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Rings-and-String Approach to the Construction of Porphyrin Arrays by Transition-Metal-Directed Threading

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Multiporphyrins[1] are particularly attractive for studying photoinduced long-range electron transfer and modeling of the photosynthetic reaction center. The vast majority of the systems described until now dispose porphyrins in a desired spacial arrangement by linking them covalently. Clearly, a modular approach to noncovalent assembly is appealing, since it should reduce synthetic work and allow the rapid construction of relatively elaborate multicomponent structures from a collection of simple modules. Recent examples of noncovalently linked systems incorporating two or more porphyrins include those based on the formation of hydrogen bonds,[2,3] as well as coordination of porphyrin-carrying ligands to metal ions.[4] To the best of our knowledge, the only system containing two different porphyrin nuclei reported in this latter group is constructed around a substitutionally inert ruthenium(II) core complex.[5]

Here, we describe an alternative principle for building multiporphyrinic assemblies. It is based on a transition-metal-directed threading reaction involving a two-chelate molecular string and two coordinating rings—each bearing a porphyrin as a pendant group—which thread and reside on the string by virtue of complexation to copper(I) ions, a strategy depicted schematically in Figure 1. It is reminiscent of the approach used to construct catenanes,[6] rotaxanes,[7] and related threaded systems.[8,9] The threaded situation of Figure 1 is the only one which permits full coordination of the metal ions, i.e., binding of two chelates per metal ion, at the stoichiometry illustrated.[8]

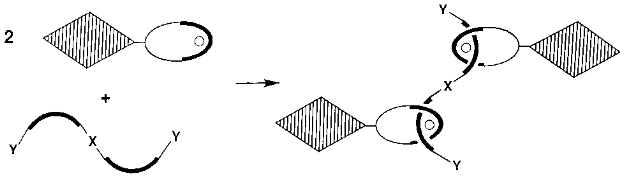
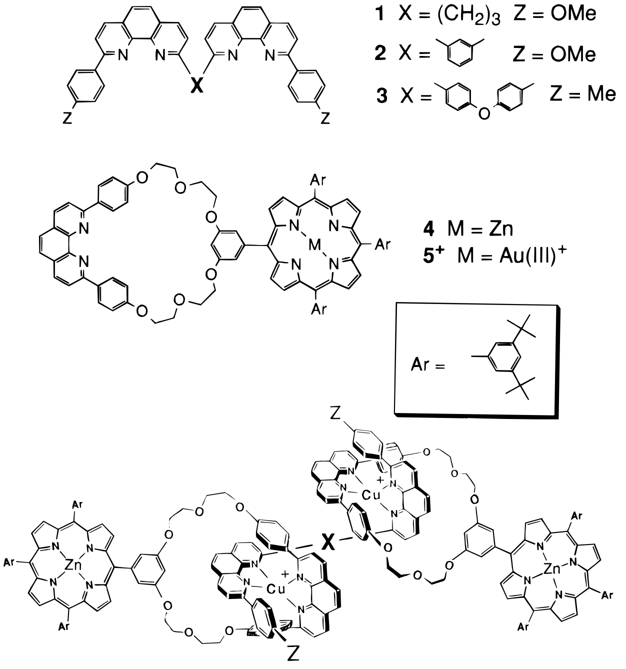


Figure 1. The construction principle. The string consists of two chelates (thick line) connected by a linker X. The terminus functions Y have to be small enough to pass through the ring in order for the string to thread the two porphyrin-appended cycles. The gathering and threading process is governed by coordination of the four chelating units of the system to the two metal centers (white circle).



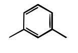
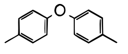
−X−	− (CH$_2$)$_3$ − **6**$^{2+}$	 **7**$^{2+}$	 **8**$^{2+}$
Yield of Threaded Complex	6%	60%	95%

Figure 2. The compounds used as the molecular strings and rings and the prototypical homoporphyrin threaded systems **6**$^{2+}$−**8**$^{2+}$ derived from **4**. The anions are PF$_6^-$ in every case.

The compounds we used as modules (Figure 2) are the three stringlike molecules[10,11] **1**−**3** and a macrocycle bearing an appended porphyrin, with either zinc(II) (**4**) or gold(III) (**5**$^+$) coordinated at its center.[12] The prototypical threaded systems **6**$^{2+}$−**8**$^{2+}$ (Figure 2) were prepared according to the schematic route in Figure 1. The stringlike molecules (0.5 equiv in CH$_2$Cl$_2$) were added to the copper(I) complex of the macrocycle **4** (in MeCN/CH$_2$Cl$_2$) at room temperature under argon. The products were purified by flash column chromatography. The efficacy of the threading process is very sensitive to the nature of the linking unit between the two chelates in the stringlike molecule. The isolated yield of **6**$^{2+}$ was only 6% (the bischelate **1** prefers to scavenge the copper(I) ion from the macrocycle to form a complex of 1:1 stoichiometry), while **7**$^{2+}$ was isolated

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[1] For key reports, see, along with references cited therein: (a) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227−6238. (b) DeGraziano, J. M.; Liddell, P. A.; Leggett, L.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* **1994**, *98*, 1758−1761. (c) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578−10592. (c) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105−1111.

[2] (a) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 345−348. (b) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 1530−1532. (c) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704−714.

[3] de Rege, P. J. F.; Williams, S. A.; Therien, M. J. *Science* **1995**, *269*, 1409−1413.

[4] (a) Woo, L. K.; Maurya, M. R. *Inorg. Chem.* **1991**, *30*, 4671−4673. (b) Mackay, G. L.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 43−44. (c) Drain, C. M.; Fischer, R.; Nolen, E. G.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 243−245. (d) Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921−1923.

[5] Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 9461−9472 and references therein.

[6] Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Bioorg. Chem. Front.*; Dugas, H., Ed. **1991**, *2*, 195−248.

[7] Chambron, J.-C.; Chardon-Noblat, S.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *Pure Appl. Chem.* **1993**, *65*, 2343−2349.

[8] Chambron, J.-C.; Dietrich-Buchecker, C. O.; Nierengarten, J.-F.; Sauvage, J.-P.; Solladié, N.; Albrecht-Gary, A.-M.; Meyer, M. *New J. Chem.* **1995**, *19*, 409−426.

[9] Threaded molecular systems not bearing stoppers at the two ends of the string have also been termed pseudorotaxanes. See, for example: Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1869−1871.

[10] The syntheses of **1** and **3** are similar to those of related compounds; see ref 8 and: Dietrich-Buchecker, C. O.; Nierengarten, J.-F.; Sauvage, J.-P.; Armaroli, N.; Balzani, V.; De Cola, L. *J. Am. Chem. Soc.* **1993**, *115*, 11237−11244.

[11] The coordination properties of **2** have been described. See: Dietrich-Buchecker, C. O.; Sauvage, J.-P.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2231−2232.

[12] The metalated porphyrins were prepared from the parent free-base porphyrin (M = 2H). Their synthesis will be described elsewhere.

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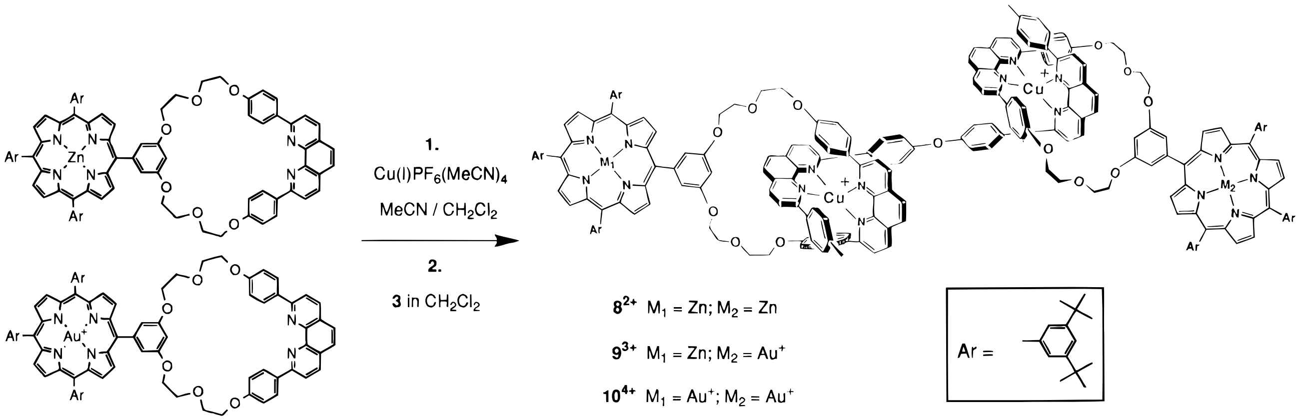

Figure 3. The threading of two different porphyrin rings onto a molecular string to generate the heteroporphyrinic complex **9**$^{3+}$. The anions are PF_6^- in every case.

in 60% yield. In the latter, the threading process competes with the formation of an extremely stable dinuclear double helix formed between copper(I) and **2**.[11] By contrast, when the copper(I) complex of **4** is combined with 0.5 equiv of **3**, an almost quantitative yield of **8**$^{2+}$ was isolated.

All the threaded systems, which have masses ranging from 4133 to 4227 amu, were unambiguously characterized using electrospray (ES) mass spectrometry and ^{1}H NMR and UV−vis spectroscopies. The ^{1}H NMR spectra of **6**$^{2+}$−**8**$^{2+}$ all show a 2:1 ring:thread stoichiometry and are characteristic of copper(I) complexes of this type.[8] It is noteworthy that although the two porphyrins are gathered by threading onto the strings, no significant interaction between the two can be detected by comparisons of the ^{1}H NMR and UV−vis spectra of **4** with those of **6**$^{2+}$−**8**$^{2+}$.

Our aim of constructing systems capable of exhibiting long-range electron transfer requires the linking of two different chromophores. Zinc(II) porphyrin is an electron donor in its excited state, while a gold(III) porphyrin is a good electron acceptor, such that their combination is well suited for the study of electron transfer processes.[7] Since the threading process for string **3** is extremely efficient, we attempted the assembly of the heteroporphyrinic **9**$^{3+}$ (Figure 3). The macrocycles **4** and **5**$^+$ (1:1 in CH_2Cl_2), incorporating zinc(II) and gold(III) porphyrins, respectively, were combined with enough $Cu(MeCN)_4PF_6$ (in MeCN) for every ring, and the molecular thread **3** was added in CH_2Cl_2 solution. A ^{1}H NMR spectrum of the crude product indicated that the macrocycles had been threaded quantitatively onto the string, affording the two homoporphyrinic systems **8**$^{2+}$ and **10**$^{4+}$ and the desired heteroporphyrinic complex **9**$^{3+}$, in the expected 1:1:2 statistical ratio. The three complexes were separated by flash column chromatography (SiO_2, CH_2Cl_2/MeOH eluent) and were isolated in yields of 20, 10, and 8% for **8**$^{2+}$, **10**$^{4+}$, and **9**$^{3+}$, respectively.[13]

The composition of **9**$^{3+}$ was confirmed by ESMS, one- and two-dimensional ^{1}H NMR spectroscopy, and UV−vis spectroscopy. The ^{1}H NMR spectrum of **9**$^{3+}$ showed a 1:1 ratio of zinc(II) : gold(III) porphyrins (whose proton resonances are at similar positions to those observed in the free macrocycles), and several signals which are unique to the ^{1}H NMR spectrum of **9**$^{3+}$ when compared with those of **8**$^{2+}$ and **10**$^{4+}$. The UV−vis spectrum of the complex has absorbances resulting from the summation of those of the component parts, again indicating essentially no interaction between the porphyrinic modules. A remarkable feature of this heteroporphyrinic system is its kinetic stability. The threaded complex **9**$^{3+}$ can be chromatographed (SiO_2, CH_2Cl_2/MeOH) without exchange of its modules, and does not detectably "scramble" to either **8**$^{2+}$ and **10**$^{4+}$ when kept in CD_2Cl_2 solution at room temperature for 24 h.

In summary, we have proved that the modular string-and-rings approach is a viable one for constructing multiporphyrinic assemblies incorporating electron donor and acceptor chromophores between which there is no covalent link. In addition, once isolated, the complexes appear to exhibit relative kinetic stability, an observation that bodes well for the use of these and similar systems for the study of long-range electron transfer processes.

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Supporting Information Available: A general synthetic procedure for the preparation and purification of the threaded complexes and related representative ^{1}H NMR spectra, ES mass spectra, and UV−vis spectra (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) The poor isolated yields for **10**$^{4+}$ and **9**$^{3+}$ reflect the difficulty in separating these two complexes, which are nonetheless relatively stable during chromatography.