A transition metal ion assembled catenane bearing linearly-arranged donor and acceptor porphyrins

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A new bis(porphyrin) has been synthezised in which a catenane is used as a spacer between the two chromophores, the donor and acceptor porphyrins being located as pendant groups, arranged linearly on each side of the catenane core.

Mimicry of electron transfer in the photosynthetic Reaction Centre[1]—specifically the primary electron transfer step between the special pair of bacteriochlorophyls and the bacteriopheophytin—is generally approached using multiporphyrins. Modulation of the electronic properties of the intervening medium between the donor and acceptor chromophores is of particular interest, and has been addressed by varying covalent[2] as well as non-covalent[3] bonds.

An approach by which the electronic properties of the medium between a donor and acceptor chromophore could be altered without having to resort to repeated synthesis of model compounds is an appealing prospect. In order to approach this goal, we designed the [2]catenane[4] depicted schematically in Fig. 1. The catenane core contains two intertwined ligands, bound to a transition metal ion. The latter should be easily exchangeable by another metal ion, providing the central complex with new electronic properties. This modular approach should allow the study of the influence of the bridge **B** between the donor **D** and acceptor **A** chromophores upon the electron transfer rate. Unlike other catenanes[5] and rotaxanes[6] incorporating porphyrins as parts of the structures which are essential for interlocking, we chose to locate them as pendant groups, in an attempt to exercise more control over the inter-porphyrin distance.

The heart of the catenane shown in Fig. 1 is similar to that described for related catenanes,[7] in which two phenanthroline residues entwine about a copper(I) ion. The tetraarylporphyrins we chose as donor and acceptor are of the zinc(II) and gold(III) variety, respectively, as these moieties have proven utility for the study of electron transfer phenomena.[8] The tetraarylporphyrin **1** was prepared from the reaction of the appropriate aldehydes with pyrrole in refluxing propionic acid. After separation, the methoxy groups of **1** were converted to alcohol functions using BBr_3 in CH_2Cl_2, affording **2**. The extended phenanthroline **6**, required for the synthesis of the macrocycle **8**, was prepared by firstly reacting **4** with 2-(2-chloroethoxy)ethanol in DMF in the presence of K_2CO_3 as a base, and then converting the resulting diol **5** to the bis(toluene-*p*-sulfonate) under standard conditions (58% yield overall). Combining these precursors, the macrocycle **8** was prepared from **2** and **6** using Cs_2CO_3 as a base in DMF at 100 °C in a yield of 47%. Metallation of the porphyrin in **8** with a gold(III) ions was achieved in refluxing glacial acetic acid using $KAuCl_4$ in the presence of NaOAc under an atmosphere of argon. After counter-ion exchange with KPF_6 and column chromatography, the orange-coloured gold(III) porphyrin **9**$^+$ was afforded in 92% yield as its hexafluorophosphate salt. The analogous macrocycle bearing a zinc(II) porphyrin (**10**) was also prepared quantitatively by reaction of **8** with $Zn(OAc)_2$ in CH_2Cl_2–MeOH.

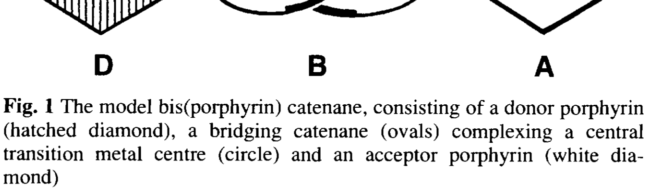
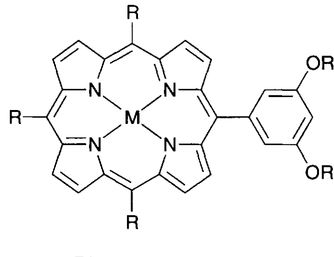
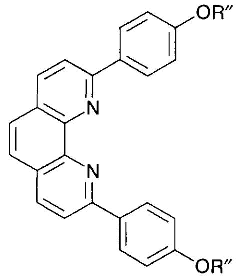


Fig. 1 The model bis(porphyrin) catenane, consisting of a donor porphyrin (hatched diamond), a bridging catenane (ovals) complexing a central transition metal centre (circle) and an acceptor porphyrin (white diamond)

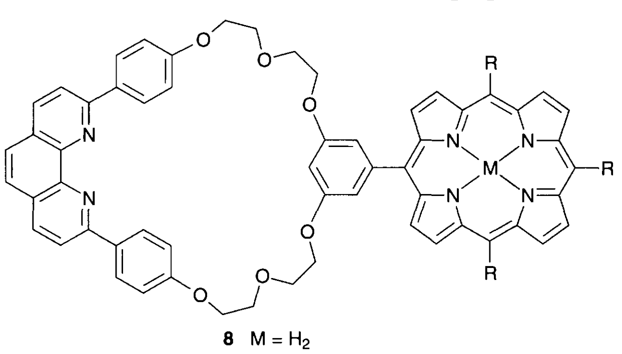
The [2]catenate was prepared according to the route shown in Scheme 1. Treatment of the macrocycle **9**$^+$ with $[Cu(MeCN)_4]PF_6$ followed by threading of the diiodide **7** [prepared from bis(sulfonate) **6** using NaI in acetone], at room temperature under argon, results in the formation of the precatenate **11**$^{2+}$ in quantitative yield. This complex was combined with the zinc(II) porphyrin **3** [prepared from **2** by treatment with $Zn(OAc)_2$] in DMF, and this solution was added slowly to a



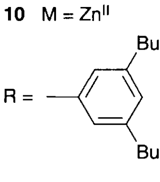
1 R′ = Me, M = H_2
2 R′ = H, M = H_2
3 R′ = H, M = Zn^{II}



4 R″ = H
5 R″ = $CH_2CH_2OCH_2CH_2OH$
6 R″ = $CH_2CH_2OCH_2CH_2OSO_2C_6H_4Me$
7 R″ = $CH_2CH_2OCH_2CH_2I$

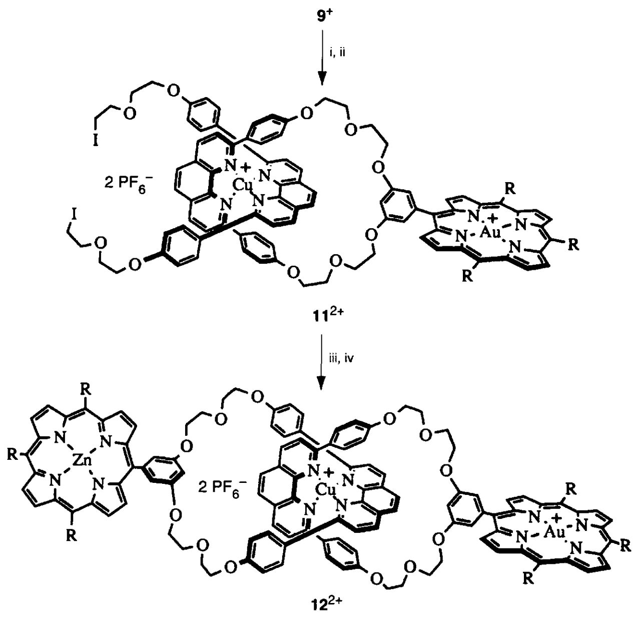


8 M = H_2
9$^+$ M = $Au^{III+}\bullet PF_6^-$
10 M = Zn^{II}



suspension of Cs_2CO_3 in DMF at 50 °C, after which the reaction was allowed to proceed for 4 days. After counter-ion exchange and column chromatography, the reaction afforded the heteroporphyrinic [2]catenate $\mathbf{12}^{2+}$ in 13% yield as its hexafluorophosphate salt, along with the homoporphyrinic [2]catenate with two appended zinc(II) porphyrins in 6% yield. The latter product results from 'scrambling' of the precatenated complexes during the course of the reaction. The component macrocycles $\mathbf{9}^{+}$ and **10** were also isolated.

The [2]catenates afforded from the reaction depicted in Scheme 1 were characterised using ^1H NMR and UV–VIS spectroscopy, as well as by fast atom bombardment (FAB) and electrospray mass spectrometry. The FAB mass spectrum of $\mathbf{12}^{2+}$ shows peaks at 3443 and 3297 for the $[M - PF_6^-]$ and $[M - 2PF_6^-]$ ions respectively, in accordance with the calculated values. Both the ^1H NMR and UV–VIS spectra of $\mathbf{12}^{2+}$ showed signals resulting from the sum of the component parts, indicating that there is no significant interaction between the two prophyrins and that the average conformation is a linear one similar to that shown in Scheme 1.



Scheme 1 *Reagents and conditions*: i, $[Cu(MeCN)_4]PF_6$, MeCN; ii, **7**, CH_2Cl_2; iii, **3**, Cs_2CO_3, DMF, 50 °C; iv, KPF_6 (aq), CH_2Cl_2

Preliminary emission measurements on $\mathbf{12}^{2+}$ reveal that the luminescence of the zinc(II) porphyrin is significantly quenched, the mechanism of the quenching reaction having to be further studied.

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