Intramolecular Electron Transfer in Peripherally Metallated Tetraphenyl Porphyrin Derivatives Containing Molybdenum Mononitrosyl Redox Centres

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Picosecond laser spectroscopy measurements on the novel complexes [Mo(NO)(L)Cl(Etpp)] [Etpp = 5-(E-substituted phenyl-10,15,20-triphenylporphyrin; L = hydrotris(3,5-dimethylpyrazol-1-yl)borate, E = para-O, meta-O, ortho-O; para-NH] indicate that the observed fluorescence quenching in these compounds is due to fast ($\tau < 30$ ps) intramolecular charge separation to produce transient species with lifetimes in the range 120–290 ps.

The control of energy and/or charge distribution within molecules or molecular arrays is of fundamental importance in the development of molecular electronic systems.[1–3] In particular, attempts to produce simple models of the early steps in photosynthesis have stimulated much interest in

charge separation processes.[4–7] However, despite the many reported examples of intramolecular electron transfer from porphyrin to organic acceptors such as quinone,[4,8,9] methyl viologen[10] or pyromellitimide,[11] examples of electron transfer to transition metal-based redox centres are very rare. The

Table 1 Redox potentials and transient lifetimes

Compound	$E_f(Mo)/V^a$	$E_f(porph.)/V^a$	Transient lifetime/ps^b	ΔG°/eV CS^c	CR^c
1, E = p-O	−0.31	1.07	220 ± 7	−0.50	−1.38
1, E = m-O	−0.32	1.09	220 ± 44	−0.47	−1.41
1, E = o-O	−0.36	1.07	120 ± 9	−0.45	−1.43
1, E = p-NH	−0.75	1.07	290 ± 110	−0.06	−1.82

^{a} Vs. standard calomel electrode (SCE), measured in dichloromethane containing 0.1 mol dm^{-3} [Bu$^n_4$N]BF$_4$ at a Pt bead electrode. Fc/Fc$^+$ = +0.54(±0.01) V, $E_f(Mo)$ is the first reduction potential associated with the {Mo(NO)} moiety and $E_f(porph.)$ is the first oxidation potential associated with the porphyrin moiety. ^{b} Measured at 740 nm following excitation at 532 nm. ^{c} CS = charge separation; CR = charge recombination.
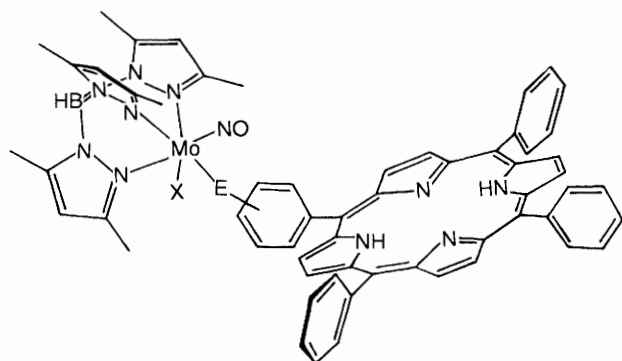
The peripherally metallated tetraphenyl derivatives **1**; X = Cl

ferricinium centres in the oxidised form of 5,10,15,20-(4-ferrocenylphenyl)porphyrin (Fc$_4$tpp) proved ineffective acceptors for an electron from the excited singlet state of the porphyrin moiety.[12] Two explanations were offered as to why electron transfer might be too slow to compete with fluorescence decay. Firstly the reaction may be so exothermic that the electron transfer rate would lie in the inverted region and, secondly, electron transfer to metal-centred electron acceptors may be inherently slow. Electron transfer to a d^{10} metal centre has since been demonstrated in the case of Ag$^+$ bound to a cyclic polyether attached to a porphyrin.[13] In our laboratories we have been studying the intramolecular interactions between non-adjacent but linked metal-containing redox centres.[3,14–21] In order to establish whether, unlike ferricinium, a molybdenum mononitrosyl centre could act as an electron acceptor towards singlet porphyrin we have prepared a series of peripherally molybdenated tetraphenylporphyrin derivatives **1**.†

The mono-functionalised species, 5-(hydroxyphenyl)-10,15,20-triphenylporphyrin (HOtpp) and 5-(aminophenyl)-10,15,20-triphenylporphyrin (H$_2$Ntpp), carrying substituents in the ortho-, meta- and para-positions, were synthesised following known procedures[22–24] and reacted with [Mo(NO)(L)Cl$_2$] to give the peripherally metallated tpp derivatives [Mo(NO)(L)Cl(Etpp)] **1**, (E = o-, m- or p-O or NH). Single crystal X-ray structural studies have been carried out on **1**, (E = p-O, o-O and o-NH) to confirm their formulations.[25] The Mo–porphyrin centroid distances are respectively 9.203, 6.689 and 6.524 Å in these three complexes.

Since the Mo(NO) moiety can potentially act as an electron acceptor we were especially interested in the observation that the normal fluorescence of the porphyrin species was quenched in the peripherally metallated species. Preliminary picosecond spectroscopic studies have thus been carried out on **1**, E = o-, m- and p-O, p-NH) to determine whether charge

† The new compounds have been characterised by elemental analyses, IR, NMR and mass spectroscopy and by electrochemical measurements.
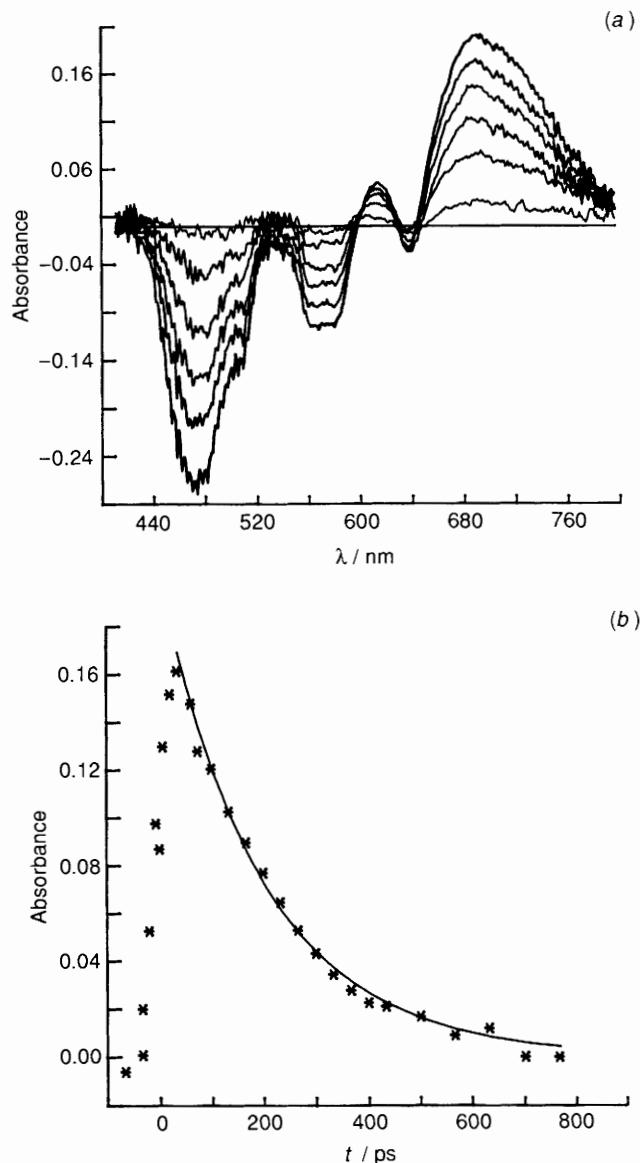

Fig. 1 (a) Time-resolved spectrum of **1**, E = para-NH, with delay times of 30, 100, 170, 240, 440 and 750 ps. (b) Kinetic trace observed at 740 nm for **1**, E = para-O.

separation is occurring in these systems. Time-correlated single-photon-counting studies of dimethylformamide solutions indicate that the fluorescence lifetimes of the molybdenated porphyrins are <15 ps, compared to ca. 12 ns measured for non-molybdenated models (MeOtpp), although there is evidence of a very minor long-lived (i.e. 10 ns) component which is ascribed to a trace (non-molybdenated) impurity. A typical picosecond time-resolved absorption spectrum is shown in Fig. 1. The transient species is non-luminescent and

cannot be attributed to a short-lived singlet state. The characteristic absorption at 740 nm in the spectrum provides evidence for the fast ($\tau < 30$ ps) formation of the porphyrin radical cation which decayed with a lifetime in the range 120–290 ps following first-order kinetics as shown in Fig. 1. The lifetimes are presented in Table 1 for the compounds studied.

We have found that very fast charge separation occurs over a distance of ca. 1 nm in these peripherally metallated porphyrins, but that charge recombination is relatively slow. A number of reasons may be proposed to account for this difference in rates. The $\Delta G°$ value for charge recombination may lie in the inverted region, the rates may reflect processes such as slow solvent reorganisation,[26] and it is possible that structural changes associated with the oxidation of the peripheral redox centre may be rate-limiting in these systems. Regarding this last possibility it is notable that the precursor molecules contain 16-electron molybdenum centres in which an sp^2 donor atom (O or N) allows mesomeric contact between the molybdenum centre and the aryl ring of the tetraphenyl-porphyrin moiety.[27–29] In the charge-separated species it would be expected that a 17-electron molybdenum centre bound to an sp^3 donor atom would be present, leading to rather different geometric arrangement.[30] Further studies are required to determine the extent of any geometric changes following charge separation in these systems.

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