Dramatic effect of the porphyrinic metal on the conformation of a two-ring threaded system

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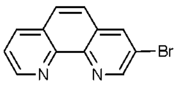
Porphyrin homodimers have been assembled by transition-metal-directed threading of porphyrin-incorporating macrocycles onto a rigid-rod bis-chelate, and the relative orientations of the porphyrins shown to be controlled by the nature of the metal that they contain.

Assemblies of naturally-occurring porphyrins or analogues held by noncovalent interactions are important components of photosynthetic systems, as light antennas, energy funnels, and electron transfer chains.[1] These facts, recently highlighted by beautiful X-ray crystal structures,[2] have stimulated the design and synthesis of multifarious porphyrin aggregates mainly based on coordination bonds, some of them showing relevant electron transfer properties.[3] In particular, the preparation and study of simple dimers of stacked porphyrins is highly significant,[4] as far as mimicking the unusual spectroscopic properties of the Special Pair of bacterial reaction centers is concerned.[5]

We have recently described the efficient assembly of porphyrin dimers by the transition-metal-controlled *threading* of macrocycles bearing *pendant* porphyrins and incorporating a 2,9-diphenyl-1,10-phenanthroline (dpp) chelate onto molecular threads containing two such dpp fragments.[6] Here we show that when a rod-like, phenanthroline-based bis-chelate and macrocycles *incorporating* metalloporphyrins in their backbone are used, the relative orientations of the porphyrins can be controlled by the nature of the metal that they contain.†

The bis-phenanthroline rigid-rod molecule **4** and the dpp-based macrocycles **9** and **10** incorporating a Zn^{II} and a Au^{III} porphyrin, respectively, as well as their precursors, are represented below. Suzuki coupling of 3-bromophenanthroline **1**[7] and diboronic acid **2**[8] in stoichiometric amounts [Pd(PPh$_3$)$_4$, aq. Na$_2$CO$_3$, EtOH–PhCH$_3$, reflux] afforded bis-phenanthroline **3** in 55% yield after chromatography.[9] This compound was further reacted with lithioanisole (3 equiv.) in THF at −5 °C.[10] After hydrolysis, MnO$_2$ aromatization and chromatographic separation from substitution isomers and homologues, bis-phenanthroline **4** was isolated in 32% yield. Direct precursors of macrocycle **8**, which incorporates a free-base porphyrin, are the phenanthroline derivative **5** and porphyrin **7**. This latter compound was obtained in quantitative yield by treatment of porphyrin **6**[11] with an excess of BBr$_3$ in CH$_2$Cl$_2$ at −78 °C. High-dilution condensation of **5** and **7** in DMF at 55 °C containing Cs$_2$CO$_3$ (5 equiv.) provided **8** in 28% yield after chromatography.[12] Insertion of Zn^{II} was carried out by reaction with Zn(OAc)$_2$·2H$_2$O (1 equiv.) in a 2 : 1 refluxing mixture of CHCl$_3$ and CH$_3$OH, to produce the Zn^{II} porphyrin-incorporating macrocycle **9** in 85% yield. The preparation of the Au^{III} porphyrin-incorporating macrocycle **10**, which could not be obtained by direct metallation of **8**, has been described elsewhere.[11]

Copper(I)-directed threading of either macrocycle **9** or **10** onto bis-phenanthroline rod **4** was carried out as follows (Scheme 1).[6,10] Equimolar amounts of Cu(CH$_3$CN)$_4$·PF$_6$ in CH$_3$CN and the desired macrocycle in CH$_2$Cl$_2$ were combined under argon. Compound **4** (0.5 equiv.) in CH$_2$Cl$_2$ was subsequently transferred to the reaction mixture. After removal of the solvents under reduced pressure, the crude material was flash-chromatographed on silica gel, affording the threaded assembly. The Zn^{II} porphyrin dimer **11** was obtained in 85% yield and its Au^{III} porphyrin analogue **12** in 50% yield. Since the threading experiments proceeded more or less quantitatively, these isolated yields show that partial dethreading takes place during chromatographic purification, especially in the case of the Au^{III}porphyrin dimer **12**.



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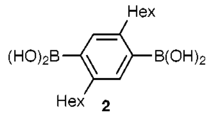

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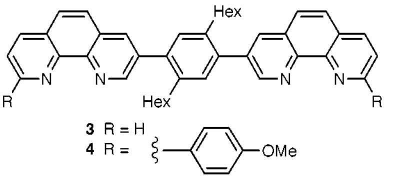

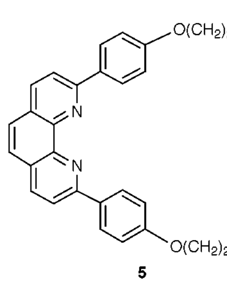

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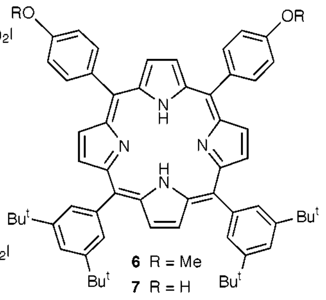
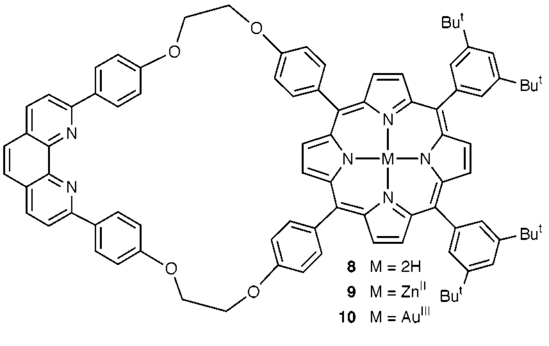
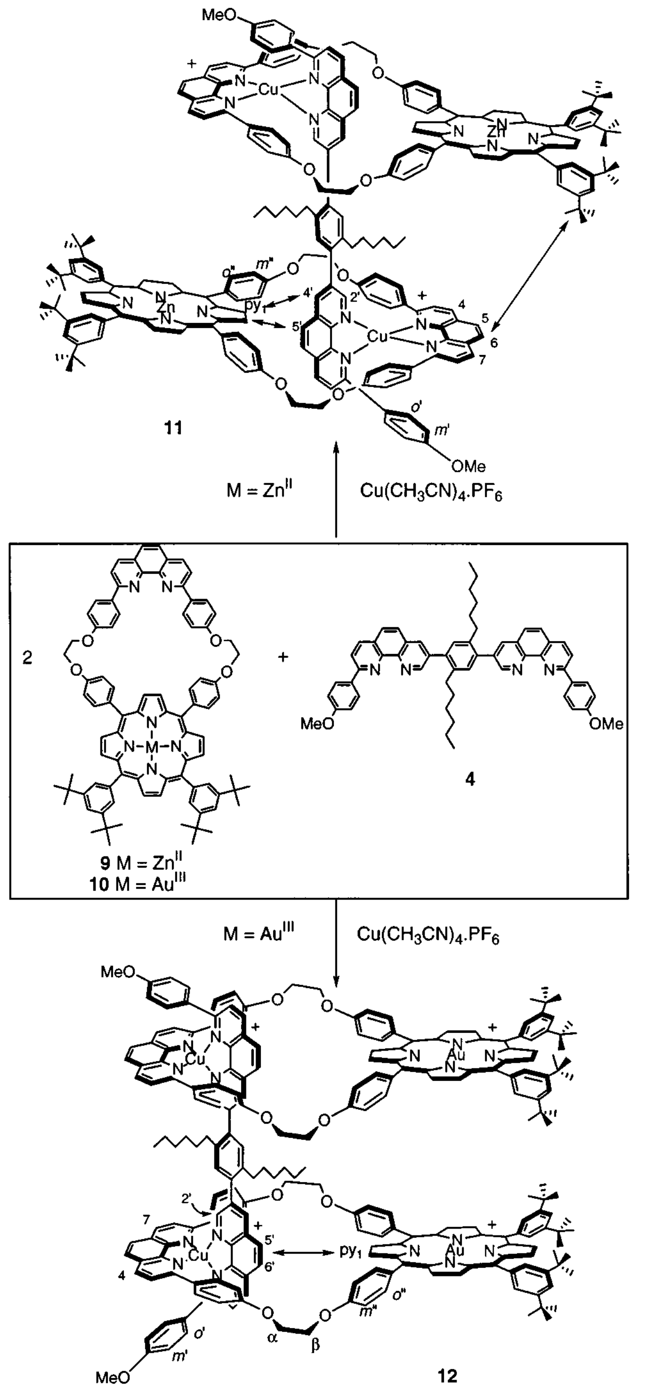


6 R = Me
7 R = H



8 M = 2H
9 M = Zn^{II}
10 M = Au^{III}

Diagnostic of macrocycle threading onto bis-phenanthroline **4** are the large upfield shifts of protons *m*′ of **4** both for **11** (−1.28 ppm) and **12** (−0.98 ppm), due to ring current effects of the phenanthroline fragment included in the macrocycles on the anisyl extremities of **4**.[13] Methyl protons of these groups are also affected, albeit to a lesser extent. As expected, threading also breaks off the symmetry plane of the macrocycle, which contains the C_2 symmetry axis. The largest resulting splittings are observed for **11**. *o*″ and *m*″ protons of the porphyrins produce two pairs of signals, indicating that the rotation of the



Scheme 1 Cu^I-directed threading of macrocycle **9** or **10** onto bis-phenanthroline **4**. Protons highlighted in the text are indicated, as well as intercomponent NOE effects.

corresponding phenylene groups is slow on the NMR timescale, and α and β protons of **11** clearly form two sets of diastereotopic pairs of atoms.

Despite these common features, the ^{1}H NMR spectra of the threaded complexes **11** and **12** showed dramatic differences, which could not be attributed solely to the different nature of the metal cation of the porphyrins. Upon threading, protons 2′ of **4** and (4,7) of the macrocycles are −2.54 and −0.59 ppm more shielded, respectively, when **11** is compared to **12**. 2D ^{1}H NMR ROESY experiments on **11** showed a remarkable intercomponent NOE crosspeak between the Zn^{II} porphyrin Bu^t groups and the pair (5,6) of protons of the phenanthroline fragment belonging to a different macrocycle, that was absent in the case of **12**. For the latter, a symmetrical correlation between py$_1$ of the Au^{III} porphyrins and the pairs (5′,6′) of protons of **4** could be observed, which, in the case of **11**, involved protons 4′ and 5′ instead.

All of these data suggest that, in the threaded system **11**, the Zn^{II} porphyrin components are roughly antiparallel, as shown in Scheme 1, each being tilted towards the phenanthroline chelate of the macrocycle maybe thanks to attractive interactions between the electron-rich Zn^{II} porphyrin of one macrocycle and the electron-deficient Cu^I-complexed phenanthroline included in the other macrocycle. The significant differences in the ^{1}H NMR spectra of **11** and **12** suggest that the Au^{III} porphyrin dimer has a conformation dramatically different from that of the Zn^{II} porphyrin dimer. The Au^{III} porphyrins being cationic, they are no longer able to stack with the Cu^I-complexed phenanthrolines, due to electrostatic repulsion. A likely conformation would be that represented in Scheme 1, in which the two Au^{III} porphyrins are roughly parallel. In conclusion, the threaded complexes **11** and **12** represent new members of the family of porphyrin dimers assembled with coordination bonds. The present study also shows that, by modifying the nature of the central metal in threaded porphyrin-containing systems, dramatic geometrical changes are induced.

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Notes and references

† All of the new compounds were characterized by ^{1}H NMR and mass spectrometry or elemental analysis, and the data are in agreement with the structures.

1 J. Deisenhofer and H. Michel, *Angew. Chem., Int. Ed. Engl.,* 1989, **28**, 829; R. Huber, *Angew. Chem., Int. Ed. Engl.,* 1989, **28**, 848; W. Kühlbrandt, *Nature,* 1995, **374**, 497; T. Pullerits and V. Sundström, *Acc. Chem. Res.,* 1996, **29**, 381.
2 J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, *J. Mol. Biol.,* 1984, **180**, 385; J. P. Allen, G. Feher, T. O. Yeates, H. Komiya and D. C. Rees, *Proc. Natl. Acad. Sci. U.S.A.,* 1987, **84**, 5730.
3 A. M. Brun, S. J. Atherton, A. Harriman, V. Heitz and J.-P. Sauvage, *J. Am. Chem. Soc.,* 1992, **114**, 4632; A. Harriman, F. Odobel and J.-P. Sauvage, *J. Am. Chem. Soc.,* 1995, **117**, 9461; A. V. Chernook, A. M. Shulga, E. I. Zenkevich, U. Rempel and C. von Borczyskowski, *Ber. Bunsenges. Phys. Chem.,* 1996, **100**, 2065; C. A. Hunter and R. K. Hyde, *Angew. Chem., Int. Ed. Engl.,* 1996, **35**, 1936; R. V. Slone and J. T. Hupp, *Inorg. Chem.,* 1997, **36**, 5422.
4 M. R. Wasielewski, U. H. Smith, B. T. Cope and J. J. Katz, *J. Am. Chem. Soc.,* 1977, **99**, 4172; Y. Kobuke and H. Miyaji, *J. Am. Chem. Soc.,* 1994, **116**, 4111; R. T. Stibrany, J. Vasudevan, S. Knapp, J. A. Potenza, T. Emge and H. J. Schugar, *J. Am. Chem. Soc.,* 1996, **118**, 3980.
5 W. W. Parson and A. Warshel, *J. Am. Chem. Soc.,* 1987, **109**, 6153; J. R. Reimers and N. S. Hush, *Chem. Phys.,* 1995, **197**, 323.
6 D. B. Amabilino, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.,* 1996, **118**, 3285.
7 Y. Saitoh, T. Koizumi, K. Osakada and T. Yamamoto, *Can. J. Chem.,* 1997, **75**, 1336.
8 M. Rehahn, A. D. Schlüter and G. Wegner, *Makromol. Chem.,* 1990, **191**, 1991.
9 P. Galda and M. Rehahn, *Synthesis,* 1996, 614.
10 J.-C. Chambron, C. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, N. Solladié, A.-M. Albrecht-Gary and M. Meyer, *New J. Chem.,* 1995, **19**, 409.
11 M. Linke, J.-C. Chambron, V. Heitz, J.-P. Sauvage and V. Semetey, *Chem. Commun.,* 1998, 2469.
12. C. O. Dietrich-Buchecker and J.-P. Sauvage, *Tetrahedron,* 1990, **46**, 503; D. B. Amabilino and J.-P. Sauvage, *New J. Chem.,* 1998, **22**, 395.
13 C. O. Dietrich-Buchecker, P. A. Marnot, J.-P. Sauvage, J.-P. Kintzinger and P. Maltèse, *Nouv. J. Chim.,* 1984, **8**, 573.

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