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Photo-induced ligand substitution at a remote site *via* electron transfer in a porphyrin-appended rhenium carbonyl supermolecule†

Anders Gabrielsson,[a] František Hartl,[b] John R. Lindsay Smith[a] and Robin N. Perutz*[a]
[a] *Department of Chemistry, University of York, York, UK YO10 5DD. E-mail: rnp1@york.ac.uk*
[b] *Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht, 166, NL-1018 WV Amsterdam, The Netherlands. E-mail: hartl@science.uva.nl*

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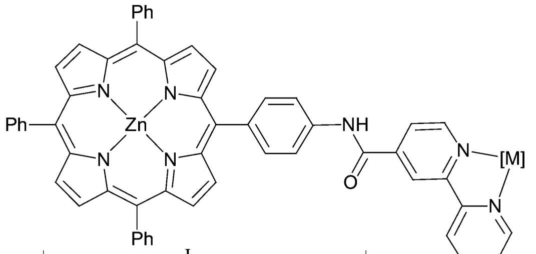
The photochemical and electrochemical properties of a Zn-porphyrin appended rhenium(I) tricarbonyl bipyridine 3-Me-pyridine complex have been investigated; visible-light sensitisation of electron transfer results in ligand substitution at a site remote from the chromophore.

Molecular dyads consisting of a photosensitiser and an electron acceptor have been used in conjunction with an external electron donor as mimics of photosynthesis.[1] Complexes of the type [Re^I(CO)$_3$(bpy)L]^n (n = 0, +1) have been studied both for reduction of carbon dioxide, and as components of supramolecular assemblies.[2–7] We show that a metalloporphyrin covalently linked to a [Re^I(CO)$_3$(bpy)L] unit sensitises the rhenium moiety towards photo-reduction. Low energy irradiation results in expulsion of a ligand at a site remote from the chromophore. Electrochemical studies are consistent with reaction *via* electron transfer.

Compound **1**$^+$OTf$^-$ was synthesised from compound **2** by removing the axial bromide ligand with AgOTf in the presence of 3-Me-pyridine in refluxing THF.† The synthesis of compound **2** has been described elsewhere.[2]



1$^+$ [M]= [*fac*-Re^I(CO)$_3$(3-Me-Py)]$^+$
2 [M]= [*fac*-Re^I(CO)$_3$Br]
3$^+$ [M]= [*fac*-Re^I(CO)$_3$(THF)]$^+$
4$^+$ [M]= [*fac*-Re^I(CO)$_3$(PrCN)]$^+$
5 [M]= No rhenium moiety

Complexes **1**$^+$ and **2** are stable towards photolysis in THF. Their UV-Vis spectra are completely dominated by the porphyrin absorption bands. The MLCT band of the Re(CO)$_3$(bpy) unit which is normally found at *ca.* 400 nm is masked by the porphyrin Soret band. Quenching of steady state fluorescence provides evidence of excited state interaction in **1**$^+$ and **2**.† On photolysis of complex **1**$^+$ with long-wavelength light (λ > 495 nm) in the presence of triethylamine, the IR spectrum reveals that a new metal carbonyl complex is formed. Comparison with [Re(CO)$_3$(bpy)(THF)]$^+$ shows that the axial ligand is displaced by the solvent to yield the THF complex **3**$^+$ (Fig. 1(a), Table 1).[8] When the photoreaction was repeated in the presence of excess bromide and triethylamine, complex **2** was formed quantitatively. While the IR spectra from these reactions show 18-electron products only, photolysis in the presence of a trace of free 3-Me-pyridine shows characteristic IR features of the radical **1**$^{\cdot}$ (Table 1). Photolysis of **1**$^+$ with Et$_3$N and excess 3-Me-pyridine in PrCN provides evidence for a rhenium bipyridine-based radical, either **1**$^{\cdot}$ or **4**$^{\cdot}$ by EPR (g = 2.003, peak-to-peak separation = 6.9 mT) and IR spectroscopy, as well as the cationic solvento complex **4**$^+$ (Table 1).[9,10]

The excitation in the visible region must occur on absorption by the porphyrin macrocycle that acts as a sensitiser towards visible light; product formation depends on electron transfer from triethylamine. In order to test this hypothesis, we

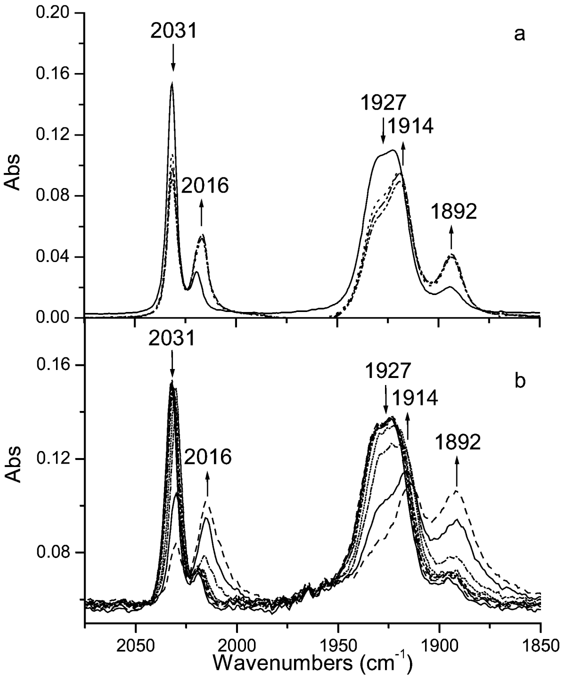


Fig. 1 (a) IR spectra recorded during the photolysis of **1**$^+$ (1.9 mM) with Et$_3$N (72 mM) in THF after 0, 5, 15, 25, 35 and 45 min (a trace of **2** is present at 2020 cm^{-1}). (b) IR spectroelectrochemistry of the reduction of **1**$^+$ (THF, [NBu$_4$][PF$_6$], OTTLE cell, 293 K).

Table 1 CO stretching frequencies of complexes under study

Complex	Solvent	ν(CO)/cm^{-1}
1$^+$	THF	2031, 1927br
1$^{\cdot}$	PrCN	2010, 1903, 1893
1$^{\cdot}$	THF	2011, 1907, 1893
2	THF	2020, 1920, 1897
2$^{\cdot -}$	THF	1998, 1888, 1868
3$^+$	THF	2016, 1914, 1892
4$^+$	PrCN	2038, ~1835
4$^{\cdot}$	PrCN	2010, 1903br, 1893br[a]
6$^+$	THF	2031, 1927br
6$^{\cdot}$	THF	2010, 1905, 1892

[a] T = 223 K.

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† Electronic supplementary information (ESI) available: energy balance, synthesis and characterisation of **1**$^+$OTf$^-$ and fluorescence spectra of **1**$^+$, **2** and **5**. See http://www.rsc.org/suppdata/cc/b2/b200127f/

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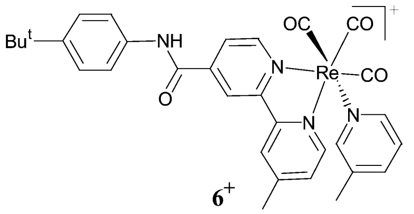
synthesised **6**$^+$ as an analogue without the porphyrin unit. Indeed, photolysis of complex **6**$^+$ in THF with visible light ($\lambda > 495$ nm) in the presence of triethylamine yields no products.



6$^+$

The electron-transfer mechanism was also tested by cyclic voltammetry together with UV-Vis and IR spectroelectrochemical studies. UV-Vis spectra show that the reversible oxidation of **1**$^+$ and **2** is based on the porphyrin macrocycle and occurs at the same potential as for **5** and Zn(TPP) (380 mV *vs*. Fc/Fc$^+$ in THF) (Fig. 2).

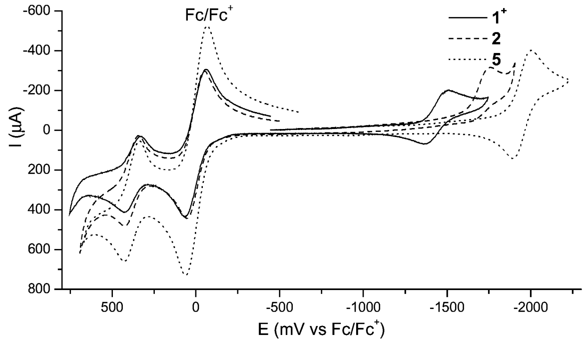


Fig. 2 Cyclic voltamograms of **1**$^+$, **2** and **5** in THF ([NBu$_4$][PF$_6$], 300 K, scan rate 100 mV s^{-1} and Fc/Fc$^+$ as internal standard).

IR spectroelectrochemistry indicates that the reduction occurs on the rhenium bipyridine site for both **1**$^+$ and **2** (compare spin distribution for [Re(CO)$_3$(bpy)L]^0).[9,10] The reduction waves for **1**$^+$ and **2** in Fig. 2 are notably different from simple models such as **6**$^+$, [Re(CO)$_3$(bpy)Br] and from **5**. For **1**$^+$ the reduction in THF is partly chemically reversible while for the model **6**$^+$ it is reversible. IR spectroelectrochemistry allows identification of the reduction products thanks to the extensive literature on [Re^I(CO)$_3$(bpy)L]^n complexes.[8,10–12] During reduction of **1**$^+$ in an OTTLE cell, three new IR bands grow in at 2016, 1914 and 1892 cm^{-1} (Fig 1(b)); since they are identical to those in the IR spectra of [Re(CO)$_3$(bpy)(THF)]$^+$ and the photoproduct (Fig. 1(a)), they are assigned to **3**$^+$.[8] The radical **1**$^\cdot$ is expected at lower frequencies and reduction at low temperature (223 K) in butyronitrile gives bands at 2010, 1903 and 1893 cm^{-1} consistent with a radical (Table 1).[10] Thus reduction of **1**$^+$ occurs at the rhenium bipyridine site whereas reduction of **5** necessarily occurs at the porphyrin. No ligand substitution occurs without reduction; hence the radical **1**$^\cdot$ must be the species that undergoes substitution. Electrode potentials listed in Table 2 reveal that, at the potential where **1**$^\cdot$ is formed, [Re(CO)$_3$(bpy)(THF)]$^\cdot$ is reoxidised to the corresponding cation. The latter should be a good model for **3**$^\cdot$/**3**$^+$. Substitution should therefore occur catalytically [eqns. (1), (2) and (3)].

$$\text{Initiation: } \mathbf{1}^+ \xrightarrow{e^- \text{ or } h\nu,\ \mathrm{Et_3N}} \mathbf{1}^\bullet \quad (1)$$

$$\text{Substitution: } \mathbf{1}^\bullet \xrightarrow{\mathrm{THF}} \mathbf{3}^\bullet + \text{3-Me-Py} \quad (2)$$

$$\text{Reoxidation: } \mathbf{3}^\bullet + \mathbf{1}^+ \longrightarrow \mathbf{1}^\bullet + \mathbf{3}^+ \text{ or } \mathbf{3}^\bullet \longrightarrow \mathbf{3}^+ + e^- \quad (3)$$

The labile nature of the axial ligand upon reduction explains why the first reduction in the cyclic voltammogram is partly chemically irreversible. At room temperature in THF, the reduced species **1**$^\cdot$ readily undergoes ligand substitution with other nucleophiles. On reduction of **1**$^+$ in the presence of bromide ions, the 3-Me-pyridine is displaced by bromide and the radical anion **2**$^{\cdot-}$ formed is reoxidised (Tables 1 and 2) to compound **2** quantitatively.

Table 2 Reduction potentials

Complex	Solvent	$E_{1/2}{}^{(\mathrm{I})}$/V (*vs*. Fc/Fc$^+$)	Ref
1$^+$	THF	−1.44[a]	[b]
2	THF	−1.75[c]	[b]
6$^+$	THF	−1.45	[b]
[Re(CO)$_3$(dmb)(3-Me-Py)]$^+$[d]	THF	−1.65	[b]
[Re(CO)$_3$(bpy)(3-Me-Py)]$^+$	MeCN	−1.47[e]	11
[Re(CO)$_3$(bpy)(THF)]$^+$	THF	−1.69	8
[Re(CO)$_3$(bpy)Br]	THF	−1.83	[b] 8

[a] Partly chemically irreversible. [b] This work. [c] Totally irreversible. [d] dmb = 4,4′-dimethyl-2,2′-bipyridine. [e] Conversion using Fc/Fc$^+$ = 380 mV *vs*. SCE in MeCN ([Et$_4$N][ClO$_4$] electrolyte).

The rhenium-free analogue **5** is effectively photo-reduced by triethylamine to the porphyrin radical anion **5**$^{\cdot-}$, confirming that Et$_3$N can transfer an electron to the excited state of this porphyrin. The driving force for intramolecular electron transfer is −0.25 eV for **1**$^+$ and *ca*. 0.06 eV for **2**.†

In spite of the similarities between **1**$^+$ and **2** noted above, there are great differences in their photochemical and electrochemical properties. Remarkably, compound **2** does not undergo photochemical reduction under the same conditions. Complex **2** is reduced at more negative potential than **1**$^+$ (Table 2) and the cyclic voltammogram shows an irreversible reduction wave in THF (Fig. 2). Nevertheless, IR spectroelectrochemistry of **2** demonstrates that the axial ligand is displaced by THF during the reduction and subsequent reoxidation giving the cationic THF complex **3**$^+$. The differences between **1**$^+$ and **2** are not yet fully understood.

In conclusion, the introduction of the porphyrin into the design of **1**$^+$ induces substitution at a remote site as a consequence of photo-induced electron transfer. This is one of the principles of supramolecular photochemistry described by Balzani and Scandola but has not previously been observed in a porphyrin metal carbonyl supermolecule.[1]

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