A New Approach to the Assembly of Electron Donor–Spacer–Acceptor Systems

Christopher A. Hunter,[a] Jeremy K. M. Sanders,*[a] Godfrey S. Beddard,[b] and Stuart Evans[b]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*

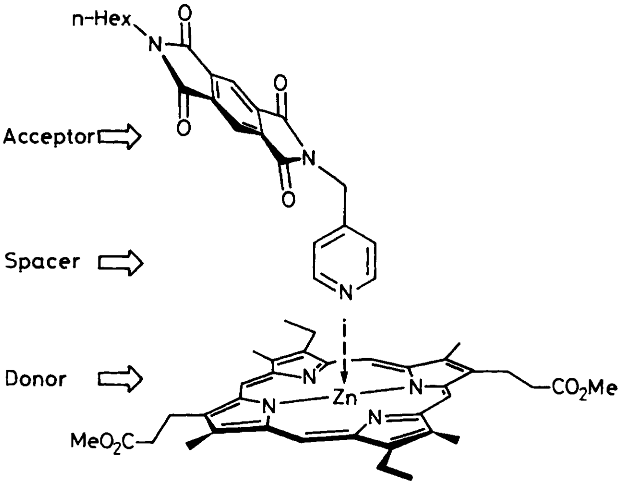
[b] *Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.*

A new range of electron donor–spacer–acceptor systems has been assembled using co-ordination chemistry to link the subunits; rates of photo-induced electron transfer to the same acceptor ligand imply that tetraphenylporphyrins and octa-alkyl porphyrins have different solvent reorganisation energies.

The design of an artificial photosynthetic system requires that we understand the factors which control the rates of electron transfer reactions.[1,2] Despite considerable efforts since Marcus first proposed his theory in 1956,[1] we still cannot use the theory on a quantitative or predictive basis. There are a large number of variables in the Marcus equation and most of these are inter-related so that it is almost impossible to vary any one factor independently. Consequently, the results obtained on any particular system do not correlate well with those obtained for different systems. The rates of electron transfer even for closely related systems can show a dramatic variation for no obvious reason, as we shall show. Many elaborate covalent systems, requiring much synthetic effort, have been described and have produced important information;[2] ultimately, however, the results have lacked generality. In this communication, we present a new versatile approach to the assembly of electron donor–spacer–acceptor systems. We use co-ordination[3,4] rather than covalent chemistry to link the organic components, giving the following attractive features. (i), The range of systems which can be investigated is not severely limited by the synthetic route, (ii), good conformational control is achieved and, (iii), a closely controlled range of systems can easily be studied because the electron donor, the electron acceptor, the spacer, and the solvent can all be varied independently.

Figure 1 illustrates our approach with Zn meso-II-porphyrin dimethyl ester (ZnDME). The ligands were synthesised by the condensation of acid anhydrides with primary amines (Scheme 1). For example, (**2**) was synthesised by refluxing equimolar quantities of pyromellitic anhydride, n-hexylamine and 4-aminomethyl pyridine in dry dimethylformamide (DMF) for 4 h. The products (**1**)—(**3**) were separated by column chromatography and recrystallised from CH_2Cl_2/hexane.† The pyridine group [or other spacer, as in (**4**)] confers the co-ordination properties, while the hexyl group confers solubility on the ligand.

When excess ligand was added to a solution of ZnDME in CH_2Cl_2, the porphyrin fluorescence was completely quenched by intramolecular photoinduced electron transfer from the porphyrin to the bound ligand (Figure 1). The binding

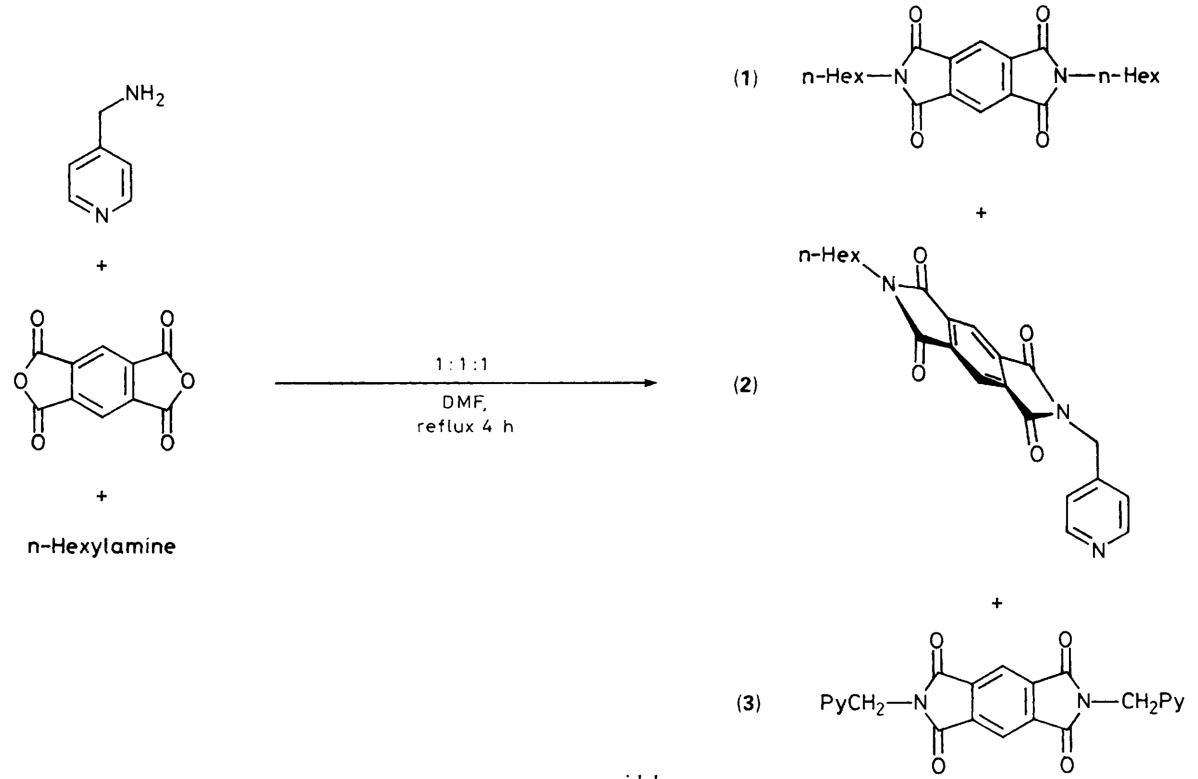


n-Hex = n-hexyl

Figure 1. An electron donor–spacer–acceptor assembly.

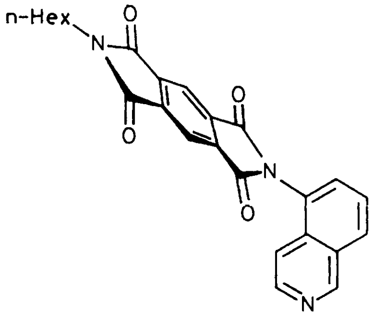
---

† All new compounds gave satisfactory NMR and mass spectra.



py = pyridyl

Scheme 1



(4)

Table 1. Rate constants of charge separation k_s and charge recombination k_r for ZnDME and ZnTPP.[a]

	ZnDME	ZnTPP
k_s^b	213	53.3
k_r	6.10	9.40
k_{SV}^c	6.35	3.81

[a] Units are 10^8 s^{-1}, measured in dichloromethane solution at 294 K. [b] k_s was measured from the experimental decay rate k_e as $k_s = k_e - k_f$ where k_f, the decay rate constant in absence of quenching ligand, was 6.25×10^8 for ZnDME and 3.71×10^8 for ZnTPP. [c] Predicted decay rate constants in the presence of Stern–Vollmer quenching of the porphyrin singlet state, $k_{SV} = k_f$[ligand] where the diffusion controlled rate constant $k_q = 10^{10}$ s^{-1}, [ligand] $= 10^{-3}$ M.

constants for the complexes studied (as observed by shifts in absorption and emission spectra) were all of the order 10^{-3} mol^{-1} dm^3 so that we were able to work at concentrations ($\sim 10^{-3}$ M) at which collisional (Stern–Vollmer) quenching of the excited singlet states was not important.‡ Furthermore, addition of a stronger binding ligand, such as piperidine, to the system shown in Figure 1 displaces (**2**) and fully restores the porphyrin fluorescence, giving these systems potential as molecular electron transfer switches.

We have synthesised a range of ligands, using different co-ordinating spacers, solubilising groups and electron acceptors. Combining these ligands with a series of zinc porphyrins, we have investigated the rates of electron transfer reactions in five solvents. In this communication, we note two interesting results which illustrate the power of the approach and a degree of hitherto unappreciated subtlety in the behaviour of electron donor–spacer–acceptor systems. Using picosecond absorption and emission spectroscopy, we measured the rate of electron transfer (k_s) from ZnDME to (**2**) to be five times faster than the corresponding rate for the transfer from zinc tetraphenyl porphyrin (ZnTPP) (Table 1). The charge recombination steps (k_r) are slower, by 5 to 50 times, than charge separation.

The two porphyrins have similar redox potentials§ and we suggest that the unusual disparity between these two systems

---

‡ A control experiment using (**1**), an acceptor molecule lacking a co-ordinating group, showed essentially no quenching of porphyrin fluorescence, confirming that the electron transfer reactions in the porphyrin–ligand complexes are intramolecular.

§ Redox values were measured *vs.* a standard calomel electrode (SCE) in dichloromethane with tetrabutylammonium tetrafluoroborate as electrolyte. Ferrocene was used as a reference redox. ZnDME: $-\Delta G_s$ 665, $-\Delta G_r$ 1445 mV; ZnTPP: $-\Delta G_s$ 595, $-\Delta G_r$ 1405 mV.

may be due to a difference in the reorganisation energy, λ; this could result from differences in solvation or solvent mobility in the two complexes. Alternatively, differences in the charge distributions of the porphyrin radical cations may be responsible.[5] Steric factors *per se* seem unlikely to be the cause of the difference: the geometries of the two adducts appear identical, and there is very little difference in closest-approach distances between donor and acceptor. The ligand bound to ZnTPP is slightly more constrained in rotational motion but it seems unlikely that this could affect electron transfer.

A second significant result is that acceptor (**4**) behaves almost identically to (**2**) when bound to ZnDME: both k_s and k_r are about 25% slower for (**4**), suggesting that an aromatic pathway does not speed up the electron transfer process.[6] A through-space pathway may also be important.[4] Clearly, the volume of data generated on systematically variable systems should make this approach exceedingly powerful and should clarify the nature of photoinduced electron transfer reactions.

We thank the D.E.N.I. and the S.E.R.C. for financial support.

Received, 21st August 1989; Com. 9/03551F

References

1 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.

2 R. J. Harrison, B. Pearce, G. S. Beddard, J. A. Cowan, and J. K. M. Sanders, *Chem. Phys.*, 1987, **116**, 429; J. A. Cowan, J. K. M. Sanders, G. S. Beddard, and R. J. Harrison, *J. Chem. Soc., Chem. Commun.*, 1987, 55; G. L. Closs, L. T. Calcaterra, N. Green, K. Penfold, and J. Miller, *J. Am. Chem. Soc.*, 1986, **108**, 3673; A. D. Joran, B. A. Leland, P. M. Felker, A. H. Zewail, J. J. Hopfield, and P. B. Dervan, *Nature*, 1987, **327**, 508; M. R. Wasielewski, M. P. Niemczyk, W. A. Svec, and M. P. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 1080; D. Gust, T. A. Moore, P. A. Liddell, G. A. Nemeth, L. R. Makings, A. L. Moore, D. Barrett, P. J. Pessiki, R. V. Bensasson, M. Rougee, C. Chachaty, F. C. De Schryver, M. Van der Auweraer, A. R. Holzwarth, and J. S. Connolly, *ibid.*, 1987, **109**, 846; K. W. Penfield, J. R. Miller, M. N. Paddon-Row, E. Cotsaris, A. M. Oliver, and N. S. Hush, *ibid.*, 1987, **109**, 5061.

3 Electron transfer between metal centres that are connected by co-ordinated ligands is well known. See, for example: T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163; R. L. Blackbourn and T. J. Hupp, *J. Phys. Chem.*, 1988, **92**, 2817; G.-H. Lee, L. D. Ciana, and A. Haim, *J. Am. Chem. Soc.*, 1989, **111**, 2535; M. M. Zulu and A. J. Lees, *Inorg. Chem.*, 1988, **27**, 1139.

4 H. L. Anderson, C. A. Hunter, and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1989, 224.

5 J. Fajer and M. S. Davis, in 'The Porphyrins,' vol. IV, ed. D. Dolphin, Academic Press, 1979, p. 197.

6 M. N. Paddon-Row, A. M. Oliver, J. M. Warman, K. J. Smit, M. P. de Haas, H. Overing, and J. W. Verhoeven, *J. Phys. Chem.*, 1988, **92**, 6958; P. Finckh, H. Heitele, M. Volk, and M. E. Michel-Beyerle, *ibid.*, 1988, **92**, 6584.