Electronic Supporting Information

Visible light promoted photocatalytic water oxidation: proton and electron collection via reversible redox dye mediator

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Experimental

Preparation of $Co(OH)_2$ based catalyst

A soluble cobalt hydroxide amino complex was prepared by dissolving 2.4g of $Co(COOCH_3)_2.4H_2O$ in 120ml of ethanol with stirring and warming to 70°C. After the mixture was allowed to cool and ammonia solution was added dropwise with stirring until the pH was raised from ~6 to 10.3 to give a clear brown/black solution. The solution was then centrifuged at 3500rpm for 6 min and the supernatant collected and microwaved to ~70°C. This resulted in the solution changing colour to a deep ruby red. The solution was allowd to cool and then filtered through a 0.22µm syringe filter and the filtrate solution air dried to form a deep red solid. This was re-suspended in water and dialysed (MWCO 12-14k dialysis tubing) against DI water for 2 hours with hourly changes of water to remove salts. The purified cobalt hydroxide amino complex was dried to form a dark red shiny solid.

Preparation of SiO_2 containing $Ru(bpy)_3^{2+}$ and DCPIP

A silica gel containing 2,6-dichlorophenolindophenol (DCPIP) and bipyridyldichlororuthenium(II) hexahydrate ($[Ru(bpy)_3Cl]Cl_2$) was prepared by adding 6 ml of TMOS to 1.5ml of 1.6mM hydrochloric acid (HCl) in a beaker whilst being stirred on electric stirrer and cooled on ice. This was left for approximately 20 minutes until a single phase was formed.

2 ml of degassed water was added to 50 mg $[Ru(bpy)_3Cl]Cl_2$ and then added to the TMOS and HCl solution. Another 2 ml of degassed water was added to 55 mg DCPIP and then filtered using a single use 0.22µm syringe filter into the beaker containing the TMOS solution whilst on ice. The solution was left overnight to form a solid precipitate which was then washed thoroughly with ethanol and ground to a fine powder in a pestle and mortar.

Solid state visible absorbance spectrophotometry of the prepared SiO_2-$Ru(byp)_3^{2+}$ showed the characteristic visible light MLCT absorbance maximum centred at 452nm.[1] Control preparations for fluorescence testing were prepared as above in absence of $[Ru(bpy)_3Cl]Cl_2$ and absence of both $[Ru(bpy)_3Cl]Cl_2$ and DCPIP.

Water oxidation using $Co(OH)_2$ based catalyst

Nitrogen degassed DI water was used to prepare an acetate buffer of pH 5.2 (50mM sodium acetate adjusted with acetic acid). A custom made three arm 50ml glass flask was taken and 120 mg of $[Co(NH_3)_5Cl]Cl_2$ (98%) electron acceptor and 45mg $[Ru(bpy)_3]Cl_2.6H_2O$ (99.95%) sensitizer added together with 25ml of buffer. The reaction flask was covered with foil to shield from light and stirred for 5 minutes to allow the electron acceptor to fully dissolve. 20mg of the dried $Co(OH)_2$ based catalyst suspended in a further 10ml of the degassed buffer was then added. The light shielded reaction flask was then left stirring for 20 minutes for the system to equilibrate. The light shield covering was then removed and the stirred flask illuminated by blue led (3W, 120 lumen, λmax 455-465 nm) held at a specific distance to give a measured $5mWcm^{-2}$ between 420-499nm (Solartech Inc. Solar Meter 9.4), at the reaction flask surface (with measured led light exposed surface area of $31.5cm^2$). O_2 release was monitored in situ using a Pyroscience Firesting O2 fibre optic O_2 sensor with an OXYROB10 oxygen probe together with a TDIP temperature sensor to give automatic compensation for minor fluctuation in reaction flask temperature. O_2 readings at 10s intervals were recorded to minimize possible photobleaching effects on the O_2 sensor. These probes were fitted into the flask aperture and reactions in air were conducted in the flask (O_2 level was zeroed after equilibration). O_2 production after light on was monitored for 100 minutes.

Micromoles of O_2 gas released into the known headspace volume was calculated from measured O_2 ppm increase. The reaction mixture pH was also simultaneously monitored using a Eutech Cyberscan pH110 with an RS232 output. Samples runs were conducted in triplicate with representative O_2 and proton release profiles shown.

During a photocatalyzed water oxidation the $[Co(NH_3)_5Cl]Cl_2$ electron acceptor decomposes with release of ammonia and $Co(OH)_2$.[2]

$$\left[Co(NH_3)_5Cl\right]^{2+} + \left[Ru(bpy)_3\right]^{2+*} \rightarrow \left[Ru(bpy)_3\right]^{3+} + Co^{2+} + 5NH_3 + Cl^-$$

Water oxidation using $Co(OH)_2$ based catalyst together with SiO2-$Ru(bpy)_3^{2+}$-DCPIP

2.50 g of ground silica solid incorporating DCPIP and $Ru(bpy)_3$ was used in a water oxidation experiment as described above with the following changes. 20 mg of $Co(OH)_2$ based catalyst was added as the catalyst in solution (no $[Co(NH_3)_5Cl]Cl_2$ electron acceptor was added). The buffer solution used was 35ml degassed water with a pH adjusted to 7.2 using dilute NH_4OH solution and the water oxidation experiment was left to run for 60 minutes.

Following the reaction the mixture was filtered and the silica gel (together with its constituents) was collected and washed. It was observed that filtrate was colourless. The collected silica gel was reused again in a water oxidation reaction however no additional $Co(OH)_x$ was added. As above 35ml of degassed water with a pH adjusted to 7.2 using dilute NH_4OH solution was used as the buffer and the experiment was left to run for 60 minutes. O_2 yields were measured as described above, measured pH of the reactions of the 60 minutes reaction showed almost no change, indicating uptake by DCPIP and conversion to DCPIPH and DCPIPH2.

For both these reactions, prior to light-on the reaction mixture contained within the flask was further degassed by sonication under vacuum for 5 minutes.

Note: Control reactions conducted in the absence of light or electron acceptor gave no measurable O_2 generation.

Chemicals

Chemical reagents were obtained from Sigma-Aldrich Co. and used as supplied.

Instrumentation

Oxygen measurements

Accurate gaseous O_2 was determined in situ and real-time with a Pyroscience Firesting O2 fibre optic oxygen meter fitted with an OXYROB10 robust O2 probe coupled with a TDIP15 temperature compensation probe. The reaction mixture pH was also simultaneously monitored using a Eutech Cyberscan pH110 with an RS232 interface. Outputs were monitored using data collection software with a linked PC.

UV/vis spectrometry

Solid state UV-vis reflectance spectrometry of powder samples over 350-700nm was conducted using a Perkin Elmer Lambda 750s UV/Vis/NIR spectrophotometer fitted with a Labsphere 60 mm integrating sphere. Background correction was made using a Labsphere certified reflectance standard. Samples in water were placed into a quartz cuvette before being examined by a Perkin Elmer UV/VIS/NIR Lambda 750S spectrophotometer at absorption wavelengths between 350-700nm and a speed of 240 nm per minute. The reference used was deionised water.

Thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA)

TGA of cobalt complex samples was conducted using a Polymer Laboratories PL-STA TGA with ISI Thermal Analysis software. The samples were heated in air at 10^{o}C per minute up to temperature of 800^{o}C and % weight loss from the samples was recorded.

Surface area analysis (BET)

Brunauer–Emmett–Teller (BET) specific surface areas from gas sorption (N_2, 77 K) were measured on Micromeritics 3-Flex gas sorption analyser. All samples were degassed at 150°C/8 h under dynamic high vacuum (10-6 mbar) prior to analysis.

Fluorescence measurements

Fluorescence measurements of samples was conducted on a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon) using a Xenon source. Emission detector photomultiplier range used was 400-750 nm with FluorEssence software used for analysis of data collected.

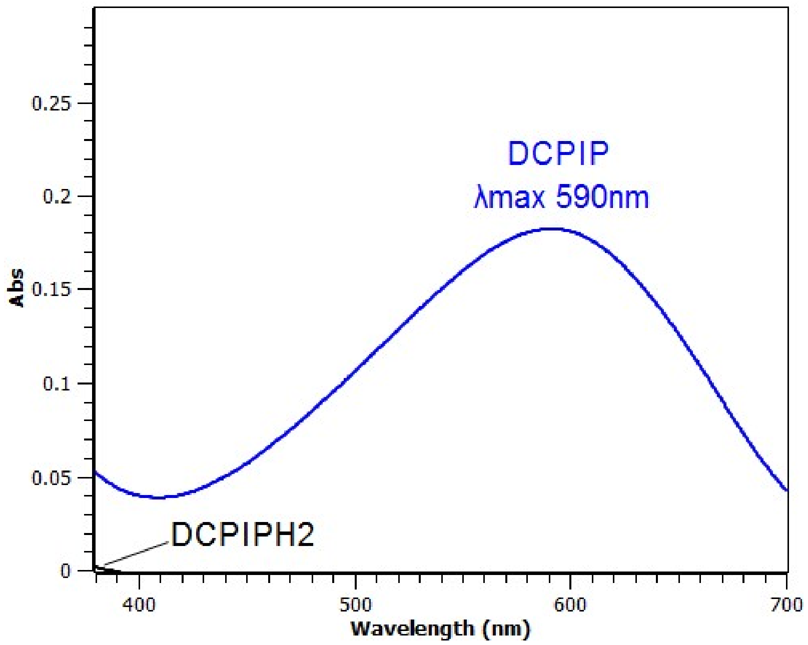

Fig. S1. Visible spectrophotometry of DCPIP in water in oxidized form with an Abs λ_{max} at 590nm, and the corresponding reduced DCPIPH2 form which was colourless.

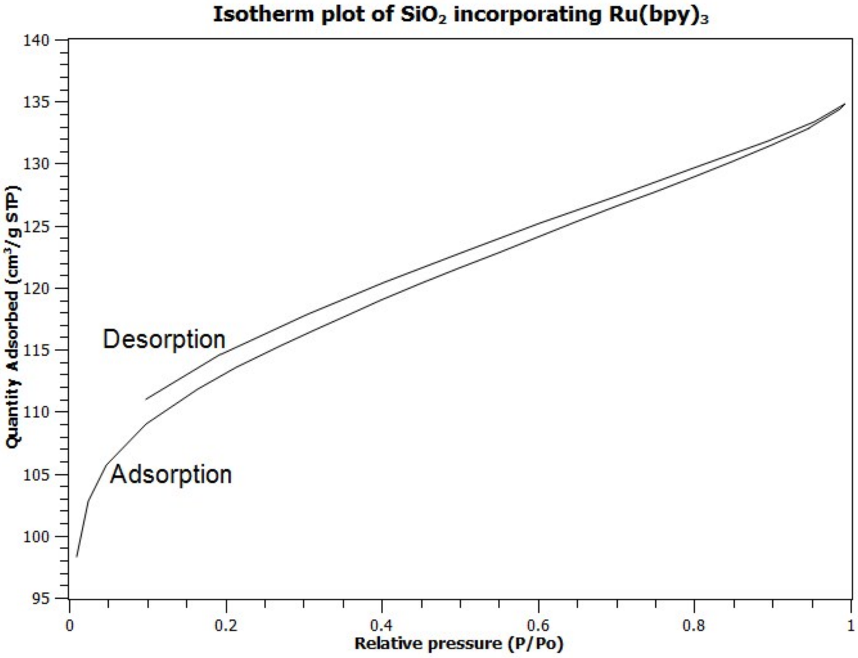

Fig. S2. N_2 BET isotherm plot of SiO_2 prepared incorporating $[Ru(bpy)_3Cl]Cl_2$. The surface area was $348 m^2/g$ and Barrett-Joyner-Halenda (BJH) pore size = 41.2Å. A Type I/II isotherm plot was obtained also indicating the silica gel was borderline micro-mesoporous.

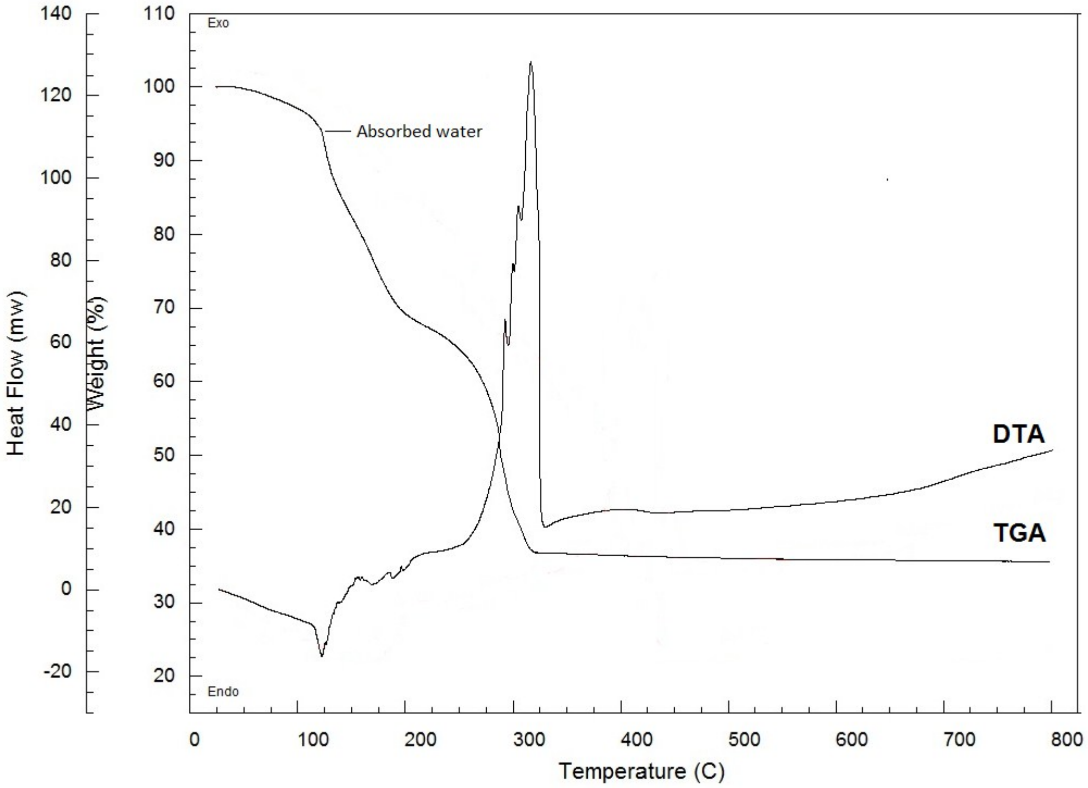

Fig. S3. TGA and DSC in air of prepared cobalt complex $Co(OH)_x(NH_3)_{(6-x)}$ showing adsorbed water of ~5wt% and thus residual mass of ~40wt%. Decomposition as shown by DTA was centred at 320°C. The residue consisted of CoO and some Co due to some reduction under heating conditions.

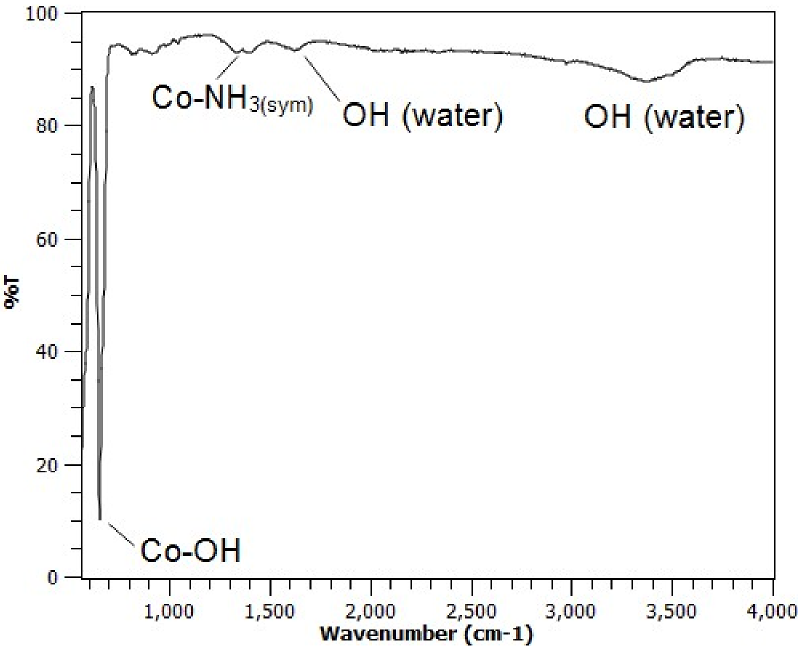

Fig. S4. FT-IR of prepared cobalt complex $Co(OH)_x(NH_3)_{(6-x)}$ showing strong absorption band at 655cm-1 due to Co-OH vibrations and weak bands at ~1330 and 1400 due to Co-NH_3(sym) deformation bands.

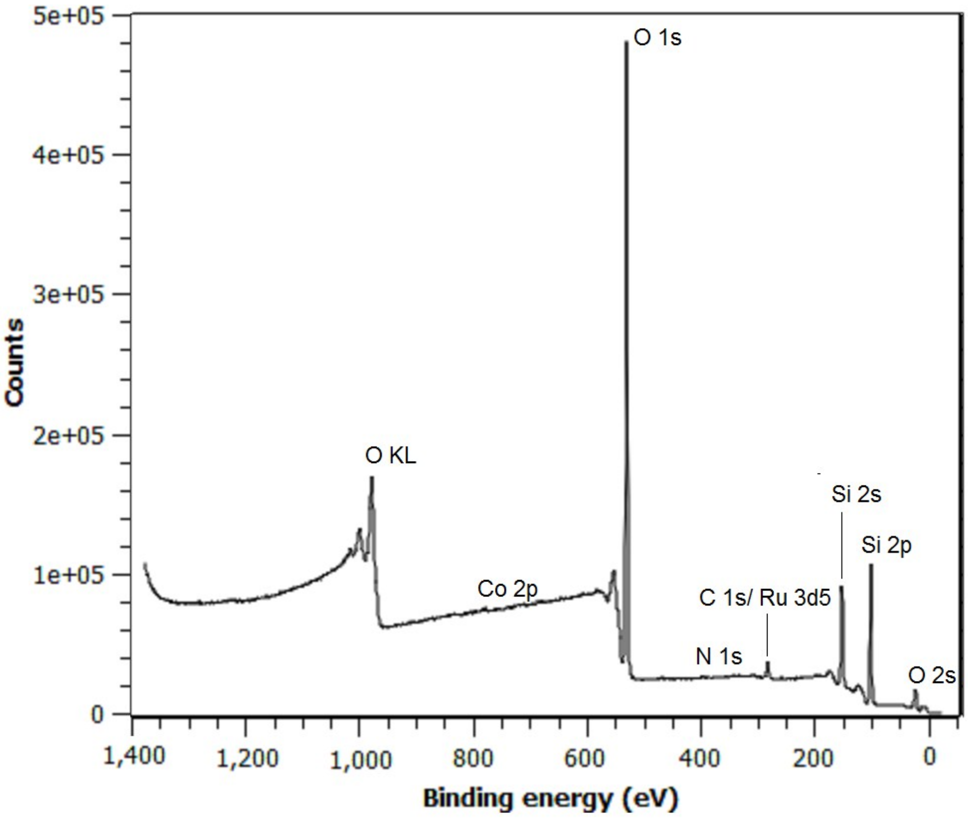

Fig. S5. XPS of prepared and washed SiO_2/DCPIP/$Ru(bpy)_3^{2+}$ composite after reaction with cobalt complex in solution. The presence of Ru and Co at low levels in the SiO_2 support is shown.

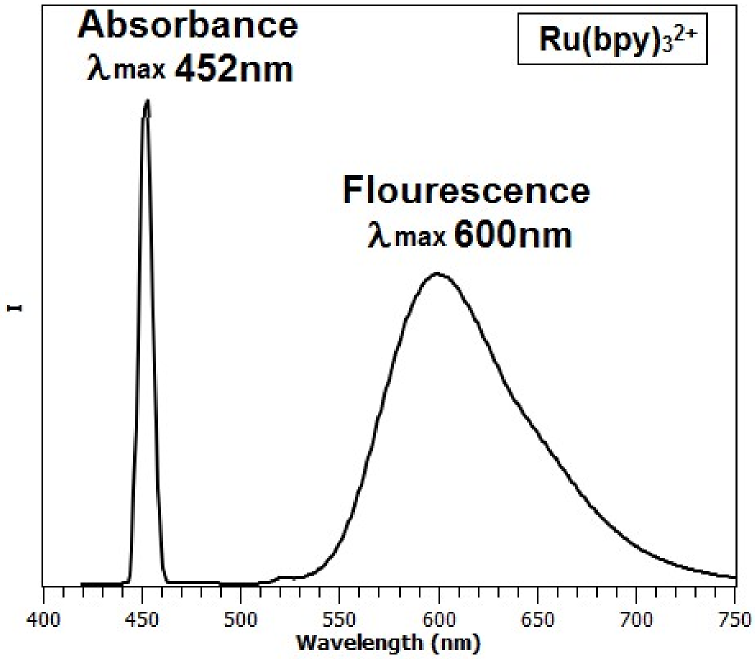

Fig. S6. Fluorescence measurement of an SiO_2-$Ru(bpy)_3^{2+}$ sample showing typical absorbance and fluorescence emission regions for $Ru(bpy)_3^{2+}$ incorporated within a microporous SiO_2 gel.[1] Electrons in the d orbitals of ruthenium are excited by visible light centred at 452nm into an orbital associated with one of the bipyridine ligands. Following internal conversions and intersystem crossing to a triplet state, (the ^{3}MLCT helps give the excited state a particularly long lifetime), the electrons relax back to the ground state with the a Stokes (red) shifted emission centred at 600nm (yellow/orange).

Turn over Frequency calculations

Prepared $Co(OH)_2$ as catalyst source (Fig. 2a)

20mg of $Co(OH)_2$ = 12.55mg Co present in the photocatalytic reaction

Moles = 12.55mg/58.93 = 0.2130×10^{-3} moles Co

Measured maximum level of O_2 generated, sustained for 300s, was 0.0597μmol per second

TOF = 0.0597μmol sec^{-1} / 0.2130×10^{-3} moles = 0.280×10^{-3} mol (O_2) sec^{-1}/ mol (Co)

TOF = 0.280×10^{-3} s^{-1}

Prepared SiO_2-DCPIP-$Ru(bpy)_3^{2+}$ sample as catalyst source (Fig. 3a)

By XPS this contained 0.62wt% Co.

Therefore 2.5g of sample = 15.5mg Co present in the photocatalytic reaction

Moles = 15.5mg/58.93 = 0.2630×10^{-3} moles Co

Measured maximum level of O_2 generated sustained for 300s was 0.0470μmol per second

TOF = 0.0470μmol sec^{-1} / 0.2630×10^{-3} moles = 0.1790×10^{-3} mol (O_2) sec^{-1}/ mol (Co)

TOF = 0.1790×10^{-3} s^{-1}

Similarly for repeat use of the sample (Fig. 3b)

TOF = 0.1566×10^{-3} s^{-1}

TOF for a sintered metal oxide used under similar reaction conditions and also using 5mWcm^{-2} light intensity was ~0.5×10^{-3} s^{-1},[3] thus the use of DCPIP as electron acceptor in this preliminary study gives TOF in the same order of magnitude and further studies on optimizing the reaction conditions to improve reaction efficiency are underway.

References

1) P. Innocenzi, H. Kozuka and T. Yoko, *Fluorescence Properties of the $Ru(bpy)_3^{2+}$ Complex Incorporated in Sol-Gel-Derived Silica Coating Film*, Journal of Physical Chemistry B, 1997, **101**(13), 2285-2291.

2) Duan, L., et al., *Visible Light-Driven Water oxidation by a Molecular Ruthenium Catalyst in Homogeneous System,* Inorganic Chemistry, 2010. **49**(1), 209-215.

3) Walsh D., et al, *Visible light promoted photocatalytic water oxidation: effect of metal oxide catalyst composition and light intensity*, Catal Sci and Technol, 2015, 5, 4560-4564.