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Novel Covalently Linked Porphyrin Trimers With Redox-Distinct Properties

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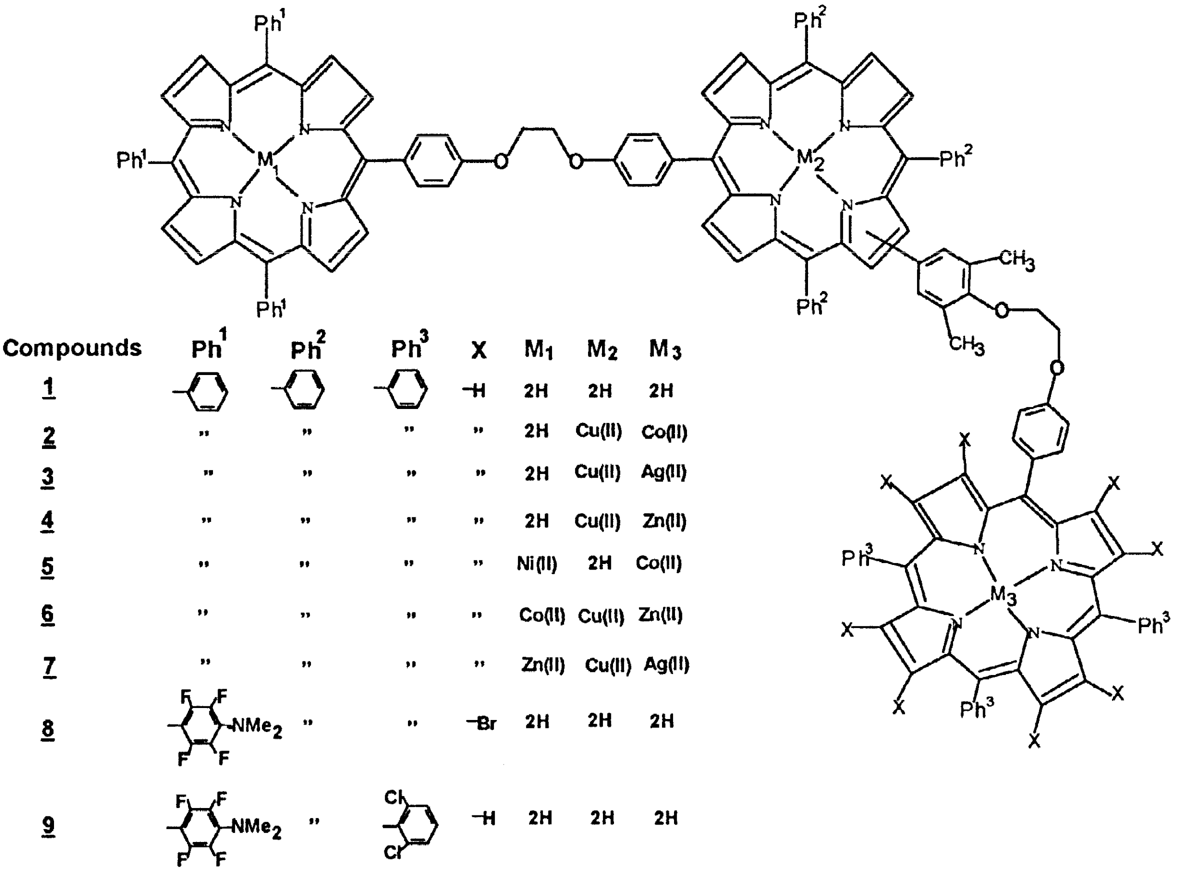
Abstract: *Two novel porphyrin trimers bearing different metal centres and/or different peripheral substituents have been synthesized. These systems display interesting spectral and electrochemical redox properties.* © 1998 Elsevier Science Ltd. All rights reserved.

Diverse porphyrin dimers and trimers have been synthesized to mimic primary functions of natural photosynthesis.[1] These porphyrin assemblies have attracted wide attention in recent years as potential molecular materials for non-linear optics[2] and for molecular scale information storage devices.[3] The nature of the porphyrin unit in the design and synthesis of these molecular assemblies is important in the display of desired properties. *Meso*-tetraphenylporphyrin offers the best molecular motif for the construction of such



Compounds	Ph¹	Ph²	Ph³	X	M₁	M₂	M₃
1				−H	2H	2H	2H
2	"	"	"	"	2H	Cu(II)	Co(II)
3	"	"	"	"	2H	Cu(II)	Ag(II)
4	"	"	"	"	2H	Cu(II)	Zn(II)
5	"	"	"	"	Ni(II)	2H	Co(II)
6	"	"	"	"	Co(II)	Cu(II)	Zn(II)
7	"	"	"	"	Zn(II)	Cu(II)	Ag(II)
8	NMe$_2$	"	"	−Br	2H	2H	2H
9	NMe$_2$	"		−H	2H	2H	2H

Figure: Structure of the trimer porphyrins.

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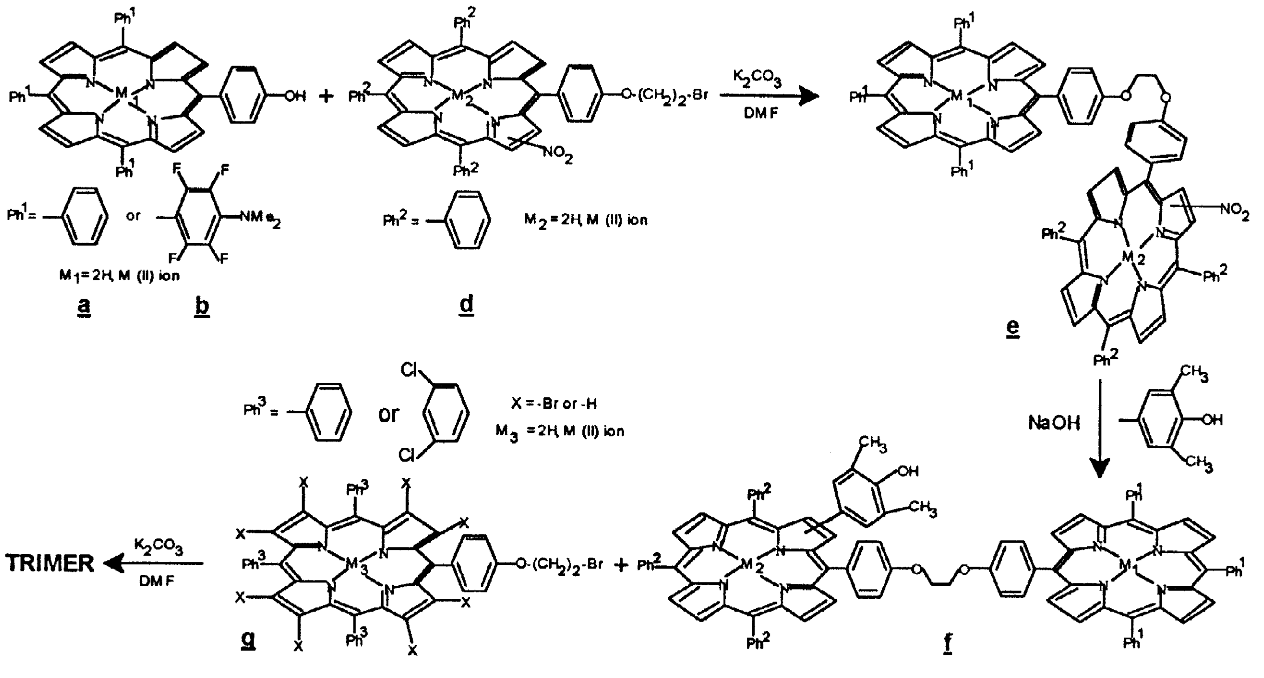
assemblies in view of its ease of synthesis and a wide choice of the modulation of the electronic structure that is possible arising from the substitution of various groups at different peripheral positions. A knowledge of a wide range of photophysical and electrochemical properties of these systems is available and this can easily be exploited for the construction of designer molecular devices. Herein, we describe a strategic synthesis of two types of porphyrin trimers (Figure). One of the types consists of three redox distinct free-base porphyrin units and the other comprises of three porphyrin units with different central metal ions. Both these types contain a flexible covalent bridge and the position of attachment of the covalent links ensures a large number of rotational degrees of freedom.

The syntheses of these trimers essentially follow the nucleophilic substitution reaction of a nitro group(at one of the β-pyrrole carbon atoms) of the preformed dimeric species with substituted phenol followed by condensation of the bromoethoxy derivative of this phenolated dimer with a third hydroxyphenylporphyrin (Scheme). The precursor porphyrin (a) was obtained by condensing respective aldehydes with pyrrole in propionic acid.[4] 5-(4-hydroxyphenyl)-10,15,20-tri(halogenated)phenylporphyrins were obtained by demethylation of the corresponding methoxy derivatives, which was obtained from respective aldehydes and pyrrole following the Lindsey procedure.[5] The porphyrin (b) was synthesised as described earlier.[6] 5[4-(2-bromoethoxyphenyl)]-10,15,20-triarylporphyrin was obtained by stirring a DMF solution of dibromoethane and the respective hydroxyporphyrin in the presence of K_2CO_3.[7] The porphyrin (d) was obtained following the reported procedure.[8] The nitro substituted dimeric porphyrin (e) was synthesized by the method of Little.[7] The dimeric porphyrin (f) was obtained in good yield by refluxing the dimeric-NO_2 compound in 2, 6-dimethylphenol



Scheme: Synthetic routes for the trimer porphyrins.

containing NaOH.[9] Finally, another β-pyrrole substituted/unsubstituted porphyrin (g) was condensed with the dimeric porphyrin (f) to get the desired trimeric porphyrins in ca. 50% yield.

All the compounds were purified either by column chromatography or preparative TLC using silica gel as stationary phase. The compounds were characterized by UV-visible, ^{1}H-NMR and FAB-MS[10] spectroscopies.

Interesting features emerge from the ^{1}H-NMR, optical and electrochemical redox studies of these trimer porphyrins. The introduction of a paramagnetic Co(II) ion in one of the porphyrin units clearly distinguishes the proximal and distal porphyrin units of the trimer. For this purpose, the proton resonances of the inner imino nitrogens are monitored. The presence of Co(II) in the porphyrin unit shifts the imino proton resonances of the neighboring porphyrin unit by 0.3 *ppm* down field relative to the proton resonances of the monomeric porphyrin at -2.75 *ppm*. However, the resonances of the inner imino protons of the distal porphyrin in the trimer remain unaffected by the presence of Co(II) ion. It is noteworthy that the paramagnetic Cu(II) and Ag(II) ions in the porphyrin trimers do not exert any influence on the proton resonances of the neighboring free-base porphyrins or their zinc(II) derivatives. The electronic absorption spectra of the trimers reveal that both the B and Q transitions are marginally red shifted (2-3 nm) and broadened (100-150 cm^{-1}) relative to that observed for the mixture of monomeric constituents. The oscillator strength (f) and absorption coefficient values (ε) of these transitions of the free-base trimers and the metal (II) derivatives were found to be increased nearly three fold compared to those of the corresponding monomers. Importantly, trimers consisting of monomeric porphyrins with large differences in the ground state absorption spectrum cover a wide range of solar spectrum with intense bands at different regions and each moiety could be selectively excited for a specific photochemistry. It is of interest to note that the presence of a non fluorescent porphyrin moiety in the terminus has marginal effect in quenching of the fluorescence from the distal free-base tetraphenylporphyrin moiety (Compound 8 and 9). This is in contrast to that observed for dioxyethylene bridged dimeric species wherein the presence of a non-fluorescent porphyrin moiety (β-pyrrole octabrominated porphyrin or 2, 6-*ortho*dichlorophenyl ring substituted porphyrin) completely quenches the fluorescence of tetraphenylporphyrin moiety due to spin-orbit coupling or other non-radiative deactivation mechanisms.

The cyclic voltammetric (CV) and differential pulse voltammetric(DPV) studies[11] of the trimer porphyrins reveal important features of the redox behaviour of the ring and metal centres of these compounds. The ring redox potentials of the individual porphyrin units constituting the trimer overlap with the neighboring potentials are found to be larger than those expected for a one-electron process. Interestingly, in a few of the trimers, multiple one-electron oxidation and/or reduction potentials are clearly distinguishable with complete reversibility. The appearance of metal centred oxidation and reductions are seen in compounds 2, 3 and 7. The five successive one-electron oxidation waves observed for compound 7 at 545, 800, 890, 1100 and 1270 mV correspond to the oxidation of Ag(II) centre followed by first ring oxidation of Zn(II) and Cu(II) centred porphyrins and second ring oxidation of Zn(II) and Cu(II) porphyrins respectively. The one-electron reductions of compounds 2 and 3 occur at -945 and -1115 mV correspond to the reduction of Co(II) and Ag(II) in the porphyrins respectively. The first and second ring reduction potentials of the free-base and Cu(II) moieties of compound 2 occur at the potentials of -1320, -1410 and -1630 and -1850 mV respectively while for the compound 3 the first and second ring reduction potentials of the free-base and Cu(II) moieties occur at -1290, -1410 and -1640, -1780 mV respectively. It is of interest to note that the differently substituted porphyrin ring reduction and oxidations are clearly distinct. These features are important in the modeling electron transfer process in multiple steps and work in this direction is in progress.

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10. m/z observed for compound 1 2064 (calc. $C_{144}H_{102}N_{12}O_4$ = 2062) and 8 3042 (calc. $C_{150}H_{97}N_{15}F_{12}O_4Br_8$ = 3039).
11. The cyclic voltammograms and differential pulse voltammograms were recorded on a BAS 100-A electrochemical analyzer. A three-electrode assembly consisting of a gold working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE) was used for redox potential measurements. Dichloromethane was used as the solvent and $TBAPF_6$ (0.1 M) was used as the supporting electrolyte. The concentrations of the porphyrins were in the range 0.1-1 mM. The solutions were purged with oxygen free nitrogen gas prior to the measurements. The uncertainity in the measurements were ± 10 mV.