432330
6	19.432	11770190	388606
Total		#####	49422918

Figure SB 46. GC trace of standard calibration gas. Carbon monoxide is at a retention time of 4.826 minutes.

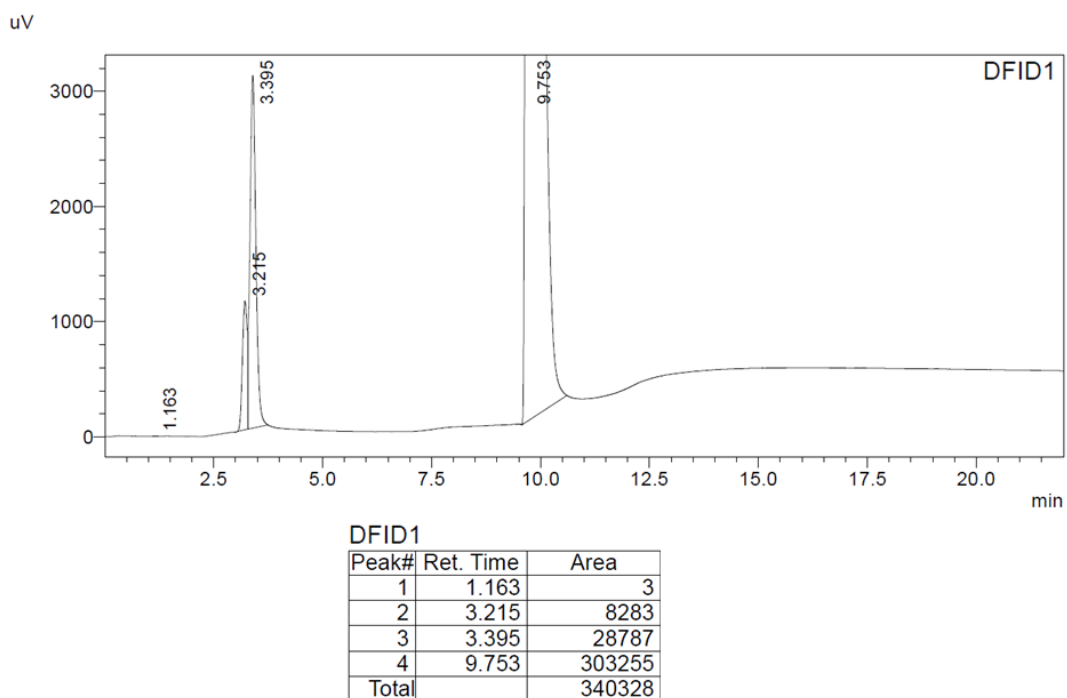


Figure SB 47. GC trace of **Ru** on NiO after 1 hour irradiation in pH 5 acetate buffer with an applied bias of -0.2 V under continuous 1 sun AM 1.5 irradiation.

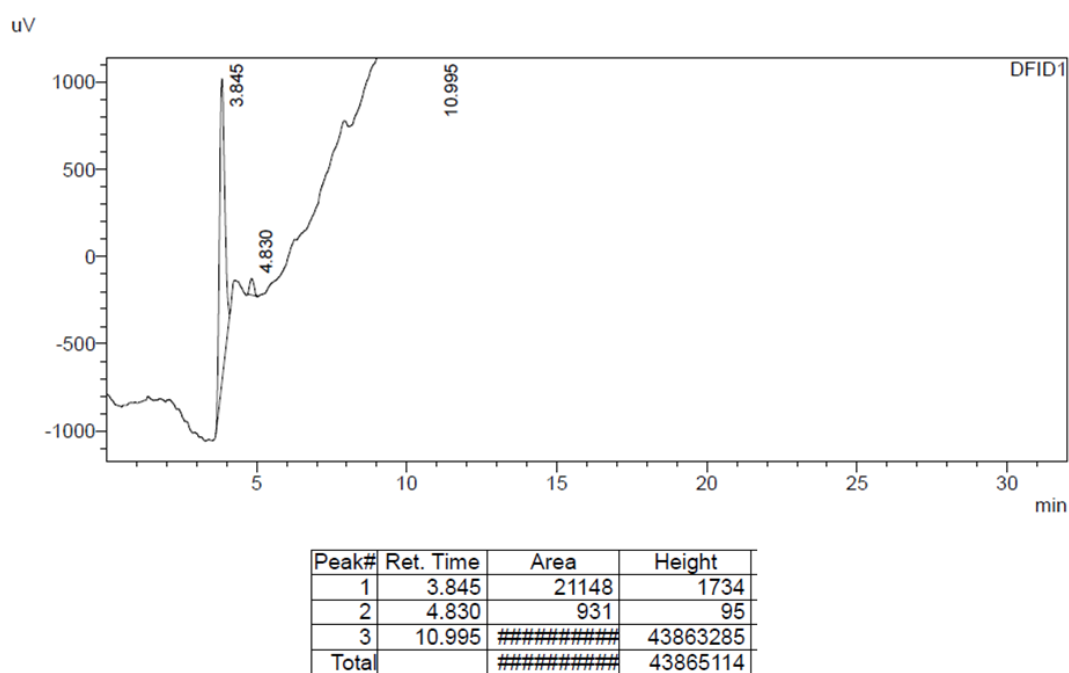
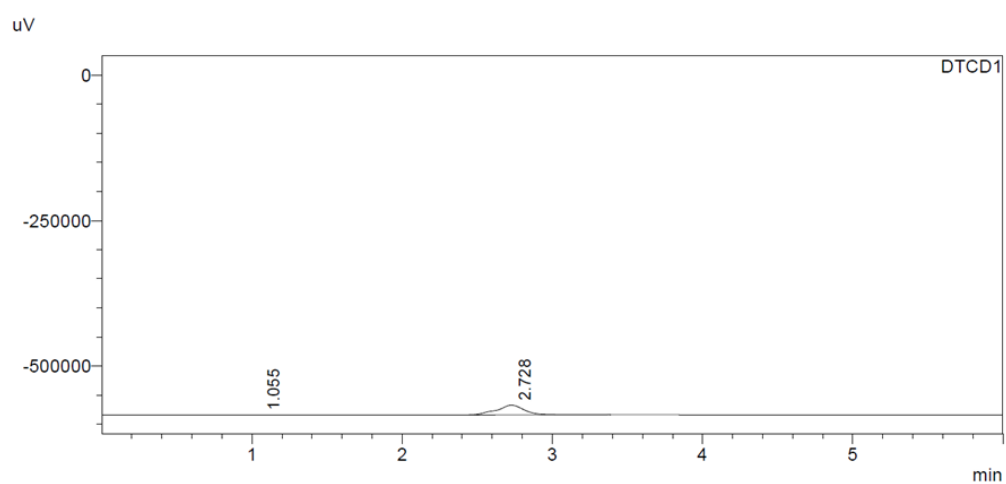


Figure SB 48. GC trace of **RuRe** on NiO after 1 hour irradiation in pH 5 acetate buffer with an applied bias of -0.2 V under continuous 1 sun AM 1.5 irradiation.



DTCD1		
Peak#	Ret. Time	Area
1	1.055	14
2	2.728	214313
Total		214327

Figure SB 49. GC trace of **RuPt** on NiO after 1 hour irradiation in pH 5 acetate buffer with an applied bias of -0.2 V under continuous 1 sun AM 1.5 irradiation. The hydrogen peak on the TCD detector is expected at approximately 1 minute.

NMR spectra

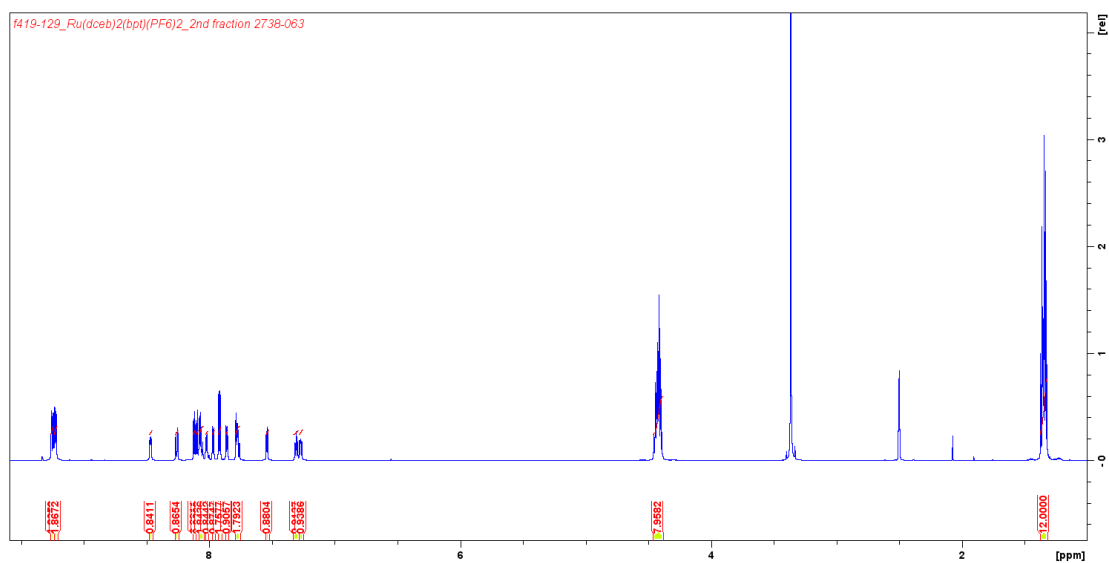


Figure SB 50. ^1H -NMR spectrum of **Ru** in DMSO- d_6 .

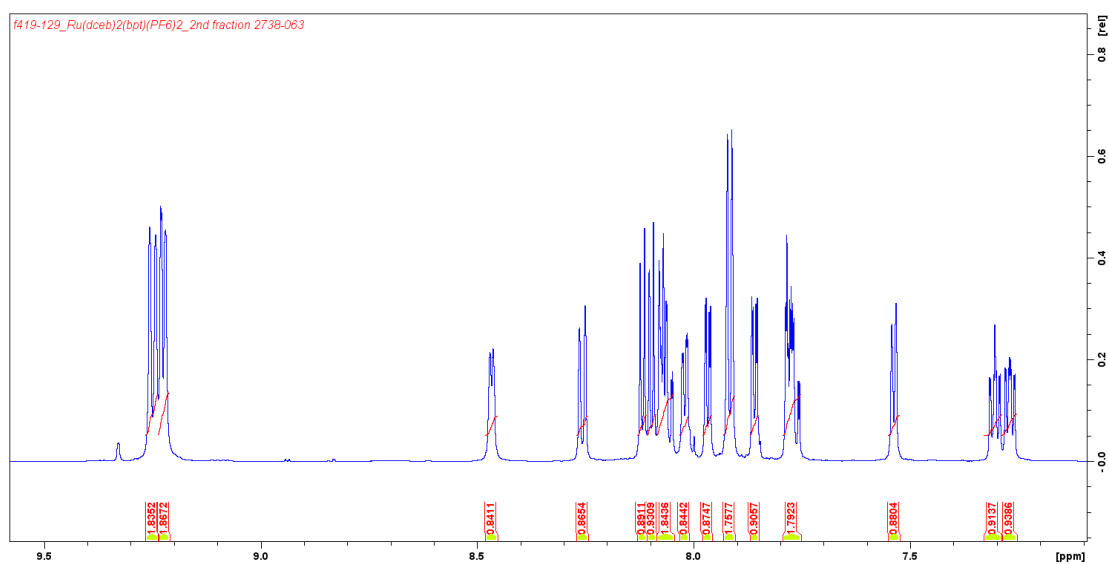


Figure SB 51. ^1H -NMR spectrum of **Ru** in DMSO- d_6 , zoom in of the aromatic region.

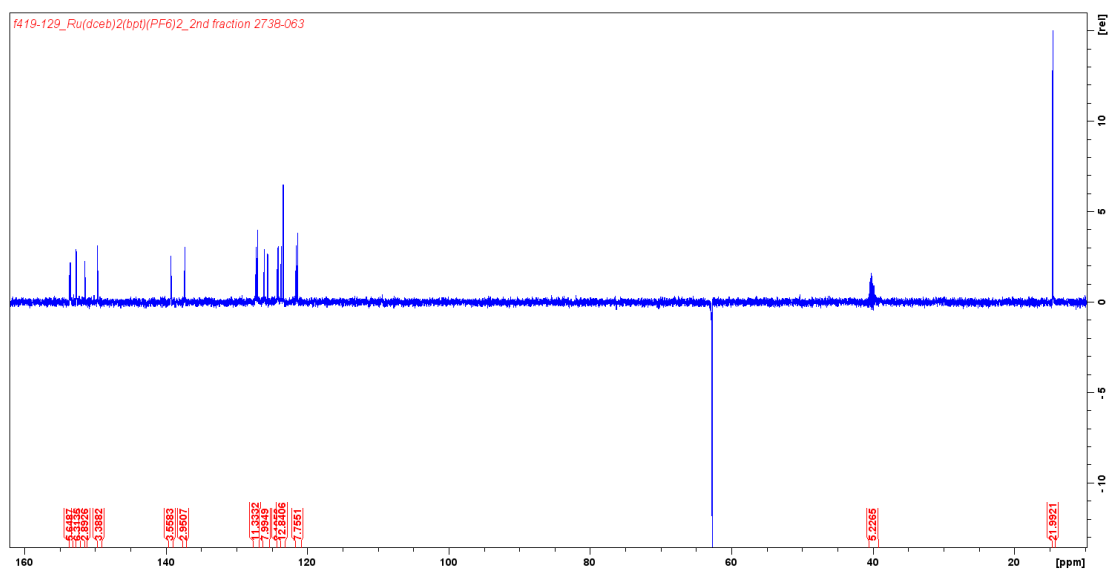


Figure SB 52. DEPT-135 ^{13}C -NMR spectrum of **Ru** in DMSO- d_6 .

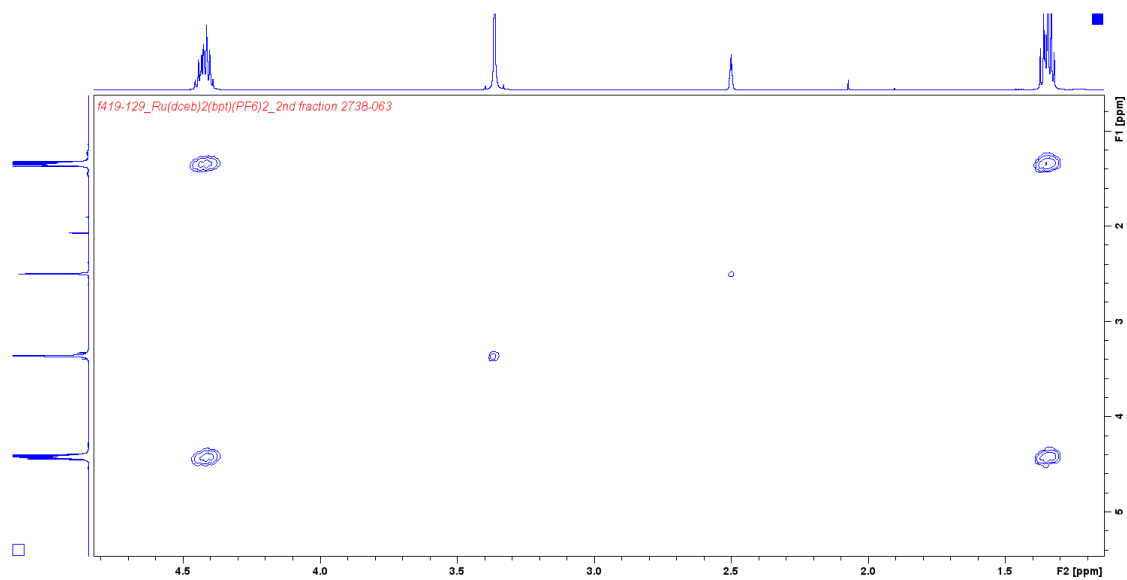


Figure SB 53. COSY spectrum of **Ru** in DMSO-d₆. 0-5 ppm range.

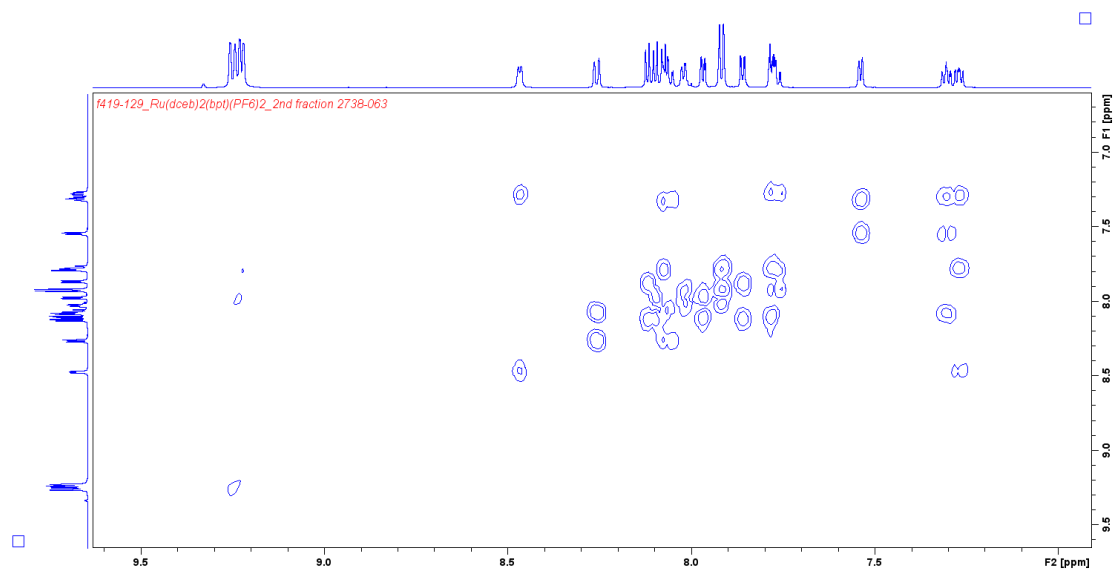


Figure SB 54. COSY NMR spectrum of **Ru** in DMSO- d_6 if the 6-9 ppm area.

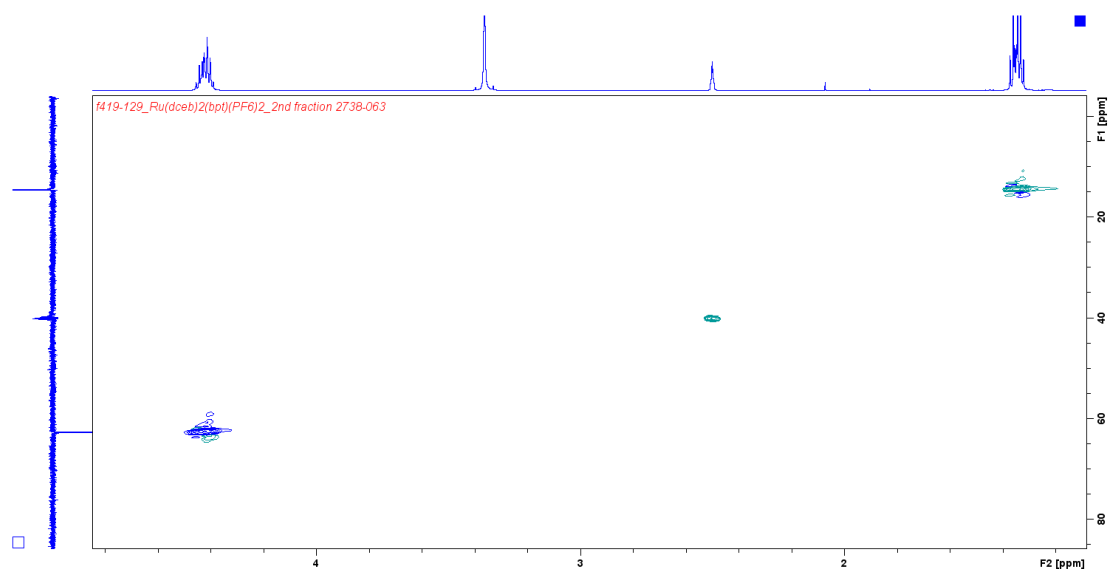


Figure SB 55. HSQC NMR spectrum of **Ru** in DMSO- d_6 focussed on the 0-5 ppm area. The ^1H -nmr spectrum (top axis) and ^{13}C - $^{135}\text{DEPT}$ spectrum (left axis) are shown for clarity.

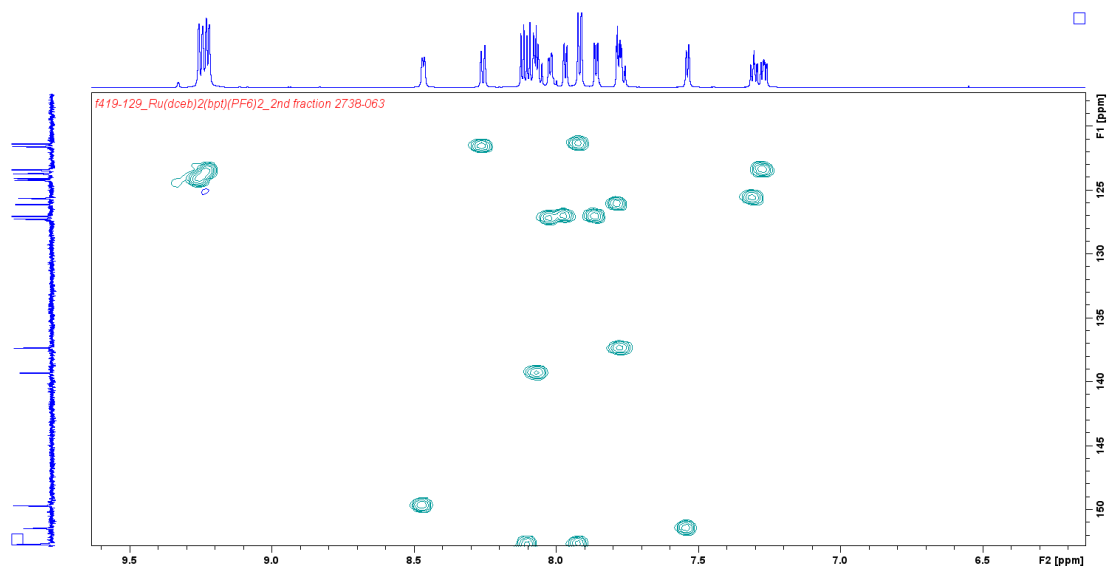


Figure SB 56. NMR HSQC spectrum of **Ru** in DMSO- d_6 focussed on the 6-10 ppm area. The ^1H -nmr spectrum (top axis) and ^{13}C -135-DEPT spectrum (left axis) are shown for clarity.

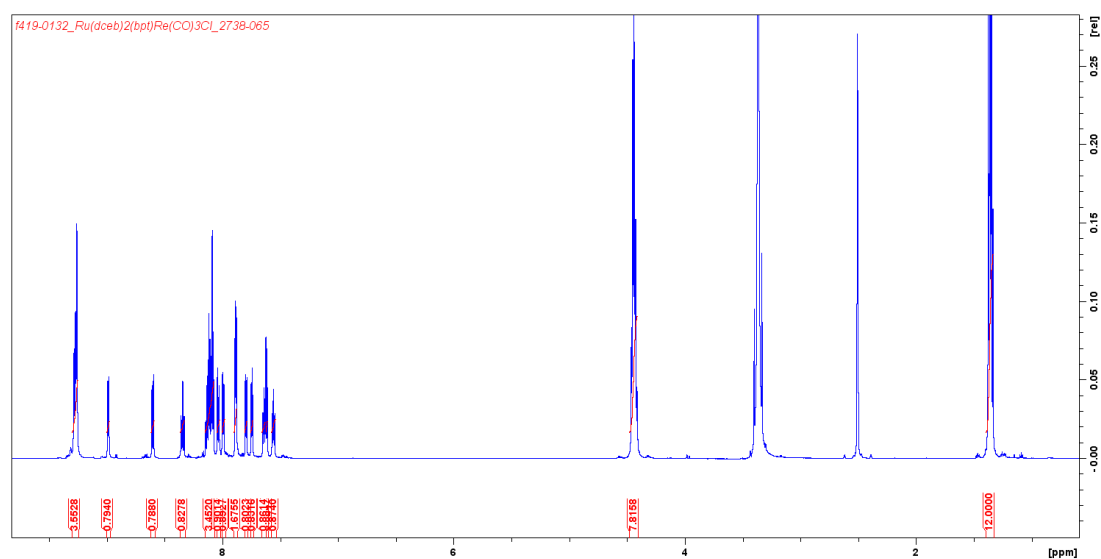


Figure SB 57. ^1H -NMR spectrum of **RuRe** in DMSO- d_6 . The signal at 3.3 ppm is residual water.

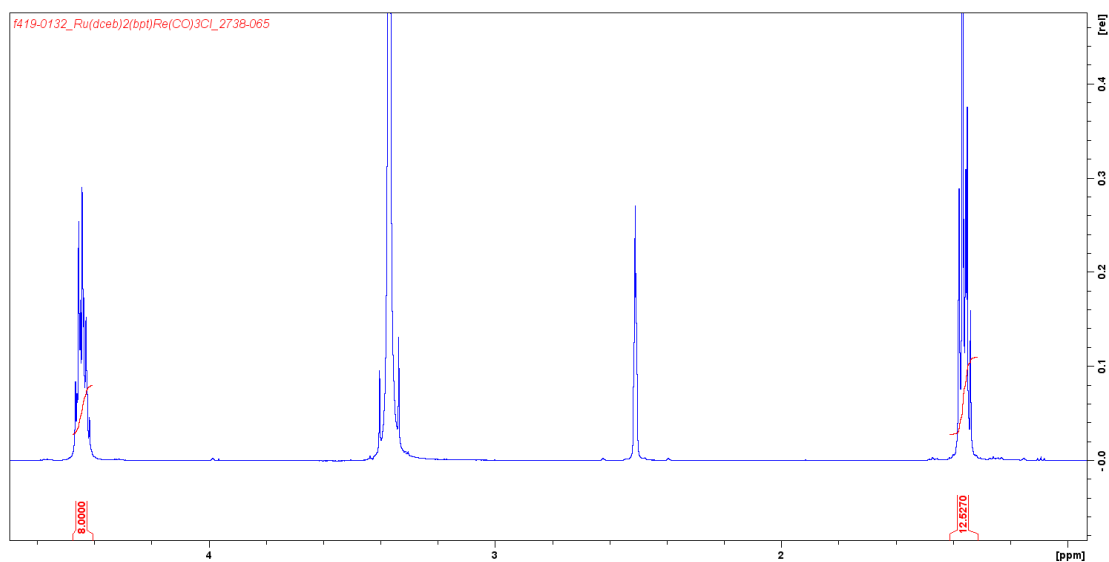


Figure SB 58 ^1H -NMR spectrum of **RuRe** in DMSO-d_6 , zoom in of the aliphatic region.

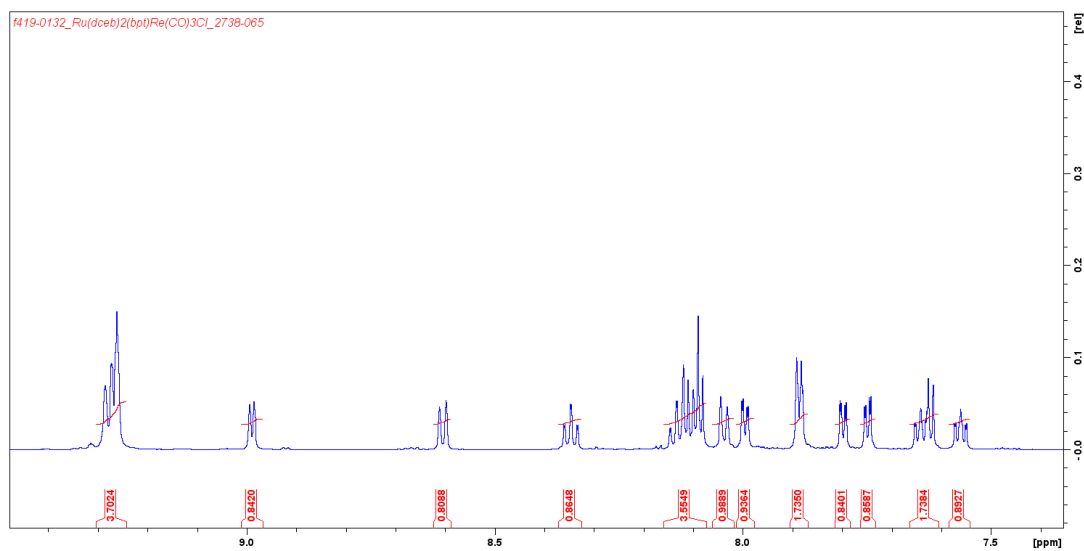


Figure SB 59. ^1H -NMR spectrum of **RuRe** in DMSO-d_6 , zoom in of the aromatic region.

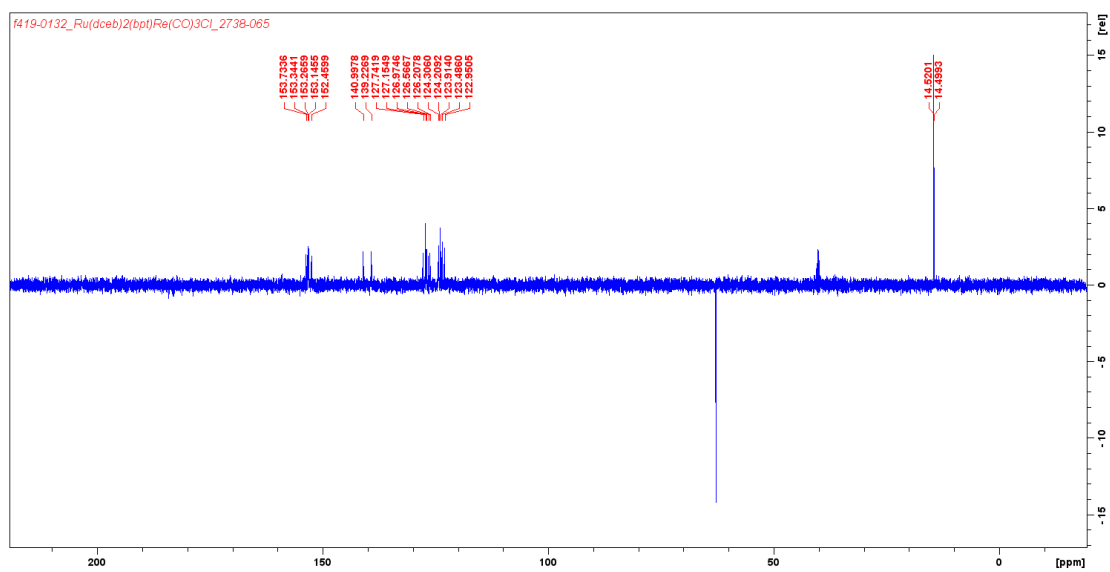


Figure SB 60. DEPT-135 ^{13}C -NMR spectrum of **RuRe** in DMSO-d_6 .

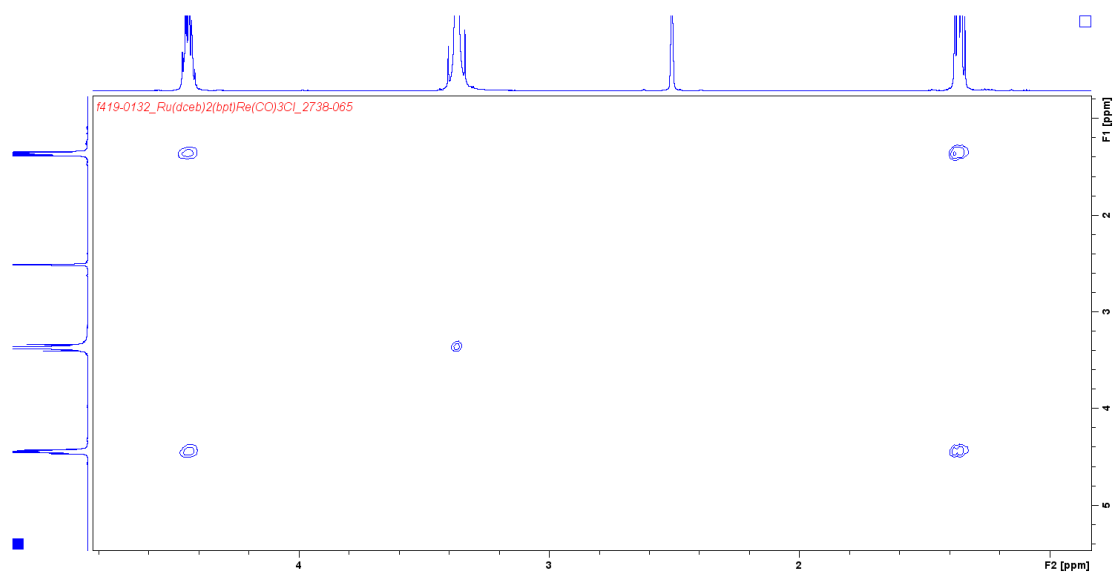


Figure SB 61. COSY ^1H -NMR spectrum of **RuRe** in DMSO-d_6 focussed on the 0-5 ppm area.

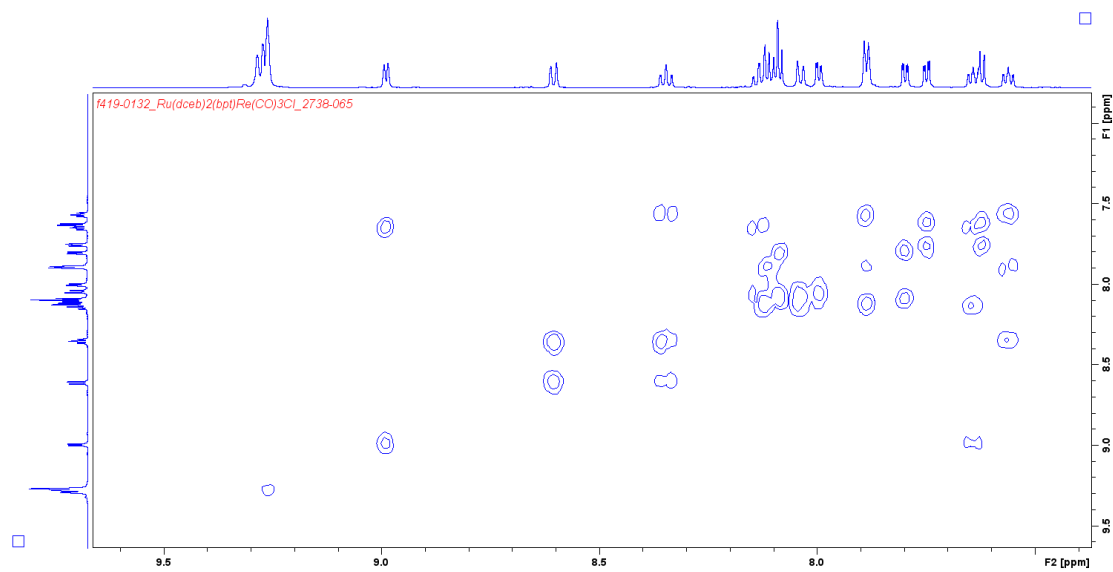


Figure SB 62. COSY NMR spectrum of **RuRe** in DMSO- d_6 focussed on the 6-9 ppm area.

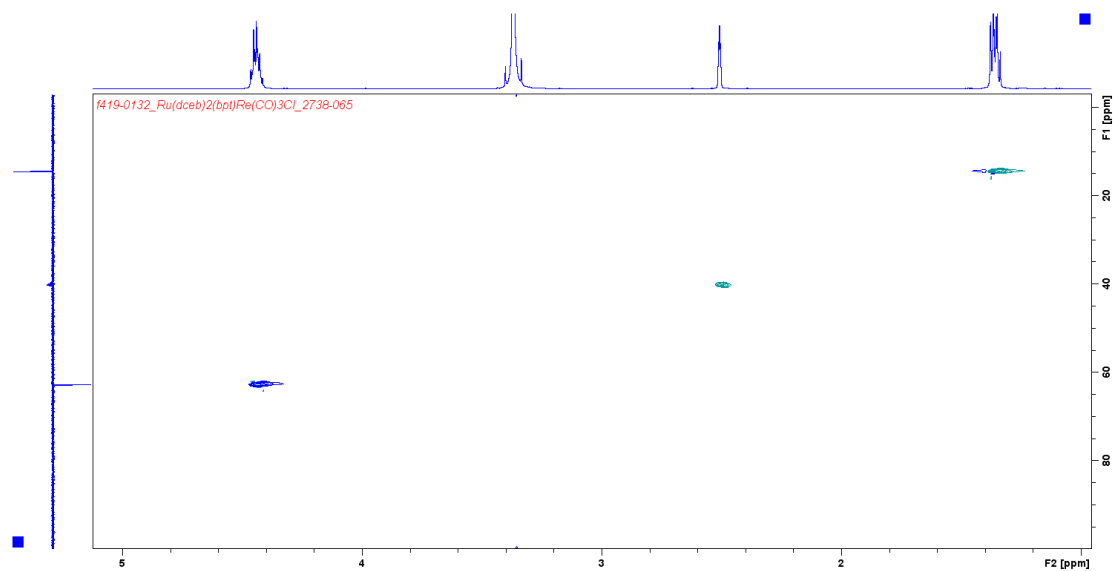


Figure SB 63. HSQC NMR spectrum of **RuRe** in DMSO- d_6 focussed on the 0-5 ppm area. The ^1H -nmr spectrum (top axis) and ^{13}C -135-DEPT spectrum (left axis) are shown for clarity.

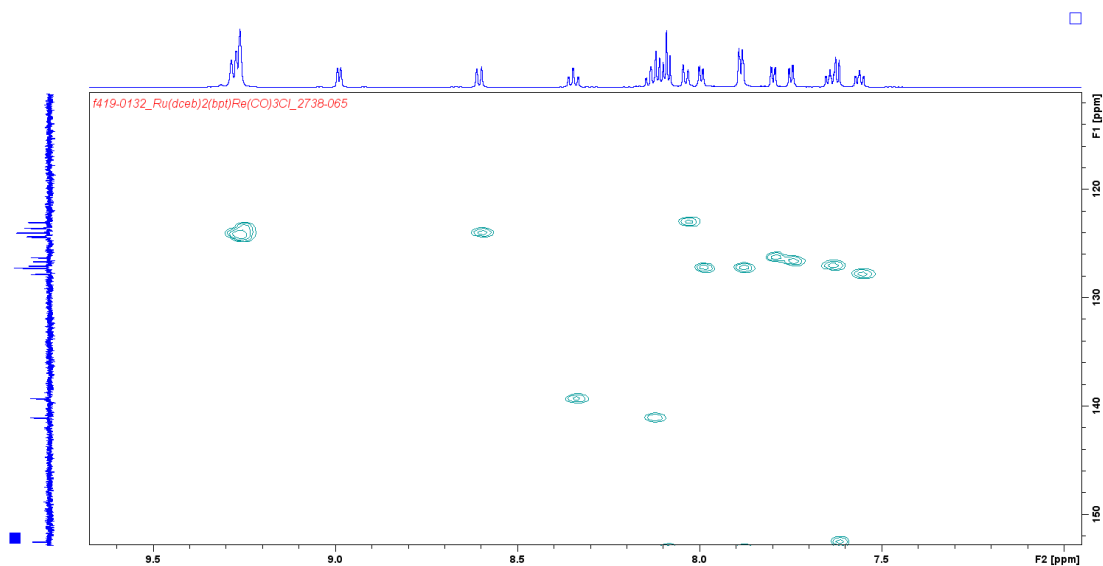


Figure SB 64. HSQC NMR spectrum of **RuRe** in DMSO- d_6 focussed on the 6-10 ppm area. The ^1H -nmr spectrum (top axis) and ^{13}C -135-DEPT spectrum (left axis) are shown for clarity.

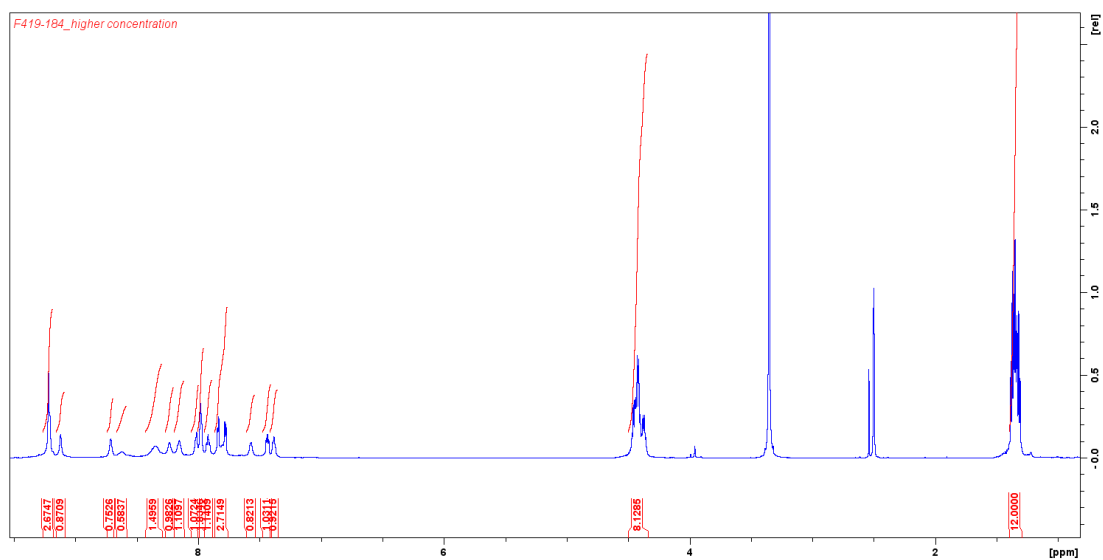


Figure SB 65. ^1H -NMR spectrum of **RuPt** in DMSO- d_6 . The signal at 2.54 is residual DMSO. The signal at 3.3 is residual water present in the deuterated solvent.

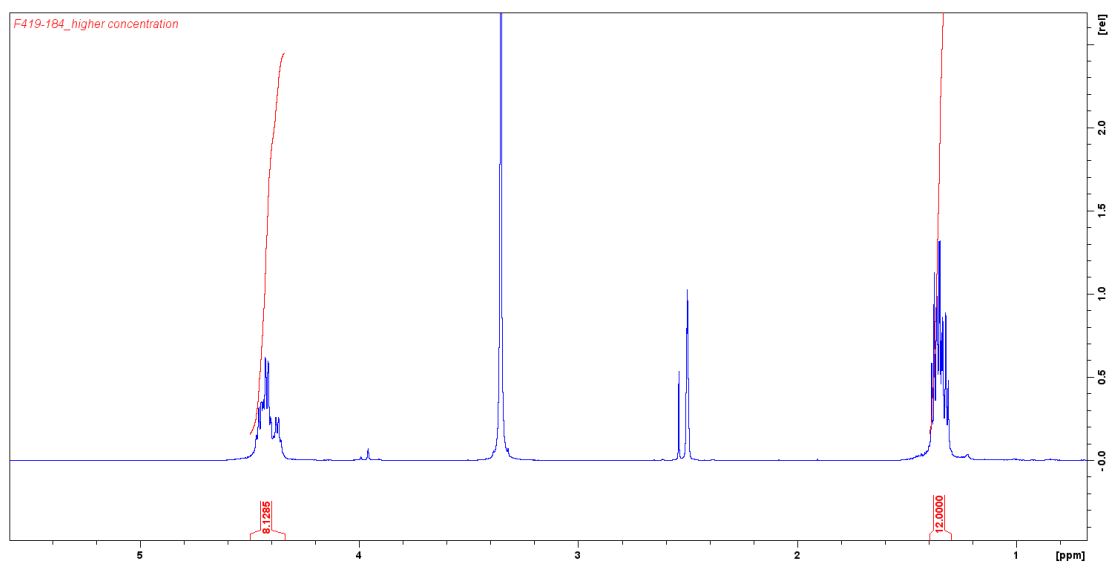


Figure SB 66 ^1H -NMR spectrum of **RuPt** in DMSO-d_6 , zoom in of the aliphatic region.

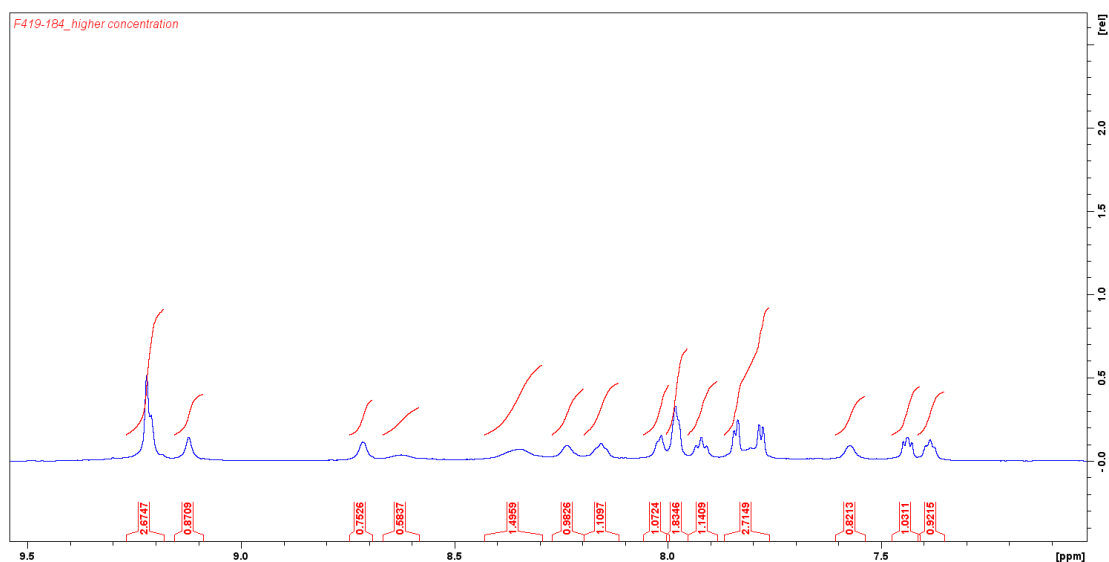


Figure SB 67 ^1H -NMR spectrum of **RuPt** in DMSO-d_6 , zoom in of the aliphatic region.

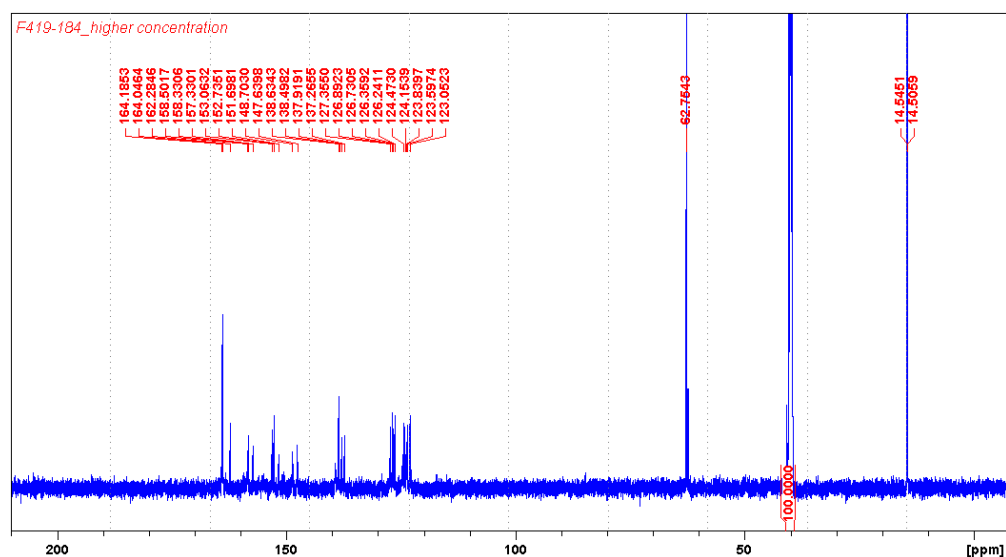


Figure SB 68. ^{13}C -NMR spectrum of **RuPt** in DMSO-d_6 . Signals at 40 ppm are residual DMSO.

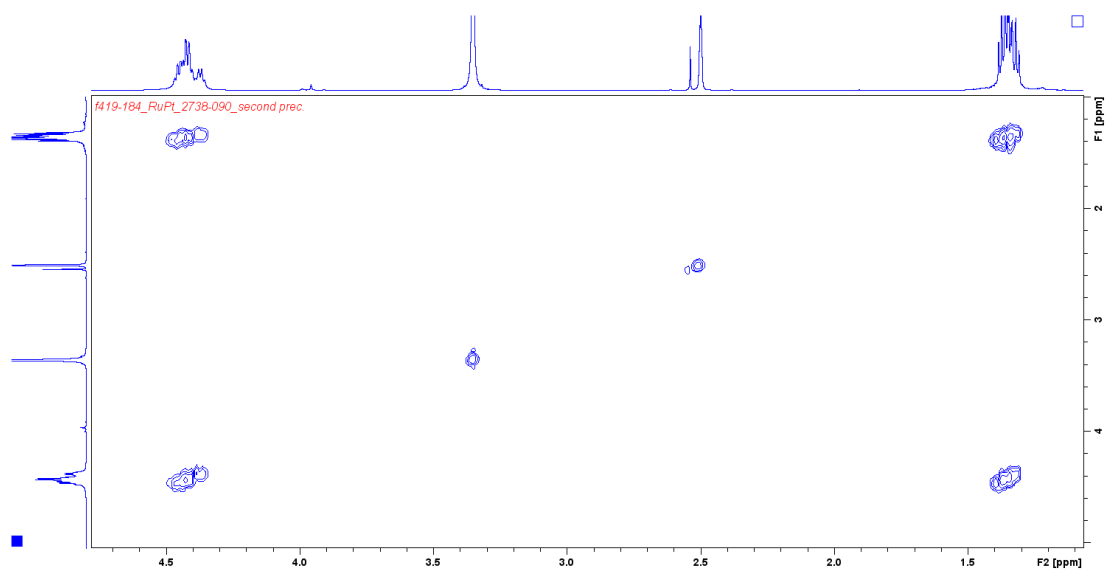


Figure SB 69. COSY NMR spectrum of **RuPt** in DMSO-d_6 focussed on the 0-5 ppm area. Signal at 2.5 and 2.54 are DMSO, signal at 3.3 is residual water.

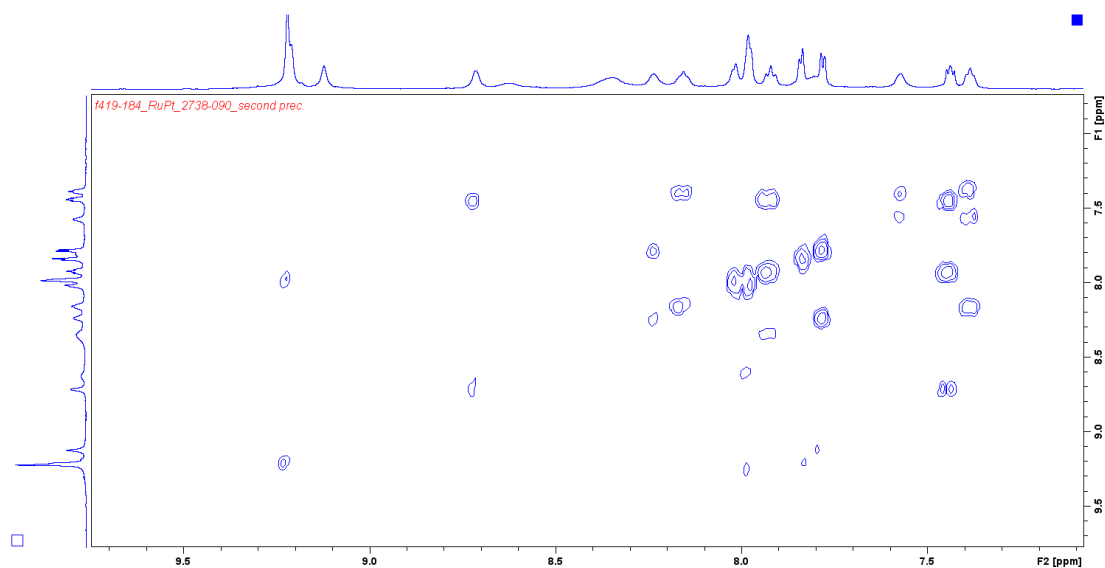


Figure SB 70. COSY NMR spectrum of **RuPt** in DMSO- d_6 focussed on the 6-11 ppm area.

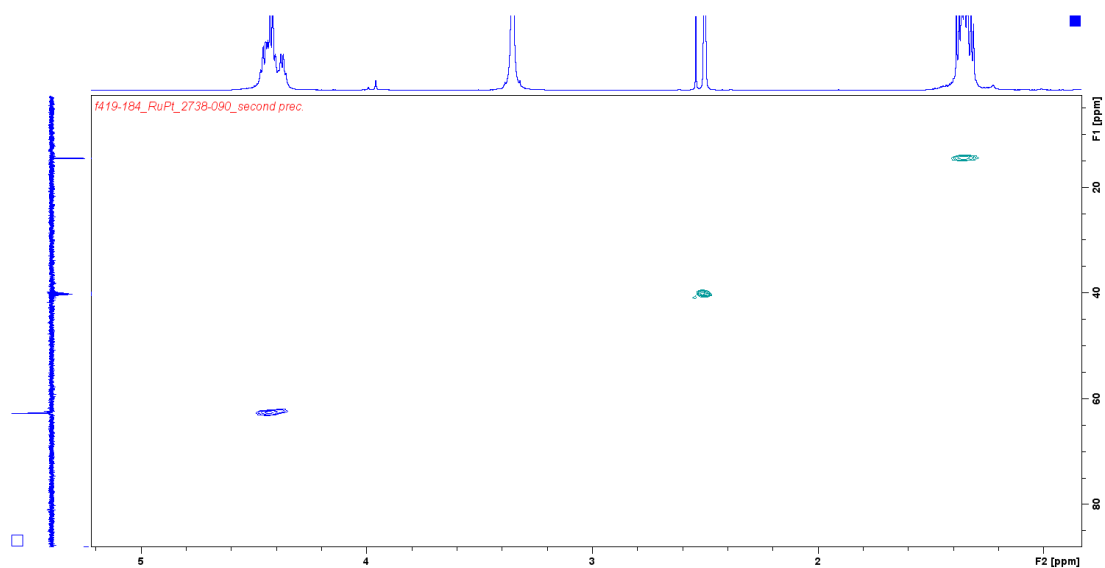


Figure SB 71. HSQC NMR spectrum of **RuPt** in DMSO- d_6 focussed on the 0-5 ppm area.

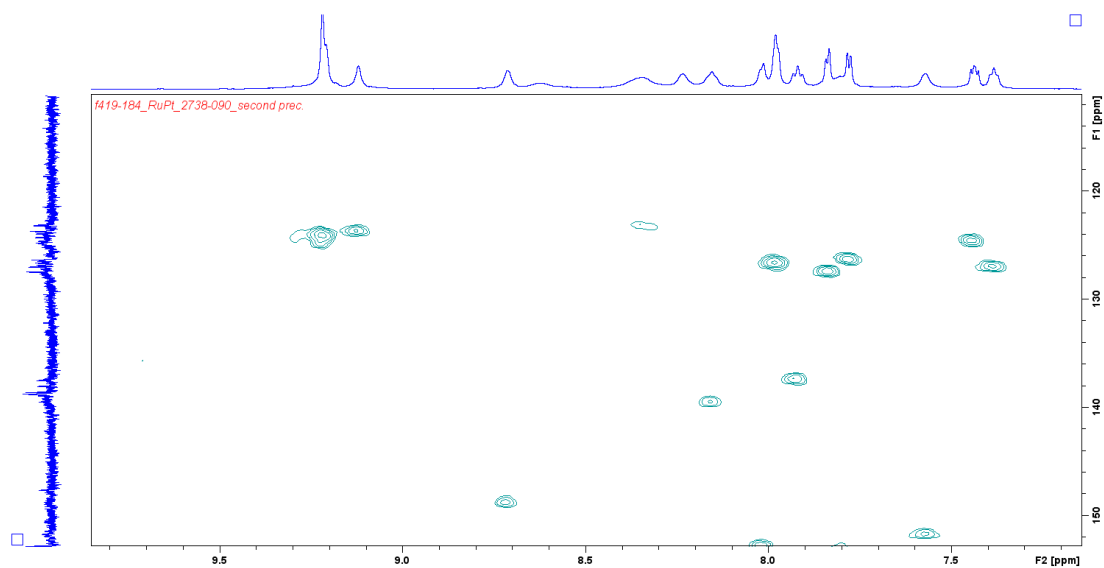


Figure SB 72. HSQC NMR spectrum of **RuPt** in DMSO- d_6 focussed on the 6-10 ppm area.

Mass spectrometry

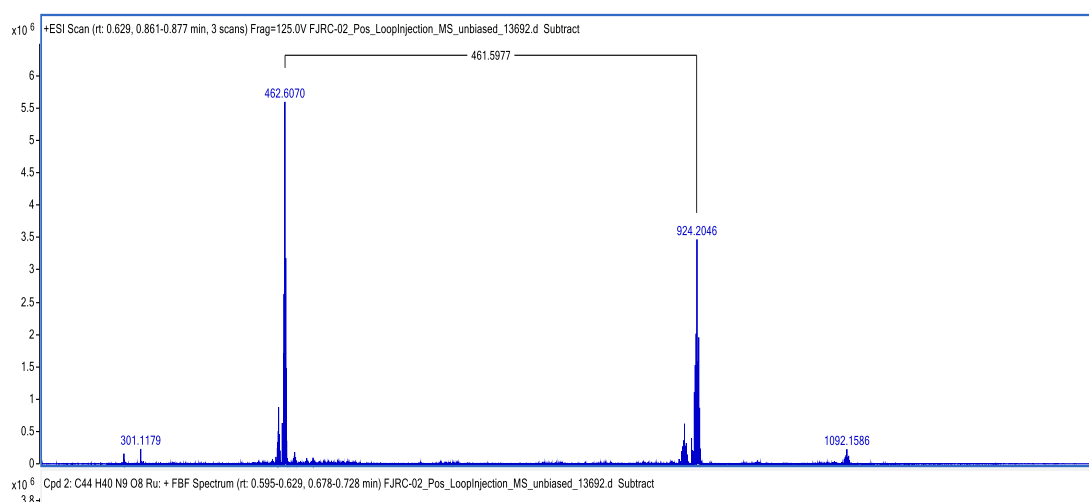


Figure SB 73. ESI-mass spectrum of **Ru** in acetonitrile. $[Ru(dceb)_2(bpt)]^{1+}$ calcd $m/z = 924.205$, found 924.2046.

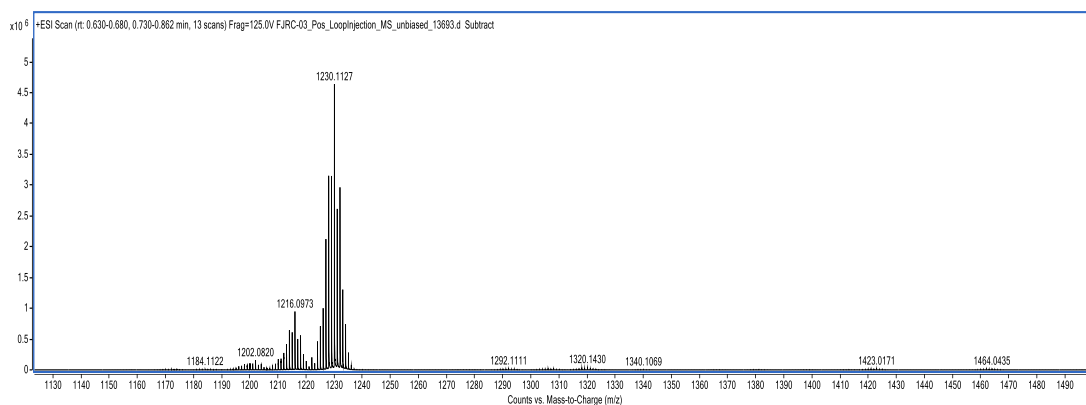


Figure SB 74. ESI mass spectrum of **RuRe** in acetonitrile. $[\text{Ru}(\text{dceb})_2(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}]^{1+}$ calcd. m/z 1230.114, found 1230.1127. $[\text{Ru}(\text{dceb})_2(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}-\text{CH}_2]$ calcd m/z 1216.098 found 1216.0973.

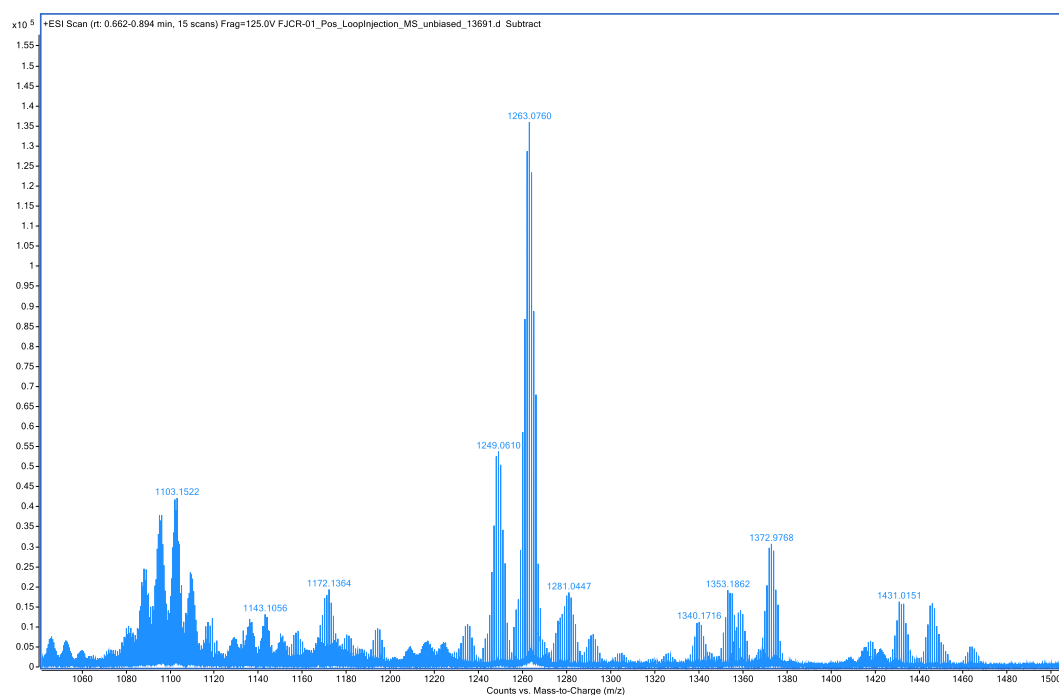


Figure SB 75. ESI mass spectrum of **RuPt** in acetonitrile. $\text{Ru}(\text{dceb})_2(\text{bpt})\text{Pt}(\text{H}_2\text{O})_2(\text{PF}_6)_2-\text{CH}_2^{1+}$ calcd. m/z 1431.103, found 1431.0151. $[\text{Ru}(\text{dceb})_2(\text{bpt})\text{PtI}_2]^{1+}$ calcd. m/z 1372.978, found 1372.9768. $[\text{Ru}(\text{dceb})_2(\text{bpt})\text{PtI}(\text{OH})(\text{H}_2\text{O})]$ calcd. m/z 1281.087, found 1281.0447 $[\text{Ru}(\text{dceb})_2(\text{bpt})\text{PtI}(\text{OH})]^{1+}$ calcd. m/z 1263.076, found 1263.076. $[\text{Ru}(\text{dceb})_2(\text{bpt})\text{PtI}(\text{OH})-\text{CH}_2]^{1+}$ calcd. m/z 1249.061, found 1249.061.

Appendix C: Ruthenium-Rhenium and Ruthenium-Palladium Supramolecular Photocatalysts for Photoelectrocatalytic CO₂ and H⁺ Reduction - Supporting Information

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S3. Transient Optical and Infrared Spectroscopy

S4. Photoelectrochemical Measurements

S5. X-Ray Photoelectron Spectroscopy

S6. Gas Chromatography Data and Calibration

S1 Experimental Section

Synthesis of Molecular Photocatalysts

3,5-di(pyridin-2-yl)-4H-1,2,4-triazole (Hbpt),¹ diethyl(2,2'-bipyridine)-4,4'-dicarboxylate (dceb),² Ru(DMSO)₄Cl₂³ and Ru(bpy)(DMSO)₂Cl₂⁴ were synthesized using reported procedures. All chemicals and solvents were purchased from Sigma Aldrich or Fluorochem and used without further purification.

Ru(DMSO)₄Cl₂³

2 g (7.65 mmol) of RuCl₃·3H₂O was added to a 100 mL flask. 50 mL of ethanol was added and the solution was refluxed for 3 hours during which the brown solution turned a dark green colour. The solution was filtered to remove any unreacted ruthenium material and the ethanol was removed under reduced pressure. The green residue was dissolved in 8 mL of dimethylsulfoxide (DMSO) and stirred at 150 °C for 2 hours. The solution turned bright orange and yellow precipitate slowly appeared. The solution was cooled to room temperature and 60 mL acetone was added to complete precipitation of product. The yellow crystalline material was collected by filtration, washed with acetone and dried under air to yield Ru(DMSO)₄Cl₂ as a yellow crystalline material (3.21 g, 6.63 mmol, 86%). ¹H-NMR (600 MHz, D₂O): 2.74 (s, 6H), 3.40 (s, 6H), 3.49 (s, 6H), 3.51 (s, 6H).

Ru(bpy)(DMSO)₂Cl₂⁴

2 g (4 mmol) of Ru(DMSO)₄Cl₂ and 0.64 g (4 mmol) of 2,2'-bipyridine were added to a 100 mL flask. 36 mL of ethanol and 4 mL of DMSO were added and the solution was refluxed for 1 hour, after which the starting suspension had fully converted to a homogeneous orange solution. Further refluxing for at least 30 minutes resulted in the precipitation of an orange powder. The powder was collected by vacuum filtration, washed with 20 mL of ethanol and dried under air to yield Ru(bpy)(DMSO)₂Cl₂ as an orange powder (1.50 g, 3.08 mmol, 77%). ¹H-NMR (600 MHz, DMSO-d₆): 2.28 (s, 3H), 2.99 (s, 3H), 3.36 (s, 3H), 3.40 (s, 3H), 7.62 (td, 1H), 7.78 (td, 1H), 8.11 (td, 1H), 8.23 (td, 1H), 8.61 (d, 1H), 8.66 (d, 1H), 9.56 (dd, 1H), 9.66 (dd, 1H).

[Ru(dceb)(bpy)(bpt)](PF₆)

0.2 g (0.41 mmol) of Ru(bpy)(DMSO)₂Cl₂ and 0.124 g (0.41 mmol) of diethyl(2,2'-bipyridine)-4,4'-dicarboxylate (dceb) were added to a 25 mL flask. 5 mL of ethanol and 5 mL of water were added and the solution was refluxed for 2 hours during which the solution changed from yellow to dark red. 0.092 g (0.41 mmol) of 3,5-di(pyridin-2-yl)-4H-1,2,4-triazole (Hbpt) was added to the solution and the solution was refluxed for a further 24 hours. The solution was allowed to cool to room temperature and the ethanol was removed under reduced pressure. An additional 10 mL of water was added after which 0.301 g (1.64 mmol) of potassium hexafluorophosphate was added. The red precipitate was collected by vacuum filtration, washed with 10 mL of water and dried. The crude product was purified by column chromatography using SiO₂ as stationary phase. Unreacted starting material was removed using acetonitrile as mobile phase. The mobile phase was changed to 10:1:0.1 acetonitrile/water/10% KNO₃ (aq.) after which the product eluted as a red band. The acetonitrile was removed under reduced pressure and a small amount of potassium hexafluorophosphate was added to complete the precipitation of a dark red powder. The powder was collected by vacuum filtration, washed with 10 mL of water and dried under air to yield [Ru(dceb)(bpy)(bpt)](PF₆) as a dark red powder (0.143 g, 0.13 mmol, 33%). ¹H-NMR (600 MHz, DMSO-d₆): 1.33-1.39 (m, 6H), 4.40-4.48 (m, 4H), 7.44 (td, 1H), 7.52 (td, 1H), 7.55-7.63 (m, 2H), 7.76-7.81 (m, 1H), 7.85-7.98 (m, 2H), 8.04-8.21 (m, 6H), 8.32 (t, 1H), 8.60 (m, 1H), 8.77-8.83 (dd, 1H), 8.84 (dd, 1H).

Mass spectrometry (ESI mode): [Ru(dceb)(bpy)(bpt)]¹⁺ calculated *m/z* = 780.162, found = 780.163. [Ru(dceb)(bpy)(Hbpt)]²⁺ calculated *m/z* = 390.585, found 390.585.

[Ru(dcb)(bpy)(Hbpt)](PF₆)₂ (PC3)

0.27 g (0.25 mmol) of [Ru(dceb)(bpy)(bpt)](PF₆) and 0.06 g (2.5 mmol, 10 eq.) of anhydrous lithium hydroxide were added to a 25 mL flask. The flask was cooled to 0 °C and 6 mL of THF and 1.5 mL of water were added. The solution was stirred overnight while being allowed to heat up to room temperature slowly. The THF was removed under reduced pressure and the solution was acidified to pH 3 using 0.1 M HCl solution. 0.184 g (1 mmol, 4 eq.) of potassium hexafluorophosphate was added resulting in the precipitation of the product as a red powder. The precipitate was collected by vacuum filtration, washed with 20 mL of water and dried under air to yield [Ru(dcb)(bpy)(Hbpt)](PF₆)₂ as a dark red powder (0.214 g, 0.21 mmol, 84%). ¹H-NMR (600 MHz, DMSO-d₆): 7.38 (m, 1H), 7.44 (m, 1H), 7.49 (m, 1H), 7.65 (m, 1H), 7.75 (m, 1H), 7.78-7.97 (m, 4H), 8.00-8.20 (m, 5H), 8.41-8.58 (m, 5H), 8.66 (t, 1H), 8.93-9.08 (m, 2H).

Mass spectrometry (ESI mode): $[\text{Ru}(\text{dcb})(\text{bpy})(\text{Hbpt})]^{2+}$ calculated $m/z = 362.555$, found = 362.554. $[\text{Ru}(\text{dcb})(\text{bpy})(\text{bpt})]^+$ calculated $m/z = 724.100$, found = 724.100.

$[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$

0.1 g (0.115 mmol) of $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})](\text{PF}_6)$, 0.032 g (0.130 mmol, 1.2 eq.) of $\text{Re}(\text{CO})_5\text{Cl}$ and 3 mL of methanol were added to a 10 mL flask. The resulting red solution was refluxed overnight resulting in precipitation of the product. The precipitate was collected by vacuum filtration, washed with cold ethanol and ether and airdried to yield $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ as a dark red solid (0.71 g, 0.058 mmol, 50%). ^1H -NMR (600 MHz, DMSO-d_6): 1.31-1.38 (m, 6H), 4.39-4.69 (m, 4H), 7.40-7.45 (m, 2H), 7.50-7.54 (m, 1H), 7.57-7.73 (m, 3H), 7.79-7.88 (m, 3H), 7.93-7.97 (m, 1H), 8.01 (t, 1H), 8.06-8.22 (m, 5H), 8.27-8.35 (m, 1H), 8.55-8.62 (dd, 1H), 8.78-8.86 (m, 2H), 8.95-8.99 (m, 1H), 9.20-9.26 (m, 2H).

Mass spectrometry (ESI mode): $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl-H}]^{-1}$ calculated m/z 1230.027 found 1230.1179

$[\text{Ru}(\text{dcb})(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ (PC1)

0.05 g (0.041 mmol) of $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ and 0.01 g of LiOH (0.39 mmol, 10 eq.) were dissolved in 5 mL of a 4:1 THF:water mixture. The mixture was stirred on ice and slowly allowed to heat to room temperature overnight while stirring. The THF was removed under reduced pressure and the solution was acidified to pH 3 with 0.1 M HCl solution. The complex was precipitated from the aqueous solution by addition of 0.025 g (0.16 mmol, 4 eq.) NH_4PF_6 . The precipitate was collected by vacuum filtration, washed with water and diethyl ether and dried under air to yield $[\text{Ru}(\text{dcb})(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ as a red solid (0.039 g, 0.034 mmol, 82%). ^1H -NMR (600 MHz, DMSO-d_6): 7.36-7.64 (m, 5H), 7.75-7.95 (m, 4H), 8.00-8.21 (m, 7H), 8.32-8.35 (1H), 8.59-8.65 (m, 1H), 8.76-8.82 (dd, 1H), 8.82-8.87 (m, 1H), 9.18-9.26 (dd, 2H) 14.2 (br, 1H, COOH). FTIR (CHCl_2) 2021, 1912, 1895, 1716 cm^{-1} .

Mass spectrometry (ESI mode): $[\text{Ru}(\text{dcb})(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}]^{1+}$ calculated $m/z = 1030.0083$, found = 1030.0142. $[\text{Ru}(\text{dcb-2H}^+)(\text{bpy})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}] + 2 \text{Na}^+$ calculated $m/z = 1218.938$, found = 1218.0245

$[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{PdCl}_2](\text{PF}_6)$

0.1 g (0.115 mmol) of $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})](\text{PF}_6)$, 0.046 g (0.138 mmol, 1.2 eq.) of $\text{Pd}(\text{DMSO})_2\text{Cl}_2$ and 5 mL of methanol were added to a 10 mL flask. The resulting red solution was refluxed overnight resulting in a precipitate to form. The precipitate was collected via filtration, washed

with cold ethanol and diethyl ether and air dried yielding **[Ru(dceb)(bpy)(bpt)PdCl₂](PF₆)** as a red solid (0.088 g, 0.068 mmol, 59%). ¹H-NMR (600 MHz, DMSO-d₆): 1.37-1.43 (m, 6H), 4.41-4.47 (m, 4H), 7.22-7.41 (m, 2H), 7.43-7.49 (m, 2H), 7.53-7.73 (m, 3H), 7.76-7.87 (m, 3H), 7.91-8.10 (m, 6H), 8.44-8.52 (m, 2H), 8.95-9.07 (m, 3H) 9.9 (t, 1H).

Mass spectrometry (ESI mode): [Ru(dceb)(bpy)(bpt)PdCl₂]¹⁺ calculated *m/z* = 956.003, found = 956.008.

[Ru(dcb)(bpy)(bpt)PdCl₂](PF₆) (PC2)

0.05 g (0.039 mmol) of **[Ru(dceb)(bpy)(bpt)PdCl(dmsO)](PF₆)** and 0.01 g of LiOH (0.39 mmol, 10 eq.) were dissolved in 5 mL of a 4:1 THF:water mixture. The mixture was stirred on ice and slowly allowed to heat to room temperature overnight while stirring. The THF was removed under reduced pressure and the solution was acidified to pH 3 with 0.1 M HCl solution. The complex was precipitated from the aqueous solution by addition of 0.025 g (0.16 mmol, 4 eq.) NH₄PF₆. The precipitate was collected by vacuum filtration, washed with water and diethyl ether and dried under air to yield **[Ru(dcb)(bpy)(bpt)PdCl₂](PF₆)** as a red solid (0.037 g, 0.030 mmol, 77%). ¹H-NMR (600 MHz, DMSO-d₆): 1.37-1.43 (m, 6H), 4.41-4.47 (m, 4H), 7.22-7.41 (m, 2H), 7.43-7.49 (m, 2H), 7.53-7.73 (m, 3H), 7.76-7.87 (m, 3H), 7.91-8.10 (m, 6H), 8.44-8.52 (m, 2H), 8.95-9.07 (m, 3H) 9.9 (t, 1H). FTIR (CH₂Cl₂) 1697 cm⁻¹.

Mass spectrometry (ESI mode): [Ru(dcb)(bpy)(bpt)PdCl₂]¹⁺ calculated *m/z* = 899.941 found 899.946

Analytical Methods

UV-visible absorption measurements were obtained on either an Ocean Optics USB 2000+ or Hitachi U3310 spectrophotometer. Steady-state fluorescence spectra were interrogated with a Hitachi F4500 instrument. Spectrophotometric grade solvents were used for all measurements and fluorescence spectra were obtained using optically thin samples. Cyclic voltammetry (CV) for PC1-3 was performed in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, glassy carbon working electrode, platinum wire counter electrode and Ag/AgNO₃ reference electrode and calibrated against ferrocene (Fc). Gas chromatography measurements were performed with a Shimadzu GC-2014 instrument where a thermal conductivity detector at 200 °C (TCD) and flame-ionisation detector (FID) at 250 °C operated in tandem. A Restek ShinCarbon ST 80/100 packed column (2 metre, 2 mm ID) was used where argon was the carrier gas. The oven temperature was 50 °C with a temperature ramp to 200 °C

(after an initial period of 2 mins at 50 °C) at a rate of 15 °C min⁻¹, followed by a final hold time of 10 mins.

XPS data was acquired using a Kratos Axis SUPRA using monochromated Al K α (1486.69 eV) X-rays at 15 mA emission and 12 kV HT (180W) and a spot size/analysis area of 700 x 300 μ m. The instrument was calibrated to gold metal Au 4f (83.95 eV) and dispersion adjusted give a binding energy (BE) of 932.6 eV for the Cu 2p_{3/2} line of metallic copper. Ag 3d_{5/2} line FWHM at 10 eV pass energy was 0.544 eV. Source resolution for monochromatic Al K α X-rays is ~0.3 eV. The instrumental resolution was determined to be 0.29 eV at 10 eV pass energy using the Fermi edge of the valence band for metallic silver. Resolution with charge compensation system on <1.33 eV FWHM on PTFE. High resolution spectra were obtained using a pass energy of 20 eV, step size of 0.1 eV and sweep time of 60 s, resulting in a line width of 0.696 eV for Au 4f_{7/2}. Survey spectra were obtained using a pass energy of 160 eV. Charge neutralisation was achieved using an electron flood gun with filament current = 0.38 A, charge balance = 2 V, filament bias = 4.2 V. Successful neutralisation was adjudged by analysing the C 1s region wherein a sharp peak with no lower BE structure was obtained. Spectra have been charge corrected to the main line of the carbon 1s spectrum (adventitious carbon) set to 284.8 eV. All data was recorded at a base pressure of below 9 x 10⁻⁹ Torr and a room temperature of 294 K. Data was analysed using CasaXPS v2.3.19PR1.0. Peaks were fit with a Shirley background prior to component analysis. Spectra are calibrated energy of all regions to the position of Au4f core level. Samples were examined at three random spot before and after photocatalysis.

Photoelectrochemical Cell

The design of the cell used for photoelectrocatalysis are outlined in Figure S1. In the static cell, a three-electrode setup was integrated into a gas-tight glass assembly, where gaseous products can be sampled by headspace injection via a septum. The working electrode was a 2 x 2 cm TEC15 (NSG) conductive glass slide with a 0.79 cm² area covered in mesoporous NiO, soaked in a dye bath solution (approx. 3 mM dye in dry acetonitrile) with the appropriate photocatalyst for 12 hours prior to the experiment. The counter-electrode was platinum wire and the reference was Ag/AgCl (3M KCl). The assembled cell was filled with a fixed amount of the desired electrolyte and bubbled with research grade CO₂ (BOC) for at least 15 minutes before commencing a photoelectrocatalysis experiment. A PalmSens EmStat3 Blue potentiostat was used to apply bias and record the current throughout the experiment. The face of the working

electrode was illuminated by AM 1.5 filtered light from a Xe-arc lamp calibrated to an intensity of 1 sun (100 mW cm^{-2}). Light chopping was accomplished with an electronic shutter.

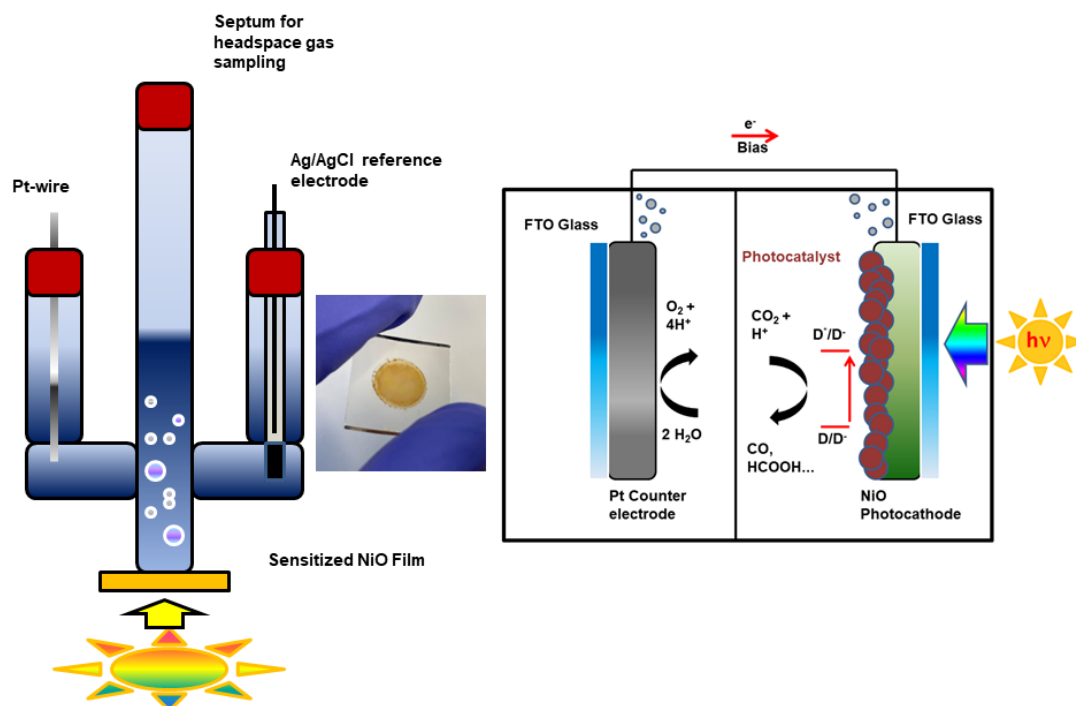


Figure SC 1. Illustration of the reaction cells used for photoelectrocatalysis.

Preparation of the Photocathode

The working electrode for all systems in this study was a mesoporous NiO semiconductor thin film on conductive glass (TEC 15 FTO, Pilkington) for photoelectrochemical experiments or polished CaF_2 windows for time-resolved infrared spectroscopy. The procedure for producing the NiO layer by doctor blading NiO sol-gel solution has been described elsewhere.⁵ NiO sol-gel precursor solution was prepared by adding anhydrous NiCl_2 (1 g, Sigma) and tri-block copolymer F108 (poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)) (1g, Sigma) to ethanol (6 ml) and ultrapure water (5 ml). The solution was left to age in a vial for two weeks and aliquots centrifuged prior to use. The NiO films have an average thickness of $1.5 \mu\text{m}$ by doctor-blading a total of three layers (annealing each layer at 450°C for 30 mins). Thickness of the thin film was determined with a Dektak³ST Surface Profile Measuring System.

Transient Absorption Spectroscopy and Time-resolved Infrared Spectroscopy

UV-visible transient absorption (TA) experiments were performed using a Helios spectrometer (HE-VIS-NIR-3200, Ultrafast Systems) at the University of Sheffield, Lord Porter laser laboratory.

Briefly, a Ti:Sapphire regenerative amplifier (Spitfire ACE PA-40, Spectra-Physics) provided 800 nm pulses (40 fs FWHM, 10 KHz, 1.2 mJ). The amplifier was seeded by a Ti:Sapphire oscillator (Mai Tai, Spectra-Physics), providing 800 nm pulses (25 fs FWHM, 84 MHz). 400 nm excitation pulses were obtained by frequency-doubling the 800-nm pulse. 500 nm pump pulses (80 fs FWHM, 2.5 KHz, 0.4 μ J) were generated by a TOPAS prime, Light Conversion, which was pumped by the 800 nm (40 fs, 10 KHz, 0.5 mJ) output of the spitfire ACE. The pump pulse was passed through a mechanical chopper with a frequency of 2.5 KHz, to allow for the probing of both pumped and unpumped sample. The pump pulse was depolarized prior to sample excitation. The pump pulses were focused onto the sample cell (fused silica with an internal path length of 2 mm), to a spot diameter of ≤ 0.3 mm. Solutions were stirred using a magnetic stirrer bar. Global fitting of transient absorption data was performed with the OPTIMUS software package using a sequential model to extract the species associated spectra and corresponding lifetimes.⁶ This approach simultaneously analyses the multiple kinetic traces for the different wavelengths using a sum of exponentials function. We used the minimum number of components required to give a good fit (i.e. minimisation of residuals).

In all experiments the cell was rastered in the two dimensions orthogonal to the direction of beam propagation to minimize localized sample decomposition. Care was taken to ensure the absorption signals measured fell within the linear region of pump laser intensity.

S2. Characterization Data for Photocatalysts

NMR spectroscopy and mass spectrometry

[Ru(bpy)(dceb)(bpt)](PF₆)

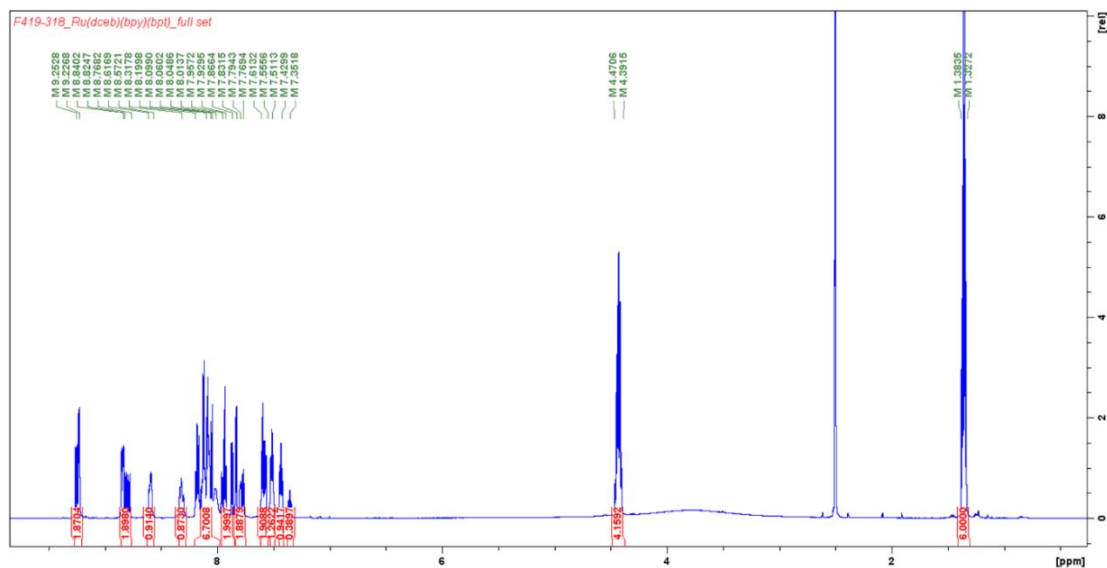


Figure SC 2. ¹H-NMR spectrum of [Ru(dceb)(bpy)(bpt)](PF₆) in dmso-d₆.

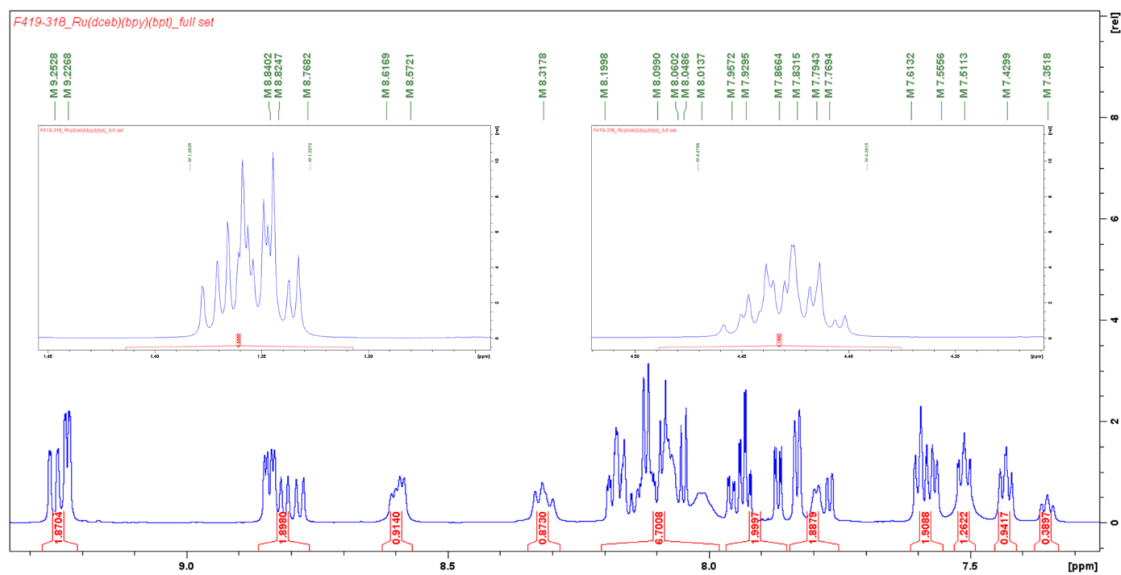


Figure SC 3. ¹H-NMR spectrum of [Ru(dceb)(bpy)(bpt)](PF₆) in dmso-d₆. The signals for the ester moieties are shown in the insets.

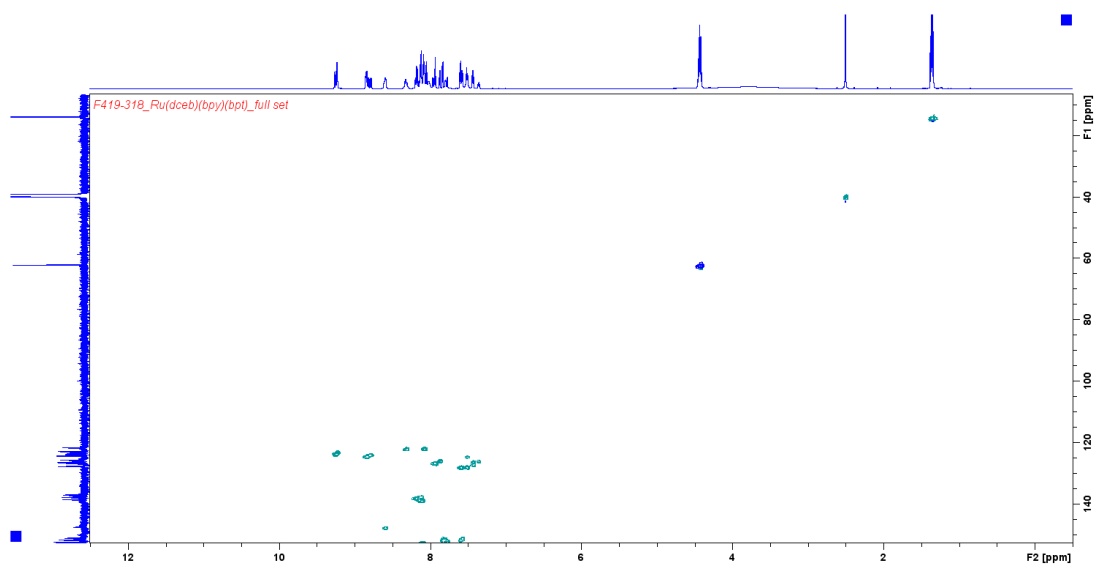


Figure SC 6. HSQC spectrum of $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})](\text{PF}_6)$ in dms0-d_6 .

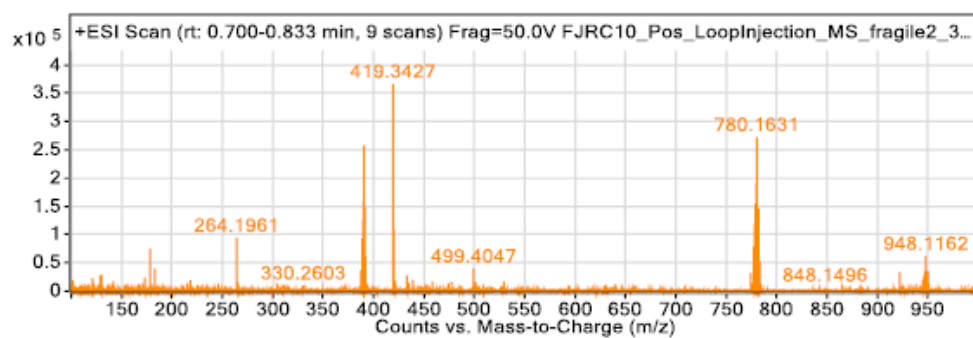


Figure SC 7. Mass spectrogram for $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})](\text{PF}_6)$. $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})]^{1+}$ calculated $m/z = 780.162$, found = 780.163. $[\text{Ru}(\text{dceb})(\text{bpy})(\text{Hbpt})]^{2+}$, calculated $m/z = 390.585$, found 390.585

$[\text{Ru}(\text{bpy})(\text{dcb})(\text{Hbpt})](\text{PF}_6)_2$ (PC3)



Figure SC 10. Mass spectrogram for $\text{Ru}(\text{dcb})(\text{bpy})(\text{Hbpt})](\text{PF}_6)_2$. $[\text{Ru}(\text{dcb})(\text{bpy})(\text{Hbpt})]^{2+}$ calculated $m/z = 362.555$, found = 362.554. $[\text{Ru}(\text{dcb})(\text{bpy})(\text{bpt})]^+$ calculated $m/z = 724.100$, found = 724.100

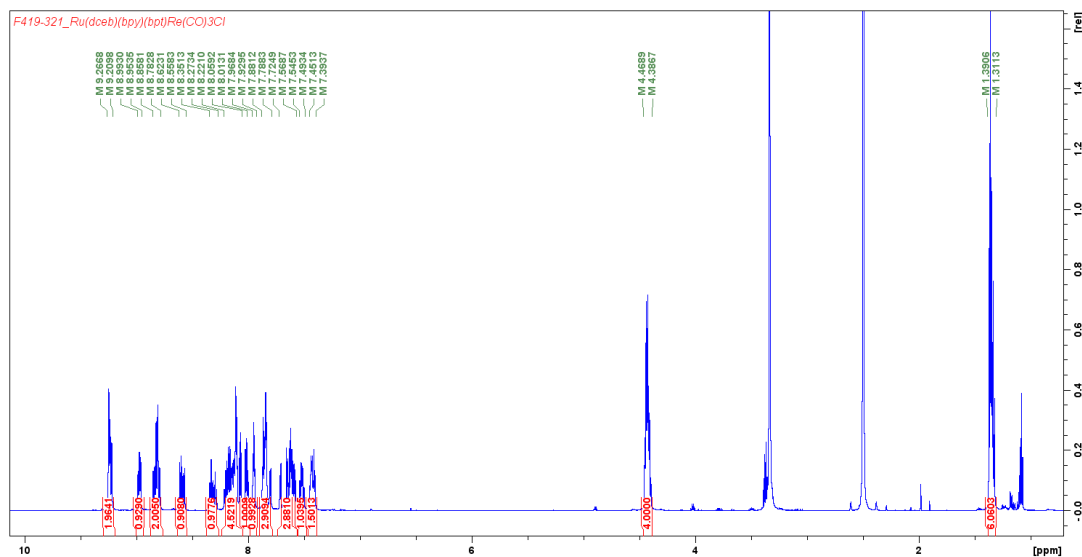


Figure SC 11. ^1H -NMR of $[\text{Ru}(\text{bpy})(\text{dceb})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ in dmsd_6 . Some residual ether was observed at 1.084 and 3.375 ppm.

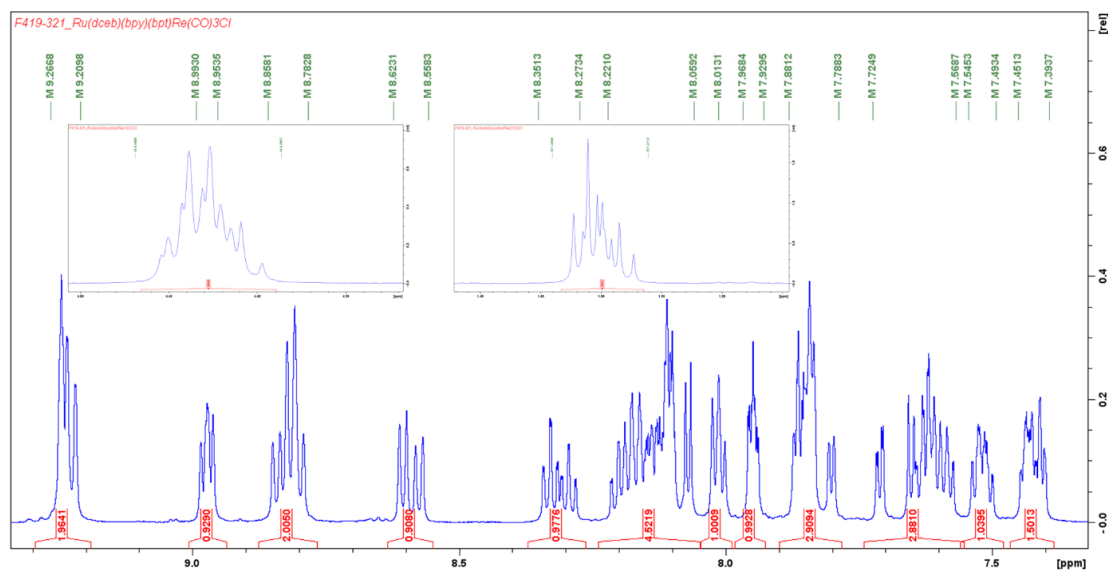


Figure SC 12. ^1H -NMR spectrum of $[\text{Ru}(\text{bpy})(\text{dceb})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ in dmsd_6 . The ester moieties are shown in the insets.

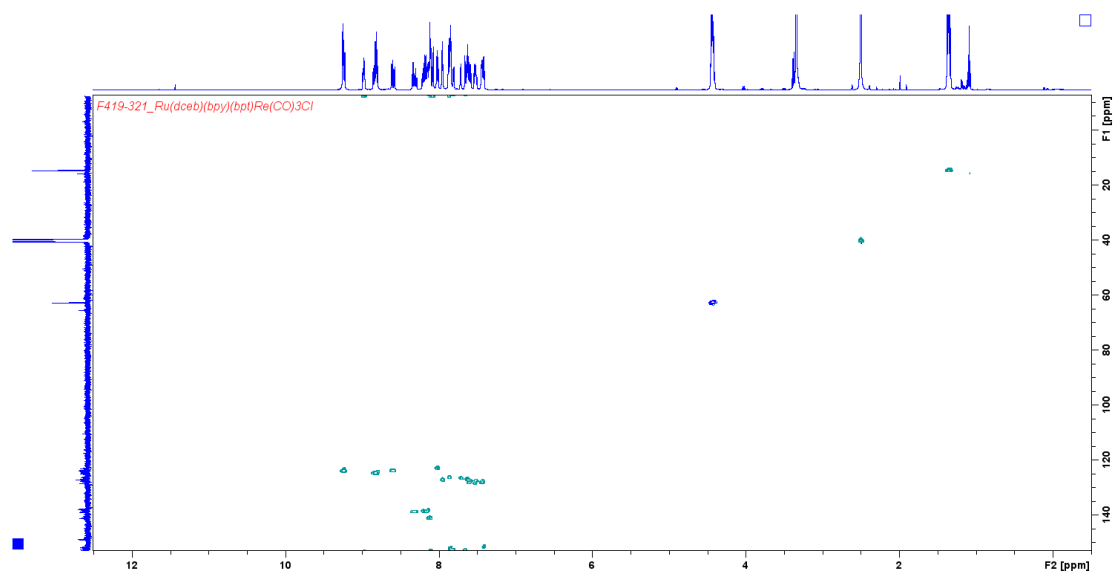


Figure SC 15. HSQC spectrum of $[Ru(bpy)(dceb)(bpt)Re(CO)_3Cl](PF_6)$ in $dmsd_6$.

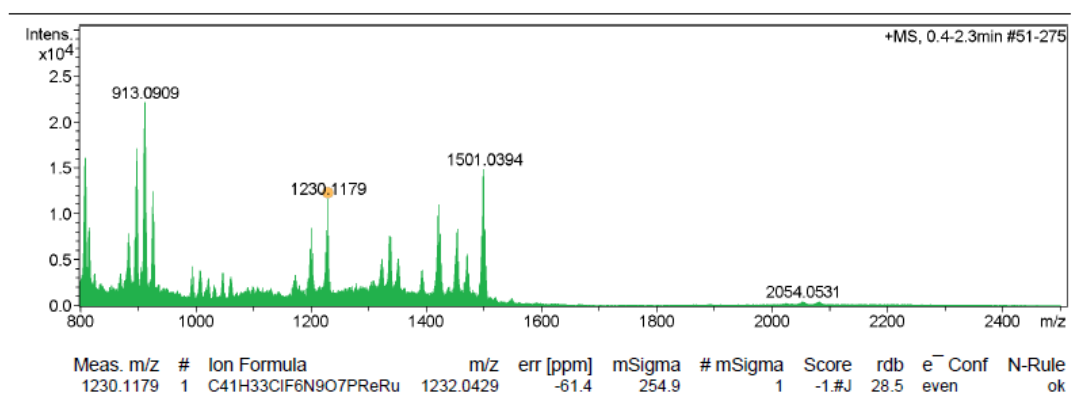


Figure SC 16. Mass spectrogram for $[Ru(bpy)(dceb)(bpt)Re(CO)_3Cl](PF_6)$. $[Ru(dceb)(bpy)(bpt)Re(CO)_3Cl-H]^{-1}$
calculated m/z 1230.027 found 1230.1179

[Ru(bpy)(dcb)(bpt)Re(CO)₃Cl](PF₆) (PC1)

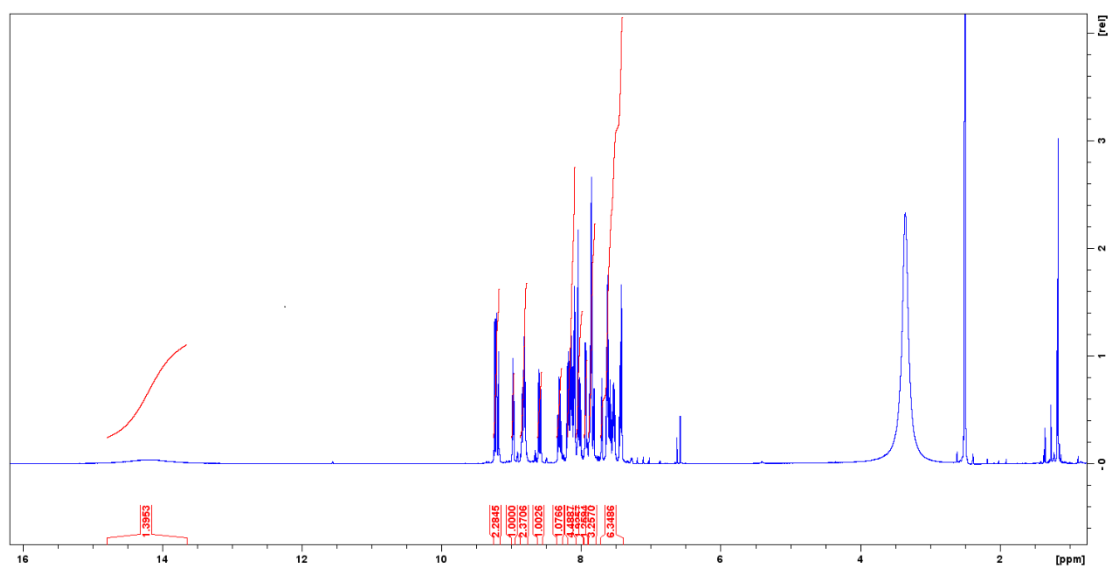


Figure SC 17. ¹H-NMR of [Ru(bpy)(dcb)(bpt)Re(CO)₃Cl](PF₆) in dmsd-d₆.

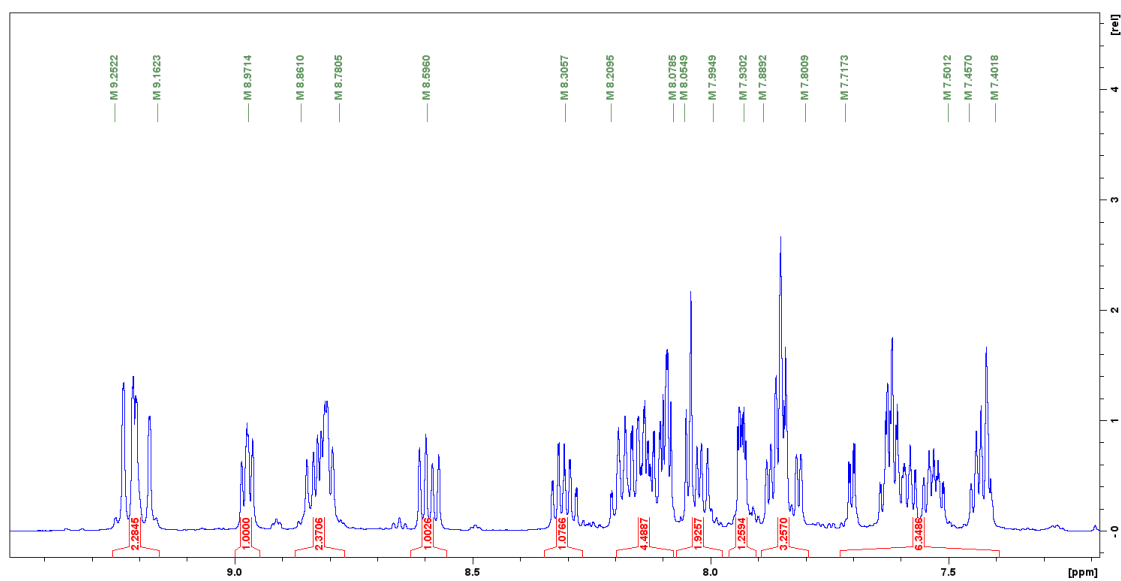


Figure SC 18. ¹H-NMR of [Ru(bpy)(dcb)(bpt)Re(CO)₃Cl](PF₆) in dmsd-d₆. Close up of the aromatic region.

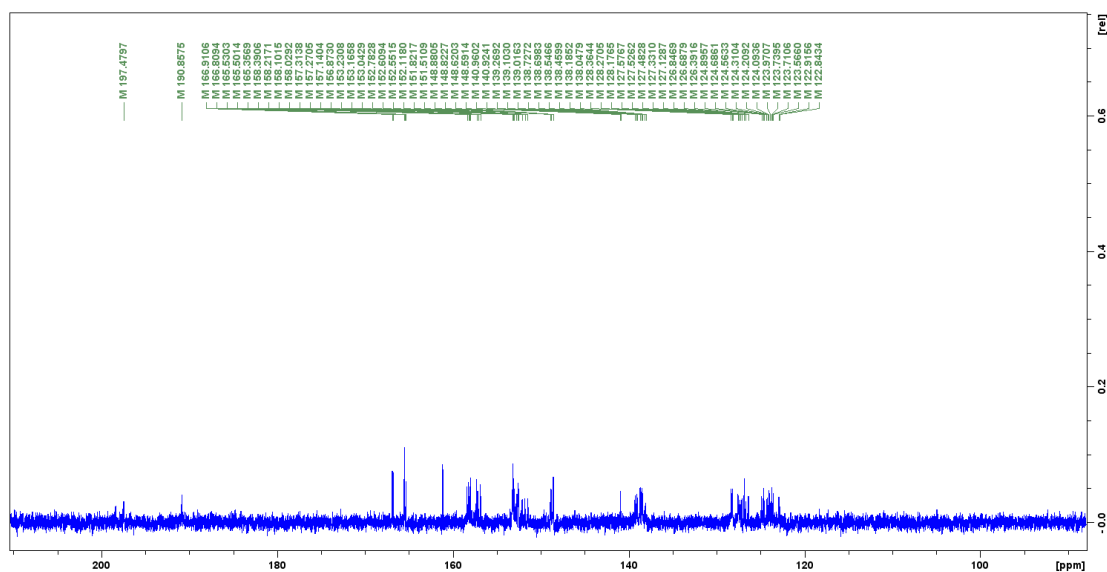


Figure SC 19. ^{13}C -NMR of $[\text{Ru}(\text{bpy})(\text{dcb})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ in dmsd-d_6 .

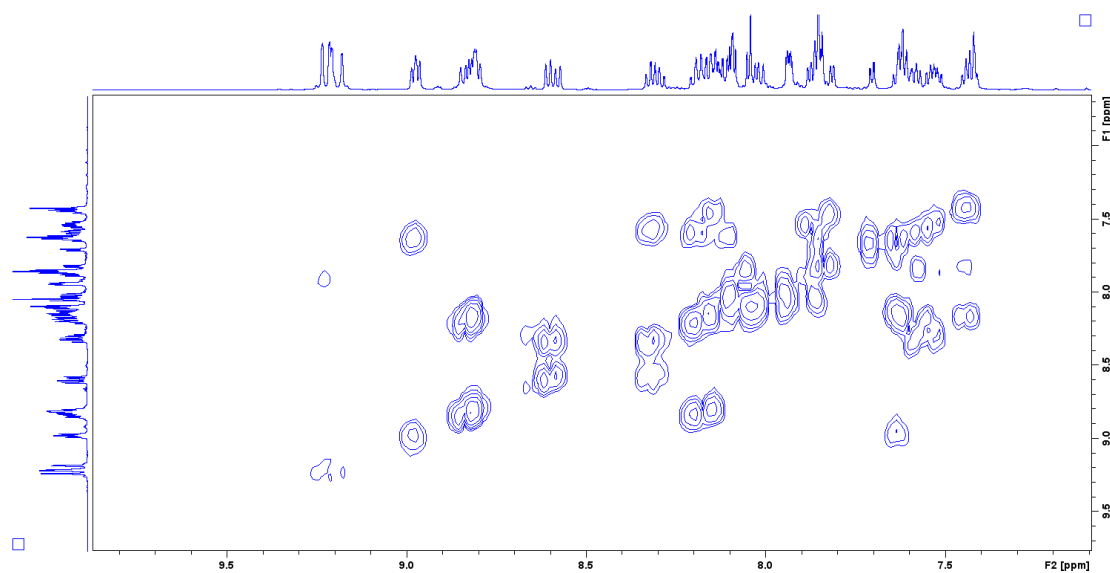
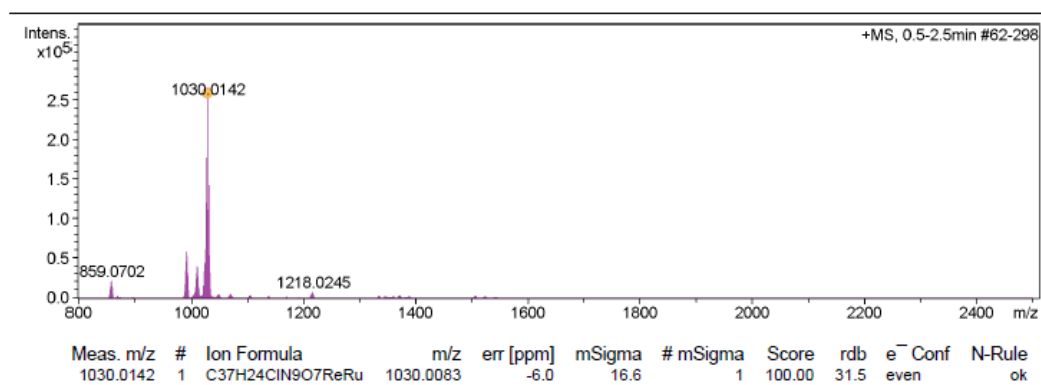


Figure SC 20. COSY spectrum of $[\text{Ru}(\text{bpy})(\text{dcb})(\text{bpt})\text{Re}(\text{CO})_3\text{Cl}](\text{PF}_6)$ in dmsd-d_6 .



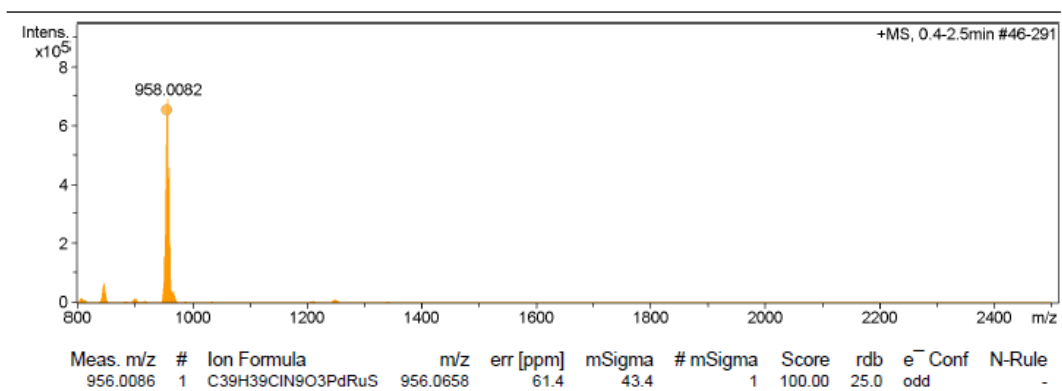


Figure SC 24. Mass spectrogram for $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{PdCl}_2](\text{PF}_6)$. $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{PdCl}_2]^{1+}$ calculated m/z = 956.003, found = 956.008.

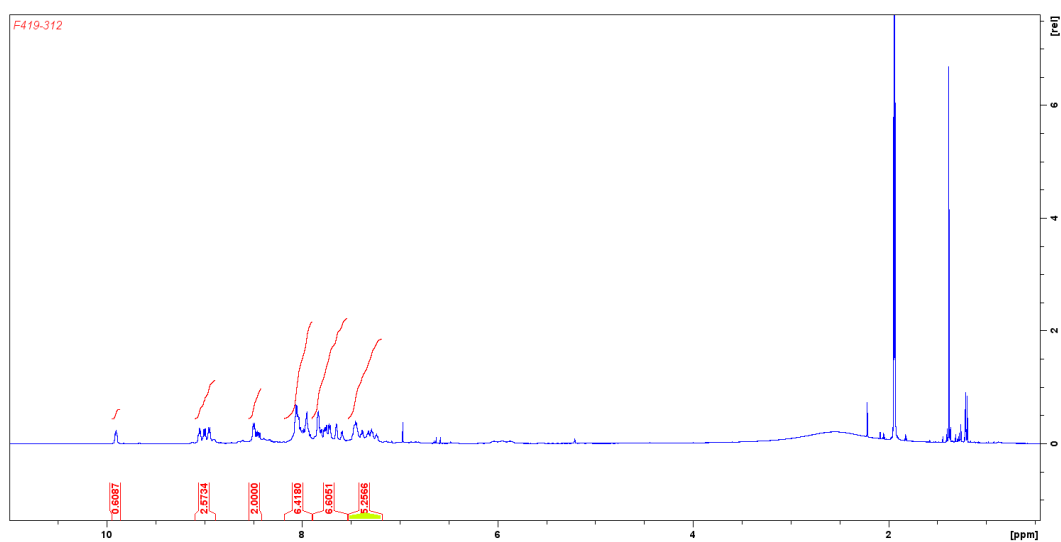
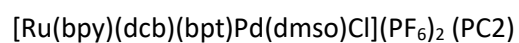


Figure SC 25. ^1H -NMR of $[\text{Ru}(\text{bpy})(\text{dcb})(\text{bpt})\text{PdCl}_2](\text{PF}_6)$ in acetonitrile- d_3

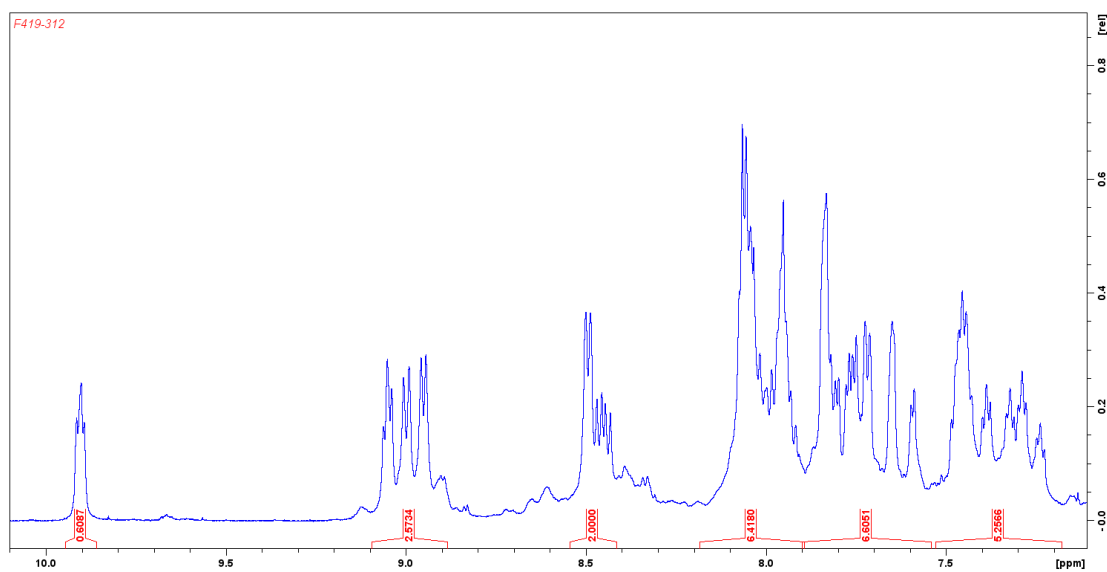


Figure SC 26. ^1H -NMR of $[\text{Ru}(\text{bpy})(\text{dcb})(\text{bpt})\text{PdCl}_2](\text{PF}_6)$ in acetonitrile- d_3 . Zoom in of the aromatic region.

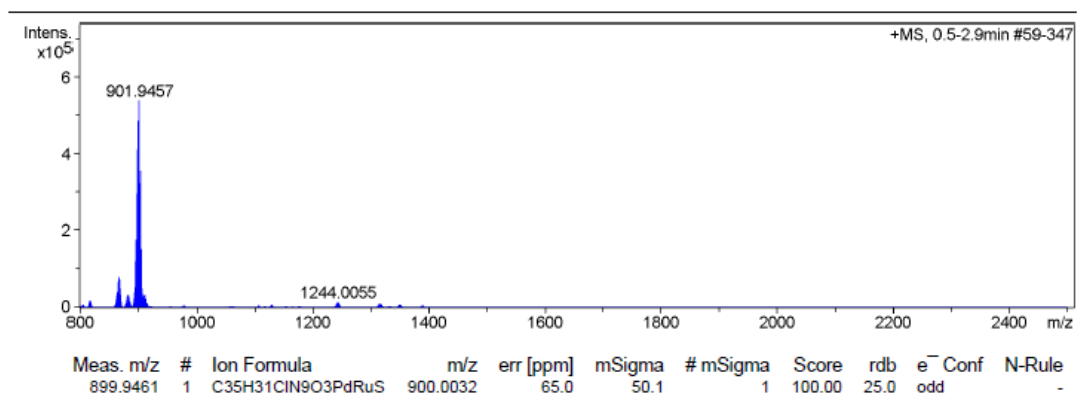


Figure SC 27. Mass spectrogram for $[\text{Ru}(\text{dceb})(\text{bpy})(\text{bpt})\text{PdCl}_2](\text{PF}_6)$. $[\text{Ru}(\text{dcb})(\text{bpy})(\text{bpt})\text{PdCl}_2]^{1+}$ calculated $m/z = 899.941$ found 899.946.

FTIR Spectra

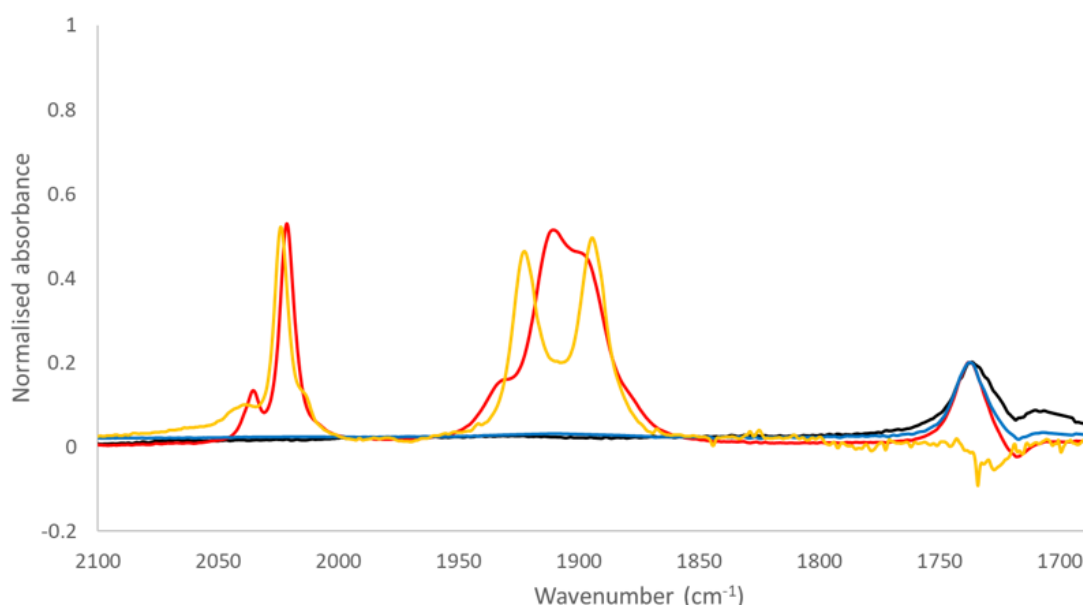


Figure SC 28. FTIR spectra of [Ru(dcb)(bpy)(Hbpt)](PF₆)₂ (black), [Ru(dcb)(bpy)(bpt)Re(CO)₃Cl](PF₆) (red), [Ru(dcb)(bpy)(bpt)PdCl₂](PF₆) (blue) and the model complex Re(Hbt)(CO)₃Cl complex in THF (yellow). Due to low solubility of this complex the FTIR spectrum was recorded in THF instead of MeCN.

UV-visible Absorption Spectroscopy

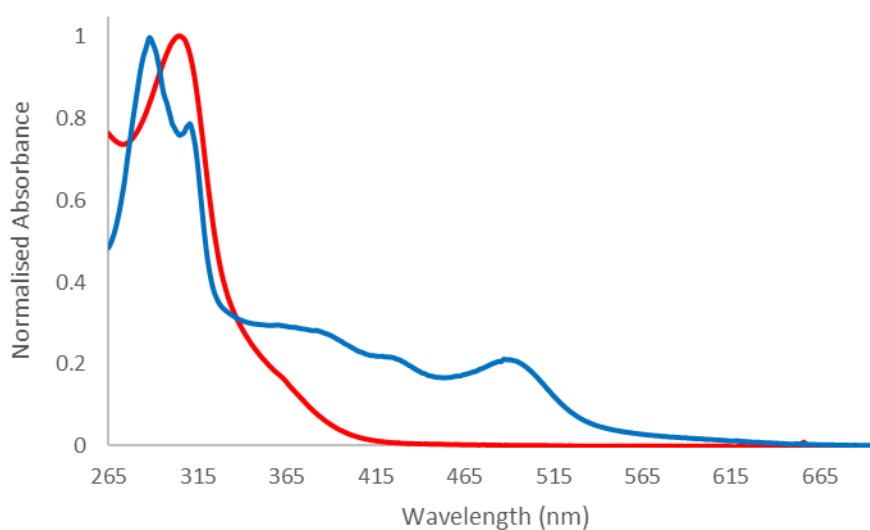


Figure SC 29. Normalised UV-Vis spectra for PC1 (blue) and Re(Hbpt)(CO)₃Cl (red) in acetonitrile.

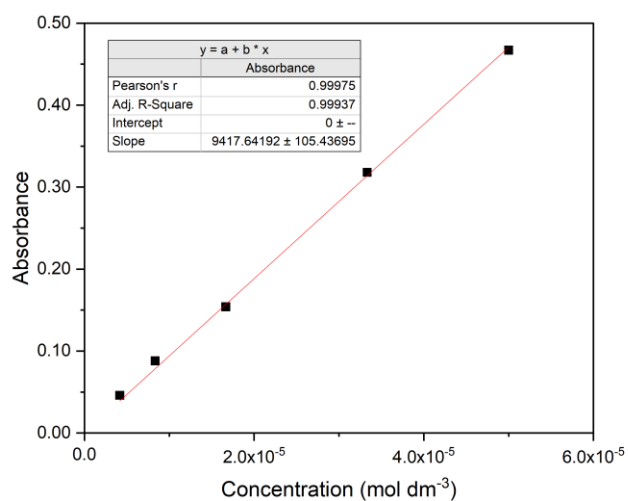


Figure SC 30. Beer-Lambert plot for PC1 in acetonitrile solution recorded at 470 nm.

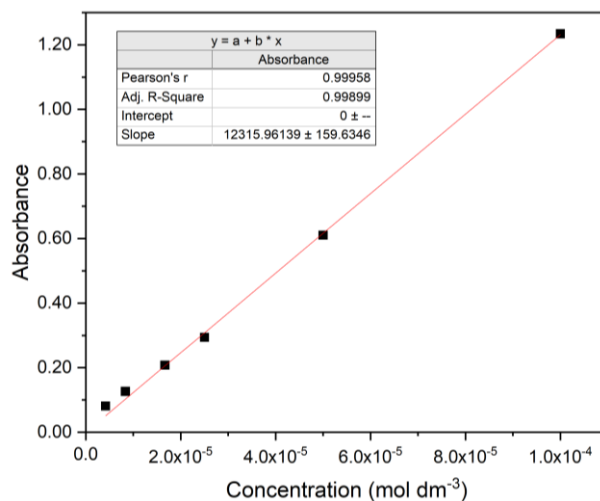


Figure SC 31. Beer-Lambert plot for PC2 in acetonitrile solution recorded at 474 nm.

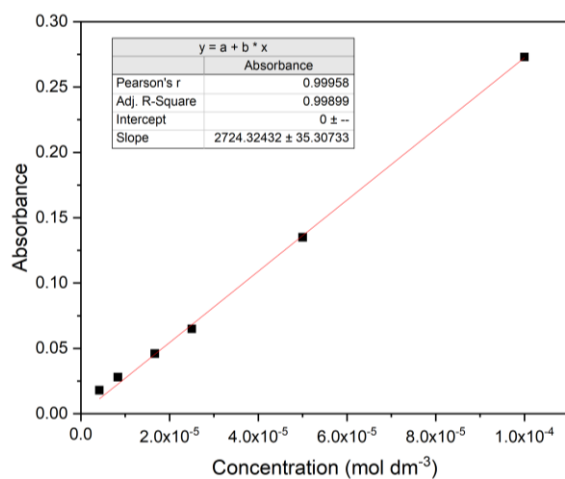


Figure SC 32. Beer-Lambert plot for PC3 in acetonitrile solution recorded at 490 nm.

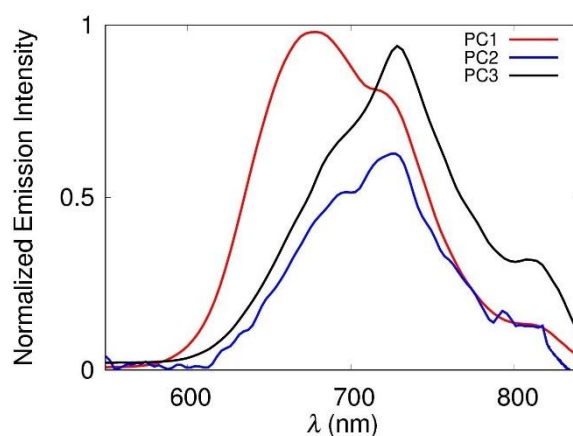


Figure SC 33. Emission spectra for the photocatalysts in optically thin (<0.1 abs at excitation wavelength) acetonitrile solution following illumination at 460 nm. Emission spectra were recorded with a Hitachi F-4500 spectrophotometer.

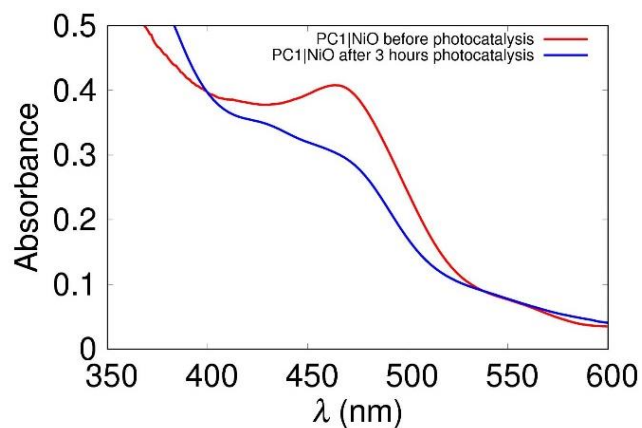


Figure SC 34. UV-visible absorption spectrum of photocatalyst PC1|NiO before and after three hours 1 sun irradiation with AM 1.5 filtered light in a photoelectrochemical cell saturated with CO_2 and an applied external bias of -0.5 V vs Ag/AgCl, in a 0.1 M pH 5 acetate buffer.

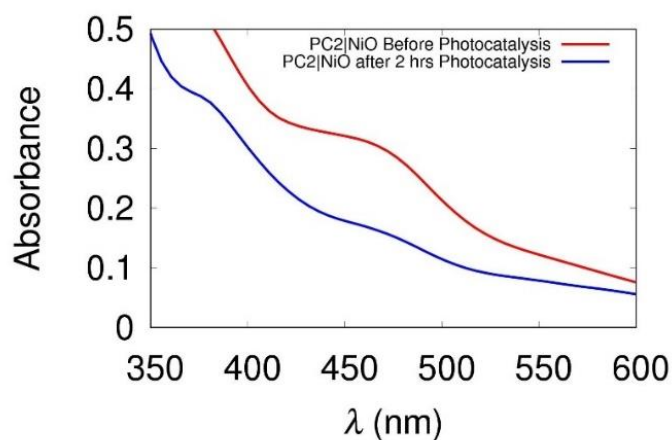


Figure SC 35. UV-visible absorption spectrum of photocatalyst PC2/NiO before and after two hours 1 sun irradiation with AM 1.5 filtered light in a photoelectrochemical cell saturated with Ar and an applied external bias of -0.5 V vs Ag/AgCl, in a 0.1 M pH 5 acetate buffer.

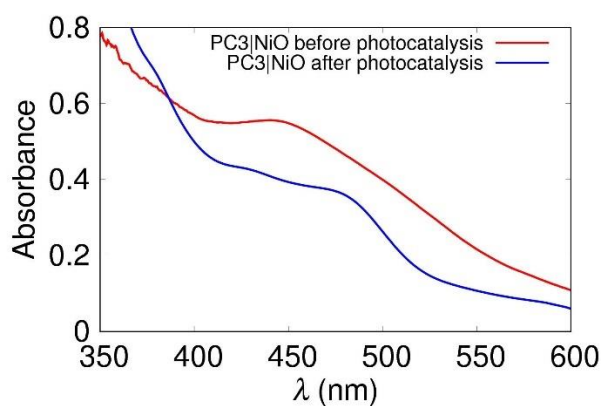


Figure SC 36. UV-visible absorption spectrum of photocatalyst PC3/NiO before and after three hours 1 sun irradiation with AM 1.5 filtered light in a photoelectrochemical cell saturated with CO_2 and an applied external bias of -0.5 V vs Ag/AgCl in a 0.1 M pH 5 acetate buffer.

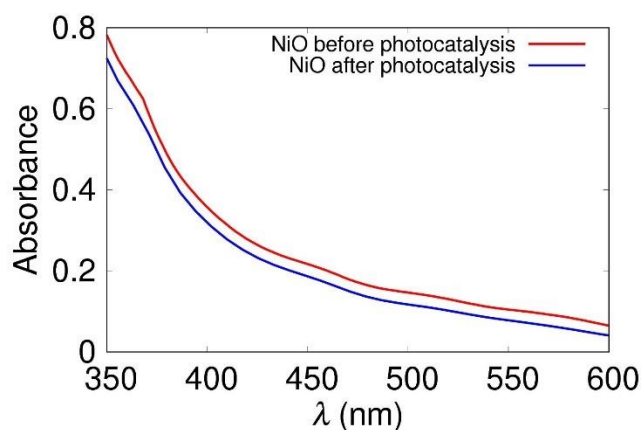


Figure SC 37. UV-visible absorption spectrum of an unsensitized NiO film before and after three hours 1 sun irradiation with AM 1.5 filtered light in a photoelectrochemical cell saturated with CO_2 and an applied external bias of -0.5 V vs Ag/AgCl in a 0.1 M pH 5 acetate buffer.

Electrochemistry

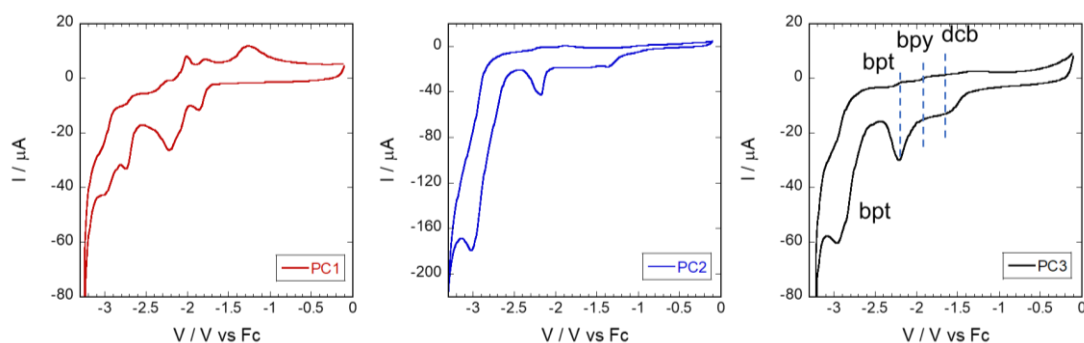


Figure SC 38. Cyclic voltammogram for PC1-3 in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, 100 mV s⁻¹ scan rate.

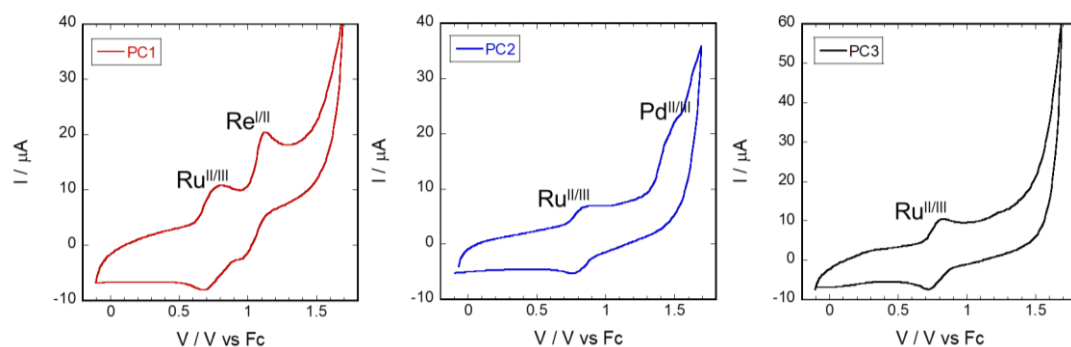


Figure SC 39. Cyclic voltammogram for PC1-3 in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, 100 mV s⁻¹ scan rate.

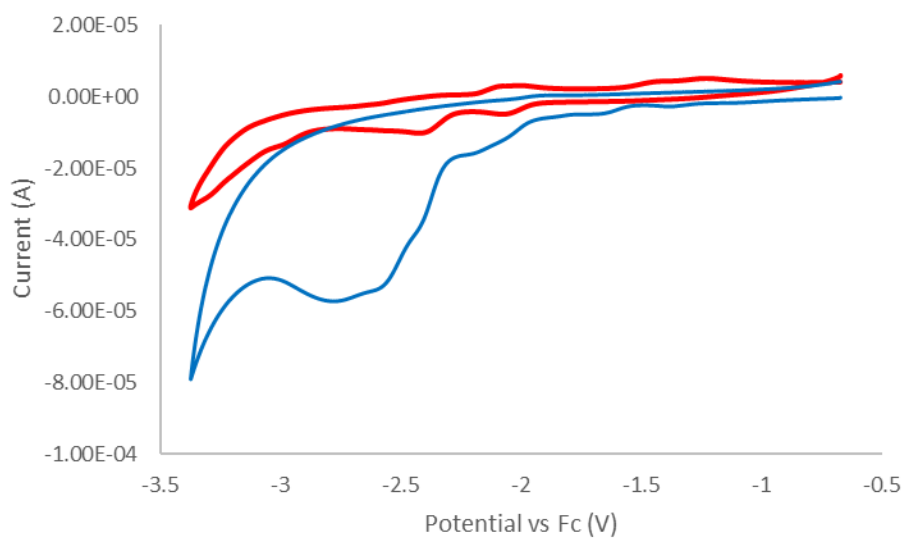


Figure SC 40. Cyclic voltammogram of PC1 in DMF with 0.1 M TBAPF₆ as supporting electrolyte following bubbling with N₂ (red) and CO₂ (blue).

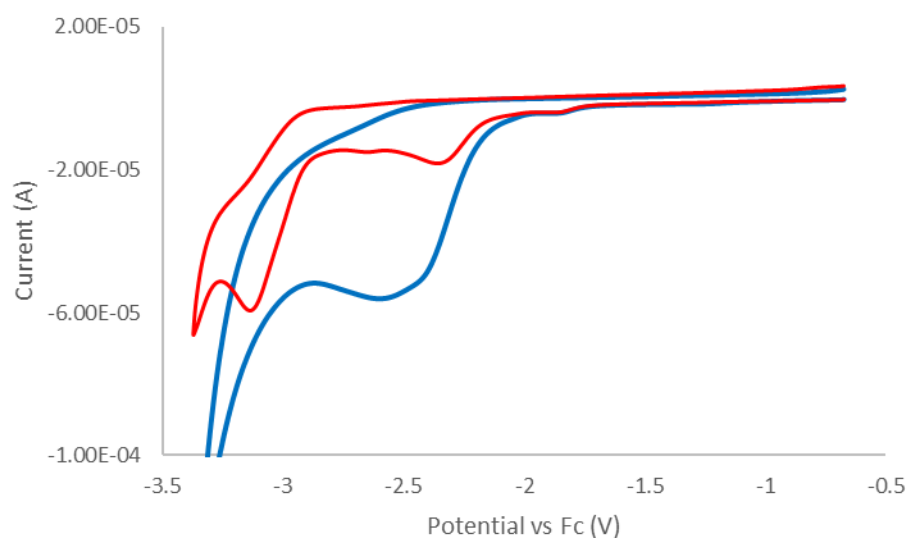


Figure SC 41. Cyclic voltammogram of $\text{Re}(\text{HBpt})(\text{CO})_3\text{Cl}$ in DMF with 0.1 M TBAPF_6 as supporting electrolyte following bubbling with N_2 (red) and CO_2 (blue).

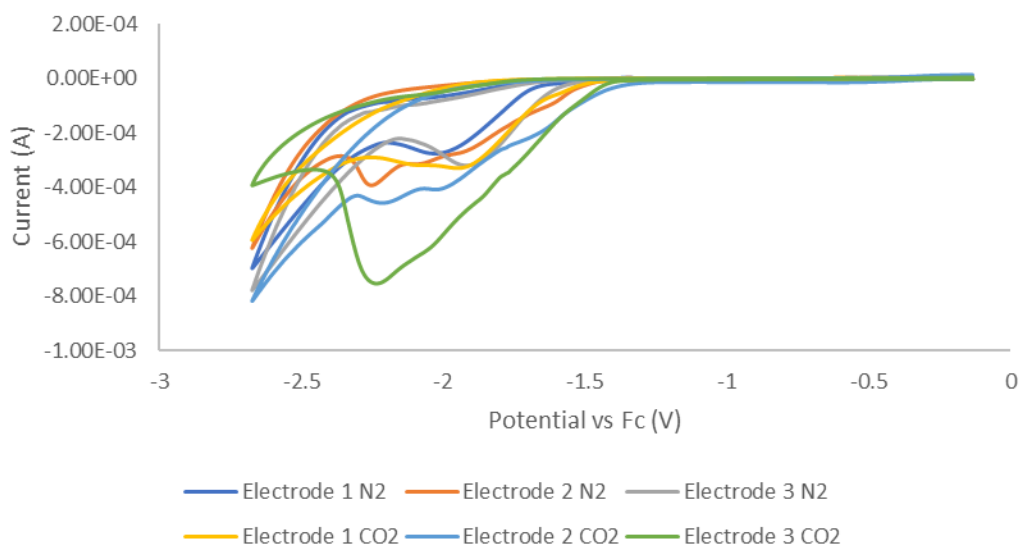
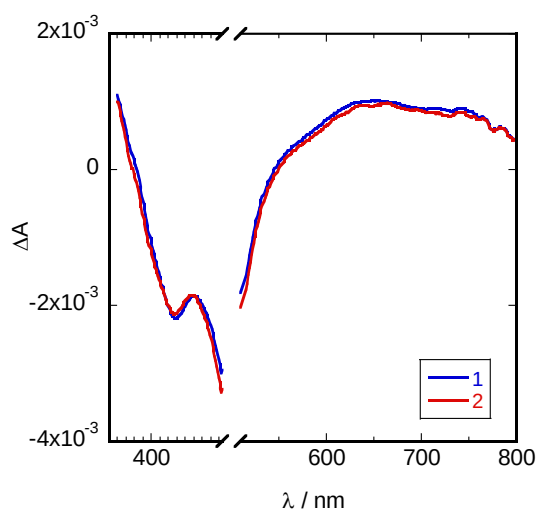
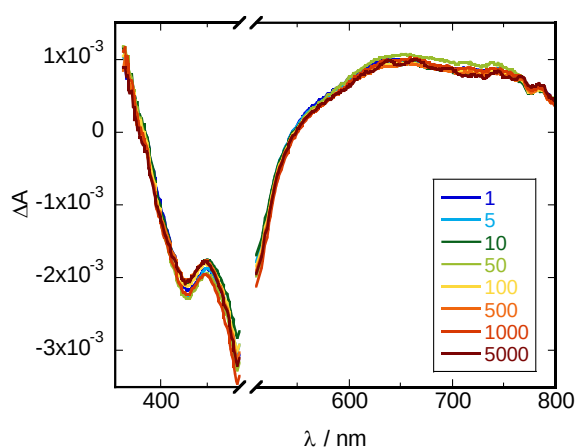


Figure SC 42. Cyclic voltammograms of RuRe dropcast on glassy carbon electrodes.

We attempted to mimic the photoelectrochemical experimental setup by dropcasting 10 mM solutions of PC1 in DMSO on glassy carbon electrodes. The electrodes were left to dry over night to form a homogeneous film of the catalyst on the electrode surface. The electrodes were tested in pH 5 buffered solutions of acetic acid/sodium acetate bubbled with nitrogen or carbon dioxide, identical to the experiments conducted for the photoelectrochemical studies on NiO. Unfortunately, rapid desorption of the catalyst layer was observed when the electrocatalysis was started. This rapid desorption made accurate determination of CO_2 reduction by a thin film of catalyst impossible. As seen in the main text, desorption of the catalyst did not occur as readily for the NiO surfaces. Potentially, the stronger interaction including covalent bonding

through pendant hydroxyl moieties on the NiO result in a stronger interaction between the catalyst and the NiO surface compared to that between the catalyst and the glassy carbon surface. Furthermore, the potentials required to reduce CO_2 electrochemically in these dropcast experiments are significantly higher than those employed for the photoelectrochemical studies on NiO. During the dropcast experiment, hydrogen formation was observed catalysed by the glassy carbon electrode, and H_2 bubble formation likely accelerated desorption of the catalyst layer from the electrode.

S3. Transient Optical and Infrared Spectroscopy



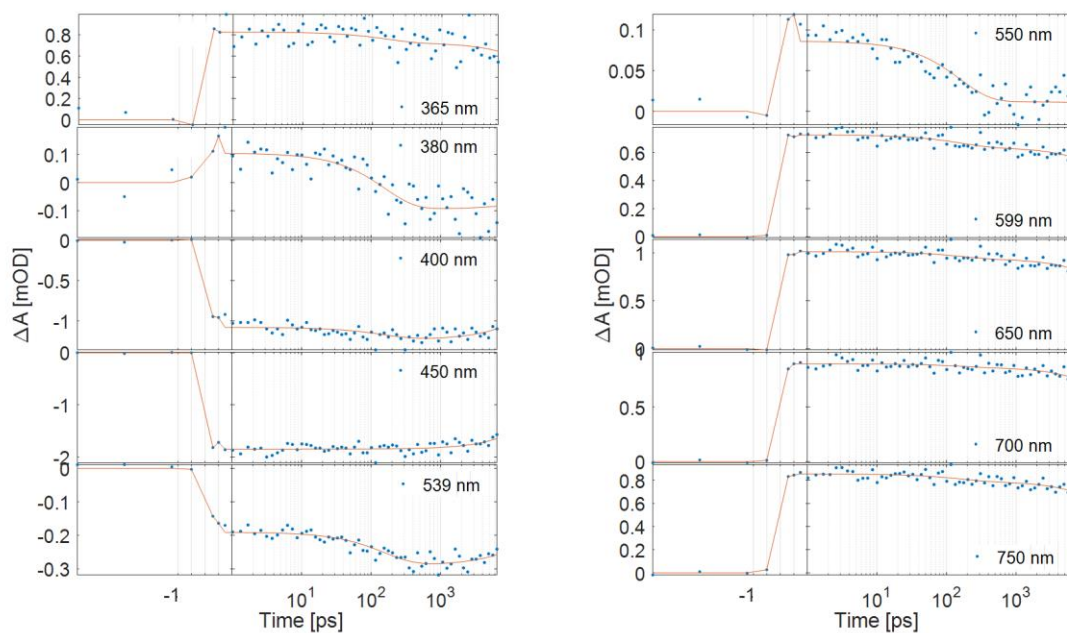
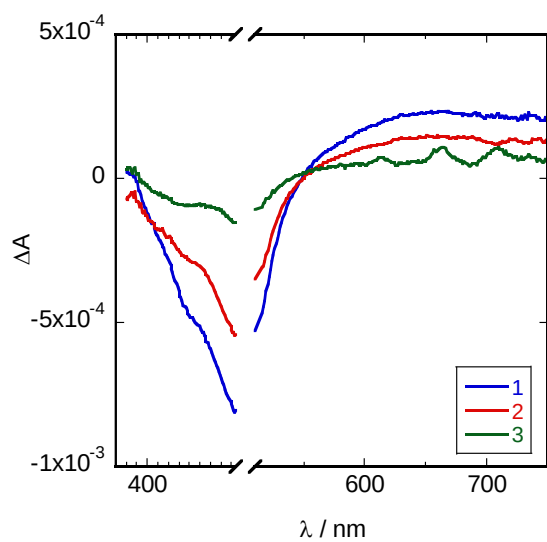
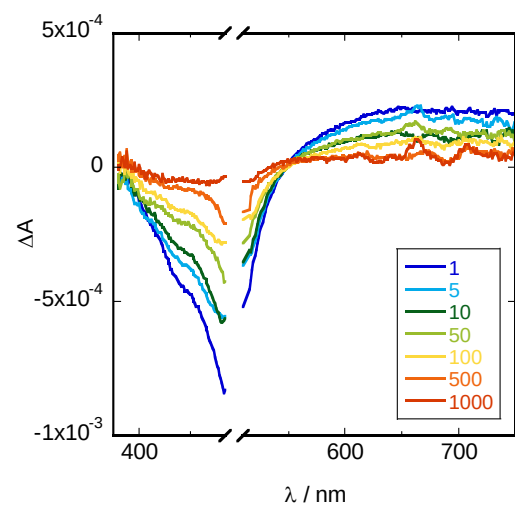


Figure SC 43. Transient absorption spectra for PC1 in acetonitrile solution with corresponding delay times in picoseconds (top left); the species associated spectra from global fitting where the numbers correspond to $1 = \tau_1 = 160$ ps, and $2 = \tau_2 \gg 1$ ns (top right); kinetic traces for selected wavelengths (bottom) with fits (orange line). The excitation wavelength was 500 nm.



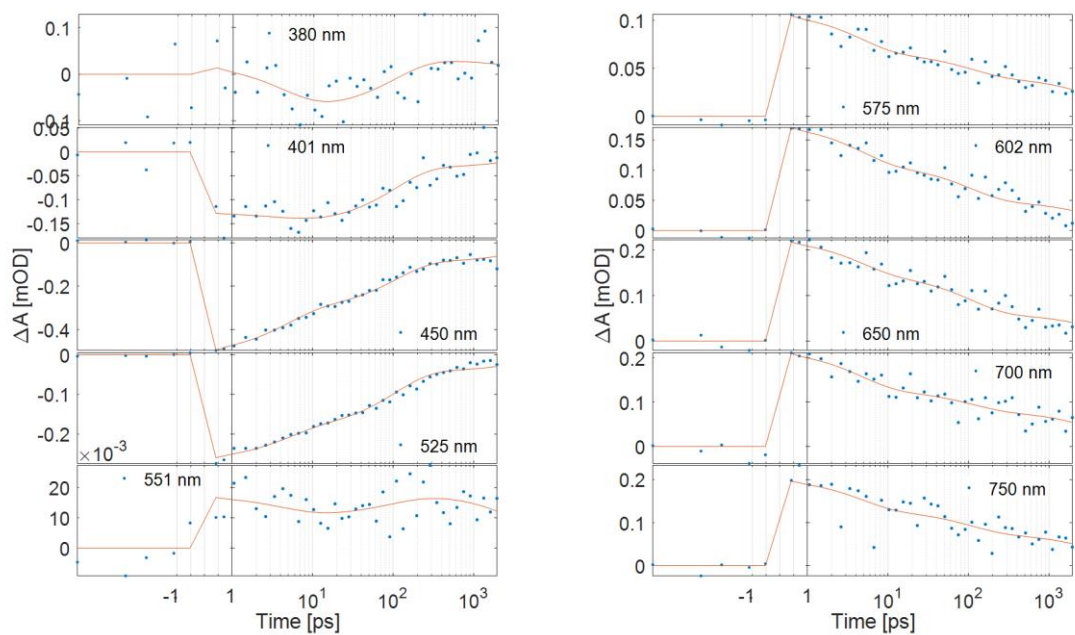
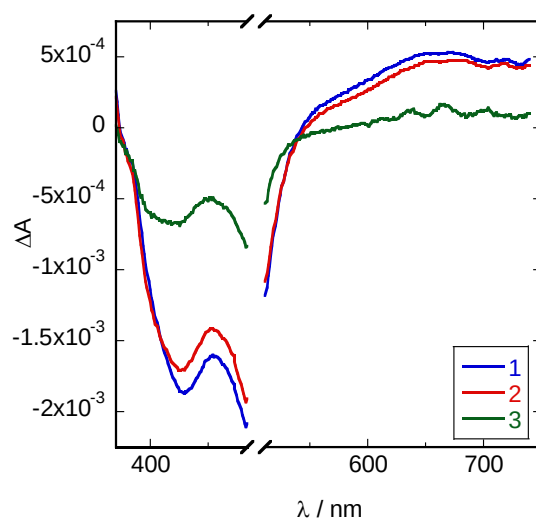
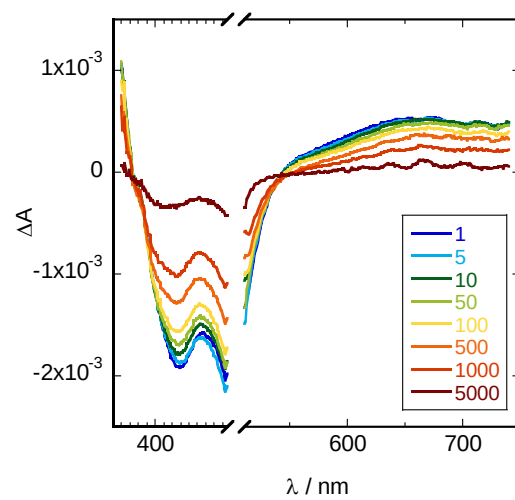


Figure SC 44 Transient absorption spectra for PC1/NiO with corresponding delay times in picoseconds (top left); the species associated spectra from global fitting where the numbers correspond to $1 = \tau_1 = 4.6$ ps, $2 = \tau_2 = 110$ ps, and $3 = \tau_3 \sim 5.1$ ns (top right); kinetic traces for selected wavelengths (bottom) with fits (orange line). The excitation wavelength was 500 nm.



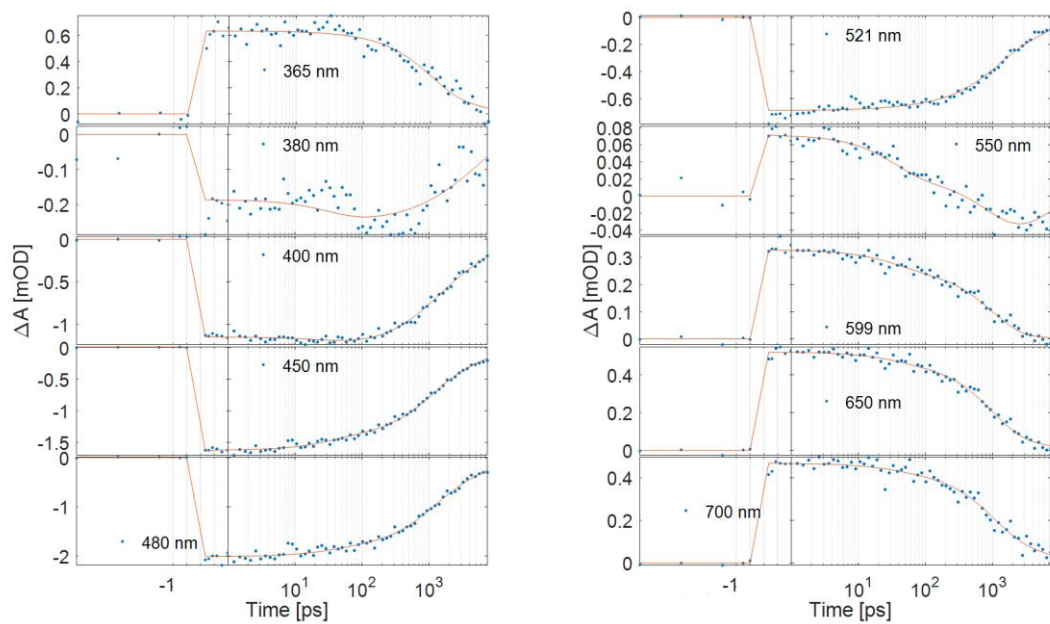
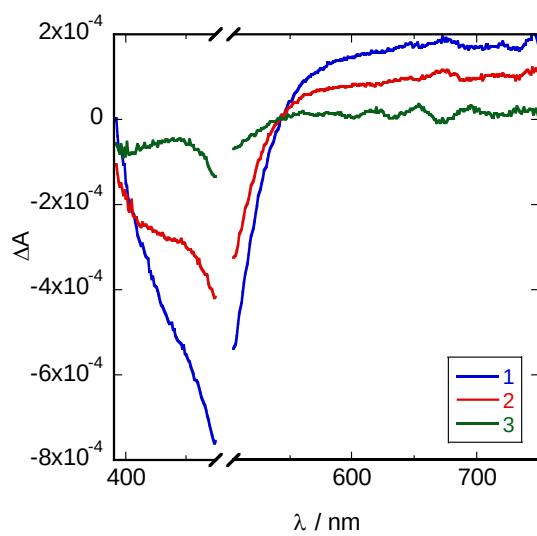
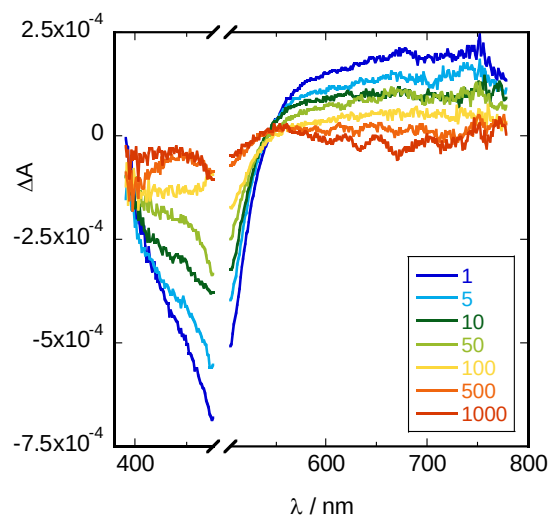


Figure SC 45. Transient absorption spectra for PC2 in acetonitrile solution with corresponding delay times in picoseconds (top left); the species associated spectra from global fitting where the numbers correspond to 1 = τ_1 = 35 ps, and 2 = τ_2 = 980 ps, 3 = τ_3 >> 1 ns (top right); kinetic traces for selected wavelengths (bottom) with fits (orange line). The excitation wavelength was 500 nm.



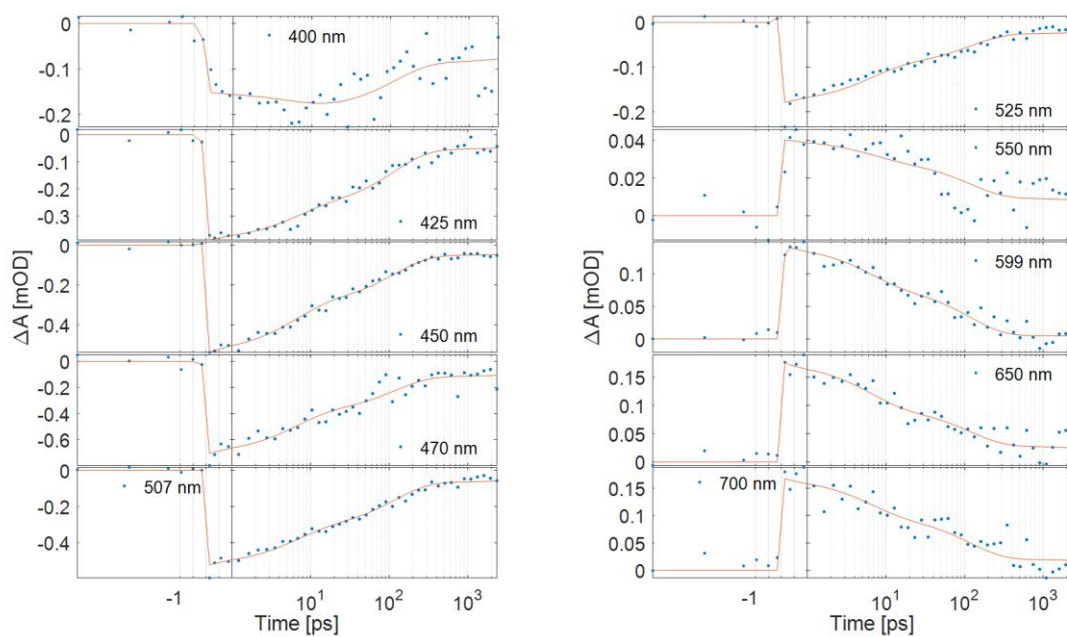
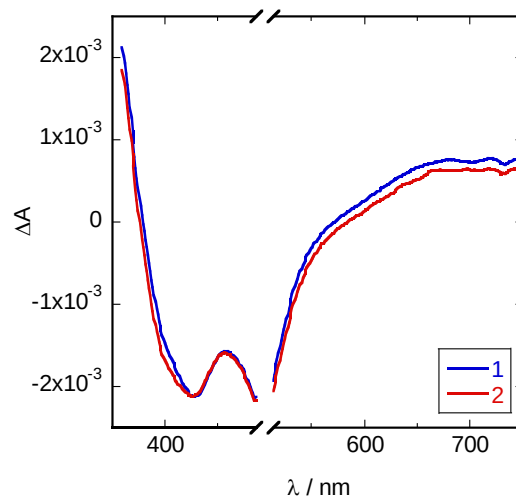
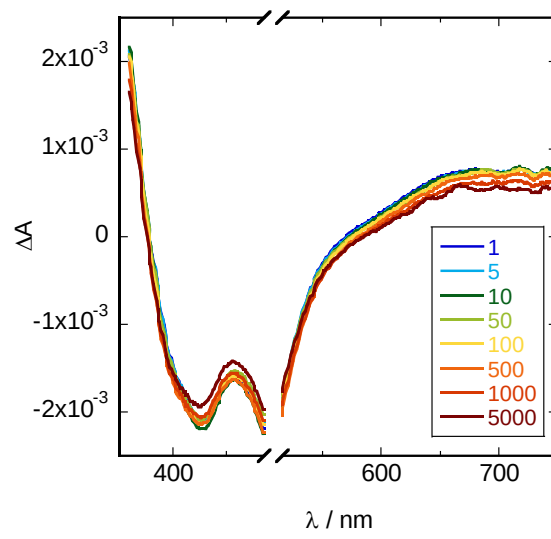


Figure SC 46. Transient absorption spectra for PC2/NiO with corresponding delay times in picoseconds (top left); the species associated spectra from global fitting where the numbers correspond to $1 = \tau_1 = 6.0$ ps, $2 = \tau_2 = 120$ ps, and $3 = \tau_3 \gg 1$ ns (top right); kinetic traces for selected wavelengths (bottom) with fits (orange line). The excitation wavelength was 490 nm.



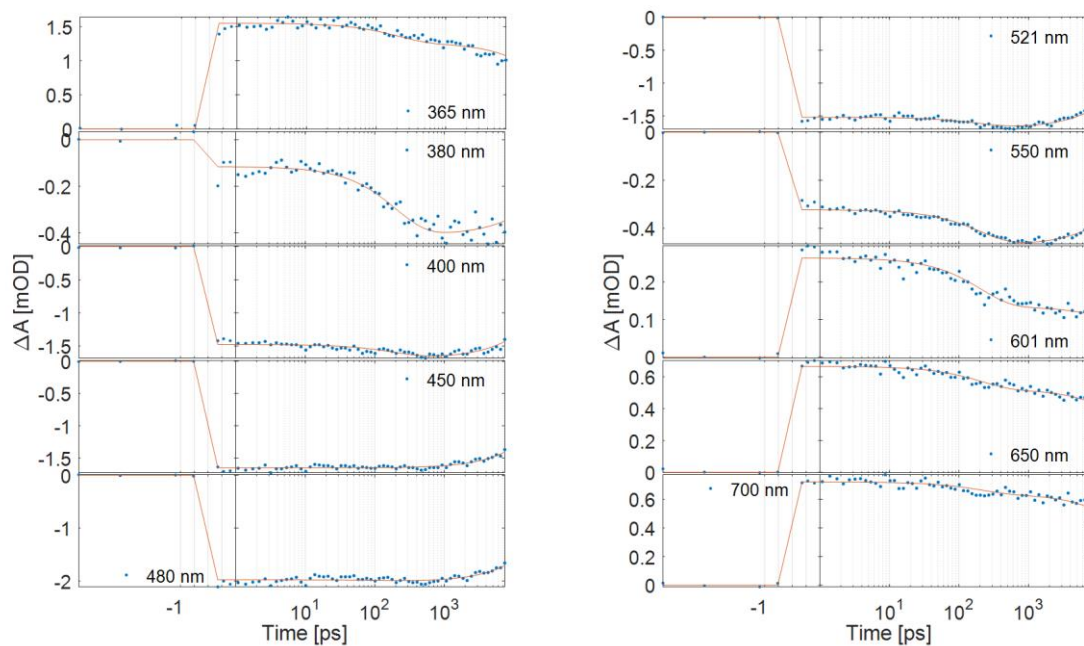
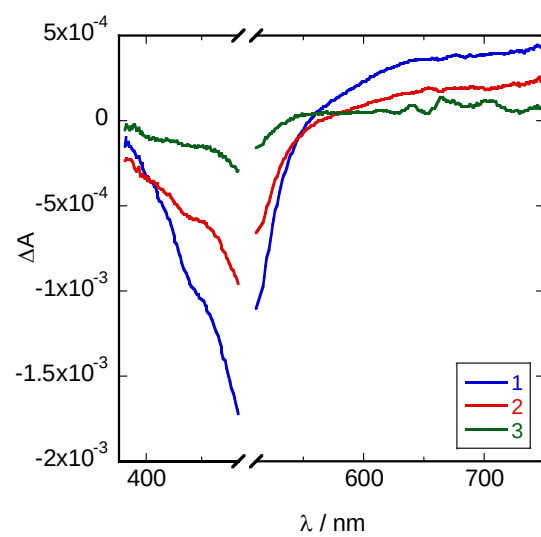
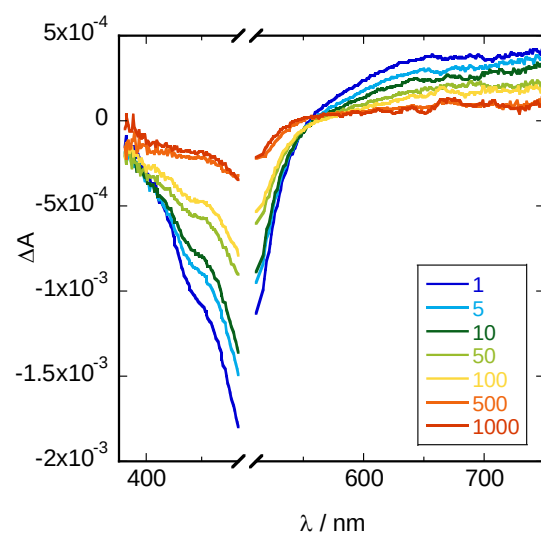


Figure SC 47. Transient absorption spectra for PC3 in acetonitrile solution with corresponding delay times in picoseconds (top left); the species associated spectra from global fitting where the numbers correspond to $1 = \tau_1 = 200$ ps, and $2 = \tau_2 \gg 1$ ns (top right); kinetic traces for selected wavelengths (bottom) with fits (orange line). The excitation wavelength was 500 nm.



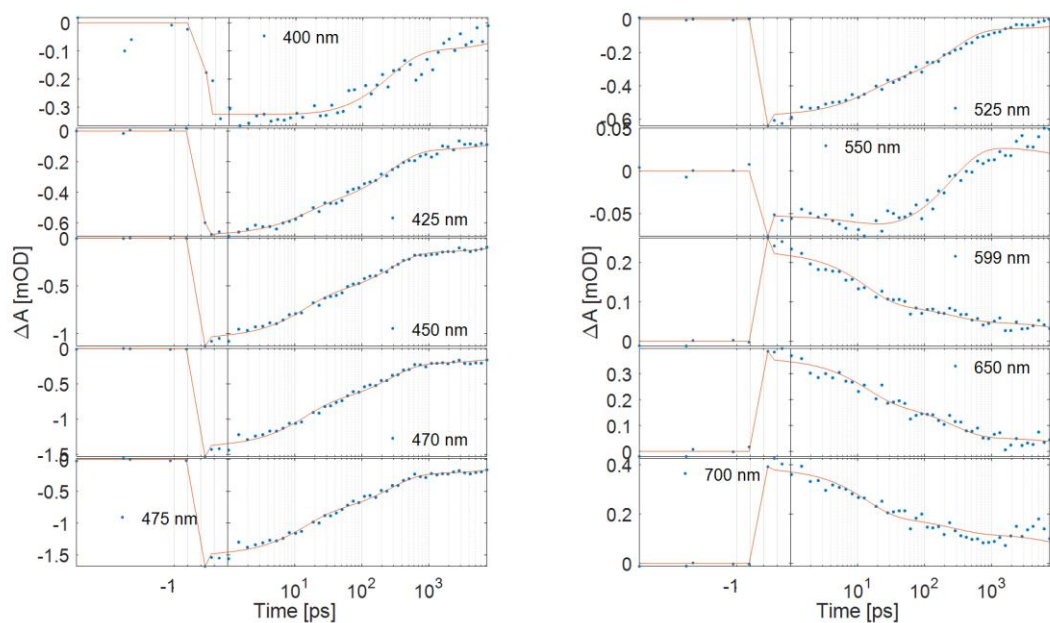


Figure SC 48. Transient absorption spectra for PC3/NiO with corresponding delay times in picoseconds (top left); the species associated spectra from global fitting where the numbers correspond to $1 = \tau_1 = 13$ ps, $2 = \tau_2 = 260$, and $3 = \tau_3 \gg 1$ ns (top right); kinetic traces for selected wavelengths (bottom) with fits (orange line). The excitation wavelength was 500 nm.

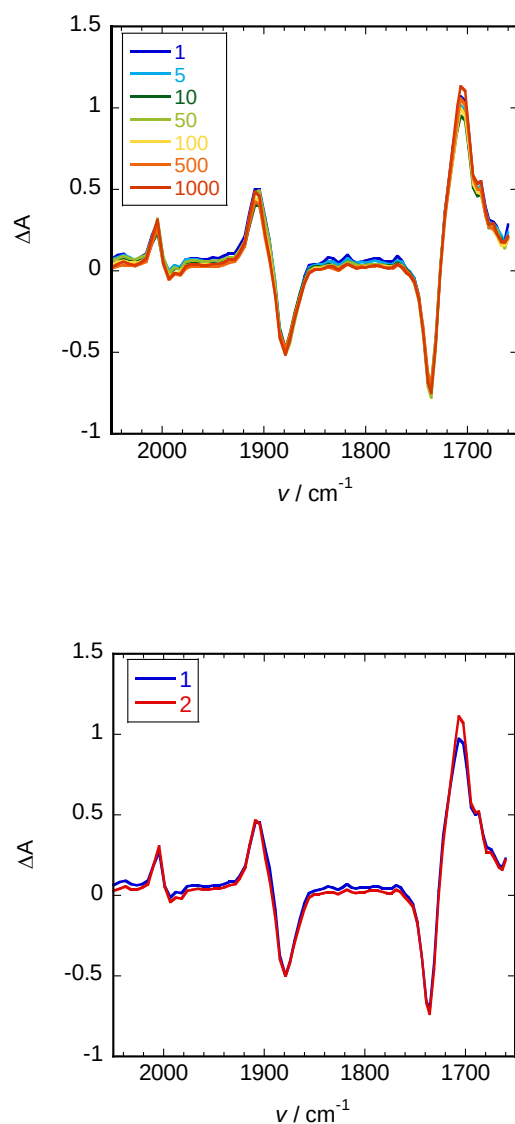


Figure SC 49. Time-resolved infrared spectra for PC1 in acetonitrile with delay times in picoseconds (left); the species associated spectra from global fitting where the numbers correspond to 1 = $\tau_1 = 130 \text{ ps}$, and 2 = $\tau_2 \gg 1 \text{ ns}$ (right). The excitation wavelength was 500 nm.

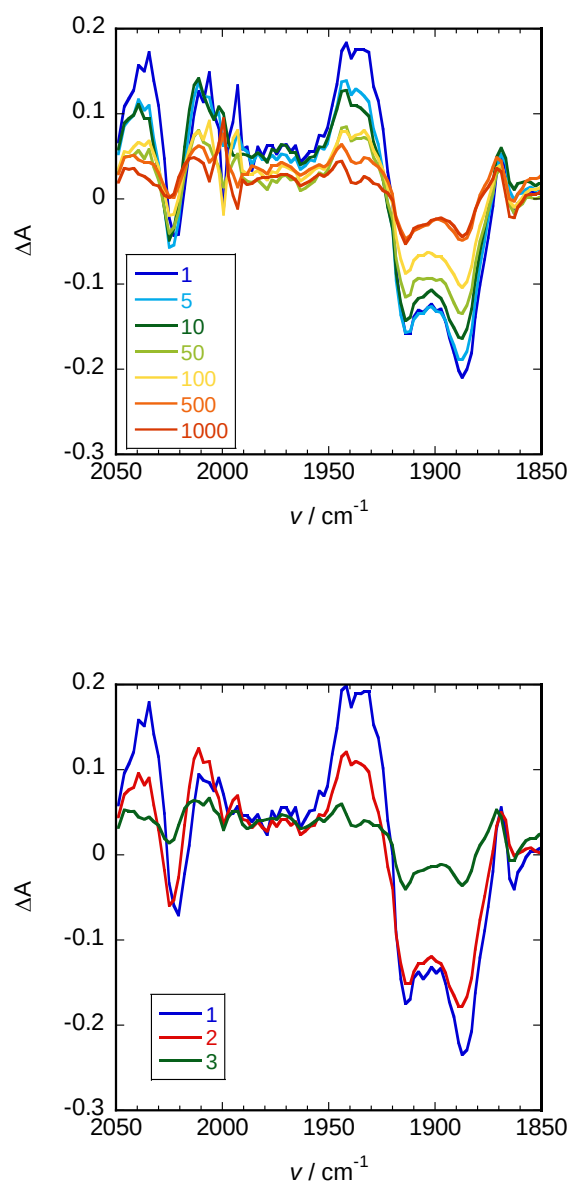


Figure SC 50. Time-resolved infrared spectra for PC1/NiO with delay times in picoseconds (left); the species associated spectra from global fitting where the numbers correspond to $1 = \tau_1 = 2.4 \text{ ps}$, $2 = \tau_2 = 150 \text{ ps}$, and $3 = \tau_3 \gg 1 \text{ ns}$ (right). The excitation wavelength was 500 nm.

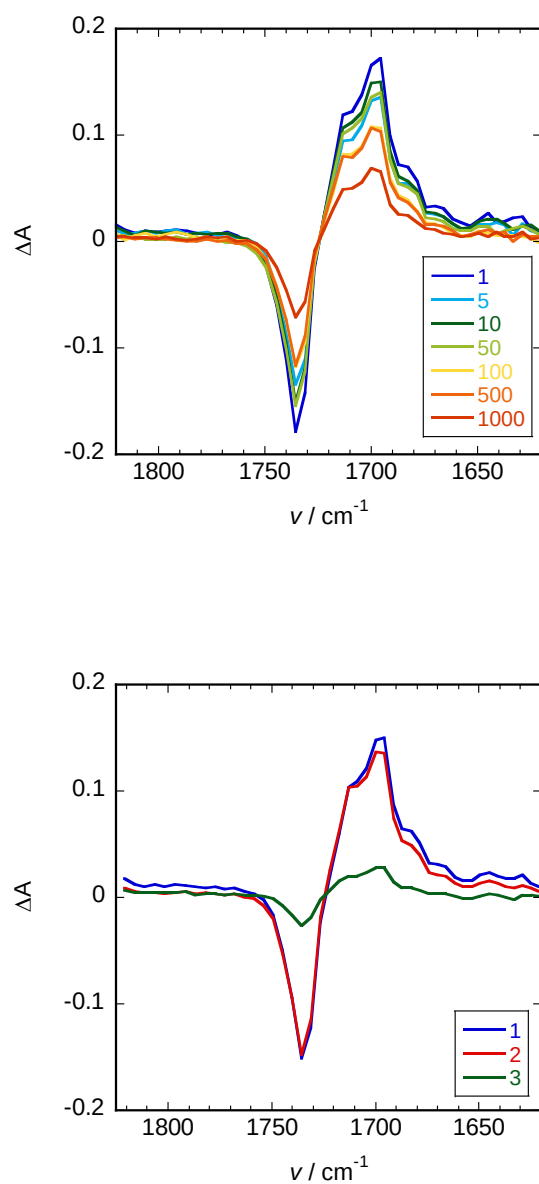


Figure SC 51. Transient infrared spectra (left) for PC2 in acetonitrile with delay times in picoseconds (left); the species associated spectra from global fitting where the numbers correspond to 1 = $\tau_1 = 22$ ps, and 2 = $\tau_2 = 1.2$ ns, 3 = $\tau_3 \gg 1$ ns (right). The excitation wavelength was 500 nm.

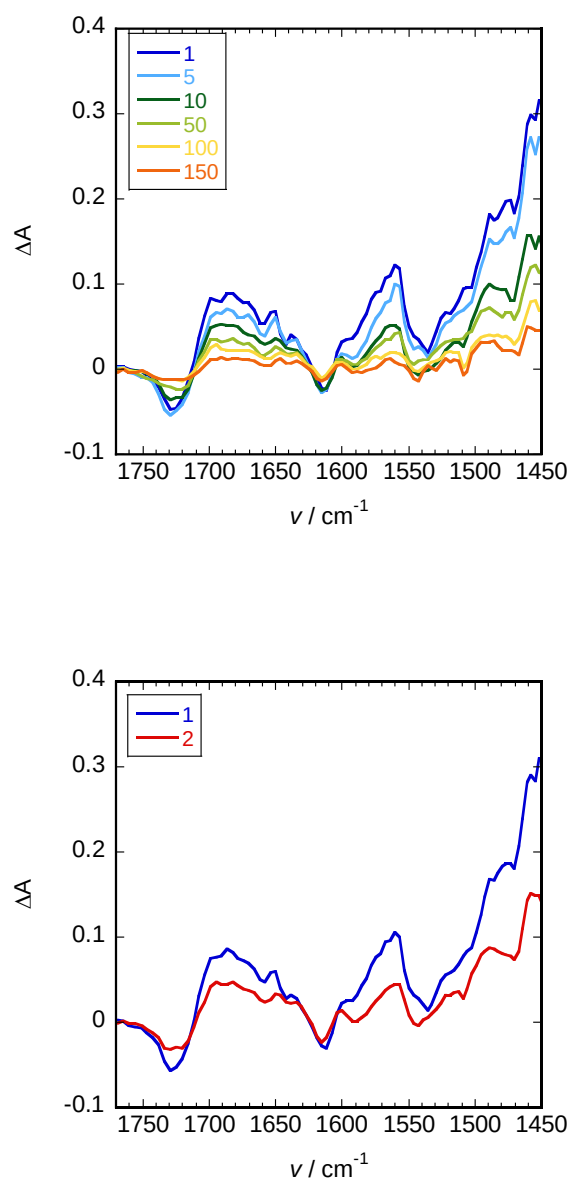


Figure SC 52. Transient infrared spectra (left) for PC2/NiO with delay times in picoseconds (left); the species associated spectra from global fitting where the numbers correspond to 1 = $\tau_1 = 7.0$ ps, 2 = $\tau_2 = 120$ ps, and 3 = $\tau_3 \gg 1$ ns (right). The excitation wavelength was 500 nm.

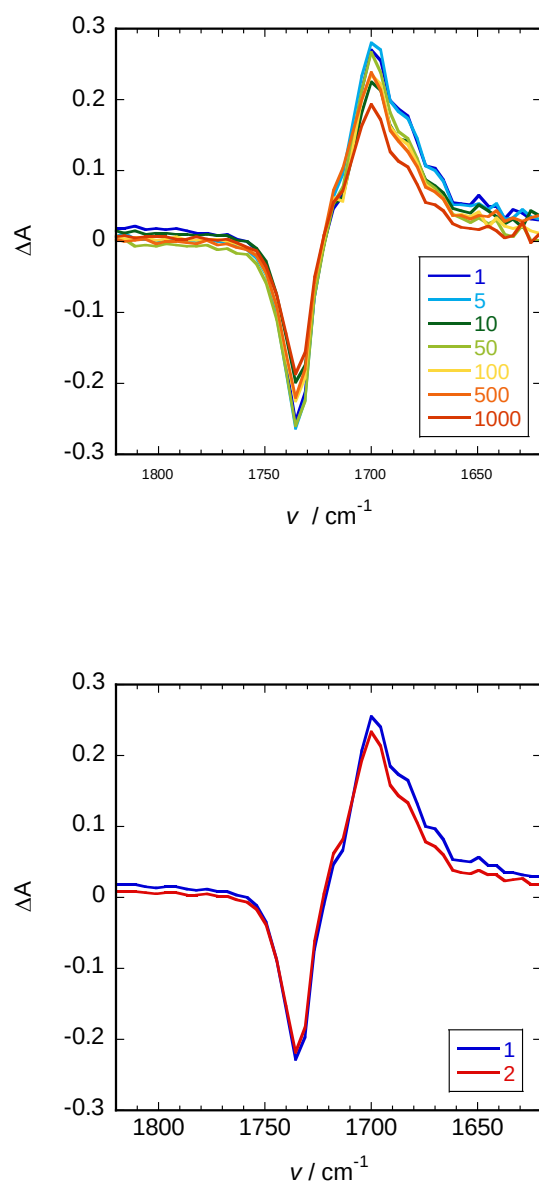


Figure SC 53. Transient infrared spectra (left) for PC3 in acetonitrile with delay times in picoseconds (left); the species associated spectra from global fitting where the numbers correspond to 1 = $\tau_1 = 14 \text{ ps}$, and 2 = $\tau_2 \gg 1 \text{ ns}$ (right). The excitation wavelength was 500 nm.

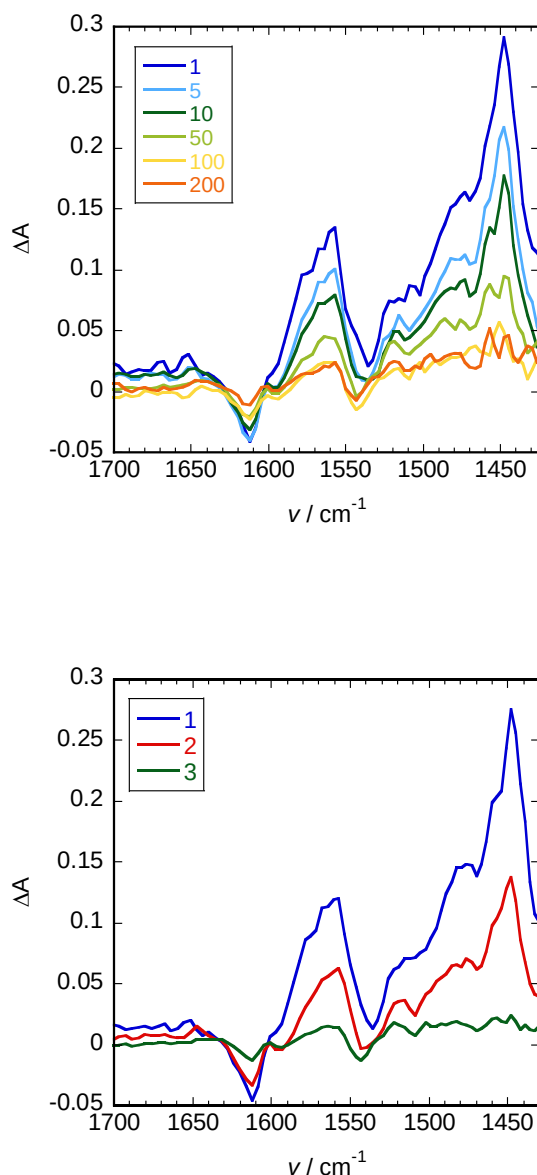


Figure SC 54. Transient infrared spectra (left) for PC3/NiO with delay times in picoseconds (left); the species associated spectra from global fitting where the numbers correspond to 1 = $\tau_1 = 7$ ps, 2 = $\tau_2 = 81$, and 3 = $\tau_3 \gg 1$ ns (right). The excitation wavelength was 500 nm.

S4. Photoelectrochemical Data

All electrochemical measurements were completed in a three-electrode setup containing a platinum counter electrode, Ag/AgCl reference electrode and a sensitized NiO film as a working electrode. Irradiation was provided by a Xe-arc lamp set at 1 sun intensity (100 mW cm^{-2}) and filtered with an AM 1.5 reference filter to simulate the solar spectrum.

The following aqueous buffer (made up in deionised water) solutions were used:

0.1 M pH 5 acetate buffer (0.07 M sodium acetate + 0.03 M acetic acid, adjusted with concentrated HCl)

0.1 M pH 8 phosphate buffer (0.0935 M K_2HPO_4 + 0.0065 M K_2HPO_4)

0.1 M pH 9.2 carbonate buffer (0.091 M sodium bicarbonate + 0.009 M sodium carbonate)

50 mM sodium hydrogen carbonate solution adjusted to pH 6.6 with concentrated HCl.

Components of the buffer solutions were obtained from Sigma-Aldrich and used as received.

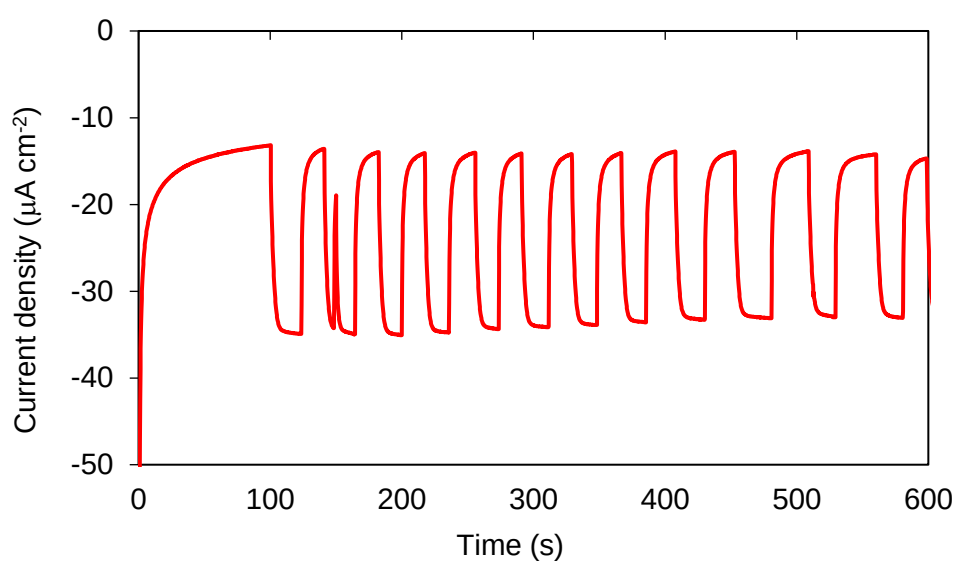


Figure SC 55. Photocurrent density of PC1/NiO with an applied external bias of -0.5 Volts vs Ag/AgCl in pH 5 acetate buffer in the presence of 10 mM tris(ethyldiamine)cobalt(III) as an electron acceptor, under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

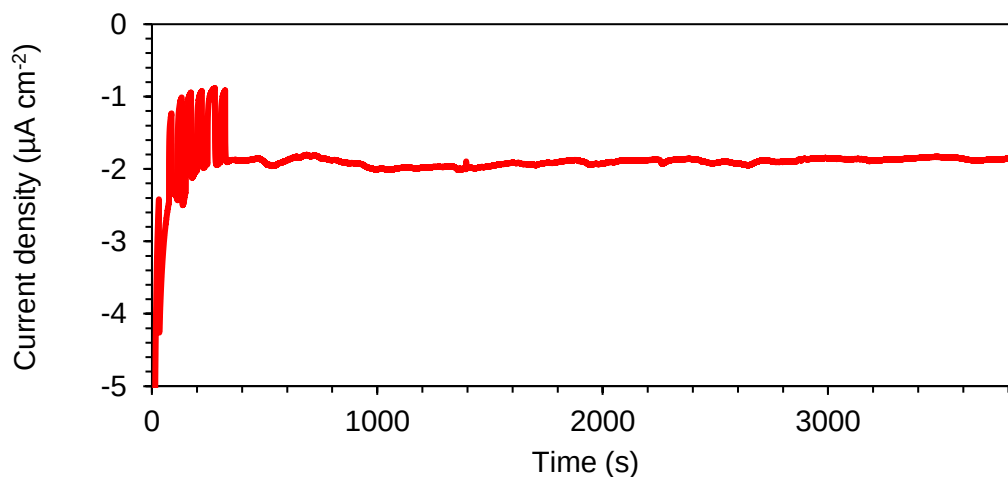


Figure SC 56. Chronoamperometry data for an unsensitized NiO in pH 5 acetate buffer (saturated with CO₂) irradiated under 1 sun AM 1.5, (100 mW cm⁻²) irradiation. The light output was chopped at the beginning of the experiment. Applied bias is -0.5 V vs Ag/AgCl.

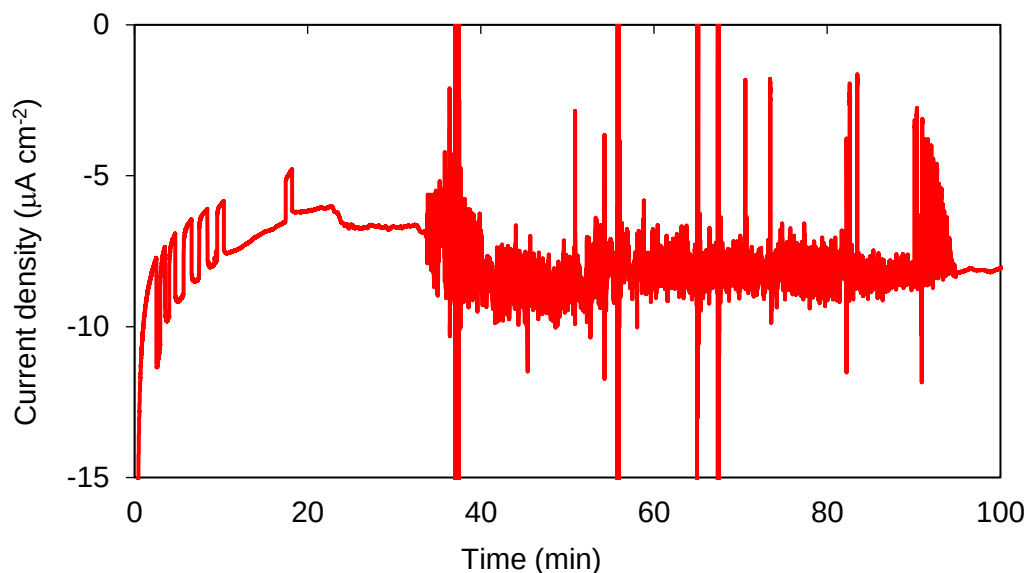


Figure SC 57. Photocurrent density of PC1/NiO with an applied external bias of -0.5 V vs Ag/AgCl in pH 5 acetate buffer under an extended period 1 sun AM 1.5, (100 mW cm⁻²) irradiation. The signal noise after 30 minutes is associated with the formation of gas bubbles on the working electrode.

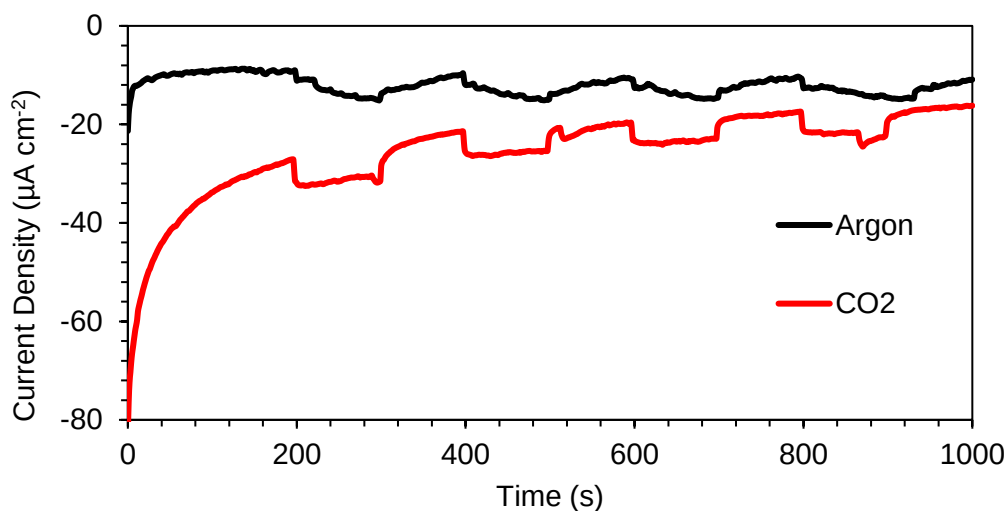


Figure SC 58. Chronoamperometry data for PC1/NiO in pH 5 acetate buffer under 1 sun AM 1.5, (100 mW cm⁻²) irradiation. The applied bias was -0.5 V vs Ag/AgCl both in the presence of argon and CO₂.

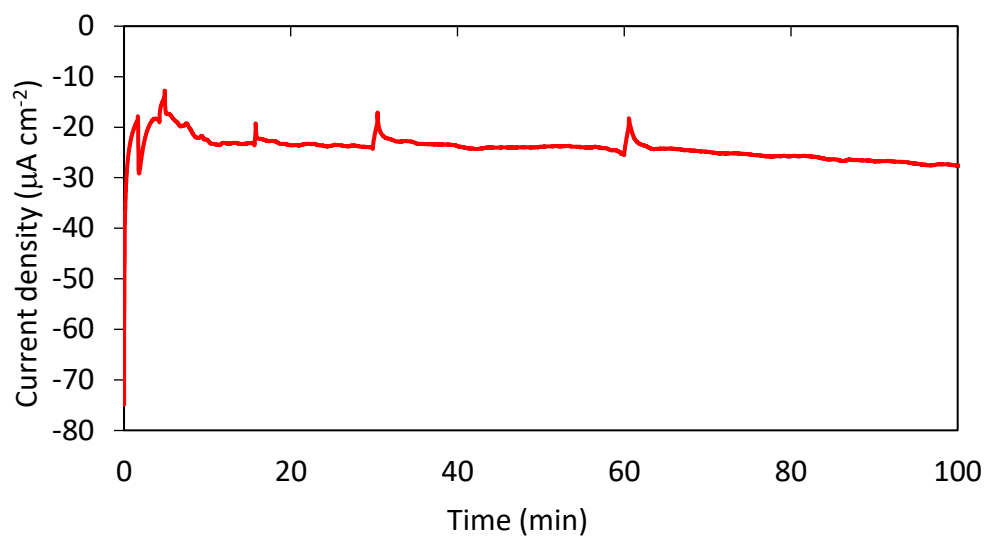


Figure SC 59. Chronoamperometry data for PC2/NiO in pH 5 acetate buffer saturated with argon and irradiated under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.5 V vs Ag/AgCl.

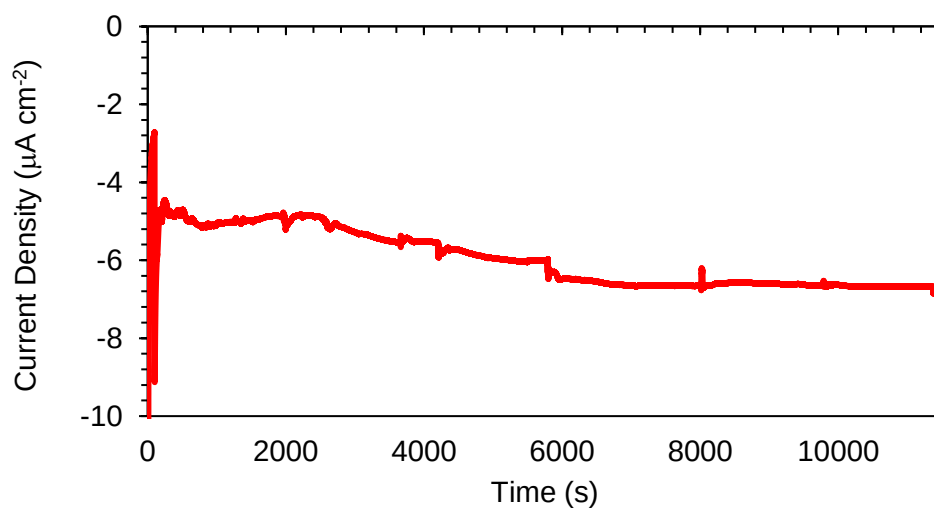


Figure SC 60. Chronoamperometry data for PC3/NiO in pH 5 acetate buffer (saturated with CO_2) under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. Applied bias: -0.5 V vs Ag/AgCl.

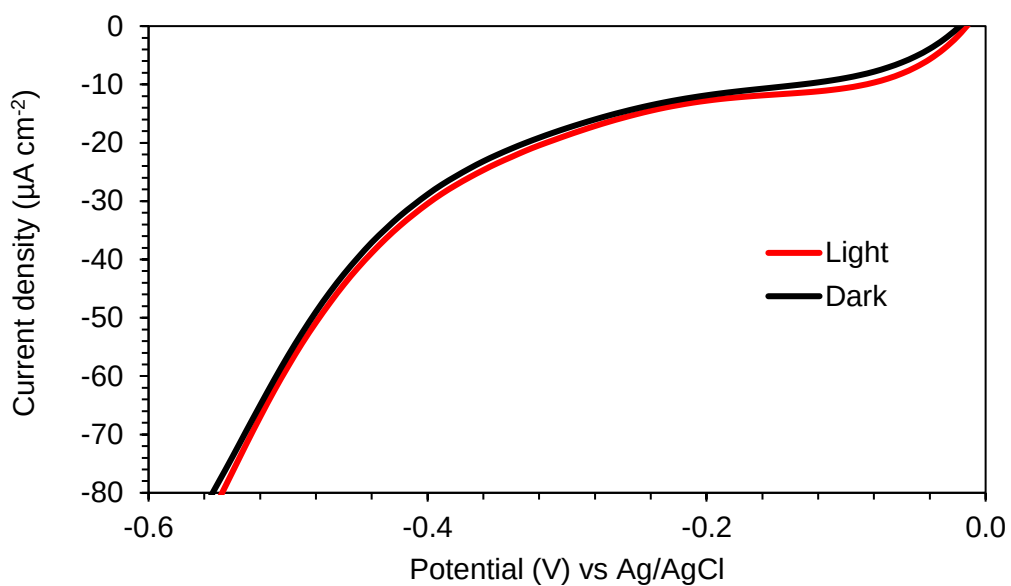


Figure SC 61. Linear sweep measurements of a bare NiO film in pH 5 acetate buffer. The light measurement was under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The cell was saturated with argon and the scan rate was 0.1 V s^{-1} .

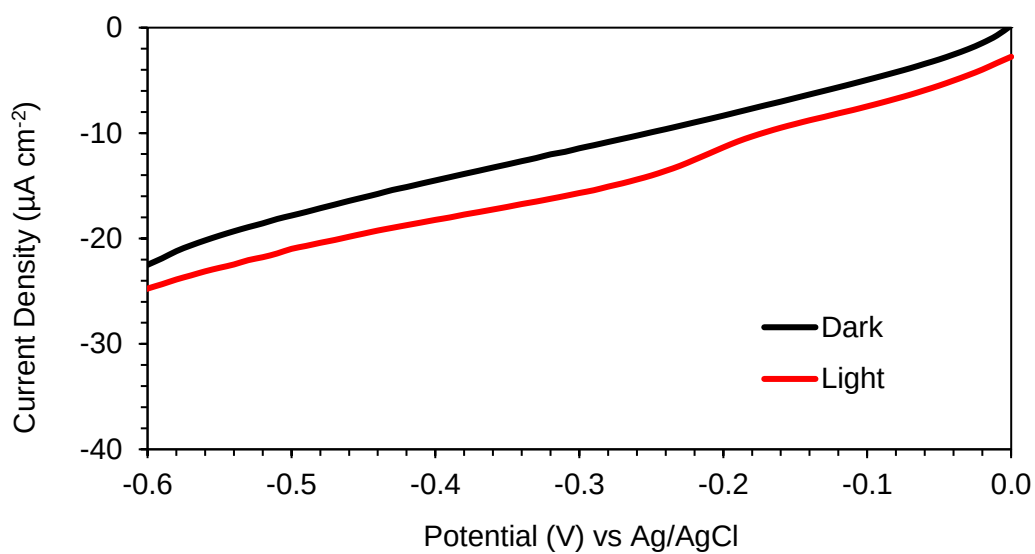


Figure SC 62. Linear sweep measurements of PC1/NiO in pH 5 acetate buffer. The light measurement was under 1 sun AM 1.5 (100 mW cm^{-2}) illumination. The scan rate was 0.1 V s^{-1} . The cell was saturated with CO_2 .

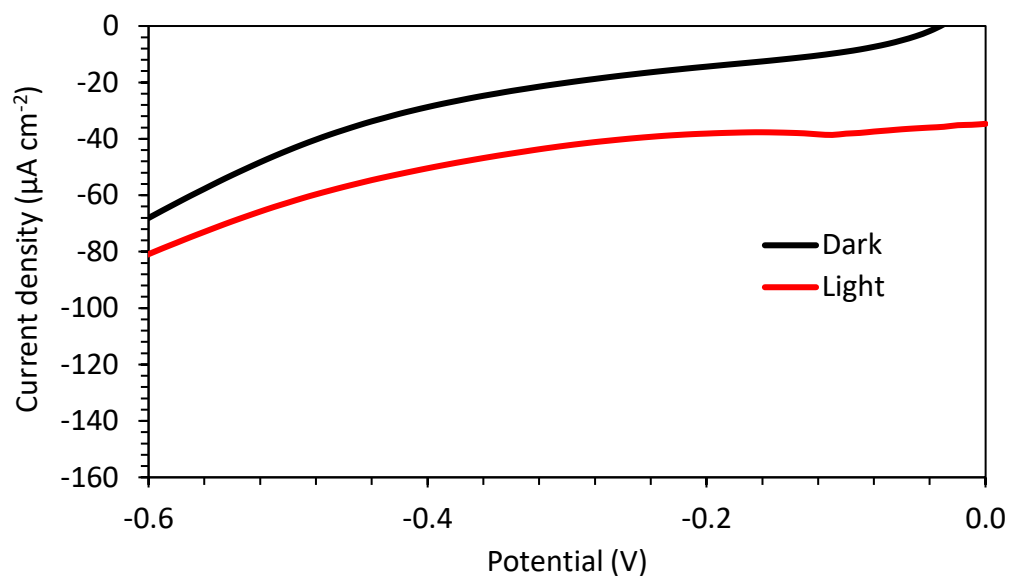


Figure SC 63. Linear sweep measurements of PC2/NiO in pH 5 acetate buffer. The light measurement was under 1 sun AM 1.5 (100 mW cm^{-2}) illumination. The scan rate was 0.1 V s^{-1} . The cell was saturated with Ar.

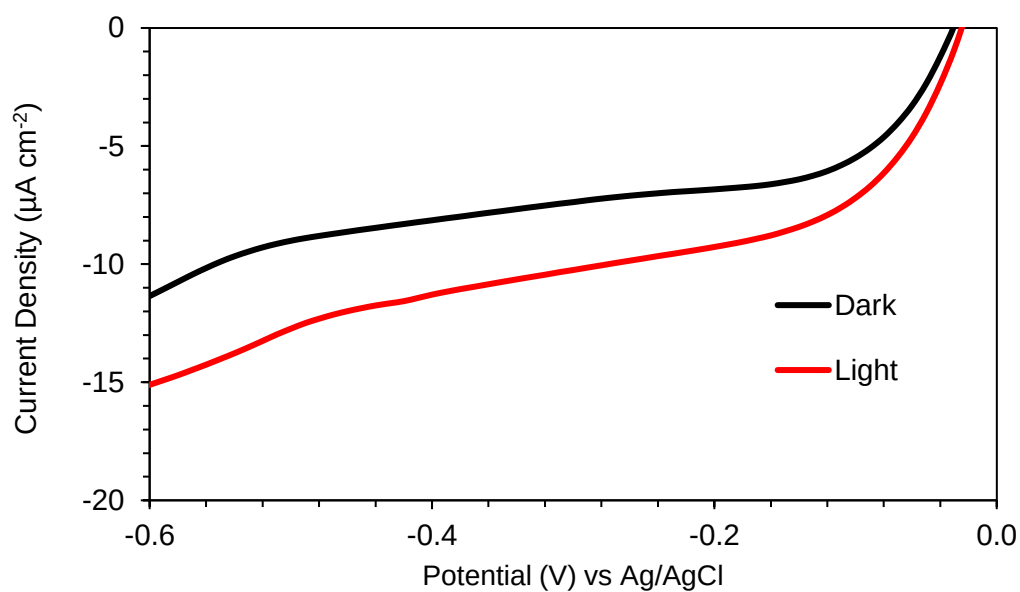


Figure SC 64. Linear sweep measurements of PC3/NiO in pH 5 acetate buffer. The light measurement was under 1 sun AM 1.5 (100 mW cm^{-2}) illumination. The scan rate was 0.1 V s^{-1} . The cell was saturated with CO₂.

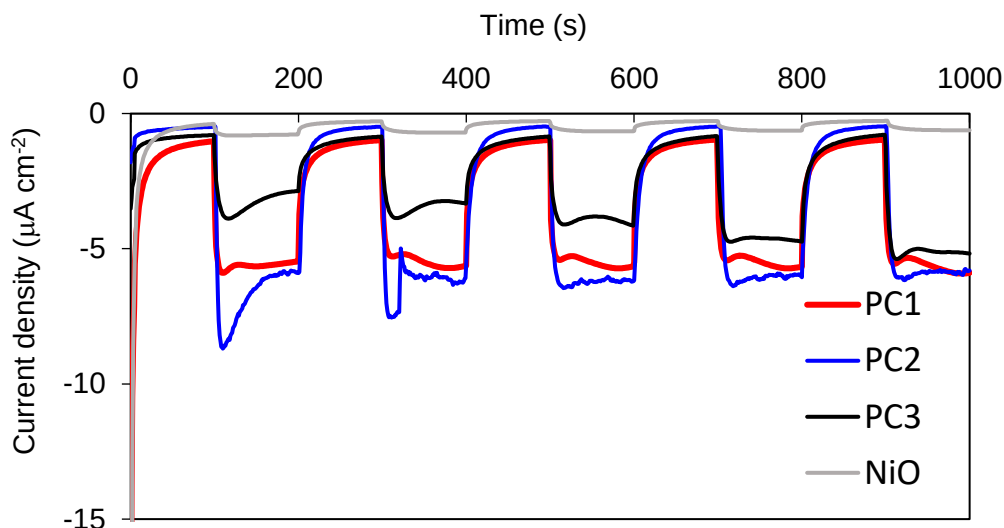


Figure SC 65. Representative example of photocurrent densities from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 0.1 M pH 5 acetate buffer under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.2 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar. Bubbles at the surface caused the noisy photocurrent signal recorded.

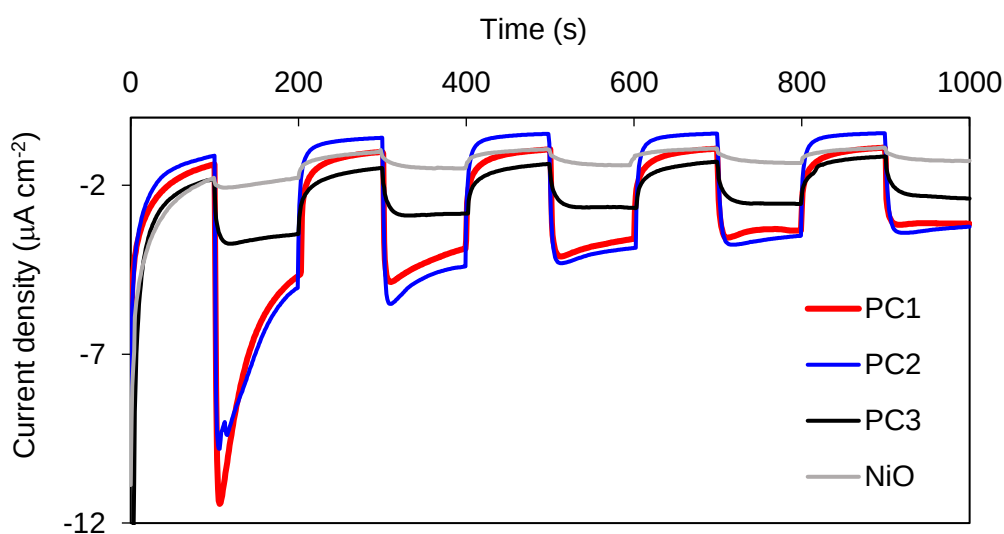


Figure SC 66. Representative example of photocurrent densities from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 50 mM pH 6.6 NaHCO_2 solution under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.2 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar.

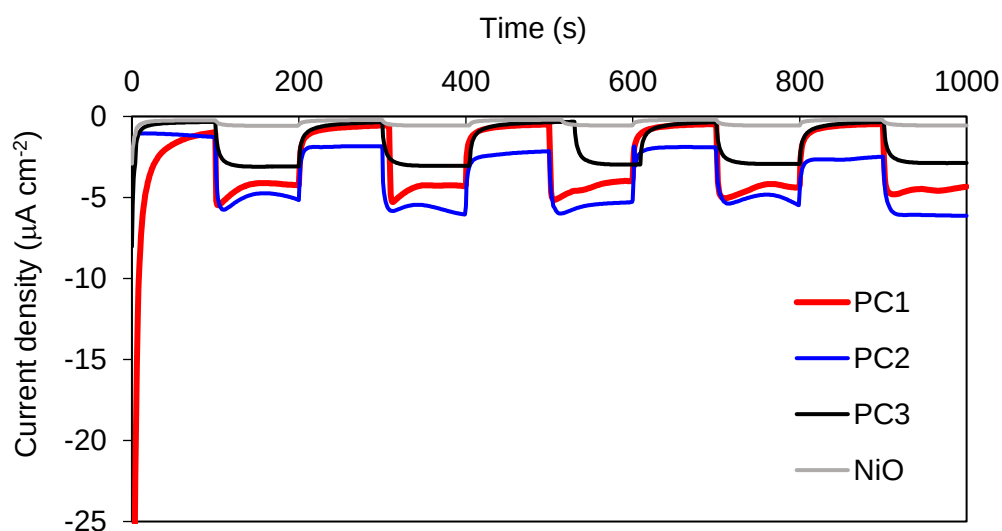


Figure SC 67. Representative example of photocurrent from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 0.1 M pH 8 phosphate buffer under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.2 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar.

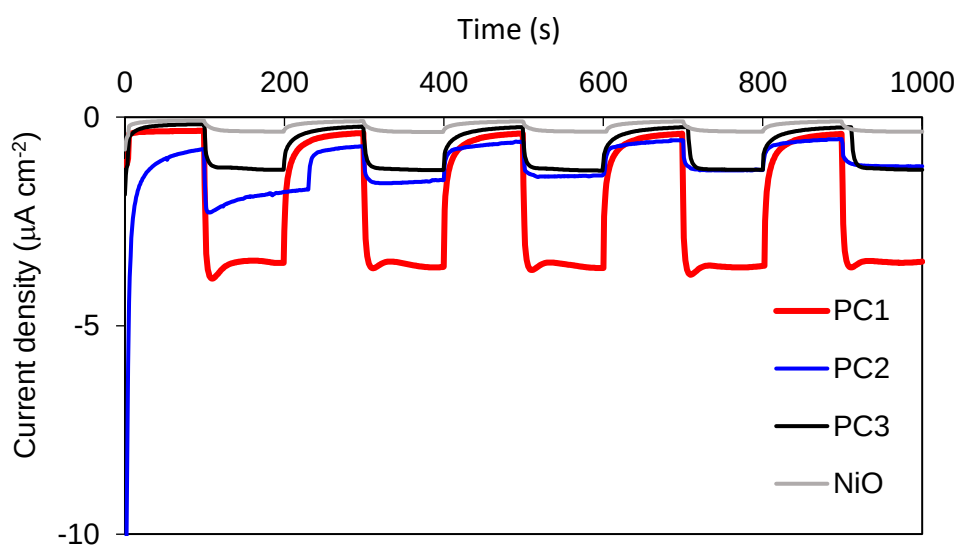


Figure SC 68. Representative example of photocurrent densities from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 0.1 M pH 9.2 carbonate buffer under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.2 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar.

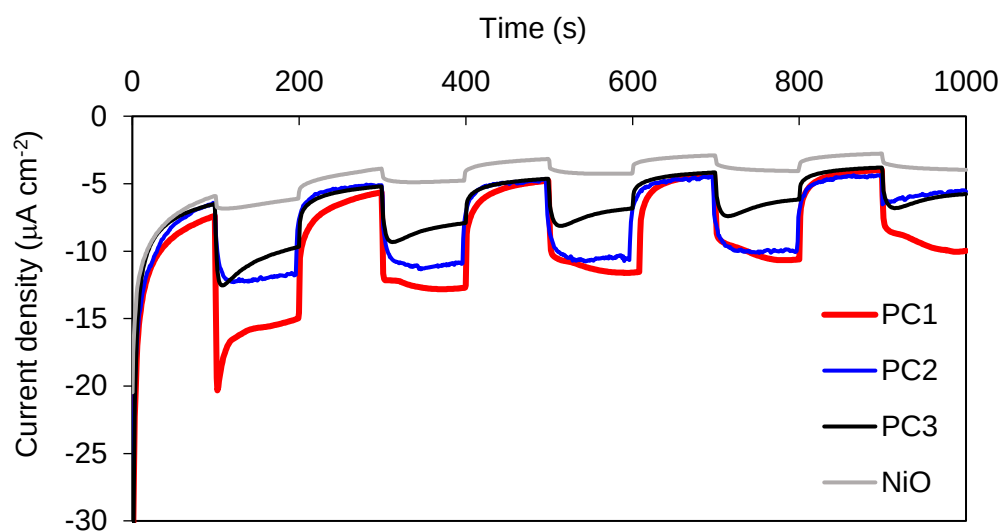


Figure SC 69. Representative example of photocurrent from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 0.1 M pH 5 acetate buffer under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.5 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar.

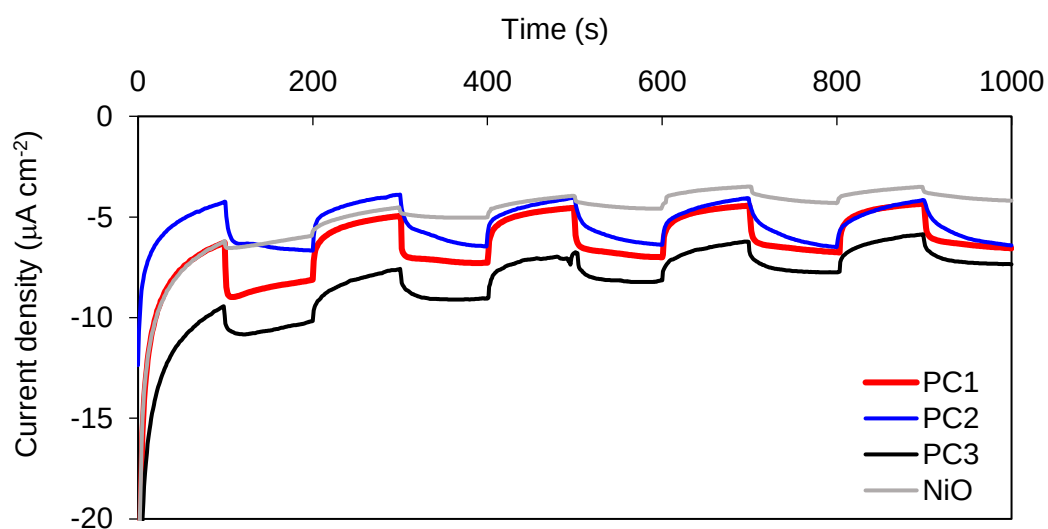


Figure SC 70. Representative example of photocurrent densities from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in $50 \mu\text{M}$ pH 6.6 NaHCO_2 solution under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.5 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar. Bubbles at the surface caused the noisy photocurrent signal recorded.

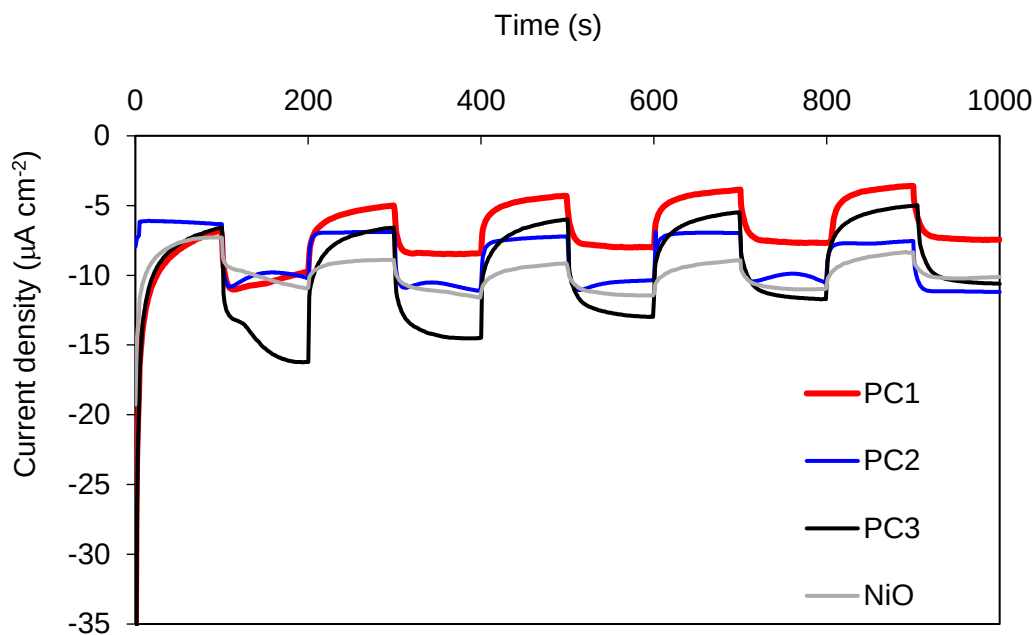


Figure SC 71. Representative example of photocurrent from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 0.1 M pH 8 phosphate buffer under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.5 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar.

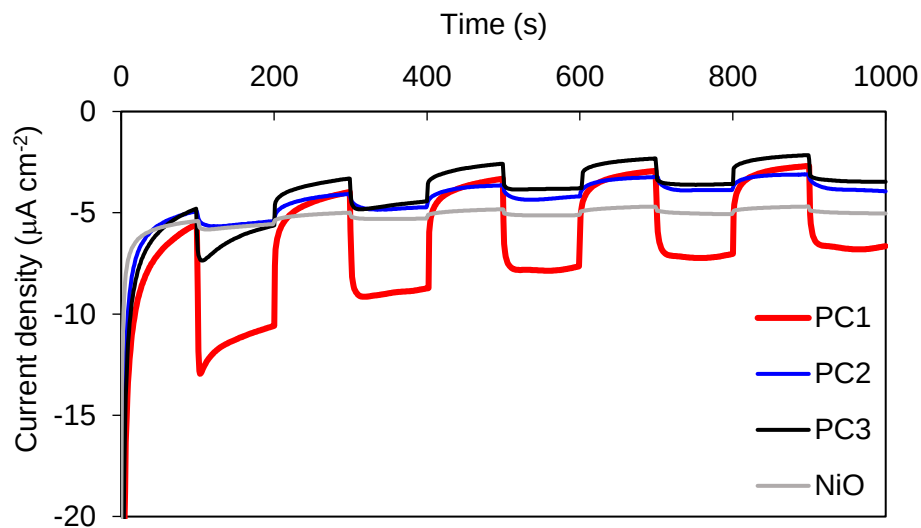


Figure SC 72. Representative example of photocurrent from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 0.1 M pH 9.2 carbonate buffer under chopped 1 sun AM 1.5, (100 mW cm^{-2}) irradiation. The applied bias was -0.5 V vs Ag/AgCl. The reaction cell was saturated with CO_2 for unsensitized NiO, PC1/NiO and PC3/NiO. In the case of PC2/NiO, the cell was saturated with Ar.

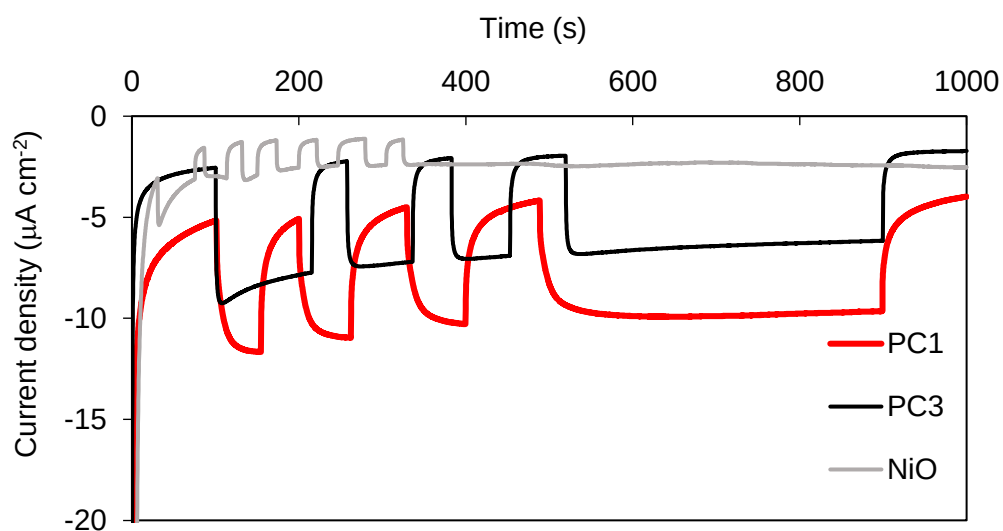


Figure SC 73. Representative example of photocurrent from photoelectrocatalysis experiments of NiO films sensitized with photocatalysts in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide under 1 sun AM 1.5, (100 mW cm⁻²) irradiation. The applied bias was -0.5 V vs Ag/AgCl. The cell was saturated with CO₂ in each case.

Table SC 1. Summary of average photocurrent densities obtained under chopped 1 sun AM 1.5, (100 mW cm⁻²) irradiation for photocatalysts systems under different conditions where the applied external bias -0.2 Volts vs Ag/AgCl. The information here is obtained from a 15 minute experiment, extracting the average.

Photocatalyst	Current density / pH 5 (μA cm ⁻²)	Current density / pH 6.6 (μA cm ⁻²)	Current density / pH 8 (μA cm ⁻²)	Current density / pH 9.2 (μA cm ⁻²)	Current density / Ionic liquid * (μA cm ⁻²)
PC1	4.6	2.9	3.8	3.1	3.3
PC2	5.7	3.5	3.7	0.9	X
PC3	4.1	1.4	6.8	1.0	3.7

*Note the ionic liquid is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

Table SC 2. Summary of average photocurrent densities obtained under chopped 1 sun AM 1.5, (100 mW cm⁻²) irradiation for photocatalysts systems under different conditions where the applied external bias -0.5 V vs Ag/AgCl. The information here is obtained from a 15 minute experiment, extracting the average.

Photocatalyst	Current density / pH 5 ($\mu\text{A cm}^{-2}$)	Current density / pH 6.6 ($\mu\text{A cm}^{-2}$)	Current density / pH 8 ($\mu\text{A cm}^{-2}$)	Current density / pH 9.2 ($\mu\text{A cm}^{-2}$)	Current density / Ionic liquid * ($\mu\text{A cm}^{-2}$)
PC1	6.80	2.6	3.70	4.73	6.50
PC2	5.88	2.3	3.9	2.7	X
PC3	3.20	1.4	3.90	1.90	5.30

*1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

S5. Gas Chromatography

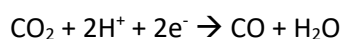
GC Method (as described in the experimental section):

Gas chromatography (GC) measurements were performed with a Shimadzu GC-2014 instrument where a thermal conductivity detector at 200 °C (TCD) and flame-ionisation detector (FID) at 250 °C operated in tandem. A Restek ShinCarbon ST 80/100 packed column (2 metre, 2 mm ID) was used with argon as the carrier gas. The initial oven temperature was 50 °C with a temperature ramp to 200 °C (after an initial period of 2 mins at 50 °C) at a rate of 15 °C min⁻¹, followed by a final hold time of 10 mins.

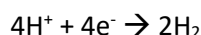
In the selection below are results for gas analysis of photocatalysis products under various conditions. For all gas chromatography measurements the injection volume was 0.5 ml. We estimate the error from gas chromatography measurements at 4 % from repeats of calibration gas standard samples. Note that carbon monoxide is detected with an FID and hydrogen is determined using a TCD.

Calculation of Faradaic Efficiency and Turnover Frequencies:

Where the quantity of evolved gaseous products was measured for a photoelectrocatalytic experiment by means of gas chromatography (either hydrogen or carbon monoxide in this case), faradaic efficiencies were determined by the method outlined below for the following reactions.



or



The faradaic efficiency $\eta_{far} = \frac{Q_{exp}}{Q_{theo}}$ where Q_{exp} reflects the number of moles of gaseous product and Q_{theo} the overall charge passed in the photoelectrocatalytic experiment. Q_{theo} is obtained directly from experimental data, integrating current over the duration of the

experiment. $Q_{\text{exp}} = n \times F \times \text{moles product}$ where n is the number of electrons involved in the reaction and F is Faraday's constant.

The turnover frequency $TOF = \frac{n_{\text{product}}}{n_{\text{catalyst}} \times t}$ where n_{product} is the number of moles of evolved gaseous product and n_{catalyst} is the number of moles photocatalyst (estimated from the dye-loading on NiO), and t is the time of the experiment.

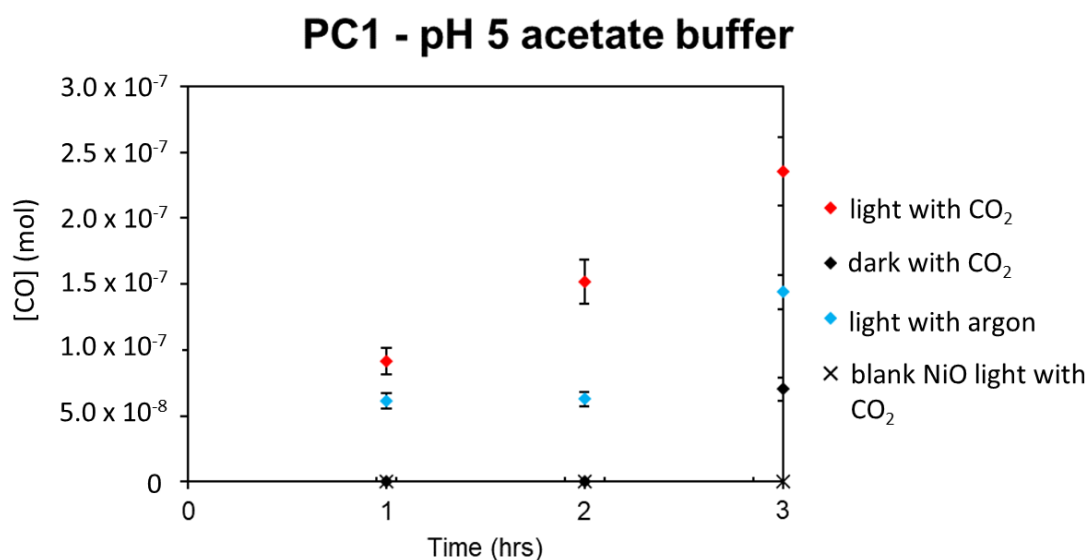


Figure SC 74. PC1/NiO thin film evolved CO detected by gas chromatography in 0.1 M pH 5 acetate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation. The experiment in the light under Ar and in the dark did produce a small amount of CO, possibly from the acetate buffer.

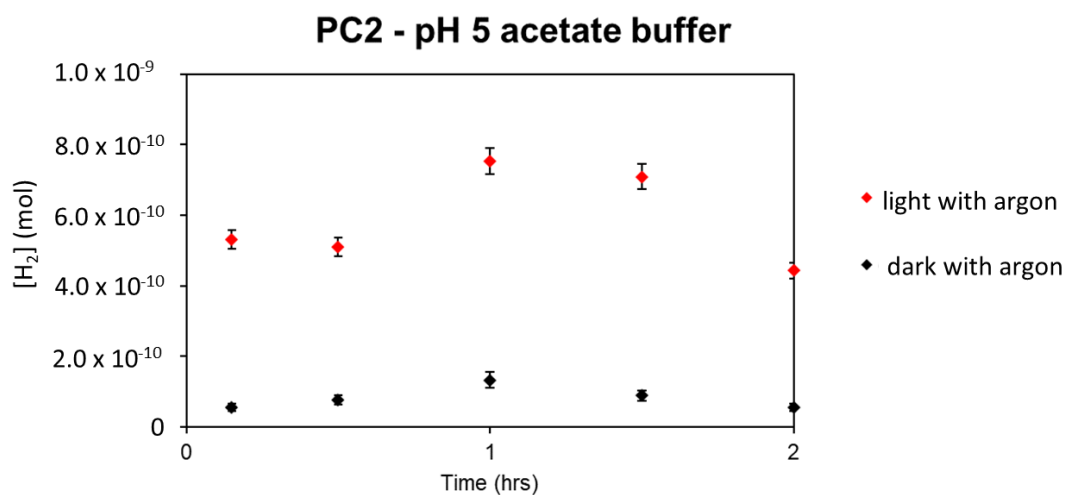


Figure SC 75. PC2/NiO thin film evolved CO detected by gas chromatography in 0.1 M pH 5 acetate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

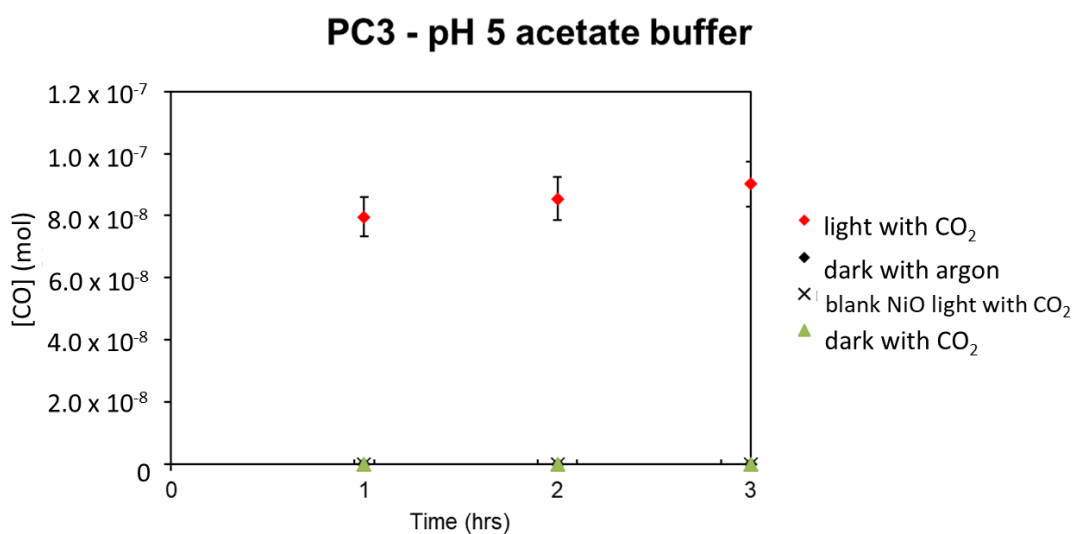


Figure SC 76. PC3/NiO thin film evolved CO detected by gas chromatography in 0.1 M pH 5 acetate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

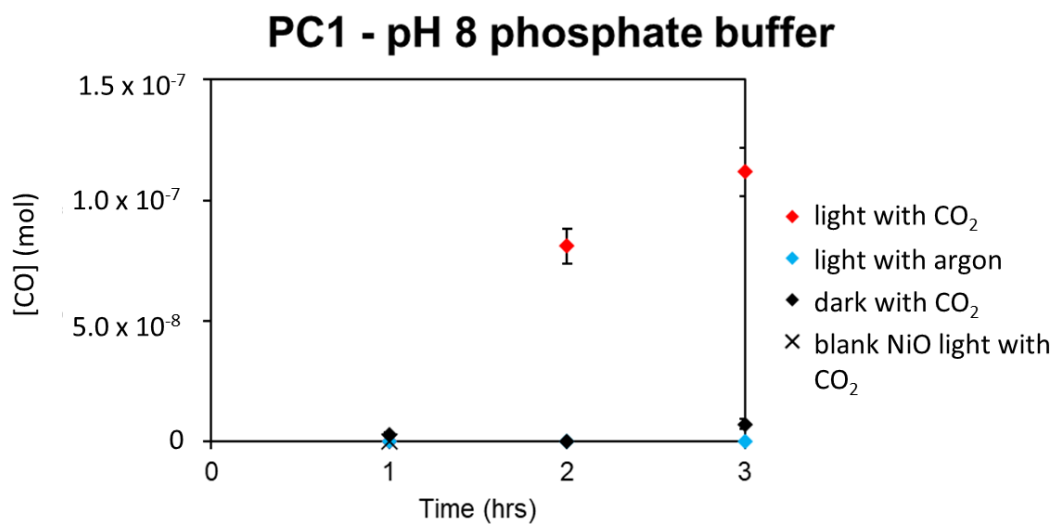


Figure SC 77. PC1/NiO thin film evolved CO detected by gas chromatography in 0.1 M pH 8 phosphate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5 (100 mW cm⁻²) irradiation.

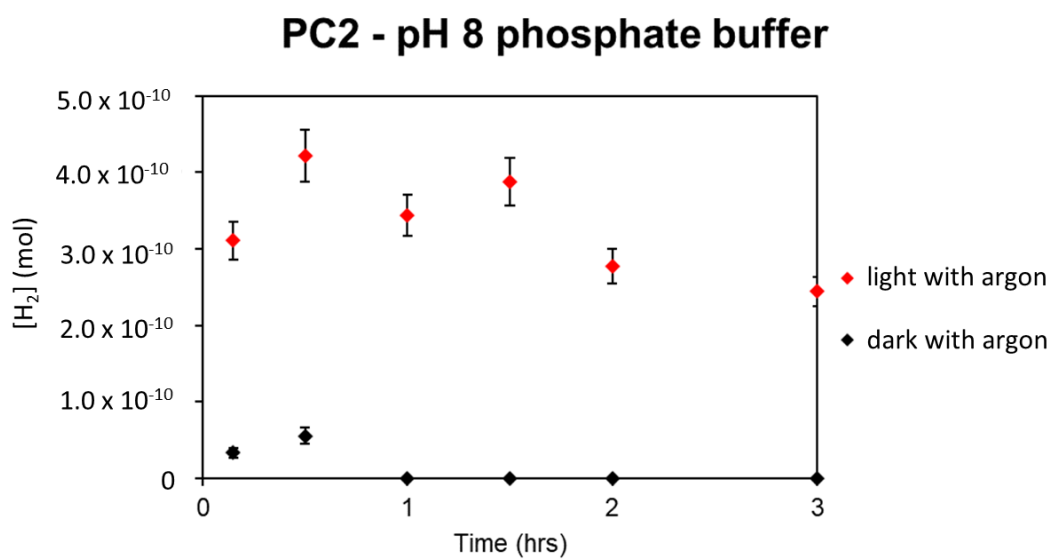


Figure SC 78. PC2/NiO thin film evolved hydrogen detected by gas chromatography in 0.1 M pH 8 phosphate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

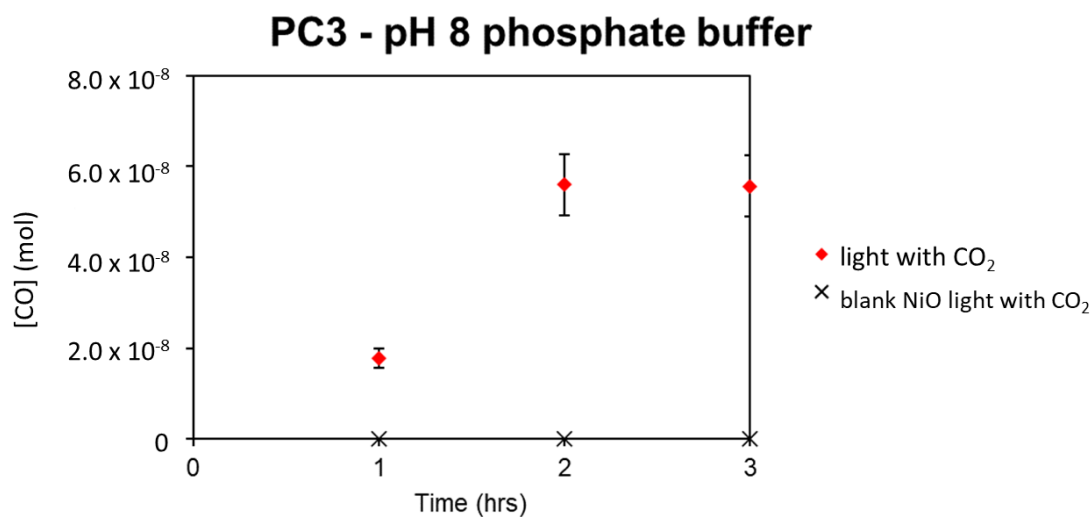


Figure SC 79. PC3/NiO thin film evolved CO detected by gas chromatography in 0.1 M pH 8 phosphate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

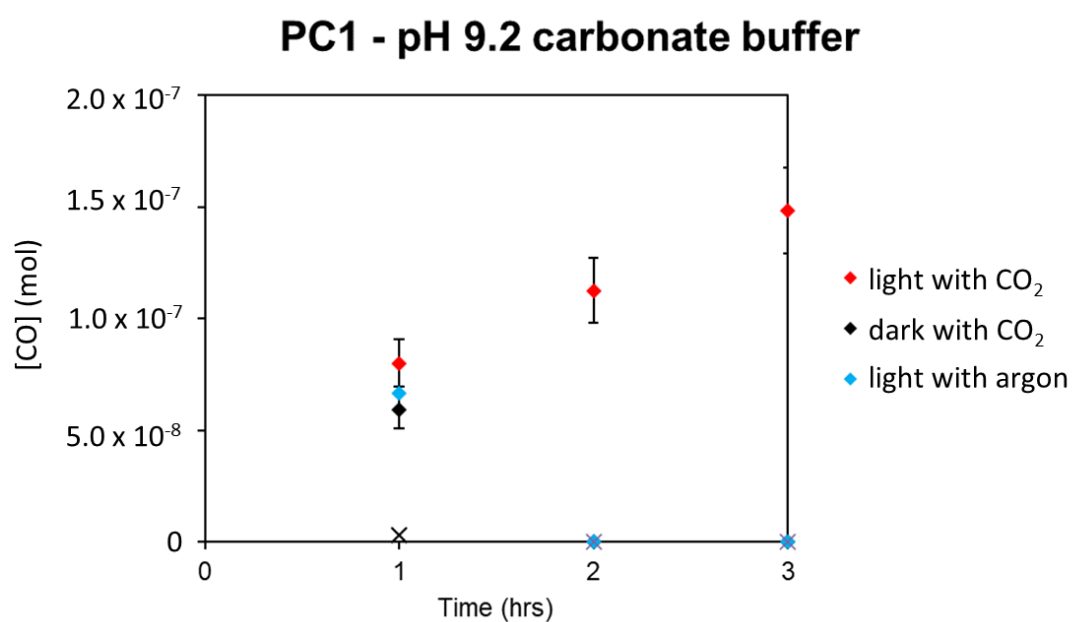


Figure SC 80. PC1/NiO thin film evolved CO detected by gas chromatography in 0.1 M pH 9.2 carbonate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

PC2 - pH 9.2 carbonate buffer

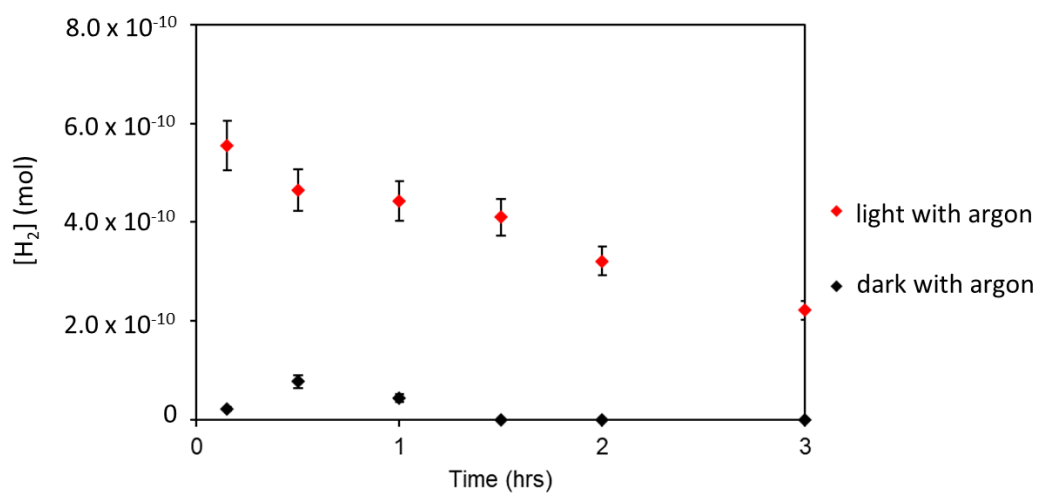


Figure SC 81. PC2/NiO thin film evolved hydrogen detected by gas chromatography in 0.1 M pH 9.2 carbonate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

PC3 - pH 9.2 carbonate buffer

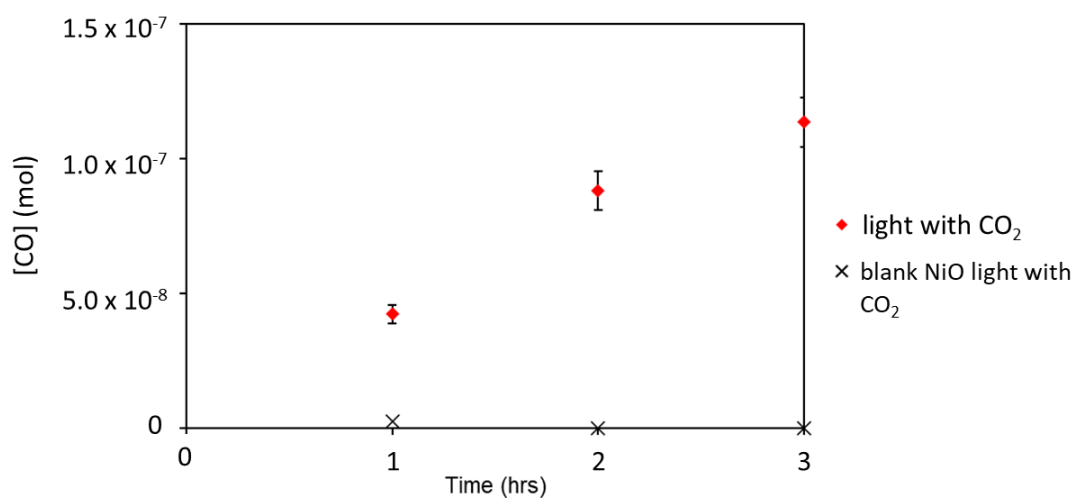


Figure SC 82. PC3/NiO thin film evolved CO detected by gas chromatography in 0.1 M pH 9.2 carbonate buffer with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

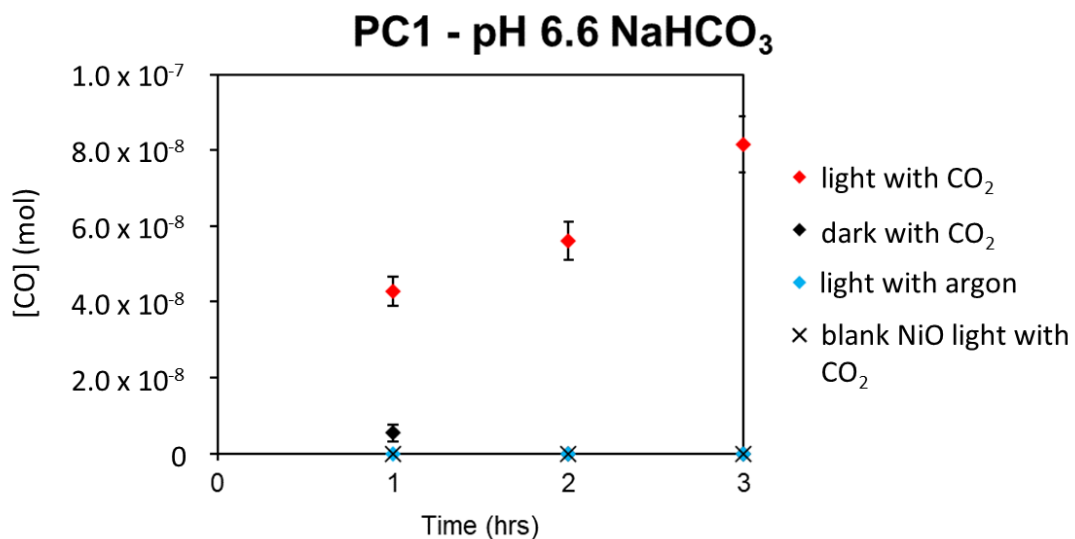


Figure SC 83. PC1/NiO thin film evolved CO detected by gas chromatography in 50 mM pH 6.6 NaHCO₃ solution with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

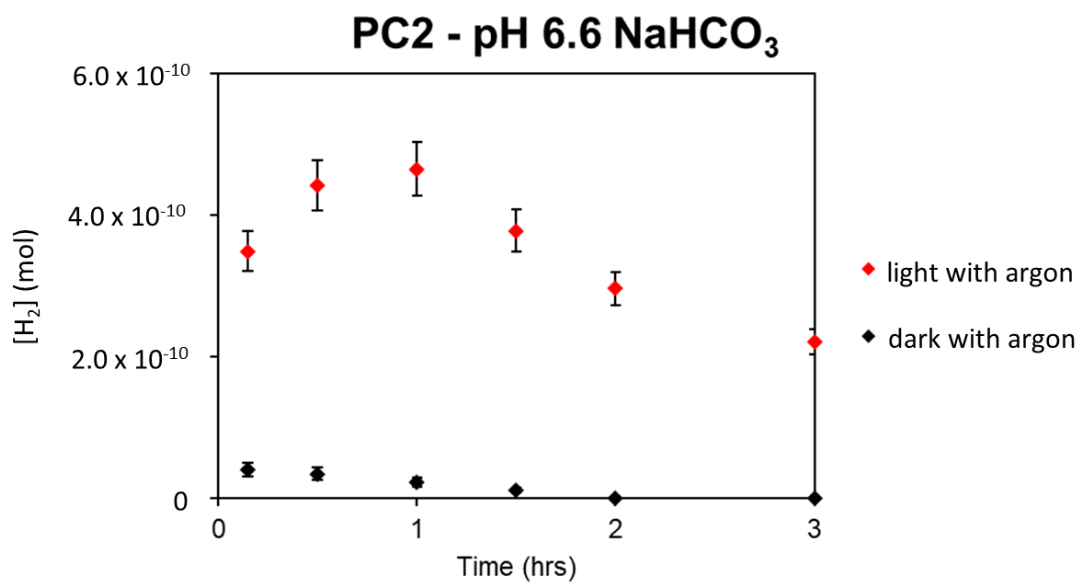


Figure SC 84. PC2/NiO thin film evolved hydrogen detected by gas chromatography in 50 μ M pH 6.6 NaHCO₃ solution with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

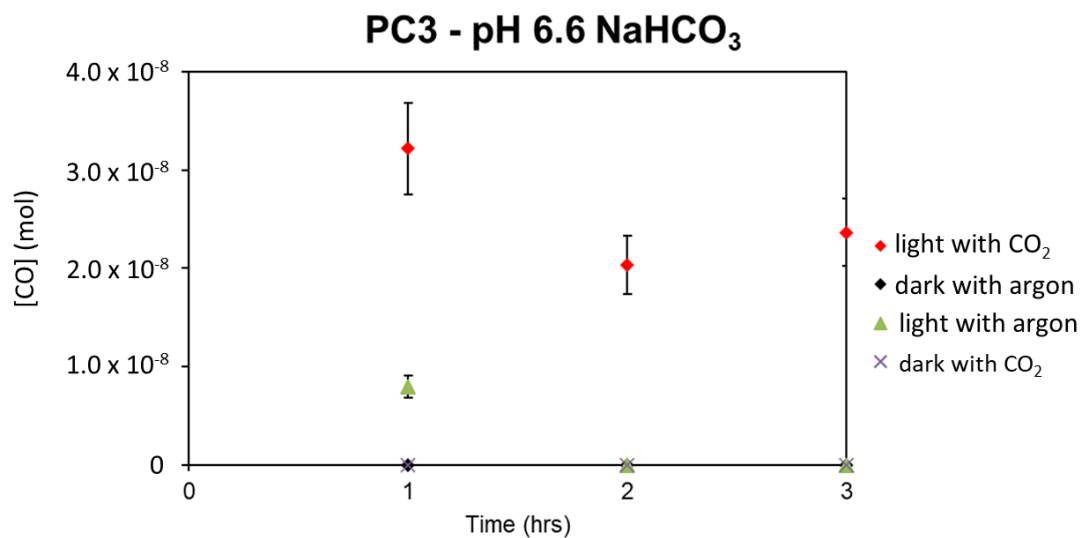


Figure SC 85. PC3/NiO thin film evolved CO detected by gas chromatography in 50 mM pH 6.6 NaHCO₃ solution with an applied bias of -0.5 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

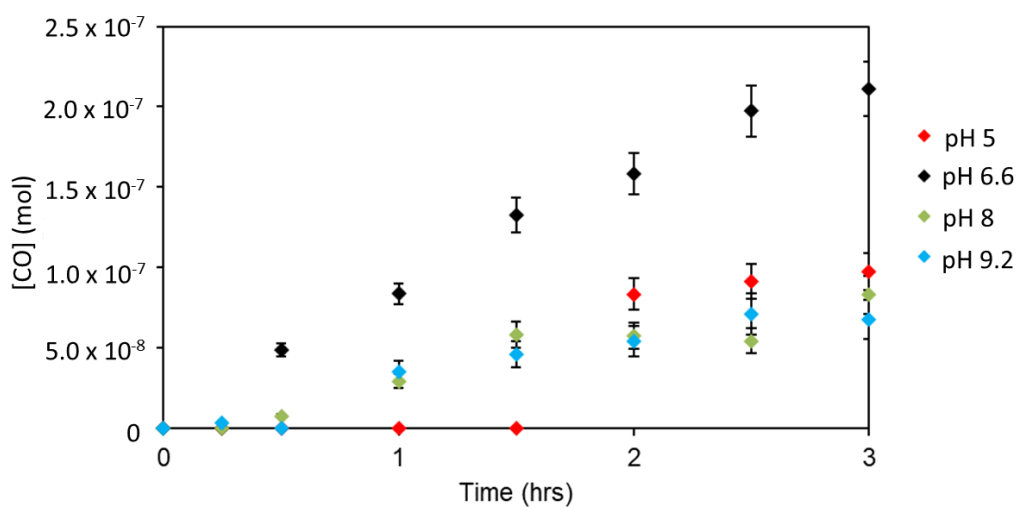


Figure SC 86. PC1/NiO thin film evolved CO detected by gas chromatography in with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation in various pH buffer solutions as described earlier. Note the pH 6.6 is 50 mM NaHCO₃ solution.

PC3 (Dark)	PC3 (Light)	PC3 (Dark)	PC3 (Light)		PC2 (Dark)	PC2 (Light)		Applied Potential (V) vs Ag/AgCl	Electrolyte	Charge (C)	Electrons (mol)	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
-0.5	-0.5	-0.5	-0.5		-0.5	-0.5		-0.5	pH 5 (with argon)	0.0447	4.63 x 10 ⁻⁷	2666	2864	3022	7.96 x 10 ⁻⁸	8.55 x 10 ⁻⁸	9.02 x 10 ⁻⁸	278	532	691	3.08 x 10 ⁻⁹	5.90 x 10 ⁻⁹	7.66 x 10 ⁻⁹
pH 5 (with CO ₂)	pH 5 (with argon)	pH 5 (with argon)	pH 5 (with CO ₂)		pH 5 (with argon)	pH 5 (with argon)		pH 5 (with argon)	pH 5 (with CO ₂)	0.0112	1.16 x 10 ⁻⁷	0	0	0	0	0	0	0	0	0	0	0	0
0.0486	0.0883	0.0112	0.0447		0.0070	0.0180		0.0070	0.0498	0.0447	4.63 x 10 ⁻⁷	2666	2864	3022	7.96 x 10 ⁻⁸	8.55 x 10 ⁻⁸	9.02 x 10 ⁻⁸	278	532	691	3.08 x 10 ⁻⁹	5.90 x 10 ⁻⁹	7.66 x 10 ⁻⁹
5.03 x 10 ⁻⁷	9.15 x 10 ⁻⁷	1.16 x 10 ⁻⁷	4.63 x 10 ⁻⁷		7.26 x 10 ⁻⁸	1.87 x 10 ⁻⁷		7.26 x 10 ⁻⁸	2.74 x 10 ⁻⁷	6.07 x 10 ⁻⁷	5.16 x 10 ⁻⁷	3058	5097	7891	9.12 x 10 ⁻⁸	1.52 x 10 ⁻⁷	2.36 x 10 ⁻⁷	481	780	919	5.33 x 10 ⁻⁹	8.65 x 10 ⁻⁹	1.02 x 10 ⁻⁸
0	349	0	2666		5	48		5	0	2056	3058	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	1082	0	2864		7	46		7	0	2102	5097	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	1396	0	3022		12	68		12	2353	4831	7891	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	1.04 x 10 ⁻⁸	0	7.96 x 10 ⁻⁸		8	64		8	0	6.14 x 10 ⁻⁸	9.12 x 10 ⁻⁸	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	3.22 x 10 ⁻⁸	0	8.55 x 10 ⁻⁸		5	40		5	0	6.27 x 10 ⁻⁸	1.52 x 10 ⁻⁷	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	3.17 x 10 ⁻⁸	0	9.02 x 10 ⁻⁸		negligible	5.32 x 10 ⁻¹⁰		negligible	7.02 x 10 ⁻⁸	1.44 x 10 ⁻⁷	2.36 x 10 ⁻⁷	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	0	0	278		-	5.1 x 10 ⁻¹⁰		-	0	2	481	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	0	0	532		-	7.53 x 10 ⁻¹⁰		-	0	69	780	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	0	0	691		-	7.10 x 10 ⁻¹⁰		-	66	142	919	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	0	0	3.08 x 10 ⁻⁹		-	4.44 x 10 ⁻¹⁰		-	0	2.22 x 10 ⁻¹¹	5.33 x 10 ⁻⁹	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	0	0	5.90 x 10 ⁻⁹						0	7.65 x 10 ⁻¹⁰	8.65 x 10 ⁻⁹	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)
0	0	0	7.66 x 10 ⁻⁹						7.32 x 10 ⁻¹⁰	1.57 x 10 ⁻⁹	1.02 x 10 ⁻⁸	CO peak (1 hr)	CO peak (2hrs)	CO peak (3hrs)	[CO] 1 hr (mol)	[CO] 2 hrs (mol)	[CO] 3 hrs (mol)	H ₂ peak (1hr)	H ₂ peak (2hrs)	H ₂ peak (3hrs)	[H ₂] / mol (1hr)	[H ₂] / mol (2hrs)	[H ₂] / mol (3hrs)

NIO Blank Film (Dark)	NIO Blank Film (Light)
-0.5	-0.5
pH 5 (with CO ₂)	pH 5 (with CO ₂)
0.0182	0.0191
1.89×10^{-7}	1.98×10^{-7}
0	0
0	0
0	0
0	0
0	0
0	0
0	0
0	0
0	0
0	0
0	0
0	0

Table SC 3. Matrix of GC experiments with the photocatalysts in 0.1 M pH 5 acetate buffer. All light experiments are under simulated 1 sun AM 1.5 light (100 mW cm⁻²).

	PC2 (Dark)	PC2 (Light)		PC1 (Dark)	PC1 (Light)	PC1 (Light)	Applied Potential (V)	
Applied Potential (V)	-0.5	-0.5		-0.5	-0.5	-0.5	Electrolyte	Electrolyte
Electrolyte	pH 6.6 NaHCO ₃ (with azoon)	pH 6.6 NaHCO ₃ (with azoon)		pH 6.6 NaHCO ₃ (with CO ₂)	pH 6.6 NaHCO ₃ (with azoon)	pH 6.6 NaHCO ₃ (with CO ₂)	Charge (C)	Charge (C)
Charge (C)	0.005	0.0345		0.00766	0.0455	0.0519	Electrons (mol)	Electrons (mol)
Electrons (mol)	5.18×10^{-8}	3.58×10^{-7}		7.94×10^{-8}	4.72×10^{-7}	5.38×10^{-7}	CO peak (1 hr)	CO peak (1 hr)
CO peak (1 hr)	7	60		340	0	2712	CO peak (2 hrs)	CO peak (2 hrs)
CO peak (2 hrs)	6	76		0	0	3569	CO peak (3 hrs)	CO peak (3 hrs)
CO peak (3 hrs)	4	80		0	0	5178	[CO] 1 hr (mol)	[CO] 1 hr (mol)
[CO] 1 hr (mol)	2	65		5.35×10^{-9}	0	4.27×10^{-8}	[CO] 2 hrs (mol)	[CO] 2 hrs (mol)
[CO] 2 hrs (mol)	0	51		0	0	5.61×10^{-8}	[CO] 3 hrs (mol)	[CO] 3 hrs (mol)
[CO] 3 hrs (mol)	0	38		0	0	8.15×10^{-8}	H ₂ peak (1 hr)	H ₂ peak (1 hr)
H ₂ peak (1 hr)	4.08×10^{-11}	3.49×10^{-10}		0	0	9	H ₂ peak (2 hrs)	H ₂ peak (2 hrs)
H ₂ peak (2 hrs)	3.49×10^{-11}	4.43×10^{-10}		0	0	0	H ₂ peak (3 hrs)	H ₂ peak (3 hrs)
H ₂ peak (3 hrs)	2.33×10^{-11}	4.66×10^{-10}		0	0	0	[H ₂] / mol (1 hr)	[H ₂] / mol (1 hr)
[H ₂] / mol (1 hr)	1.16×10^{-11}	3.78×10^{-10}		0	0	5.24×10^{-11}	[H ₂] / mol (2 hrs)	[H ₂] / mol (2 hrs)
[H ₂] / mol (2 hrs)	0	2.97×10^{-10}		0	0	0	[H ₂] / mol (3 hrs)	[H ₂] / mol (3 hrs)
[H ₂] / mol (3 hrs)	0	2.21×10^{-10}		0	0	0		

NIO Blank Film (Dark)	NIO Blank Film (Light)	Applied Potential (V)	PC3 NIO (Dark)	PC3 (Dark)	PC3 (Light)	PC3 (Light)
-0.5	-0.5		-0.5	-0.5	-0.5	-0.5
pH 6.6 NaHCO ₃ (with CO ₂)	pH 6.6 NaHCO ₃ (with CO ₂)	Electrolyte	pH 6.6 NaHCO ₃ (with CO ₂)	pH 6.6 NaHCO ₃ (with argon)	pH 6.6 NaHCO ₃ (with argon)	pH 6.6 NaHCO ₃ (with CO ₂)
N/A	0.0171	Charge (C)	0.0644	0.0423	0.0765	0.0934
-	1.77×10^{-7}	Electrons (mol)	6.67×10^{-7}	4.38×10^{-7}	7.93×10^{-7}	9.68×10^{-7}
0	0	CO peak (1 hr)	0	0	503	2045
0	0	CO peak (2 hrs)	0	0	0	1294
0	0	CO peak (3 hrs)	0	0	0	1502
0	0	[CO] 1 hr (mol)	0	0	7.91×10^{-9}	3.22×10^{-8}
0	0	[CO] 2 hrs (mol)	0	0	0	2.04×10^{-8}
0	0	[CO] 3 hrs (mol)	0	0	0	2.36×10^{-8}
0	0	H ₂ peak (1 hr)	0	0	20	50
0	0	H ₂ peak (2 hrs)	0	0	0	100
0	0	H ₂ peak (3 hrs)	0	0	0	23
0	0	[H ₂] / mol (1 hr)	0	0	1.16×10^{-10}	2.91×10^{-10}
0	0	[H ₂] / mol (2 hrs)	0	0	0	5.82×10^{-10}
0	0	[H ₂] / mol (3 hrs)	0	0	0	1.34×10^{-10}

Table SC 4. Matrix of GC experiments with the photocatalysts in 50 μ M pH 6.6 NaHCO₃ solution. All light experiments are under simulated 1 sun AM 1.5 light (100 mW cm⁻²).

PC1 (Dark)	PC1 (Light)	PC1 (Light)	Applied Potential (V) vs Ag/AgCl
-0.5	-0.5	-0.5	
pH 8 (with CO ₂)	pH 8 (with argon)	pH 8 (with CO ₂)	Electrolyte
0.0136	0.0237	0.0350	Charge (C)
1.41×10^{-7}	2.46×10^{-7}	3.63×10^{-7}	Electrons (mol)
187	0	0	CO peak (1 hr)
0	0	5023	CO peak (2 hrs)
451	0	6941	CO peak (3 hrs)
3.01×10^{-8}	0	0	[CO] 1 hr (mol)
0	0	8.09×10^{-8}	[CO] 2 hrs (mol)
7.26×10^{-9}	0	1.12×10^{-7}	[CO] 3 hrs (mol)
0	89	63	H ₂ peak (1hr)
0	0	259	H ₂ peak (2 hrs)
0	0	279	H ₂ peak (3 hrs)
0	5.09×10^{-10}	3.61×10^{-10}	[H ₂] / mol (1 hr)
0	0	1.48×10^{-9}	[H ₂] / mol (2 hrs)
0	0	1.60×10^{-9}	[H ₂] / mol (3 hrs)

PC2 (Dark)	PC2 (Light)	Applied Potential (V)
-0.5	-0.5	Electrolyte
pH 8 (with argon)	pH 8 (with argon)	Charge (C)
0.0234	0.2300	Electrons (mol)
2.43×10^{-7}	2.39×10^{-6}	H ₂ peak (15 mins)
3	28	H ₂ peak (30 mins)
5	38	H ₂ peak (1 hrs)
0	31	H ₂ peak (1.5 hrs)
0	35	H ₂ peak (2 hrs)
0	25	[H ₂] / mol (15 mins)
negligible	3.10×10^{-10}	[H ₂] / mol (30 mins)
-	4.21×10^{-10}	[H ₂] / mol (1 hrs)
-	3.44×10^{-10}	[H ₂] / mol (1.5 hrs)
-	3.88×10^{-10}	[H ₂] / mol (2 hrs)
-	2.77×10^{-10}	

NIO Blank Film (Dark)	NIO Blank Film (Light)	PC3 (Dark)	PC3 (Light)	Applied Potential (V) vs Ag/AgCl
-0.5	-0.5	-0.5	-0.5	Electrolyte
pH 8 (with CO ₂)	pH 8 (with CO ₂)	pH 8 (with CO ₂)	pH 8 (with CO ₂)	Charge (C)
N/A	0.0270	0.0093	0.0293	Electrons (mol)
N/A	2.80×10^{-7}	9.63×10^{-8}	3.04×10^{-7}	CO peak (1 hr)
-	0	0	186	CO peak (2 hrs)
-	0	0	50	CO peak (3 hrs)
-	0	0	0	[CO] 1 hr (mol)
-	0	0	3.00×10^{-9}	[CO] 2 hrs (mol)
-	0	0	8.05×10^{-10}	[CO] 3 hrs (mol)
-	0	0	0	H ₂ peak (1 hr)
		0	0	H ₂ peak (2 hrs)
		0	0	H ₂ peak (3 hrs)
		0	0	[H ₂] / mol (1 hr)
		0	9.73×10^{-10}	[H ₂] / mol (2 hrs)
		0	0	[H ₂] / mol (3 hrs)
		0	1.57×10^{-9}	
		0	0	

Table SC 5. Matrix of GC experiments with the photocatalysts in 0.1 M pH 8 phosphate buffer. All light experiments are under simulated 1 sun AM 1.5 light (100 mW cm⁻²).

PC3 (Dark)	PC3 (Light)	PC3 (Dark)	PC3 (Light)	Applied Potential (V) vs Ag/AgCl	PC2 (Dark)	PC2 (Light)	Applied Potential (V)	PC1 (Dark)	PC1 (Light)	PC1 (Light)	Applied Potential (V) vs Ag/AgCl
-0.5	-0.5	-0.5	-0.5	Electrolyte	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	Electrolyte
pH 9.2 (with argon)	pH 9.2 (with argon)	pH 9.2 (with CO ₂)	pH 9.2 (with CO ₂)	Electrolyte	pH 9.2 (with argon)	pH 9.2 (with argon)	Electrolyte	pH 9.2 (with CO ₂)	pH 9.2 (with argon)	pH 9.2 (with CO ₂)	Electrolyte
0.0080	0.0207	0.0200	0.0460	Charge (C)	0.0070	0.0120	Charge (C)	0.0092	0.0256	0.0329	Charge (C)
8.29E x 10 ⁻⁸	2.157E x 10 ⁻⁷	2.17E x 10 ⁻⁷	4.77 x 10 ⁻⁷	Electrons (mol)	7.25 x 10 ⁻⁸	1.24 x 10 ⁻⁷	Electrons (mol)	9.52 x 10 ⁻⁸	2.65 x 10 ⁻⁷	3.41 x 10 ⁻⁷	Electrons (mol)
0	76	0	2649	CO peak (1 hr)	2	50	H ₂ peak (15 mins)	369	416	5010	CO peak (1 hr)
0	0	0	5515	CO peak (2 hrs)	7	42	H ₂ peak (30 mins)	0	0	7035	CO peak (2hrs)
0	0	0	7108	CO peak (3 hrs)	4	40	H ₂ peak (1 hrs)	0	0	9277	CO peak (3hrs)
0	0	0	4.23 x 10 ⁻⁸	[CO] 1 hr (mol)	0	37	H ₂ peak (1.5 hrs)	5.90 x 10 ⁻⁸	6.65 x 10 ⁻⁸	8.01 x 10 ⁻⁸	[CO] 1 hr (mol)
0	0	0	8.8 x 10 ⁻⁸	[CO] 2 hrs (mol)	0	29	H ₂ peak (2 hrs)	0	0	1.1 x 10 ⁻⁷	[CO] 2 hrs (mol)
0	1.22 x 10 ⁻⁹	0	1.14 x 10 ⁻⁷	[CO] 3 hrs (mol)	Negligible	5.54 x 10 ⁻¹⁰	[H ₂] / mol (15 mins)	0	0	1.48 x 10 ⁻⁷	[CO] 3 hrs (mol)
0	0	0	136	H ₂ peak (1 hr)	-	4.66 x 10 ⁻¹⁰	[H ₂] / mol (30 mins)	0	0	87	H ₂ peak (1hr)
0	0	0	218	H ₂ peak (2 hrs)	-	4.43 x 10 ⁻¹⁰	[H ₂] / mol (1 hrs)	0	0	253	H ₂ peak (2hrs)
0	0	0	301	H ₂ peak (3 hrs)	-	4.10 x 10 ⁻¹⁰	[H ₂] / mol (1.5 hrs)	0	0	256	H ₂ peak (3hrs)
0	0	0	8.2 x 10 ⁻¹⁰	[H ₂] / mol (1 hr)	-	3.21 x 10 ⁻¹⁰	[H ₂] / mol (2 hrs)	0	0	5.25 x 10 ⁻¹⁰	[H ₂] / mol (1hr)
0	0	0	1.31 x 10 ⁻⁹	[H ₂] / mol (2 hrs)				0	0	1.53 x 10 ⁻⁹	[H ₂] / mol (2hrs)
0	0	0	1.81 x 10 ⁻⁹	[H ₂] / mol (3 hrs)				0	0	1.54 x 10 ⁻⁹	[H ₂] / mol (3hrs)

	NiO Blank (Dark)	NiO Blank (Light)
	-0.5	-0.5
	pH 9.2 (with CO ₂)	pH 9.2 (with CO ₂)
	N/A	0.0210
	N/A	$2.18\text{E} \times 10^{-7}$
	-	157
	-	0
	-	0
	-	2.51×10^{-6}
	-	0
	-	0

Table SC 6. Matrix of GC experiments with the photocatalysts in 0.1 M pH 9.2 carbonate buffer. All light experiments are under simulated 1 sun AM 1.5 light (100 mW cm⁻²).

	PC1 (under CO ₂)	PC2 (under Ar)	PC3 (under CO ₂)
$\eta_{\text{Far}}/\%$ (CO)	91	-	39
$\eta_{\text{Far}}/\%$ (H ₂)	2.0	0.24	1.7
[CO]/ $\mu\text{mol h}^{-1} \text{cm}^{-2}$	0.1 (± 0.011)	-	0.038 (± 0.003)
[H ₂]/ $\text{nmol h}^{-1} \text{cm}^{-2}$	4.3 (± 0.473)	0.95 (± 0.0475)	3.2 (± 0.256)
TOF (CO) h^{-1}	1.8	-	0.8
TON (H ₂) h^{-1}	0.08	0.007	0.07

Table SC 7. Faradaic efficiencies ($\eta_{\text{Far}}/\%$), and turnovers per hour per catalytic centre (TOF) for CO and H₂ production during photoelectrocatalysis for the photocatalysts in 0.1 M pH 5 acetate buffer under 1 sun AM1.5 illumination (100 mW cm⁻²). The applied bias to these systems was -0.5 V vs Ag/AgCl.

	PC1 (under CO ₂)	PC2 (under Ar)	PC3 (under CO ₂)
$\eta_{\text{Far}}/\%$ (CO)	30	-	4.9
$\eta_{\text{Far}}/\%$ (H ₂)	nil	<0.1	<0.1
[CO]/ $\mu\text{mol h}^{-1} \text{cm}^{-2}$	0.035 (± 0.0031)	-	0.01 (± 0.00145)
[H ₂]/ $\text{nmol h}^{-1} \text{cm}^{-2}$	Nil	Very low	Very low
TOF (CO) h^{-1}	0.63	Nil	0.21
TOF (H ₂) h^{-1}	Nil	Nil	Nil

Table SC 8. Faradaic efficiencies ($\eta_{\text{Far}}/\%$), and turnovers per catalyst per hour (TOF) for CO and H₂ production during photoelectrocatalysis for the photocatalysts in 50 μM pH 6.6 NaHCO₃ solution under 1 sun AM1.5 illumination (100 mW cm⁻²). The applied bias to these systems was -0.5 V vs Ag/AgCl.

	PC1 (under CO ₂)	PC2 (under Ar)	PC3 (under CO ₂)
$\eta_{\text{Far}}/\%$ (CO)	61.6	-	28.1
$\eta_{\text{Far}}/\%$ (H ₂)	0.44	<0.1	0.4
[CO]/ $\mu\text{mol h}^{-1} \text{cm}^{-2}$	0.047 (± 0.0042)	-	0.024 (± 0.0028)
[H ₂]/ $\text{nmol h}^{-1} \text{cm}^{-2}$	0.67 (± 0.060)	0.18 (± 0.014)	0.66 (± 0.079)
TOF (CO) h^{-1}	0.86	-	0.50
TOF (H ₂) h^{-1}	0.013	0.003	0.013

Table SC 9. Faradaic efficiencies ($\eta_{\text{Far}}/\%$), and turnovers per catalyst per hour (TOF) for CO and H₂ production during photoelectrocatalysis for the photocatalysts in 0.1 M pH 8 phosphate buffer under 1 sun AM1.5 illumination (100 mW cm⁻²). The applied bias to these systems was -0.5 V vs Ag/AgCl.

	PC1 (under CO ₂)	PC2 (under Ar)	PC3 (under CO ₂)
$\eta_{\text{Far}}/\%$ (CO)	87.0	-	47.6
$\eta_{\text{Far}}/\%$ (H ₂)	0.45	0.2	0.38

$[\text{CO}_2]/\mu\text{mol h}^{-1} \text{ cm}^{-2}$	0.062 (± 0.080)	-	0.048 (± 0.004)
$[\text{H}_2]/\text{nmol h}^{-1} \text{ cm}^{-2}$	0.065 (± 0.008)	0.2 (± 0.018)	0.077 (± 0.006)
TOF (CO) h^{-1}	1.14	-	1.02
TOF (H_2) h^{-1}	0.013	0.003	0.017

Table SC 10. Faradaic efficiencies ($\eta_{\text{Far}}/\%$), and turnovers per catalyst per hour (TOF) for CO and H_2 production during photoelectrocatalysis for the photocatalysts in 0.1 M pH 9.2 carbonate buffer under 1 sun AM1.5 illumination (100 mW cm^{-2}). The applied bias to these systems was -0.5 V vs Ag/AgCl.

Calibration of Gas Chromatography Measurements

The main gaseous products of interest in this study were carbon monoxide and hydrogen. Calibration of the gas chromatograph's flame ionization detector (FID) and thermal conductivity detector (TCD) was accomplished by dosing known mixtures of a certified standard gas (BOC) containing 5,000 ppm propylene, 5,000 ppm methane, 5,000 ppm ethylene, 5,000 ppm methane, 10,000 ppm carbon monoxide, 10,000 ppm hydrogen and the balance carbon dioxide.

Calibration was done by taking the glass reaction cell described in earlier in the manuscript and injecting known amounts of the standard gas into the headspace with each electrolyte present. The gas is allowed to equilibrate for 5 mins, then a headspace sample of 0.5 ml is withdrawn as one would do during the photoelectrocatalysis experiments.

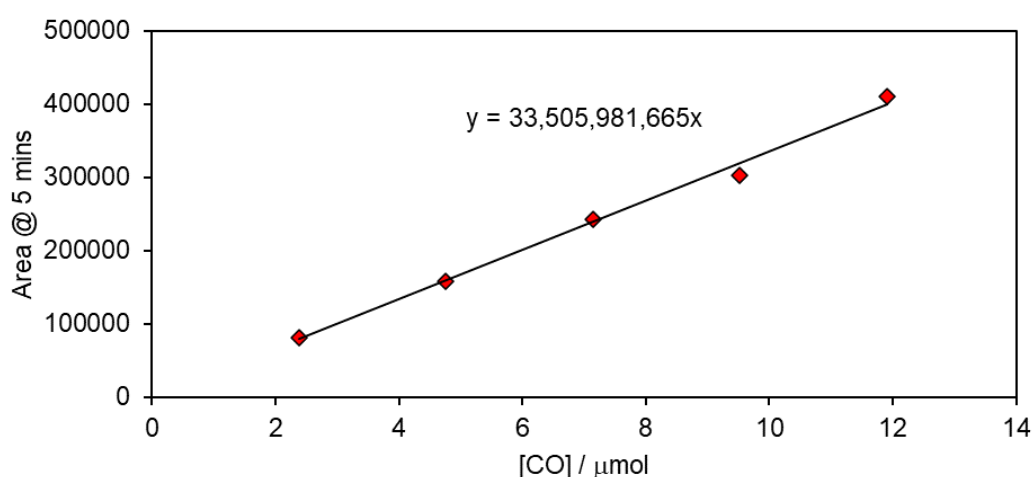


Figure SC 87. Calibration chart for carbon monoxide concentration measured by gas chromatography using a flame ionization detector. Sampling was from the PEC cell headspace containing pH 5 acetate buffer.

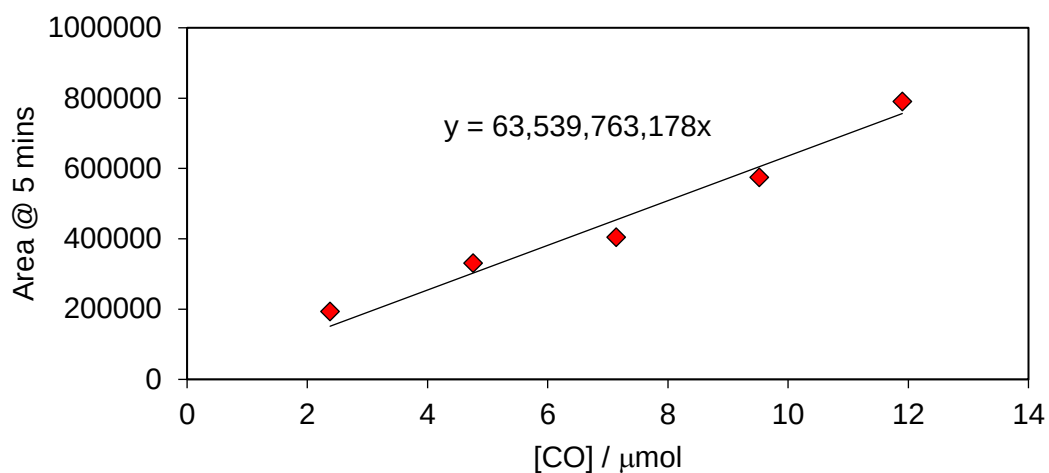


Figure SC 88. Calibration chart for carbon monoxide concentration measured by gas chromatography using a flame ionization detector. Sampling was from the PEC cell headspace containing 50 μM pH 6.6 NaHCO_3 solution.

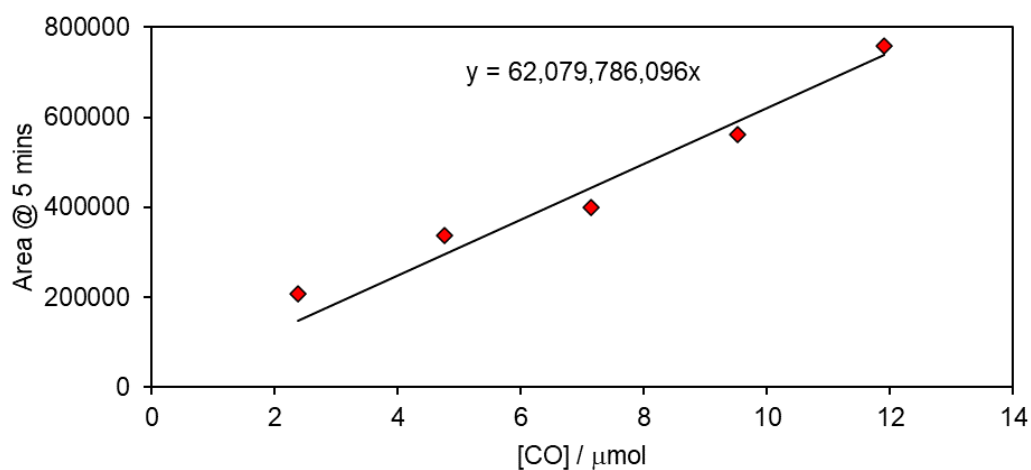


Figure SC 89. Calibration chart for carbon monoxide concentration measured by gas chromatography using a flame ionization detector. Sampling was from the PEC cell headspace containing pH 8 phosphate buffer.

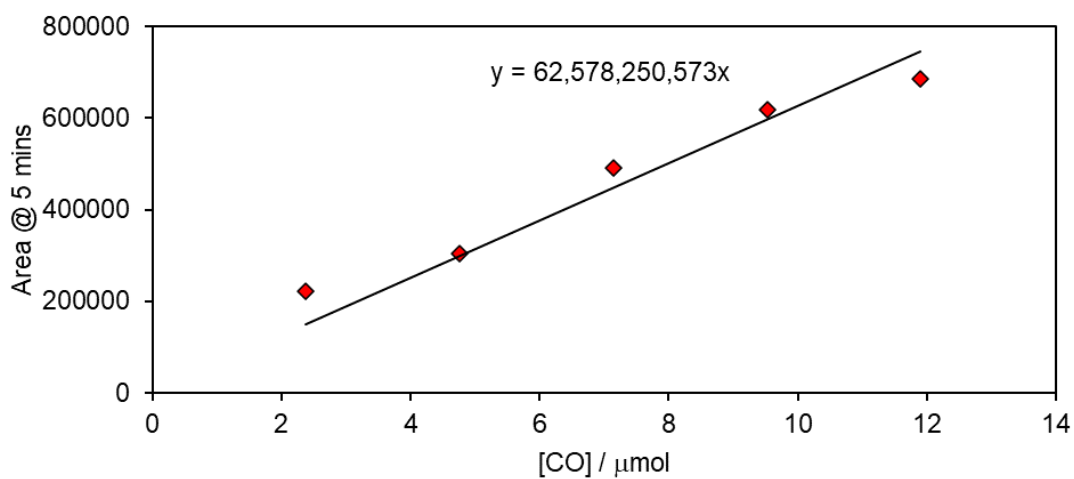


Figure SC 90. Calibration chart for carbon monoxide concentration measured by gas chromatography using a flame ionization detector. Sampling was from the PEC cell headspace containing pH 9.2 carbonate buffer.

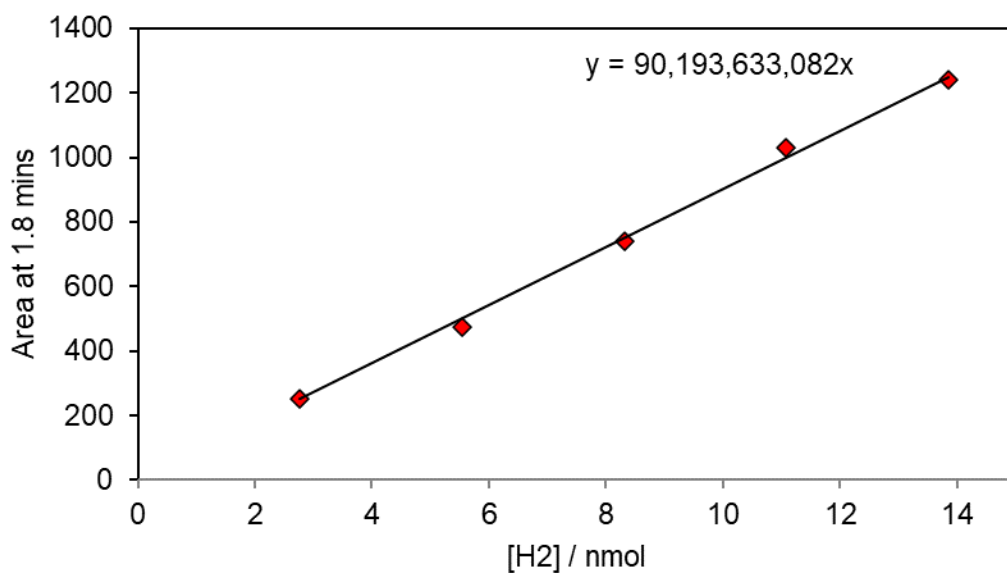


Figure SC 91. Calibration chart for hydrogen concentration measured by gas chromatography using a thermal conductivity detector. Sampling was from the PEC cell headspace containing pH 5 acetate buffer.

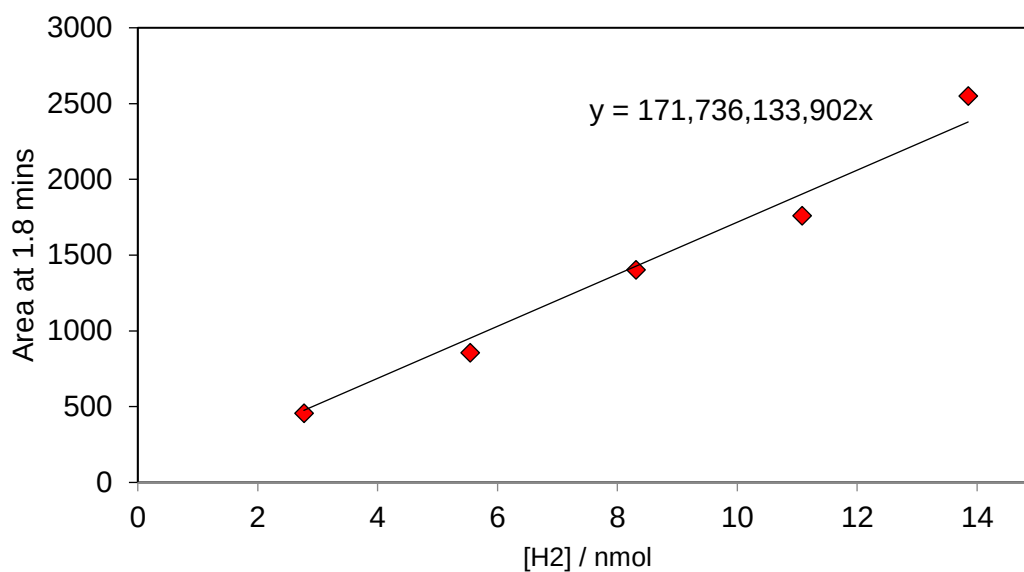


Figure SC 92. Calibration chart for hydrogen concentration measured by gas chromatography using a thermal conductivity detector. Sampling was from the PEC cell headspace containing 50 μ M pH 6.6 NaHCO₃ solution.

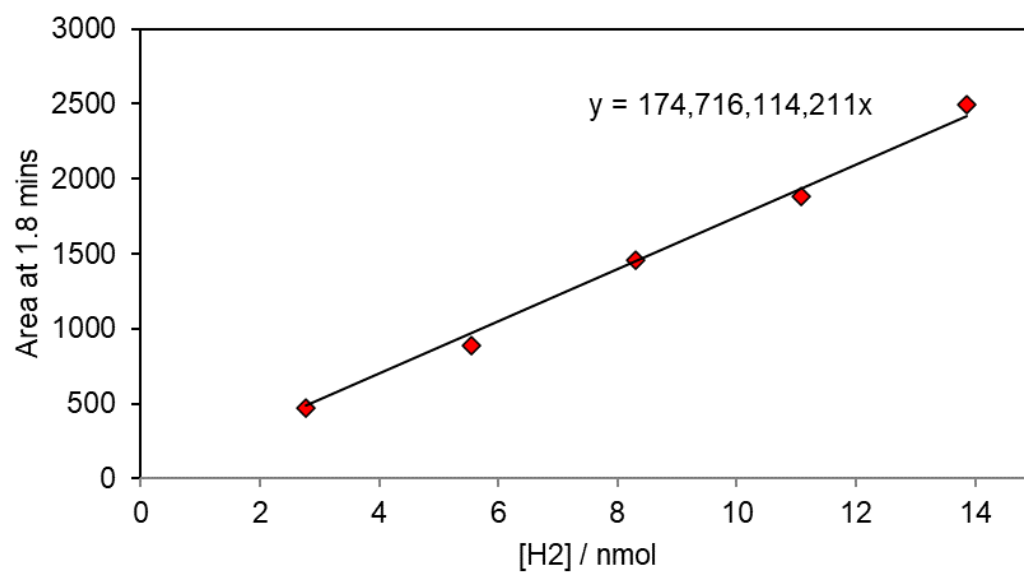


Figure SC 93. Calibration chart for hydrogen concentration measured by gas chromatography using a thermal conductivity detector. Sampling was from the PEC cell headspace containing pH 8 phosphate buffer.

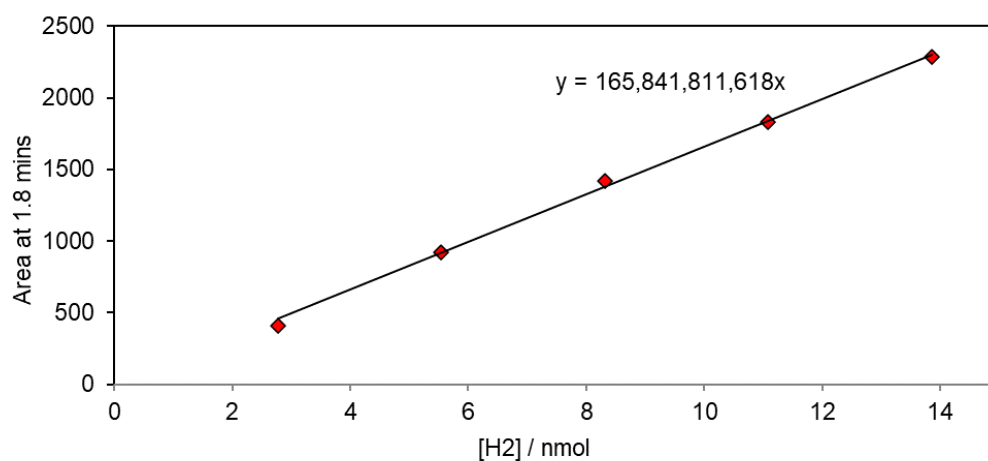


Figure SC 94. Calibration chart for hydrogen concentration measured by gas chromatography using a thermal conductivity detector. Sampling was from the PEC cell headspace containing pH 9.2 carbonate buffer.

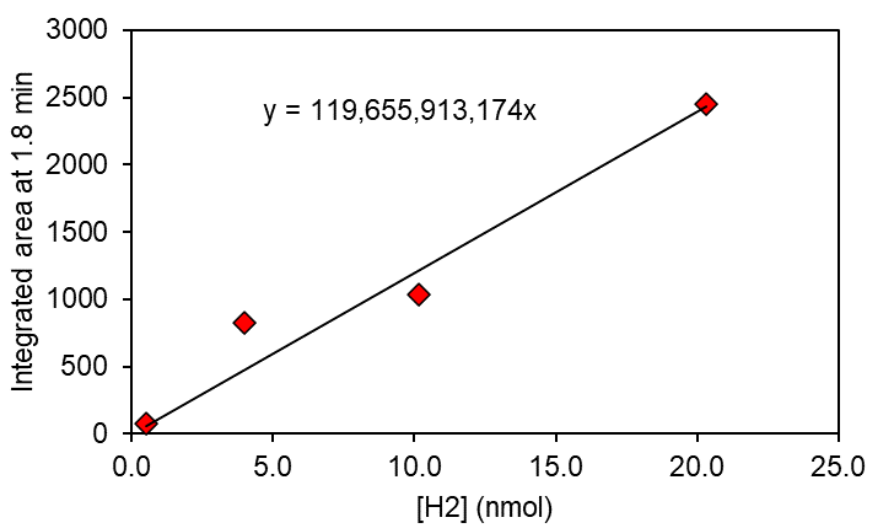


Figure SC 95. Calibration chart for hydrogen concentration measured by gas chromatography using a thermal conductivity detector. Here, low concentration calibrated H_2 gas standard mixtures of H_2/N_2 were injected from a gas bag.

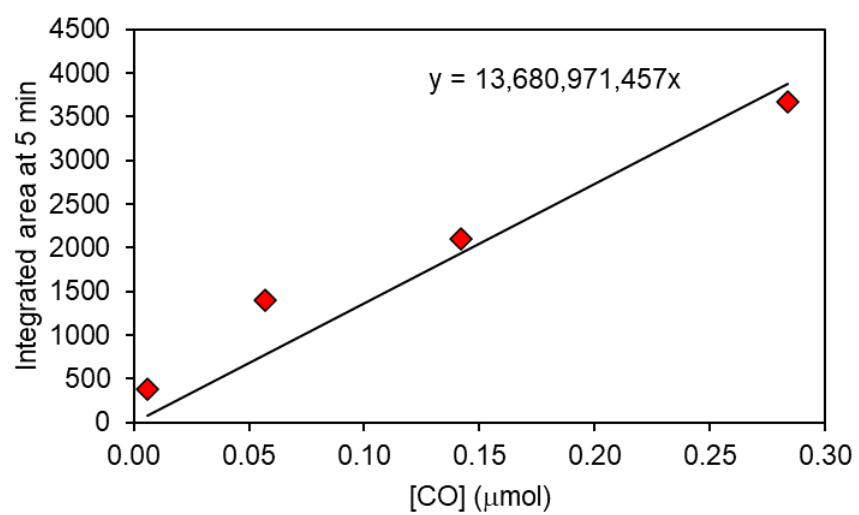


Figure SC 96. Calibration chart for carbon monoxide concentrations measured by gas chromatography using a flame ionization. Here, low concentration calibrated CO gas standard mixtures of H_2/N_2 were injected from a gas bag.

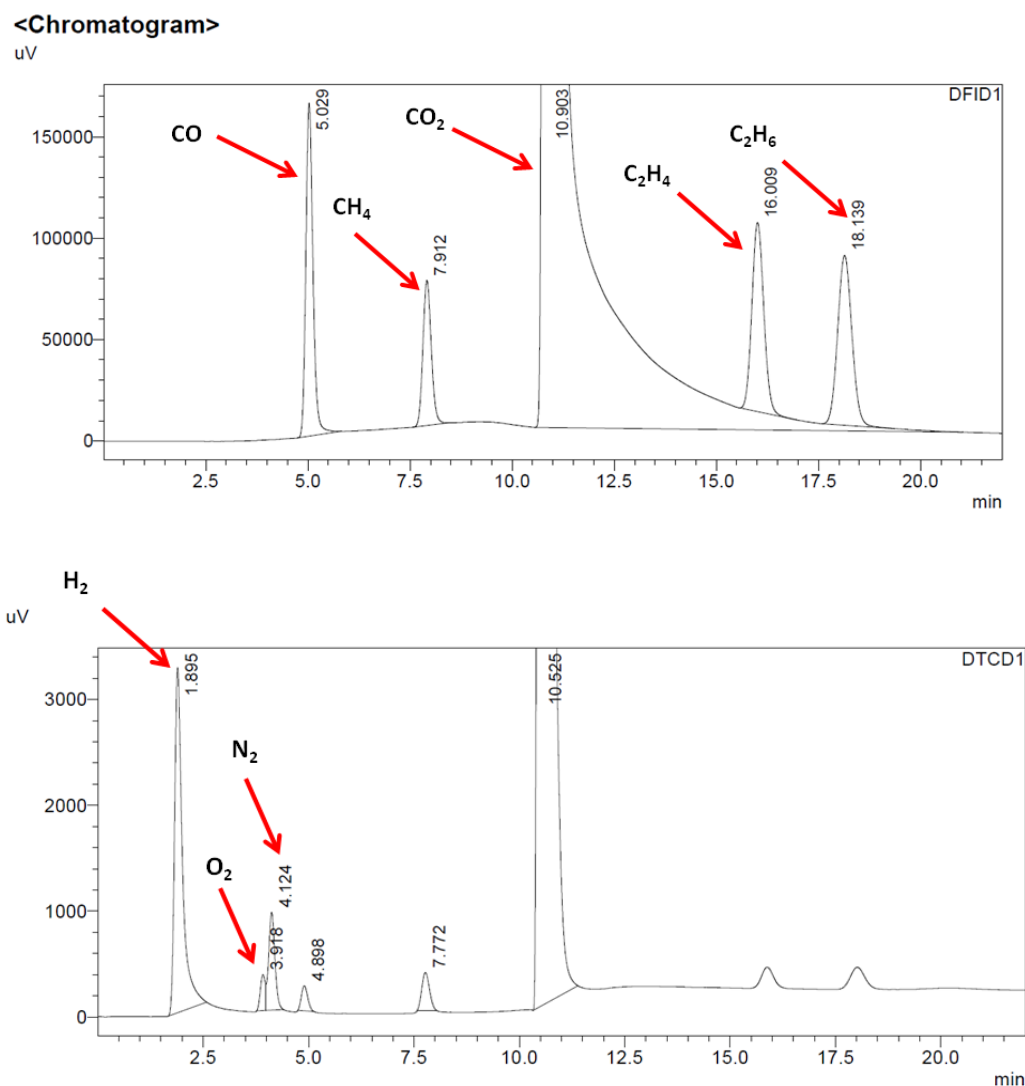


Figure SC 97. Representative gas chromatogram traces from calibration of carbon monoxide from a standard mixture. The upper panel shows a trace from the flame-ionization detector, the bottom panel displays the output from the thermal conductivity detector. Major components of the gas mixture have been identified by comparing with manufacturers specifications of the column used (Restek ShinCarbon Restek ShinCarbon ST 80/100).

¹³CO₂ Isotope Labelled Gas Analysis of Products from PC1|NiO

In order to establish the true origin of carbon products evolved from the system PC1|NiO the regular CO₂ feedstock was substituted for ¹³CO₂, and gaseous products monitored with GC-MS analysis. The assumption was that any CO produced by photoelectrocatalysis would be isotopic ¹³CO and other products due to degradation of the photocatalyst would be ¹²C. The photocatalysis experiment performed with ¹³CO₂, feedstock was PC1 in pH 5 acetate buffer with an applied bias of -0.5 V and -0.2 V vs Ag/AgCl. The conclusion of the data tabulated below is that there is a mixture of genuine photocatalysis and some ¹²C due to impurities in the gas

stream and potential degradation of the photocatalyst, consistent with the UV-vis and XPS studies.

GC-MS analysis details

*Instrument: Agilent 8890 GC system with 5977B GC/MSD mass spec

*Column: HP-PLOT-Q

For experiment at -0.2 V

*Injection: 400 microlitres manual injection with gas tight syringe

*Oven: 50 degrees for 2 mins then increase 10 degrees per minute to 100 degrees and hold 3 mins. Solvent delay 0.5 min.

*Inlet temp 100 degree, flow 1 ml per min, transfer line 280 degrees, injection volume 1 microlitre, carrier gas helium. SIM and scan mode used, range of mass 1.6 to 150, ions monitored 44, 45, 28, 29, 12C, 13C.

For the experiment at -0.5 V vs Ag/AgCl

*Injection: 40 microlitres manual injection with gas tight syringe

*Oven: 40 degrees for 10 mins then increase 40 degrees per minute to 120 degrees and hold 5 mins. Solvent delay 0.5 min.

*Inlet temp 100 degree, flow 1 ml per min, transfer line 230 degrees, injection volume 1 microlitre, carrier gas helium. SIM and scan mode used, range of mass 1.6 to 150, ions monitored 44, 45, 28, 29, 12C, 13C.

Note that with the above GC-MS method it was not possible to effectively separate carbon monoxide from residual air in the reaction vessel. This presents a challenge in distinguishing between N₂ in air (m/z 28), ¹²CO (m/z 28) and ¹³CO (m/z 29). We could not obtain clear chromatographic separation of the gases due to the column that was available. To separate the ¹³CO from ¹²CO and N₂ we used the extracted ion chromatogram (EIC) by plotting the intensity of the signal observed at 12, 13, 28 and 29 ions separately. To separate the ¹³CO from ¹²CO and nitrogen, we used an extracted ion chromatogram (EIC) and plotted the area of the signal observed at 12, 13, 28 and 29 ions separately. The main evidence that we were producing ¹³CO was that the area of the ¹³CO peak increases against the ¹²CO peak (from EIC, example below), while the portion of air was constant.

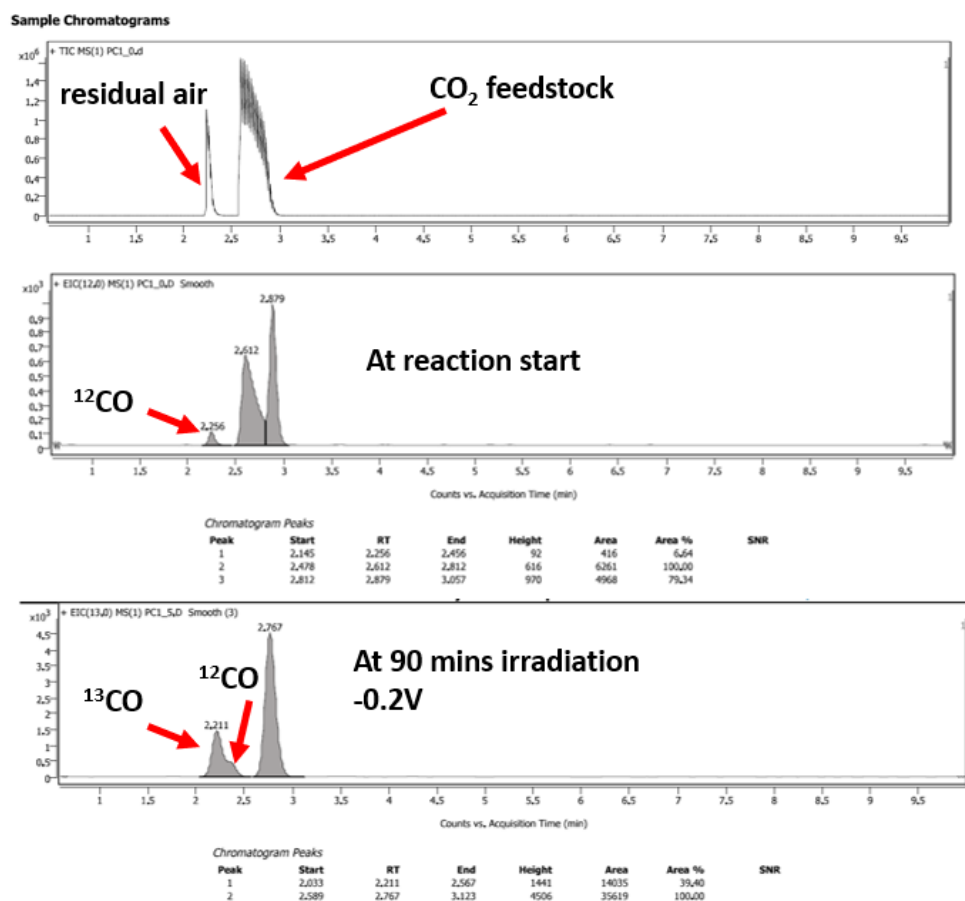


Figure SC 98. Example of GC-MS Analysis PC1 @ pH 5 -0.2 V vs Ag/AgCl.

PC1	^{12}CO	^{13}CO	$^{13}\text{CO}/^{12}\text{CO}$
@ pH 5 -0.5 V vs Ag/AgCl			
0 min	10905	60985	5.59
30 min	20049	96587	4.82
60 min	30799	148363	4.82
90 min	39593	81318	2.05
120 min	19980	95012	4.76

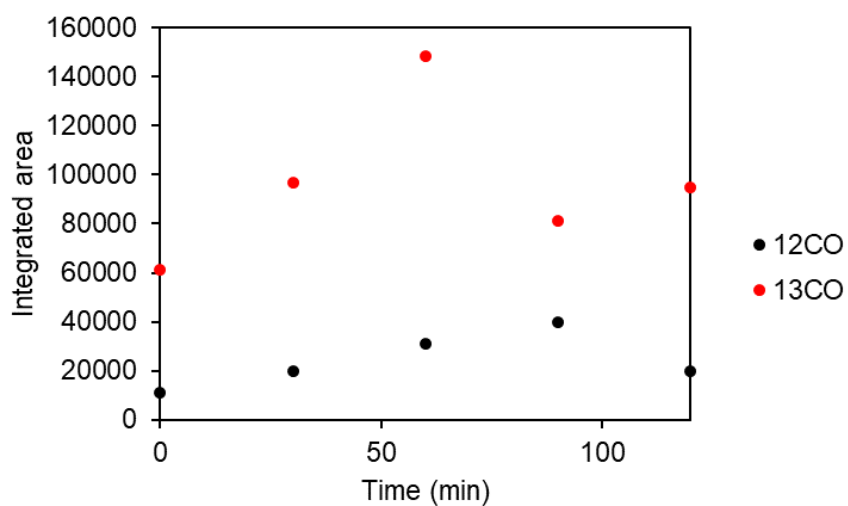


Figure SC 99. Evolution of ¹³CO vs ¹²CO evolved from photoelectrocatalysis reaction of PC1 in pH 5 acetate buffer under 1 sun AM 1.5 irradiation and an applied external bias of −0.5 V vs Ag/AgCl as monitored by GC-MS.

PC1	¹² CO	¹³ CO	¹³ CO/ ¹² CO
@ pH 5 -0.2 V vs Ag/AgCl			
0 min	415	4127	9.95
15 min	1578	6563	4.16
30 min	1934	8978	4.64
60 min	1948	9621	4.94
90 min	2665	14035	5.27

120 min	2725	9737	3.57

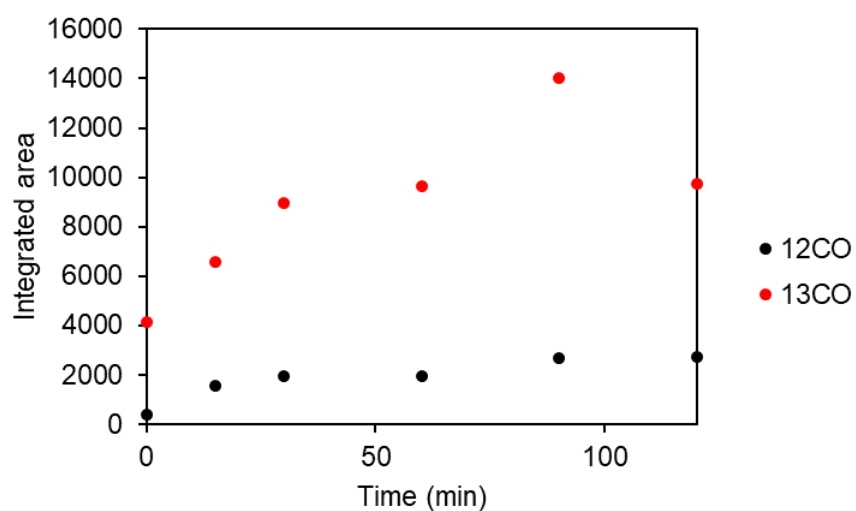


Figure SC 100. Evolution of ¹³CO vs ¹²CO evolved from photoelectrocatalysis reaction of PC1 in pH 5 acetate buffer under 1 sun AM 1.5 irradiation and an applied external bias of −0.2 V vs Ag/AgCl as monitored by GC-MS.

PC1	¹² CO	¹³ CO	¹³ CO/ ¹² CO
@ pH 8 -0.2 V vs Ag/AgCl			
0 min	238	1811	7.61
15 min	523	3405	6.51
30 min	663	4626	6.98

60 min	1024	5686	5.55
90 min	989	7225	7.30
120 min	1073	6257	5.83
180 min	1455	6287	4.32

Feedstock gas ($^{13}\text{CO}_2$) pure	^{12}CO	^{13}CO	$^{13}\text{CO}/^{12}\text{CO}$	$^{13}\text{CO}_2$
repeat 1	3282	17430	5.31	295300000
repeat 2	2684	14410	5.37	292500000
repeat 3	2183	10351	4.74	292900000

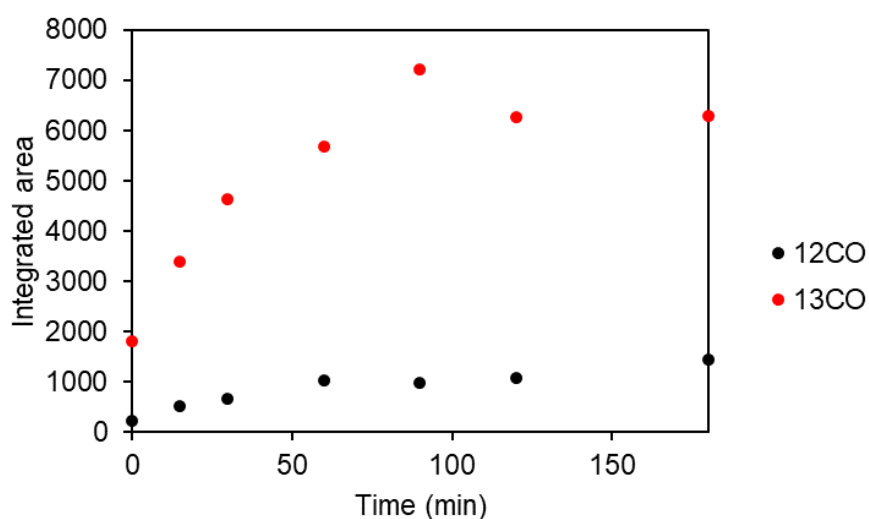
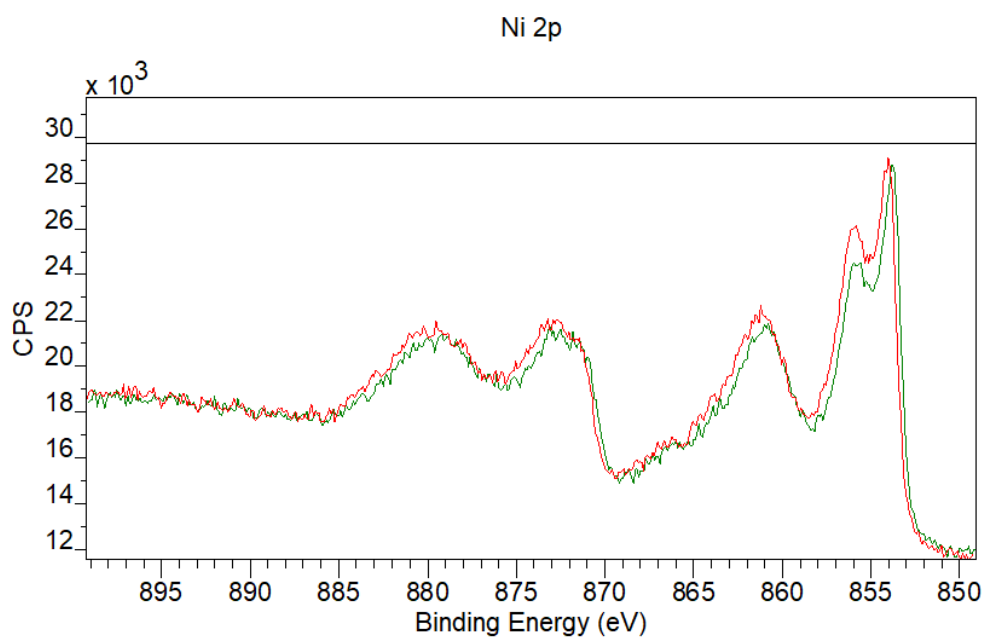


Figure SC 101. Evolution of ^{13}CO vs ^{12}CO evolved from photoelectrocatalysis reaction of PC1 in pH 8 phosphate buffer under 1 sun AM 1.5 irradiation and an applied external bias of -0.2 V vs Ag/AgCl as monitored by GC-MS.

S6. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were obtained for the photocatalysts on NiO both before and after photoelectrocatalysis experiments as described in the main manuscript. The films had been irradiated with 1 sun intensity illumination AM 1.5 light for 1000 seconds under chopped light conditions in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl . The adventitious carbon signal located at 284.8 eV was used to calibrate samples.



Figure

SC 102. Unsensitized NiO thin film nickel 2p region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

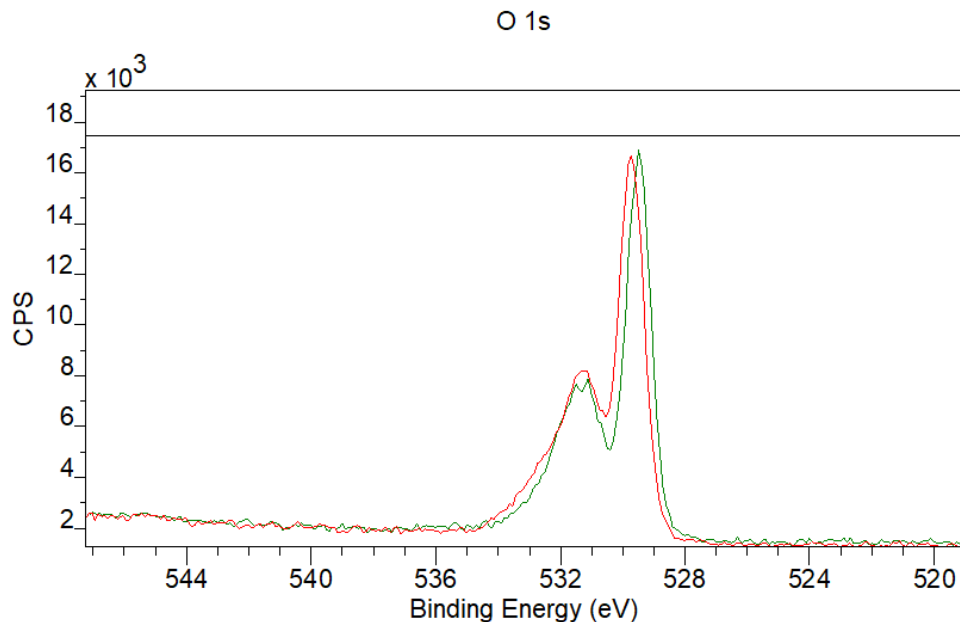


Figure SC 103. Unsensitized NiO thin film oxygen 1s region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

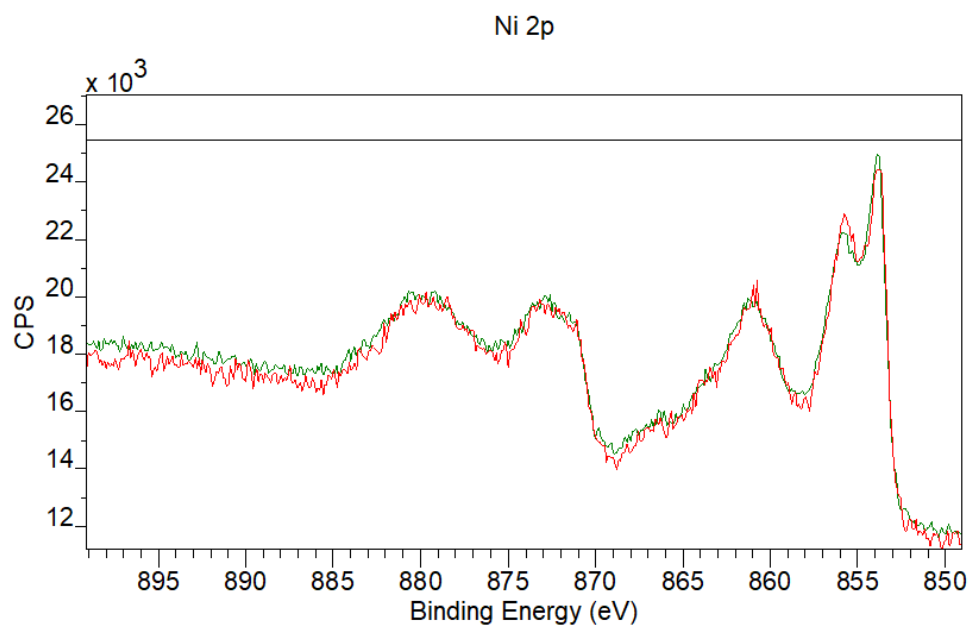


Figure SC

104. PC1/NiO thin film nickel 2p region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

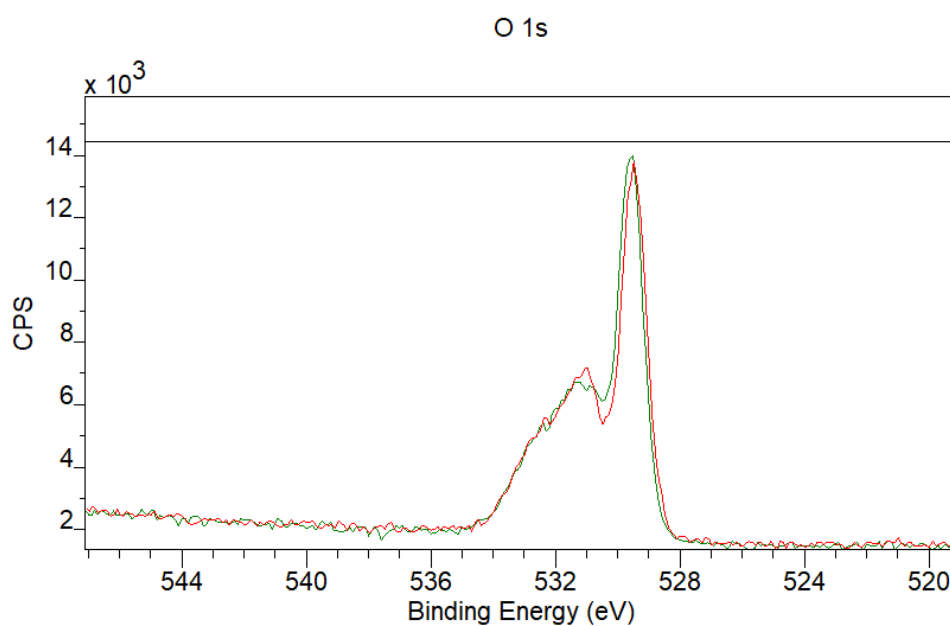


Figure SC 105. PC1/NiO thin film oxygen 1s region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

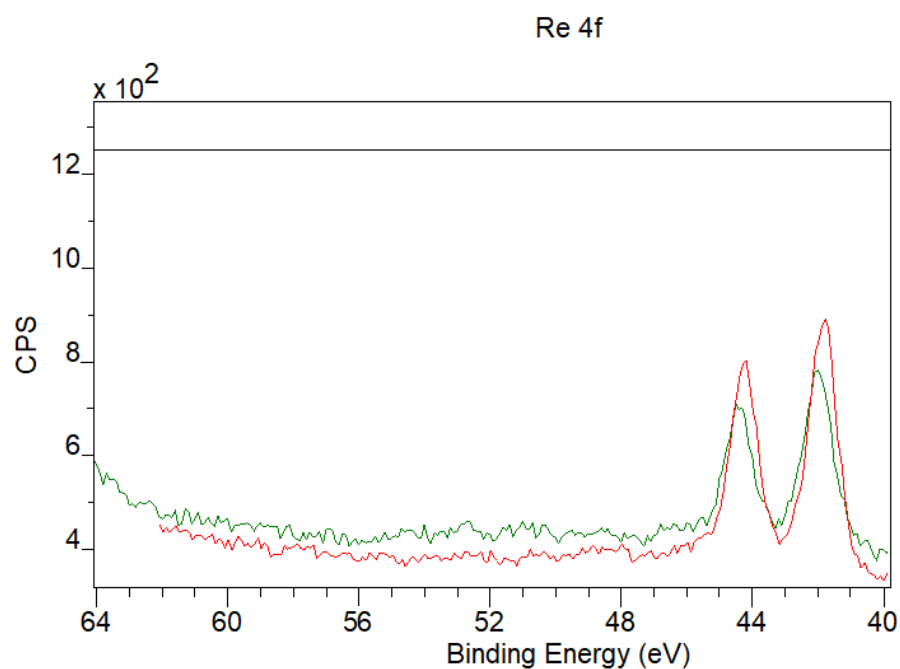


Figure SC 106. PC1/NiO thin film rhenium 4f region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

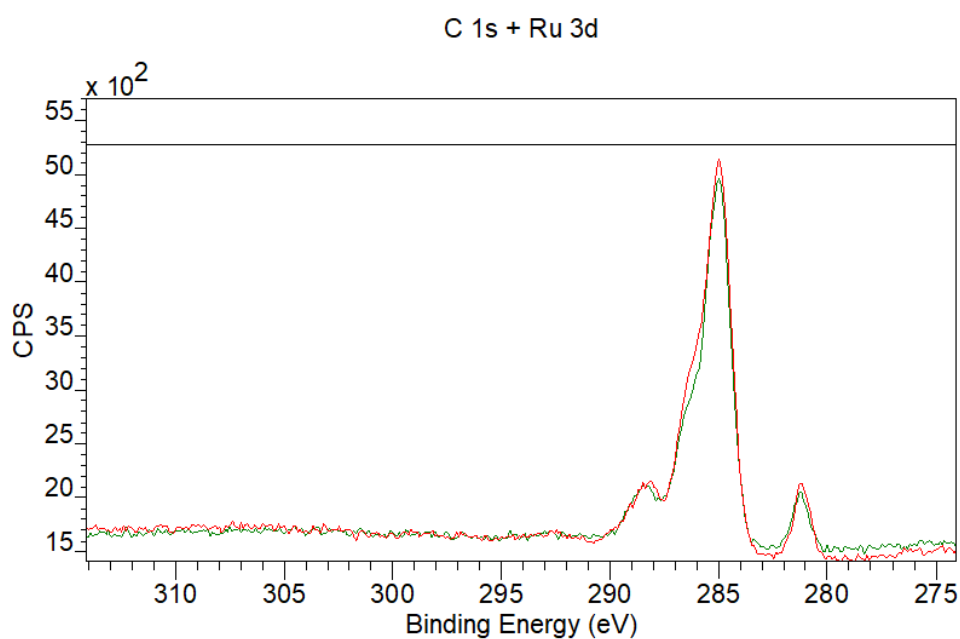


Figure SC 107. PC1/NiO thin film carbon 1s and ruthenium 3d regions before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

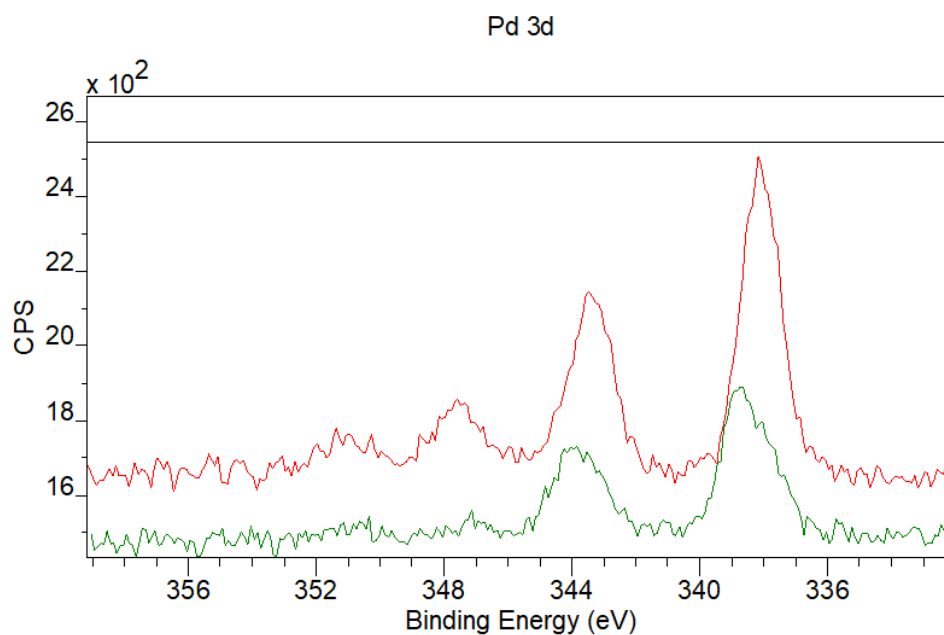


Figure SC 108. PC2/NiO palladium 3d region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

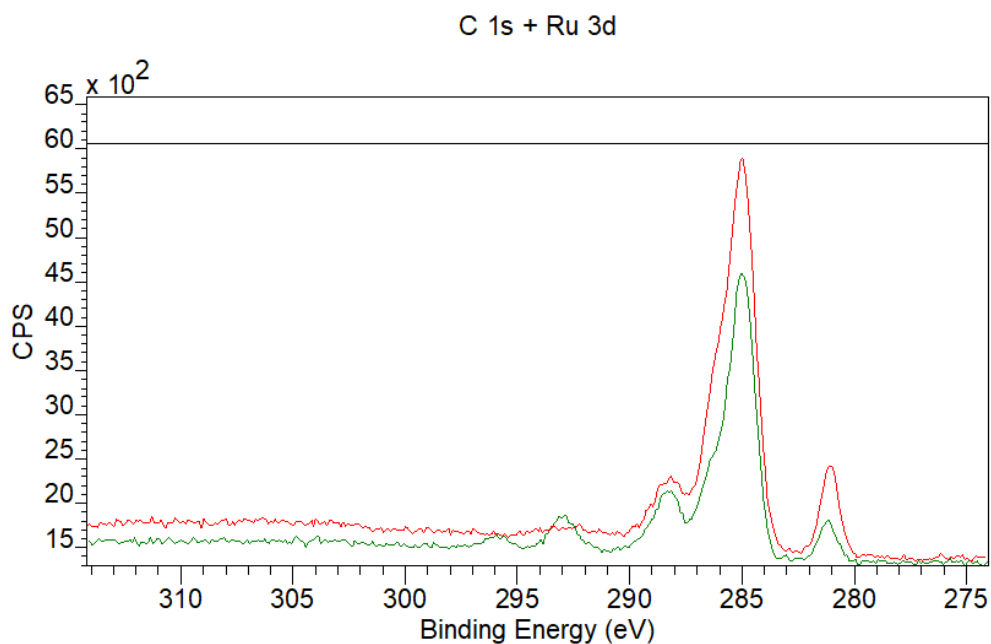


Figure SC 109. PC2/NiO carbon 1s and ruthenium 3d regions before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm^{-2}) irradiation.

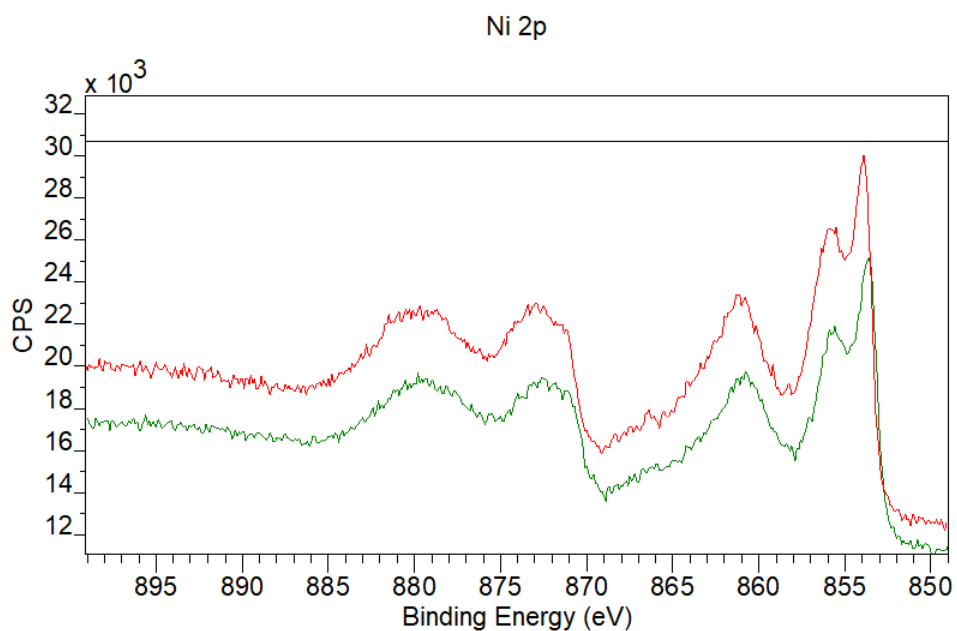


Figure SC

110. PC2/NiO nickel 2p region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

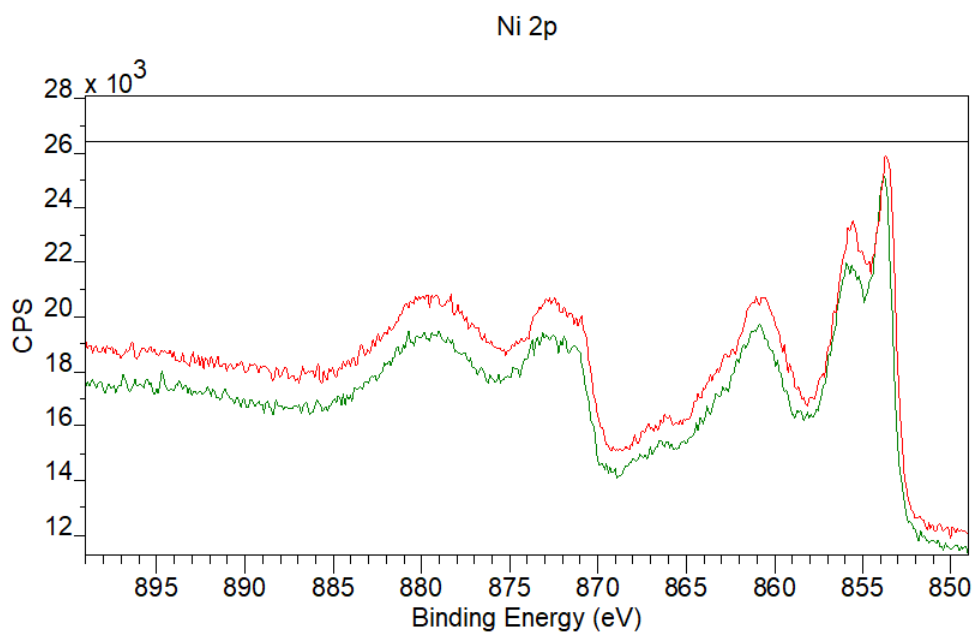


Figure SC 111. PC3/NiO thin film nickel 2p region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

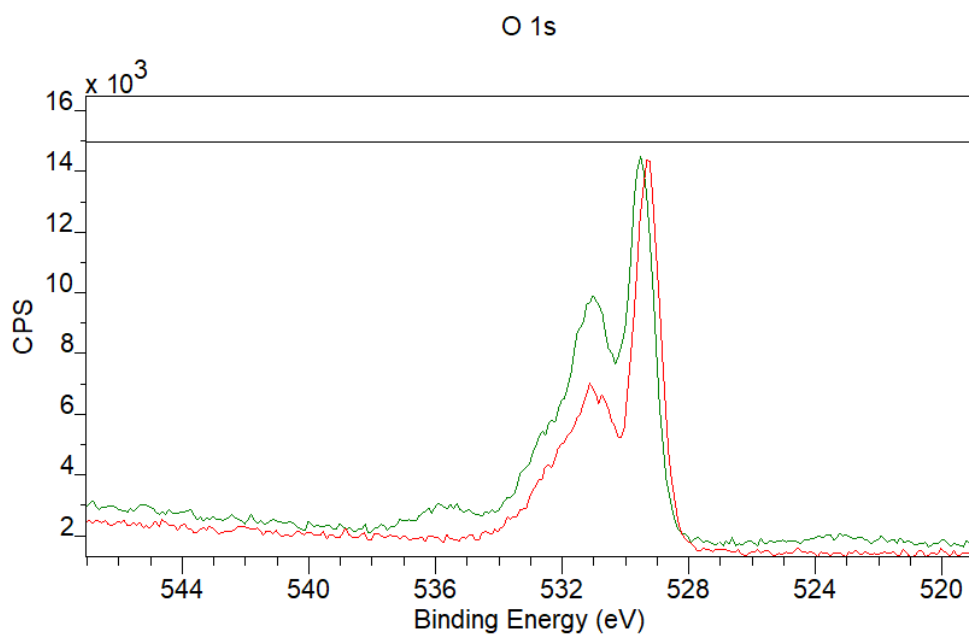


Figure SC 112. PC3/NiO thin film oxygen 1s region before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

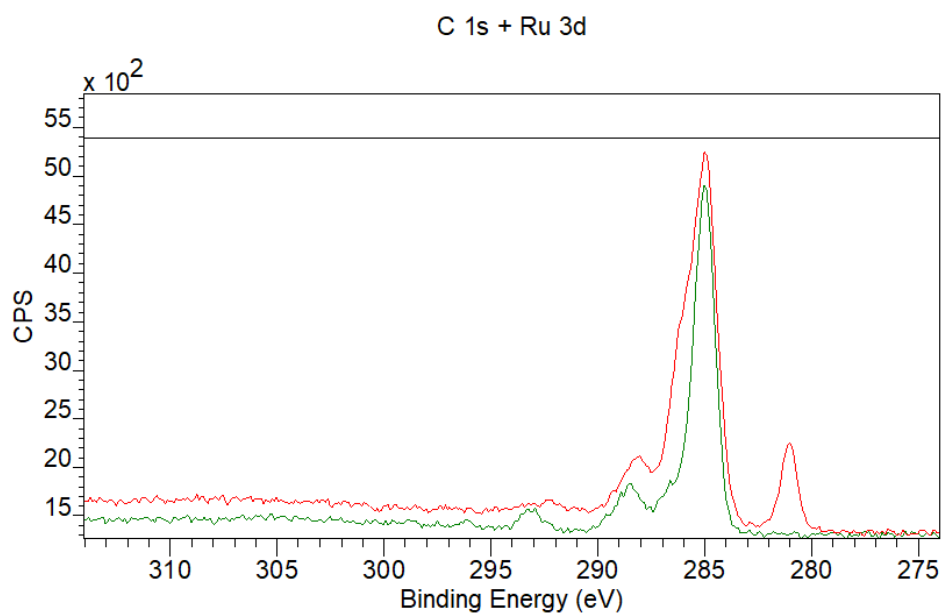


Figure SC 113. PC3/NiO thin film carbon 1s and ruthenium 3d regions before photoelectrocatalysis (red trace), after photoelectrocatalysis (green trace) in 0.1 M pH 5 acetate buffer with an applied bias of -0.2 V vs Ag/AgCl under 1 sun AM 1.5, (100 mW cm⁻²) irradiation.

References

- 1 J. F. Geldard and F. Lions, *J. Org. Chem.*, 1965, **30**, 318–319.
- 2 L. Hammarström, T. Norrby, G. Stenhagen, J. Mårtensson, B. Åkermark and M. Almgren, *Journal of Physical Chemistry B*, 1997, **101**, 7494–7504.
- 3 I. Bratsos and E. Alessio, in *Inorganic Syntheses*, Wiley Blackwell, 2010, vol. 35, pp. 148–163.
- 4 M. Toyama, T. Takizawa, I. Morita, N. Nagao, Y. Kuramochi and H. Ishida, *Chemistry - A European Journal*, 2019, **25**, 16582–16590.
- 5 S. Sumikura, S. Mori, S. Shimizu, H. Usami and E. Suzuki, *J Photochem Photobiol A Chem*, 2008, **199**, 1–7.
- 6 C. Slavov, H. Hartmann and J. Wachtveitl, *Anal Chem*, 2015, **87**, 2328–2336.

Appendix D: A novel naphthalene-diimide rhenium carbonyl compound; a spectroscopic, electrochemical and CO₂ reduction study – supporting information

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Re(oppt)(CO) ₃ Cl.....	D-12
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ATR-IR spectra

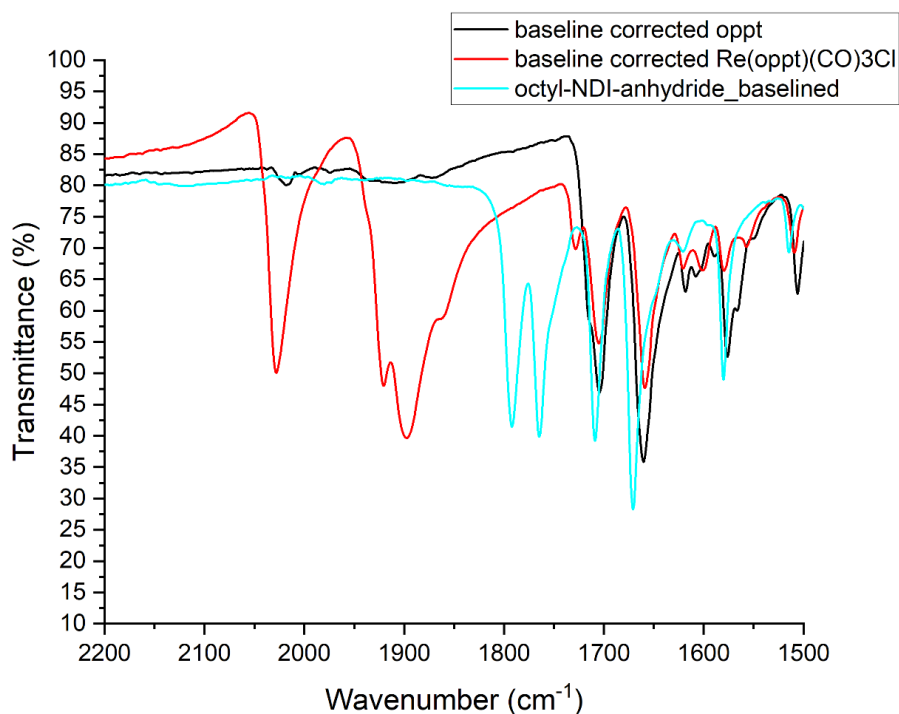


Figure SD 1. ATR-IR spectra of the oppt ligand, Re(oppt)(CO)₃Cl and Pt(oppt)I₂.

Table SD 1. FT-IR and ATR-IR shifts for oppt, $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$.

Compound	FT-IR shifts in dichloromethane (cm^{-1})	ATR-IR shifts
Oppt ligand	1666, 1705, 1719	1660, 1705, 1717
$\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$	1669, 1708, 1725, 1899, 1922, 2023	1659, 1706, 1728, 1861 1897, 1921, 2028

Electrochemistry

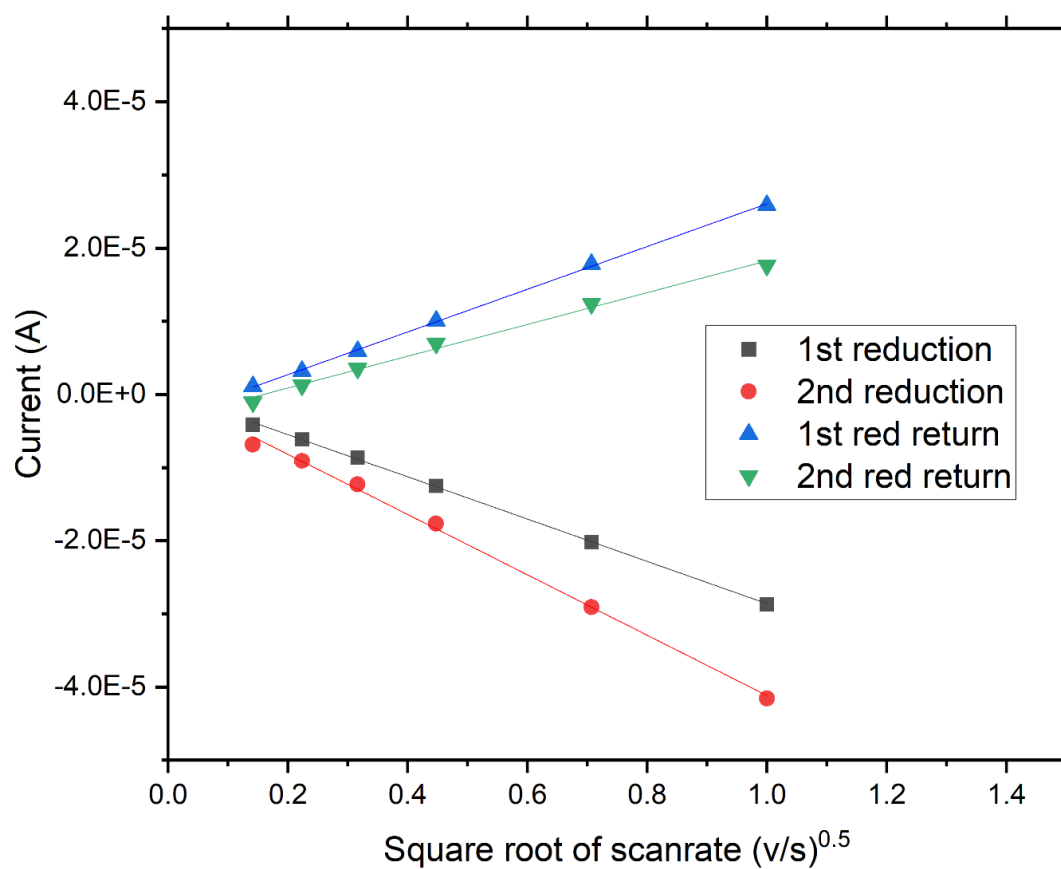


Figure SD 2. Scanrate dependence study for the oppt ligand. The reduction and oxidation waves for the 1st and 2nd reduction at -0.95 (grey), -1.03 (blue), -1.32 (red) and -1.40 V (green).

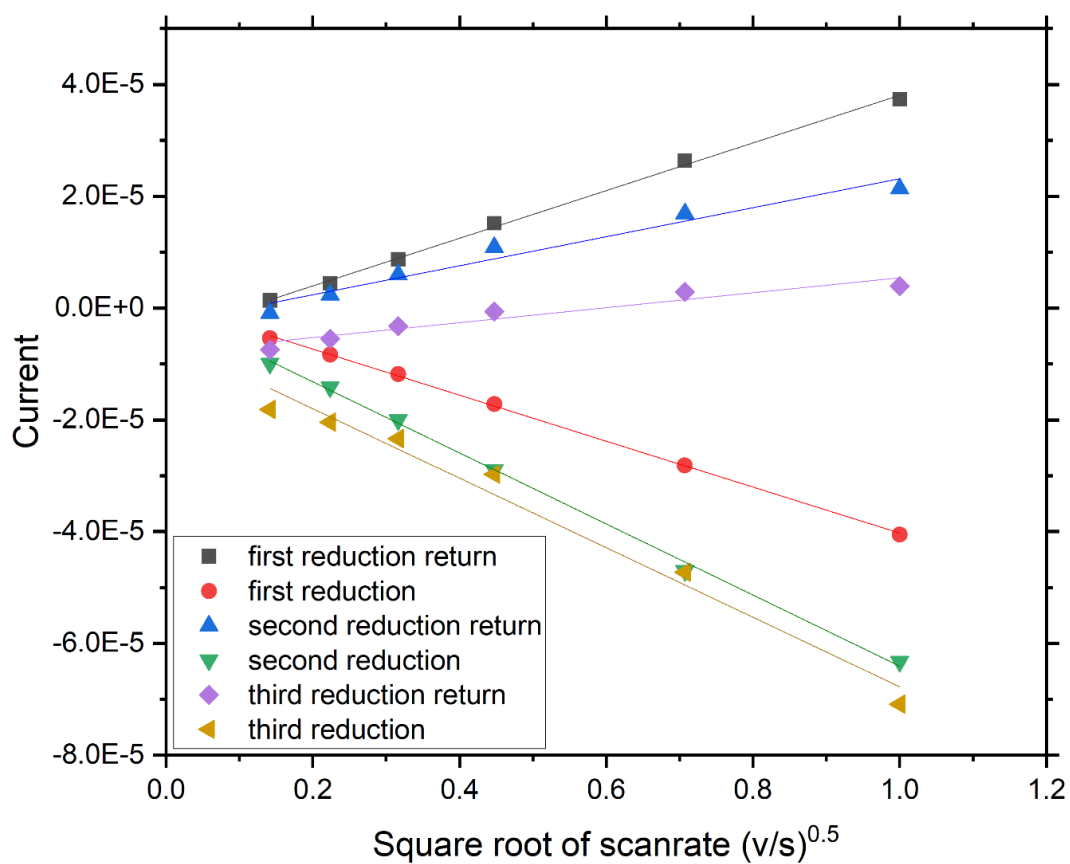


Figure SD 3. Scanrate dependence study for $\text{Re}(\text{oppt}(\text{CO})_3\text{Cl})$. The reduction and oxidation waves for the 1st, 2nd and 3rd reduction are shown at -0.89 (red), -1.03 (black), -1.31 (green), -1.4 (blue), -2.03 (yellow) and -2.17 V (purple).

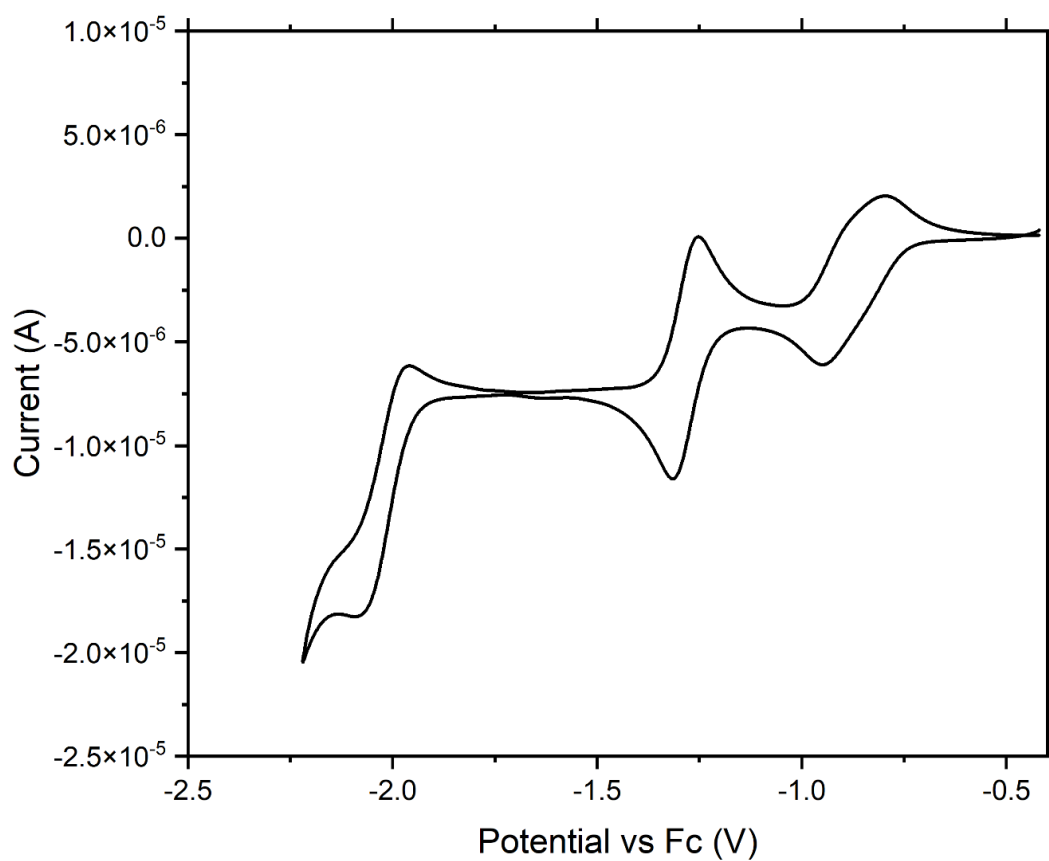


Figure SD 4. Cyclic voltammogram for the reductive processes of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ at 0.02 v/s. Measurement performed in deaerated dichloromethane with 0.1 M TBAPF_6 as supporting electrolyte.

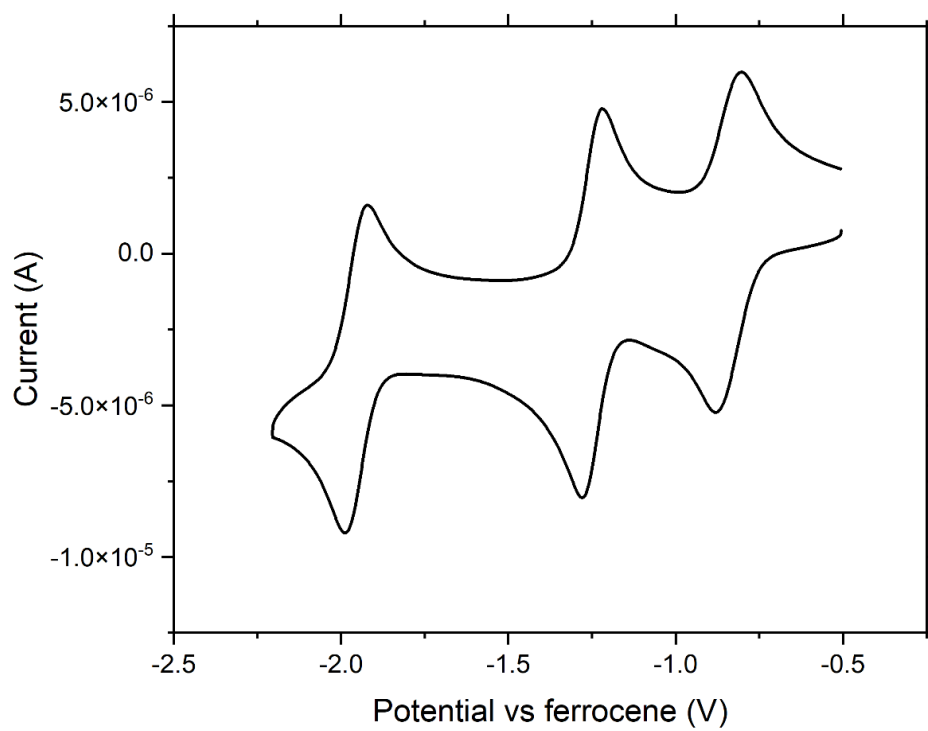


Figure SD 5. Cyclic voltammogram of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in DMF with 0.1 M TBAPF_6 as supporting electrolyte.

Single photon counting lifetime studies

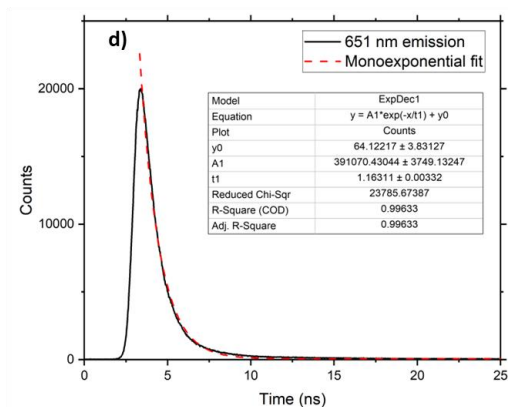
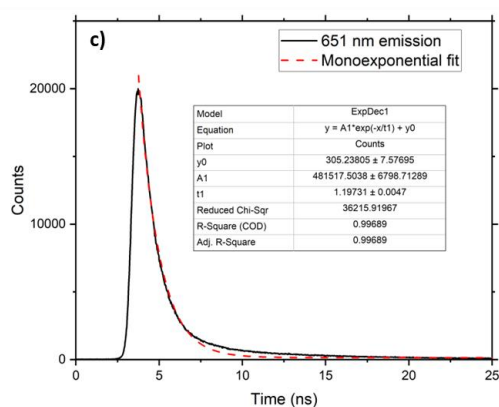
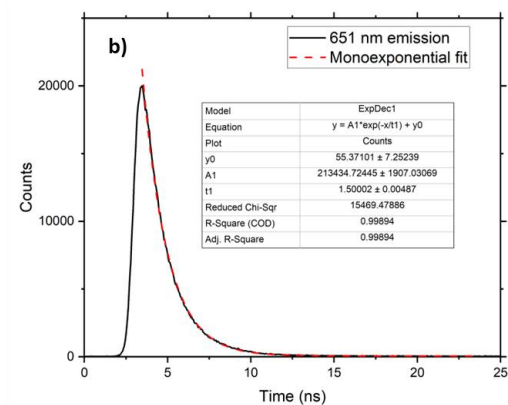
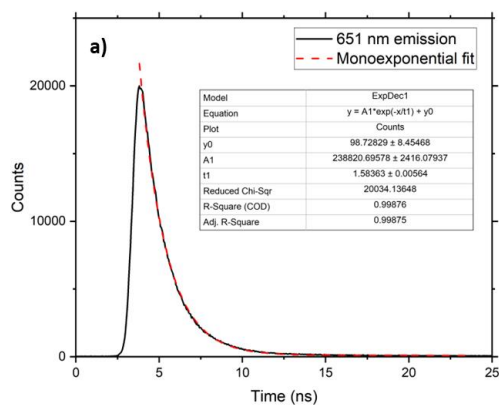


Figure SD 6. Overview of the 651 nm emission lifetimes for the oppt ligand at a) 375 nm excitation in aerated dichloromethane, b) at 510 nm excitation in aerated dichloromethane, c) at 375 nm excitation in deaerated dichloromethane and d) at 510 nm excitation in deaerated dichloromethane.

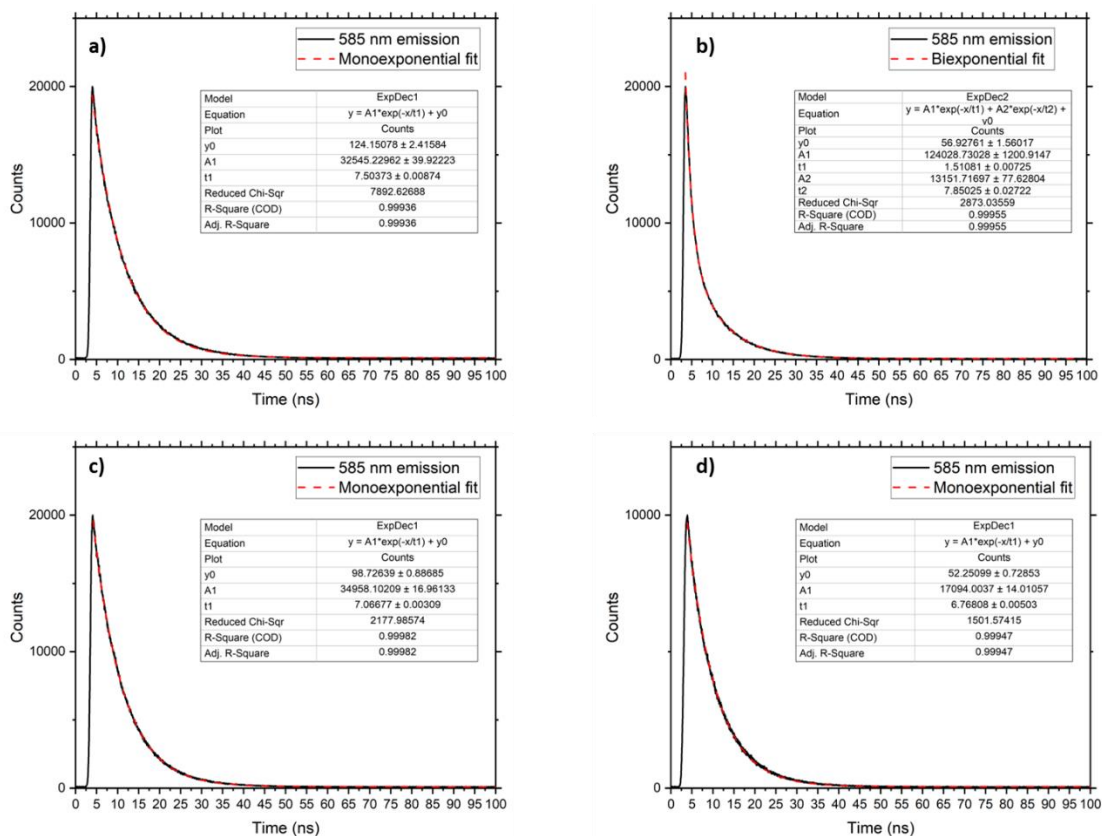


Figure SD 7. Overview of the 585 nm emission lifetimes for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ at a) 375 nm excitation in aerated dichloromethane, b) at 510 nm excitation in aerated dichloromethane, c) at 375 nm excitation in deaerated dichloromethane and d) at 510 nm excitation in deaerated dichloromethane.

Transient absorption spectroscopy

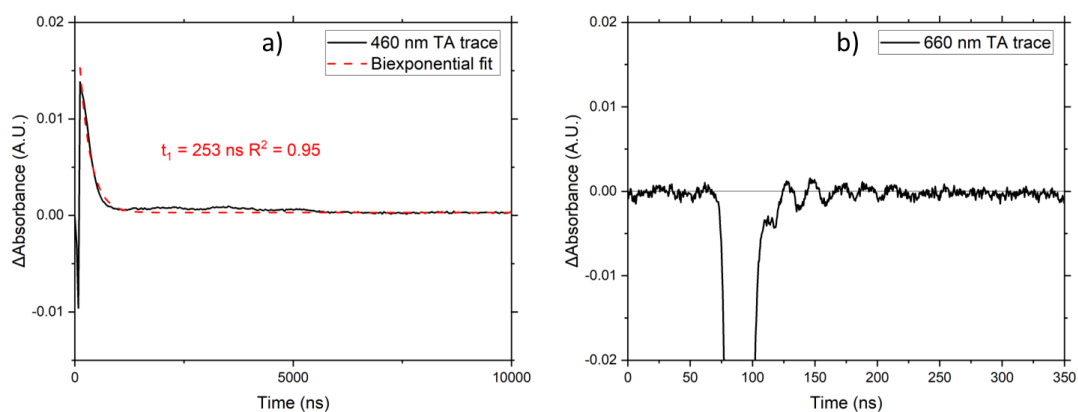


Figure SD 8. a) Transient absorption trace at 460 nm for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in deaerated dichloromethane following 355 nm excitation. b) transient absorption trace at 660 nm for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in deaerated dichloromethane following 532 nm excitation.

Ps-Time resolved infrared spectroscopy

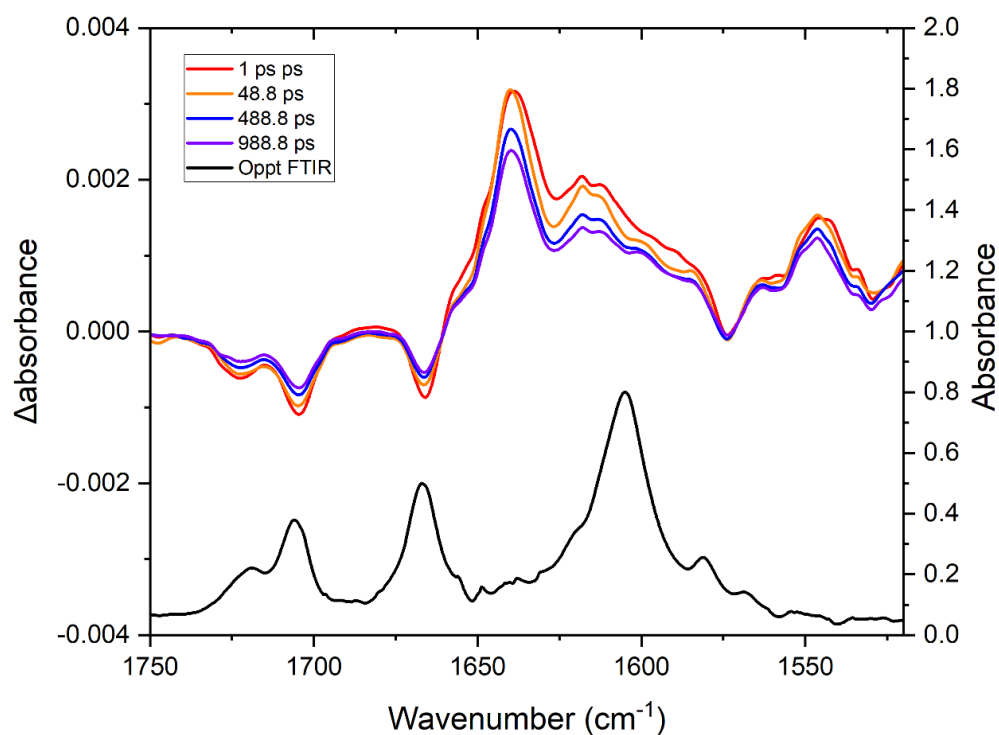


Figure SD 9. ps-TRIR spectrum for the oppt ligand in dichloromethane solution following 400 nm excitation.

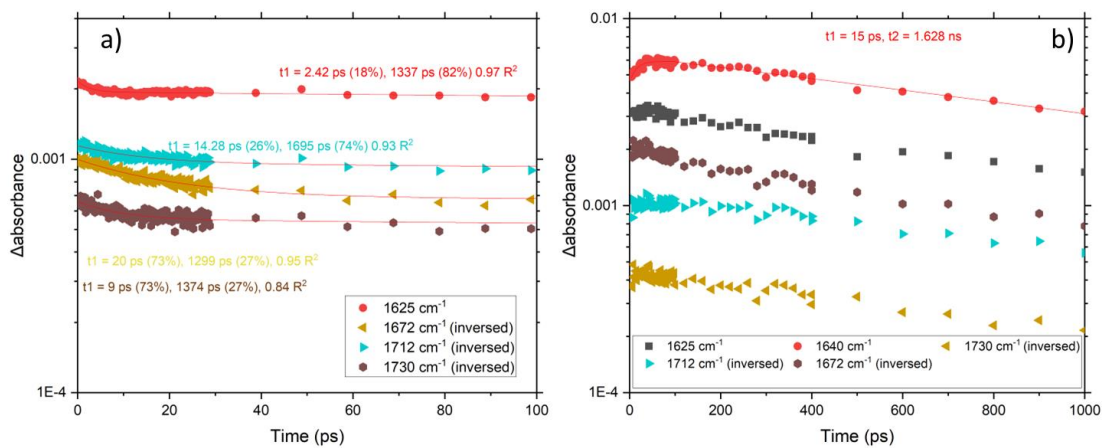


Figure SD 10. TRIR kinetic traces for selected bleaches and absorptions for oppt following a) 400 nm and b) 510 nm excitation in aerated dichloromethane.

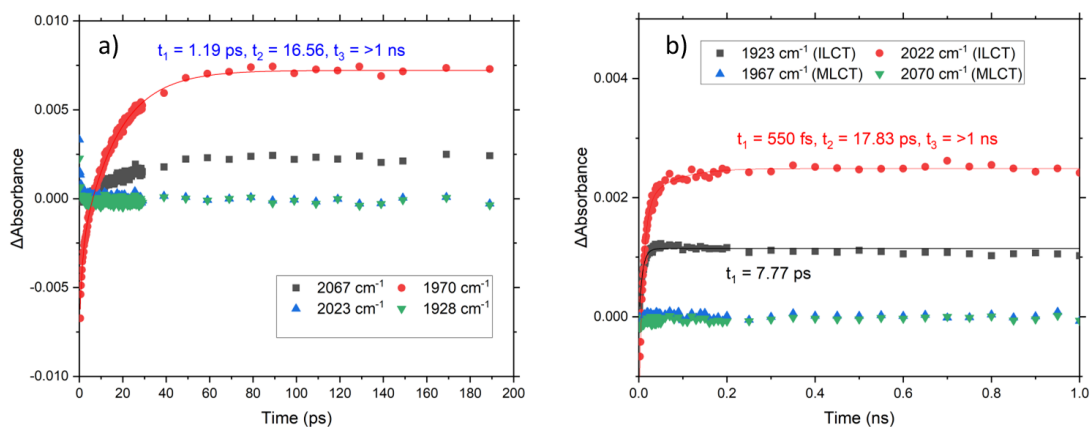


Figure SD 11. TRIR kinetic traces for selected bleaches and absorptions for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ following a) 400 nm and b) 510 nm excitation in aerated dichloromethane.

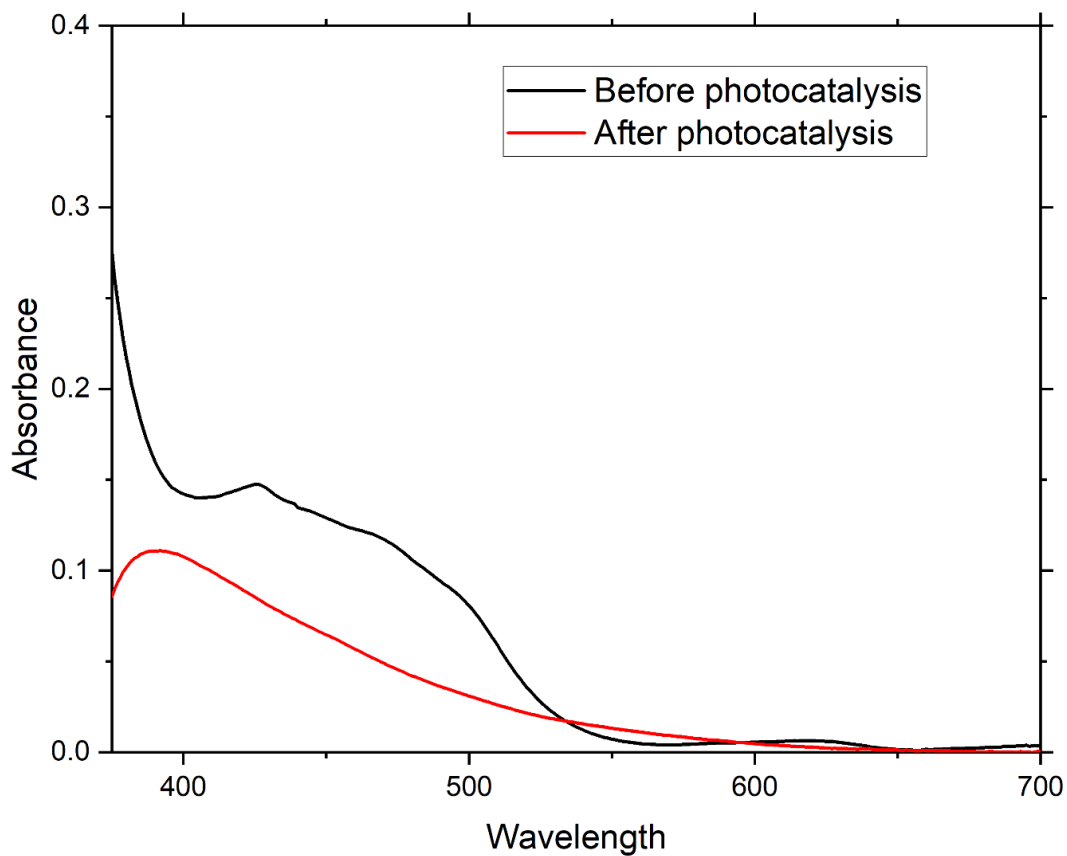


Figure SD 12. UV-Vis spectrum of the photocatalytic solution before (black) and after (red) 24 hours of photocatalysis at 470 nm irradiation.

NMR spectroscopy

2-octylbenzo[10',1''][3,8]phenanthrolino[3',2':1,2]imidazo[4,5-f][1,10]phenanthroline-1,3,6(2H)-trione (oppt)

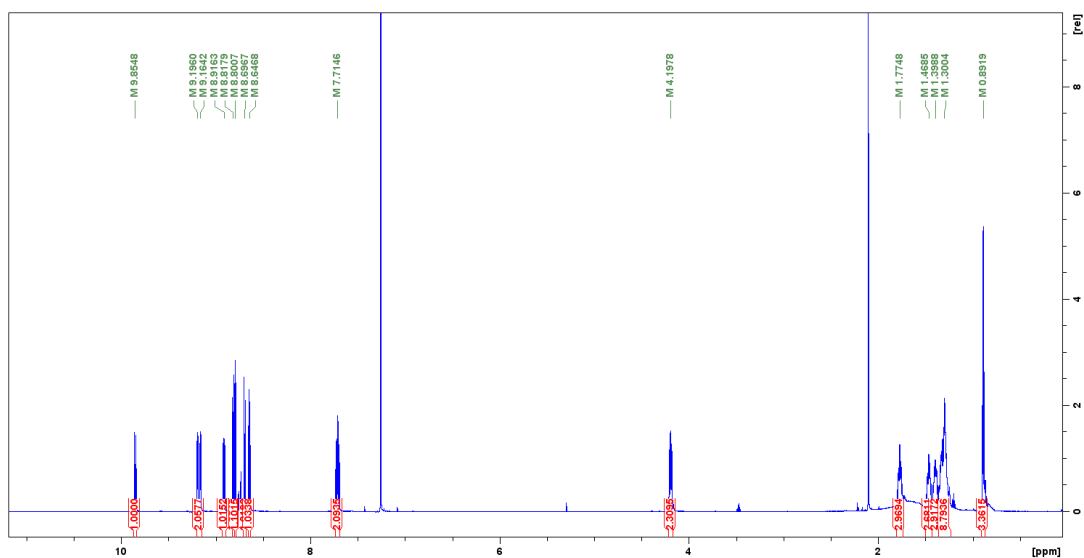


Figure SD 13. ^1H -NMR spectrum of the oppt ligand in CDCl_3 .

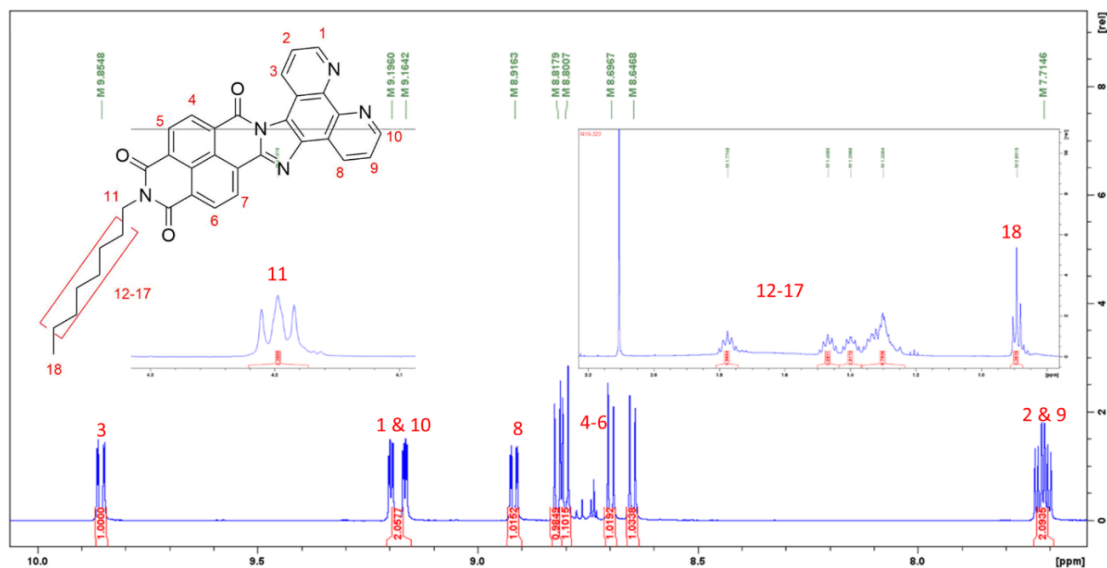


Figure SD 14. ^1H -NMR of the oppt ligand in CDCl_3 . Close up of the aromatic region with the aliphatic signals shown in the insets.

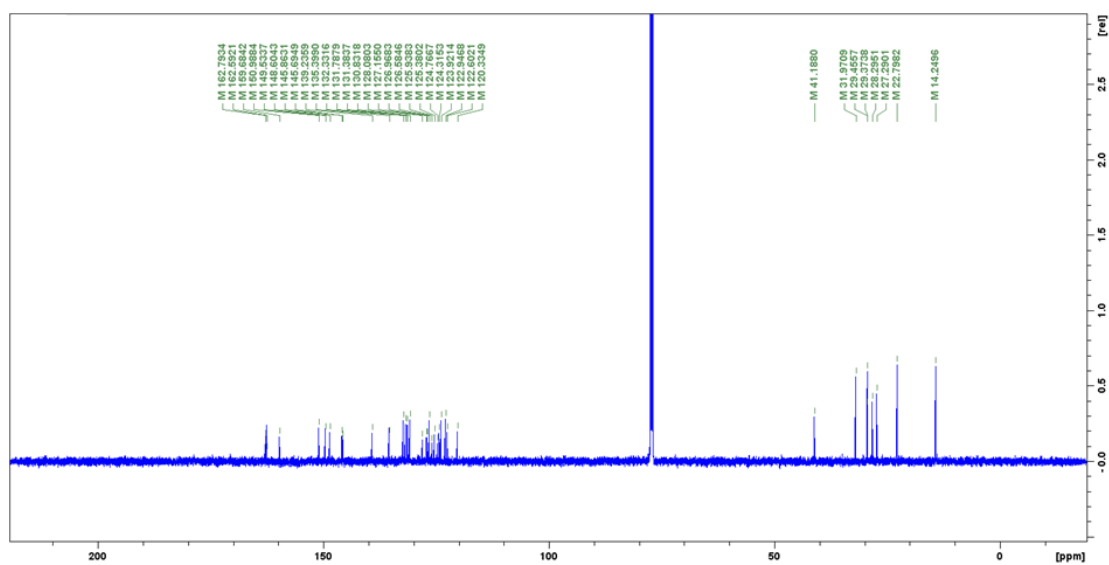


Figure SD 15. ^{13}C -NMR spectrum of the oppt ligand in CDCl_3 .

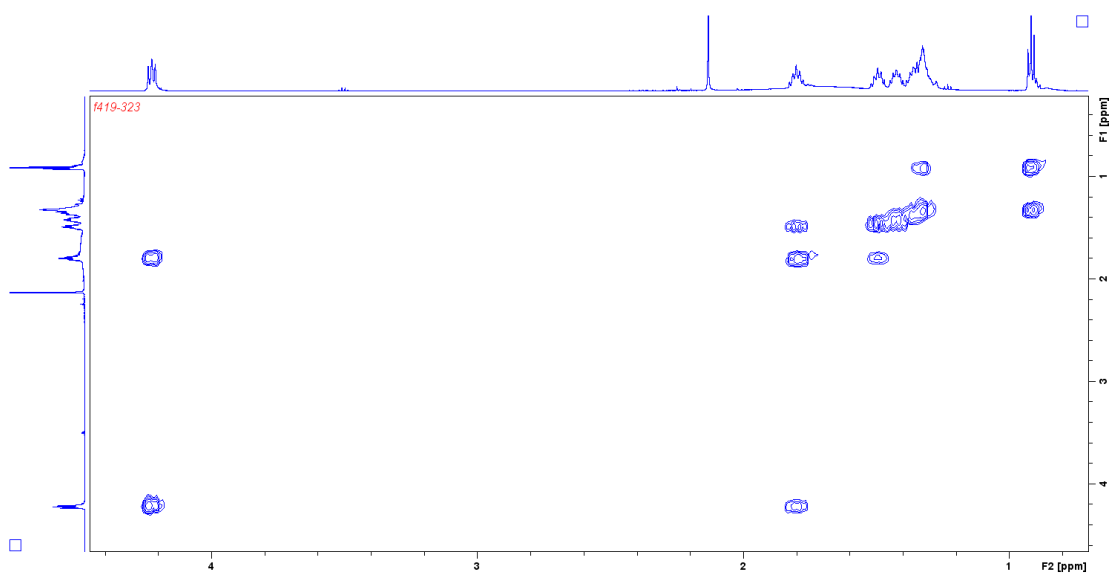


Figure SD 16. COSY spectrum of the oppt ligand in CDCl_3 , zooming in on the aliphatic region.

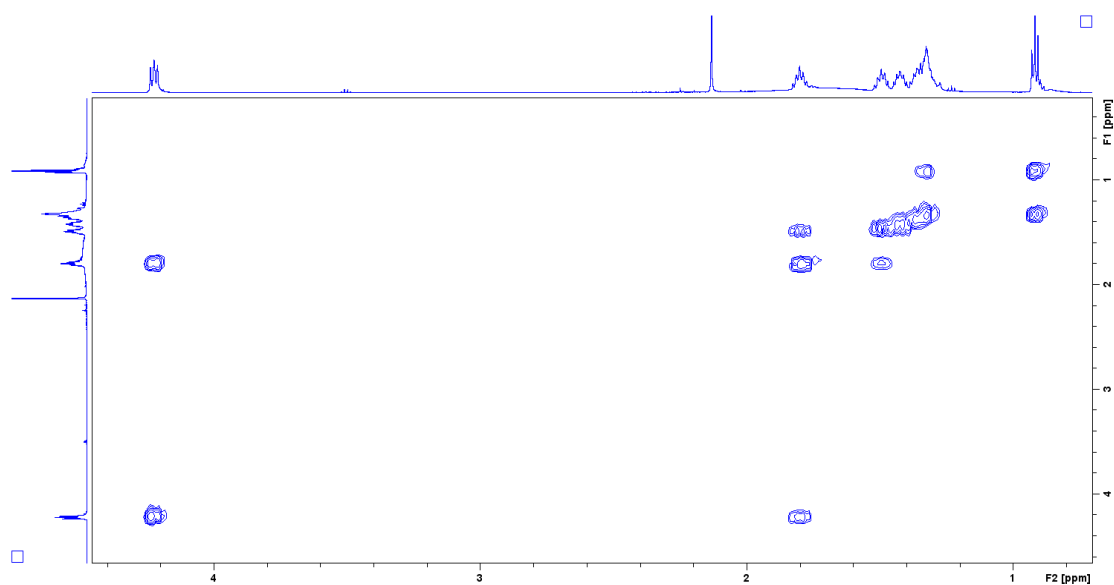


Figure SD 17. COSY spectrum of the oppt ligand in CDCl_3 , zooming in on the aromatic region.

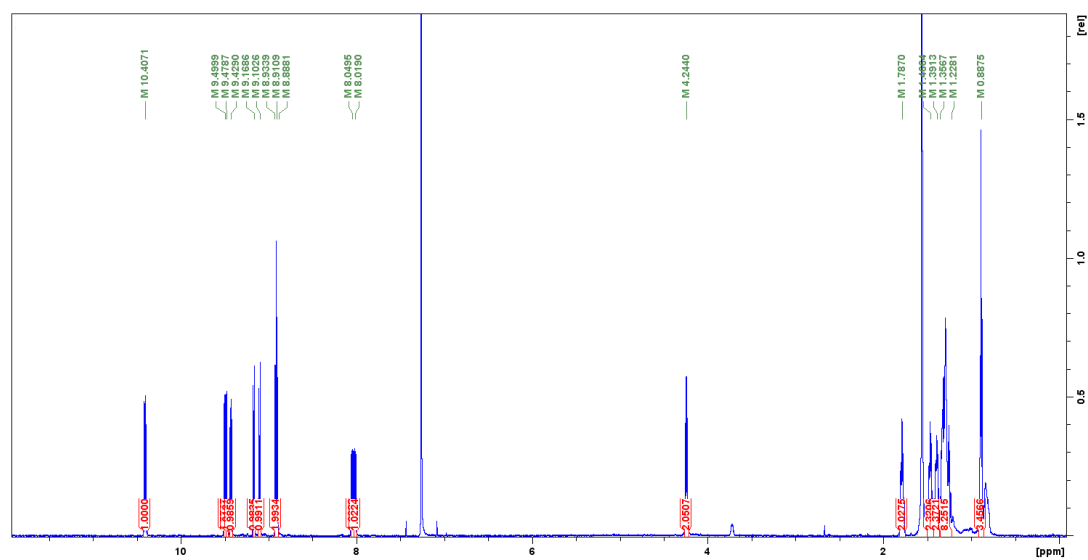
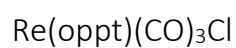


Figure SD 18. ^1H -NMR spectrum of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in CDCl_3 .

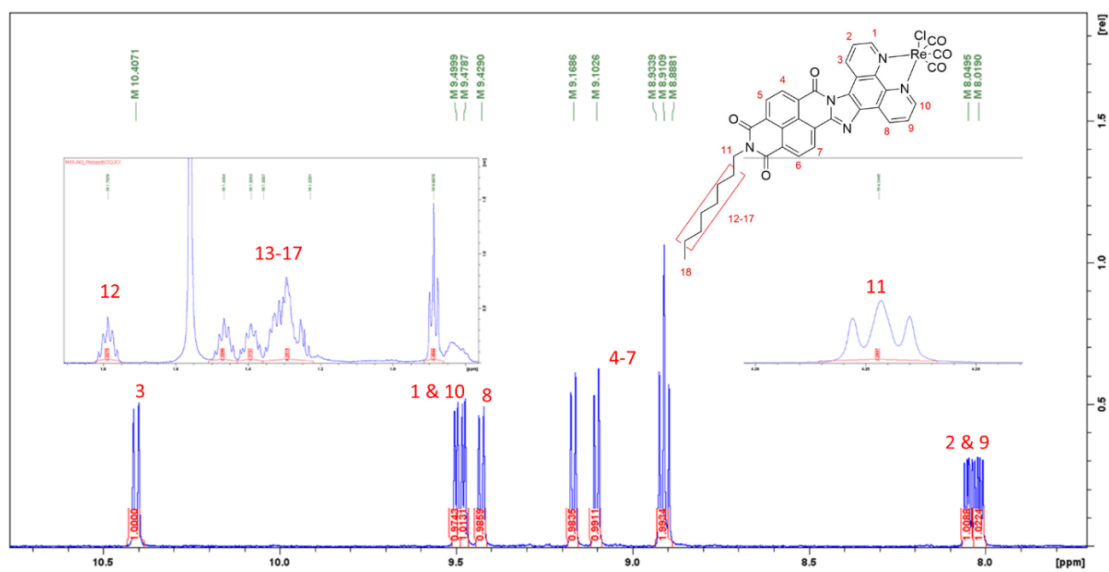


Figure SD 19. ^1H -NMR of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in CDCl_3 . Zoom in of the aromatic region with the aliphatic signals shown in the insets.

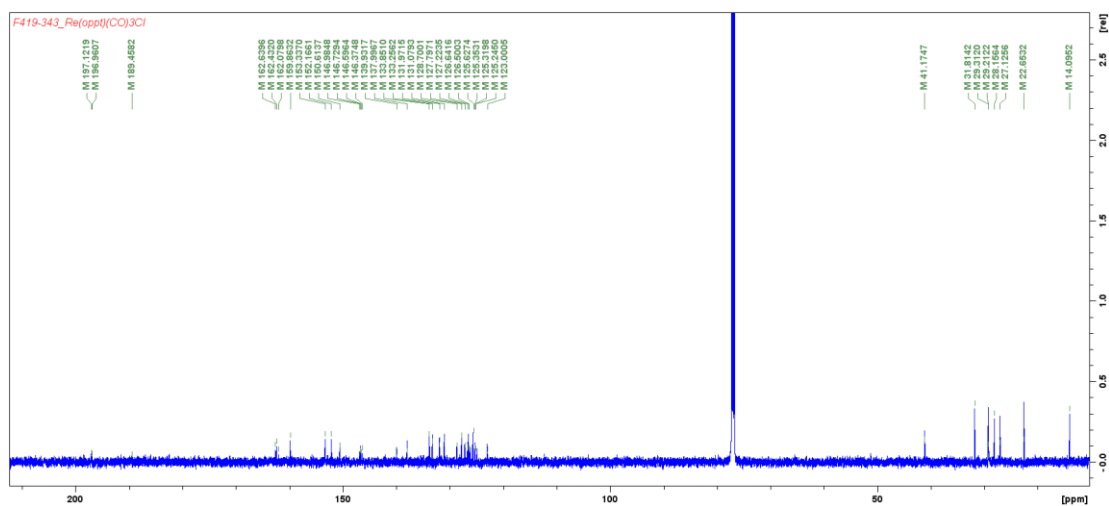


Figure SD 20. ^{13}C -NMR of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ in CDCl_3 .

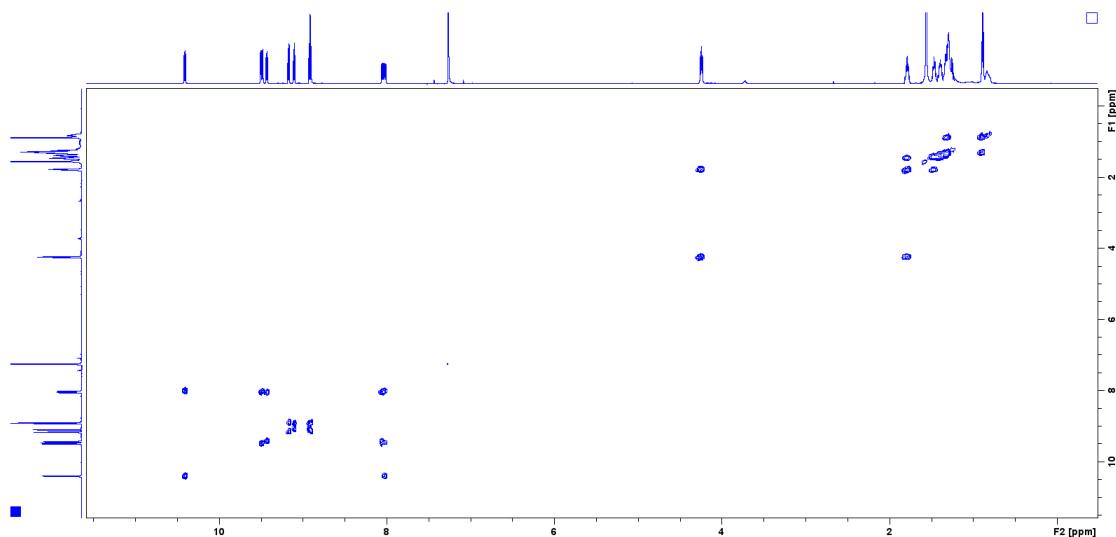


Figure SD 21. COSY spectrum of $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$ ligand in CDCl_3 .

Mass spectrometry

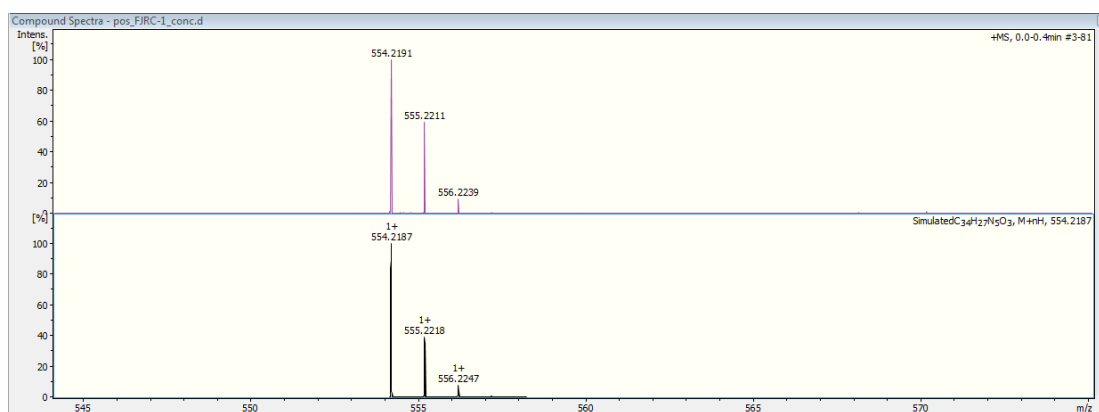


Figure SD 22. Found (top) and calculated (bottom) mass spectrogram of the *oppt* ligand+ H^+ complex in positive mode mass spectrometry.

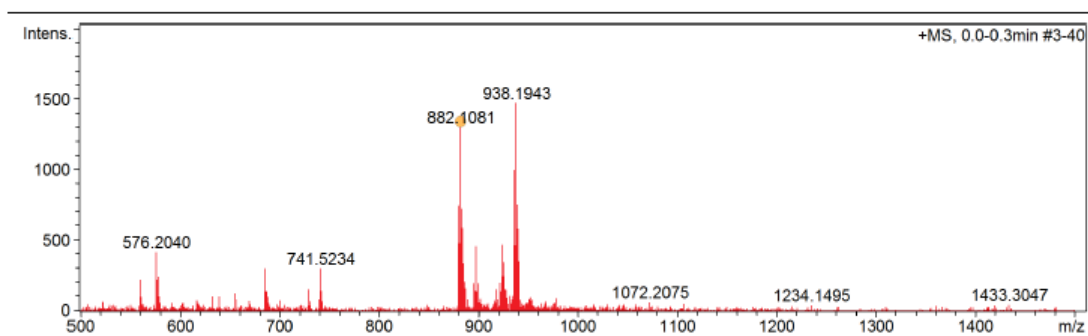


Figure SD 23. Mass spectrogram for $\text{Re}(\text{oppt})(\text{CO})_3\text{Cl}$. [$\text{Re}(\text{oppt})(\text{CO})_3\text{Cl} + \text{Na}^+$] calculated $m/z = 882.1100$, found = 882.1081.