COMMUNICATION

ChemComm
www.rsc.org/chemcomm

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*

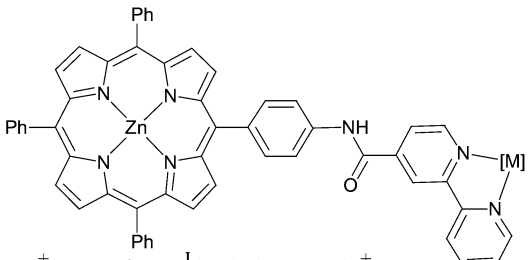
[b] *Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht, 166, NL-1018 WV Amsterdam, The Netherlands. E-mail: hartl@science.uva.nl*

Received (in Cambridge, UK) 3rd January 2002, Accepted 6th March 2002
First published as an Advance Article on the web 2nd April 2002

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 $\mathbf{1}^+OTf^-$ 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*-$Re^{I}(CO)_3Br$]

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 ($\lambda > 495$ 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_3N 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

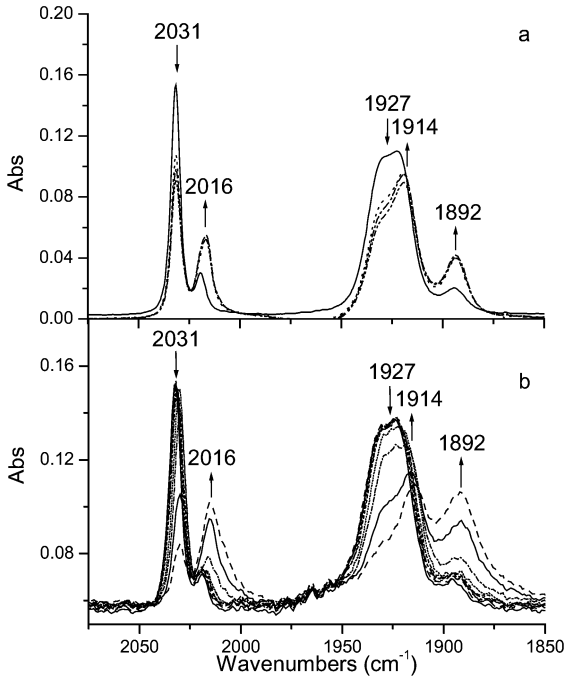


Fig. 1 (a) IR spectra recorded during the photolysis of **1**$^+$ (1.9 mM) with Et_3N (72 mM) in THF after 0, 5, 15, 25, 35 and 45 min (a trace of **2** is present at 2020 cm^{-1}). (b) IR spectroelectrochemistry of the reduction of **1**$^+$ (THF, $[NBu_4][PF_6]$, OTTLE cell, 293 K).

Table 1 CO stretching frequencies of complexes under study

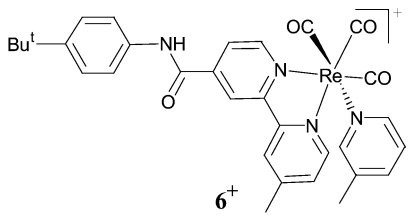
Complex	Solvent	ν(CO)/cm^{-1}
1$^+$	THF	2031, 1927br
1$^{\cdot}$	PrCN	2010, 1903, 1893
1$^{\cdot}$	THF	2011, 1907, 1893
2	THF	2020, 1920, 1897
2$^{\cdot-}$	THF	1998, 1888, 1868
3$^+$	THF	2016, 1914, 1892
4$^+$	PrCN	2038, ~1835
4$^{\cdot}$	PrCN	2010, 1903br, 1893br[a]
6$^+$	THF	2031, 1927br
6$^{\cdot}$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

[a] T = 223 K.

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

DOI: 10.1039/b200127f

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



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 $\mathbf{1}^+$ 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).

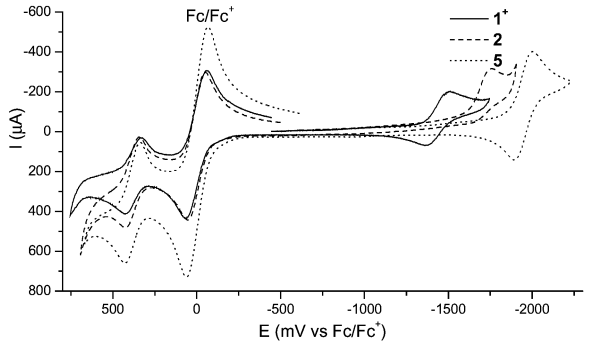


Fig. 2 Cyclic voltamograms of $\mathbf{1}^+$, **2** and **5** in THF ($[NBu_4][PF_6]$, 300 K, scan rate 100 mV s^{-1} and Fc/Fc$^+$ as internal standard).

IR spectroelectrochemistry indicates that the reduction occurs on the rhenium bipyridine site for both $\mathbf{1}^+$ and **2** (compare spin distribution for $[Re(CO)_3(bpy)L]^0$).[9,10] The reduction waves for $\mathbf{1}^+$ and **2** in Fig. 2 are notably different from simple models such as $\mathbf{6}^+$, $[Re(CO)_3(bpy)Br]$ and from **5**. For $\mathbf{1}^+$ the reduction in THF is partly chemically reversible while for the model $\mathbf{6}^+$ 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 $\mathbf{1}^+$ 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 $\mathbf{3}^+$.[8] The radical $\mathbf{1}^\cdot$ 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 $\mathbf{1}^+$ occurs at the rhenium bipyridine site whereas reduction of **5** necessarily occurs at the porphyrin. No ligand substitution occurs without reduction; hence the radical $\mathbf{1}^\cdot$ must be the species that undergoes substitution. Electrode potentials listed in Table 2 reveal that, at the potential where $\mathbf{1}^\cdot$ is formed, $[Re(CO)_3(bpy)(THF)]^\cdot$ is reoxidised to the corresponding cation. The latter should be a good model for $\mathbf{3}^\cdot/\mathbf{3}^+$. Substitution should therefore occur catalytically [eqns. (1), (2) and (3)].

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

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

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

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 $\mathbf{1}^\cdot$ readily undergoes ligand substitution with other nucleophiles. On reduction of $\mathbf{1}^+$ in the presence of bromide ions, the 3-Me-pyridine is displaced by bromide and the radical anion $\mathbf{2}^{\cdot-}$ formed is reoxidised (Tables 1 and 2) to compound **2** quantitatively.

Table 2 Reduction potentials

Complex	Solvent	$E_{1/2}^{(1)}$/V (*vs*. Fc/Fc$^+$)	Ref
$\mathbf{1}^+$	THF	−1.44[a]	[b]
2	THF	−1.75[c]	[b]
$\mathbf{6}^+$	THF	−1.45	[b]
$[Re(CO)_3(dmb)(3\text{-Me-Py})]^+$[d]	THF	−1.65	[b]
$[Re(CO)_3(bpy)(3\text{-Me-Py})]^+$	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 ($[Et_4N][ClO_4]$ electrolyte).

The rhenium-free analogue **5** is effectively photo-reduced by triethylamine to the porphyrin radical anion $\mathbf{5}^{\cdot-}$, confirming that Et_3N can transfer an electron to the excited state of this porphyrin. The driving force for intramolecular electron transfer is −0.25 eV for $\mathbf{1}^+$ and *ca*. 0.06 eV for **2**.†

In spite of the similarities between $\mathbf{1}^+$ 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 $\mathbf{1}^+$ (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 $\mathbf{3}^+$. The differences between $\mathbf{1}^+$ and **2** are not yet fully understood.

In conclusion, the introduction of the porphyrin into the design of $\mathbf{1}^+$ 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]

We thank Mr T. Mahabiersing and Dr A. Whitwood for help with the experiments and COST Action D14, project D14/0001/19 for funding.

Notes and references

1 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.
2 C. J. Aspley, J. R. Lindsay Smith and R. N. Perutz, *J. Chem. Soc., Dalton Trans*., 1999, 2269.
3 R. V. Slone and J. T. Hupp, *Inorg. Chem*., 1997, **36**, 5422.
4 R. V. Slone, K. D. Benkstien, S. Belanger, J. T Hupp, I. A. Guzei and A. L. Rheingold, *Coord. Chem. Rev*., 1998, **171**, 221.
5 J. L. Allwood, A. K. Burrell, D. L. Officer, S. M. Scott, K. Y. Wild and K. C. Gordon, *Chem. Commun*., 2000, 747.
6 V. W. W. Yam, *Chem. Commun*., 2001, 789.
7 S. S. Sun, E. Robson, N. Dunwoody, A. S. Silva, I. M. Brinn and A. J. Lees, *Chem. Commun*., 2000, 201.
8 G. J. Stor, F. Hartl, J. W. M. van Outersterp and D. J. Stufkens, *Organometallics*, 1995, **14**, 1115.
9 W. Kaim and S. Kohlmann, *Inorg. Chem*., 1990, **29**, 2909.
10 J. W. M. van Outersterp, F. Hartl and D. J. Stufkens, *Organometallics*, 1995, **14**, 3303.
11 L. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. DeGraff, *Inorg. Chem*., 1990, **29**, 4335.
12 F. P. A. Johnson, M. W. George, F. Hartl and J. J. Turner, *Organometallics*, 1996, **15**, 3374.