'Axial-bonding Type' Hybrid Porphyrin Trimers: Design, Synthesis and Modulation of Redox and Photophysical Properties

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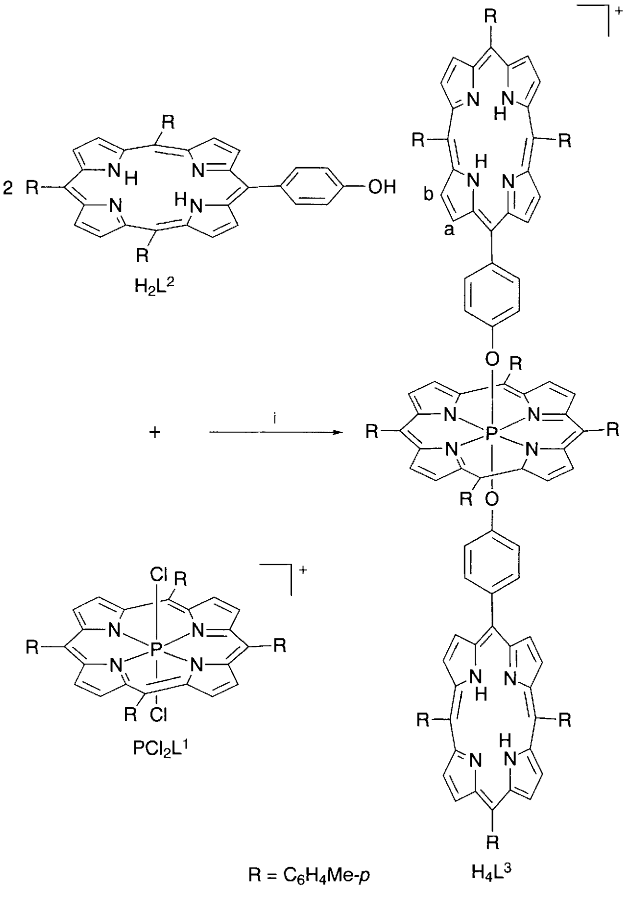
Utilising the axial bond formation capability of a phosphorus(v) porphyrin, new hybrid porphyrin trimers are readily synthesised and a systematic control of their redox and photophysical properties demonstrated.

Porphyrin oligomers have been employed as components of supramolecular structures in studies related to molecular catalysis, molecular electronics, biomimetic photosynthesis *etc.*[1] However, in many such oligomers, the monomeric porphyrin subunits have been fixed at their peripheral *meso* or pyrrole-β carbon position(s) thus necessitating extensive, and often cumbersome, synthetic efforts to achieve a systematic variation of their molecular architecture. During our studies on porphyrin-based photosynthetic model systems,[2] it occurred to us that utilisation of the axial bond (covalent[3]) on the resident central metal ion of a porphyrin could reduce the difficulty involved in the synthesis of porphyrin oligomers. We reasoned that a six-coordinated, bis-axially ligated metalloid–porphyrin can be conveniently employed for the synthesis of homologous porphyrin arrays and that a proper choice of two different porphyrins should result in the formation of hybrid (unsymmetrical) analogues. Axial-bonding type, homologous porphyrin oligomers have been known in the literature but, many of them were obtained only as solid-state polymers.[4] While this manuscript was being prepared, a report describing the synthesis of novel, axial-bonding 'wheel-and-axle' type porphyrin arrays appeared but, even these soluble oligomers were composed of only one type of porphyrin in their arrays.[5] Thus, to the best of our knowledge, hybrid porphyrin oligomers, which are essential for fine-tuning the redox and photophysical properties of supramolecular systems, have not been synthesised so far utilising the axial-bond formation approach. This is achieved in the present study which reports on the synthesis, electrochemistry and fluorescence properties of hybrid trimers in which a phosphorus(v) porphyrin has been axially ligated, *via* aryloxy bridges, with either two free-base (H_4L^3, Scheme 1), zinc(II) (Zn_2L^3) or copper(II) (Cu_2L^3) porphyrins.

Refluxing a pyridine solution containing readily accessible[6] dichloro (5,10,15,20-tetratolylporphyrinato)phosphorus(v) chloride PCl_2L^1 and an excess of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin H_2L^2 for 5 h and evaporating the solvent gave a brown residue which upon purification by column chromatography [silica gel: $CHCl_3$ and $CHCl_3$–MeOH (9/1, *v*/*v*) as eluents] afforded the desired trimer, H_4L^3, as its hydroxide salt,† in ≈ 50% yield (Scheme 1). The dizinc and the dicopper analogues, Zn_2L^3 and Cu_2L^3 were prepared in quantitative yields by treating $[H_4L^3][OH]$ with the corresponding metal acetates in refluxing CH_2Cl_2–MeOH (1 : 1, *v*/*v*) and were purified by column chromatography.

The trimeric porphyrin $[H_4L^3][OH]$ was characterised by mass,† UV–VIS, ^1H NMR (one- and two-dimensional) and ^{31}P NMR spectroscopic methods. The proton decoupled ^{31}P NMR ($CDCl_3$, external H_3PO_4) signal observed for the compound at δ −194, which is in the typical range expected for six-coordinated phosphorus compounds,[7] suggests that the two axial bridges are attached to the central phosphorus atom to complete octahedral coordination. In the ^1H NMR spectrum ($CDCl_3$,



Scheme 1 *Reagents and conditions*: i, pyridine, reflux, 5 h

Table 1 UV–VIS, fluorescence and redox potential data

Compound	$\lambda_{max}{}^a$/nm Q bands	B band	$E_{\frac{1}{2}}{}^b$/V P^V(por)	$H_2/Zn^{II}/Cu^{II}$(por)	$\Phi_f{}^c$
H_2L^2	647, 592, 553, 517	419		1.01, −1.25	0.13
PCl_2L^1	618, 571	445	−0.33, −0.71		0.03
$P(OC_6H_4Me\text{-}p)_2L^1$	610, 566	439	−0.49, −0.95		7×10^{-3}
H_4L^3	648, 612,^{d} 591, 555, 518	442, 420	−0.46, −0.98	1.03, −1.22	6×10^{-4}
ZnL^2	598, 549	422		0.74, −1.40	0.035
Zn_2L^3	618,^{d} 599, 559	442, 424	−0.46, −1.02	0.72, −1.43	2×10^{-4}
CuL^2	570, 539	416		0.88, −1.33	
Cu_2L^3	613, 569, 540	441, 417	−0.46, −1.02	0.94, −1.36	

^{a} Solvent, CH_2Cl_2. Error limit, ±1 nm. ^{b} Measured in CH_2Cl_2, 0.1 mol dm^{-3} NBu_4ClO_4 on a Pt-working electrode *versus* SCE. Error limit, ±0.02 V. ^{c} Solvent, CH_2Cl_2. Error limit, ±10%. ^{d} Shoulder.

$SiMe_4$) the eight equivalent pyrrole-β protons of the phosphorus porphyrin resonate at δ 9.34 as a doublet due to a four-bond coupling with the phosphorus atom ($^4J_{PH}$ = 3.4 Hz). On the other hand, the pyrrole-β proton signals of the free-base porphyrins are shifted upfield (relative to those of H_2L^2 ref. 2) and are also split into a singlet at δ 8.82 (8H) and a pair of doublets at δ 8.59 (4 H) and 7.88 (4 H), $^3J_{HH}$ = 4.8 Hz. This observation is in contrast to observations made earlier for various face-to-face porphyrins including the 'wheel-and-axle' type systems for which a single resonance peak was observed for all the eight pyrrole-β protons present on a given ring.[5] We conclude that, in the case of our trimer, four pyrrole-β protons of type a and four others of type b (both facing the central porphyrin, see Scheme 1), are differently affected by the ring current of the central phosphorus porphyrin, and resonate as two separate doublets and that the remaining eight pyrrole-β protons on the two free bases, being equivalent, resonate as a singlet. It should be noted that this analysis intrinsically assumes a symmetric (but, a non-parallel) orientation of the two axial free bases with respect to the plane of the central porphyrin ring. The assumption is consistent with the general symmetry observed in the ^1H NMR spectrum and specifically, with the symmetry observed for the resonances due to protons on the axial aryloxy bridges [δ 6.83 (d, 4H) for protons *meta* to the 'oxo' group and δ 2.72 (d, 4H) for protons *ortho* to the 'oxo' group; $^3J_{HH}$ = 7.9 Hz] and for those due to the inner imino protons of the axial free-base porphyrins [δ −2.99 (s, 4 H)]. The protons on the aryloxy bridges of this trimer simultaneously experience the shielding effect of the central porphyrin[6a] and the deshielding effect of the axial porphyrins suggesting that the orientation is certainly not of a face-to-face (parallel) type in which case an additive shielding effect as reported for the axial protons of the 'wheel-and-axle' type porphyrins would be expected.[5]

The UV–VIS spectrum of each trimer was found to be similar to that of a solution containing a 2:1 molar ratio of the corresponding precursors (H_2L^2, ZnL^2, $CuL^2:PCl_2L^1$),‡ Table 1. This suggests the absence of an exciton coupling between the porphyrin rings in these trimers and is consistent with the EPR spectrum of Cu_2L^3 which is indistinguishable from that of CuL^2. The electrochemical redox potentials of the three hybrid trimers were also found to be in the same range as those of their corresponding monomeric analogues, Table 1. By contrast, UV–VIS absorption maxima, EPR spectral parameters and redox potentials of face-to-face dimers or oligomers differ considerably from those of the monomers[1c,5] further establishing the unique structural arrangement in our system.

Data given in Table 1 also suggest that while the phosphorus porphyrin in each trimer is reduced at almost the same potential for the three compounds the axial porphyrins are seen to undergo electron transfer reactions at different potentials for the H_4L^3, Zn_2L^3 and Cu_2L^3 species. Similarly, whilst H_2L^2, ZnL^2 and PCl_2L^1 are moderately fluorescent, both H_4L^3 and Zn_2L^3 show weak fluorescence when excited either at 450 nm (phosphorus porphyrin) or at 415 nm (free-base/Zn^{II} porphyrin). The weak fluorescence observed for these bichromophoric complexes can be understood in terms of an energy transfer from the phosphorus porphyrin to the axial porphyrin subunits and a photoinduced electron transfer (PET) in the reverse direction.§ Finally, Cu_2L^3 is non-fluorescent probably due to the presence of paramagnetic copper ions in this system.

In summary, these results suggest that the present method of synthesis is useful for the construction of novel hybrid-type porphyrin arrays and that the redox and photophysical properties of these systems are tuneable systematically. Branched-chain, multi-porphyrin arrays are currently being synthesised adopting the axial-bond formation approach reported here.

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Footnotes

† The FAB-mass spectrum of the compound showed a minor peak at *m/z* 2059 ascribable to $[M + OH]^+$ ($M = H_4L^3$, $C_{142}H_{106}N_{12}O_2P$) thus confirming the presence of OH^- as the counter anion; the major molecular ion peak at *m/z* 2043 ($[M + H]^+$).

‡ $P(OC_6H_4Me\text{-}p)_2L^1$ (ref 6*a*) can also be regarded as a suitable phosphorus-containing model compound for comparative purposes (Table 1).

§ The excitation spectrum of H_4L^3 showed absorption due to the central phosphorus(V) porphyrin in its B-band region, when the fluorescence was monitored at the emission maximum of the free-base porphyrins (650 nm). The free-energy changes for PET from the ground states of the free-base and zinc(II) porphyrins to the singlet phosphorus(V) porphyrin in these trimers were calculated to be −0.53 and −0.80 eV, respectively. Similarly, PET reactions from the singlet excited states of the free-base and zinc(II) porphyrins to the ground-state phosphorus(V) porphyrin were found to be exergonic by 0.40 and 0.87 V, respectively (singlet-state energies of the free-base, zinc(II) and phosphorus(V) porphyrins are 1.89, 2.07 and 2.00 eV, respectively).

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