Pyromellitimide-Bridged Porphyrins as Model Photosynthetic Systems. 1. Synthesis and Steady State Fluorescence Properties.

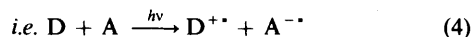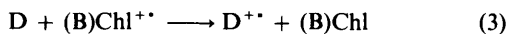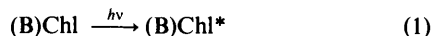James A. Cowan and Jeremy K. M. Sanders *
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A two-step synthesis of pyromellitimide-bridged porphyrins is described. These compounds offer a convenient route to model photosynthetic systems of predetermined geometry. Very strong quenching of the fluorescence emission bands on irradiation at the Soret wavelength is suggestive of electron transfer interactions.

Electron transfer reactions are of paramount importance for the proper functioning of living systems, one of the most important examples of such phenomena being photosynthesis. Photosynthesis involves energy trapping of sunlight and the use of this energy to produce a potential gradient *via* charged species which can then drive slower biochemical processes leading to chemical products.

The photosynthetic apparatus of green plants, involving two photosystems which contain chlorophyll (Chl), is more complicated than that for bacteria which has one photosystem containing bacteriochlorophyll (BChl). However the basic reaction scheme for each photosystem (PS) is similar and can be summarised thus:
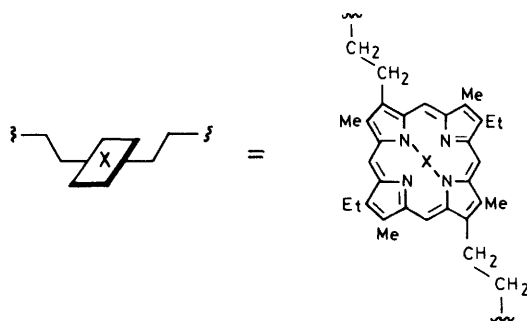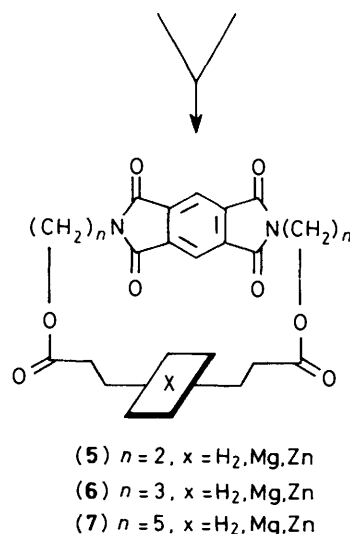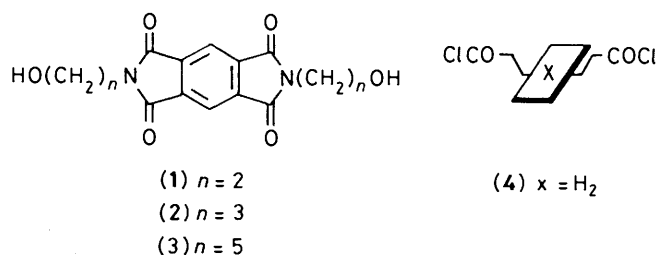
$$(B)Chl \xrightarrow{h\nu} (B)Chl^* \tag{1}$$

$$(B)Chl^* + A \longrightarrow (B)Chl^{+\cdot} + A^{-\cdot} \tag{2}$$

$$D + (B)Chl^{+\cdot} \longrightarrow D^{+\cdot} + (B)Chl \tag{3}$$

$$i.e.\ D + A \xrightarrow{h\nu} D^{+\cdot} + A^{-\cdot} \tag{4}$$

The terminal electron accepting unit in bacteria and PS-II in plants is thought to be a quinone or Fe–quinone complex. This has led to the synthesis of several pendant type porphyrin quinone laboratory models[1–6]; however, such systems suffer from two main disadvantages. Firstly the electronic properties of tetraphenylporphyrin (TPP) complexes, which are often used due to their ease of synthesis, differ appreciably from β-substituted porphyrins. Primarily, however, the attachment of a quinone to a porphyrin with a single loose sidearm leads to great difficulties in interpreting the importance of porphyrin–quinone geometry relative to the photochemical event. We have, in our laboratory, tried to circumvent these problems by synthesizing quinone and methyl viologen bridged mesoporphyrins of predetermined geometry.[7–10] However, both of these systems suffer from synthetic or aggregation problems, and the metallated species suffer co-ordination complications.

We have now synthesized a series of pyromellitimide-bridged porphyrins which are very amenable synthetically and have few co-ordination or aggregation problems.

Pyromellitic anhydride is an electron accepting molecule with an $E_0 = -0.55$ V[11] which is only slightly lower than that of benzoquinone $E_0 = -0.51$ V[12] and moreover the bis-imide derivative can be readily made in a one step reaction[13] from pyromellitic dianhydride and terminal amino alcohols to give diols (1)—(3) suitable for bridging with the meso diacid.

Results and Discussion

Although yields of 94% have been reported[13] for the synthesis of the bis-imide diol (1) we did not achieve more than 53% yield using these procedures in the synthesis of (1)—(3). High dilution

(1) $n = 2$
(2) $n = 3$
(3) $n = 5$

(4) $x = H_2$

(5) $n = 2$, $x = H_2$,Mg,Zn
(6) $n = 3$, $x = H_2$,Mg,Zn
(7) $n = 5$, $x = H_2$,Mg,Zn

Scheme.

coupling[14] of these diols with mesoporphyrin II bis-acid chloride gave the bridged compounds in reasonable yields (35—42%) [see the Scheme]. The reaction could be carried out in dichloromethane with 10% DMF to solubilise the diol.

The synthesis of the short chain ($n = 2$) compound (Scheme)

Table 1. Fluorescence of pyromellitimide-bridged porphyrins[a]

Compd.	Relative fluorescence[b] ($\times 10^{-3}$)	Compd.	Relative fluorescence[c] ($\times 10^{-3}$)	Compd.	Relative fluorescence[d] ($\times 10^{-3}$)
H$_2$ (5)	1.6	Mg (5)	5.6	Zn (5)	1.5
H$_2$ (6)	5.5	Mg (6)	8.6	Zn (6)	5.0
H$_2$ (7)	13.4	Mg (7)	1.3	Zn (7)	6.5

[a] Relative to corresponding H$_2$, Mg or Zn mesoporphyrin II dimethyl ester. [b] At 620 nm. [c] At 580 nm. [d] At 570 nm.

Table 2. ^{1}H Chemical shifts in pyromellitimide bridged porphyrins

	δ_{NH}	δ_{Hpyro}	δ_{Hpyro} (+Py)
Pyromellitimide		8.0	
Meso-II-ester	−3.85		
H$_2$ (5)	−4.76	4.38	
Mg (5)		4.22	4.28
Zn (5)		4.3	4.29
H$_2$ (6)	−4.16	6.7	
Mg (6)		5.4	6.68
Zn (6)		6.22	6.76
H$_2$ (7)	−4.08	7.3	
Mg (7)		6.1	6.95
Zn (7)		6.4	7.14

also produced ca. 5% yield of a dimeric product, as suggested by the highfield shift of the NH signal in the n.m.r. spectrum. Dimers were not formed when longer chains were used, presumably because the chains were not rigid enough. The resulting free base bridged porphyrins were then metallated with magnesium or zinc by established methods.[15]

Fluorescence experiments were performed on the free base and metallated compounds in order to obtain evidence for charge transfer interactions. Each series of free base or metallated bridged porphyrins was compared with the corresponding unbridged compound as reference. The emission wavelength did not vary in going from unbridged to bridged material. The results are detailed in Table 1, and show quenching of the main emission bands of the free base, magnesium and zinc derivatives of the order of several hundred fold, undoubtedly due to electron transfer interactions. Reference mixtures of free base, magnesium and zinc mesoporphyrin II esters with a pyromellitimide derivative show no significant quenching effects. In order to relate the quenching factors noted above with the inter-chromophore spacing, the geometries of these compounds were studied by n.m.r. spectroscopy using the pyromellitimide proton signal as a probe. This is shifted to higher field by the porphyrin ring current[16] as the bridge draws nearer to the porphyrin. The chemical shifts for the NH protons in the free base porphyrins are also given in Table 2.

For the free base and zinc compounds, fluorescence quenching follows the order $n = 2 > n = 3 > n = 5$, in agreement with the relative chromophore separation determined by n.m.r. With the magnesium derivative, the quenching order is $n = 5 > n = 2 > n = 3$ which is at slight variance with the order determined by n.m.r. Since the photochemical event will be governed by the most favourable geometry for the interacting groups, which may not be the time averaged configuration determined by n.m.r., the discrepancy can be understood in terms of the longer, more flexible $n = 5$ chain allowing closer approach to the porphyrin, presumably by transient co-ordination to magnesium. It can be noted that n.m.r. results show, in general, a smaller inter-chromophore spacing for the magnesium as compared to the zinc complexes.

Addition of pyridine leads to shifts in $\delta(H_{pyro})$ as shown in Table 2. This implies[16] the presence of some intramolecular co-ordination in the $n = 3$ and $n = 5$ metal derivatives. However such co-ordination is again certainly transient since the absorption spectra show no shifts in the Soret region characteristic of metal-ligand binding and further, no significant change was observed in fluorescence quenching on addition of external ligands. CPK models also demonstrate the difficulty in rotating the bridge in these molecules.

An interesting point arises from the ease of metallation of these compounds. Whereas the quinone and bipyridyl bridged porphyrins readily incorporate zinc and magnesium, the pyromellitimide compounds do not, more especially in the case of magnesium. It is possible that whereas in the case of quinone or bipyridyl the metal is entering a relatively polar environment with a perpendicular bridge displaying a co-ordinating group to the incoming metal, in the case of pyromellitimide we have, in addition to the statistical restriction with one face blocked, the bridging molecule face to face with the porphyrin, generating a relatively non polar environment. The n.m.r. data for the free base porphyrins also indicate that the NH protons lie in the shielded region of the pyromellitimide moiety, as indicated by the high field shift relative to mesoporphyrin II ester.

A final point to note from the n.m.r. spectra is the unusually large separation of the meso-H signals in the bridged molecule as compared to the meso ester. In the quinone or bipyridyl series this is observed[16b] only where intramolecular co-ordination forces the bridge to lie in a strongly constrained manner.

In conclusion, the use of pyromellitimide diols as bridging units offers a quick and convenient two-step synthesis of model photosynthetic systems of controlled geometry, for future study by a variety of physical methods.

Experimental

^{1}H N.m.r. spectra of the pyromellitimide diols were obtained at 60 MHz (Varian EM 360) in [^{2}H$_6$] DMSO, and those of porphyrin compounds were obtained in deuteriochloroform at 400 MHz using a Bruker WH 400 instrument. Chemical shifts are in δ units (p.p.m. from SiMe$_4$). High resolution mass spectra were obtained on an MS.50 instrument. Melting points were recorded on a Buchi melting point apparatus. The bridged porphyrins were purified by elution through 0.04—0.063 mm silica. Metallated porphyrins were purified over a column of neutral alumina UG1.

Fluorescence spectra were obtained on a Perkin-Elmer Fluorescence Spectrometer MPF-3. Samples for study were prepared in dichloromethane solution and the concentration adjusted until an absorbance of 0.5 ± 0.05 was obtained at the Soret absorption wavelength. Emission spectra were then obtained and the results corrected to account for slight absorbance differences.

Dichloromethane was distilled from either calcium hydride or phosphorus pentaoxide. AnalaR DMF was dried over barium oxide and molecular sieves.

Synthesis. N,N'-Bis(2-hydroxyethyl)pyromellitimide (1).*—Pyromellitic dianhydride (1.82 g) and 2-aminoethanol (1 ml) were added to DMF (8 ml). The solution was refluxed for 4 h and poured into ice–water (150 ml), to give a white precipitate. After filtration, the solid was recrystallised from DMF–water to give (1) (0.94 g, 46%), m.p. 278—279 °C (lit.,[13] 271 °C), δ 8.0 (2 H, s), 4.6 (2 H, br), and 3.6 (8 H, s).

N,N'-Bis(3-hydroxypropyl)pyromellitimide (2).—Similarly, pyromellitic dianhydride (2.14 g) and 3-aminopropanol (1.53 ml)

* Pyromellitimide is benzene-1,2,4,5-tetracarboxdi-imide.

in DMF (10 ml) gave (2) (1.4 g, 53%) m.p. 240—241 °C, δ 8.0 (2 H, s), 4.3 (2 H, br), 3.5 (8 H, m), and 1.8 (4 H, m) (Found: C, 57.5; H, 4.6; N, 8.3. $C_{16}H_{14}N_2O_6$ requires C 57.8; H 4.8; N 8.4%).

N,N'-Bis(5-hydroxypentyl)pyromellitimide (3).—Similarly, pyromellitic dianhydride (1.1 g) and 5-aminopentanol (1.5 ml) in DMF (5 ml) gave (3) (0.525 g, 32%) m.p. 209—210 °C, δ 8.0 (2 H, br), 4.2 (2 H, br), 3.5 (8 H, br) and 1.5 (12 H, br) (Found: C, 61.2; H, 6.0; N, 6.9. $C_{20}H_{22}N_2O_6$ requires C, 61.8; H 6.2; N. 7.2%).

2-Hydroxyethylpyromellitimide Bridged Porphyrin (5).—To a three-necked flask containing dry DMF (50 ml), dry CH_2Cl_2 (100 ml) and dry 4-(N,N-dimethylamino)pyridine (0.7 g), were added slowly via dropping funnels, solutions of (1) (148 g) in dry CH_2Cl_2 (400 ml)–dry DMF (100 ml) and mesoporphyrin II bis-acid chloride in dry CH_2Cl_2 (500 ml).

The acid chloride was prepared by treating mesoporphyrin II (275 mg) in dry CH_2Cl_2 (100 ml) with oxalyl chloride (1 ml) and stirring under N_2(gas) for 1 h. After the removal of the solvent and an excess of oxalyl chloride under reduced pressure and finally high vacuum (the compound was redissolved in a little CH_2Cl_2 and the solvent was again removed under reduced pressure if any traces of oxalyl chloride remained) the acid chloride was redissolved in dry CH_2Cl_2 (500 ml). Solutions were transferred to dropping funnels, under N_2(gas), via two-way needles. The porphyrin solutions were protected from light with aluminium foil and with the whole system under N_2(gas) a steady rate of addition with stirring was maintained over a period of ca. 8 h and then stirred overnight. After removal of the solvent under reduced pressure, the compound was redissolved in CH_2Cl_2 and eluted with CH_2Cl_2–MeOH (95:5) through SiO_2 to give a mixture of two components. The title compound was isolated as the faster running band from 2 mm silica preparative plates using CH_2Cl_2–MeOH (99:1) as the eluant and recrystallised from CH_2Cl_2–MeOH to give (5) (142 mg, 35%) (Found: M^+, 834.3377 $C_{48}H_{46}N_6O_8$ requires M, 834.3360); δ 10.08, 9.92 (mesoH) and -4.76 (NH, br).

The other dimeric component [as suggested by n.m.r. δ 9.45 (mesoH); -5.6 (NH, br)] was isolated (25 mg).

3-Hydroxypropylpyromellitimide Bridged Porphyrin (6).—Similarly, using mesoporphyrin II bis acid chloride (300 mg) and compound (2) (160 mg) gave the title compound, after elution through SiO_2 with CH_2Cl_2 to remove a minor impurity followed by CH_2Cl_2—MeOH (99:1) to give the product. Recrystallisation from CH_2Cl_2—MeOH gave (6) (166 mg, 37%) (Found: M^+, 862.3690 $C_{50}H_{58}N_6O_8$ requires M, 862.3716); δ 10.11, 9.62 (mesoH) and -4.16 (NH, br).

5-Hydroxypentylpyromellitimide Bridged Porphyrin (7).—Similarly, mesoporphyrin II bis acid chloride (300 mg) and compound (3) (206 mg) led to the desired product, after elution through SiO_2 with $CHCl_3$. Recrystallisation from CH_2Cl_2–MeOH gave (7) (205 mg, 42%) (Found: M^+, 918.4316 $C_{54}H_{58}N_6O_8$ requires M, 918.4302); δ 10.1, 9.72 (mesoH), and -4.099 (NH, br).

Procedure for the Introduction of Mg.—The porphyrin (10 mg) was added to dry pyridine (3 ml) containing $Mg(ClO_4)_2$ (20 mg) and the solution was refluxed overnight or until reaction had proceeded to completion as determined by u.v.-visible absorption spectroscopy. The solution of the magnesium porphyrin was poured onto aqueous saturated $Mg(CO_3)_2$, extracted with Et_2O, dried ($MgSO_4$) and reduced to dryness. The solid was redissolved in CH_2Cl_2 and eluted through dry Al_2O_3 with CH_2Cl_2-MeOH (9:1). After removing the solvent, finally under high vacuum, the compound was recrystallised from CH_2Cl_2–pentane. Yields were in the range 80—90%. Products gave satisfactory mass and u.v.-visible spectra.

Procedure for the Introduction of Zn.—The porphyrin (10 mg) was added to CH_2Cl_2 (3 ml)–MeOH (1 ml) containing Zn $(OAc)_2$ (5 mg) and refluxed, with stirring, for 15 min. After removing the solvent and redissolving in CH_2Cl_2, the solution was eluted over dry neutral Al_2O_3 using CH_2Cl_2-MeOH (95:5). Recrystallisation from CH_2Cl_2–pentane gave yields in the range 80—90%. Products gave satisfactory mass and u.v.-visible spectra.

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