Modelling the Photosynthetic Reaction Centre: Photoinduced Electron Transfer in a Pyromellitimide-bridged 'Special Pair' Porphyrin Dimer

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Coproporphyrin-I has been bridged across one face by mesoporphyrin-II and across the other by a pyromellitimide, the resulting doubly-bridged compound showing rapid electron transfer between the 'special pair' porphyrin dimer and the pyromellitimide acceptor; both the excited singlet and charge-separated states have been observed in picosecond absorption and emission experiments, and a closely related side-by-side analogue lacks these 'special pair' properties, electron transfer being *ca.* 1000 times slower.

The primary step in bacterial photosynthesis involves electron transfer from an excited 'special pair' of bacteriochlorophyll molecules to an electron acceptor within the reaction centre.[1] There are now many synthetic analogues containing a monomeric porphyrin covalently linked to an acceptor,[2—8] but we are not aware of any that contain a dimeric unit in a well defined geometrical relationship.[9] We now report the synthesis and some properties of (**1**), a molecule that consists of a cofacial porphyrin dimer bridged by a pyromellitimide electron acceptor. We also describe the side-by-side analogue (**2**) which has very different properties.

The synthesis (Scheme 1) builds on our earlier syntheses[6,10] of the pyromellitimide-bridged porphyrin (**3**) and the cofacial dimer (**4**). The key step is reaction, under high dilution, of 1 mol. equiv. of coproporphyrin-I tetra-acid chloride (**5**) with a solution containing 1 mol. equiv. of the mesoporphyrin-II diol (**6**) and 2 mol. equiv. of benzyl alcohol. The only cyclic products, obtained in a combined yield of 15%, are the '*trans*' cofacial dimer (**7**) and the '*cis*' side-by-side isomer (**8**).†

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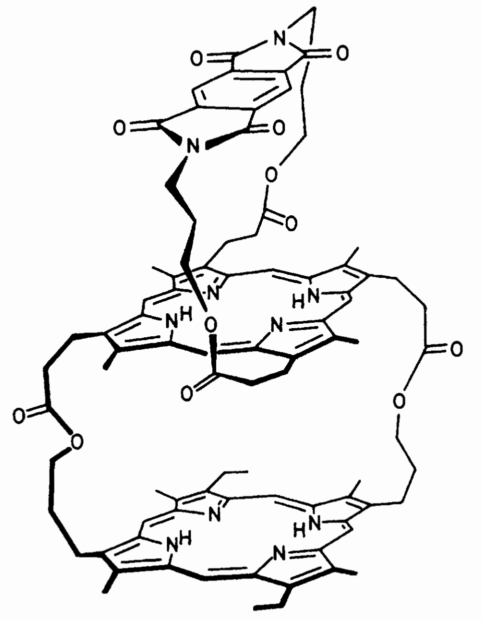
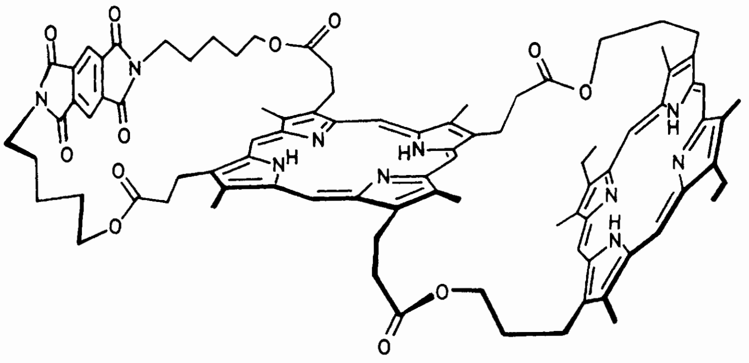
† All new compounds had satisfactory spectroscopic properties and mass spectra.



(1)



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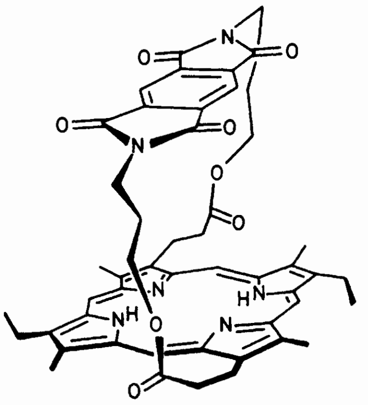

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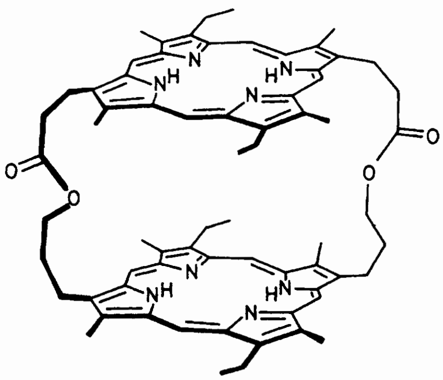

(4)

Following debenzylation (H_2, Pd black, 92%), the bis acids (**9**) and (**10**) were separated by preparative t.l.c.‡ Addition of a pyromellitimide bridging group gave (**1**) and (**2**)§ in 38% yield.

This statistical route is less elegant than the alternative approach which uses differentially protected esters of coproporphyrin-I.[11] However, it has the merits not only of brevity and simpler starting materials but it also provides analogues with radically different geometry.

Both (**1**) and (**2**) are produced as a pair of diastereoisomers. N.m.r. spectroscopy of (**1**) shows that the diastereoisomers have similar geometries, the porphyrin moieties being arranged in the same offset, but closely stacked, manner that is characteristic of (**4**) and other cofacial dimers.[12]¶ Preliminary reactions using zinc acetate in CH_2Cl_2–MeOH reveal that the outer porphyrin face is metallated readily, while the centre face, being sterically protected, can only be metallated with difficulty. This result should allow an easy entry into mixed metal derivatives analogous to the dimers we have recently described.[10]

As might be expected, the fluorescence decay profile and n.m.r. spectrum of (**2**) are not readily interpreted in terms of a single geometry. An even spread of *meso* proton chemical shifts within the range δ 8—10 is indicative of the type of orientation shown. Metallation experiments confirm that both porphyrin faces are freely accessible to solvent.

Compound (**3**) exhibits a 'normal' electronic absorption spectrum for a porphyrin, while the simple cofacial dimer (**4**)

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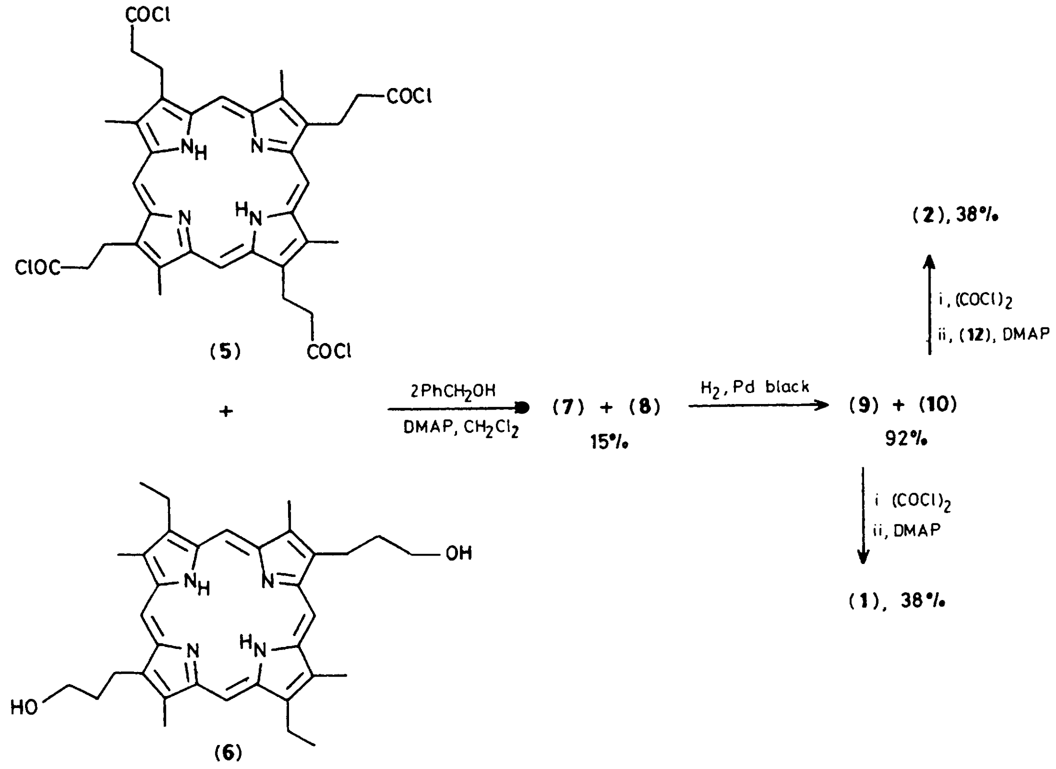
‡ Reactions of (**5**) and (**6**) in the absence of benzyl alcohol did not give significant yields of (**9**) and (**10**) after workup.

§ This geometry needs a longer pyromellitimide linking chain but this has only a small effect on the photochemistry.[6,13]

¶ This conclusion is based on the observation that half of the *meso* proton signals are strongly shifted upfield to δ 7.6—8.1, while the remainder are found at δ 9.1—9.5.



Scheme 1. DMAP = 4-dimethylaminopyridine.

Table 1. U.v.-visible absorption properties.[a]

	$\lambda_{max.}$/nm		
Compound	Pyro	Soret	Q
(1)	236	386	504, 536, 573, 626
(2)	236	392	500, 533, 569, 622
(3)	234	399	498, 533, 567, 621
(4)	—	385	501, 535, 569, 623

[a] CH_2Cl_2 solution.

Table 2. Fluorescence properties and electron transfer rates.

Compound	ϕ_f,[a] rel.	k_{sep}/s^{-1} [c]	k_{rec}/s^{-1} [c]
(1)	5×10^{-3}	$(1.1—3.6) \times 10^{11}$	$(8.8—78) \times 10^9$
(2)	0.24	$(3.8—6.5) \times 10^8$	$<10^7$
(3)[b]	5×10^{-3}	$(5—80) \times 10^{10}$	$(4—100) \times 10^9$
(4)	1.0	$<5 \times 10^6$	—
(10)	0.94	—	—

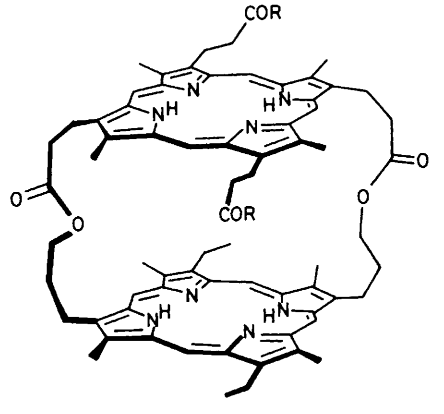
[a] Excitation at Soret wavelength; fluorescence at 626 nm. [b] Fluorescence at 621 nm. [c] Rates are solvent dependent, being fastest in non-polar solvents; excitation at 576 nm.

shows evidence for porphyrin–porphyrin interactions in its blue-shifted Soret and red-shifted Q bands (Table 1). The spectrum of (**1**) is similar to that of (**4**), whereas the side-by-side analogue (**2**), with smaller band shifts, shows evidence for much weaker porphyrin–porphyrin interactions.

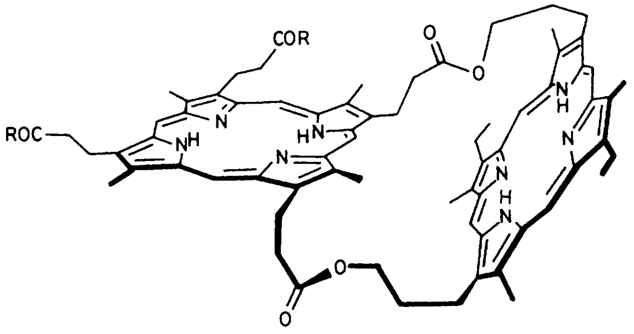
The most notable characteristic of (**1**), however, is its remarkably low fluorescence intensity (Table 2). Picosecond spectroscopy shows that fluorescence quenching in (**3**) and related bridged porphyrins is due to electron transfer from the excited porphyrin to the attached acceptor (Scheme 2 and Table 2).[7,13] Given that (**4**) exhibits fluorescence that is comparable to that from monomeric porphyrins, one might have expected substantial fluorescence from the outer porphyrin face of (**1**), even if the centre face were quenched by electron transfer. The fact that fluorescence from both faces is so effectively quenched demonstrates that, photochemically, the two porphyrins are acting in concert as a 'special pair', with fast dipole–dipole energy transfer coupling the porphyrin excited states. In the charge separated state, electron transfer between P and P^+ should occur rapidly, perhaps at a rate comparable with P^+–A^- recombination. In this sense the unpaired electron can be thought of as delocalised over both porphyrins. By contrast, adding the pyromellitimide acceptor to the side-by-side dimer (**10**) leads to relatively little fluorescence quenching in (**2**), and slow electron transfer.

These conclusions are supported by picosecond absorption and emission measurements (Table 2). The S_1 excited states of (**1**) and (**3**) are extremely short lived as a result of electron transfer; the resulting charge-separated states are also rather short lived. By contrast, the simple cofacial dimer (**4**) and the '*cis*' molecule (**2**) have long lived excited states and comparatively slow rates of electron transfer.

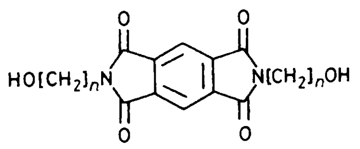
The results reported here demonstrate that mere proximity between donor and acceptor is not a sufficient condition for



(7) R = OCH$_2$Ph
(9) R = OH



(8) R = OCH$_2$Ph
(10) R = OH



(11) n = 3
(12) n = 5

electron transfer. There is also a strong geometrical requirement.

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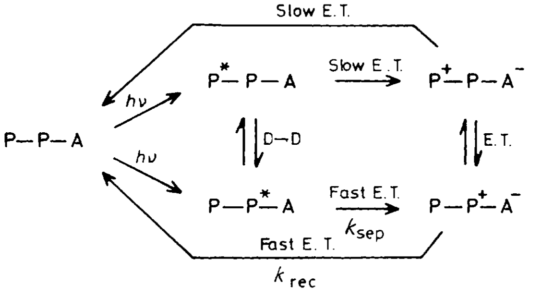

D–D = fast dipole–dipole energy transfer
E.T. = electron transfer

Scheme 2

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