Remote site photosubstitution in metalloporphyrin–rhenium tricarbonylbipyridine assemblies: photo-reactions of molecules with very short lived excited states[†]

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The synthesis is reported of a series of metalloporphyrins (and the corresponding free-base porphyrin), mono-*meso*-substituted with a bipyridyl group *via* an amide link at the 4-position of one phenyl group: $[Re(CO)_3(Pic)Bpy-MTPP][OTf]$, where M = Mg, Zn, Pd or 2H, Pic = 3-picoline, Bpy = 2,2'-bipyridine, TPP = tetraphenylporphyrin. The photochemical reactions of the assemblies with the sacrificial electron donor triethylamine have been investigated by IR spectroscopy and compared to the behaviour of analogues of the type **Bpy-MTPP** without rhenium. Selective long-wavelength irradiation of the metalloporphyrin unit in the presence of excess picoline leads to reduction at the rhenium bipyridine centre. In the absence of 3-picoline, the latter is not reduced, but substituted by added halide or by the THF solvent. Mechanistic analysis highlights the differences between the zinc and magnesium chelate on the one hand and the palladium porphyrin on the other. The free-base assembly, **[Re(CO)_3(Pic)Bpy-H_2TPP)[OTf]** is unreactive. The zinc and magnesium porphyrin assemblies initially coordinate Et₃N before undergoing photo-induced inner-sphere electron transfer from the triethylamine to form a charge-shifted excited state of the assembly. In contrast, the palladium-based dyad reacts *via* outer-sphere reductive quenching of a porphyrin-based excited state. The substitution products are postulated to form by a mechanism involving an electron-transfer chain.

Introduction

One of the main challenges facing research into photo-induced electron transfer is to devise systems that can utilise the energy stored in the charge-separated state to initiate chemical reactions for artificial photosynthesis.¹⁻⁸ A common strategy is to produce supramolecular assemblies capable of forming long-lived charge-separated states. Multiple electron-transfer steps down an energy gradient in these multi-component systems may yield spatial charge separation and states with lifetimes sufficient for potential utilisation.

We have recently investigated various combinations of (metallo)porphyrins peripherally anchored to transition metal carbonyls.⁹⁻¹² In a previous paper,¹² we addressed the rate of photo-induced charge separation and the lifetime of the charge-separated state in assemblies with a transition metal centre linked to a metal-loporphyrin [**Re(CO)**₃(**Pic)Bpy-MTPP**[**IOTf**] (Scheme 1; M = Zn, Mg; Pic = 3-picoline; Bpy = 2,2'-bipyridine; TPP = tetraphenyl-porphyrin). A related triad has been synthesised incorporating both rhenium and ruthenium bipyridine units appended to a zinc porphyrin.¹³ Our own studies demonstrated ultra-fast charge separation and a charge-separated state with a lifetime of tens of

picoseconds in this type of assembly. Conventional expectations would exclude this system from productive reaction because of its short excited-state lifetime, yet we have already shown that one of these assemblies reacts photochemically at a site remote from the light absorbing unit in the presence of Et₃N as a sacrificial donor.^{11,12} Triethylamine is capable of coordinating to the metal atom of some metalloporphyrins so transforming the reaction from an intermolecular to an intramolecular electron transfer. The implication is that short-lived charge-separated states may react usefully, if they are coordinated to a sacrificial electron donor such as triethylamine.

Rhenium complexes of the type $[\text{Re}^{(1)}(\text{CO})_3 \text{L}(\text{bpy})]^{+/0}$ (where L is an anionic or neutral ligand and bpy) have been used extensively for photochemical redox reactions.^{14–22} The long-lived ³MLCT excited state readily accepts electrons from sacrificial electron donors (typically a tertiary amine) forming the reduced radical complex with the electron centred on the bipyridine ligand. When the axial ligand is triphenylphosphine, the photochemical reduction with triethanolamine (TEOA) leads to substitution of the phosphine ligand by a nucleophile (DMF or TEOA). The radical complex that is formed initially is a stronger reductant than the parent phosphine complex and capable of reducing another phosphine complex; consequently the ligand substitution becomes catalytic (Scheme 2).¹⁸

Rhenium polypyridyl complexes $[\text{Re}(\text{CO})_3 L(\text{N}-\text{N})]^{+/0}$ (N–N = chelating nitrogen ligand) have found use in the electrochemical or photochemical reduction of carbon dioxide to carbon monoxide, formate or oxalate.^{15,18,20,21,23-25} IR spectroelectrochemistry and time-resolved IR spectroscopy showed that the reaction proceeds *via* the reduced complex $[\text{Re}(\text{CO})_3 L(\text{bpy})]^{-0/-}$, the axial ligand L

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[†] Electronic supplementary information (ESI) available: Fig. S1: UV/vis spectra observed on photolysis of **Bpy-ZnTPP** and **[Re(CO)₃(Pic)Bpy-ZnTPP][OTf]**. Fig. S2: IR spectra observed on photolysis of **[Re(CO)₃(Pic)Bpy-ZnTPP][OTf]** in THF + Et₃N. Fig. S3: EPR spectrum after photolysis of **[Re(CO)₃(Pic)BpyZnTPP][OTf]** in THF with 5% Et₃N and 3-picoline. For ESI see DOI: 10.1039/b806267f



Re(CO)₃XBpy-MTPP X = CI, Br



[Re(CO)₃(Pic)Bpy-MTPP][OTf]

M = Mg, Zn, Pd or 2H

Scheme 1

$[\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{bpy})]^* \xrightarrow{\text{hv, triethanolamine}} [\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{bpy})]^{\bullet}$	Initiation
$[Re(CO)_3(PPh_3)(bpy)]^{\bullet} + L \longrightarrow [Re(CO)_3(L)(bpy)]^{\bullet} + PPh_3$	Radical substitution
$[Re(CO)_3(L)(bpy)]^{\bullet} + [Re(CO)_3(PPh_3)(bpy)]^{+}$	Cabolitation
→ [Re(CO) ₃ (L)(bpy)] ⁺ + [Re(CO) ₃ (PPh ₃)(bpy)] [•]	Propagation

L = DMF or triethanolamine

Scheme 2 Catalytic substitution *via* photo-induced electron transfer (after reference 18).

is labilised upon reduction and is usually substituted by a solvent molecule (in coordinating solvents).^{26,27} This was also confirmed through EPR spectroscopy.²⁸⁻³¹ Addition of carbon dioxide and a proton forms a formate complex, or a formate bridged dimer.³² Other active catalysts that have been suggested include a hydride complex and a metal–metal bonded dimer.³³ It has been found that replacement of the axial halide with a phosphine, phosphite or acetonitrile ligands also gives an active catalyst, and improvements have been made through analysis of the reaction mechanism.^{18,21,34} Recently, a Ru–Re heterometallic complex has been demonstrated to be active for CO₂ reduction with visible irradiation with high quantum yield.³⁵

Porphyrins form another class of chromophores whose photochemistry have been extensively studied in the presence of sacrificial electron donors such as amines, NADH and ascorbic acid.³⁶⁻⁴² Iron and cobalt porphyrins have also shown activity in photochemical CO₂ reduction.^{32,33} In some cases, it has been suggested that initial reduction takes place *via* axial binding of Our aim is to utilise the knowledge gathered about porphyrin and rhenium polypyridyl complexes to construct assemblies capable of long-wavelength absorption *via* the porphyrin chromophore and to sensitise a reaction at a remote rhenium centre. The $[Re^{(1)}(CO)_3L(bpy)]^{+/0}$ complexes used for photo-induced electrontransfer catalysis barely absorb natural sunlight. In contrast, the porphyrins exhibit spectra with extremely high extinction coefficients in the visible region making them very efficient light harvesters.

Our light absorbing groups are (metallo)porphyrins and the purpose of the rhenium centre is to act both as an electron acceptor and as a reacting centre. This allows for almost independent tuning of the light absorbing characteristics of the porphyrin and the reactivity of the rhenium unit. Our use of an appended bipyridine unit ensures that dissociation from the rhenium unit is not an issue, whereas dissociation becomes a concern if a metal carbonyl is coordinated to an appended pyridine.¹⁰ Similarly, dissociation can occur when the link is made by axial coordination at the metal of the metalloporphyrin.46,49 In this publication, we have widened the range of porphyrins to include palladium and free-base porphyrins, thus extending the range of redox potentials and emission properties. We compare assemblies made from the palladium and free-base systems with the zinc and magnesium analogues mentioned previously. We show here that the choice of the porphyrin-chelated metal does indeed have profound implications for the mechanism and efficiency of the photo-reduction.11,12

Experimental

Solvents for general use were used as obtained from Fisher. Solvents for Schlenk-line work were dried by refluxing over sodium–benzophenone (benzene, toluene, pentane, THF), over P_2O_5 (acetonitrile, butyronitrile), or over CaCl₂ then P_2O_5 (dichloromethane). After refluxing they were distilled and stored under argon. Triethylamine (BDH) was dried over CaH₂ and stored over 4 Å molecular sieves. CDCl₃ and CD₂Cl₂ were either used as obtained from Fluorochem or Goss, or dried over P_2O_5 . Dried NMR solvents were transferred into an NMR tube fitted with a PTFE stopcock (Young) on a high-vacuum line, and sealed under argon.

Chemicals were obtained from the following suppliers: benzophenone, tetraphenylporphyrin (Acros Organics); $\text{Re}_2(\text{CO})_{10}$, Celite, activated alumina, $[\text{NBu}_4][\text{X}]$ (X = Cl, Br), 3-picoline, 4*tert*-butylaniline and anhydrous magnesium bromide (Aldrich); zinc acetate, magnesium sulfate, sodium carbonate and thionyl chloride (Fisons); silver trifluoromethanesulfonate (Avocado); silica gel 60 and TLC plates F₂₅₄ (Merck).

The procedures for infrared, electronic absorption, fluorescence and NMR spectroscopy have been described previously.^{10,12} NMR assignments were made with the aid of 2D-spectra. Photochemical reactions were performed at room temperature in an IR cell or UV cuvette using a 125 W medium-pressure mercury vapour lamp with a water filter (10 cm) and Schott cut-off filters. Syntheses of **Bpy-H₂TPP**, [**Re**(**CO**)₃(**Pic**)**Bpy-ZnTPP**][**OTf**] and [**Re**(**CO**)₃(**Pic**)**Bpy-MgTPP**][**OTf**] were described in references 11 and 12 (see Scheme 1). Concentrations used for photochemical experiments in UV cuvettes were typically 5×10^{-5} to 1×10^{-4} mol dm⁻³; corresponding IR spectra were measured in cells with a 50 µm pathlength at concentrations *ca*. 10 times higher, that is 5×10^{-4} to 1×10^{-3} mol dm⁻³.

Synthesis of 5-(4-nitrophenyl)-10,15,20triphenylporphyrinatopalladium(II): NO₂-PdTPP

5-(4-Nitrophenyl)-10,15,20-triphenylporphyrin, $NO_2-H_2TPP^{50}$ (1.0 g, 1.52 mmol) and palladium(II) acetate (0.36 g, 1.60 mmol) were heated in toluene (150 mL) at reflux overnight. The solvent was removed and the purple material was purified by column chromatography under acidic conditions to remove free-base porphyrins (Si-60, dichloromethane–hexane–trifluoroacetic acid 60:40:1) to give bright red **NO₂-PdTPP** (1.18 g, 1.50 mmol, 99%).

¹H NMR (270 MHz, CDCl₃); δ 7.70–7.76 (9 H, m, *m*-, *p*-phenyl); 8.13–8.16 (6 H, m, *o*-phenyl); 8.32 (2 H, d. *J* 8.3 Hz, *m*-nitrophenyl); 8.59 (2 H, d, *J* 8.3 Hz, *o*-nitrophenyl); 8.67 (2 H, d, *J* 4.7 Hz, β-pyrrolic); 8.81 (4 H, s, β-pyrrolic); 8.83 (2 H, d, *J* 4.7 Hz, β-pyrrolic).

Synthesis of 5-(4-aminophenyl)-10,15,20triphenylporphyrinatopalladium(π): NH₂-PdTPP

NO₂-PdTPP (1.18 g, 1.54 mmol) was suspended in hydrochloric acid (10 mL, 10 M), ethanol (50 mL) and dichloromethane (100 mL). Tin dichloride dihydrate (2.2 g, 9.3 mmol) was added and the mixture was heated at reflux for 2 d, cooled, diluted with water (100 mL) and made alkaline with concentrated sodium hydroxide solution (10 mol dm⁻³) while cooling on ice. Dichloromethane (200 mL) was added, the mixture was shaken and allowed to settle, the aqueous phase was removed, the organic layer was washed with water (2 × 500 mL) and dried (MgSO₄). Removal of the solvent gave a bright red solid. Column chromatography (Si-60, dichloromethane) gave the product NH₂- PdTPP as a red solid (0.57 g, 0.78 mmol, 50%).

¹H NMR (270 MHz, CDCl₃): δ 3.95 (2 H, s, br, NH₂); 7.00 (2 H, d, *J* 8.1 Hz, *m*-aminophenyl); 7.69–7.75 (9 H, m, *m*-, *p*-phenyl); 7.92 (2 H, d, *J* 8.1 Hz, *o*-aminophenyl); 8.15–8.18 (6 H, m, *o*-phenyl); 8.80 (4 H, s, β-pyrrolic); 8.80 (2 H, d, *J* 4.9 Hz, β-pyrrolic); 8.91 (2 H, d, *J* 4.9 Hz, β-pyrrolic).

ESI-MS: $m/z = 692 (100\%, MH^+)$.

Synthesis of 5-[4-(4-methyl-2,2'-bipyridine-4'carboxyamidyl)phenyl]-10,15,20triphenylporphyrinatopalladium(II): Bpy-PdTPP

A solution of 4-methyl-2,2'-bipyridine-4'-carboxylic acid, **Bpy-COOH** (0.034 g, 0.16 mmol) in thionyl chloride (3 mL) was heated at reflux under an inert atmosphere for 2 h. The excess thionyl chloride was removed *in vacuo* and the yellow residue was dried under vacuum for 1 h at 100 °C to give the acid chloride. A solution of **NH₂-PdTPP** (0.12 g, 0.16 mmol) in dichloromethane (5 mL, dry), pyridine (5 mL, dry) was added to the yellow solid by cannula and the solution was heated at reflux under argon for

1 h and then left overnight at room temperature. The solvent was removed, the purple residue was re-dissolved in dichloromethane (25 mL), washed with water (150 mL), and dried (MgSO₄). The solvent was removed *in vacuo* and the product was purified by column chromatography (Si-60, dichloromethane, with 10% v/v tetrahydrofuran) to yield the bright red compound, **Bpy-PdTPP** (60 mg, 64 mmol, 40%).

¹H NMR (500 MHz, CD₂Cl₂ 10% CD₃CN): δ 2.44 (3 H, s, Bpy CH₃); 7.20 (1 H, d, *J* 4.0 Hz, Bpy), 7.70–7.77 (9 H, m, *p*-, *m*-phenyl); 7.88 (1 H, dd, *J* 4.3 Hz, Bpy); 8.11–8.13 (10 H, m, *m*-, *p*-phenyl and bridging phenyl); 8.32 (1 H, s, Bpy); 8.55 (1 H, d, *J* 4.6 Hz, Bpy); 8.79–8.80 (6 H, s and d, 6 β-pyrrolic); 8.84 (1 H, d, *J* 4.6 Hz, Bpy); 8.87 (2 H, d, *J* 4.64 Hz, β-pyrrolic); 8.97 (1 H, s, Bpy); 9.17 (1 H, br, CONH).

UV/vis (THF): $\lambda_{max}/nm (\epsilon/dm^3 mol^{-1} cm^{-1}) = 416 (312\,000),$ 488 (6300), 523 (44 800), 553 (6400).

ESI-MS: $m/z = 930 (100\%, C_{56}H_{37}N_7O^{106}Pd, MH^+).$

HR-FAB-MS: For $C_{56}H_{37}N_7O^{104}Pd$, observed mass 927.2093, calculated 927.2099, difference 0.6 mD.

Synthesis of 5-{4-[rhenium(1)tricarbonylbromide-4-methyl-2,2'bipyridine-4'-carboxyamidyl]phenyl}-10,15,20triphenylporphyrinatopalladium(II): Re(CO)₃BrBpy-PdTPP

Rhenium pentacarbonylbromide (0.025 g, 0.062 mmol) and **Bpy-PdTPP** (0.048 g, 0.052 mmol) were heated in toluene (20 mL, dry) at 60 °C under argon overnight. A red precipitate was formed which was insoluble in common organic solvents and was used without further purification in the next step.

$\label{eq:synthesis} Synthesis of 5-\{4-[rhenium(1)tricarbonyl(3-picoline)-4-methyl-2,2'-bipyridine-4'-carboxyamidyl]phenyl\}-10,15,20-triphenylporphyrinatopalladium(II) trifluoromethanesulfonate:$ $[Re(CO)_3(Pic)Bpy-PdTPP][OTf] \end{tabular}$

The compound **Re(CO)**₃**BrBpy-PdTPP** (0.05 g, 0.039 mmol) was suspended in a mixture of tetrahydrofuran (30 mL, dry) and 3picoline (0.5 mL). AgOTf (0.06 g, 0.258 mmol) was added, the reaction mixture was heated under argon at reflux for 1 h, the solvent was removed, the solid was redissolved in dichloromethane (3 mL) and purified by column chromatography (Si-60, CH₂Cl₂ with 20% v/v THF) to yield [**Re(CO)**₃(**Pic)Bpy-PdTPP**][**OTf**] (0.05 g, 0.035 mmol, 90%).

¹H NMR (500 MHz, CD₂Cl₂, labelling of hydrogen atoms in Scheme 1): δ 2.30 (3 H, s, Bpy CH₃); 2.75 (3 H, 3-picoline CH₃); 7.28 (1 H, dd, *J* 8.0 and 5.6 Hz, 3-picoline H₂); 7.61 (1 H, d, *J* 5.6 Hz, Bpy H_{5'}); 7.68 (1 H, d, *J* 8.0 Hz, 3-picoline H₄); 7.78–7.83 (9 H, m, 9 *m*-, *p*-phenyl); 7.97 (1 H, d, *J* 5.6 Hz, 3-picoline H₆); 8.15 (1 H, s, 3-picoline H₂); 8.21–8.26 (8 H, m, 6 *o*-phenyl and 2 bridging C₄H₆); 8.38 (2 H, d, *J* 8.6 Hz, 2 bridging C₄H₆); 8.51 (1 H, dd, *J* 5.6 and 1.3 Hz, Bpy H₅); 8.75 (1 H, s, Bpy H_{3'}); 8.88 (4 H, s, β-pyrrolic H_a and H_b); 8.90 (2 H, d, *J* 5.0 Hz, β-pyrrolic H_c); 8.97 (2 H, d, *J* 5.0 Hz, β-pyrrolic H_d); 9.00 (1 H d, *J* 5.6 Hz, Bpy H_{6'}); 9.25 (1 H, d, *J* 1.3 Hz, Bpy H₃); 9.35 (1 H, d, *J* 5.6 Hz, Bpy H₆) 10.75 (1 H, s, br, CONH).

UV/vis (THF): λ_{max} /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 416 (288 000), 488 (5300), 523 (33 600), 553 (5300).

ESI-MS: m/z = 1293 (100% [M, major contribution from $C_{65}H_{44}N_8O_4{}^{106}Pd{}^{187}Re]^+$), 1200 (10% [M – (Pic)]⁺).

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HR-FAB-MS: For $C_{65}H_{44}N_8O_4{}^{104}Pd{}^{185}Re$, observed mass 1289.2022 calculated 1289.2055, difference 3.3 mD.

$\label{eq:synthesis} Synthesis of 5-\{4-[rhenium(1)tricarbonyl(3-picoline)-4-methyl-2,2'-bipyridine-4'-carboxyamidyl]phenyl\}-10,15,20-triphenylporphyrin trifluoromethanesulfonate: [Re(CO)_3(Pic)Bpy-H_2TPP][OTf]$

The complex $[Re(CO)_3(Pic)Bpy-MgTPP]|OTf]^{12}$ was demetallated by elution through a silica column (Si-60 Fluorochem, dichloromethane 2 v/v % methanol). The solvent was removed to yield $[Re(CO)_3(Pic)Bpy-H_2TPP]|OTf]$ quantitatively.

¹H NMR (500 MHz, CD₂Cl₂, labelling of hydrogen atoms in Scheme 1): δ –2.75 (2 H, s, inner NH); 2.31 (3 H, s, Bpy CH₃); 2.76 (3 H, 3-picoline CH₃); 7.27 (1 H, dd, *J* 7.6 and 6.0 Hz, 3-picoline H₂); 7.60 (1 H, d, *J* 5.6 Hz, Bpy H_{3'}); 7.68 (1 H, d, *J* 7.6 Hz, 3-picoline H₄); 7.78–7.85 (9 H, m, 9 *m*-, *p*-phenyl); 7.96 (1 H, d, *J* 5.6 Hz, 3-picoline H₆); 8.15 (1 H, s, 3-picoline H₂); 8.26–8.32 (8 H, m, 6 *o*-phenyl and 2 bridging C₄H₆); 8.42 (2 H, d, *J* 8.3 Hz, 2 bridging C₄H₆); 8.51 (1 H, dd, *J* 5.6 and 1.7 Hz, Bpy H₃); 8.77 (1 H, s, Bpy H_{3'}); 8.91 (4 H, s, β-pyrrolic H_a and H_b); 8.93 (2 H, d, *J* 5.6 Hz, β-pyrrolic H_c); 9.00 (2 H, d, *J* 5.6 Hz, β-pyrrolic H_d); 8.99 (1 H d, *J* 5.6 Hz, Bpy H_{6'}); 9.35 (2 H, m, Bpy H₃ and H₆); 10.85 (1 H, s, br, CONH).

UV/vis (THF): λ_{max} /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 373 (23 700 sh), 418 (237 000), 514 (19 800), 549 (11 100), 592 (6900), 647 (5900).

ESI-MS: $m/z = 1189 (100\% \text{ M}^+), 1096 (25\% [M - (Pic)]^+).$

HR-FAB-MS: For $C_{65}H_{46}N_8O_4^{185}$ Re, observed mass 1187.3167 calculated 1187.3171, difference 0.4 mD.

Synthesis of 4-methyl-2,2'-bipyridine-4'-carboxyamidyl-(4-*tert*-butylphenyl): Bpy-amide

BpyCOOH (0.57 g, 2.66 mmol) was converted to the corresponding acid chloride by reaction with thionyl chloride (10 mL) at reflux for 4 h. The excess thionyl chloride was removed and the resulting solid was dried under vacuum at 100 °C for 1 h. CH_2Cl_2 (50 mL) and Et_3N (15 mL) was added. The solution turned black and a precipitate formed. To this suspension 4-*t*-Bu-aniline was added (0.8 g, 5.36 mmol) and the mixture was heated overnight at reflux. The solvent was removed and the crude material was purified by column chromatography (CH_2Cl_2 basic alumina hydrated) and recrystallised from CH_2Cl_2 –hexane to give **Bpy-amide** (0.63 g, 1.8 mmol, 69%).

¹H NMR (500 MHz, CD_2Cl_2): δ 1.34 (9 H, *t*-Bu); 2.67 (3 H, s, Bpy CH₃); 7.46 (2H, d, *J* 8.7 Hz, bridging C₆H₄); 7.67 (1 H, d, *J* 5.8 Hz, Bpy H_{3'}); 7.76 (2 H, d, *J* 8.7 Hz, bridging C₆H₄); 8.17 (1 H, dd, *J* 5.1 Hz, Bpy H₅); 8.40 (1 H, s, br, CONH); 8.42 (1 H, s, Bpy H_{3'}); 8.67 (1 H, d, *J* 5.8 Hz, Bpy H_{6'}); 8.85 (1 H, s, Bpy H₃); 8.95 (1 H, d, *J* 5.6 Hz, Bpy H₆).

ReBr(CO)₃(Bpy-amide)

A benzene solution (50 mL) of **Bpy-amide** (0.63 g, 1.8 mmol) was heated with $\text{Re}(\text{CO})_5\text{Br}$ (0.75 g, 1.8 mmol) at reflux overnight, cooled to 0 °C and the resulting yellow precipitate was collected by filtration (0.53 g, 0.76 mmol, 42%).

¹H NMR (250 MHz, (CD₃)₂CO): δ 1.47 (9 H, *t*-Bu); 2.59 (3 H, s, Bpy CH₃); 7.31 (1 H, d, *J* 6.2 Hz, Bpy H_{3'}); 7.41 (2H, d, *J* 7.5 Hz, bridging C₆H₄); 7.74 (2 H, d, *J* 7.5 Hz, bridging C₆H₄); 8.17 (1 H, dd, *J* 6.2 and 2.1 Hz, Bpy H₃); 8.73 (1 H, s, Bpy H_{3'}); 8.98 (1 H, d,

J 5.6 Hz, Bpy H₆'); 9.03 (1 H, d *J* 2.1 Hz, Bpy H₃); 9.26 (1 H, d, *J* 6.2 Hz, Bpy H₆); 10.03 (1 H, s, br, CONH).

IR (THF): 2020, 1920 and 1897 cm⁻¹.

[Re(CO)₃(Pic)Bpy-amide][OTf]

ReBr(CO)₃(**Bpy-amide**) (0.1 g, 0.14 mmol) and AgOTf (0.185 g, 0.7 mmol) were dissolved in dry THF (20 mL) and 3-picoline (0.1 mL) was added. The mixture was heated at reflux for 4 h. The solvent and excess picoline were removed under vacuum and the solid was suspended in CH₂Cl₂ (50 mL). AgBr was removed by filtration, excess AgOTf was removed by washing with water (3 × 50 mL); the organic phase was dried with MgSO₄ and the solvent was removed. The crude material was purified by column chromatography (basic alumina hydrated CH₂Cl₂, 2% v/v MeOH) to yield the desired product as a pale yellow solid (0.07 g, 0.11 mmol, 76%).

¹H NMR (500 MHz, CDCl₃): δ 1.32 (9 H, *t*-Bu); 2.26 (3 H, s, Bpy CH₃); 2.69 (3 H, 3-picoline CH₃); 7.23 (1 H, dd, *J* 7.3 and 5.8 Hz, 3-picoline H₅); 7.38 (2H, d, *J* 7.3 Hz, bridging C₆H₄); 7.49 (1 H, d, *J* 5.8 Hz, Bpy H_{5'}); 7.60 (1 H, d, *J* 7.3 Hz, 3-picoline H₄); 7.81 (1 H, d, *J* 5.6 Hz, 3-picoline H₆); 7.82 (2 H, d, *J* 7.3 Hz, bridging C₆H₄); 8.04 (1 H, s, 3-picoline H₂); 8.26 (1 H, d, *J* 5.1 Hz, Bpy H_{5'}); 8.65 (1 H, s, Bpy H_{3'}); 8.86 (1 H d, *J* 5.8 Hz, Bpy H_{6'}); 9.06 (1 H, s, Bpy H₃); 9.14 (1 H, d, *J* 5.6 Hz, Bpy H₆); 10.27 (1 H, s, br, CONH).

IR (THF): 2031 and 1927 cm⁻¹.

Results

Syntheses

The syntheses of Bpy-MTPP, Bpy-H₂TPP and [Re(CO)₃(Pic)Bpy-**MTPP**[**OTf**] (M = Mg, Zn) have been described previously.^{11,12} The free base [Re(CO)₃(Pic)Bpy-H₂TPP][OTf] was made by demetallation of [Re(CO)₃(Pic)Bpy-MgTPP[[OTf], achieved by elution through a silica column. A different route was required to synthesise **Bpy-PdTPP** from that employed for its Zn and Mg analogues since palladium is known to coordinate strongly to bipyridine ligands. Consequently palladium needs to be inserted into the porphyrin before the Bpy ligand is attached. Furthermore, complexation of the porphyrin to palladium frequently leads to reduction of the porphyrin macrocycle to chlorin and bacteriochlorin.51 Several different methods of inserting palladium into porphyrins have been reported in the literature.^{51,52} Our strategy utilised Pd(OAc)₂ to react with NO₂-H₂TPP releasing a weak acid upon metal insertion. A weakly coordinating solvent, toluene, was also employed to facilitate metal insertion. This procedure was almost quantitative and afforded no chlorin according to the UV/vis spectrum, simplifying the purification process. Reduction of NO2-PdTPP to NH2-PdTPP was achieved by modifying the biphasic procedure used for the free-base analogue NO₂-H₂TPP. For the reduction of NO₂-PdTPP, ethanol was necessary as an emulsifying agent to increase the reaction rate to an acceptable level. The amide coupling to form **Bpy-PdTPP** followed the same procedure as for Bpy-H₂TPP.¹² Subsequent steps followed the same route as for [Re(CO)₃(Pic)Bpy-ZnTPP][OTf] (Scheme 3).¹²

We have shown previously that the complexes $[Re(CO)_3-(Pic)Bpy-MTPP][OTf] (M = Zn, Mg)$ exhibit ground state UV/vis



and IR spectra that correspond to their component parts with no significant interaction between the porphyrin and rhenium bipyridine units.¹² The UV/vis absorption of the rhenium tricarbonylbipyridine moiety is, however, masked by the porphyrin. It is well established that zinc porphyrins take up a solvent molecule or add a nucleophile as a fifth ligand, and the magnesium porphyrins usually form octahedral complexes with two added ligands.^{53,54} In contrast, the palladium porphyrins remain 4-coordinate in solution.⁵⁵

Emission spectroscopy and energetics of electron transfer

The fluorescence spectra of **Bpy-MTPP** and **[Re(CO)₃(Pic)Bpy-MTPP][OTf]** (M = Mg, Zn) have been reported previously.¹² In essence, the presence of the rhenium unit quenches the porphyrin emission by electron transfer from the excited porphyrin to the rhenium moiety and there is no emission from the rhenium bipyridine unit. The redox potentials of the palladium and freebase porphyrin S₁ excited states are more positive than those of their zinc and magnesium analogues (Table 1) affecting the energetics of emission quenching.

Palladium porphyrins emit from both the singlet and triplet excited states in solution at room temperature, allowing simultaneous observation of singlet and triplet quenching by standard steady-state emission spectroscopy.⁵⁸ The emission spectra of **Bpy-PdTPP** and **[Re(CO)₃(Pic)Bpy-PdTPP][OTf]** both show narrow bands at 560 and 607 nm in butyronitrile due to fluorescence and one band at 686 nm due to phosphorescence (${}^{3}Q_{1,0}$ could not be observed with the instrumentation used, Fig. 1a). Importantly, the emission of the rhenium-appended palladium porphyrin is not quenched significantly. Fig. 1b shows the emission spectra of **Bpy-H₂TPP** and **[Re(CO)₃(Pic)Bpy-H₂TPP][OTf]** in butyronitrile. It is clear that the presence of the rhenium moiety also has little effect on the fluorescence of the free-base porphyrin.

Table 1Redox potentials and free energy change for intramolecularelectron transfer from porphyrin S_1 or T_1 excited states to the rheniumbipyridine unit in THF. The ground state values are for **Bpy-MTPP** and**MTPP**^{a,b}

	Redox potentials for ground and excited states (V vs. Fc/Fc ⁺)			$\Delta G/eV$	
Compound	$\overline{E_{\text{ox}}}$	$E_{ox}(\mathbf{S}_1)$	$E_{ox}(\mathbf{T}_1)$	$\overline{\mathbf{S}_1}$	T ₁
[Re(CO) ₃ (Pic)Bpy-ZnTPP] ⁺ [Re(CO) ₃ (Pic)Bpy-MgTPP] ⁺ [Re(CO) ₃ (Pic)Bpy-PdTPP] ⁺ [Re(CO) ₃ (Pic)Bpy-H ₂ TPP] ⁺	$0.38^a \\ 0.24^a \\ 0.74^b \\ 0.66^b$	-1.68 -1.76 -1.47 -1.25	-1.22 -1.24 -1.06 -0.77	-0.24 -0.32 -0.03 0.19	0.22 0.20 0.38 0.67

^a Values for Bpy-MTPP.¹² ^b Literature values for MTPP.^{56,57}



Fig. 1 Emission spectra of **Bpy-MTPP** and $[Re(CO)_3(Pic)Bpy-MTPP][OTf]$ corrected for photomultiplier response in rigorously degassed butyronitrile. (a) M = Pd, excitation at 522 nm; (b) M = 2H, excitation at 590 nm.

Photochemistry

It is well documented that the excited state of zinc porphyrins can be quenched reductively by tertiary amines. We report the results of photochemical experiments monitored *in situ* by IR spectroscopy in the CO-stretching region and, in some cases, by UV/vis spectroscopy. We quote conversion levels that should be regarded as semi-quantitative. As expected, THF solutions of **Bpy-ZnTPP**, **Bpy-MgTPP** or **Bpy-H**₂**TPP** containing 5–10% triethylamine changed colour on photolysis ($\lambda > 495$ nm) and showed spectra consistent with reduction to chlorins. The excited states of palladium porphyrins are stronger oxidants than those of the excited states of the zinc porphyrins by 0.5 eV.^{37,59} The photo-reduction of palladium porphyrins with NADH has a quantum yield three orders of magnitude greater than for the zinc derivative.¹⁶ The absorption spectra of **Bpy-PdTPP** exhibited new bands after photolysis ($\lambda > 495$ nm) with triethylamine consistent with photo-reduction of the porphyrin.

Visible (λ > 495 nm) irradiation of a THF solution of [Re(CO)₃(Pic)Bpy-ZnTPP][OTf] with triethylamine (20 eq.) produced changes in both the IR and electronic absorption spectra of the complex. When the experiment was performed under identical conditions to those for Bpy-ZnTPP, the IR spectra changed within a few minutes, but the absorption spectra displayed formation of chlorins only after times exceeding 60 min, a much longer time scale than for Bpy-ZnTPP (Fig. S1[†]). Monitoring of the reaction by IR spectroscopy revealed that the carbonyl bands at 2031 and 1927 cm⁻¹ were reduced in intensity, and two new bands emerged at 2016 and 1892 cm⁻¹ (Fig. S2[†]).¹¹ The stretching frequencies of transition metal carbonyls reflect the electron density of the metal centre. The appearance of new bands at lower frequency shows that the photochemical reaction of [Re(CO)₃(Pic)Bpy-ZnTPP|[OTf] with triethylamine induces a reaction at the rhenium bipyridine unit. The conversion was not quantitative but reached 13% after 30 min and 41% after 120 min irradiation, according to the IR spectrum (the conversion figures here and elsewhere are based on depletion of the precursor).⁶⁰ Prolonged photolysis led to decomposition of the porphyrin rather than an increased conversion.

When the photolysis of $[Re(CO)_3(Pic)Bpy-ZnTPP][OTf]$ ($\nu(CO) = 2031 \text{ cm}^{-1} \text{ sharp}, 1927 \text{ cm}^{-1} \text{ broad})$ with Et₃N (20 eq.) was undertaken in the presence of nucleophiles such as chloride ions, the IR bands of $[Re(CO)_3(Pic)Bpy-ZnTPP][OTf]$ disappeared and three new bands appeared at 2019, 1918 and 1895 cm⁻¹ (Fig. 2). The shift to low frequency of the product bands and the splitting of the lower frequency band are characteristic; the product can readily be assigned to $Re(CO)_3(ClBpy-ZnTPP$ from the resemblance to the IR spectrum of $Re(CO)_3(bpy)Cl$. In the presence of $[NBu_4][Br]$, the starting material decayed rapidly upon photolysis with Et₃N and the product was formed quantitatively within 10 min, compared to 84% in the same time with $[NBu_4][Cl]$. The IR spectrum of the photo-product was identical to that of $Re(CO)_3BrBpy-ZnTPP$.

When free 3-picoline (1 eq. with respect to the rhenium complex) was present in addition to Et_3N , bands appeared at 2011, 1907 and 1893 cm⁻¹ together with the bands observed in the absence of 3-



Fig. 2 IR spectra in the CO-stretching region observed before (black line) and after 5, 10, 15, 20 and 30 min photolysis (colours displayed in figure) of **[Re(CO)₃(Pic)Bpy-ZnTPP][OTf]** in THF with Et₃N (20 eq., $\lambda > 495$ nm) in the presence of [NBu₄][CI].

picoline in THF. The new product was highly air-sensitive and exposure to air regenerated the spectrum of the parent complex quantitatively. When the concentration of added 3-picoline was increased only one product was observed but the rate of conversion was decreased. On photolysis in a THF solution containing 1% 3-picoline (*ca.* 100 eq.) and 5% Et₃N (*ca.* 500 eq), the conversion was one order of magnitude slower than without added 3-picoline.

The IR bands of products from the photolysis reactions and some rhenium complexes are summarised in Table 2. It is evident that in the presence of halides the picoline ligand was replaced with a halide ligand. Furthermore, in the absence of free 3picoline or halide, a complex with very similar IR spectrum to that of [Re(CO)₃(THF)(bpy)]⁺ was formed.⁶¹ The product formed in the absence of picoline and halides is consequently assigned as [Re(CO)₃(THF)Bpy-ZnTPP][OTf]. In the presence of 3-picoline, the product can be identified as the radical [Re(CO)₃(Pic)Bpy-ZnTPP]⁺ by comparison with the spectroelectrochemically generated radical.¹¹

When $[Re(CO)_3(Pic)Bpy-MgTPP][OTf]$ was photolysed in the presence of Et₃N in THF, the observed behaviour was the same as that of the zinc analogue. In the absence of added 3-picoline, the cationic THF complex was obtained. If 3-picoline was added to

Precursor complex	Added reagent	Product v(CO)/cm ⁻¹	Assignment
[Re(CO)₃(Pic)Bpy-ZnTPP +	_	2016, 1914, 1892	[Re(CO) ₃ (THF)Bpy-ZnTPP] ⁺
[Re(CO) ₃ (Pic)Bpy-ZnTPP] ⁺	Pic	2011, 1907, 1893	[Re(CO) ₃ (Pic)Bpy-ZnTPP] [•]
[Re(CO) ₃ (Pic)Bpy-ZnTPP] ⁺	Br-	2020, 1920, 1897	Re(CO) ₃ BrBpy-ZnTPP
[Re(CO) ₃ (Pic)Bpy-ZnTPP] ⁺	Cl-	2019, 1918, 1895	Re(CO) ₃ ClBpy-ZnTPP
Related complexes (no photolysis or added reagent)		$v(CO)/cm^{-1}$	
Related complexes (no photolysis of added reagent)		V(CO)/ elli	
[Re(CO) ₁ (Pic)Bpv-ZnTPP] ⁺		2031, 1927 br	
[Re(CO) ₃ (Pic)Bpy-ZnTPP] ⁺ [Re(CO) ₁ (Pic)(Me ₂ bpy)] ^{+ a}		2031, 1927 br 2031, 1925 br	
[Re(CO) ₃ (Pic)Bpy-ZnTPP] ⁺ [Re(CO) ₃ (Pic)(Me ₂ bpy)] ^{+ a} [Re(CO) ₃ (THF)(bpy)] ^{+ 61}		2031, 1927 br 2031, 1925 br 2018, 1915, 1891	
Re(CO) ₃ (Pic)Bpy-ZnTPP]* [Re(CO) ₃ (Pic)(Me ₂ bpy)]* ^a [Re(CO) ₃ (THF)(bpy)]* ⁶¹ Re(CO) ₃ BrBpy-ZnTPP		2031, 1927 br 2031, 1925 br 2018, 1915, 1891 2020, 1920, 1897	

Table 2 IR bands of the photolysis products (hv > 495 nm with Et₃N) of [Re(CO)₃(Pic)Bpy-ZnTPP][OTf] with IR bands of rhenium reference complexes in THF

the solution, the emerging bands of $[Re(CO)_3(Pic)Bpy-MgTPP]^*$ were observed. As for the zinc chelate, the rate of photolysis was considerably decreased upon addition of 3-picoline to the solution. Fig. 3 illustrates the spectrum with 5% Et₃N and 1% 3-picoline; the yield was only 13% after 30 min but reached 31% after 90 min.



Fig. 3 IR spectra in the CO-stretching region observed before (black line) and after 10, 30, 60 and 90 min (colours displayed in figure) photolysis of **[Re(CO)₃(Pic)Bpy-MgTPP][OTf]** with $\lambda > 495$ nm in THF containing 1% 3-picoline and 5% Et₃N (*ca.* 100 and 500 eq., respectively).

Photolysis of the rhenium-appended compound $[Re(CO)_3-(Pic)Bpy-PdTPP][OTf]$ in the presence of 3-picoline (1%) and Et₃N (5%) in THF caused rapid changes. Photolysis with visible light for 6 min gave $[Re(CO)_3(Pic)Bpy-PdTPP]^{\cdot}$ with almost quantitative conversion (Fig. 4). The radical was identified from its IR spectrum in the same way as for the Mg and Zn analogues. Furthermore, addition of excess 3-picoline or the use of butyronitrile as a solvent caused no significant reduction in the rate of the photolysis reaction. In the absence of nucleophiles, the solvent complex was formed photochemically. Addition of bromide to the solution gave $Re(CO)_3BrBpy-PdTPP$ in quantitative yield.



Fig. 4 IR spectra in the CO-stretching region observed before (black line) and after 6 min photolysis (red line) with $\lambda > 495$ nm of [Re(CO)₃(Pic)Bpy-PdTPP][OTf] in THF containing 1% 3-picoline and 5% Et₃N (*ca.* 100 and 500 eq., respectively). * indicates impurity.

Photolysis of [Re(CO)₃(Pic)Bpy-H₂TPP][OTf] with Et₃N with $\lambda >$ 495 nm in THF produced negligible change after 60 min (Fig. 5).



Fig. 5 IR spectra in the CO-stretching region observed before (black line) and after 60 min irradiation (red line) of $[\text{Re(CO)}_3(\text{Pic})\text{Bpy-H}_2\text{TPP}][\text{OTf}]$ with $\lambda > 495$ nm in THF containing 1% 3-picoline and 5% Et₃N (*ca.* 100 and 500 eq., respectively).

With the aim of establishing the site of reduction unambiguously, in situ photolysis of [Re(CO)₃(Pic)Bpy-ZnTPP][OTf] was performed in an EPR cavity. A THF solution of [Re(CO)₃(Pic)Bpv-ZnTPP][OTf] and excess 3-picoline containing 5% Et₃N was photolysed in the EPR cavity with an Xe lamp $(\lambda > 400 \text{ nm})$. No EPR signal was present prior to photolysis, but during photolysis an unusual feature developed (Fig. S3[†], g = 2.003, peak-to-peak separation = 6.9 mT). This spectrum corresponds well with the reported EPR spectrum of neutral rhenium tricarbonylbipyridine-based radicals.62 There are two rhenium isotopes with spin 5/2 (181 Re 62.6%, 183 Re 37.4%) and comparable magnetic moments. The spectrum for each rhenium isotopomer is coupled further with 3 nitrogen nuclei and at least six of the protons, thus accounting for the unresolved spectrum. The EPR experiment established unambiguously that the reduction occurred exclusively on the rhenium bipyridine moiety. A porphyrin-based π -radical anion would have produced a narrow line spectrum with rich hyperfine splitting.63

The rhenium moiety does not absorb light at the wavelengths employed in these experiments ($\lambda > 495$ nm); consequently the absorption of a photon by the porphyrin unit results in substitution at a remote site *via* a sensitisation mechanism. As a control, we synthesised the model compound [**Re**(**CO**)₃(**Pic**)(**Bpyamide**)]⁺; it did not undergo any reaction when photolysed with long wavelength light ($\lambda > 495$ nm) in the presence of triethylamine.



Discussion

Product assignment

The bipyridine-appended porphyrins were all stable towards prolonged exposure to irradiation with ultraviolet and visible light when pure, both under argon and air.⁶⁴ The bipyridine-appended metalloporphyrins described here all underwent similar changes in the absorption spectra of the Q-band region upon photolysis in the presence of triethylamine consistent with reduction to chlorins and related species.^{36-42,65}

Like their rhenium-free analogues, the rhenium-appended porphyrins were stable towards prolonged irradiation when pure, both under argon and air. Spectroelectrochemical experiments have shown that oxidation occurs at the porphyrin moiety of the rhenium-appended assemblies, whereas reduction occurs at the rhenium bipyridine moiety since it has a lower (more positive) reduction potential than that of the metalloporphyrin unit.^{11,12} Consequently, photochemical reduction with triethylamine was expected to result in reduction of the rhenium moiety. IR spectroscopy is a useful tool for following changes located on the rhenium subunit while the electronic absorption spectra give information about processes located on the porphyrin moiety. Upon photolysis with triethylamine in THF, all the assemblies were partially converted to the cationic solvent complexes [Re(CO)₃(THF)Bpy-MTPP]⁺ except for the free-base system. The emerging IR spectrum varied according to the presence of excess picoline or added nucleophiles (Table 2). The reductively-induced reaction with nucleophiles was confirmed by adding [NBu₄][X] (X = Cl or Br) to the solution, which produced $Re(CO)_3(X)Bpy$ -MTPP rapidly and quantitatively. The latter was identified by IR spectroscopy and mass spectrometry. These products result from formal substitution, yet no substitution was detected when the compounds were photolysed in the absence of Et₃N. Likewise, the complexes were stable towards thermal substitution in refluxing THE

When the photolysis was performed in THF with added 3picoline, the rhenium bipyridine-centred radical **[Re(CO)₃(Pic)-Bpy-MTPP]**^{*} was identified as photo-product by comparison with spectroelectrochemically generated radicals.^{11,12} The requirement for excess picoline in order to observe the radical is explained below; in brief, the radical is harder to reduce than the cations and is more labile with respect to picoline substitution. We deduce that the substitution must arise *via* a reduced intermediate **[Re(CO)₃(Pic)Bpy-MTPP]**^{*}.

In order to observe the radical some picoline has to be added to the reaction mixture, but a high picoline concentration has a negative effect on the rate of photo-reduction of the Zn and Mg assemblies. The Mg and Zn derivatives need to pre-coordinate triethylamine to the axial position of the metalloporphyrin in order for the photo-reaction to take place (see below). Any free picoline in the solution is a good competitor for this site and thus acts as an inhibitor for photo-reduction. In stark contrast, the picoline concentration has no significant impact on the rate of photoreduction of the palladium analogue since this assembly operates by another mechanism that does not require pre-coordination of the reductant.

Coordination of nitrogen ligands to metalloporphyrins

The ability of zinc porphyrins to coordinate an additional nitrogen ligand is well established. The stability constants have been critically assessed in *The Porphyrin Handbook*.⁶⁶ Values of $\log_{10} K$ (*K* is the stability constant) for ZnTPP are as follows: triethylamine 1.10 in benzene, 3-picoline 3.81 in benzene, pyridine 3.84 in

dichloromethane. No values are available for THF or MeCN solvents, nor are there values for magnesium porphyrins except for MgTPP + pyridine in benzene ($\log_{10} K = 3.30$). We can safely deduce that a significant fraction of the zinc porphyrins will have coordinated Et₃N when it is present at 5–10% in solution. Moreover, 3-picoline will displace Et₃N even when its concentration is considerably lower than that of Et₃N.

Photophysics in the absence of Et₃N

In our previous publication on the photophysics of $[Re(CO)_3(Pic)Bpy-MTPP]^+$ (M = Mg or Zn) in the absence of Et₃N, we found that excitation in the long wavelength absorption bands of the porphyrin moiety resulted in electron transfer from porphyrin to rhenium bipyridine on an ultrafast time scale.¹² In the case of the magnesium porphyrin, the IR bands of the chargeseparated excited state are observed after 1.5 ps and decay in *ca*. 20 ps. For the zinc analogue, the corresponding rise takes *ca*. 5 ps and the decay 40 ps. The charge-separated excited state may be approximated by the description [Re⁺(CO)₃(Pic)Bpy^{•-}-MTPP^{•+}]. A further state, identified in the IR spectra at a stage when the transient absorption signal has disappeared, is assigned to a species that remains vibrationally excited but is in the ground electronic state.12 The assembly returns to its initial state (vibrational and electronic ground state) with a time constant of 35-55 ps. The system is reversible in the absence of an added electron donor.12

The excited states of $[\text{Re}(\text{CO})_3(\text{Pic})\text{Bpy-MTPP}]^+$ (M = Zn, Mg) are quenched by intramolecular electron transfer.¹² The energetics of this process are determined by the fluorescence energy, E_{00} and the excited state redox potential (eqn (1)). The free base assembly $[\text{Re}(\text{CO})_3(\text{Pic})\text{Bpy-H}_2\text{TPP}]^+$ is expected to have a more positive oxidation potential than its zinc or magnesium analogues by *ca*. 300–400 mV on the basis of literature comparisons (Table 1). Moreover, its S₁ excited state potential is also substantially more positive. Intramolecular electron-transfer quenching of the excited state of $[\text{Re}(\text{CO})_3(\text{Pic})\text{Bpy-H}_2\text{TPP}]^+$ is calculated to have a positive free energy and is therefore unlikely. The calculations show that the palladium analogue has a Gibbs free energy for intramolecular electron transfer close to 0 V.

$$[\operatorname{Re}^{+}(\operatorname{CO})_{3}(\operatorname{Pic})Bpy-MTPP]^{*} \rightarrow [\operatorname{Re}^{+}(\operatorname{CO})_{3}(\operatorname{Pic})Bpy^{-\bullet}-MTPP^{+\bullet}]$$
(1a)

$$\Delta G^{\circ}_{ox} = F E_{ox}^{\circ} (\text{MTPP}) - F E_{red}^{\circ} (\text{ReBpy}) - E_{00}^{*}$$
(1b)

These free-energy calculations are fully consistent with the emission experiments. Quenching of the S_1 state results in a large decrease of the emission quantum yield for the Zn and Mg assemblies.¹² Furthermore, the emission of [Re(CO)₃(Pic)Bpy-PdTPP]⁺ is not quenched and [Re(CO)₃(Pic)Bpy-H₂TPP]⁺ exhibits negligible quenching.

Electron transfer from a sacrificial donor

In the presence of Et_3N , productive photo-reaction at the rhenium site is observed on irradiation of the zinc or magnesium porphyrins. The short lifetime of the charge-separated state prevents its participation in outer-sphere electron-transfer reaction; furthermore the porphyrin T_1 state of [**Re(CO)**₃(**Pic)Bpy-MTPP**]⁺ (M = Mg, Zn) is not populated significantly. Nevertheless, intermolecular electron transfer is compatible with ultrafast back-electron transfer provided that (a) triethylamine coordinates to zinc or magnesium prior to absorption and (b) electron transfer from the metalloporphyrin to the bipyridine is followed rapidly by irreversible electron transfer from the triethylamine to the metalloporphyrin (Scheme 4).¹² This mechanism is an excited state version of an inner-sphere electron-transfer reaction.



The triethylamine is a successful sacrificial electron donor due to the rapid and irreversible dissociation from the metal and decomposition of the radical cation NEt_3^{*+} that prevents the non-productive back-electron transfer. The exact decomposition pathway is complicated but most likely involves the abstraction of a proton by a second molecule of Et_3N as a first step.⁶⁷⁻⁶⁹

The photo-reduction of the free-base porphyrin $[Re(CO)_3-(Pic)Bpy-H_2TPP]^+$ is inefficient compared with the metallated derivatives; virtually no conversion was observed after 1 h irradiation. In this case, pre-coordination is not possible and the energetics for photo-induced electron transfer from the porphyrin to the rhenium-bipyridine moiety are unfavourable.

The palladium porphyrin [Re(CO)₃(Pic)Bpy-PdTPP]⁺ undergoes photo-reaction very efficiently in the presence of triethylamine and picoline even though [Re(CO)₃(Pic)Bpy-PdTPP]⁺ is not capable of intramolecular photo-induced electron transfer from the excited porphyrin to the rhenium unit and cannot precoordinate triethylamine. Indeed, [Re(CO)₃(Pic)Bpy-PdTPP]⁺ is the most rapidly reduced of the assemblies studied. Clearly, this complex must operate by a different mechanism. The singlet and triplet excited states of the palladium porphyrin are significantly better oxidants than the corresponding states of the magnesium or zinc porphyrins.⁵⁹ The lack of fluorescence and phosphorescence quenching indicates that the lifetimes of the palladium excited states are little changed by appending the rhenium moiety. Palladium porphyrins exhibit very weak short-lived (picosecond) fluorescence and intense (high quantum yield) phosphorescence.59,70 The room-temperature phosphorescence lifetime of PdTPP is 385 µs.⁷¹ Thus, triethylamine must be able to reduce the palladium assembly without prior charge separation. Furthermore, the long lifetime of the triplet state means that an outer-sphere bimolecular reaction can proceed efficiently. Kalyanasundaram reported that the photo-reduction of palladium porphyrins with NADH has a quantum yield three orders of magnitude greater than that of the zinc derivative.37 We conclude that the reaction of the palladium assemblies proceeds by intermolecular electron transfer from triethylamine to the assembly in an excited state. The triplet state will be most significant in this process because of its longer

lifetime. The unpaired electron in the product is localised at the rhenium bipyridine moiety.

Electron-transfer chain

The ligand L on rhenium complexes of the type $[\text{Re}(\text{CO})_3-\text{L}(\text{byy})]^{+/0}$ has a substantial influence on the reduction potential of the rhenium–bipyridine unit which, in turn, can explain the ligand substitution behaviour. The starting material $[\text{Re}(\text{CO})_3(\text{Pic})\text{Bpy-ZnTPP}]^+$ is reduced at -1.44 V vs. Fc/Fc⁺ in THF, while the reduction potential for $\text{Re}(\text{CO})_3\text{BrBpy-ZnTPP}$ is -1.75 V^{11} The complex $[\text{Re}(\text{CO})_3(\text{THF})\text{Bpy-ZnTPP}]^+$ was not synthesised but simple bipyridine compounds can be used as good models for the rhenium Bpy-MTPP complexes; $[\text{Re}(\text{CO})_3(\text{THF})(\text{bpy})]^+$ is reduced at -1.69 V in THF.⁶¹ Furthermore, radicals of the type $[\text{Re}(\text{CO})_3(\text{L}(\text{bpy})]^{-0'-}$ (L = Cl⁻, Br⁻, pyridine, Pic) readily undergo ligand substitution reactions at room temperature.²⁶

These considerations lead us to propose an electron-transfer chain mechanism shown in Scheme 5, that is reminiscent of Scheme 2.¹⁸ The radical [Re(CO)₃(Pic)Bpy-ZnTPP][•] may be generated as in Scheme 4 (Scheme 5, step 1). This radical can react with the solvent to form [Re(CO)₃(THF)Bpy-ZnTPP]⁺ (Scheme 5, step 2), which in turn is capable of reducing [Re(CO)₃(Pic)Bpy-**ZnTPP**]⁺ to its radical form (Scheme 5, step 3). The other product from the reduction, [Re(CO)₃(THF)Bpy-ZnTPP]⁺, is unable to undergo photo-induced charge shift as the THF complex has a significantly more negative reduction potential. This change in potential has been demonstrated quantitatively for simpler rhenium complexes.²⁶ The THF ligand in [Re(CO)₃(THF)Bpy-ZnTPP]⁺, however, is labile and can be displaced by added picoline, regenerating the starting complex [Re(CO)₃(Pic)Bpy-ZnTPP]⁺. We therefore have the steps required for an electrontransfer chain leading ultimately to the photosubstitution of the picoline ligand (Scheme 5). The equilibrium in step 2 can be shifted to the left by adding a small excess of 3-picoline making the radical species [Re(CO)₃(Pic)Bpy-MTPP][•] observable by IR and EPR spectroscopy. The chain may be terminated by oxidation of the radical species by other electron acceptors (step 4). The yield of substitution product may be reduced by replacement of THF in [Re(CO)₃(THF)Bpy-ZnTPP]⁺ by picoline (Scheme 5, step 5) since the THF is fairly labile.

When Cl⁻ or Br⁻ is present the corresponding halide complex [Re(CO)₃(X)Bpy-ZnTPP]⁻ is formed in the substitution step and steps 2 and 3 are replaced by 2a and 3a. The propagation step is likely to be faster for halides since the radical anion [Re(CO)₃(X)Bpy-ZnTPP]⁻ is a better reductant than the neutral radical [Re(CO)₃(THF)Bpy-ZnTPP]⁻. In the presence of halide, there is no equivalent of step 5. Thus the catalytic cycle is much more efficient with halide.

In support of these steps, electrochemical reduction of the rhenium complexes resulted in the replacement of the ligand by a solvent molecule (THF) and re-oxidation to the cationic THF complex.¹¹ On reduction of **[Re(CO)₃(Pic)Bpy-ZnTPP][OTf]** in the presence of bromide, **Re(CO)₃BrBpy-ZnTPP** was formed.

We have been able to develop this mechanism for the zinc porphyrin assemblies since considerable electrochemical data are available. The electron-transfer chain mechanism is expected to apply the magnesium and palladium assemblies as well.



Scheme 5 Electron-transfer chain mechanism.

Conclusions

The experiments reported in this paper on metalloporphyrins appended with rhenium tricarbonylbipyridine moieties exhibit several striking features. (1) The complexes are photo-stable in the absence of Et_3N but photo-reactive with it. (2) The reactions occur at the rhenium centre although the metalloporphyrins act as the light absorbers. (3) Analysis of the products by IR spectroscopy reveals substitution at rhenium unless excess 3-picoline is added. Only with excess picoline are radical products observed. (4) Two different mechanisms are observed depending on the metal chelated by the porphyrin. When the picosecond charge separation and back-reaction are taken into account, it becomes clear that the magnesium and zinc porphyrins pre-coordinate Et₃N, and are reduced on photolysis to the rhenium bipyridine picoline radical complex with dissociation of Et₃N^{•+}. An electron-transfer chain allows substitution of picoline and eventual re-oxidation to the closed shell Re^(I) products. This catalytic substitution is especially efficient with halides as the incoming ligand. In the presence of excess 3-picoline, the reaction is halted at the radical stage. The palladium porphyrin derivative contrasts with the magnesium and zinc complexes; it shows negligible fluorescence quenching implying a long-lived excited state and its excited state is a weaker reductant. Moreover, it shows emission from both singlet and triplet states in liquid solution. This assembly reacts with Et₃N by intermolecular electron transfer. Thus the reactions of the excited magnesium and zinc derivatives may be considered as inner-sphere electron-transfer reactions while the reactions of the palladium derivatives proceed by an outer-sphere mechanism. Finally, it is important to stress that a charge-separated state with a very short lifetime does not preclude productive reaction in the presence of a sacrificial electron donor that can pre-coordinate to the metalloporphyrin.

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References

- 1 V. Balzani and F. Scandola, in *Supramolecular Photochemistry*, ed. T. J. Kemp, Ellis Horwood, Chichester, 1991.
- 2 D. Gust, T. A. Moore and A. L. Moore, Acc. Chem. Res., 2001, 34, 40.
- 3 T. J. Meyer, Prog. Inorg. Chem., 1983, 30, 389.
- 4 M. D. Ward, Chem. Soc. Rev., 1997, 26, 365.
- 5 M. R. Wasielewski, Chem. Rev., 1992, 92, 435
- 6 T. S. Balaban, in *Light-harvesting nanostructures*, ed. H. S. Nalwa, American Scientific Publishers, Valencia, California, 2004, vol. 4, pp. 505–559.
- 7 J. H. Alstrum-Acevedo, M. K. Brennaman and T. J. Meyer, *Inorg. Chem.*, 2005, 44, 6802.
- 8 M. H. V. Huynh, D. M. Dattelbaum and T. J. Meyer, *Coord. Chem. Rev.*, 2005, **249**, 457.
- 9 C. J. Aspley, J. R. Lindsay Smith and R. N. Perutz, J. Chem. Soc., Dalton Trans., 1999, 2269.
- 10 C. J. Aspley, J. R. Lindsay Smith, R. N. Perutz and D. Pursche, J. Chem. Soc., Dalton Trans., 2002, 170.

- 11 A. Gabrielsson, F. Hartl, J. R. Lindsay Smith and R. N. Perutz, Chem. Commun., 2002, 950.
- 12 A. Gabrielsson, F. Hartl, H. Zhang, J. R. Lindsay Smith, M. Towrie, A. Vlček, Jr. and R. N. Perutz, J. Am. Chem. Soc., 2006, 128, 4253.
- 13 X. Liu, L. J. J. Pan, C. R. Y. Na, W. Gao and S. L., *Tetrahedron Lett.*, 2006, **62**, 3674.
- 14 J. Hawecker, J.-M. Lehn and R. Ziessel, J. Chem. Soc., Chem. Commun., 1983, 536.
- 15 J. Hawecker, J. M. Lehn and R. Ziessel, *Helv. Chim. Acta*, 1986, 69, 1990.
- 16 K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, San Diego, 1992.
- 17 Photosenitization and Photocatalysis Using Inorganic and Organometallic Compounds, ed. K. Kalyanasundaram and M. Grätzel, Kluwer Academic Publishers, Dordrecht, 1993.
- 18 H. Hori, F. P. A. Johnson, K. Koike, K. Takeuchi, T. Ibusuki and O. Ishitani, J. Chem. Soc., Dalton Trans., 1997, 1019.
- 19 C. Luo, D. M. Guldi, H. Imahori, K. Tamaki and K. Sakata, J. Am. Chem. Soc., 2000, 122, 6535.
- 20 C. Kutal, M. A. Weber, G. Ferraudi and D. Geiger, *Organometallics*, 1985, 4, 2161.
- 21 K. Koike, H. Hori, M. Ishizuka, J. R. Westwell, K. Takeuchi, T. Ibusuki, K. Enjouji, H. Konno, K. Sakamoto and O. Ishitani, *Organometallics*, 1997, 16, 5724.
- 22 L. A. Lucia, K. Abboud and K. S. Schanze, *Inorg. Chem.*, 1997, **36**, 6224.
- 23 J. Grodkowski, D. Behar, P. Neta and P. Hambright, *J. Phys. Chem. A*, 1997, **101**, 248.
- 24 M. Hammouche, D. Lexa, M. Momenteau and J. M. Saveant, J. Am. Chem. Soc., 1991, 113, 8455.
- 25 J. Hawecker, J. M. Lehn and R. Ziessel, J. Chem. Soc., Chem. Commun., 1984, 328.
- 26 F. P. A. Johnson, M. W. George, F. Hartl and J. J. Turner, Organometallics, 1996, 15, 3374.
- 27 K. Koike, N. Okoshi, H. Hori, K. Takeuchi, O. Ishitani, H. Tsubaki, I. P. Clark, M. W. George, F. P. A. Johnson and J. J. Turner, J. Am. Chem. Soc., 2002, 124, 11448.
- 28 S. Berger, A. Klein and W. Kaim, Inorg. Chem., 1998, 37, 5664.
- 29 S. Ernst and W. Kaim, J. Am. Chem. Soc., 1986, 108, 3578.
- 30 W. Kaim and S. Kohlmann, Inorg. Chem., 1990, 29, 2909.
- 31 W. Kaim and S. Kohlmann, Chem. Phys. Lett., 1987, 139, 365.
- 32 Y. Hayashi, S. Kita, B. S. Brunschwig and E. Fujita, J. Am. Chem. Soc., 2003, **125**, 11976.
- 33 E. Fujita and J. T. Muckerman, Inorg. Chem., 2004, 43, 7636
- 34 H. Takeda, K. Koike, H. Inoue and O. Ishitani, J. Am. Chem. Soc., 2008, 130, 2023.
- 35 S. Sato, K. Koike, H. Inoue and O. Ishitani, *Photochem. Photobiol. Sci.*, 2007, 6, 454.
- 36 K. Kalyanasundaram, Inorg. Chem., 1984, 23, 2453.
- 37 K. Kalyanasundaram, J. Photochem. Photobiol., A, 1988, 42, 87.
- 38 G. R. Seely and M. Calvin, J. Chem. Phys., 1955, 23, 1068.
- 39 A. Harriman and G. Porter, J. Chem. Soc., Faraday Trans. 2, 1979, 75, 1543.
- 40 D. Mauzerall, J. Am. Chem. Soc., 1960, 82, 1832.

- 41 D. Mauzerall, J. Am. Chem. Soc., 1962, 84, 2437.
- 42 Y. Harel, J. Manassen and H. Levanon, *Photochem. Photobiol.*, 1976, 23, 337.
- 43 T. Dhanasekaran, J. Grodkowski, P. Neta, P. Hambright and E. Fujita, J. Phys. Chem. A, 1999, 103, 7742.
- 44 L. Flamigni, A. M. Talarico, J.-C. Chambron, V. Heitz, M. Linke, N. Fujita and J.-P. Sauvage, *Chem.-Eur. J.*, 2004, 10, 2689.
- 45 C. Monnereau, J. Gomez, E. Blart, F. Odobel, S. Wallin, A. Fallberg and L. Hammarström, *Inorg. Chem.*, 2005, 44, 4806.
- 46 E. Iengo, F. Scandola and E. Alessio, *Struct. Bonding*, 2006, **121**, 105.
 47 M. Ghirotti, C. Chiorboli, M. T. Indelli, F. Scandola, M. Casanova, E.
- Iengo and E. Alessio, *Inorg. Chim. Acta*, 2007, **360**, 1121.
- 48 S. J. Lee and J. T. Hupp, *Coord. Chem. Rev.*, 2006, **250**, 1710.
- 49 J. T. Hupp, *Struct. Bonding*, 2006, **121**, 145.
- 50 W. J. Kruper, T. A. Chamberlin and M. Kochanny, *J. Org. Chem.*, 1989, **54**, 2753.
- 51 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.
- 52 D. W. Thomas and A. E. Martell, J. Am. Chem. Soc., 1959, 81, 5111.
- 53 W. R. Scheidt and Y. J. Lee, Struct. Bonding, 1987
- 54 M. O. Senge and W. W. Kalisch, Inorg. Chem., 1997, 36, 6103.
- 55 A. M. Stolzenberg, L. J. Schussel, J. S. Summers, B. M. Foxman and J. L. Petersen, *Inorg. Chem.*, 1992, **31**, 1678.
- 56 A. Giraudeau, H. J. Callot and M. Gross, *Inorg. Chem.*, 1979, 18, 201.
- 57 J. Takeda and M. Sato, Chem. Lett., 1995, 939.
- 58 J. B. Callis, M. Gouterman, Y. M. Jones and B. H. Henderson, J. Mol. Spectrosc., 1971, 39, 410.
- 59 K. Kalyanasundaram and M. Neumann-Spallart, J. Phys. Chem., 1982, 86, 5163.
- 60 It would be possible to measure quantum yields but it is difficult because there are only minor changes in the visible spectrum but big changes in the IR spectrum, resulting in a big inner filter effect. We have not undertaken such measurements at this stage. However, we point out relative yields wherever possible.
- 61 G. J. Stor, F. Hartl, J. W. M. van Outersterp and D. J. Stufkens, Organometallics, 1995, 14, 1115.
- 62 A. Klein, C. Vogler and W. Kaim, Organometallics, 1996, 15, 236.
- 63 D. F. Bocian and J. Seth, J. Am. Chem. Soc., 1994, 116, 143.
- 64 Difficulties in removing the amine used during the synthesis of Bpy-MgTPP accounted for changes in the electronic absorption spectrum after photolysis with bands emerging at 455 and 620 nm consistent with the formation of chlorins (ref. 65 and 66).
- 65 G. Balducci, G. Chottard, C. Gueutin, D. Lexa and J. M. Saveant, *Inorg. Chem.*, 1994, 33, 1972.
- 66 M. Tabata and J. Nishimoto, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 9, ch. 60, p. 221.
- 67 C. D. Russell, J. Am. Chem. Soc., 1963, 35, 1291.
- 68 S. G. Cohen, A. Parola and G. H. Parsons, Jr., Chem. Rev., 1973, 73, 141.
- 69 S. G. Cohen and R. J. Baumgarten, J. Am. Chem. Soc., 1965, 87, 2996.
 70 G. Khalil, M. Gouterman, S. Ching, C. Costin, L. Coyle, S. Gouin, E. Green, M. Sadilek, R. Wan, J. Yearyean and B. Zelelow, J. Porphyrins Phthalocyanines, 2002, 6, 135.
- 71 A. Harriman, J. Chem. Soc., Faraday Trans. 2, 1981, 77, 1281.