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Synthesis of Unsymmetrical Porphyrin Dimers Containing β-Octaalkyl and *meso*-Tetraphenylporphyrin Subunits

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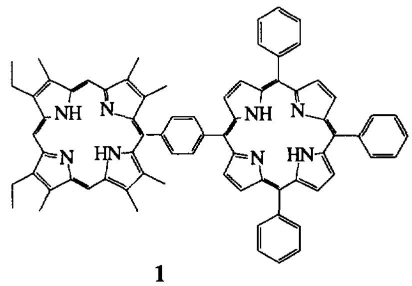
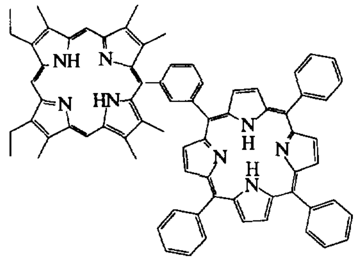
Abstract: Methodology for synthesis of phenyl-linked unsymmetrical dimers containing 8,12-diethyl 2,3,7,12,13,17,18-hexamethylporphyrin and *meso*-tetraphenylporphyrin subunits is reported. Hetero metal complexes of these dimers can be prepared by following two different routes.

The X-ray analysis of the reaction center of photosynthetic bacteria[1] has revealed the steric arrangements of these systems, but the complete understanding of the dynamic of the photosynthetic processes is far from complete. Model systems, able to mimick their natural counterpart, but easier to understand, have been developed, in order to define the factors influencing the fate of the electron transfer (ET) process.[2] Among them, covalently linked porphyrin dimers have been very useful as idealized photosynthetic reaction centers: much information about the importance of proximity, geometry and redox potential on the efficiency of the ET have been obtained from the study of these compounds.[3] Furthermore, metal complexes of porphyrin dimers with an *o*-phenylene spacer show interesting redox properties with potential catalytic applications[4] and, on the other hand, porphyrin dimers have been reported as useful photosensitizers in the photodynamic therapy of cancer.[5] More recently unsymmetrical dimers, where two different macrocycles are covalently linked, have been proposed, in order to obtain fast initial charge transfer and a slow back reaction, so giving a long-lived charge separated state, easier to investigate.[6]



1



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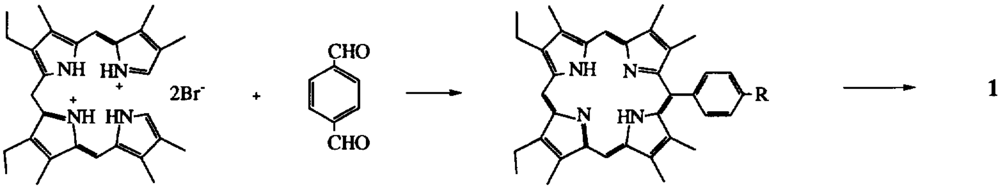
Our attention has been focused on unsymmetrical dimers where β-alkyl and meso-tetraaryl porphyrins are covalently linked, because they represent two extremes in the electronic properties of such macrocycles, with an inversion in the HOMOs of the macrocyclic π system.[7] In this Communication we report a general route to the synthesis of the porphyrin dimers 1 and 2 and their homo and hetero metal complexes.

The first step in the synthesis of **1** is the formation of the porphyrin aldehyde **3**. This compound was obtained from the acid catalyzed condensation of terephthalaldehyde with the a,c-biladiene **4** in ethanol.
No dimeric species were formed in this reaction, as previously reported in the literature:[8] the products were a mixture of **3** (18% yield) and **5** (49% yield), but **3** can be quantitatively obtained from **5** after acid hydrolysis. **3** was then condensed with benzaldehyde and pyrrole (1:19:20 ratio) following Adler's method,[9] to obtain, after chromatographic separation from the expected meso-tetraphenylporphyrin (TPP), **1** in acceptable yield (12 % based on the starting porphyrin **3**). Dimer **2** was obtained in a similar way, using isophthalaldehyde for the initial condensation with **4**, to afford the *meta*-substituted porphyrin-aldehyde and the corresponding diethyl acetal (21 and 43% yield respectively): subsequent cyclization afforded **2** with a yield slightly lower than **1**, but still acceptable (9 %).



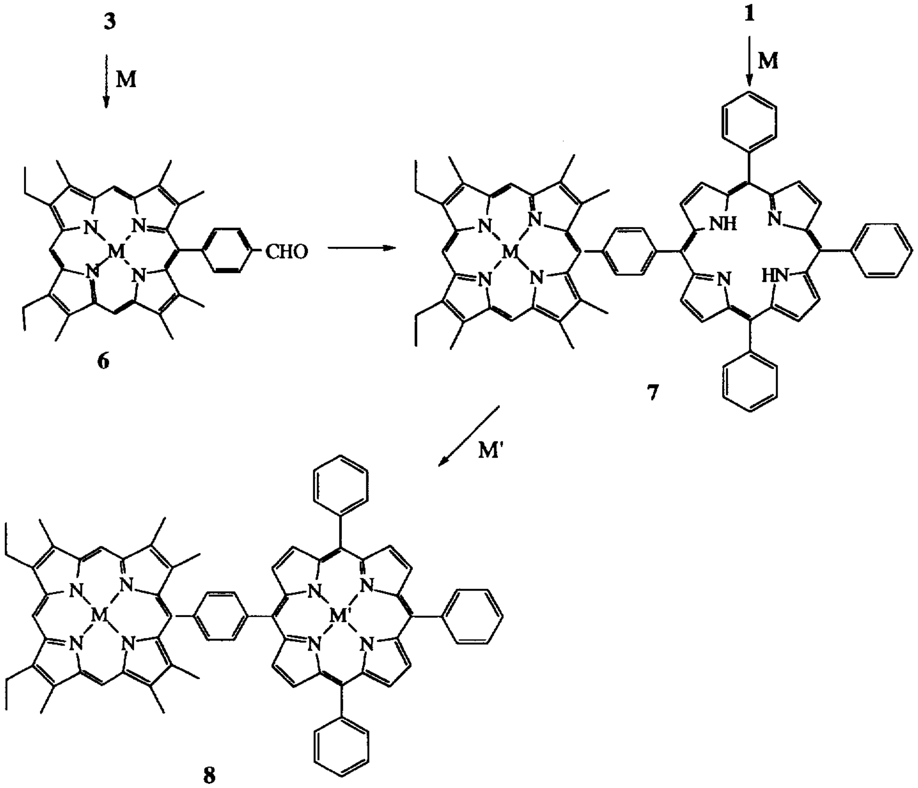
4

3. R = CHO
5. R = $CH(OEt)_2$

Symmetric metal complexes of **1** and **2** (M=M'=Cu, Zn, Ni and Co) were prepared following literature methods[10]. Heterometallated complexes of **1** and **2** can be achieved following two different routes: the first one consists in the preliminary metallation of **3** with a metal of stability class II or higher[10] to afford **6** (M=Ni, Cu, Co); this restriction is necessary to avoid demetallation during the Adler reaction conditions, necessary to obtain **7**. The further insertion of a different metal affords the desired heterometallated dimer **8** (M'=Ni, Co, Cu, Zn). The second route differs in the first step where the selective metalation of the dimer is performed: stoichiometric amount of a suitable metal carrier affords the monometalated dimer **7** (M=Zn, Ni, Cu and Co); by this route we synthesized the Zn complex of **7** and then the corresponding complexes of **8** (M≠M'=Zn, Ni, Cu and Co), so avoiding the limitation of the first approach. It is relevant to note that the first macrocycle to be metallated is the β-alkyl substituted porphyrin, as expected for its better donor properties. The regiochemistry of these metallations was confirmed by spectroscopic results: the FAB mass spectra showed the coordination of only one metal and the visible spectra of the mono-metallated dimers displayed the absorption around 650 nm, typical of TPP free base;[11] in addition, in the ^1H NMR spectra the resonances of the β-alkyl fragment presented a shift attributable to metallation, whereas those of the TPP were practically unchanged.

In the ^1H NMR spectra of **1**[12] and **2**[13] the resonances attributable to the β-alkyl fragment do not show significant variations from **3** or an analogous symmetrical dimer[3f], whereas those of the TPP moiety are split because of the reduced symmetry of the macrocycle; the resonances of the aryl bridge in **1** resonate as a doublet of doublets, different from the analogous symmetrical dimers, where they appear as a singlet.[3f,14] It is interesting to note that the inner N-H pyrrole signals display two different sets of resonances: the singlet at lower field is attributable at the meso-tetraphenyl moiety, as revealed from **7** where this peak disappears, whereas the resonances of the β-alkyl fragment are present as two broad singlets at higher field, demonstrating slow tautomerization in the NMR time scale. The FAB mass spectra (3-nitrobenzylalcohol) of **1** and **2** are characterized by a cluster of peaks centered at m/e 1063, corresponding to the M^+ peak. The visible spectra of **1** and **2** in the Q region are a superposition of the absorptions of the two macrocycle, with no significant shifts. The situation of the B bands is different: in this case the spectrum of **1** displays a slight broadening of the band, with a maximum centered at 421 nm (ε=4.01x10^5) and a shoulder around 410 nm (ε=1.80x10^5). This splitting is more evident in the case of **2**, where two absorptions at 422 (ε=3.98x10^5) and 406 nm (ε=2.49x10^5) were revealed: these features have been previously studied in detail for similar dimers of porphyrins and it was demonstrate that the two macrocycles cannot be considered as independent because of the presence of electronic interactions.[3e,f] These splittings become more pronounced in the complexes: the copper complex of 1, for example, displays two peaks at 405 and 425 nm.

Further developments of this approach to unsymmetrical dimers are in progress. All the new compounds were characterized by NMR, visible spectroscopy, FAB mass spectrometry and elemental analysis.



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10. Buchler, J.W. in *The Porphyrins*, Dolphin, D. ed., Academic Press: New York, 1978, p. 389 and references therein.

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12. Dimer **1**: ^{1}H-NMR (δ ppm, CDCl$_3$): 10.24 (s, 2H), 10.01 (s, 1H), 9.31, 9.12 (each d, 4H), 8.95 (m, 4H), 8.57, 8.39 (each d, 4H), 8.32-8.26 (m, 6H), 7.85-7.75 (m, 9H), 4.08 (q, 4H), 3.52 (s, 12H), 3.04 (s, 6H), 1.92 (t, 6H), -2.58 (s, 2H) -2.99, -3.18 (each br s, 2H).

13. Dimer **2**: ^{1}H-NMR (δ ppm, CDCl$_3$): 10.18 (s, 2H), 9.92 (s, 1H), 9.33, 8.99 (each d, 4H), 8.91 (s, 1H), 8.82 (s, 4H), 8.68, 8.51 (each d, 2H), 8.28-8.12 (m, 6H), 7.82-7.68 (m, 10H), 4.02 (q, 4H), 3.60 (s, 12H), 3.09 (s, 6H), 1.83 (t, 6H), -2.77 (s, 2H) -3.10, -3.29 (each br s, 2H).

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