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Porphyrins acting as external and internal ligands: preparation of conjugated trimetallic dimeric porphyrins

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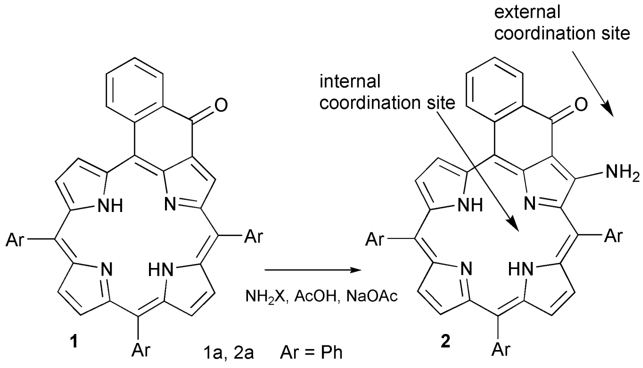
A porphyrin bearing a peripheral enaminoketone function allows the preparation of conjugated dimeric porphyrins linked through metal ions.

Multiporphyrin assemblies are involved in several biological processes such as photosynthesis or electron transfer. Mimicking those assemblies and their activity has been a challenge for chemists and numerous examples of multiporphyrin compounds have been described in recent years.[1–22] The connection between porphyrin nuclei may involve C–C bonds, hydrogen bonds, direct metal–metal or μ-X bonds, catenation of porphyrin *ansa*-derivatives, coordination of appropriate peripheral substituents to metal centers, *etc.* More recently, after the molecular wires described earlier by Crossley and Burn,[8] several groups are pursuing efforts to obtain conjugated oligoporphyrinic molecules directly linked through one, two or even three covalent bonds.[10–13] This covalent approach suffers some drawbacks: synthetic and separation problems, iterative reactions to obtain larger molecules, variations of the linking bonds limited to C–C or C–N.

The use of coordination bonds[15–21] has the advantage of offering an additional choice: each metal center may present its own geometry and coordination number depending on the element and its oxidation level, in addition to the variations due to the nature of the internal coordination sites of the porphyrins.

Here we describe a substituted porphyrin acting both as an internal (with the four pyrrole nitrogens) and as an external (with an enaminoketone moiety) ligand. The external coordination site is coplanar and fully conjugated to the porphyrin aromatic system.[22] In contrast to most systems assembled with metal ions, where little or no interaction is observed in the ground state between the porphyrins, the porphyrin–porphyrin conjugation in our dimers linked by metal ions will be illustrated by their electronic spectra and electrochemical behaviour.

meso-Tetraarylporphyrins bearing a keto group located on an additional ring attached to an aryl substituent and a pyrrolic β-carbon have been known since 1980 but their reactivity has been little investigated.[23–26] In the course of a search for extended porphyrin chromophores we reacted ketone **1** with nitrogen nucleophiles. Under mild acid catalysis, reagents of the general composition $H_2N–X$ (X = OH, NHTs, OSO_3H) gave in variable yield enaminoketone **2**, the highest yield (90%) being observed with hydroxylamine *O*-sulfonic acid–AcOH–NaOAc in refluxing CH_2Cl_2. Enaminoketone **2a** showed a UV–VIS similar to the starting material (λ_{max} = 451, 568, 614 and 709 nm). The β-N–H NMR signals could be detected at δ 9.0 (N–H involved in a hydrogen bond with the carbonyl group) and δ 5.48 (free N–H, shielded by a vicinal phenyl ring).

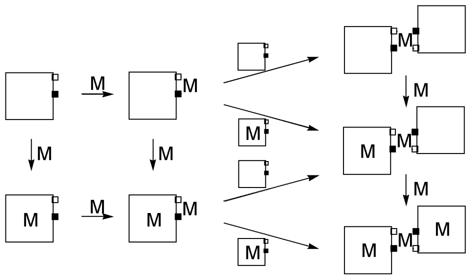


1a, 2a Ar = Ph
1b, 2b Ar = $C_6H_3Bu^t_2$-3,5

Enaminoketone **2** presents remarkable coordinating properties: in addition to the internal 4N tetradentate macrocyclic coordination site, the enaminoketone group is a potential N+O chelating external site (an analog of the acetylacetonate ligand) that might couple porphyrins to form homo- or hetero-polymetallic complexes. One would predict that the coordination at the enaminoketone site should be favoured over the introduction of metal ions in the core of the porphyrin, but one also expects the stability of the internal complex to be of orders of magnitude higher for the same metal ion; in particular with first row transition metals the porphyrin–metal–porphyrin connection is expected to be of low stability. Accordingly, heterometallation may be performed along two routes by using as an intermediate either an internal complex or the porphyrin base dimer (Scheme 1).

Metallation of **2a** (R = Ph) with nickel acetylacetonate (one or more equiv.) rapidly gave a highly insoluble product containing one metal and two porphyrins formulated as **3a** (M^1 = Ni; M^2 = M^3 = H_2). Treatment with acetic acid, which is unable to remove nickel from the 4N site of a porphyrin, quantitatively regenerated the starting material. However, on prolonged reaction in refluxing toluene with a 1:1 porphyrin/nickel ratio, metallation of the porphyrin occurred and gave mononuclear **Ni–2a**, while excess reagent gave trinuclear **3a** (M^1 = M^2 = M^3 = Ni). The formation of **Ni–2a** is best explained by the low stability of the nickel bridge—it did not survive chromatographic conditions—and the slow formation of the most stable metallation product. The same trinuclear compound **3a** (M^1 = M^2 = M^3 = Ni) was formed when **Ni–2a** was treated with an excess of nickel acetylacetonate. Similarly, several trimetallic bisporphyrins were prepared (Ni/Cu/Ni; Ni/V=O/Ni; Ni/Pd/Ni).

There remained the question of the relative arrangement of the porphyrins around the metal, since the dimers may have a center or a plane of symmetry. COSY and NOESY experiments



Scheme 1 Metallation of enaminoketone **2** (squares): vertical arrows = metallation of internal site of porphyrin, slow and irreversible under the reaction conditions; horizontal arrows = metallation of external site (fast and possibly reversible reactions).

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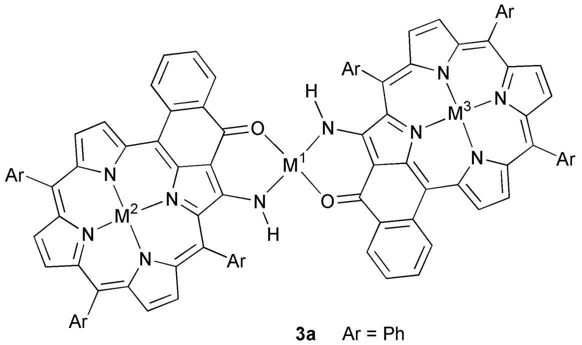

3a Ar = Ph
3b Ar = $C_6H_3Bu^t_2$-3,5

confirmed the structure and the dimeric nature of **3**. Additional information was obtained when we turned to the more soluble *meso*-tri(3,5-di-*tert*-butyl)phenylporphyrin series. Heating equimolecular amounts of palladium(II) acetate and enaminoketone **2b** in refluxing toluene for 3 h led almost exclusively to **3b** (M^1 = Pd; M^2 = M^3 = H_2). Again, NMR experiments (ROESY) confirmed the relative position of the porphyrins: HH ROESY cross signals were observed between two protons of the cyclised phenyl ring and the *para* proton and the *tert*-butyl protons of a *meso*-aryl group belonging to the other porphyrin. This compound survived chromatographic purification and is a good starting material for heterometallic dimer preparation. Indeed, metallation with zinc acetate gave the mono- and bis-metallated **3b** (M^1 = Pd; M^2 = Zn; M^3 = H_2 or Zn).

These new porphyrin dimers all showed similar electronic spectra and an electrochemical behaviour indicative of the conjugation introduced through the connecting metal between the two aromatic rings. For example, the lowest energy band of **3a** (M^{1-3} = Ni) shifts to 700 nm (ε = 33000 $dm^3\ mol^{-1}\ cm^{-1}$) in comparison to the band observed at 649 nm (ε = 18500 $dm^3\ mol^{-1}\ cm^{-1}$) for **Ni–2a** (Fig. 1). The HOMO–LUMO gap estimated from these data is reduced to 1.77 eV in the dimer **3a** (M^{1-3} = Ni) compared to 1.91 eV for the monomer **Ni–2a** (already a very low value compared to the gap reported for nickel porphyrins, $E \approx 2.3$ eV). The corresponding bases such as **3b** (M^1 = Pd; M^2 = M^3 = H_2) display bands at even longer wavelengths (730 nm, ε = 39000 $dm^3\ mol^{-1}\ cm^{-1}$), which can be compared with that of **2b** (711 nm, ε= 8500 $dm^3\ mol^{-1}\ cm^{-1}$).

The monomer **Ni–2a** showed two one-electron oxidations at 0.46 and 0.83 V *vs.* Fc/Fc$^+$. In trimetallic **3a** (M^{1-3} = Ni), the first oxidation is split into two one-electron oxidation waves (one electron per porphyrin) at 0.32 and 0.50 V, indicative of a strong interaction between the two porphyrins. The removal of the first electron therefore occurs at a potential 0.14 V lower than for the monomer (a value equal to the difference between the gaps taken from the electronic spectra). A two-electron oxidation (or rather twice a one-electron oxidation of each porphyrin ring) is further observed at 0.68 V. It seems that the removal of the first two electrons from the dimer has led to a disruption of the conjugation between the two rings. The dimer (already oxidised by two electrons) now behaves like two independant nickel monomers. All waves are quasi-reversible (ΔE_p = 60–90 mV), showing that dimer **3a** (M^{1-3} = Ni) remains intact during this overall four-electron oxidation–reduction process.

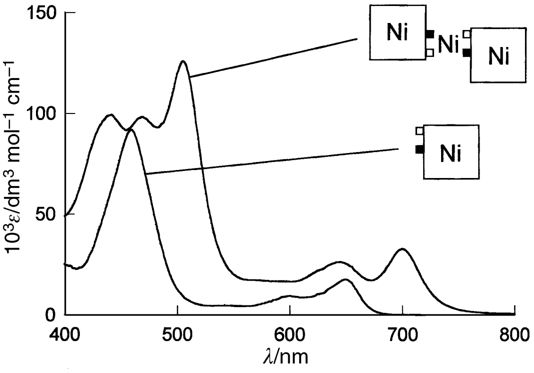

Fig. 1 UV–VIS spectrum of **3a** (M^{1-3} = Ni) and **Ni–2a**.

In conclusion, we confirmed that efficient porphyrin–porphyrin interaction could be achieved *via* metal coordination. The synthesis of bis-enaminoketoporphyrins where two external coordination sites are located in divergent directions is in progress. These compounds should allow the preparation of more highly conjugated oligomers.

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