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# A modular approach to porphyrin oligomers using metal ions as connectors†

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**Porphyrins bearing two external coordination sites allowed the stepwise preparation of polymetallic oligomers connected by metal centers.**

Multiporphyrin assemblies are involved in several biological processes such as photosynthesis, electron transfer or oxygen transport. Numerous models, mimicking their geometry or their activity, have been described.[1–4] More recently, porphyrins have also been considered as building blocks for molecular materials because these macrocycles are more polarisable aromatics than the smaller heterocycles (thiophene, pyrrole, . . .) used before. Specific electronic, magnetic or optical properties are expected for oligomeric molecules if significant interactions are present between the individual porphyrins.

The connections between porphyrin nuclei may involve covalent, coordination or hydrogen bonds. Little or no interactions in the ground state has been observed so far for oligomers linked through coordination[2] or hydrogen bonds.[3] On the other hand, several examples of porphyrin oligomers connected by one or more C–C bonds showed large interactions leading to spectacular modifications of the electronic properties.[4]

The use of coordination bonds presents several inherent advantages compared to covalent bonds: the number of possible metals and/or ligands, the multiple coordination geometries available, the ease of synthesis, the reversibility of the formation of most linkages. In addition, the characteristics of each connecting metal will tune the electronic, magnetic and geometric properties of the products.

Such an approach has been developed in the related porphyrazine series[5] and peripherally metallated macrocycles as well as porphyrazine dimers have been prepared and studied.

We earlier described[6] a series of dimers based on porphyrins bearing an enaminoketone external coordination site fully conjugated with the macrocycle. To build higher oligomers, the preparation of porphyrins bearing two divergent external coordination sites was an obvious choice.

Bis-functionalised porphyrins could not be obtained by the usual synthetic route (formylation, cyclisation and amination).[7] The required bis-enaminoketones were prepared from nickel porphyrins substituted at the *meso*-positions by two *o*-carbomethoxyphenyl groups (in 5,10 or 5,15 positions) and two 3,5-di-*tert*-butylphenyl groups (used for solubility reasons). This synthetic route was developed for the preparation of mono-enaminoketones[8] and is compatible with acid-stable metals. Hydrolysis of the ester group (LiOH in dioxane–water), acid chloride formation (oxalyl chloride) and Friedel–Crafts reaction ($SnCl_4$) gave the corresponding cyclic diketones. Amination of the diketones proceeded in high yield using 4-amino-4*H*-1,2,4-triazole and base.[9] The four possible bis-enaminoketones were characterised which, depending on the relative arrangement of the external sites, may give linear or bent porphyrin–porphyrin connections.

All four bis-enaminoketones could be metallated easily at their external coordination sites by using palladium(II) bis-acetylacetonate ($Pd(acac)_2$).

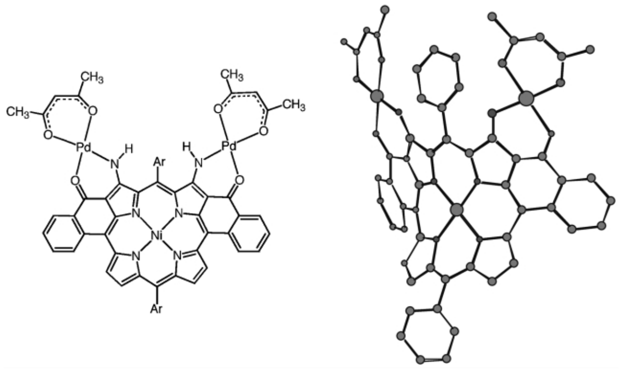
Suitable crystals and an X-ray structure of a typical trimetallic compound[10] where the two external enaminoketones are complexed by two Pd(acac) fragments could be obtained (Scheme 1).

The geometry of the porphyrin macrocycle is best described as saddle-shaped. Two opposite *meso* carbon atoms (5,15 and 10,20) are oriented either down- or up-wards and the angles C5–Ni–C15 or C10–Ni–C20 are close to 153°. The coordination geometry around the palladium is square planar with the Pd–N bond being slightly shorter than the three Pd–O bonds (1.96 Å compared to 1.98, 1.99 and 2.00 Å).

Only one series of compounds, built from the centrosymmetric nickel bis-enaminoketone **1** (Scheme 2) with palladium(II) as connecting metal ion, and thus leading to a linear arrangement of porphyrins, will be described below.

If the metallation of the external coordination sites is not run to completion, mono- and di-metallated porphyrins **2** (28%) and **3** (36%), as well as remaining starting material **1** (25%) could be easily separated chromatographically. The porphyrin : acac stoichiometry in these products was confirmed by their $^1H$ NMR spectra. Doubly metallated nickel dienaminoketone **5**, bearing labile acetate ligands, was produced, but not isolated and characterised—thus the ligands are denoted X—when the starting material **1** was added to an excess palladium acetate. Alternatively, displacement of the acetylacetonate ligands of **3** in boiling acetic acid gave a solution which may contain a similar intermediate. Compounds **2** and **3**, which can be described as mono- and di-protected bis-enaminoketones, represent, along with the bis-metallated porphyrin **5**, the building blocks necessary for the selective preparation of higher oligomers. The use of either the acetate (labile ligand) or the acetylacetonate ligand (less labile) allows the desired oligomer to be obtained almost specifically.

Indeed, reaction of porphyrin **2** with palladium acetate gave, in one step, dimer **4** containing five metal centers in 50% yield. Trimer **6** was in turn obtained in 45% isolated yield when deprotected **5** was treated with porphyrin **2**.



**Scheme 1** Bis-palladium complex of a nickel bis-enaminoketoporphyrin (Ar = 3,5-di-*tert*-butylphenyl; hydrogen atoms, *tert*-butyl groups and solvent molecules are omitted in the X-ray structure drawing (right) for clarity).

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† Electronic supplementary information (ESI) available: preparation and spectroscopic data for compounds **4** and **6**. Crystallographic data for the bis-palladium complex shown in Scheme 1. See http://www.rsc.org/suppdata/cc/b1/b109357f/

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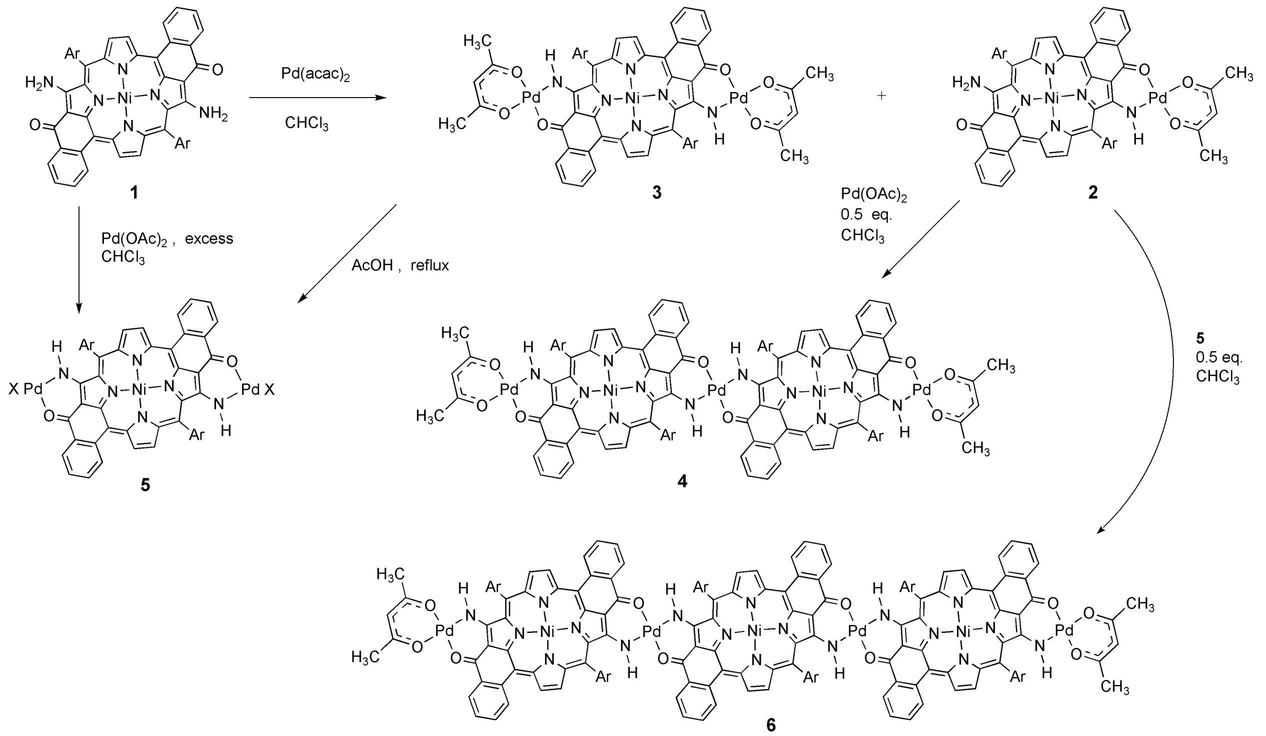

**Scheme 2** General synthetic routes to monomer **3**, dimer **4** and trimer **6**.

**Table 1** Electronic data for compounds **1**, **2**, **3**, **4** and **6**

| Compound | $\lambda$/nm($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) | | | |
|---|---|---|---|---|
| **1** | 488 (140000) | 667 (19200) | ~690sh (~14000) | 758 (39500) |
| **2** | 500 (96000) | 675 (17200) | 725 (9700) | 803 (33000) |
| **3** | 514 (95000) | 678 (24600) | 775 (9500) | 863 (50100) |
| **4** | 532 (196000) | 682 (52000) | 784 (19600) | 877 (65500) |
| **6** | 540 (300000) | 684 (83800) | 789 (31200) | 881 (116000) |

All oligomers were characterised by FAB-MS and $^1$H NMR. All signals of each oligomer could be unambiguously attributed by combining $^1$H–$^1$H COSY and ROESY experiments (see NMR data in ESI†).

With respect to that of the starting porphyrin **1**, electronic spectra (Table 1) of compounds **1**–**4** and **6** show large red shifts due to two cumulating effects: (a) the metallation of the porphyrin external site (**1**, **2**, **3** sequence), (b) the sequential replacement of acac ligands by porphyrin macrocycles (**3**, **4**, **6** sequence). The most spectacular shift was observed on the two long wavelength bands along the **1**, **2**, **3** sequence and confirm the very strong electronic effect of the coplanar coordination to the porphyrin ring. On the other hand, the effect on the Soret band is limited. Sequential replacement of acac ligands by chelating porphyrins resulted in a moderate red-shift of all bands, but a strong increase of the absorption along the **3**, **4**, **6** sequence.

These preliminary results demonstrate that this modular approach to coplanar porphyrin oligomers containing up to three macrocycles through coordination bonds is feasible and is expected to be suitable for building higher homologs, including polymeric polymetallic materials. Depending on the relative positions of the external coordination sites, linear as well as angular chains may be built. Use of porphyrins bearing other substituents opens routes to hybrid (variations concerning the organic part and/or metals involved) or ramified chains. Extension of this work in these directions is currently in progress.

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