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Systematic synthesis and photochemistry of tetraaryl porphyrins mono-substituted with a transition metal carbonyl: characterisation of a zinc porphyrin–rhenium carbonyl complex†

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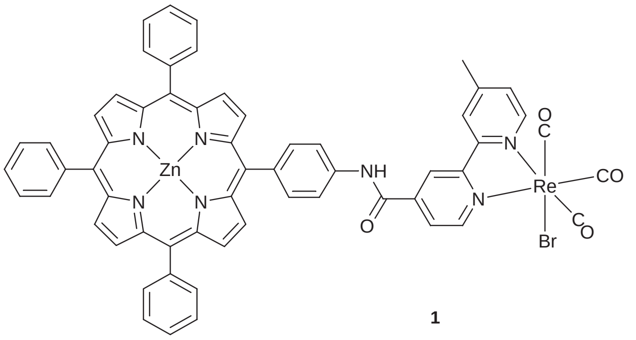
A systematic synthesis designed to connect a metalloporphyrin to a metal carbonyl moiety is demonstrated through a zinc tetraphenyl porphyrin substituted with $Re(CO)_3$(4′-methyl-2,2′-bipyridyl)Br *via* an amide bond; the emission and excited state absorption spectra are dominated by porphyrin transitions.

Supramolecular systems containing porphyrins have been designed to mimic electron or energy transfer processes in photosynthesis.[1] They include systems in which the porphyrin is coordinated to a peripheral transition metal complex.[2–5] Our aim is to exploit the opportunities of combining a porphyrin and a single metal carbonyl into the same molecule and to investigate the intramolecular photochemical interaction between the two chromophores. Metal carbonyls have their own photochemistry and the benefit of structure-sensitive IR bands. The examples of porphyrins coordinated to a transition metal carbonyl described so far have the following transition metal carbonyl groups on the periphery of various porphyrins: $Cr(CO)_3$, $W(CO)_5$, $RuCl_2(DMSO)_2CO$, $Re(CO)_3Cl$ and (μ-H)-$Os_3(CO)_{10}$. In most, the porphyrin is substituted by several metal carbonyl groups and only a few have been investigated photochemically.[6–10] We report here a versatile synthesis capable of systematic variation which satisfies the following requirements: (i) it provides a simple route to monofunctionalised metalloporphyrin with established photochemistry suitable for coordination to a single metal carbonyl; (ii) it uses an adaptable linker between metalloporphyrin and metal carbonyl; (iii) it uses an accessible metal carbonyl with established photochemistry which can be linked by displacement of labile ligands.

We have demonstrated these principles with the synthesis of a mono-substituted metalloporphyrin, **1**, coordinated to a $Re(CO)_3Br$ moiety *via* an amido–bipyridyl linker unit. Tetraphenylporphyrin, H_2tpp, was converted into 5-(4-aminophenyl)-10,15,20-triphenylporphyrin[11] and metallated with zinc acetate to give the zinc amino porphyrin. This was reacted with the acid chloride of 4′-methyl-2,2′-bipyridyl-4-carboxylic acid, prepared by selective oxidation of 4,4′-dimethyl-2,2′-bipyridine using SeO_2 and $AgNO_3$,[12] to give zinc 5-[4-(4′-methyl-2,2′-bipyridyl-4-carboxyamidyl)phenyl]-10,15,20-triphenylporphyrin, **2**. Refluxing **2** with $Re(CO)_5Br$ in benzene gave the desired compound **1** in 12% overall yield.‡



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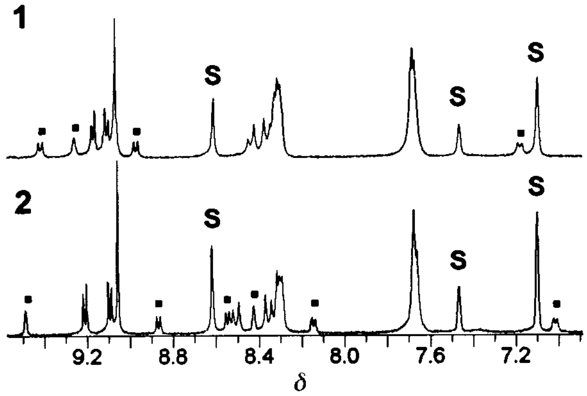
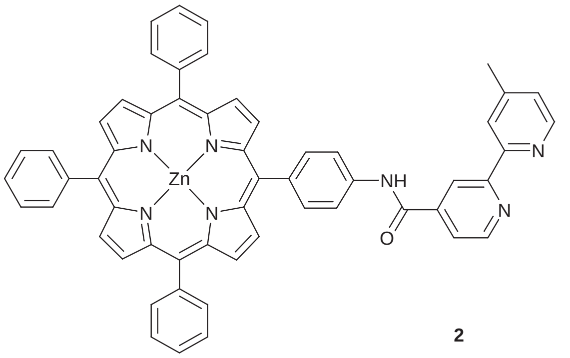


Fig. 1 The ^1H NMR spectra of zinc porphyrins **1** (top trace) and **2** (bottom trace) in [$^2H_5$]pyridine. S: pyridine resonances; ■: resonances due to bipyridyl protons.



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NMR spectra were recorded in [$^2H_5$]pyridine,§ since **1** is insoluble in other, less strongly coordinating solvents. The resonances due to the bipyridyl protons are significantly shifted in the ^1H NMR spectrum of **1** compared to those of **2**, whereas the resonances due to the metalloporphyrin macrocyclic protons are barely affected by peripheral coordination to rhenium (Fig. 1). This suggests that **1** has an extended conformation which was confirmed by models and NOESY experiments.

The $Re(CO)_3$ unit is detected in the ^{13}C NMR spectrum recorded in [$^2H_5$]pyridine by the three carbonyl resonances observed at δ 198.8, 198.4 and 190.5. The carbonyl region of the IR spectrum exhibits three peaks at 2020, 1920 and 1897 cm^{-1} as expected for a *fac*-$Re(CO)_3X$(diimine) complex (X = halide).[13]

Coordination of the $Re(CO)_3Br$ unit to the bipyridyl substi-

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† *Supplementary data available*: Characterisation data for complex **2**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/2269/, otherwise available from BLDSC (No. SUP 57579, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

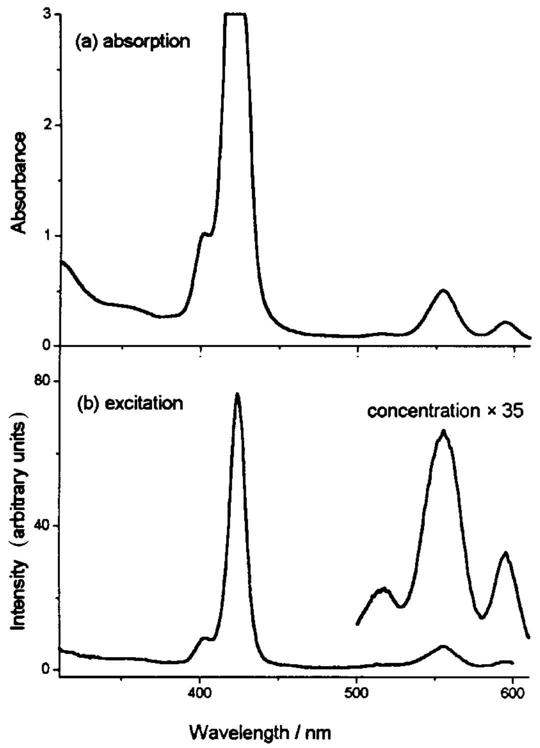

Fig. 2 UV–Vis absorption (a) and excitation (b) spectra of metalloporphyrin **1** in THF.

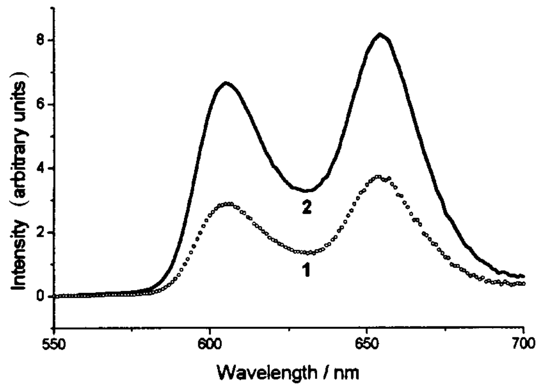

Fig. 3 The corrected emission spectra of **1** (••••) and **2** (——) in THF.

tuted metalloporphyrin (**2**) results in a colour change from purple to red and in a slight broadening of the Soret band. The UV–Vis spectrum of **1** is shown in Fig. 2(a). The Re to bipyridyl MLCT band anticipated at 350 to 420 nm[14] is masked by porphyrin bands.¶ The steady-state fluorescence spectra of **1** and **2** were recorded with excitation either at 355 nm, where both the metalloporphyrin and rhenium-based chromophores are expected to absorb, or at 556 nm, a metalloporphyrin Q-band absorption. The emission spectra (corrected for instrument response) are typical of a metalloporphyrin with peaks at 606 and 656 nm. The emission intensities of solutions of **1** in THF, using either 355 or 556 nm excitation, are *ca.* 50% lower than solutions of **2** which have an equal absorbance at the excitation wavelength (Fig. 3). The excitation spectrum of **1** [Fig. 2(b)] is in good agreement with the UV–Vis absorption spectrum [Fig. 2(a)]. Emission from the ^{3}MLCT excited state of $Re(CO)_3(bpy)Br$ (bpy = 2,2′-bipyridine) was observed at 620 nm but no emission due to the ^{3}MLCT excited state was detected in this region for **1**.

A preliminary time-resolved absorption and emission study of zinc porphyrin **1** has been carried out in THF solution using a YAG laser with a 10 ns pulse length and excitation at 355 nm. Zinc porphyrin **2** and $Re(CO)_3(bpy)Br$ were studied as controls. No significant differences between the transient spectra of the two zinc porphyrins were seen. The spectra are characteristic of

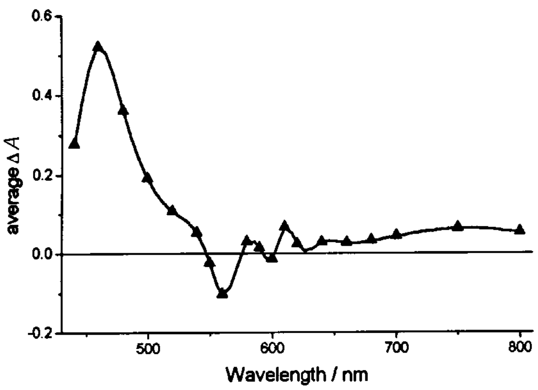

Fig. 4 The transient absorption spectrum of metalloporphyrin **1** recorded 0.8 μs after pulsed excitation at 355 nm with a YAG laser.

the porphyrin $^3(\pi\pi^*)$ excited states with intense absorption at 460 nm (Fig. 4), red-shifted from the Soret absorption of the ground state at 422 nm. Bleaching is seen in the Q-band region and weak, broad transient absorption extends into the near infra-red. There was no evidence of excited state absorption due to Re-to-bipyridylporphyrin MLCT transitions, presumably because these bands would be very weak in comparison with the very intense absorption of the zinc porphyrin transients.

The decays of the $^3(\pi\pi^*)$ metalloporphyrin excited states of both zinc porphyrins fit bi-exponential functions. The $^3(\pi\pi^*)$ excited states of metalloporphyrins are known to decay by triplet–triplet quenching and unimolecular decay resulting in approximately bi-exponential kinetics.[15] Both metalloporphyrins decay with essentially the same lifetimes: $\tau_1 = 3 \times 10^{-6}$ and $\tau_2 = 2 \times 10^{-5}$ s.

Time-resolved emission from the ^{3}MLCT excited state of the model, $Re(CO)_3Br(bpy)$, is detected between 580 and 670 nm with a lifetime of 63 ns. No emission could be detected in this region for zinc porphyrin **1** under these conditions. Either the rhenium-based emission has been quenched by the metalloporphyrin chromophore or the lifetime of the emission has become shorter than the instrumental limits. For comparison, Slone and Hupp reported that the $Re(CO)_3Cl$ units in their molecular squares with $Re(CO)_3Cl$ "corners" and 5,15-bis(4-pyridyl)porphyrin "sides" had only a structural rather than a direct photophysical role.[9]

The versatility of the synthesis of **1** opens the way to new complexes of the type porphyrin–linker–metal carbonyl with designed spatial arrangement of their components and tunable electronic and photophysical properties. Analogues of **2** with pyridyl groups in place of the bipyridyl have already been synthesised in a similar manner from the amino-porphyrin precursor. Work is currently underway to coordinate these porphyrins to peripheral $W(CO)_5$ groups and to study the interaction of the excited states of the porphyrin chromophore and the pentacarbonyl group.

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Notes and references

‡ Synthesis of **1**: Zinc porphyrin **2** (100 mg, 0.112 mmol) and $Re(CO)_5Br$ (46 mg, 0.112 mmol), were placed in a Schlenk tube equipped with a magnetic flea under Ar. Benzene (15 mL) was added and the solution heated to ≈65 °C with stirring under Ar. After 4 h the solvent was removed under reduced pressure to give **1** in quantitative yield. UV–Vis λ_{max}/nm (pyridine) 409 (sh, ε/dm^3 mol^{-1} cm^{-1} 38 000), 429 (Soret, 465 000), 522 (Q_3, 3200), 562 (Q_2, 17 000) and 602 (Q_1, 10 000). IR (THF) ν_{max}/cm^{-1} 2020 (CO), 1920 (CO) and 1897 (CO). ^{1}H NMR (500 MHz; solvent [$^2H_5$]pyridine; referenced to [$^2H_5$]pyridine at δ 7.1) δ 11.90 (1 H, s, amide NH), 9.41 (1 H, d, *J* 5.88 Hz, bpy^a), 9.22 (1 H, s, bpy^{b*}),

9.16 (2 H, d, J 4.80 Hz, β-pyrrole), 9.10 (2 H, d, J 4.80 Hz, β-pyrrole), 9.07 (4 H, s, β-pyrrole), 8.97 (1 H, d, J 5.88 Hz, bpy^{c}), 8.43 (2 H, d, J 8.43 Hz, bridging phenyl^{d}), 8.37 to 8.26 (m, two protons on phenyl bridge, six *o*-phenyl and two bpy^{e}*), 7.67 (9 H, m, *m*/*p*-phenyl), 7.18 (1 H, d, J 5.13 Hz, bpy^{f}), 2.17 (3 H, s, bpy CH_3). ^{13}C NMR (126 MHz; solvent [$^{2}H_5$]pyridine; referenced to [$^{2}H_5$]pyridine at δ 123.9) δ 198.8 (ReCO), 198.4 (ReCO), 190.46 (ReCO), 164.1 (amide CO), 157.6 (C), 155.7 (C), 154.7 (CH^{a}), 153.3 (CH^{c}), 152.7 (C), 151.1, 146.8 (C), 144.3 (C), 140.8 (C), 139.1 (C), 136.2, 136.0, 135.5 (CH^{e}), 132.8 (CH, β-pyrrole), 132.7 (CH, β-pyrrole), 129.0 (CH), 128.2 (CH^{f}), 127.4 (CH, *m*/*p*-phenyl), 126.0 (CH), 125.8 (CH), 124.2, 123.1 (CH^{b}), 121.8 (C), 121.2 (C), 119.7 (CH^{d}), 21.5 (bpy CH_3). ^{1}H and ^{13}C NMR resonances marked with $^{a-f}$ are correlated in the 2-D ^{1}H–^{13}C HETCOR spectrum. Resonances marked with * are concentration dependent. ES-MS *m*/*z* 1239 (100%, $C_{59}H_{37}N_7O_4ZnBrRe$), 887 [18, M − $Re(CO)_3Br$]. Further characterisation data (including elemental analysis) are supplied as supplementary data (SUP 57579).

§ The spectrum illustrated (Fig. 1) and listed was recorded at 2×10^{-2} mol dm^{-3}. On dilution to 4×10^{-3} mol dm^{-3}, some resonances shift indicating that there is intermolecular interaction between the porphyrin molecules in solution. Note also that in pyridine, the solvent is coordinated to the zinc atom in the porphyrin.

¶ $Re(CO)_3$(diimine)X complexes have extinction coefficients of $2–4 \times 10^{-3}$ dm^{3} mol^{-1} cm^{-1} for the MLCT bands. The porphyrin absorbance is *ca.* 2×10^{4} dm^{3} mol^{-1} cm^{-1} in this region, even at wavelengths where the porphyrin absorbs least.

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