Ultrafast Charge Separation in a Photo-Reactive Rhenium Appended Porphyrin Assembly Monitored by Picosecond Transient Infrared Spectroscopy

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Synthesis of 5-[4-(4-methyl-2,2'-bipyridine-4'-carboxyamidyl)phenyl]-10,15,20-triphenylporphyrinato zinc(II): Bpy-ZnTPP.

Table S1. ^{1}H NMR Chemical shifts and assignments for **Bpy-MgTPP** and **Bpy-ZnTPP** in pyridine-d_5.

Figure S1: ^{1}H NMR spectrum (400 MHz) of **[Re(CO)$_3$(Pic)Bpy-ZnTPP][OTf]** in CD_2Cl_2.

Figure S2. ^{1}H COSY NMR spectrum of **[Re(CO)$_3$(Pic)Bpy-ZnTPP][OTf].**

Figure S3 ^{1}H NMR spectrum (500 MHz) of **[Re(CO)$_3$(Pic)Bpy-MgTPP][OTf]** in CD_2Cl_2

Figure S4 Electronic absorption spectra of **Bpy-MgTPP** and **[Re(CO)$_3$(Pic)Bpy-MgTPP][OTf]** in THF.

Figure S5 UV/vis spectroelectrochemical oxidation of **Bpy-ZnTPP** in THF with electrolyte [NBu$_4$][PF$_6$]

Synthesis of 5-[4-(4-methyl-2,2'-bipyridine-4'-carboxyamidyl)phenyl]-10,15,20-triphenylporphyrinato zinc(II): Bpy-ZnTPP. A modification of the method developed by Aspley *et al*.[75,77] was employed for **Bpy-ZnTPP**. **Bpy-H_2TPP** (0.17, 0.2 mmol) and zinc acetate dihydrate (0.2 g, 0.9 mmol) were heated at reflux in a mixture of trichloromethane (25 cm^3) and methanol (5 cm^3) for 1 h. The reaction mixture was cooled, diluted with dichloromethane (100 cm^3), washed with EDTA solution (2 g in 200 cm^3 10% sodium carbonate solution), water (3 × 200 cm^3), dried ($MgSO_4$), and the solvent removed. The residue was purified by column chromatography (Si-60, dichloromethane with 2% v/v methanol) to yield **Bpy-ZnTPP** (0.17 g, 0.19 mmol, 96%). The spectroscopic data were in agreement with those reported by Aspley *et. al*.[77]

^{1}H NMR (500 MHz, THF-d_8): δ 2.61 (3 H, s, Bpy CH_3); 7.35 (1 H, d, br, 3.8 Hz, Bpy); 7.86-7.89 (9 H, m, *m*-, *p*-phenyl); 8.10 (1H, dd, *J* 4.76 and 1.6 Hz, Bpy); 8.33-8.36 (6 H, m, 6 *o*-phenyl); 8.41 (2 H, d, 8.58 Hz, *m*-bridging phenyl); 8.59 (1 H, s, Bpy); 8.79 (1 H, d, 4.76 Hz, Bpy); 8.97 (4 H, s, β-pyrrolic a and b); 8.99 (3 H, m, 2 β-pyrrolic and 1 Bpy); 9.08 (2 H, d, *J* 4.45 Hz, β-pyrrolic d); 9.25 (1H, s, Bpy); 11.90 (1 H, s, br, CONH).

ESI-MS: *m/z* = 888 (100 % MH^+)

Table S2. ^{1}H NMR Chemical shifts and assignments for **Bpy-MgTPP** and **Bpy-ZnTPP** in pyridine-d_5.

Bpy-MgTPP	**Bpy-ZnTPP**[a]	Assignment
2.15, s	2.15, s	3 H, Bpy CH_3
7.02, d	7.01, d	1 H, Bpy
7.66, m	7.68, m	9 H *m*-, *p*–phenyl
8.14, d	8.14, d	1 H, Bpy
8.30, m	8.30, s	6 H, *o*–phenyl
8.35, d	8.36, d	2 H, bridging C_6H_4
8.43, s	8.43, s	1 H, Bpy
8.48, d	8.50, d	2 H, bridging C_6H_4
8.55, d	8.54, d	1 H, Bpy
8.87, d	8.86, d	1 H, Bpy
9.03, s	9.06, s	4 H, β–pyrrole a and b
9.06, d	9.09, d	2 H, β–pyrrole c
9.17, d	9.20, d	2 H, β–pyrrole c
9.48, s	9.48, s	1 H, Bpy
11.80, s, br	11.86, s	1 H, CONH

[a] Ref 77

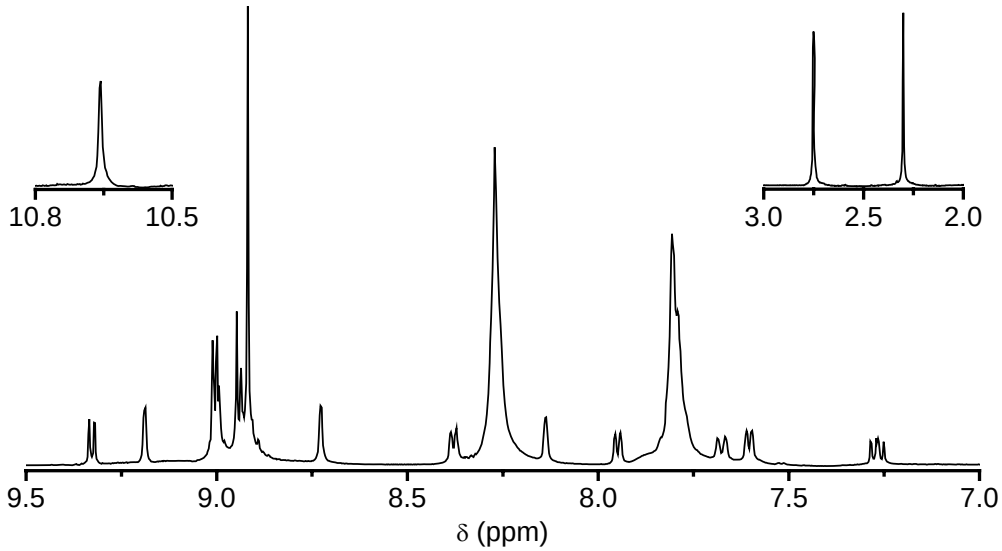

Figure S1: ^{1}H NMR spectrum (400 MHz) of **[Re(CO)$_3$(Pic)Bpy-ZnTPP][OTf]** in CD_2Cl_2.

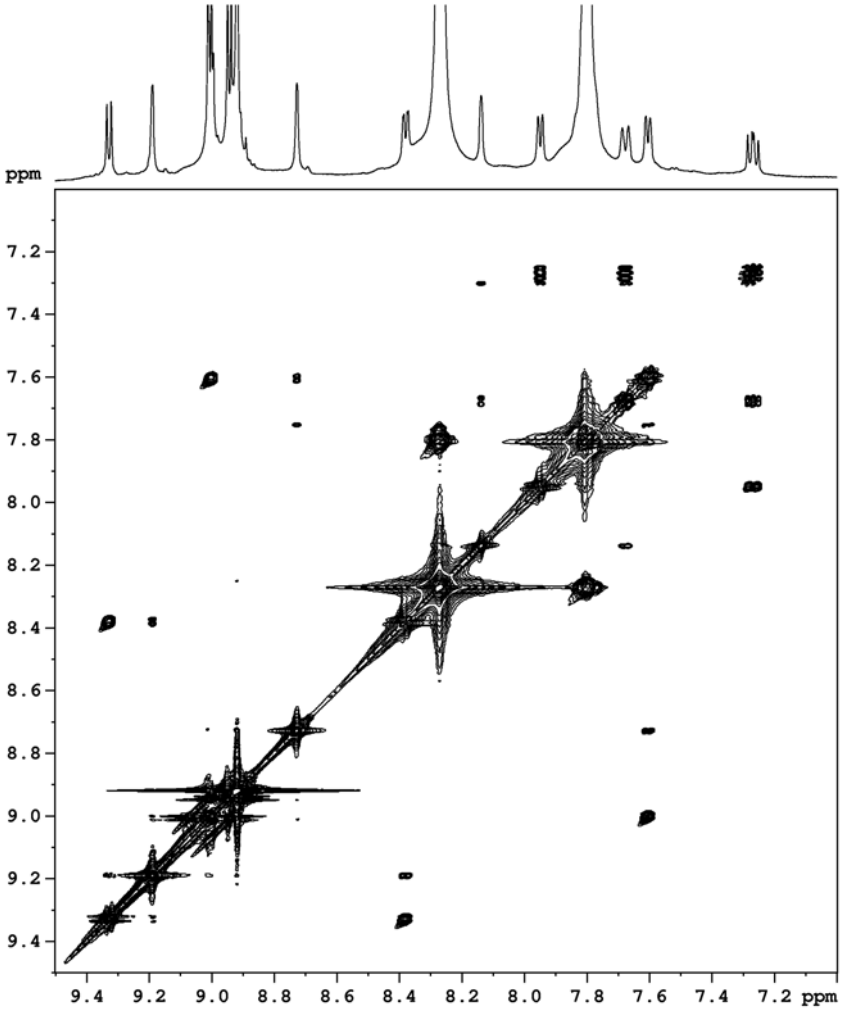

Figure S2. ^{1}H COSY NMR spectrum of **[Re(CO)$_3$(Pic)Bpy-ZnTPP][OTf].**

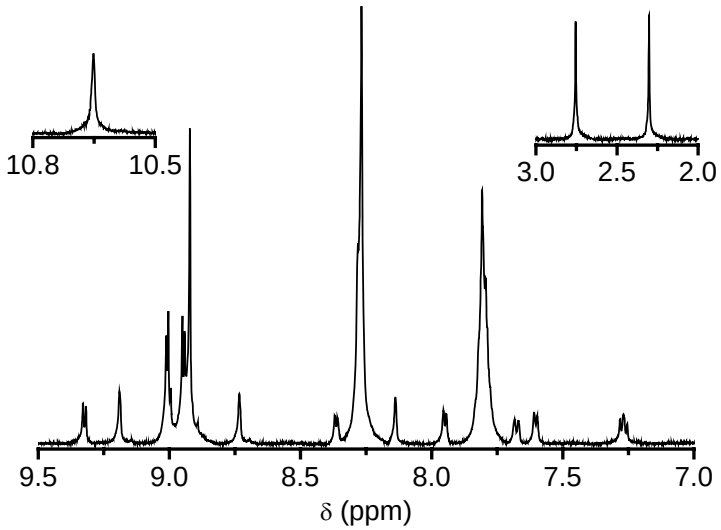

Figure S3 ^{1}H NMR spectrum (500 MHz) of **[Re(CO)$_3$(Pic)Bpy-MgTPP][OTf]** in CD_2Cl_2

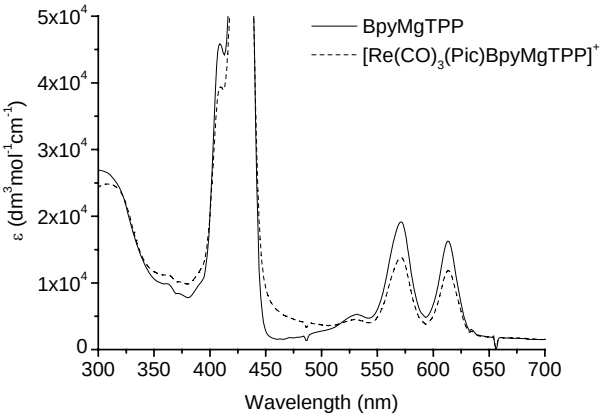

Figure S4 Electronic absorption spectra of **Bpy-MgTPP** and **[Re(CO)$_3$(Pic)Bpy-MgTPP][OTf]** in THF.

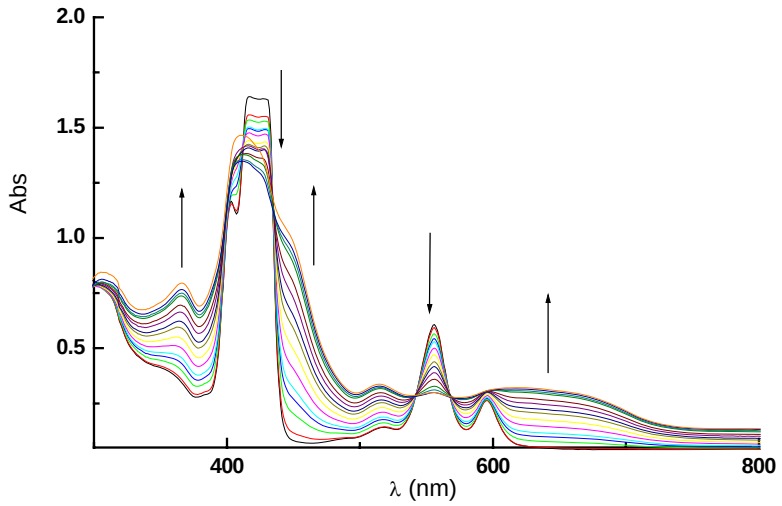

Figure S5 UV/vis spectroelectrochemical oxidation of **Bpy-ZnTPP** in THF with electrolyte $[NBu_4][PF_6]$