Electronic Supplementary Information for Dalton Transactions

Supplementary Data

Porphyrin-cobaloxime complexes for hydrogen production, a Photo- and Electrochemical

Study, coupled with Quantum Chemical Calculations

Jennifer C. Manton, Conor Long, Johannes G. Vos and Mary T. Pryce.*

School of Chemical Sciences,

Dublin City University,

Dublin 9, Ireland.

* To whom correspondence should be addressed:

Fax: +353 1 7005503; Tel: +353 1 7008005; E-mail: mary.pryce@dcu.ie

1. Using fluorescence to determine the quantum yield for cleavage of the Co-N(pyridyl) bond in the porphyrin-cobaloxime complexes studied

All quantum yields were carried out using a liquid-phase potassium ferrioxalate actinometer. The actinometer was prepared by mixing three volumes of 1.5 M $K_2C_2O_4$ solution with one volume of 1.5 M $FeCl_3$ solution in water, and stirring in complete darkness. The precipitated $K_3Fe(C_2O_4)_3.3H_2O$ was then recrystallised three times from hot water and dried in a current of warm air. To prepare 1 L of 0.006M $K_3Fe(C_2O_4)_3.3H_2O$ solution, 2.947 g of the precipitate was dissolved in 800 mL water, 100 mL 1.0 N sulphuric acid was added and filled to the mark with water, again in complete darkness. The 0.15 M actinometric solution required 73.68 g of precipitate to be added to the same volumes of liquid. For all quantitative work the preparation and manipulation of the ferrioxalate solutions must be carried out in a darkroom, using a red photographic safelight. The light intensity in a photochemical reaction is determined by irradiating ferrioxalate solution and monitoring the subsequent change in absorbance at 510 nm. Irradiation was achieved using band pass filtering of the output of a 150 W Hg arc lamp. A carousel was used to house both the actinometer and sample cells so that they were equally exposed to a uniform amount of irradiation throughout the duration of each experiment. The carousel operated inside a black box to prevent any stray light reaching the sample or actinometer solutions. An autopipette was to ensure all volumes were accurately measured.

For each actinometeric measurement a quartz cuvette was charged with 3 mL (V_1) of ferrioxalate solution. The cell was placed in the carousel and irradiated for the time shown in the results section. After the allocated irradiation time (t), the solution was well mixed and an aliquot volume (0.5 mL, V_2) was pipette into a volumetric flask (10 mL, V_3). Buffer solution of volume equal to half the volume of photolyte placed in the flask was added (0.25 mL), so too was 2 mL phenanthroline solution (0.1 % by weight solution in water). The solution was diluted with distilled water to the volume mark (V_3) and mixed well. The flask was wrapped in tinfoil and the solution was allowed develop. After one hour, the absorbance of the solution was measured in a 1cm cell at 510 nm using a spectrophotometer using a blank iron free solution as a reference.

The number of Fe^{2+} ions (n_{Fe}^{2+}) formed during photolysis can be calculated from:

$$n_{Fe}^{2+} = \frac{6.023 \times 10^{20} \, V_1 \, V_3 \, \log_{10}(I_0/I)}{V_2 \, l \, \varepsilon}$$

where

V_1 = Volume of actinometer solution irradiated (mL)

V_2 = Volume of aliquot taken for analysis (mL)

V_3 = Final volume to which the aliquot V_2 is diluted (mL)

$\log_{10}(I_0/I)$ = measured optical density of the solution (taking into account the inner filter effect due to abs of 1 at λ_{ex})

l = path length of the spectrophotometer cell used (cm)

ε = experimental value of the molar extinction coefficient of Fe^{2+} complex, determined from the slope of the calibration plot (approx. equal to 1.11×10^4 l mol^{-1} cm^{-1}).

The number of quanta absorbed by the actinometer (n_a) per second is obtained from

$$n_a = n_{Fe}^{2+} / \Phi_\lambda t$$

where t is the time in seconds

Φ_λ is the quantum yield of Fe^{2+} formation.

For sample **1a**, a solution of known concentration (5×10^{-7} M) was prepared so that the optical density was 0.1 ± 0.1 AU at the Soret absorbance band (418 nm) in a solution of THF, triethylamine (33 % (v/v)) along with deionised water (10 % (v/v)) to replicate the conditions of the photolysis experiments. Each sample cuvette was accurately charged with 3 mL this solution. The sample cell was placed in the carousel, along with the 3mL actinometric solutions in cells, and all were irradiated in parallel. As the cobaloxime derivative **1a** is non-emissive, the change in the fluorescence spectrum as the Co-N(pyridyl) bond is cleaved forming free **1** and cobaloxime was monitored. The rate of formation of **1** from **1a** was monitored at 5 time points (1, 2, 3, 5, 10, 15 mins).

Utilising standard solutions of **1** between 4.5×10^{-7} M to 1×10^{-8} M, a standard curve based on the emission profile of **1** was compiled and the emission increase of the irradiated samples was compared to yield the concentration of **1a** converted to **1** and free cobaloxime within the timescale of the experiment.

Accounting for the inner filter effect

As both complexes **1** and **1a** absorb at the λ_{ex} utilised during this experiment, the inner filter effect due to the absorbance of **1** must be considered. The percentage of light absorbed by **1** at the various time points was calculated and factored into the quantum yield calculations.
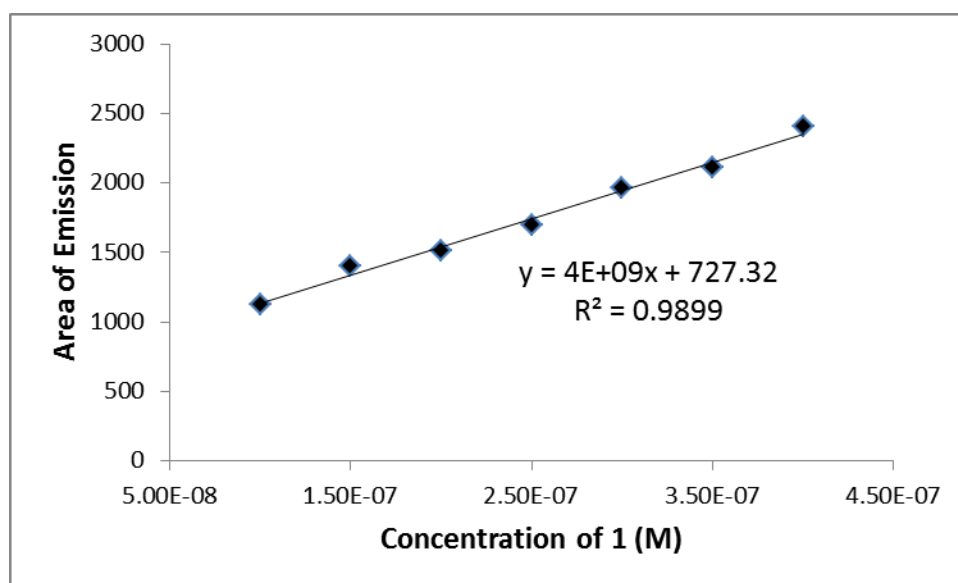

The plot shows Area of Emission vs. Concentration of 1 (M) with the fitted line equation:

$$y = 4E+09x + 727.32$$
$$R^2 = 0.9899$$

Figure S1- Standard curve of area under emission vs. concentration of **1** in THF with 33% TEA and 33% H_2O present.

2. Photocatalytic Hydrogen Turnover Number Experiment

1×10^{-4} M solutions of the catalysts/ photosensitisers were prepared in completely dry and deaerated THF. 1.2 mL of the catalyst/ photosensitiser solution, 0.2 mL (10%) H_2O and 0.6 mL (33%) TEA were added to a suitable gas tight vial and irradiated at various (350, 470 or > 470 nm) wavelengths for an average of 20 hours. Alternatively for the 0% water experiments 0.2 mL of THF was added to replace the water. For the photolysis reaction in THF, the septa capped deoxygenated photolysis reaction vial (5 mL full volume) containing 2 mL of the reaction solution was used. The solutions were photolysed using an LED light arrays. After 20 h photolysis time, the amount of hydrogen produced was measured by gas chromatography using gas tight syringe. Samples of the syringe (500 µL) were injected into a series CP-3800 Gas Chromatograph equipped with a 5 Å molecular sieves column and polymer supported silica column purchased from Varian Inc. (UK) using ultra-high purity nitrogen as the carrier gas. The signals were amplified with a Varian Star Workstation Chromatography Data system. The system was calibrated for hydrogen signal sensitivity by hydrogen standard measurements. The total amount of hydrogen produced in a photolysis experiment was obtained by the sum of hydrogen found in the gas phase (hydrogen found in the solution phase was assumed to be negligible).

Photocatalytic Hydrogen Turnover Number Calculations

- To calculate the concentration (in ppm) of hydrogen generated:

$$\frac{\text{Average Area of H}_2 \text{ Peak}}{x \text{ ppm}} = \frac{\text{Area of standard H}_2 \text{ peak}}{\text{Conc. in ppm of H}_2 \text{ standard}}$$

- To calculate the number of moles of H_2 produced the ideal gas law is applied ($PV = nRT$):

- TON:

$$\frac{\text{No. moles of H}_2 \text{ produced}}{\text{No. moles catalyst used}}$$

3. UV-vis absorption spectra of 1a and 2a at time = 0, 3 and 24hr during photocatalytic experiments.
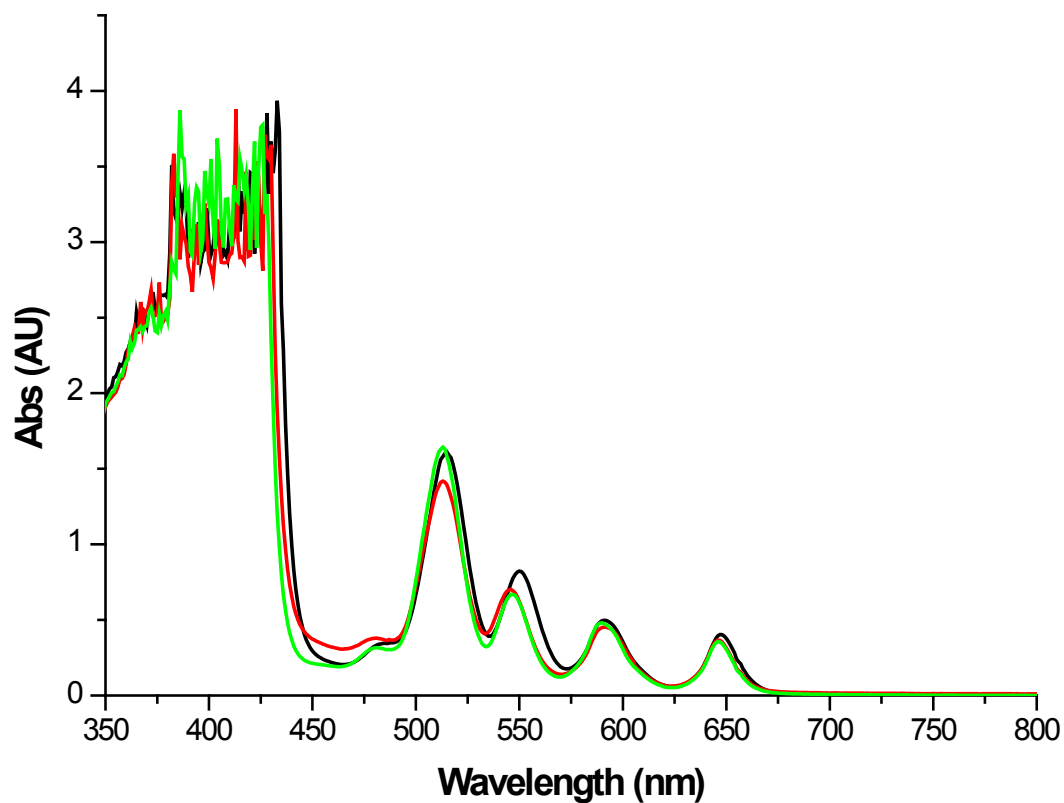

Figure S2- Electronic absorbance spectra of **1a** following irradiation at 470 nm for 0 hr (black line), 3 hr (red line) and 24 hr (green line). Conc. = 1 x 10^{-4} M in THF, TEA (33%(v/v)) and H_2O (10%(v/v))
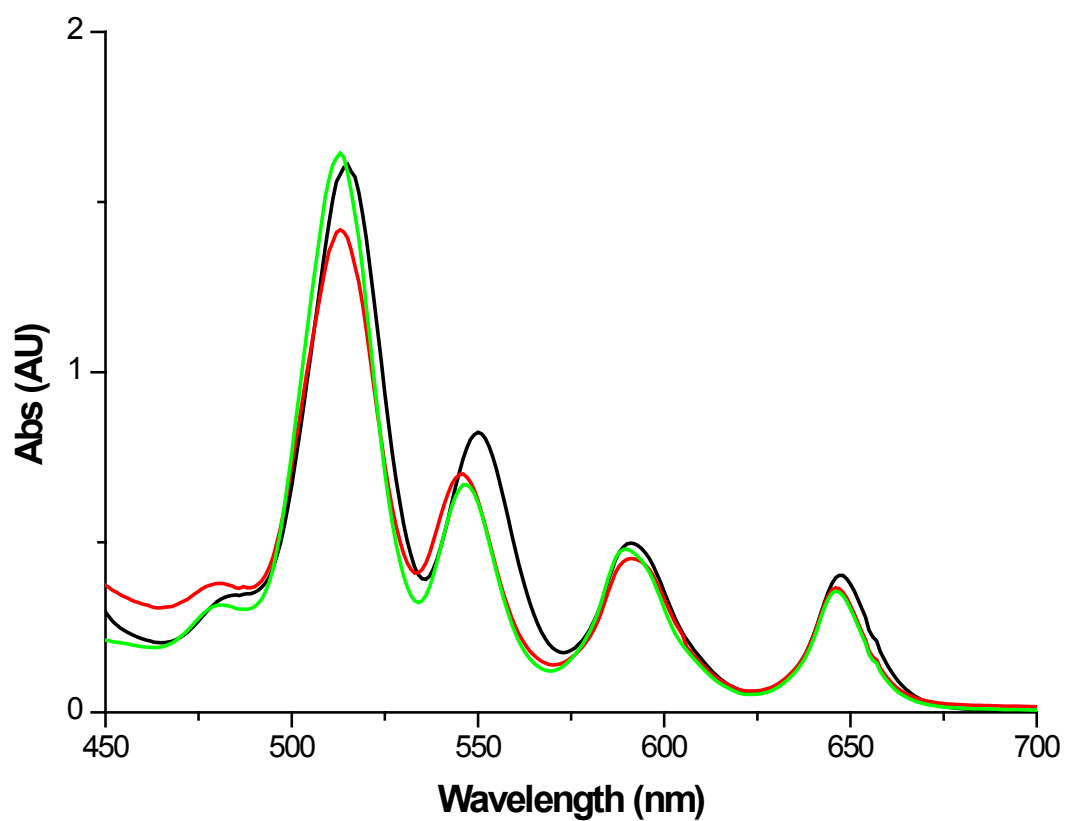
Figure S3- Electronic absorbance spectra of **1a** following irradiation at 470 nm for 0 hr (black line), 3 hr (red line) and 24 hr (green line). Conc. = 1 x 10^{-4} M in THF, TEA (33%(v/v)) and H_2O (10%(v/v))
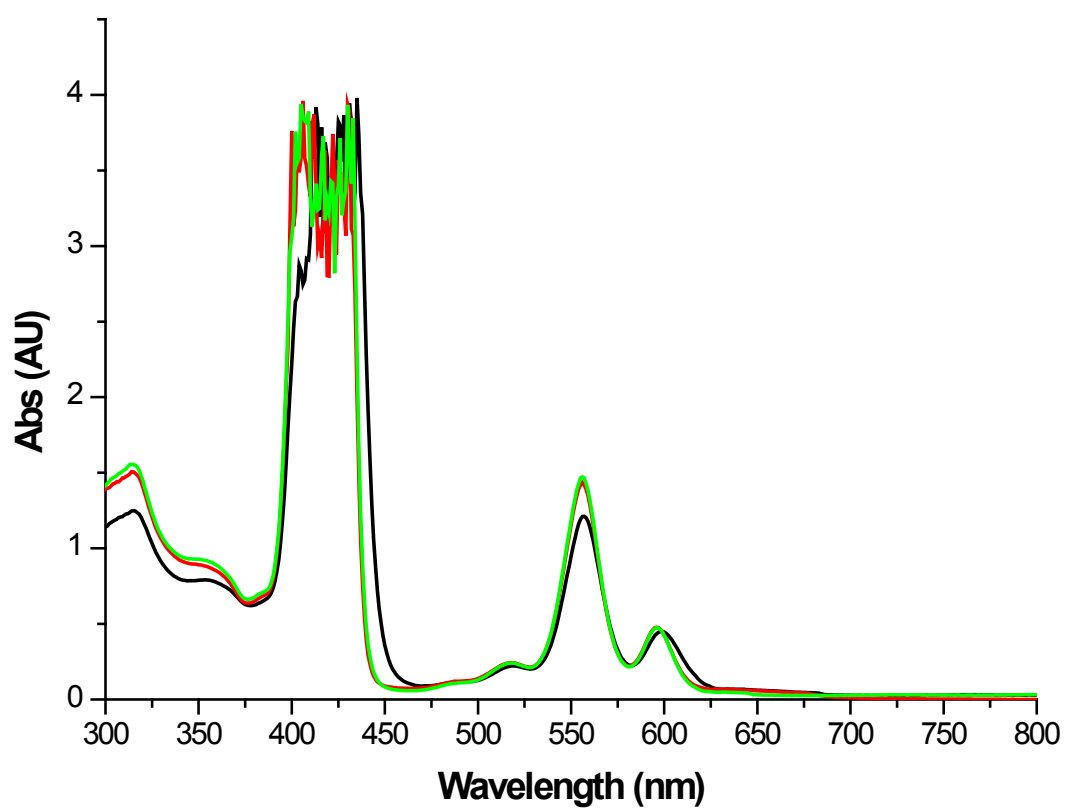
Figure S4- Electronic absorbance spectra of **2a** following irradiation at λ_{exc}. 470 nm for 0 hr (black line), 3 hr (red line) and 24 hr (green line). Conc. = 1 x 10^{-4} M in THF, TEA (33%(v/v)) and H_2O (10%(v/v))
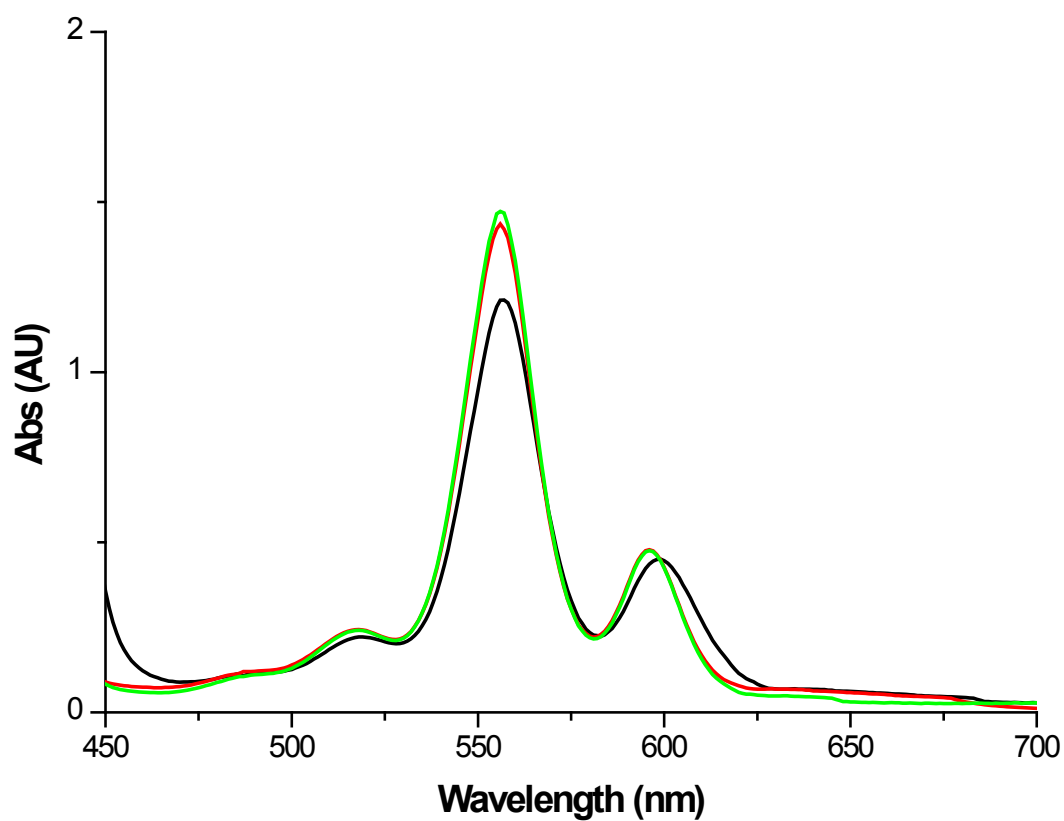
Figure S5- Electronic absorbance spectra of **2a** following irradiation at 470 nm for 0 hr (black line), 3 hr (red line) and 24 hr (green line). Conc. = 1 x 10^{-4} M in THF, TEA (33%(v/v)) and H_2O (10%(v/v))

4. Electrocatalytic Hydrogen Turnover Number (TON) Experiment

All electrocatalytic experiments were carried out in a 2 necked V-shaped electrochemical cell, using a glassy carbon working electrode with an area of $0.07cm^2$, a platinum wire counter electrode and a Ag/AgCl reference electrode filled with 3 M KCl.

A 1×10^{-4} M solution of each sample was prepared in dimethylformamide (DMF). 1.5 µL of this sample was then drop cast on the surface of the glassy carbon electrode and allowed to dry overnight is complete darkness. The V-shaped cell was filled with 15 mL of 0.1 M NaH_2PO_4 buffer at pH 2.0. The sample coated glassy carbon electrode, along with the platinum wire counter and Ag/AgCl reference electrodes, were placed into the cell and the cell was sealed with a suba-seal in each neck. The buffer was degassed with BIP grade argon for 20 min prior to each experiment. Bulk electrolysis experiments were carried out -1.2 V vs. Ag/AgCl.

Electrocatalytic Hydrogen Turnover Number Calculations

- Electrochemical calculation of number of moles of H_2 produced:

After bulk electrolysis the current change (I_t) over the duration of the experiment can be measured. According to Faraday's laws of electrolysis:

$$n = \left(\frac{It}{F} \right) \left(\frac{1}{z} \right)$$

n = number of moles of H_2 produced.

F = Faraday's constant (96485 C mol^{-1}).

z = the valence number of ions of the substance (electrons transferred per ion).

- Electrochemically determined H_2 generation TON:

$$\text{TON} = \frac{\text{No. moles of } H_2 \text{ produced}}{\text{No. moles catalyst used}}$$

- GC determined H_2 generation TON:

As with the photocatalytic studies the GC was used to determine the electrocatalytic TON of H_2.

- **Determination of the Efficiency of the System:**

The efficiency of the system refers to the efficacy of the system to produce H_2 relative to the current passed during the experiment. This is measured by calculating the TON which has been determined using Faradays law of electrolysis, and comparing this result with the TON which has been calculated through injection of the headspace into the GC, measuring the actual number of moles of H_2 gas produced.

The efficiency =

$$\frac{\text{Electrochemically Determined TON}}{\text{GC Determined TON}} \times 100$$

- **Determination of Current Density:**

Current density is a measurement of the flow of current per unit area. During a bulk electrolysis experiment the average current throughout the experiment is measured. The area of the electrode surface has been measured to be 0.07 cm^2.

Therefore the current density =

$$\frac{\text{Average Current During Bulk Electrolysis (mA)}}{\text{Area of Electrode Surface (cm}^2)}$$