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Synthesis of Accurate Distance Models of the Primary Donor - Primary Acceptor Pair of Bacterial Photosynthetic Reaction Centres

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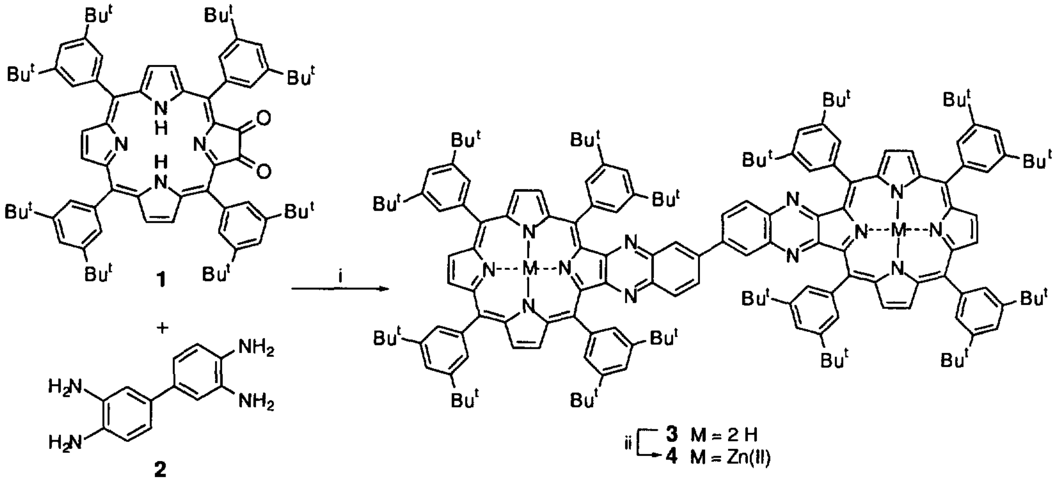
Abstract: The synthesis of **4** and **9**, in which two porphyrins are joined by a biquinoxalinyl bridge and by a quinoxaline Tröger's base, respectively, provide systems which have interporphyrin centre-centre and edge-edge distances that very closely match those between the primary donor - primary acceptor tetrapyrrolic pair in bacterial photosynthetic reaction centres. Copyright © 1996 Elsevier Science Ltd

A number of recent studies involving bis-porphyrin systems have been directed towards modelling of features revealed in the X-ray crystal structures of the photosynthetic reaction centre (PRC) of the purple bacterium *Rhodopseudodomonas viridis* and of *Rhodobacter sphaeroides*.[1-6] There is a very similar arrangement of the macrocyclic components that brings about charge separation in the two systems. In particular there is a special pair of bacteriochlorophyll of approximate C_2 symmetry which is the primary electron donor and a nearby bacteriopheophytin which is the primary acceptor.[7] A number of factors relating to this donor-acceptor pair will influence the charge separation process; some of these are the redox driving forces, modulating properties of nearby groups, the nature of the intervening medium and the relative geometry of the pair. The X-ray structure revealed that the chromophores of this donor-acceptor (D-A) pair on the redox-active L-side have a centre-centre distance of 16.5 Å and an intermolecular edge-edge shortest distance of 9.5 Å.[8]

Previously no synthetic systems have been described that closely model these intermacrocyclic distances. We now report the synthesis of the bis-metalloporphyrin systems, **4** and **9**, with centre-centre and macrocycle edge-edge distances that match very closely those found between the primary donor - primary acceptor tetrapyrrolic pair in PRC's.

We have shown earlier that the porphyrin-2,3-dione **1** reacts with 1,2,4,5-benzenetetramine to give extended porphyrin systems[9] and with *o*-phenylenediamine to give quinoxalinoporphyrins.[10] As expected, other diamino-arenes react with the porphyrin-2,3-dione **1** to give corresponding quinoxalinoporphyrins. We used this reaction to synthesise the biquinoxalinyl-bridged bis-porphyrin **3**[11] in 89% yield by condensing 2 equivalents of the porphyrin-2,3-dione **1** with 3,3'-diaminobenzidine **2** (Scheme 1). Treatment of **3** with excess zinc(II) acetate dihydrate afforded the dizinc(II) bis-porphyrin **4** in 86% yield. Dicopper(II) and dinickel(II) derivatives of **3** have also been prepared. Compounds **3** and **4** are shown in Scheme 1 in their *anti*-conformation (χ = 180°) about the biaryl linking bond.



i) CH_2Cl_2, 2 h. ii) $Zn(OAc)_2.2H_2O$, MeOH, CH_2Cl_2, 4 h.

Scheme 1

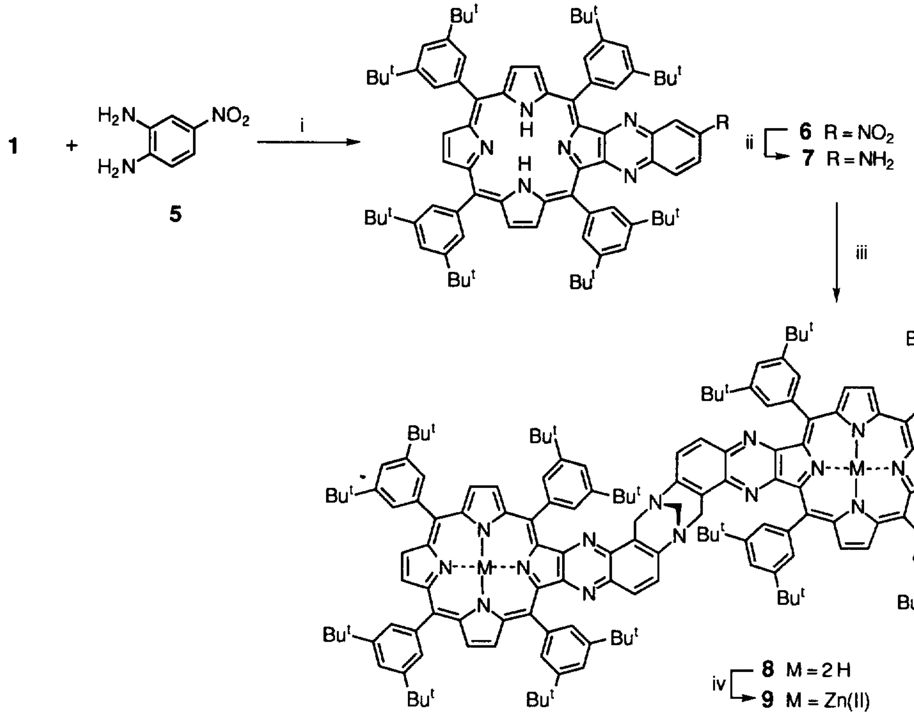
The two porphyrins can rotate with respect to each other about the biaryl bond of **4** but this has only a very small effect on the edge-edge or centre-centre distances in the compound. Molecular modelling of bis-porphyrin **4** using the energy-minimization program SPARTAN[12] yielded an unconstrained minimized structure with the interplane angle $\chi = 32°$ and a centre-centre distance of 18.8 Å and an edge-edge distance of 10.4 Å. Molecular modelling of bis-porphyrin **4** in its three extreme conformations, the *syn*-planar ($\chi = 0°$), the *anti*-planar ($\chi = 180°$), and the orthogonal ($\chi = 90°$), yielded the interporphyrin centre-centre and edge-edge distance ranges given in Table 1.

Table 1. Distance (Å) between macrocyclic rings in a PRC and in compounds **4** and **9**

System	Edge-Edge[a]	Centre-Centre
D-A Pair in PRC[8]	9.5	16.5
Biquinoxalinyl Bis-porphyrin **4** (χ = 0 - 180°)	10.4-11.2	18.4-19.5
Tröger's Base Quinoxalinoporphyrin **9**	9.8	16.8

[a] The shortest distance between β-pyrrolic positions of the two (reduced) porphyrins.

In order to fully constrain the geometry it is necessary to double-pin each of the porphyrins to a rigid linker. The diazocine bridge of Tröger's base achieves this fixation. We have shown previously that a porphyrin-appended Tröger's base analogue results from condensation of a 2-aminoporphyrin with formaldehyde; this bis-porphyrin has a centre-centre distance of only 8.3-8.9 Å.[13] In order to more closely mimic the geometry of the D-A pair in the PRC, we sought to separate the porphyrin rings via an expanded bridge. Condensation of the porphyrin-2,3-dione **1** with 1,2-diamino-4-nitrobenzene **5** gave the nitroquinoxalinoporphyrin **6** (95% yield) which was subsequently reduced with $SnCl_2$/HCl. The resultant aminoquinoxalinoporphyrin **7** (71% yield) was reacted with formaldehyde to produce the expanded quinoxaline-bridged Tröger's base analogue **8**[14] in 88% yield (Scheme 2). Metallation with zinc(II) acetate dihydrate produced the dizinc(II) compound **9** in 73% yield. Monozinc(II), dinickel(II), dipalladium(II) and mixed metal zinc(II)-gold(III) derivatives of **8** have also been prepared.



i) CH_2Cl_2, pyridine. ii) $SnCl_2$, HCl, CH_2Cl_2. iii) CH_2O, HCl, EtOH, THF, reflux, 18 h.
iv) $Zn(OAc)_2.2H_2O$, MeOH, CH_2Cl_2, reflux.

Scheme 2

Molecular modelling[12] generated an energy-minimized structure for **9** in which the two quinoxalinoporphyrin units are arranged at an 96° interplanar angle with the distances shown in Table 1. This angle lies in the range seen in the X-ray structures of simpler Tröger's base derivatives (92-104°).[15] The centre-centre distance of about 16.5 Å in the dizinc(II) compound **9** has been measured independently by use of bidentate ligands as 'molecular rulers' as will be described elsewhere.[16]

Most synthetic models of the D-A pair have been based on the linkage of two metalloporphyrin units but generally they have been linked by a flexible bridge so that the intermacrocycle distance is not controlled.[1-6] In contrast, the models reported here not only have remarkably similar edge-edge and centre-centre distances to those found in the PRC but also a constrained geometry. Studies of photoinduced electron-transfer in Zn(II)-free base and Zn(II)-Au(III) derivatives of **3** and **8** should provide information about the influence of the intervening medium on the process. The syntheses reported in this paper further illustrate the versatility of the α-dione **1** as a component in building interesting porphyrin arrays.[9,17]

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