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Additional experimental detail - Photocatalytic experiments:

The photocatalytic apparatus consisted of a double manifold Schlenk line in which a premier grade CO_2 cylinder and vacuum pump were attached, a large sample preparation chamber containing a vial holder and Schlenk flasks with concentrated sample, for each required component (Cat, PS and sacrificial donor (SD)). The viscosity of triethanolamine resulted in the requirement of its dilution in a 1:1 ratio with the solvent utilised within experiments, prior to sample preparation. Triethylamine and MeCN were refluxed with CaH_2 and distilled prior to their uses. In the cases of DMF and DMA, anhydrous solvents (Sigma-Aldrich) were used without further purification. Triethanolamine was also used without further purification.

Following preparation of the concentrated samples in separate Schlenk flasks, each flask was degassed by vacuum and refilled with CO_2 for whichever was greater of either three cycles or until bubbling under vacuum was no longer apparent. The sample chamber was also evacuated and refilled three times with CO_2. The individual samples were introduced in the order of photosensitiser, catalyst and sacrificial donor (to a final concentration of 100 μM w.r.t catalyst, 134 μM of **1** where present) upon high flow of CO_2 (to avoid air entering the sample chamber), whereby the final ratio of solvent to sacrificial donor was 5:1 v/v. The single-piercable sample lids were applied and the vials were placed at a constant distance from the LED light sources. The process was repeated until samples (in triplicate) were prepared for each of the 355 nm, 470 nm and > 400 nm light sources and the dark control. The vial size was in total, 4.9 ml, with 2 ml occupied by the sample. The λ = 355 nm and 470 nm samples were irradiated with fan assistance to avoid potential heating. Ambient light was shielded from solutions at all times during preparation, irradiation and sampling. The λ = 355 and 470 nm LED strips were manufactured in-house. The power output of the λ = 355 nm, 470 nm and > 400 nm LED sources was measured to be 3, 62 and 12 W m^{-2} respectively with a Delta Ohm HD2102.2 photoradiometer equipped with either an LP471 UVA or LP471 RAD irradiance probe. Sample irradiation was undertaken for 21 hours.

Gas chromatography was undertaken with a Shimadzu GC-2010, equipped with a micropacked column (Restek ShinCarbon ST, of length 2 m and ID 0.53 mm) and a barrier ionisation detector (BID). The oven of the GC containing the column was maintained at 30 ^{0}C during the course of approximately 6 minute runs in the absence of CO_2. Where samples contained CO_2, the run time was extended to 24 minutes. The carrier gas (helium, BIP grade, Air Products) was passed through the column at a rate of 10 ml min^{-1}. Approximate retention times of the gases of interest were 0.7 mins, 2.2 mins, 5.5 mins and 17 mins for H_2, CO, CH_4 and CO_2 respectively. The BID was maintained at 220 ^{0}C. The GC contains a sample loop of approximate 250 μl volume. The injection method allows for purging the void volumes with sample, followed by filling of the loop. 100, 1,000 and 10,000 ppm standard mixes of gases (H_2, O_2, CO, CH_4, CO_2, balance of He) were procured from Scientific and Technical Gases (STG) and were used to quantify the gases generated in photocatalytic studies. Samples and standards were introduced to the GC sampling loop with a valve-lock gas-tight 1 ml syringe (Valco VICI A-2).

The concentration (ppm) of the headspace of a gas was calculated by dividing the standard concentration (ppm) by the standard integrated area, and multiplying by the sample integrated area.

The number of moles in the headspace within the sample was calculated with Equation S.1. Henry's law was not applied to account for dissolved gases.

$$n = \frac{\left(\left(\frac{PV}{RT}\right) sample\ concentration\ in\ ppm\right)}{1{,}000{,}000} \qquad \text{Equation S.1}$$

Whereby P = 101,325 Pa, V is the volume of the headspace (m^3), R is the gas constant of 8.314 Pa m^3 mol^{-1} K^{-1} and T is temperature (K).

NMR spectra

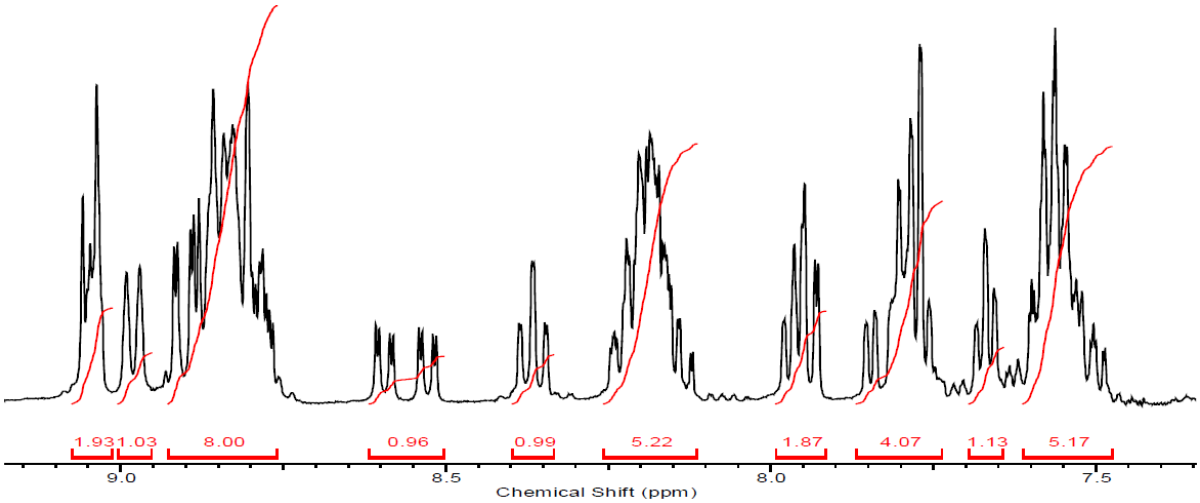

Figure S1: ^{1}H NMR (400 MHz) spectrum of **5** in DMSO-d_6

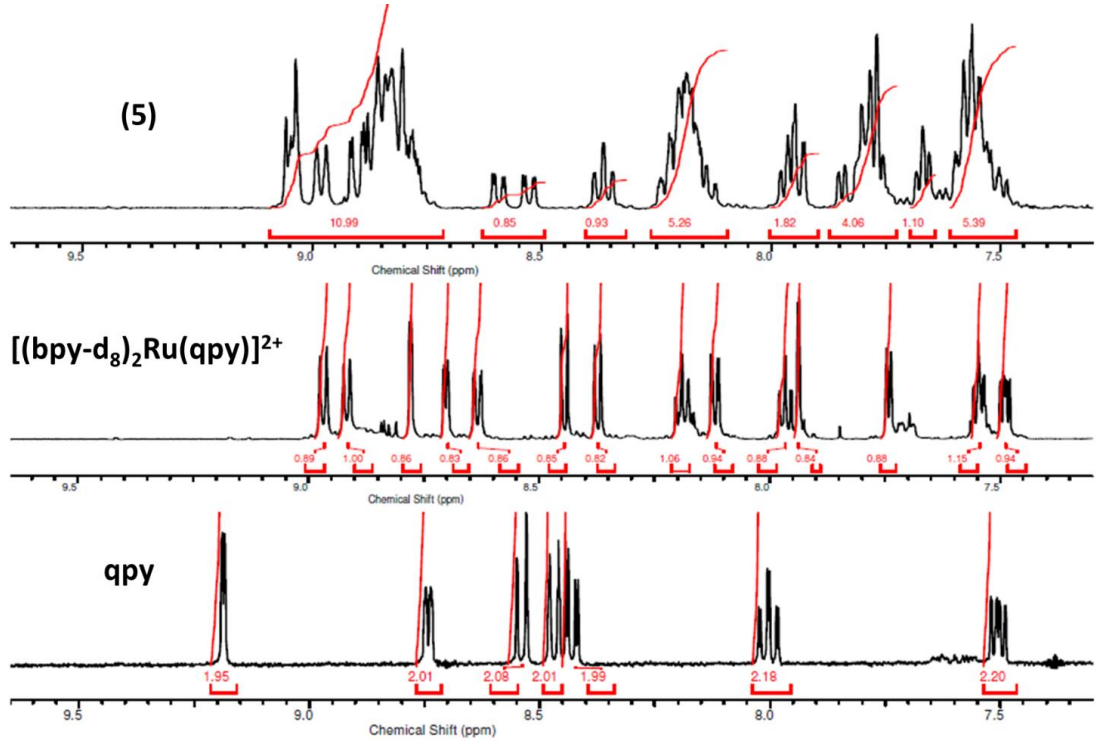

Figure S2: ^{1}H NMR (400 MHz) spectrum of **5**, $[(bpy\text{-}d_8)_2Ru(qpy)]^{2+}$ and qpy in DMSO-d_6

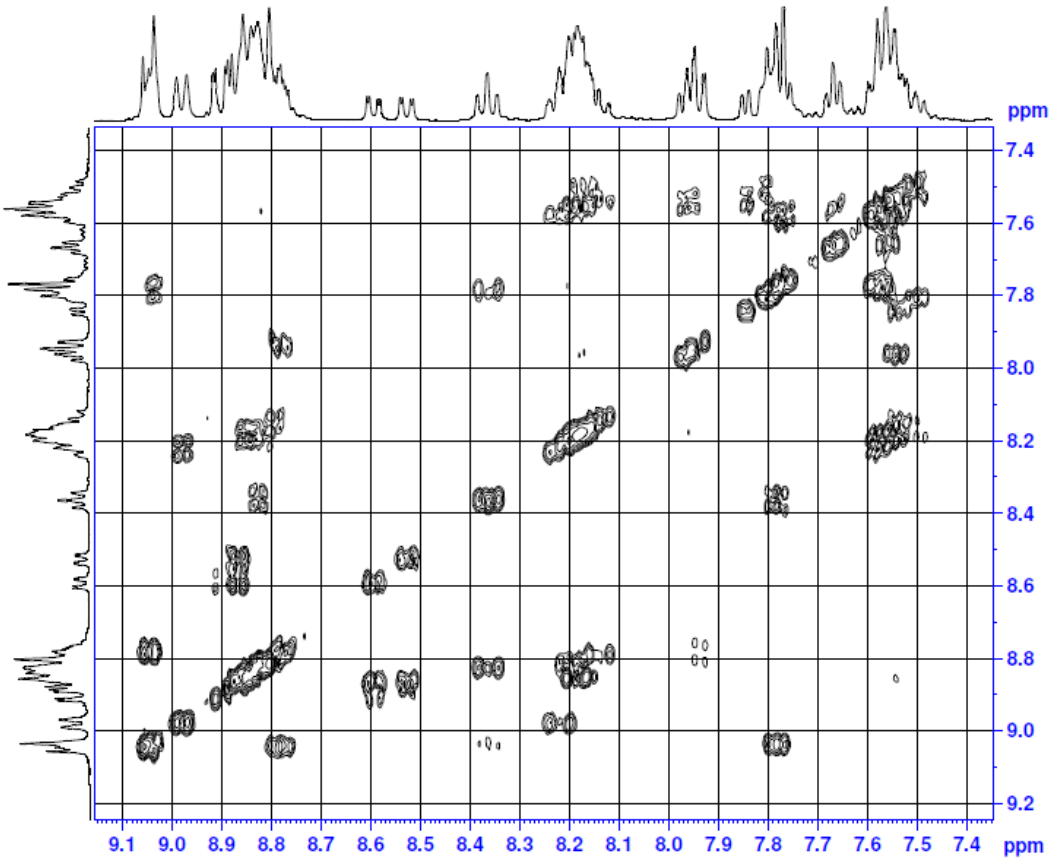

Figure S3: ^{1}H COSY NMR (400 MHz) spectrum of **5** in DMSO-d_6

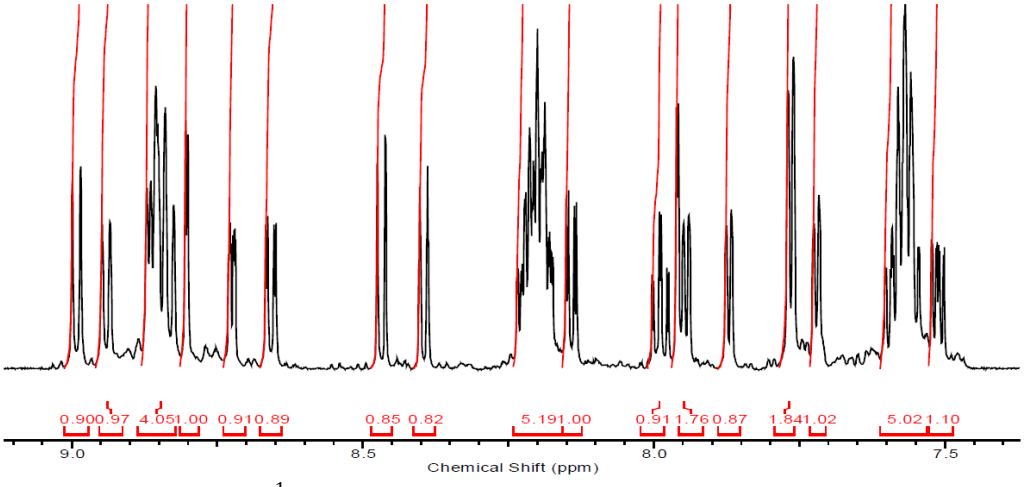

Figure S4: ^{1}H NMR (400 MHz) spectrum of **3** in DMSO-d_6

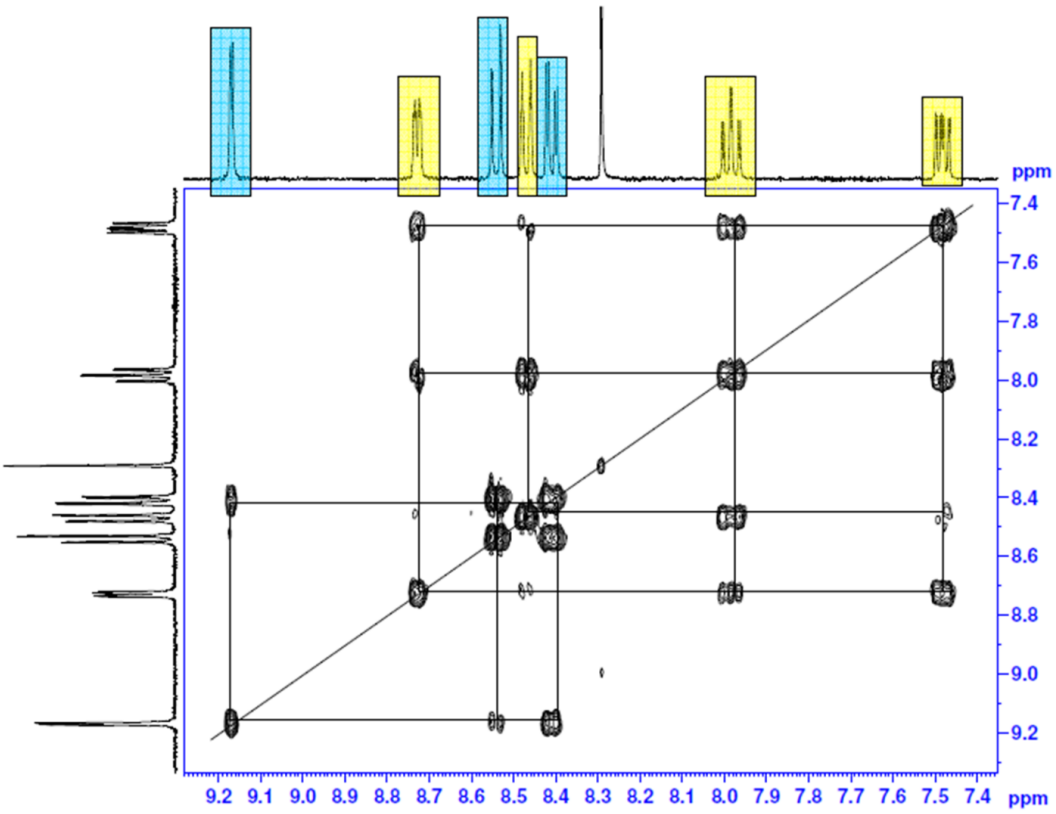

Figure S5: ^{1}H COSY NMR (400 MHz) spectrum of 2,2’:5’,3’’:6’’,2’’’-quaterpyridine (qpy) in DMSO-d_6

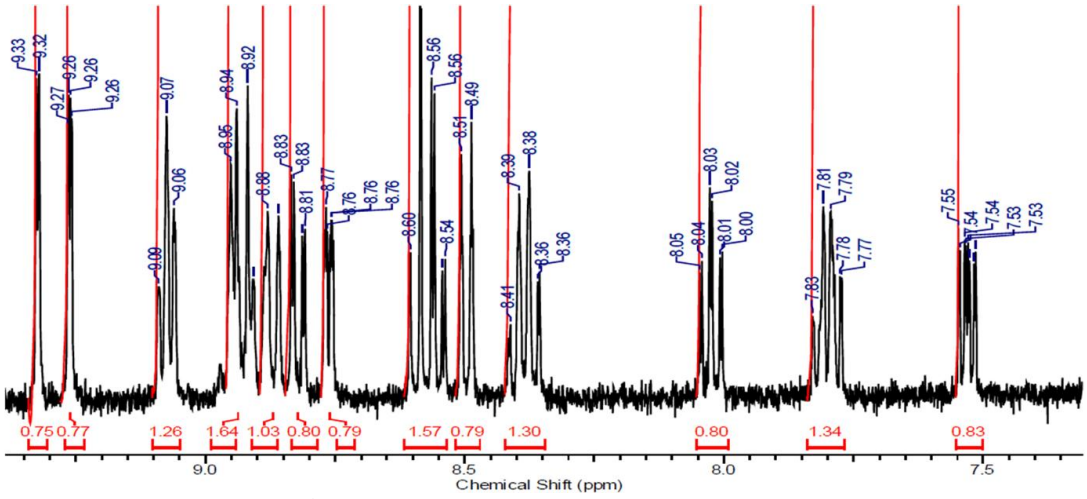

Figure S6: ^{1}H NMR (400 MHz) spectrum of **4** in DMSO-d_6

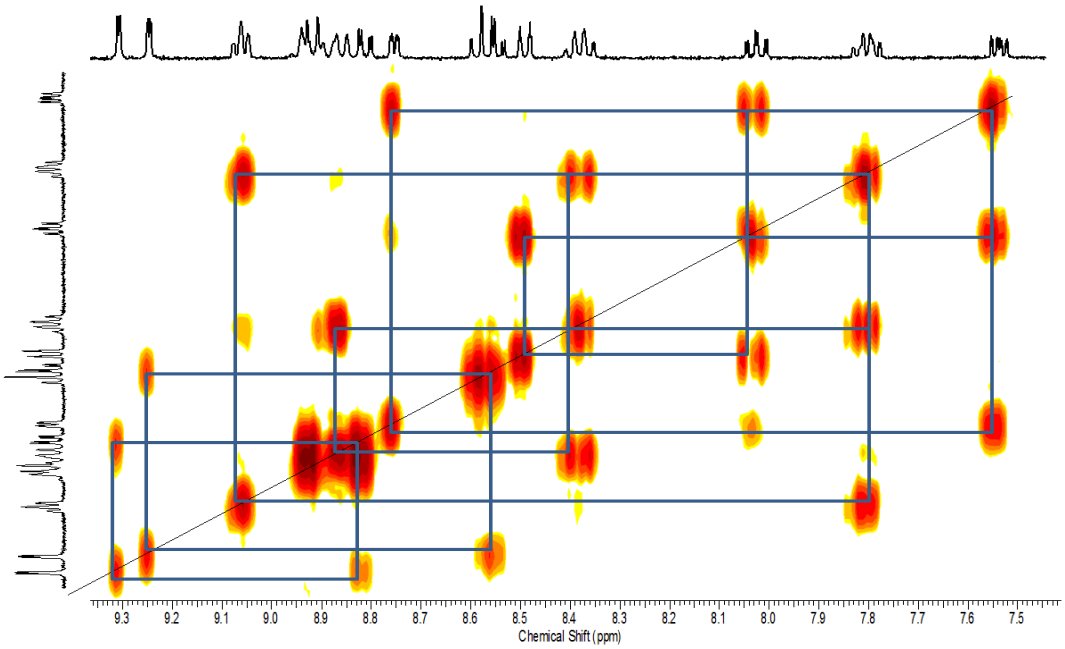

Figure S7: ^{1}H COSY NMR (400 MHz) spectrum of **4** in DMSO-d_6

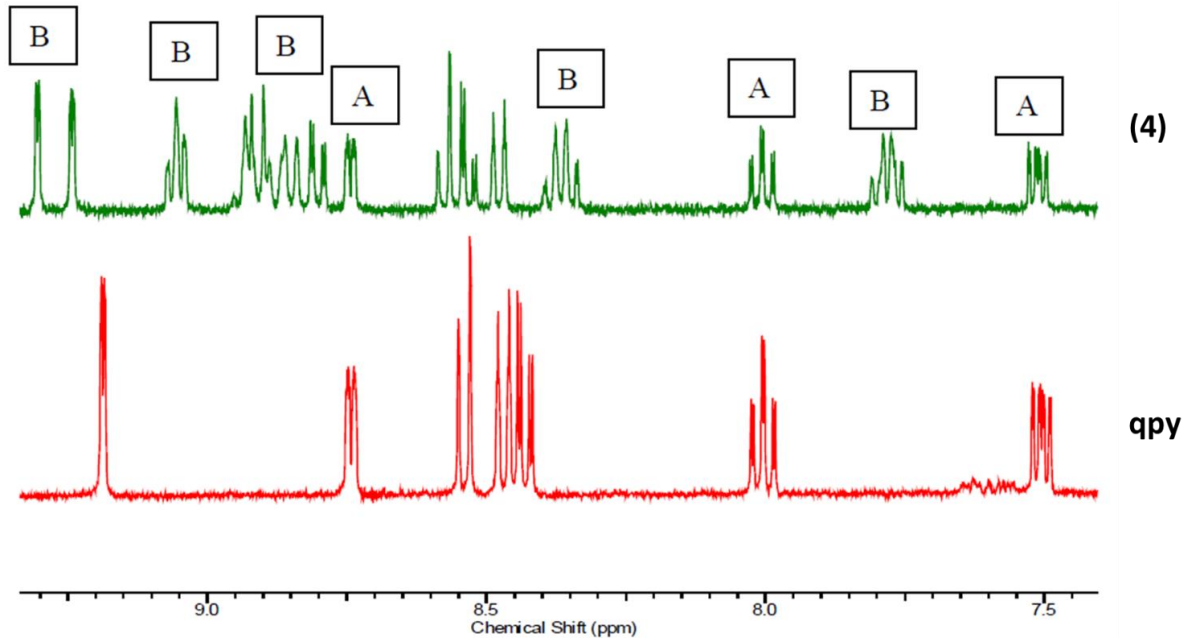

Figure S8: ^{1}H NMR (400 MHz) spectrum of **4** and qpy in DMSO-d_6. B attributed to Re-bound, A attributed to uncomplexed bpy of qpy.

Infrared spectroscopy

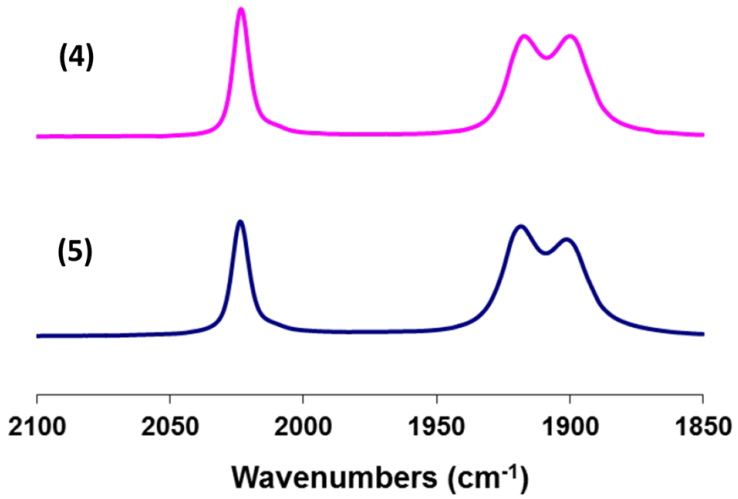

Figure S9: FTIR spectra of **4** (pink) and **5** (blue) in MeCN

Time resolved infrared spectroscopy (TRIR)

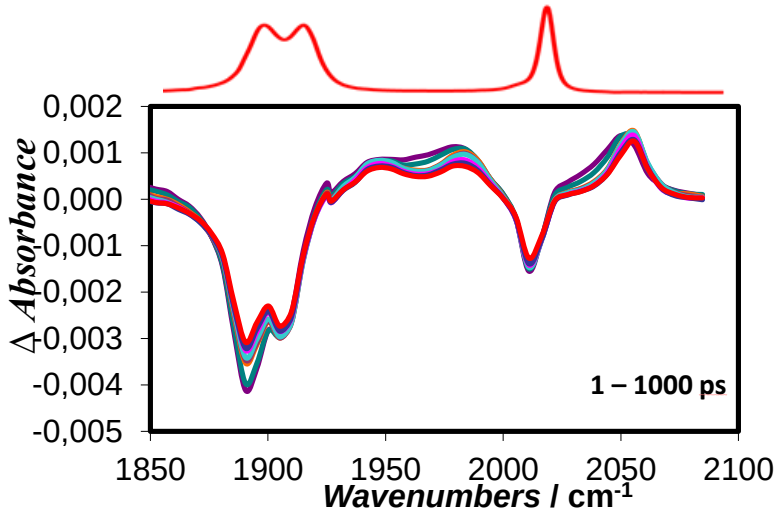

Figure S10: Time resolved infra-red difference spectra following laser photolysis (λ_{exc} = 320 nm) for **4** in MeCN. The spectrum above illustrates the parent υ(CO) stretches at t = 0 ps in MeCN.

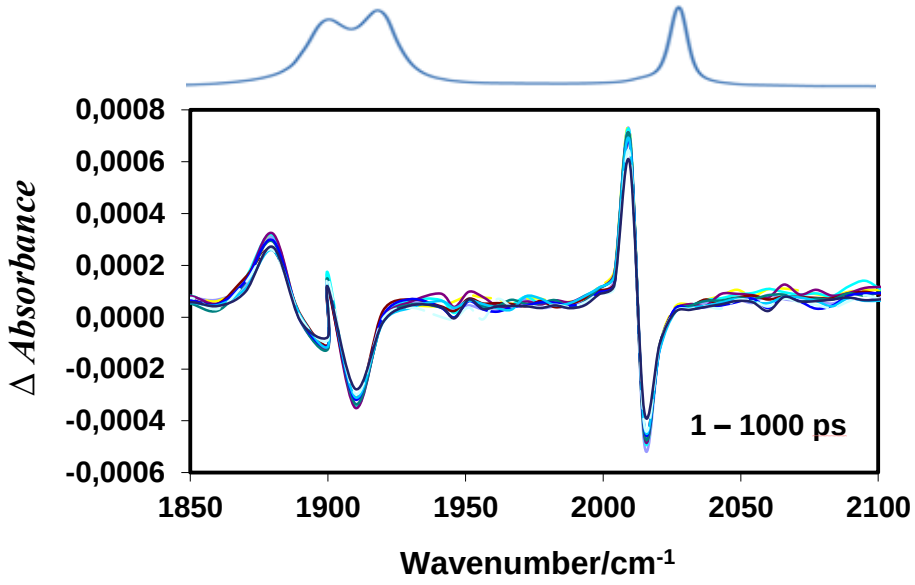

Figure S11: Time resolved infra-red difference spectra following laser photolysis (λ_{exc} = 450 nm) for **5** in MeCN. Above spectrum illustrates the parent υ(CO) streches at t = 0 ps in MeCN.

Computational studies

A plot of the behaviour of the twenty lowest energy singlet excited states along the Re to trans-CO stretching reaction coordinate showing that all accessible excited states are bound with respect to the metal to CO interaction.

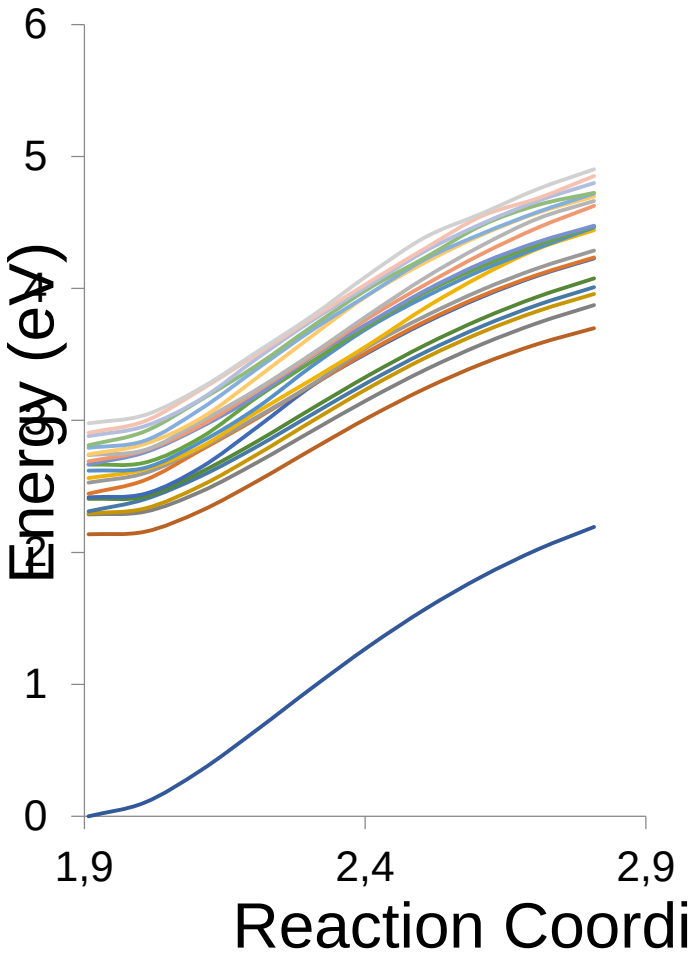

Figure S12. The calculated energy change along the reaction coordinate involving stretching of the Re to trans-CO ligand from 1.91 to 2.81 Å (bottom plot) and the twenty lowest energy singlet excited states all of which are bound states with respect to *trans*-CO loss.

The Optimised coordinates of the singlet ground state of **5**.

C	-1.035330	1.870118	-2.346877
C	-0.566401	3.172134	-2.530823
C	0.684251	3.494653	-1.999171
C	1.435691	2.520747	-1.317547
C	-0.275902	0.925422	-1.621042
C	2.784382	2.854091	-0.807621
C	3.387313	4.119589	-0.974507
C	4.675861	4.356383	-0.477182
H	5.141358	5.328697	-0.602786
C	5.351016	3.313281	0.183914
C	4.707407	2.079928	0.323781
H	-1.983478	1.564739	-2.768079
H	-1.154491	3.905027	-3.072871
H	5.190745	1.257128	0.831922
N	3.450654	1.849181	-0.153801
H	2.868308	4.919922	-1.485456
H	1.070846	4.496807	-2.125573
C	4.642722	-1.420699	-1.272858
C	3.279452	-0.379849	-2.893335
C	4.894884	-1.599482	0.170988
C	5.483054	-1.927284	-2.283078
C	4.083897	-0.851414	-3.938091
H	2.424463	0.254483	-3.090526
C	5.953182	-2.365637	0.694432
C	5.201677	-1.650381	-3.629493
H	3.841780	-0.592652	-4.963421
C	6.139626	-2.442790	2.083299
C	4.214688	-1.002301	2.353986
H	5.844411	-2.033881	-4.415441
C	5.257109	-1.742205	2.926870
H	6.952746	-3.031105	2.496390
H	3.516456	-0.451558	2.970253
H	5.367231	-1.768050	4.005674
N	3.531351	-0.666355	-1.584667
H	6.626274	-2.897793	0.032391
H	6.354174	-2.519205	-2.027683
C	0.704380	-0.395686	2.438357
C	1.545856	1.809353	2.444438
C	0.724165	-1.702917	1.754565
C	-0.004360	-0.146452	3.627284
C	0.886945	2.102968	3.643909
H	2.142736	2.559261	1.943869

C	0.137297	-2.866825	2.287840
C	0.091214	1.110558	4.242584
H	0.979721	3.092067	4.078826
C	0.288246	-4.090437	1.622955
C	1.563889	-2.934852	-0.071933
H	-0.455291	1.313921	5.157825
C	1.026342	-4.127106	0.424408
H	-0.154579	-4.993226	2.031411
H	2.131240	-2.921162	-0.994159
H	1.184545	-5.055966	-0.113625
N	1.412849	-1.741525	0.565018
N	1.464465	0.588949	1.848025
H	-0.429592	-2.818149	3.208009
H	-0.641751	-0.909198	4.053410
N	4.026800	-0.928291	1.006430
N	0.967776	1.228203	-1.111110
Ru	2.438097	0.044475	0.065534
H	6.350366	3.448995	0.583087
C	-0.885265	-0.447499	-1.607334
C	-0.208770	-1.485279	-2.266608
C	-2.854328	-1.767035	-1.496837
C	-0.870241	-2.690415	-2.544313
H	0.808451	-1.324567	-2.595855
C	-2.208268	-2.822819	-2.169879
H	-0.363367	-3.494358	-3.068913
H	-2.744240	-3.733965	-2.400893
C	-4.286334	-1.847107	-1.129797
C	-5.118801	-2.921697	-1.496374
C	-6.106942	-0.756587	-0.099209
C	-6.477101	-2.901927	-1.145062
H	-4.729674	-3.764908	-2.053223
C	-6.981398	-1.797448	-0.437053
H	-6.457922	0.106914	0.450824
H	-7.126453	-3.726515	-1.421612
H	-8.024650	-1.736833	-0.147520
N	-4.788644	-0.779461	-0.433090
N	-2.193160	-0.594323	-1.194710
Re	-3.352061	0.709971	0.198582
Cl	-2.722219	-1.131498	1.861816
C	-1.946672	1.896010	0.740497
C	-3.955166	1.973246	-1.097270
C	-4.475698	1.502020	1.551252
O	-4.326057	2.756547	-1.912781
O	-1.072053	2.638840	1.058579
O	-5.171187	1.949994	2.392785

Electrochemistry

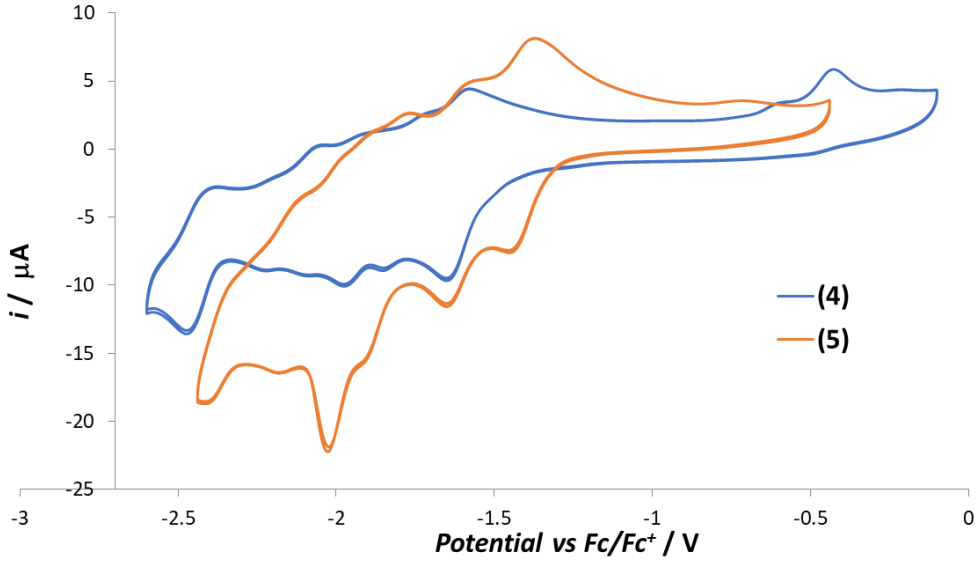

Figure S13: Cyclic voltammetry of **4** and **5** (beyond the Ru and Re qpy-based reductions) in MeCN/0.1 M $TBAPF_6$, ν = 100 mV s^{-1}.

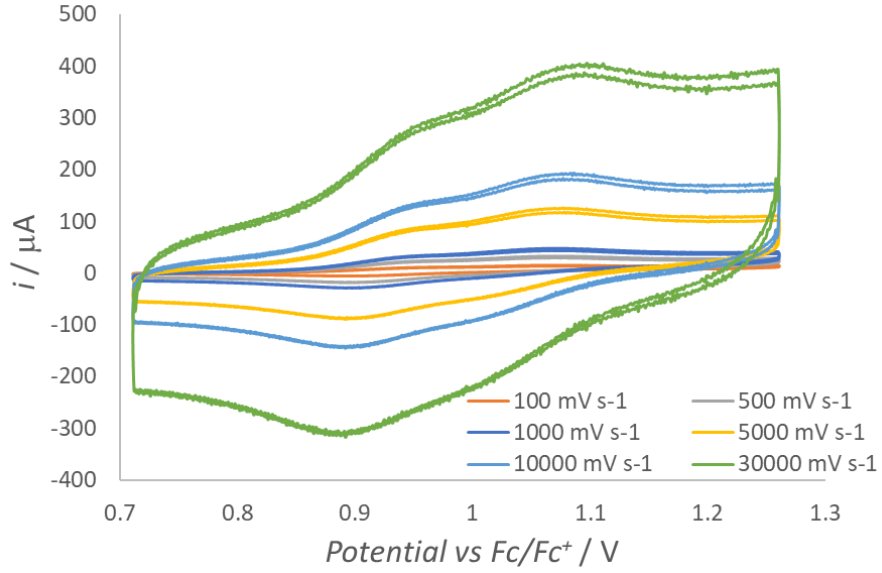

Figure S14: Cyclic voltammetry of **5** in MeCN/0.1 M $TBAPF_6$, with varied scan rate from 100 mVs^{-1} to 30 Vs^{-1}

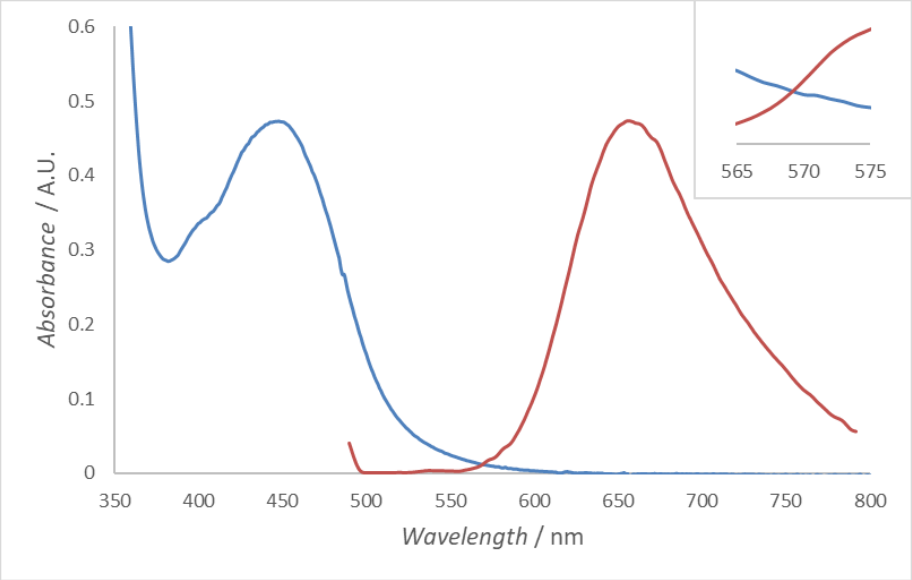

Figure S.15: Absorbance and emission spectra (λ_{excit} of 470 nm) of **5** in MeCN at room temperature, Absorption (Blue) and Emission (Red), MLCT and emission λ_{max} normalised to the same height[1]

Photocatalytic experiments

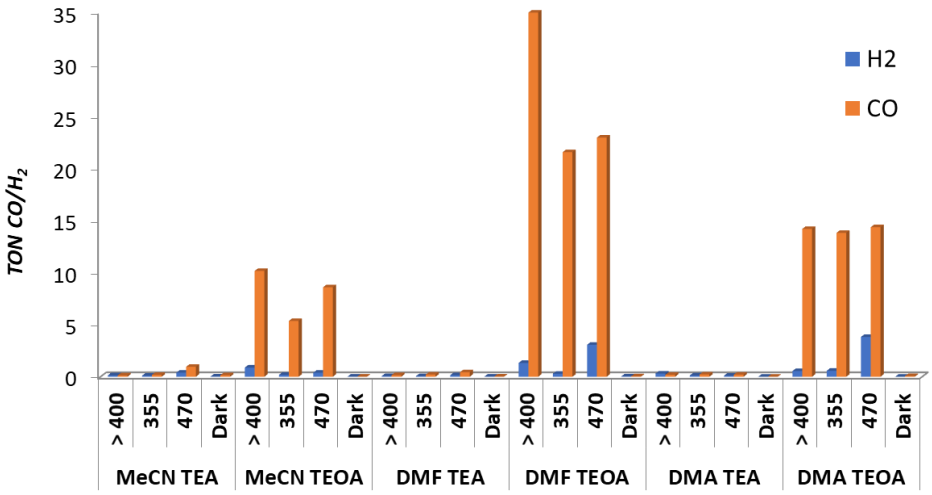

Figure S16: The effect of different solvents and sacrificial donors on H_2 and CO production from CO_2 in 134 μM **1** with 100 μM **2** (at λ = 355, 470 and > 400 nm), with an irradiation time of 21 hours

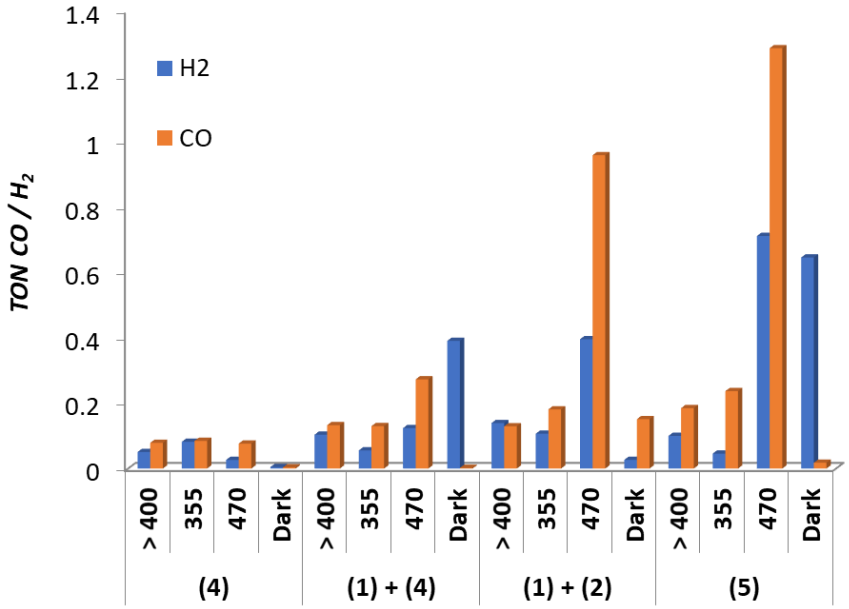

Figure S17: H_2 and CO TON values produced in 5:1 MeCN/TEA by 100 μM **4**, 134 μM **1** with 100 μM **4**, 134 μM **1** with 100 μM **2** and 100 μM **5** (at λ = 355, 470 and > 400 nm), with an irradiation time of 21 hours

References

[1] A. Islam, H. Sugihara, H. Arakawa, *J. Photochem. Photobiol. Chem.* **2003**, *158*, 131–138.