Supporting Information (revised 27.6.12)

CO_2 photoreduction with long-wavelength light: dyads and monomers of zinc porphyrin and rhenium bipyridine

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Experimental

General Procedures. Chemicals were obtained from the following suppliers: pyridine, EDTA, AgOTf, (Aldrich); 3-picoline (BDH Chemicals); CO_2 CP grade (BOC); thionyl chloride, silica 60 (Fluka); sodium sulfate, sodium carbonate, sodium hydrogen carbonate, (Fisher); $Zn(OAc)_2.H_2O$, (Fisons); 4 Å molecular sieves (Merck), tetraphenylporphyrin (Frontier) tetraphenylchlorin (TCI).

Solvents for general use were obtained from Fisher. Solvents were dried by refluxing over sodium wire (benzene, THF) or over CaH_2 (dichloromethane).

CD_2Cl_2, CD_3OD and THF-d_8 were used as obtained (Aldrich) and $CDCl_3$ was dried over 4 Å molecular sieves.

Pyridine was dried over 4 Å molecular sieves.

4'-methyl-2,2'-bipyridine-4-carboxylic acid[1], $Re(CO)_5Br$[2], 5-(4-aminophenyl)-10,15,20-triphenylporphyrin[3], **Dyad 1**[4,5] and zinc tetraphenylchlorin[6] were synthesised by literature methods. The synthesis of zinc tetraphenylchlorin was modified to include a water wash (5x) to remove $Zn(acac)_2$ and subsequent drying under high vacuum. The formation of zinc tetraphenylchlorin during photolysis was verified by comparison with ^1H and ^{13}C NMR spectra of an authentic sample

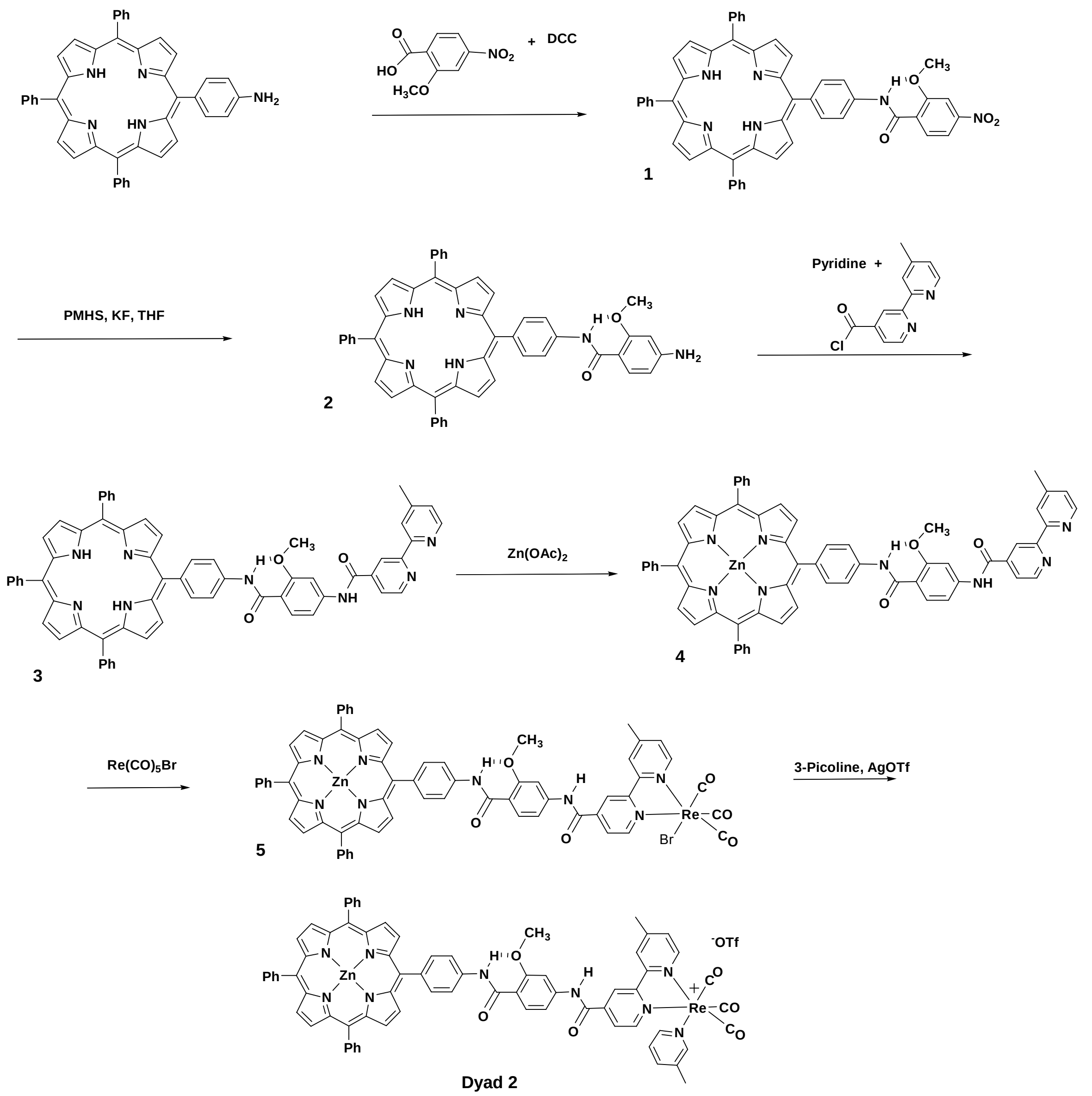
NMR spectra were run on a Bruker AV500 (^1H at 500.23 MHz) spectrometer or Bruker ECS400 (400 MHz). The spectra were referenced to residual protiated solvent at δ 7.26 ($CDCl_3$), δ 1.72 ([$^2H_8$] THF), δ 5.32 (CD_2Cl_2) and δ 3.31 (CD_3OD).

IR spectra were recorded on a Mattson RS FTIR instrument, averaging 64 scans at resolution 2 cm^{-1}. UV−visible absorption spectra were measured using an Agilent 8453 spectrometer. ESI mass spectra were recorded on a Bruker micrOTOF instrument, EI on a Waters GCT premier and reaction mixture ESI on a Bruker Esquire 6000. Mass values are quoted for ^{64}Zn, ^{185}Re and ^{79}Br.

Irradiation of all samples was by an ILC 302 UV lamp. Light from the lamp was directed through a water filter (10 cm) followed by various optical filters. Analysis of gas samples from CO_2 reduction was by gas chromatography on a UNICAM PRO GC+ with a thermal conductivity detector and a Restek ShinCarbon ST 100/120 micropacked column. The amount of CO produced was determined using a calibration plot. Known volumes of CO were mixed with a mimic experimental solution 3 mL DMF:TEOA 5:1 (v/v) and sampled to GC. Quantification was by comparison of integrations against a 1% CH_4 internal standard. Corrections were made for temperature and the change in headspace pressure at each injection TONs were calculated as reported previously.[7]

Electrochemistry was performed in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ (TBAP) electrolyte. The setup comprised reference electrode (Ag/AgCl, 3 M), working electrode (platinum disc) and counter electrode (platinum wire). Ferrocene was used as internal standard. All scans were made at 100 mV/sec. Electrochemistry experiments used a BASi Epsilon with C3 cell stand.

Dyad 2 was synthesised as shown in **Scheme S 1**. Details follow.



Scheme S 1 Synthesis of **Dyad 2**

5-[4-[(2-methoxy-4-nitro-phenylcarbonyl)-amino]phenyl]-10,15,20-triphenyl porphyrin. 1 Dicyclohexylcarbodiimide (1.00 g, 4.85 mmol) was added to a stirred solution of 2-methoxy-4-nitrobenzoic acid (0.80 g, 4.05 mmol) in acetonitrile (25 cm^3) at 0 ^{o}C. After 15 minutes the reaction was brought to room temperature and stirred for ~24h until the reaction was complete by TLC (10:1 chloroform:acetonitrile v/v). The solution was filtered and the solid by-product was washed thoroughly with acetonitrile and the washings added to the filtrate. Removal of the solvent yielded a pale yellow solid, which was used without further purification. The anhydride residues were taken up in acetonitrile (20 cm^3) and added dropwise to an ice-cold solution of free base 5-(4-aminophenyl)-10,15,20-triphenylporphyrin, (0.40 g, 0.635 mmol) in chloroform with stirring. The reaction was heated at reflux for 48 h. The solvent was removed and the purple residue was extracted into dichloromethane and washed with 2 M sodium hydroxide (3 × 250 cm^3), water and brine. The organic fraction was dried over sodium sulfate and the solution was then concentrated *in vacuo* and purified by column chromatography (Si-60, 10:1 chloroform:acetonitrile v/v) to give **1** (0.44 g, 0.54 mmol, 86%).

λ_{abs}(DMSO)/nm 420 (ε/dm^3 mol^{-1} cm^{-1} 511000), 518 (20800), 552 (11200), 592 (6130) and 647 (5560);
λ_{em}(DMSO)/nm 654 and 719;
ν_{max}(KBr disc)/cm^{-1} 3448br w, 3374br w, 3316br w, 3083w, 3061w, 3026m, 2924s and 2852w; ν_{max}(ATR)/cm^{-1} 1676s, 1589s, 1521s, 1471s, 1440m, 1400m, 1344s, 1311m, 1259s, 1177m, 1156m, 1101br s, 1056m, 1022s, 1002s, 981s, 964s, 867m, 798s, 750m, 728s and 699s;
δ_H (500 MHz; $CDCl_3$, see ESI) 9.99 (1H, s, NH), 8.89 (8H, m, β-pyrrole), 8.58 (1H, d, *J* = 8.4 Hz, phenyl), 8.29 (2H, d, *J* = 8.0 Hz, *o*-aminophenyl) 8.26 (6H, m, *o*-phenyl), 8.11 (2H, d, *J* = 8.2 Hz, *m*-aminophenyl) 8.05 (1H, dd, *J* = 2.3, 8.8 Hz, phenyl), 7.78 (9H, m, *m*-/*p*-phenyl), 7.96 (1H, d, *J* = 2.0 Hz, phenyl), 4.31 (3H, s, OCH_3) and –2.74 (2H, br s, inner NH);
δ_C (176 MHz; $CDCl_3$) 161.5, 157.3, 150.6, 142.2, 142.1 138.8, 137.4, 135.3, 134.6, 133.9, 127.8, 127.3, 126.7, 120.3, 120.2, 119.3, 118.9, 116.5, 107.0 and 57.2
m/z (ESI^+) 809.5 ($M + H^+$, 100%); *m/z* (ESI^-) 807.4 ($M - H^+$, 100%); *m/z* (HR ESI^+) 809.2895 ($M + H^+$. $C_{52}H_{37}N_6O_4$ requires 809.2871, difference 2.4 mDa).

5-[4-[(2-methoxy-4-amino-carboxyamidyl)phenyl]phenyl]-10,15,20-triphenyl porphyrin 2. To a flame 500 cm^3 round bottom flask under Ar was added **1** (2.48 g, 3.07 mmol) and $Pd(OAc)_2$ (33.7 mg, 153 µmol). Dry degassed THF was added (140 cm^3) with stirring. The system was purged with N_2. A solution of KF (356 mg, 6.14 mmol) in degassed water (6.43 cm^3) was added. A balloon of Ar was fitted and polymethylhydrosiloxane (740 µL, 12.2 mmol) was added dropwise (gas evolved). The solution was stirred at RT for 2 hrs 45 mins after which it was judged complete by TLC. When following by TLC a third rather intense spot is observed at approx. 1 hour but this disappeared by 2 hr 45 mins.

The reaction was opened to air, diluted with 10 – 20 cm^3 ether and stirred for 5 minutes. Water and ether was added and the product back-extracted into ether. This was filtered through a mixed plug of neutral alumina (bottom layer) and celite (top layer) flushing with EtOAc followed by CH_2Cl_2/CH_3CN. The product was purified by column chromatography (Si-60, CH_2Cl_2/CH_3CN 10/1) (2.15 g, 2.76 mmol, 90%).

λ_{abs}(DMSO)/nm 421 (ε/dm^3 mol^{-1} cm^{-1} 368000), 518 (19800), 552 (12300), 592 (7140) and 648 (8100)

λ_{em}/nm (DMSO) 656 and 720;

ν_{max}(KBr disc)/cm^{-1} 3437br m, 3341br m, 3056w, 3017w, 2975w, 2938w, 2924m and 2899w;

ν_{max}(ATR)/cm^{-1} 1663m, 1595s, 1516s, 1472s, 1441m, 1400m, 1349m, 1309s, 1270s, 1245s, 1206m, 1178s, 1156m, 1134s, 1094m, 1072m, 1029s, 1002s, 981s, 965s, 877m, 847m, 827m, 799s, 726s, 701s and 658s

^{1}H NMR (400 MHz, $CDCl_3$): δ –2.78 (2 H, br s, pyrrole NH), 4.12 (3 H, s, OCH_3), 6.32 (1 H, d, phenyl), 6.45 (1 H, dd, phenyl), 7.74 (9 H, m, *m*-/ *p*-phenyl), 8.04 (2 H, d, *m*-aminophenyl

δ_C (176 MHz; $CDCl_3$) 161.5, 157.3, 150.6, 142.1, 138.8, 137.4, 135.3, 134.6, 133.8, 128.0, 127.3, 126.7, 120.3, 119.4, 118.7, 118.2, 117.4, 116.6, 107.1 and 57.5

m/z (ESI$^+$) 779.4 (M + H$^+$, 100%); *m/z* (ESI$^-$) 777.3 (M – H$^+$, 100%); *m/z* (HR ESI$^+$) 779.3102 (M + H$^+$. $C_{52}H_{39}N_6O_2$ requires 779.3129, difference 2.7 mDa).

5-[4-[(2-methoxy-4-(4-methyl-2,2’-bipyridine-4’-carboxyamidyl) carboxyamidyl) phenyl] phenyl]-10,15,20-triphenyl porphyrin 3. 4-methyl-2,2’-bipyridine-4-carboxylic acid (52.7 mg, 0.248 mmol) was heated at reflux in thionyl chloride (4.65 cm^3) under an inert atmosphere for 2 hours. Excess thionyl chloride was removed under reduced pressure revealing a yellow solid, which was dried for a further 30 minutes. Porphyrin **2** (193 mg, 0.248 mmol) was dissolved in the minimum amount of dry dichloromethane and added by cannula to the yellow solid. Dry pyridine was added (7.75 cm^3) and the solution heated at reflux for 2 hours under an inert atmosphere and then left overnight at room temperature. The solvent was removed under reduced pressure and the product was re-dissolved in dichloromethane, washed with saturated sodium hydrogen carbonate solution, brine and water followed by drying over sodium sulfate. The solvent was removed and the product purified by column chromatography (Si-60, dichloromethane, Et_3N, methanol). The second fraction was collected and the solvent removed yielding the desired compound (103 mg, 0.105 mmol, 53 %)

^{1}H NMR (500 MHz, $CDCl_3$): δ –2.76 (2 H, s, pyrrole NH); 2.48 (3 H, s, bpy CH_3); 4.26 (3 H, s, OCH_3), 7.19 (1 H, m, bpy); 7.22 (1 H, *o*-methoxyphenyl); 7.75 (9 H, m, *m-/p*-phenyl); 7.90 (1 H, dd, bpy); 8.08 (2 H, d, *m*-amidophenyl); 8.13 (2H, d, *m*-methoxyphenyl); 8.21 (8H, m, *o*-phenyl + *o*-amidophenyl); 8.33 (1 H, s, bpy); 8.43 (1 H, d, bpy); 8.46 (1 H, s, bpy amide); 8.58 (1 H, d, bpy); 8.83 (6H, m, β-pyrrole); 8.89 (3 H, m, bpy, β-pyrrole); 10.15 (1 H, s, porphyrin amide)

ESI-MS: *m/z* = 975.3758 (M + H^+, 100%), (M + H^+. $C_{64}H_{46}N_8O_3$ requires 975.3766, difference 0.8 mDa)

5-[4-[(2-methoxy-4-(4-methyl-2,2'-bipyridine-4'-carboxyamidyl) carboxyamidyl) phenyl] phenyl]-10,15,20-triphenyl porphyrinatozinc(II) 4. In a modification of a literature procedure,[5] porphyrin **3** (260 mg, 0.267 mmol) was dissolved in 15 % methanol in chloroform. Zinc acetate dihydrate (264 mg, 1.20 mmol) was added and the solution heated at reflux for 1 hour and then allowed to cool. The product was diluted further with dichloromethane and washed with a solution of 1 % EDTA (m/v) in 10 % sodium carbonate solution and then with water. The product solution was dried over magnesium sulfate and the solvent removed (244 mg, 0.235 mmol, 88 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (3 H, s, bpy CH_3); 4.26 (3 H, s, OCH_3); 7.18 (1 H, d, 5-methoxyphenyl); 7.22 (1 H, d, bpy 5'); 7.75 (9 H, m, *m-/p*-phenyl); 7.89 (1 H, d, bpy 5); 8.08 (2 H, d, *m*-amidophenyl); 8.11 (1 H, s, 3-methoxyphenyl); 8.21 (8 H, m, *o*-phenyl); 8.33 (1 H, s, bpy 3'); 8.39 (1 H, s, 6-methoxyphenyl); 8.41 (1 H, s, bpy amide); 8.58 (1 H, d, bpy 6'); 8.80 (1 H, s, bpy 5'); 8.90 (1 H, d, bpy 6); 8.95 (7 H, m, β-pyrrole + bpy 3); 9.02 (2 H, d, β-pyrrole); 10.15 (1 H, s, porphyrin amide)

ESI-MS: *m/z* = 1037.2904 (M+H$^+$, 98%), (M + H$^+$. $C_{64}H_{44}N_8O_3Zn$ requires 1037.2901, difference 0.7 mDa)

5-[4-[(2-methoxy-4-([rhenium (I) tricarbonyl (bromide)]4-methyl-2,2'-bipyridine-4'-carboxyamidyl) carboxyamidyl) phenyl] phenyl]-10,15,20-triphenyl porphyrinatozinc(II) 5. In a modification of a literature procedure,[8] porphyrin **4** (109 mg, 0.105 mmol) and Re(CO)$_5$Br (43 mg, 0.105 mmol) were placed in a Schlenk tube under argon and dry benzene (15 cm^3) was added by cannula. The mixture was heated to 65 ˚C under argon for 12 hours. The solvent was removed to yield the desired product (142 mg, 0.102 mmol, 97 %).

^{1}H NMR (400 MHz, THF-*d*$_8$): 2.67 (3 H, s, bpy CH$_3$); 4.29 (3 H, s, OCH$_3$); 7.45 (1 H, d, 6-methoxyphenyl); 7.58 (1 H, bpy); 7.79 (9 H, m, *m-/p*-phenyl); 8.11 (1 H, d, bpy); 8.20 (1 H, 3-methoxyphenyl); 8.24 (8 H, *m*-amidophenyl); 8.37 (1 H, d, 5-methoxyphenyl); 8.67 (1 H, s, bpy); 8.89 (6 H, m, β-pyrrole); 8.98 (3 H, m, β-pyrrole + bpy); 9.04 (1 H, s, bpy); 9.30 (1 H, d, bpy); 10.23 (1 H, s, amide); 10.30 (1 H, s, amide).

ESI-MS: *m/z* = 1407.1208 (M + Na$^+$, 24%), (M + Na$^+$. $C_{67}H_{44}N_8O_6ZnReBr$ requires 1407.1280, difference 8 mDa)

IR (ν/cm^{-1}) (THF) 2020 (s), 1920 (s), 1898 (s) (ν(CO)).

5-[4-[(2-methoxy-4-([rhenium (I) tricarbonyl (3-picoline)]4-methyl-2,2'-bipyridine-4'-carboxyamidyl) carboxyamidyl) phenyl] phenyl]-10,15,20-triphenyl porphyrinatozinc(II) triflate (Dyad 2) In a modification of a literature procedure,[4] porphyrin **5** (142 mg, 0.102 mmol) was dissolved in a mixture of dry THF (13 cm^3), 3-picoline (0.63 cm^3) and AgOTf (130 mg, 0.504 mmol) and heated at reflux under argon for 1 hour. The solution was filtered and evaporated to dryness. The residue was then dried under vacuum overnight. The product was purified on sephadex LH20 eluting with THF (60 mg, 0.039 mmol, 54 %)

^{1}H NMR (500 MHz, CD$_2$Cl$_2$ + CD$_3$OD): δ 2.25 (3 H, s, pic CH$_3$); 2.7 (3 H, s, bpy CH$_3$); 4.25 (3 H, s, methoxy CH$_3$); 7.22 (1 H, dd, 5-pic); 7.55 (1 H, d, bpy 5'); 7.65 (1 H, 4-pic); 7.75 (10 H, m, *m-/p*-phenyl + 3-methoxyphenyl); 7.87 (1 H, d, 6-pic); 7.95 (1 H, dd, 5-methoxyphenyl); 8.06 (2 H, d, *m*-amidophenyl); 8.10 (1 H, s, bppy amide); 8.22 (8 H, m, *o*-phenyl); 8.28 (1 H, d, 6-methoxyphenyl); 8.37 (1 H, dd, bpy 5); 8.70 (1 H, s, bpy 3’); 8.89 (6 H, m, β-pyrrole); 8.96 (2 H, d, β-pyrrole); 8.98 (1 H, d, bpy 2’); 9.17 (1 H, d, bpy 3); 9.34 (1 H, d, bpy 6); 10.27 (1 H, s, porphyrin amide)

λ_{abs}(CH_2Cl_2)/nm 303 (ε/dm^3 mol^{-1} cm^{-1} 4510), 420 (29700), 504 (458), 548 (1740) and 581 (526)

ESI-MS: *m/z* = 1398.2754 (M^+, 30%), (M+ $C_{73}H_{51}N_9O_6ZnRe$ requires 1398.2778, difference 2.4 mDa) (**Figure S 1**).

IR (ν/cm^{-1}) (THF) 2032 (s), 1923 (s, broad) (ν(CO)).

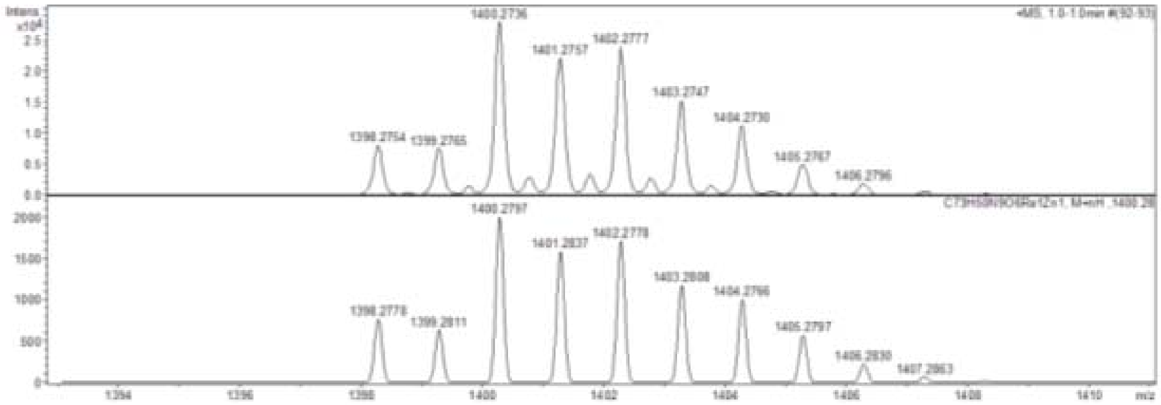


Figure S 1 Mass spectrum of **Dyad 2** observed (above) and calculated (below)

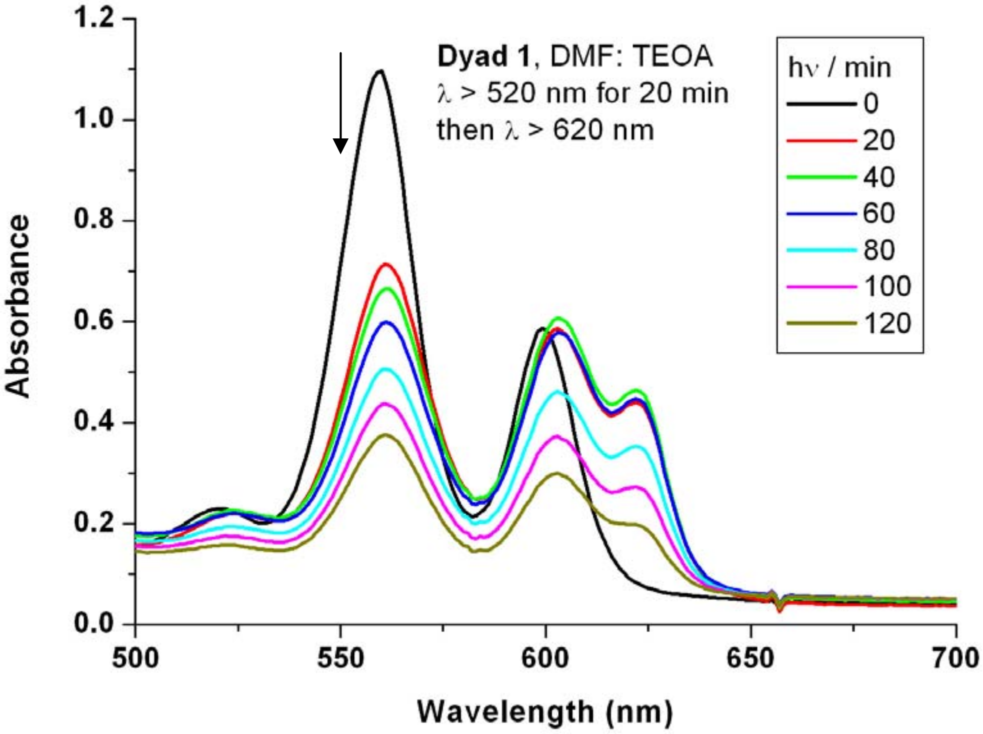


Figure S 2 Visible absorption spectrum of **Dyad 1** during CO_2 photoreduction, λ_{ex} > 520 nm for 20 min, then λ_{ex} > 610 nm.

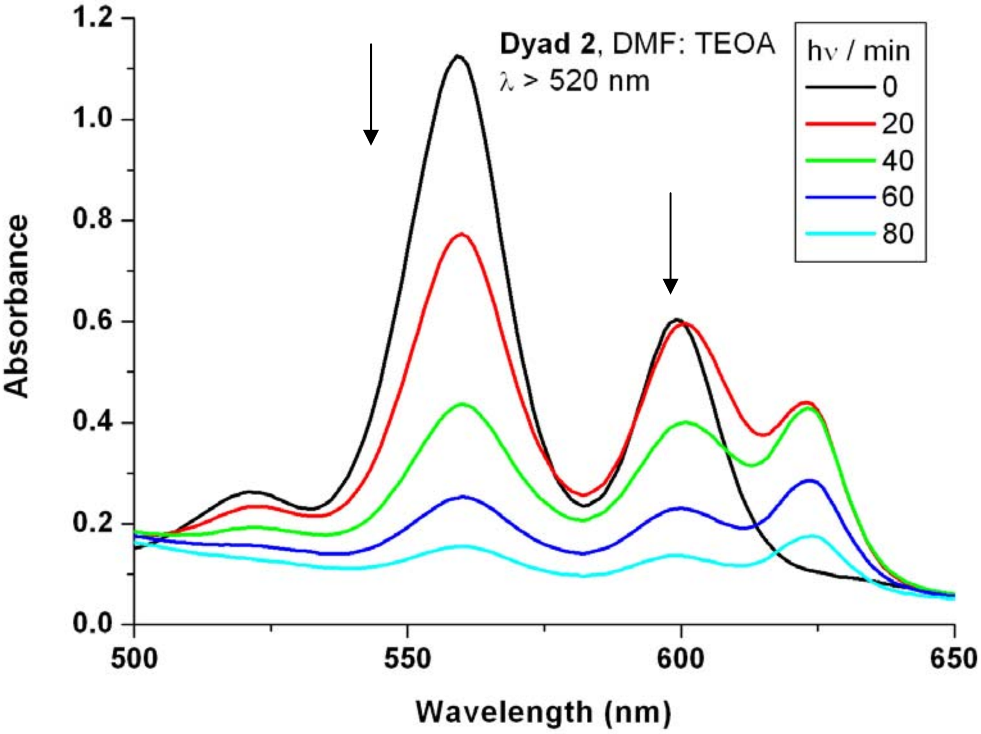


Figure S 3 Visible absorption spectrum of **Dyad 2** during CO_2 photoreduction λ_{ex} > 520 nm

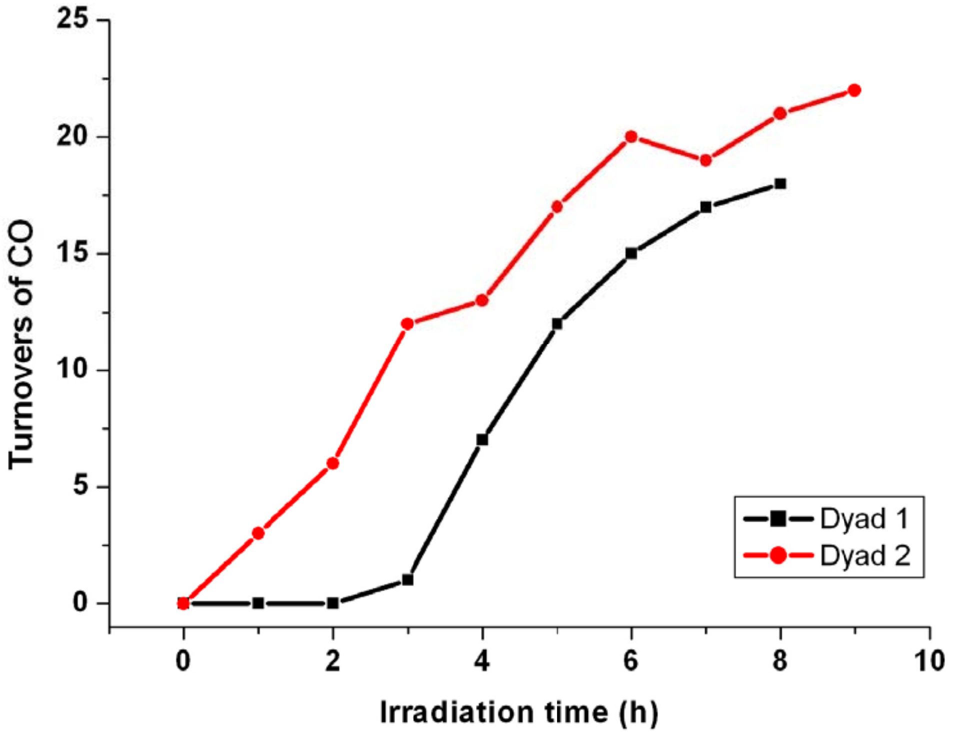


Figure S 4 CO production of **Dyad 1** and **Dyad 2** under irradiation (λ > 520 nm) with lower intensity projector lamp

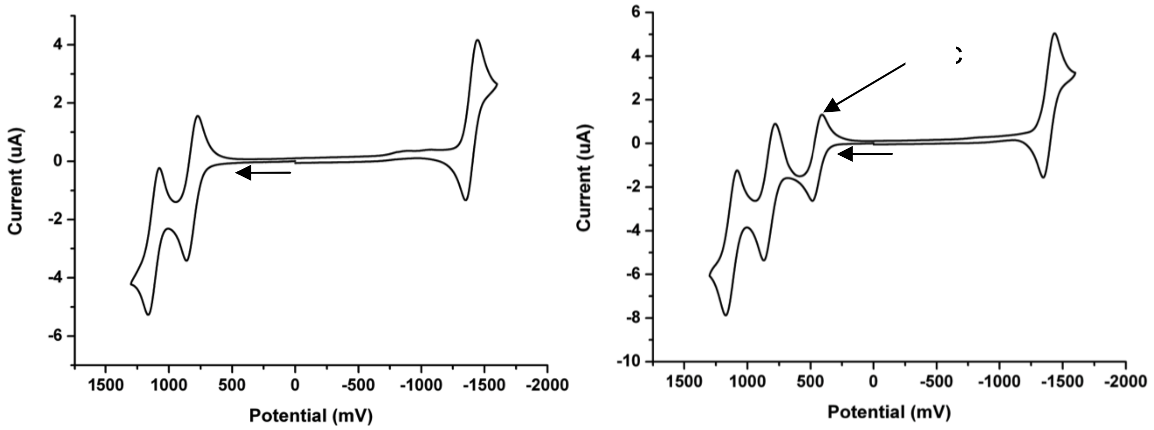


Figure S 5 Cyclic voltammogram of ZnTPP with (right) and without (left) ferrocene (Fc) internal standard. All scans start at 0 V.

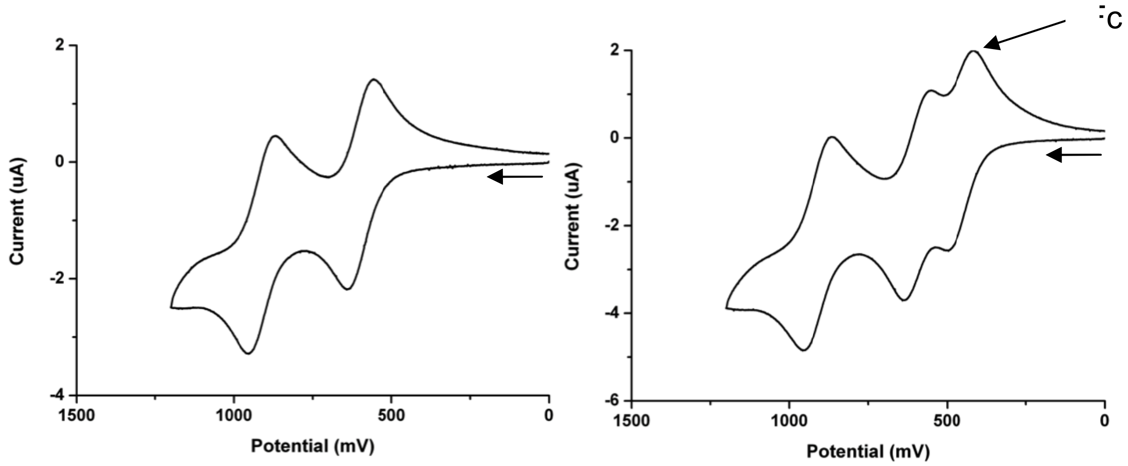


Figure S 6 Cyclic voltammogram of ZnTPC with (right) and without (left) ferrocene internal standard

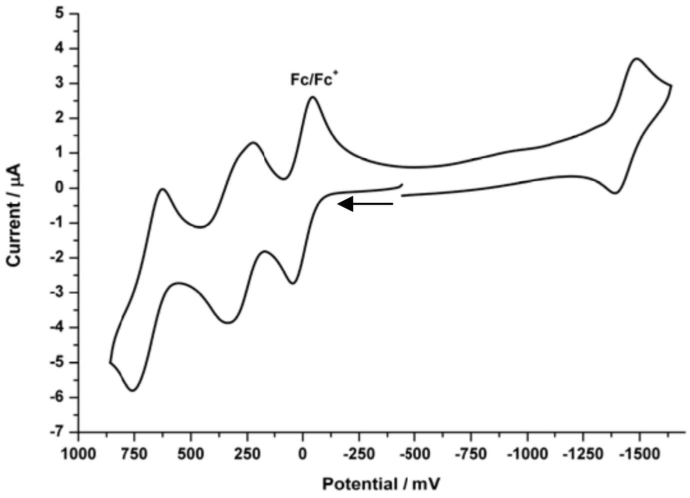


Figure S 7 Cyclic voltammogram of **Dyad 1** with ferrocene

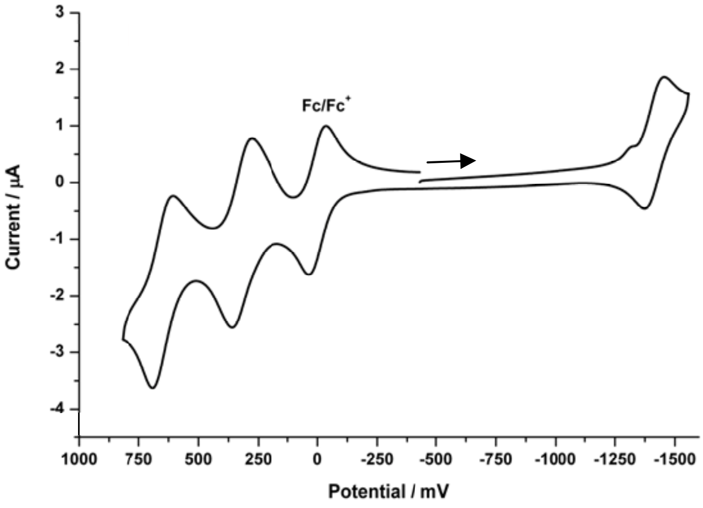


Figure S 8 Cyclic voltammogram of **Dyad 2** with ferrocene

Table S 1 Redox potentials and highest energy emission maxima (corrected) of sensitisers and catalyst with the estimated change in free energy of electron transfer. Measured in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$, reference electrode (Ag/AgCl, 3 M), vs $E_{1/2}(Fc^+/Fc)$

Complexes	$E_{1/2}^{ox}$/V	$E_{1/2}^{red}$/V	E_{00}/eV	ΔG_{ox}*/eV[a]
ZnTPP + $[Re(CO)_3(Pic)Bpy][PF_6]$	+0.38	-1.57[7]	2.06	-0.11
ZnTPC + $[Re(CO)_3(Pic)Bpy][PF_6]$	+0.14	-1.57[7]	1.97	-0.26
Dyad 1	+0.28	-1.44	2.07	-0.35
Dyad 2	+0.32	-1.42	2.06	-0.32

[a] *Calculated via* $\Delta G_{ox}* = E_{ox} - E_{red} - E_{00}$

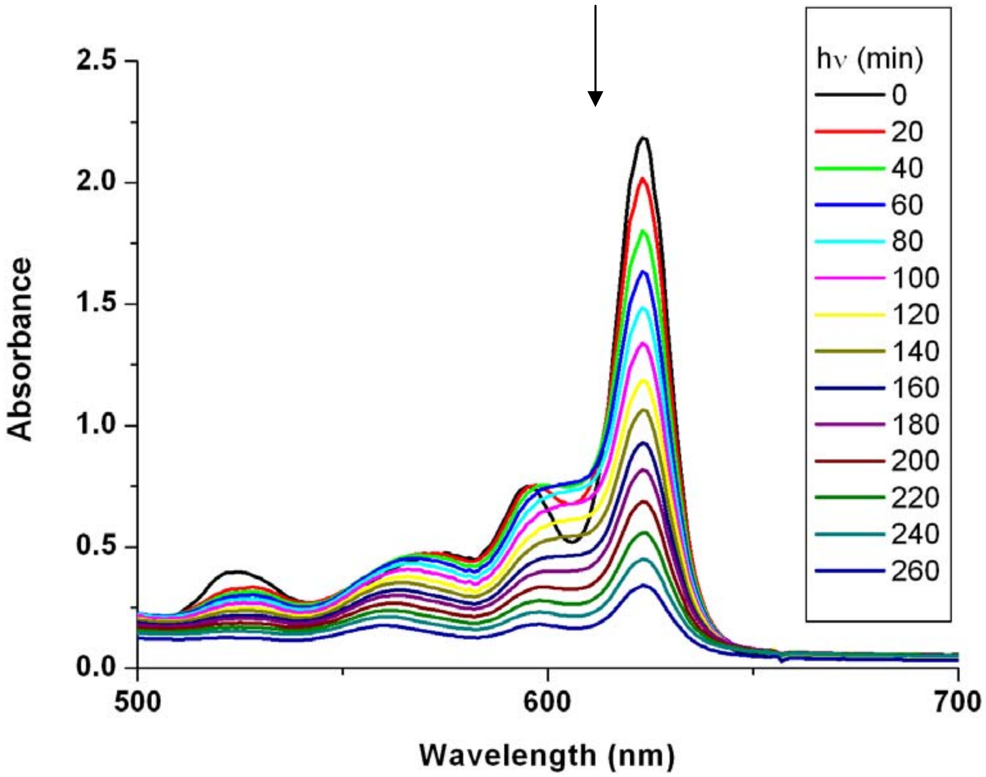


Figure S 9 Visible absorption spectrum of ZnTPC + $[Re(CO)_3(Pic)Bpy][PF_6]$ during CO_2 photoreduction (λ > 520 nm)

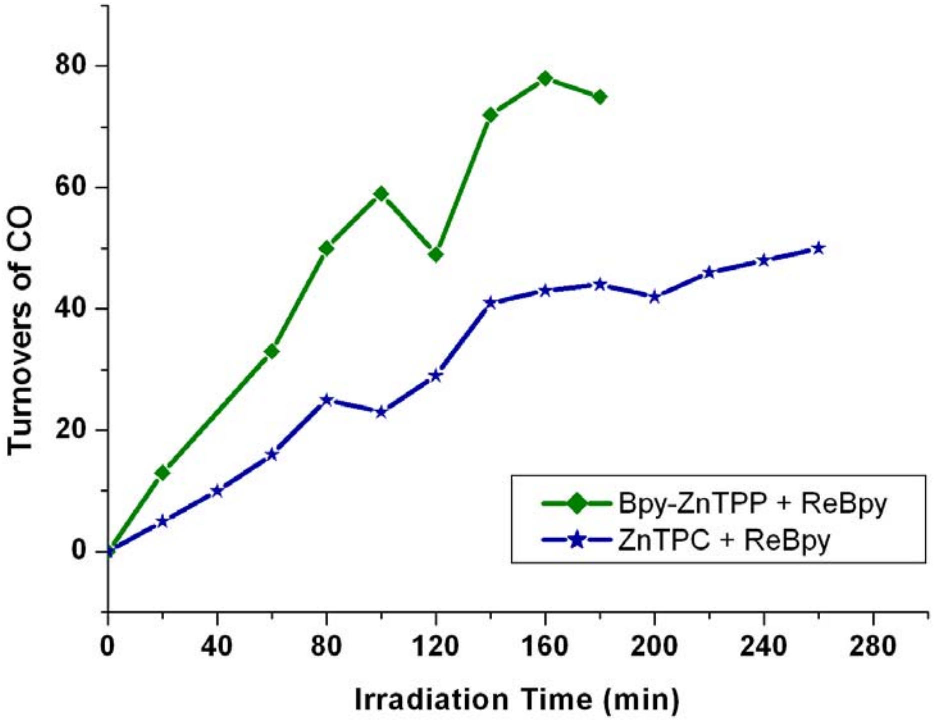


Figure S 10 Longer duration photolysis with ZnTPC + ReBpy and Bpy-ZnTPP + ReBpy.

Mass Spectrometric Data

ESI-MS of Dyad 1 reaction mixture (0.25 mM, DMF/TEOA 5/1, λ > 520 nm)

Irradiation time: 0 min

Observed 1251.0 ($C_{65}H_{44}N_8O_4ZnRe$ requires 1251.2) M^+

Irradiation time: 5 min

Observed 1158.0 ($C_{59}H_{37}N_7O_4ZnRe$ requires 1158.2) $[M – Picoline]^+$

Observed 1251.0 ($C_{65}H_{44}N_8O_4ZnRe$ requires 1251.2) M^+

Observed 1307.0 ($C_{65}H_{52}N_8O_7ZnRe$ requires 1307.3) $[M – Picoline + TEOA]^+$

Irradiation time: 10 and 15 min

Observed 1158.0 ($C_{59}H_{37}N_7O_4ZnRe$ requires 1158.2) $[M – Picoline]^+$

Observed 1251.0 ($C_{65}H_{44}N_8O_4ZnRe$ requires 1251.2) M^+

Observed 1307.0 ($C_{65}H_{52}N_8O_7ZnRe$ requires 1307.3) $[M – Picoline + TEOA]^+$

ESI-MS of Dyad 2 reaction mixture (0.25 mM, DMF/TEOA 5/1, λ > 520 nm)

Irradiation time: 0 min

Observed 1400.0 ($C_{73}H_{51}N_9O_6ZnRe$ requires 1400.3) M^+

Irradiation time: 5 and 10 min

Observed 1307.0 ($C_{67}H_{44}N_8O_6ZnRe$ requires 1307.2) [M – Picoline]$^+$

Observed 1400.0 ($C_{73}H_{51}N_9O_6ZnRe$ requires 1400.3) M$^+$

Observed 1456.0 ($C_{73}H_{59}N_9O_9ZnRe$ requires 1456.3) [M – Picoline + TEOA]$^+$

ESI-MS of 2 components [Re(CO)$_3$(Pic)Bpy][PF$_6$] + Bpy-ZnTPP reaction mixture (0.25 mM, DMF/TEOA 5/1, λ > 520 nm)

Irradiation time: 0 min

Observed 519.9 ($C_{19}H_{15}N_3O_3Re$ requires 520.1) [Re(CO)$_3$(Pic)Bpy]$^+$

Irradiation time: 5 and 15 min

Observed 519.9 ($C_{19}H_{15}N_3O_3Re$ requires 520.1) [Re(CO)$_3$(Pic)Bpy]$^+$

Observed 575.9 ($C_{19}H_{23}N_3O_6Re$ requires 576.1) [Re(CO)$_3$(TEOA)Bpy]$^+$

Observed 888.0 ($C_{56}H_{37}N_7OZn$ requires 888.2) [Bpy-ZnTPP +H]$^+$

Detection of formic acid

Solution phase IR spectroscopy was used to detect formic acid. In order to observe a signal at 1712 cm^{-1} the DMF/TEOA 5/1 solution was diluted to 80% CH_2Cl_2 by volume. Using an authentic sample mimicking 10 turnover numbers of formic acid, a signal was observed at 1712.52 cm^{-1}.

A catalyst mixture of ZnTPP + ReBpy in the standard conditions was irradiated for 2 hours. It was then diluted to 80% CH_2Cl_2 and a solution IR spectrum was taken. A signal at 1712.52 cm^{-1} was not observed.

1. D. G. McCafferty, B. M. Bishop, C. G. Wall, S. G. Hughes, S. L. Mecklenberg, T. J. Meyer and B. W. Erickson, *Tetrahedron*, 1995, **51**, 1093-1106.
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