ORGANIC
LETTERS

2000
Vol. 2, No. 16
2435−2438

Self-Assembly of Oligomeric Porphyrin Rings

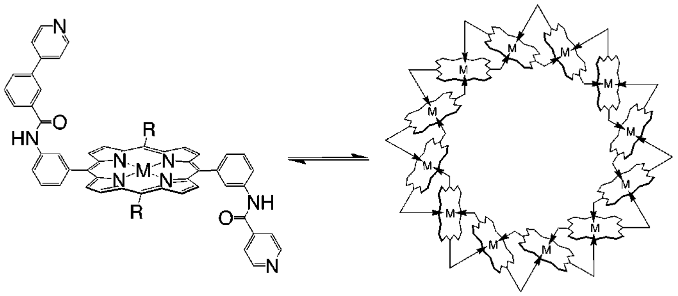
**Richard A. Haycock, Christopher A. Hunter,* David A. James,
Ulrike Michelsen, and Liam R. Sutton**

*Krebs Institute for Biomolecular Science, Department of Chemistry,
University of Sheffield, Sheffield S3 7HF, U.K.*

c.hunter@shef.ac.uk

Received May 18, 2000

ABSTRACT



A cobalt porphyrin equipped with two different but geometrically complementary pyridine ligands self-assembles to form an unusually stable complex with approximately 12 porphyrin monomers arranged in a macrocyclic array.

Porphyrin arrays have attracted considerable interest as synthetic targets due to the potential for exploitation as photochemical devices.[1] Organized oligomeric assemblies of the related chlorophyll chromophores are used in biological light-harvesting complexes and reaction centers for the trapping and conversion of solar energy in photosynthesis.[2] A number of synthetic strategies have been developed for the construction of multiporphyrin assemblies, and self-assembly has emerged as one of the most promising approaches.[3] We recently reported the self-assembly of long-chain polymers from a cobalt porphyrin symmetrically functionalized with two pyridine ligands, Co**1** (Figure 1).[4] We now describe the synthesis of an unsymmetrically functionalized analogue and show that it exhibits completely different self-assembly properties.

---

(1) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 10418; **1995**, *117*, 704. Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198. Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578. Li, J. Z.; Ambroise, A.; Yang, S. I.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927. Kuciauskas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604. Maruo, N.; Uchiyama, M.; Kato, T.; Arai, T.; Nishino, N.; Akisada, H. *Chem. Commun*. **1999**, 2057. Mak, C. C.; Pomeranc, D.; Sanders, J. K. M.; Montalti, M.; Prodi, L. *Chem. Commun*. **1999**, 1083. Darling, S. L.; Mak, C. C.; Bampos, N.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *New J. Chem*. **1999**, 23, 359. Mak, C. C.; Bampos, N.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3020. Nakano, A.; Osuka, A.; Yamazaki, I.; Yamazaki, T.; Nishimura,Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 3023. Kumar, R. K.; Goldberg, I. *Angew. Chem., Int. Ed.* **1998**, *37*, 3027. Huck, W. T.; Rohrer, A.; Anikumar, A. T.; Fokkens, R. H.; Nibbering, N. M. M.; Van Veggel, F. C. J. M.; Reinhoudt, D. N. *New J. Chem*. **1998**, *22*, 165. Biemans, H. A. M.; Rowan, A. E.; Verhoeven, A.; Vanoppen, P.; Latterini, L.; Foekema, J.; Schenning, A. P. H. J.; Meijer, E. W.; de Schryver, F. C.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1998**, *120*, 11054. Sugiura, K.; Tanaka, H.; Matsumoto, T.; Kawai, T.; Sakata, Y. *Chem. Lett*. **1999**, *11*, 1193.

(2) Deisenhofer, J.; Michel, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 829. Huber, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 848. McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornethwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517.

(3) Hunter, C. A.; Sarson, L. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316. Chi, X.; Guerin, A. J.; Haycock, R. A.; Hunter, C. A.; Sarson, L. D. *J. Chem. Soc., Chem. Commun.* **1995**, 2567. Drain, C. M.; Nifiatis, F.; Vasenko, A.; Batteas, J. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2344. Reek, J. N. H.; Schenning, A. P. H. J.; Bosman, A. W.; Meijer, E. W.; Crossley, M. J. *Chem. Commun*. **1998**, 11.

(4) Michelsen, U.; Hunter, C. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 764.

10.1021/ol000129d CCC: $19.00

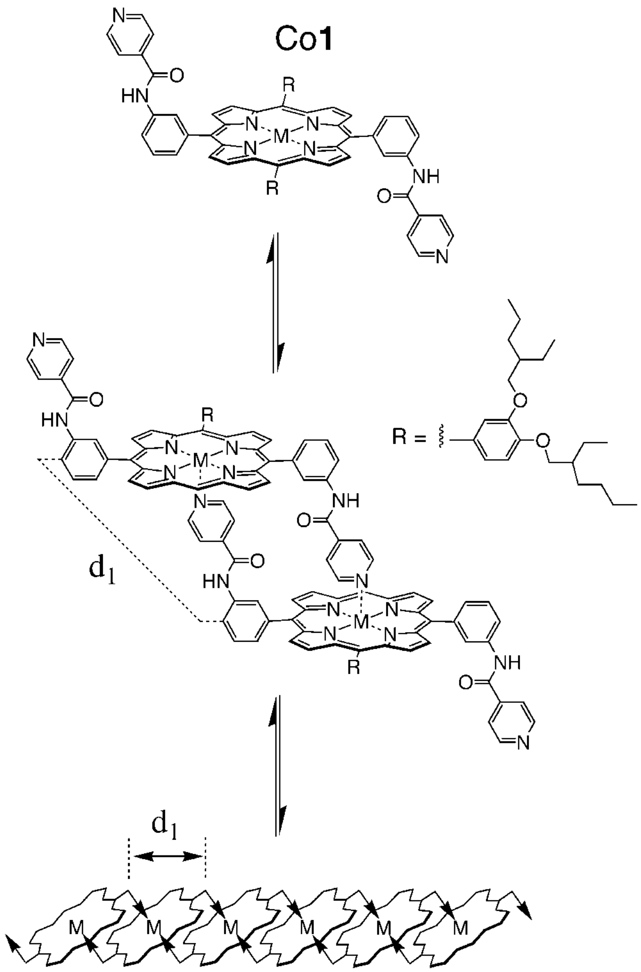
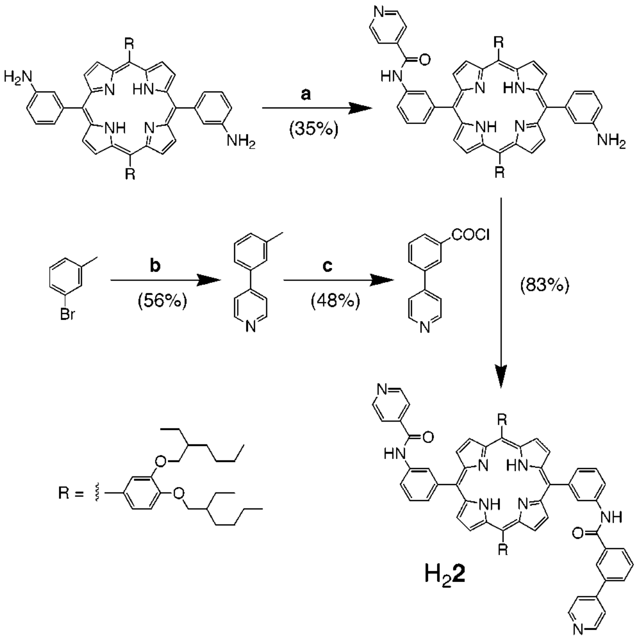


Figure 1. Self-assembly of Co**1** to form long-chain polymeric complexes, showing the key monomer−monomer interaction interaction in detail and a cartoon of the corresponding polymer. The structural parameter d_1 used for calibration of the GPC data is indicated.

H_2**2** was prepared from the corresponding diaminoporphyrin using sequential acid chloride couplings as illustrated in Scheme 1. Metalation with cobalt acetate in chloroform/methanol afforded Co**2** in quantitative yield. We have previously shown that the best method for characterizing the assembly properties of cobalt porphyrin oligomers is gel permeation chromatography (gpc),[5] and Figure 2 shows the results obtained for Co**2**.

Scheme 1[a]



[a] Conditions: 4-pyridinecarbonyl chloride; (b) i. Mg, ii. 4-bromopyridine; (c) i. $KMnO_4$, ii. $SOCl_2$.

The behavior of this system is remarkably different from the other symmetrically substituted porphyrin derivatives which we have studied. Figure 2a shows a typical concentration profile for the symmetrical derivative Co**1**. The retention times for Co**1** are significantly shorter than those for the corresponding porphyrin monomer Co**3** and porphyrin dimer $(\text{Co}\mathbf{4})_2$ and are indicative of polymerization. As the concentration of cobalt porphyrin increases, the length of the polymeric assembly increases as expected.[4] In contrast, the retention time for Co**2** is relatively insensitive to concentration (Figure 2b). A single species is formed over the concentration range 5−500 μM, and only when the concentration increases further do higher molecular weight polymers begin to emerge. The behavior of Co**2** is characteristic of a cooperative self-assembly process to form a special structure with unusual stability. The most likely candidate is a macrocyclic architecture, where the intramolecular interactions formed in the cyclization process confer additional stability relative to the intermolecular interactions required to make open-chain polymers.[6] We have endeavored to obtain some supporting evidence for this hypothesis by studying the dimerization of model compounds.

H_2**4** and H_2**5** were prepared from the corresponding aminoporphyrins according to Scheme 2 and were quantitatively metalated with zinc acetate. UV/visible dilution studies were used to determine the association constants for the zinc porphyrin dimers. The Zn**4**·Zn**5** association constant ($1.0 \pm 0.2 \times 10^6$ M^{-1}) is significantly larger than the self-dimerization constants for the formation of Zn**5**·Zn**5** ($4 \pm 1 \times 10^4$ M^{-1}) and Zn**4**·Zn**4** ($4 \pm 1 \times 10^5$ M^{-1}). Thus, the two different ligand side arms constitute a geometrically

---

(5) Other techniques have proved less suitable for characterizing these systems: the major species detected by mass spectrometry (FAB, ESMS, or Maldi) is always the monomer; the molecular weights of the oligomers are too high for reliable vapor pressure osmometry; the paramagnetic cobalt(II) center makes the ^{1}H NMR spectra very broad; ligand coordination can be detected by UV/visible absorption spectroscopy, but this only confirms that the cobalt centers are fully bound to pyridine in these compounds.

(6) Chi, X.; Guerin, A. J.; Haycock, R. A.; Hunter, C. A.; Sarson, L. D. *J. Chem. Soc., Chem. Commun.* **1995**, 2563.

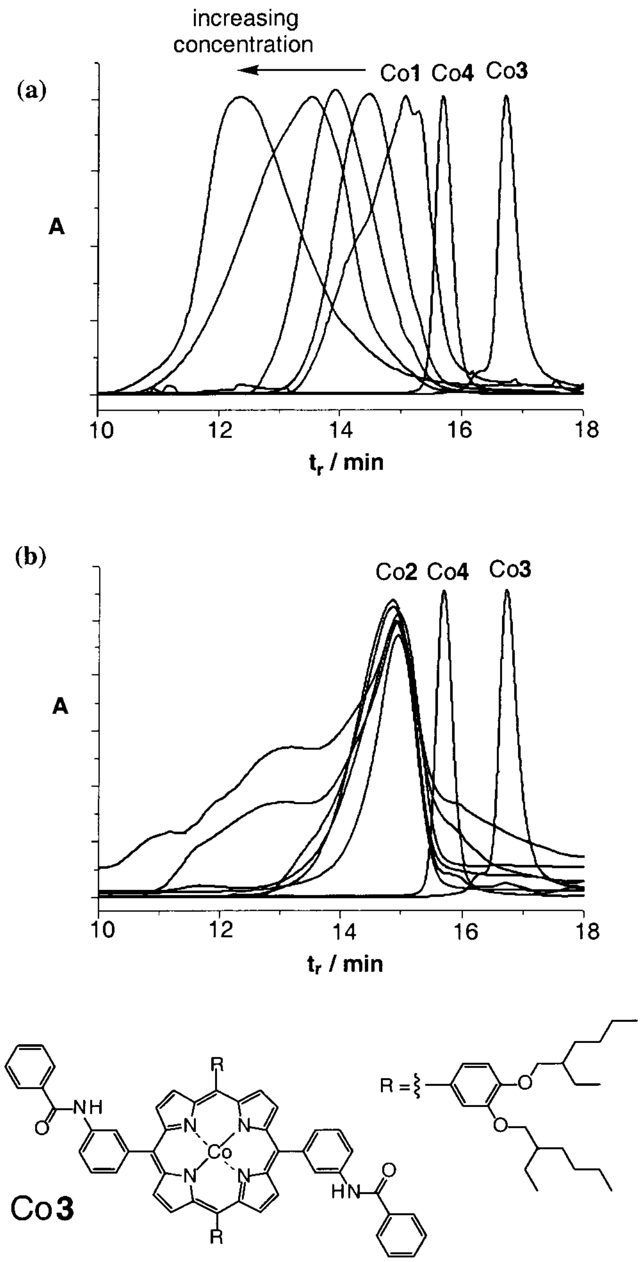
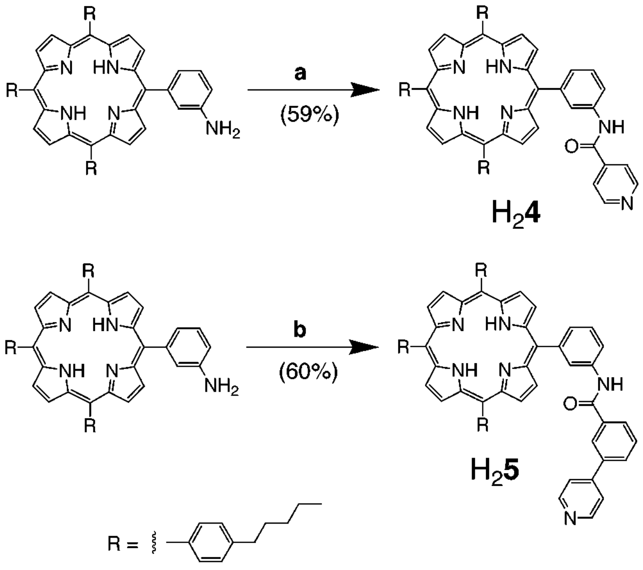


Figure 2. Normalized GPC traces (5 μm mixed bed column) for (a) Co**1** at concentrations between 55 and 7000 μM and (b) Co**2** at concentrations between 5 and 2000 μM. t_R is the retention time and A is the absorbance at 440 nm. Both figures show the corresponding GPC traces for reference compounds Co**3** and Co**4**. Co**3** cannot oligomerize because it is functionalized with benzoyl rather than pyridyl side arms as shown.[4] Co**4** is functionalized with only one pyridyl side arm and therefore forms a dimer (see Scheme 2 for structure).[4]

Scheme 2[a]



[a] (a) 4-Pyridinecarbonyl chloride; (b) 3-(4-pyridyl)benzoyl chloride.

complementary pair, and this leads to preferential formation of the heterodimer shown in Figure 3. Models show that the heterodimer can adopt a strain-free conformation which is not accessible to the other two homodimers (compare the ideal metal−pyridine bond angles in Figure 3 with those in Figure 1 which are highly distorted). This structure leads to an inclination of about 30° between the planes of the two porphyrins in the heterodimer (Figure 3) which is clearly consistent with proposed macrocyclization of Co**2**. The two different ligands in Co**2** are attached trans across the porphyrin, and so the 30° bend at the level of the monomer−monomer interaction must propagate in the same direction

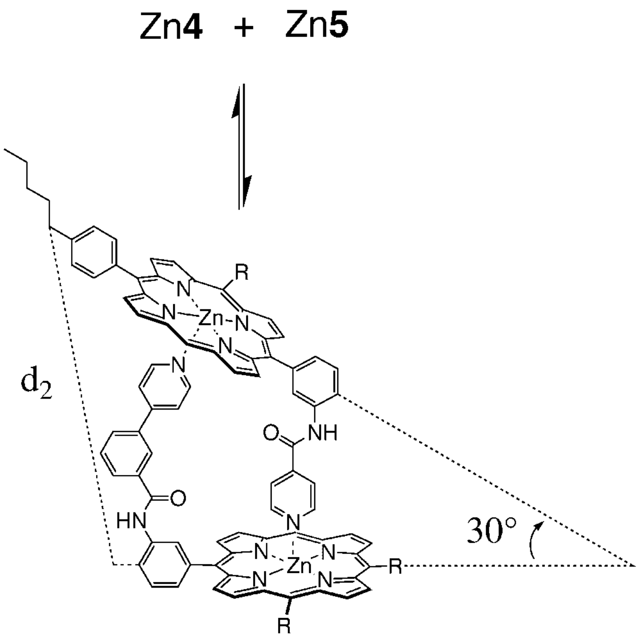


Figure 3. Model compounds Zn**4** and Zn**5** form a 1:1 complex rather than homodimers due to the complementarity of the two different ligand side arms. This leads to an inclination of about 30° between the planes of the two porphyrins. The structural parameter d_2 used for calibration of the GPC data is indicated.

along the oligomer, leading to either a macrocyclic or helical structure. This suggests that the stable structure observed by GPC is a cyclic dodecamer (Figure 4).

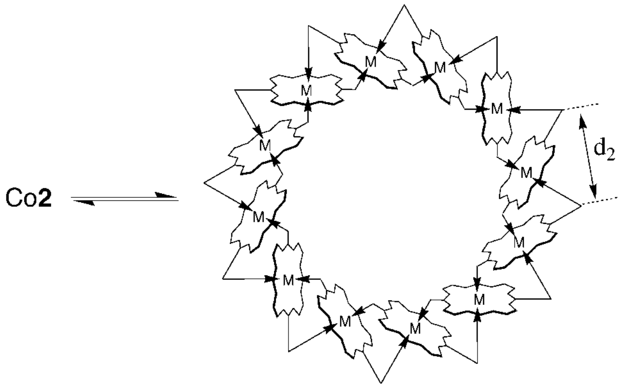


Figure 4. Co**2** self-assembles to form a macrocyclic oligomer. A bend of 30° at the level of the Co**2** monomer−monomer interaction leads to the dodecamer shown, and this structure is consistent with the GPC retention time (the structural parameter d_2 used for calibration of the GPC data is indicated).

The GPC results can be calibrated using the Co**1**−Co**4** chain stopper system as described previously,[4] and this calibration was used to estimate the size of the self-assembled structure formed by Co**2**. Since the dimensions of a macrocyclic oligomer scale with the diameter of the ring, whereas the dimensions of a linear polymer simply increase with length, a geometric correction must be applied to the retention time calibration in order to relate these two systems:

$$t_R \text{ for Co}\mathbf{1} = c \log(Nd_1) \quad (1)$$

$$t_R \text{ for Co}\mathbf{2} = c \log(Nd_2/\pi) \quad (2)$$

where c is a constant, N is number of monomer units in the assembly, and d_1 and d_2 are the monomer repeat lengths illustrated in Figures 1, 3, and 4. The repeat lengths were determined by using models which assume that the porphyrin side arms all lie flat in one plane ($d_1 \approx 14$ Å and $d_2 \approx 19$ Å). The GPC data in Figure 2 together with eqs 1and 2 give a value of $N = 11.5$ for the Co**2** assembly which is close to the expected value for a monomer−monomer wedge angle of 30°.

These experiments show that changing the geometry of the monomer unit can have dramatic effects on the structure and self-assembly properties of cobalt porphyrin arrays. Co**1** which is symmetrically substituted with two identical ligand side arms forms linear polymers (Figure 1). Co**2** which is unsymmetrically functionalized with complementary but different ligand side arms self-assembles at much lower concentrations to form a more stable structure which resists polymerization. The best explanation based on the results obtained from GPC, modeling, and the behavior of zinc porphyrin model compounds is the formation of a macrocyclic dodecamer (Figure 4) which only opens up to form higher molecular weight polymers once the concentration increases above the effective molarity for macrocylisation (about 0.5 mM).[7] The macrocyclic architecture resembles the bacterial light-harvesting complexes LH1 and LH2 where close coupling of the chromophores around the ring facilitates rapid and efficient energy transfer over long distances.[2,8] The chromophores are too far apart to show strong excitonic coupling in the UV/visible absorption spectrum, and unfortunately, cobalt quenches the porphyrin fluorescence, which makes any analysis of the energy transfer properties of these synthetic analogues problematic. However, the approach can clearly be applied to other metalloporphyrin-ligand combinations, and work on such systems is in progress.

Acknowledgment. This research was supported by the EPRSC (R.A.H., U.M.), the BBSRC (D.A.J., L.R.S.), and the Lister Institute (C.A.H.).

Supporting Information Available: Spectroscopic data for H_2**2**, Co**2**, Zn**4**, and Zn**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL000129D

---

(7) Given the accuracy of the gpc experiment and the width of the peaks, it is not possible to pin down the structure to a dodecamer as opposed to another cyclic oligomer close in size or a mixture of two or three such species. However, the structure is clearly a macrocycle of approximately these dimensions.

(8) van Grondelle, R.; Dekker, J. P.; Gillbro, T.; Sundstrom, V. *Biochim. Biophys. Acta Bioenergetics* **1994**, *1187*, 1. Karrasch, S.; Bullough, P. A.; Ghosh, R. *EMBO J.* **1995**, *14*, 631. Oling, F.; Boekema, E. J.; Dezarate, I. O.; Visschers, R.; van Grondelle, R.; Keegstra, W.; Brisson, A.; Picorel, R. *Biochim. Biophys. Acta Bioenergetics* **1996**, *1273*, 44.