Letter

Self-assembly of chiral-twisted porphyrin dimers

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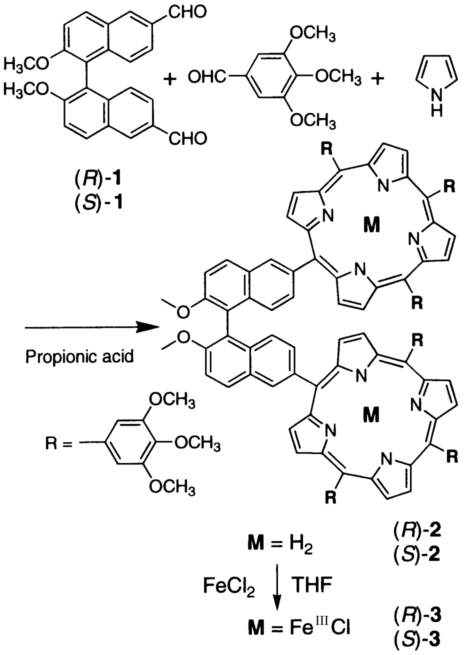
Chiral-twisted iron(III) porphyrin dimers were self-assembled to high-molecular-weight polynuclear species through the intermolecular formation of μ-oxo dimers.

There have been considerable efforts made in the design and synthesis of multiple porphyrin arrays through covalent and non-covalent bonds.[1,2] These porphyrin arrays are synthetic models for photosynthetic reaction centers, light-harvesting antenna complexes, and enzymatic reaction centers. Steric control of angles and distances among porphyrin moieties can enhance such properties as efficient electron and energy transfer in the porphyrin arrays and catalytic activities.[1–3] Porphyrin dimers have also been used in the design of supramolecular hosts for amino acids, diamines, and sugars.[4]

Chiral porphyrins bearing chiral groups covalently linked to achiral porphyrin moieties have been studied as enantioselective catalysts.[5] Optically active binaphthyl groups produce a strong chiral field around porphyrin moieties. We have prepared novel chiral porphyrin dimers (*R*)- and (*S*)-**2**, in which two porphyrin moieties are linked by a chiral binaphthyl spacer. The optically active binaphthyl spacer provides a bias of a twisted nature to the porphyrin dimers and controls the angles and distances between the two porphyrin moieties. Herein, we report the synthesis and characterization of chiral-twisted porphyrin dimers, and their self-assembly through the intermolecular formation of a μ-oxo dimer between iron porphyrin moieties. The self-assembly of chiral-twisted iron porphyrin dimers (*R*)- and (*S*)-**3** may result in optically active porphyrin assemblies.

A pair of chiral-twisted porphyrin dimers (*R*)- and (*S*)-**2** were enantioselectively prepared from (*R*)- and (*S*)-1,1′-binaphthol (commercially available, >99% ee) (Scheme 1). Dinuclear compounds (*R*)- and (*S*)-**2** were obtained by fusing **1** (1 mmol), 3,4,5-trimethoxybenzaldehyde (6 mmol), and pyrrole (8 mmol) in propionic acid under reflux for 72 h, followed by purification by basic alumina and gel-permeation (Bio-Beads SX-3) chromatography in a 5% yield. All products were characterized by FT-IR, mass spectrometry, and ^{1}H NMR. For preparation of the iron(III) complexes (*R*)- and (*S*)-**3**, the free-base **2** and $FeCl_2$ were refluxed in THF for 48 h. The metallation was monitored by UV-Vis and MALDI-TOF-MS spectral changes. The iron porphyrin dimers (*R*)- and (*S*)-**3** were obtained in a 60% yield after purification by column chromatography and treatment with methanoic HCl. Fig. 1 shows the CD spectra of (*R*)- and (*S*)-**2** in CH_2Cl_2. The two enantiomers of the chiral-twisted porphyrin dimers displayed mirror images of the intense CD spectra in the 400–450 nm range. One enantiomer (*R*)-**2** showed a positive sign of the CD at 427 nm corresponding to the Soret band of the porphyrin moiety in the absorption spectra. This result implies the absence of racemization, and the opposite twisted nature of (*R*)- and (*S*)-**2**. The linkage of two porphyrin moieties by the optically active binaphthyl spacer results in the generation of a regulated arrangement (see illustration in Fig. 1).[6]

It is well-known that Fe(III) porphyrin complexes form stable μ-oxo dimers in basic aqueous solution with the two porphyrin planes set at a distance of approximately 0.38 nm.[7] The absorption spectrum of (*R*)-**3** in CH_2Cl_2 changed in response to mixing with aqueous solutions at various pH. The



Scheme 1

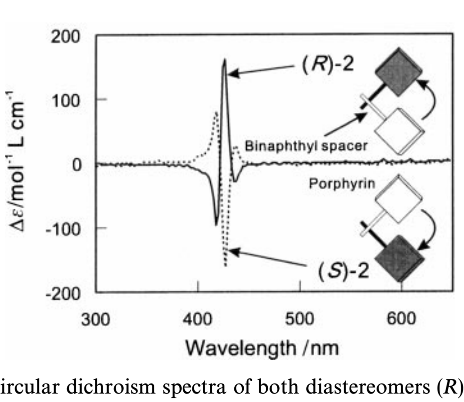


Fig. 1 Circular dichroism spectra of both diastereomers (*R*)- and (*S*)-**2** in CH_2Cl_2.

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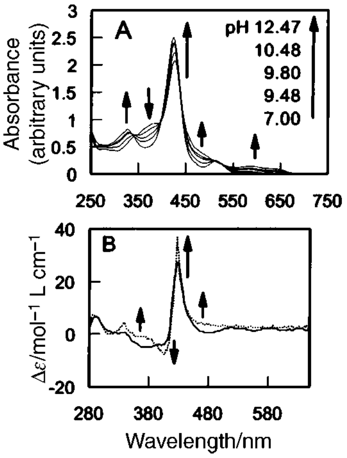
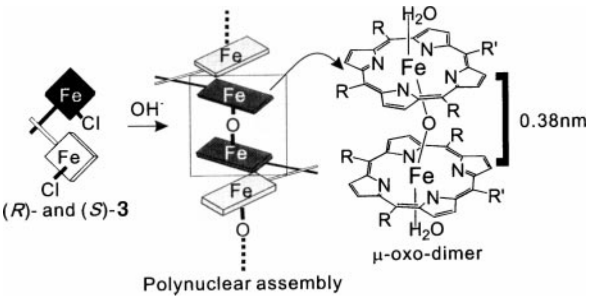


Fig. 2 (A) Absorption spectral changes of (*R*)-**3** by mixing with aqueous solutions at various pH: pH = 7.0, 9.5, 9.8, 10.5, 12.4. (B) Circular dichroism spectra of (*R*)-**3** and assembled (*R*)-**3** in CH_2Cl_2.



Scheme 2

absorbance of the Soret band increased with increasing pH and saturated at pH 12.4 (Fig. 2A). The isosbestic points showed an equilibrium between the two species at different pH. IR spectroscopy of (*R*)-**3** after treatment with a basic aqueous solution displayed a new band at 850 cm^{-1}, indicating the formation of a μ-oxo dimer between the two Fe(III) porphyrin moieties.[8] Furthermore, a mononuclear tetrakis(3,4,5-trimethoxyphenyl)porphyriniron(III) complex has also been converted to the μ-oxo dimer under the same conditions and was characterized by MALDI-TOF-MS and IR.[9] The examination of CPK molecular models revealed that the intramolecular formation of μ-oxo dimers in (*R*)- and (*S*)-**3** is sterically impossible.[10] The absorption spectra above pH 12.4 provided strong evidence of intermolecular formation of μ-oxo dimers between two iron porphyrin moieties in differently twisted porphyrin dimers. The twisted porphyrin dimer could have assembled into the porphyrin assembly as shown in Scheme 2. Fig. 2B shows the CD spectral change of (*R*)-**3** when mixed with a basic aqueous solution at pH 12.4. Iron complexes (*R*)- and (*S*)-**3** exhibited positive and negative CD signs for the Soret band, respectively. The magnitude of the CD signals for the Soret band of (*R*)-**3** increased as a result of the formation of the μ-oxo dimer, and the CD spectral change corresponds to the absorption spectral change. An opposite response of the CD spectra was observed in the formation of the μ-oxo dimer of (*S*)-**3**. The molecular weight (M_w) and polydispersity (M_w/M_n) were roughly estimated to be 6.0×10^4 g mol^{-1} and 2.35 by gel permeation chromatography (GPC) analysis referenced to a polystyrene standard. MALDI-TOF-MS spectroscopy of the assemblies gave only the fragment (*R*)- and (*S*)-**3** (*m*/*z* 2050), in which no peaks corresponding to oligonuclear complexes were detected. Therefore, the chiral-twisted iron(III) porphyrin dimers formed high-molecular-weight assemblies through the formation of the μ-oxo dimer between two iron porphyrin moieties.

In conclusion, we have demonstrated the spontaneous formation of optically active porphyrin assemblies through the formation of μ-oxo dimers among chiral-twisted porphyrin dimers. Predetermined design of the building blocks can lead to large porphyrin assemblies through self-assembling processes. Optically active porphyrin assemblies should be of great interest in chiral recognition and enantioselective catalytic processes by the use of their chiral grooves.

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References

1 See for example: (*a*) A. Osuka, S. Marumo, N. Magata, S. Taniguchi, T. Okada, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki, *J. Am. Chem. Soc.*, 1996, **118**, 155; (*b*) D. L. Officer, A. K. Burrel and D. C. W. Reid, *Chem. Commun.*, 1996, 1657; (*c*) A. Vidal-Ferran, N. Bampos and J. K. M. Sanders, *Inorg. Chem.*, 1997, **36**, 6117; (*d*) S. I. Yang, R. K. Lammi, J. Seth, J. A. Riggs, T. Arai, D. Kim, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Phys. Chem. B*, 1998, **102**, 9426.

2 See for example: (*a*) P. J. F. deRege, S. A. Williams and M. J. Therien, *Science*, 1995, **268**, 1409; (*b*) D. B. Amabilino, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1996, **118**, 3285; (*c*) A. P. H. J. Schenning, F. B. G. Benneker, H. P. M. Geurts, X. Y. Liu and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1996, **1187**, 8549; (*d*) C. M. Drain, K. C. Russell and J.-M. Lehn, *Chem. Commun.*, 1996, 337; (*e*) H.-y. Liu, J.-w. Huang, X.-d. Jiao, G.-t. Luo, L.-n. Ji, *Chem. Commun.*, 1997, 1575; (*f*) T. Arai, K. Takei, N. Nishino and T. Fujimoto, *Chem. Commun.*, 1996, 2133.

3 See for example: (*a*) J. P. Collman, J. E. Hutchison, M. A. Lopez, A. Tabard, R. Guilard, W. K. Seok, J. A. Ibers and M. L'Her, *J. Am. Chem. Soc.*, 1992, **114**, 9869; (*b*) L. Ruhlmann, A. Nakamura, J. G. Vos and J.-H. Fuhrhop, *Inorg. Chem.*, 1998, **37**, 6052.

4 (*a*) M. J. Crossley, T. W. Hambley, L. G. Mackay, A. C. Try and R. Walton, *J. Chem. Soc., Chem. Commun.*, 1995, 1077; (*b*) M. Takeuchi, T. Imada and S. Shinkai, *Angew. Chem., Int. Ed.*, 1998, **37**, 2069; (*c*) X. Huang, B. H. Rickman, B. Borhan, N. Berova and K. Nakanishi, *J. Am. Chem. Soc.*, 1998, **120**, 6185; (*d*) Y. Kuroda, A. Kawashima, Y. Hayashi and H. Ogoshi, *J. Am. Chem. Soc.*, 1997, **119**, 4929.

5 L. Pu, *Chem. Rev.*, 1998, **98**, 2405 and refs. therein.

6 N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy-Exciton Coupling in Organic Spectrochemistry*, Oxford University Press, Oxford, 1983.

7 B. Cheng, J. D. Hobbs, P. G. Debrunner, J. Erlebacher, J. A. Shelnutt and W. R. Scheidt, *Inorg. Chem.*, 1995, **34**, 102.

8 M. Takeuchi, T. Imada and S. Shinkai, *J. Am. Chem. Soc.*, 1996, **118**, 10658.

9 J. W. Buchler, *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier, Amsterdam, 1975.

10 Fe–Fe distance in **3** was estimated to be *ca.* 1.1 nm by CPK models.

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