Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 251 (2007) 2743–2752

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Chiral self-discriminative self-assembling of *meso–meso* linked diporphyrins

Chihiro Maeda, Taisuke Kamada, Naoki Aratani, Atsuhiro Osuka*

Department of Chemistry, Graduate School of Science, Kyoto University, Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Sakyo-ku, Kyoto 606-8502, Japan

Received 21 November 2006; accepted 11 February 2007
Available online 1 March 2007

Contents

Abstract

We have explored a variety of self-assembled cyclic porphyrin arrays mainly as biomimetic models of light harvesting antenna in photosynthetic systems. The key reaction is Ag(I)-promoted coupling reaction of 5,15-diaryl zinc(II) porphyrin that provides a *meso–meso* linked diporphyrin. *meso*-Pyridine-appended zinc(II) porphyrins **M1**–**M3** and their *meso–meso* linked dimers **D1**–**D3** assemble spontaneously in non-coordinating solvents into tetrameric porphyrin squares **S1**–**S3** and porphyrin boxes **B1**–**B3**, respectively. In the latter case, it has been demonstrated that four molecules of *R*-diporphyrin assemble into *R*-box and four molecules of *S*-diporphyrin assemble into *S*-box *via* rigorous homochiral self-sorting process. Efficient excitation energy transfer along these cyclic porphyrin arrays has been revealed by the time-resolved transient absorption and fluorescence measurements. We have also demonstrated that the *meso*-cinchomeronimide appended Zn(II) porphyrin **CIM** forms a cyclic trimer, while the corresponding diporphyrins **CID** exhibit high-fidelity self-sorting assembling to form discrete cyclic trimer, tetramer, and pentamer with large association constants, through perfect discrimination of enantiomeric and conformational differences of the *meso*-cinchomeronimide substituents.

Keywords: Porphyrin; Self-sorting; Self-assembly; Chiral recognition

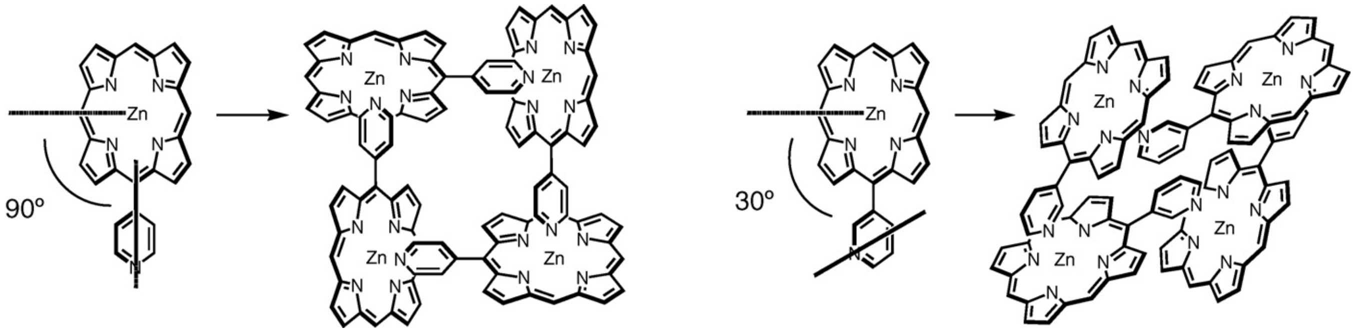
1. Introduction

Photosynthesis starts by the absorption of a photon by light-harvesting (antenna) complexes that usually comprise of a large number of pigments embedded in protein matrices [1]. This process is followed by a rapid and efficient energy migration over many pigments within the antenna system until a reaction center is encountered. At the reaction center charge separation takes place for fixation of the solar energies harvested. Photosynthetic organisms often utilize electronically coupled chromophores to capture dilute sunlight as well as enhance the energy transfer efficiency as seen in chlorosomes [2], LH1 [3], and LH2 [4] in bacterial antenna systems. In these cases, photosynthetic pigments form aggregates whose excitation leads to the formation of excitons with quantum-mechanical coherence extending over many chromophores.

---

* Corresponding author. Tel.: +81 75 753 4008; fax: +81 75 753 3970.
E-mail address: osuka@kuchem.kyoto-u.ac.jp (A. Osuka).

0010-8545/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2007.02.017



Scheme 1. Tetrameric aggregates of 4-pyridyl and 3-pyridyl porphyrins [14].

For model systems of the photosynthetic systems, in the last two decades, covalently and non-covalently linked multi-(metallo)porphyrin arrays have been extensively explored [5,6]. The covalent approach to construct multi-porphyrin arrays has advantages of robust stability and precise control in the spatial arrangement. The judicious choice of a spacer will allow fine control of electronic interactions between chromophores. However, in general, as the size and complexity of these systems grow, the covalent strategy becomes increasingly inefficient and tedious.

Supramolecular chemistry, using a strategy of non-covalent self-assembly of molecular units, has been developed as a highly promising means for the construction of two- or three-dimensional architectures. Those supramolecules have specific structures, properties, and functions [7]. Inspired by the non-covalent nature of natural photosynthetic systems, the self-assembly approach has been increasingly attempted in the mimicry of light-harvesting and charge separation systems [8].

Recently, our group has reported a variety of *meso–meso* linked porphyrin arrays, in which rapid energy transfer was achieved. Here we described the self-assembling behaviors of metalloporphyrins, especially focusing on our work that achieves high fidelity self-sorting assembling.

2. Self-assembly of metalloporphyrins

Molecules having both coordinating donor and acceptor in themselves can show self-assembled behavior. Especially, the coordination interaction between zinc(II) porphyrin and pyridine is particularly useful for its easy manipulation, relatively large association, and a favorable tendency not to spoil the photo-excited-state dynamics of porphyrins [9]. Interesting examples so far reported include oligomeric conjugated porphyrin ladders developed by Anderson and co-workers that exhibit very large two-photon absorption cross-section [10], energy-transfer and electron-transfer assemblies reported by Hunter and co-workers [11] and giant porphyrin arrays and large porphyrin wheels as a model of light-harvesting antenna reported by Kobuke and co-workers, where an imidazolyl substituent is used instead of a pyridyl substituent [12]. Fujita et al. reported a porphyrin-based hollow framework which can accommodate neutral organic molecules in an aqueous solution [13]. Tsuda et al. reported a thermochromic system, *via* the self-assembly of a π-extended zinc porphyrin complex with a metal ligating 3-pyridyl group [14]. This system exhibits a multicolor thermochromism upon heating by taking advantage of the absorption spectral change capability due to thermal-induced axial coordination dynamics. There are also several reports for the assembly of infinite structures [15].

Spatial control of porphyrinic pigments is crucial in supramolecular design, since it directly leads to control of the electronic interactions between chromophores. In this respect, a precise spatial control of porphyrin pigments with ample electronic interactions still remains challenging. For use as light-harvesting antennae, careful avoidance of energy sink that deactivates the excited state is another important requirement. Molecular self-assembly can translate the covalent connectivity and molecular shape of the components into tertiary structure.

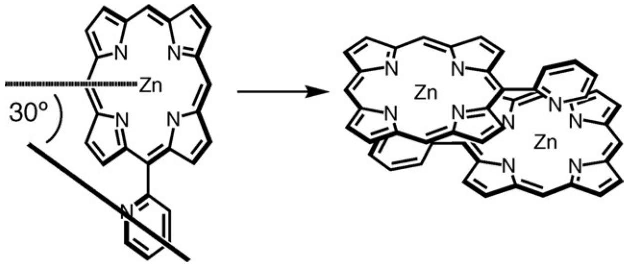
3. Key features for molecular design of self-assembly

To construct desired molecular assembly, an inclination between the porphyrin plane and the ligand plays a key role. Changing the geometry of the monomer unit can have dramatic effects on the structure and self-assembly properties. Another important point is favorable entropic factors for formation of discrete cyclic aggregates rather than polymeric aggregates.

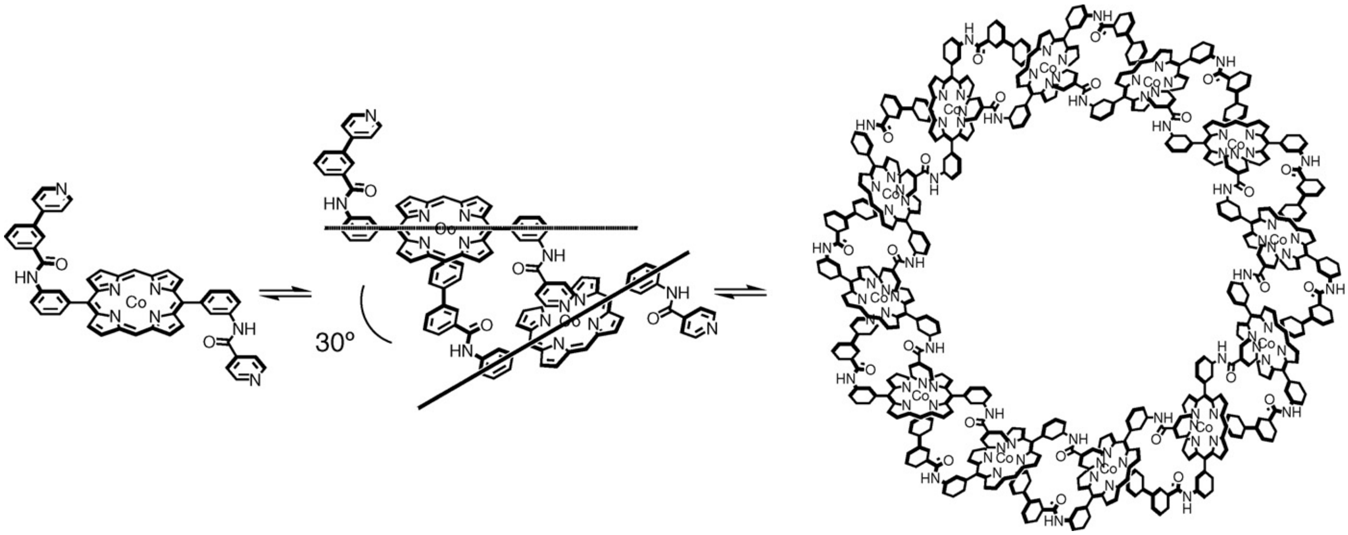
For example, 4-pyridyl porphyrin which has an inclination of 90° between the planes of the two porphyrins tends to form a square assembly, while 3-pyridyl porphyrin which has an inclination of 30° or 150° between the two porphyrin planes forms a rhombus one (Scheme 1) [14].

In the case of 2-pyridyl porphyrin, it is hard to make assembly if we consider its rigid structure. In real, it can deform to form a dimeric aggregate (Scheme 2) [16].

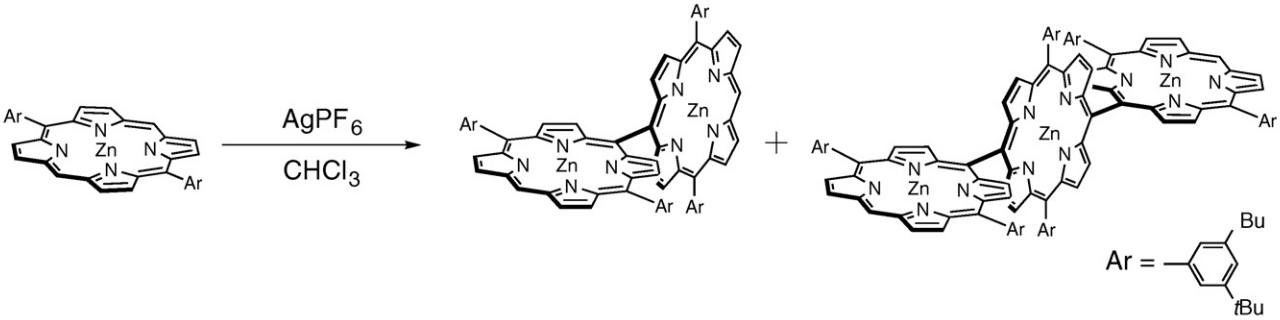
One of the most elegant examples is a dodecameric porphyrin ring synthesized by Hunter and co-workers [17]. A cobalt



Scheme 2. A dimeric aggregate of 2-pyridyl porphyrin [16].



Scheme 3. A dodecameric porphyrin ring synthesized by Hunter and co-workers [17].



Scheme 4. Synthesis of *meso–meso* linked porphyrin arrays [19].

porphyrin equipped with two different but geometrically complementary pyridine ligands self-assembles to form a stable complex with 12 porphyrin monomers arranged in a macrocyclic array (Scheme 3). The two kinds of pyridyl arms are attached trans across the porphyrin with a strain-free conformation, and so the 30° bend at the level of the monomer–monomer interaction must propagate in the same direction along the oligomer, leading to a macrocyclic structure.

4. *meso–meso* Linked porphyrin arrays

During the past decade, we have explored various porphyrin arrays on the basis of the Ag(I)-promoted *meso–meso* coupling reaction of 5,15-diaryl Zn(II)-porphyrins, which includes 3D-extending windmill arrays [18], extremely long arrays [19], and cyclic arrays [20] (Scheme 4). We have also reported that further oxidation of single *meso–meso* linked porphyrin arrays under stronger conditions (DDQ and $Sc(OTf)_3$) provided *meso–meso*, β–β, β–β, triply linked porphyrin arrays (porphyrin tapes) [21], whose Q-like bands, the lowest electronic absorption bands, exhibit continuous red-shifts, reaching deeply into the infrared region due to the extensive π-conjugation over the molecules.

The molecular component of a *meso–meso* linked diporphyrin is quite attractive because of its perpendicular conformation, which leads to unique architectures (Fig. 1). In addition, the two porphyrins in the component are strongly coupled mainly with Coulombic interaction but not π-conjugation [19]. This encourages the possibility that properly self-

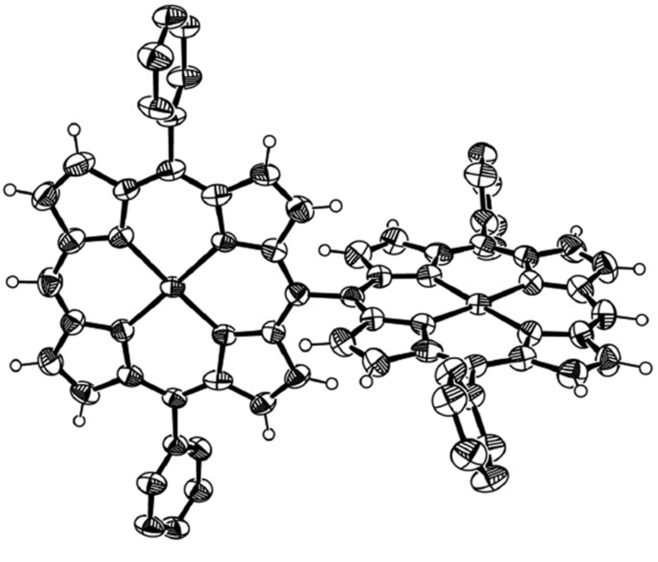
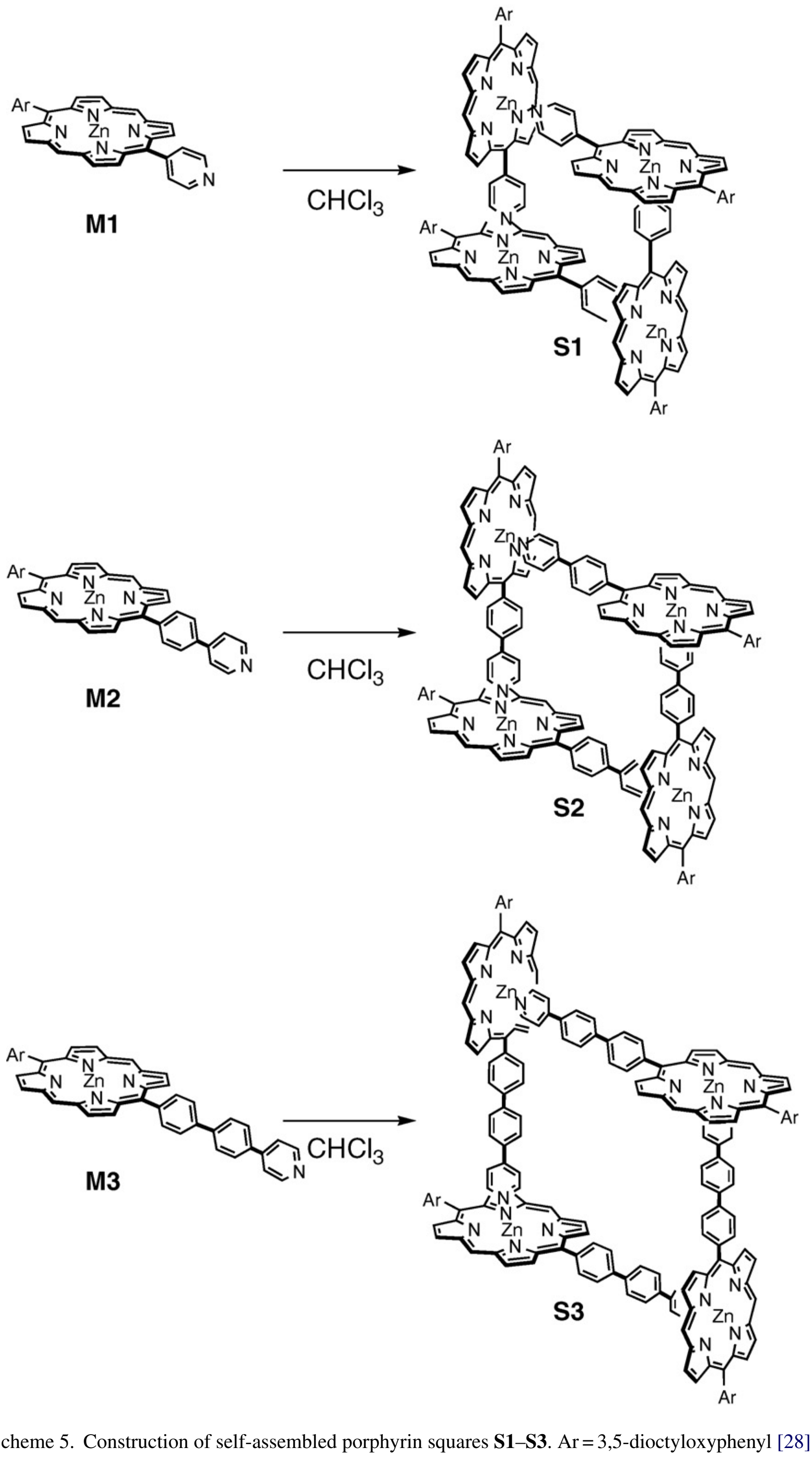


Fig. 1. Crystal structure of *meso–meso* linked Cu(II) porphyrin dimer [19e]. Substituents of phenyl groups are omitted for clarity.

assembled *meso*–*meso* linked zinc(II) porphyrins serve as a model for light-harvesting antennae. We have investigated rigid and three-dimensional self-assembling behaviors of zinc(II) diporphyrin having pyridyl derivatives as mentioned below. Complementary multiple coordination interactions arising from *meso*–*meso* linked diporphyrin framework help increase the association constants, such that the aggregates can be manipulated like covalently linked molecules.

5. Self-sorting

Self-sorting is high fidelity recognition of self from non-self and is a common and fundamental property in biological systems [22]. Self-sorting assembling process with discrimination of subtle structural differences among similar isomers may lead to largely different tertiary architectures of variable functions. Structural diversity thus attained plays an important role in



Scheme 5. Construction of self-assembled porphyrin squares **S1**–**S3**. Ar = 3,5-dioctyloxyphenyl [28].

many biological processes. Protein and DNA build complicated system to pass through a precisely correct molecular recognition process and find out a partner. In particular, a complex formed *via* self-assembly process among the living bodies makes very complicated and precise structure, and plays an important role in life activity. Aggregates formed *via* self-sorting process are mainly built thermodynamically through non-covalent bond such as hydrogen bonds, metal coordination interactions, or hydrophobic interactions. In recent years, therefore, diverse efforts have been made towards synthetic supramolecular systems that achieve such high fidelity self-sorting assembling [23–26].

Metalloporphyrins bearing a coordinating sidearm have been used as an effective platform to build various supramolecular structures with aids of multiple coordination interactions of central metal ions with coordinating sidearms as already mentioned above. However, such metalloporphyrins have been scarcely tested for self-sorting process.

6. Porphyrin boxes constructed from *meso–meso* linked diporphyrins

Recently, we have explored three-dimensional porphyrin boxes that are formed *via* rigorous enantiomeric self-sorting assembling of racemic 4-pyridine-appended *meso–meso* linked Zn(II) diporphyrins, in which the structural matching of 90° dihedral angle between the diporphyrin and the 4-pyridyl group plays a key role towards the formation of box-shaped assemblies [27–29].

First, we showed that a series of 5-*p*-pyridyl-15-(3,5-dioctyloxyphenyl) zinc(II) porphyrin **M1**–**M3** form cyclic porphyrin tetramer **S1**–**S3** in non-coordinating solvents such as chloroform or benzene, which was confirmed by ^{1}H NMR spectra and UV–vis absorption spectra (Scheme 5). The related structure of 5-*p*-pyridyl-15-(3,5-di-*tert*-butylphenyl) zinc(II) porphyrin was also confirmed by X-ray crystal structure analysis (Fig. 2) [27].

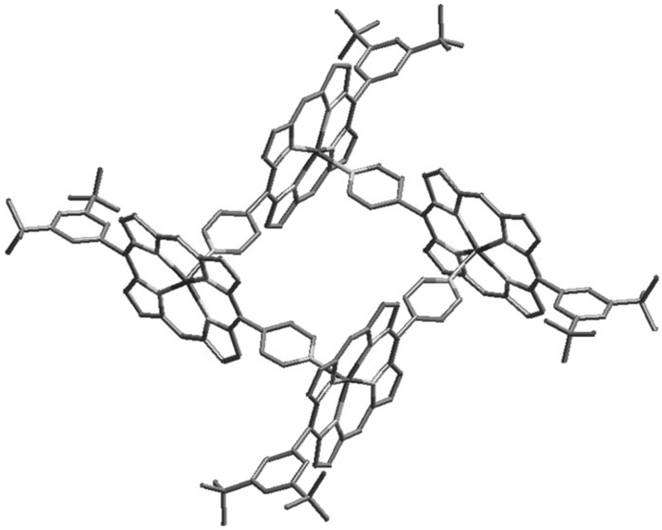


Fig. 2. Crystal structure of 5-*p*-pyridyl-15-(3,5-di-*tert*-butylphenyl) zinc(II) porphyrin [27].

The Ag(I)-promoted coupling reaction of **M1**–**M3** gave *meso–meso* coupled diporphyrin **D1**–**D3** along with higher oligomers. **D1** also aggregated to form tetrameric conformation with the larger association constant and rigidity (Scheme 6). Quantitative self-assembly of **D1** as its tetramer **B1** was confirmed by ^{1}H NMR spectroscopy in $CDCl_3$ and cold spray ionization mass spectroscopy (CSI-MS) [27]. On the basis of the practical concentration independence of its fluorescence spectral shape (up to 1.0×10^{-8} M), the association constant of **B1** was estimated to be at least $>10^{25}\,M^{-3}$ in $CHCl_3$. Formation of porphyrin boxes **B2** and **B3** from **D2** and **D3** was similarly indicated by ^{1}H NMR spectra in $CDCl_3$. Complementary multiple coordination interactions arising from *meso–meso* linked diporphyrin framework help increase the association constants, such that the boxes can be manipulated like covalently linked molecules.

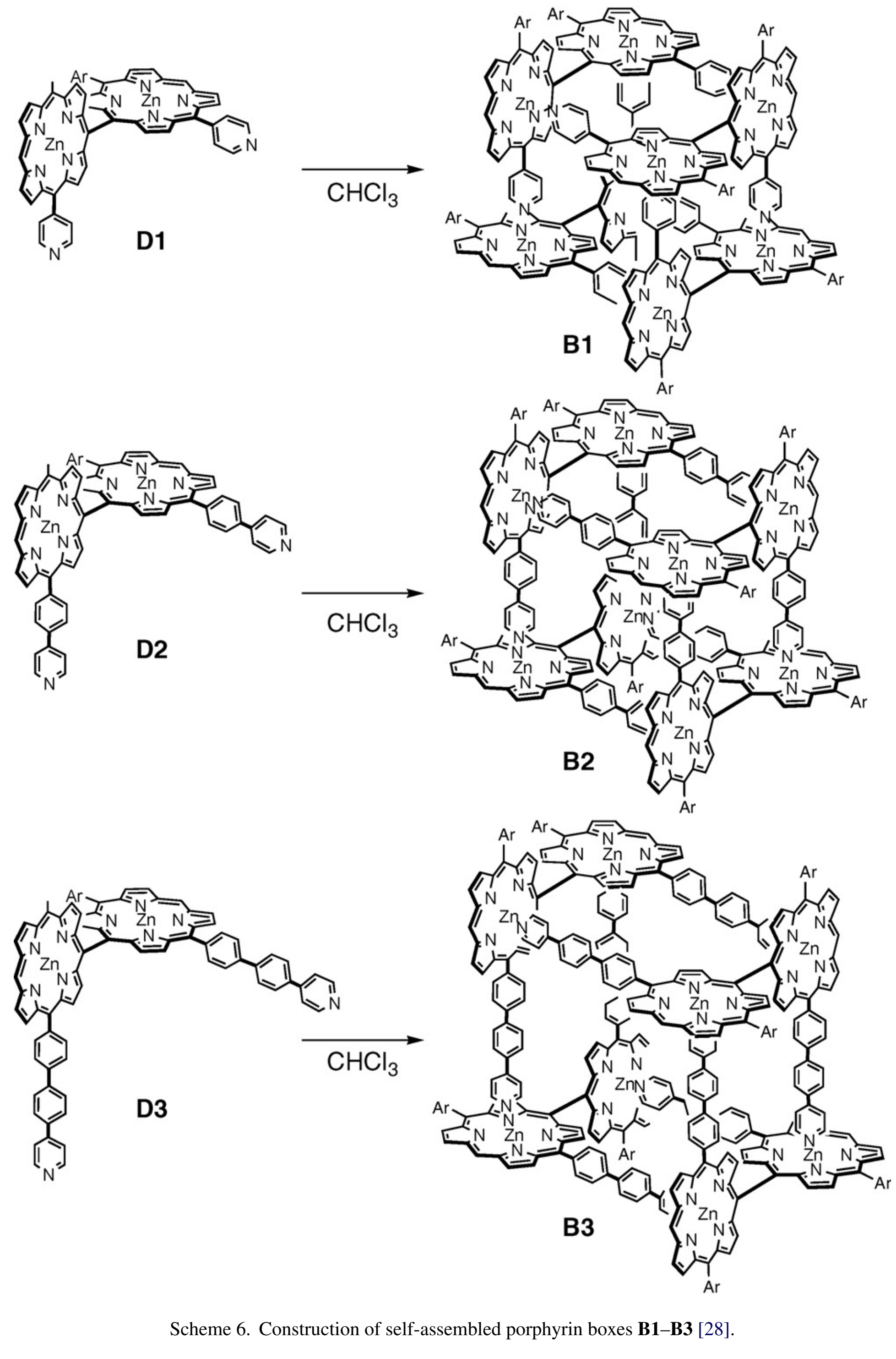
Owing to the different *meso*-aryl substituents, **D1**–**D3** are all chiral, and hence, two enantiomers are present in equal abundance in solution, since a free rotation around the *meso–meso* linkage is strictly prohibited [30]. Accordingly, the chiral porphyrin boxes **B1**–**B3** are formed by homochiral self-sorting assembly of the respective (*R*)- and (*S*)-isomers of **D1**–**D3**. Actually the optical resolution of **B1** and **B2** has been accomplished with a chiral HPLC setup. In the case of **B2**, the first fraction exhibited Cotton effects, negative at 469 nm, positive at 454 nm, and negative at 435 nm, and second fraction exhibited the reverse Cotton effects at the same wavelengths. The CD spectra of optically separated **B1** are similar to those of **B2**, but the intensity at 450 nm is doubled reflecting a shorter pyridyl arm, thus providing evidence for the exciton coupling between the non-covalent neighboring porphyrin rings.

Excitation energy migration processes within **B1**–**B3** have been investigated by the steady-state and time-resolved spectroscopic methods. Both the pump-power dependence on the femtosecond transient absorption and the transient absorption anisotropy decay profiles have been directly associated with the excitation energy migration process within the **B1**–**B3** boxes. Consequently, the excitation energy hopping rates between the zinc(II) diporphyrin units have been estimated for **B1** $(48\,ps)^{-1}$, **B2** $(98 \pm 3\,ps)^{-1}$, and **B3** $(361 \pm 6\,ps)^{-1}$.

7. *meso*-Cinchomeronimide appended *meso–meso* linked diporphyrin

As mentioned in Section 3, one strategy to create assemblies of different shape is to displace the positions of coordinating nitrogen atoms from the porphyrin plane. This idea drove us to examine self-sorting assembling behaviors of 10,10′-cinchomeronimide-appended *meso–meso* linked Zn(II) diporphyrin **CID** (**D** represents dimer) [31].

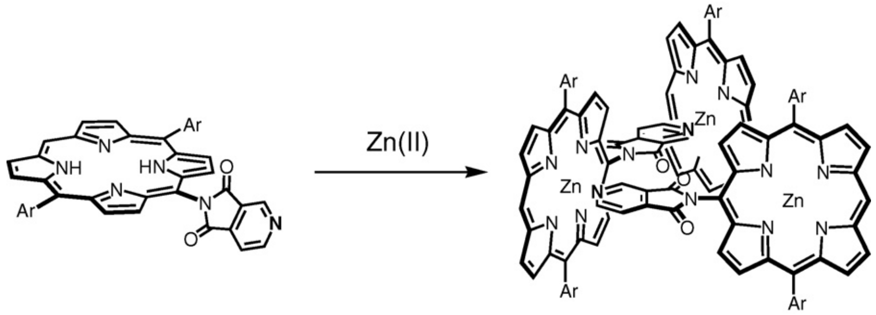
First, 10-cinchomeronimide-substituted 5,15-bis(3,5-di-*tert*-butylphenyl) Zn(II)-porphyrin **CIM** (**M** represents monomer) was prepared. ^{1}H NMR spectrum of **CIM** in $CDCl_3$ is very simple, featuring a simple set of peaks with large upfield shifts for the imide protons, which indicates the coordination of the



Scheme 6. Construction of self-assembled porphyrin boxes **B1**–**B3** [28].

pyridyl group to Zn(II) porphyrin (Scheme 7). X-ray-quality crystals of **CIM** were grown by vapor diffusion of acetonitrile into its toluene solution. The crystal structure revealed a triangular complex formed by complementary coordination of the cinchomeronimide group to the Zn(II) atom with a dihedral angle of 61° between the porphyrin mean planes (Fig. 3). The pyridyl group is coordinated to the Zn center with an angle of 88.8° and the Zn center is displaced 0.272 Å out of the N4 plane that is slightly domed.

Next, *meso–meso* linked diporphyrin **CID** bearing two cinchomeronimide groups at 10,10′-positions was prepared from 5,10-bis(3,5-di-*tert*-butylphenyl)porphyrin. Importantly, the free rotation of the cinchomeronimide group is considerably restricted due to the steric hindrance of the two imide-carbonyl groups, which gives rise to three different stable atropisomers (*in–in*, *in–out*, and *out–out*) with respect to the orientation of the nitrogen atom in the pyridine moiety. In addition, a free rotation around the *meso–meso* linkage is severely pro-



Scheme 7. Construction of self-assembled porphyrin triangle **CIM** [31].

hibited, thus making all the isomers to be chiral (*R* and *S*). Therefore, six isomers are present in a solution of **CID**; *R*-$\mathbf{CID}_{\text{in–in}}$, *S*-$\mathbf{CID}_{\text{in–in}}$, *R*-$\mathbf{CID}_{\text{in–out}}$, *S*-$\mathbf{CID}_{\text{in–out}}$, *R*-$\mathbf{CID}_{\text{out–out}}$, and *S*-$\mathbf{CID}_{\text{out–out}}$ (Scheme 8).

Gel permeation chromatography (GPC) of this mixture revealed three distinct fractions (I, II, and III) in a 1:2:1 ratio in the order of increasing molecular weight. GPC analysis with polystyrene standards indicated the molecular weights of the fractions I, II, and III to be 4.8×10^3, 6.1×10^3, and 7.6×10^3 Da, which roughly correspond to trimeric, tetrameric, and pentameric aggregates of **CID**, respectively.

^{1}H NMR spectra of the fractions I, II, and III are different from one another. It is important to note that only single sets of the signals were observed for the fractions I and III, while two sets of the signals were detected for fraction II. ^{1}H NMR spectrum of as-prepared **CID** is a simple sum of those of the fractions I, II, and III in a ratio of ca. 1:2:1, indicating that these aggregates are stable in $CDCl_3$ solution and there is no scrambling of diporphyrin fragments.

We have found that chiral separation of the fraction I was possible through a chiral HPLC column and reasonably nice crystals of the fraction I were obtained by slow diffusion of acetonitrile into a toluene solution of the chiral fraction I (Fig. 4). X-ray diffraction analysis on this crystal provided preliminary data, which indicated a pair of trimers in the unit cell. Each trimer was constructed by complementary coordination of three molecules of an *in–in* conformer (*R*-$\mathbf{CID}_{\text{in–in}}$). Largely due to the disorder of many solvent molecules contained in the crystal, the X-ray data remain preliminary level but the main skeletal structure should be certain.

As more convincing information, we have succeeded in X-ray crystal diffraction analysis of the fraction III. After many attempts, X-ray-quality crystals were obtained by slow diffusion of acetonitrile into a toluene solution of optically pure *R*-$\mathbf{CID}_{\text{out–out}}$. The crystal structure thus determined shows a symmetric pentameric aggregate consisting of five molecules of *R*-$\mathbf{CID}_{\text{out–out}}$ (Fig. 5). The aggregate (*R*-$\mathbf{CID}_{\text{out–out}}$)$_5$ exhibits

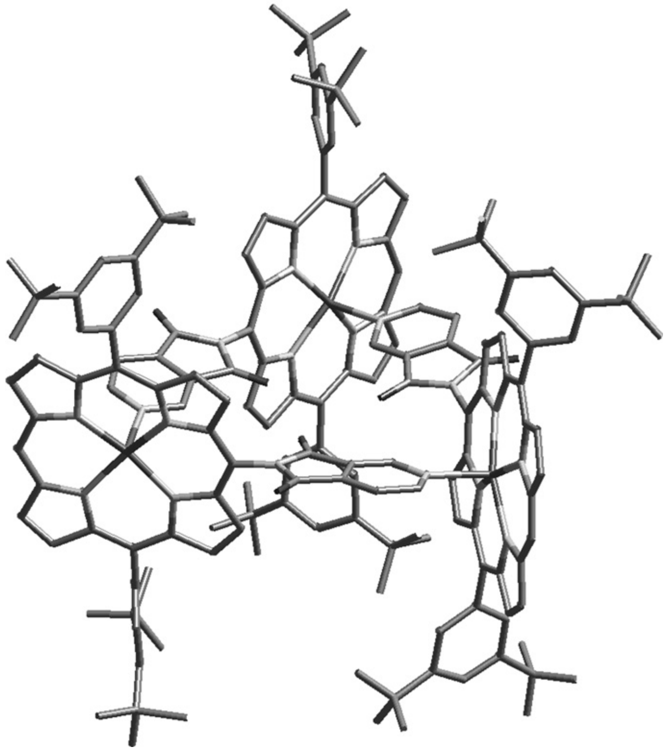


Fig. 3. Crystal structure of **CIM** [31].

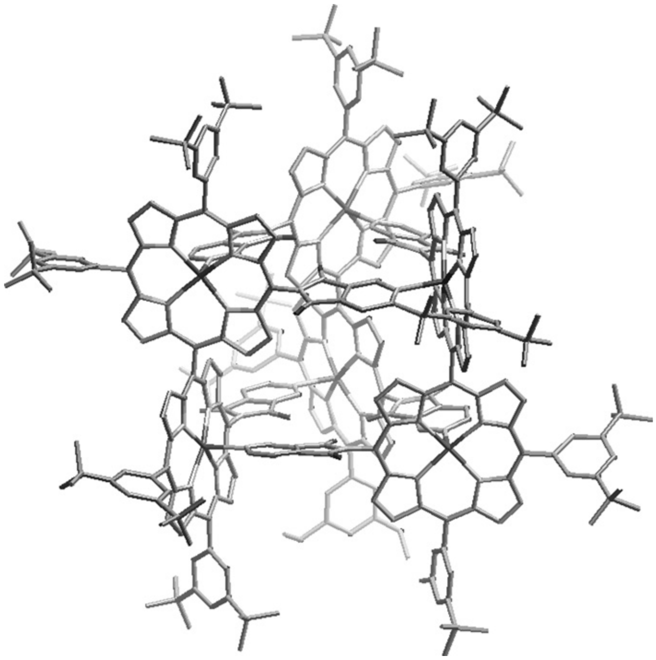
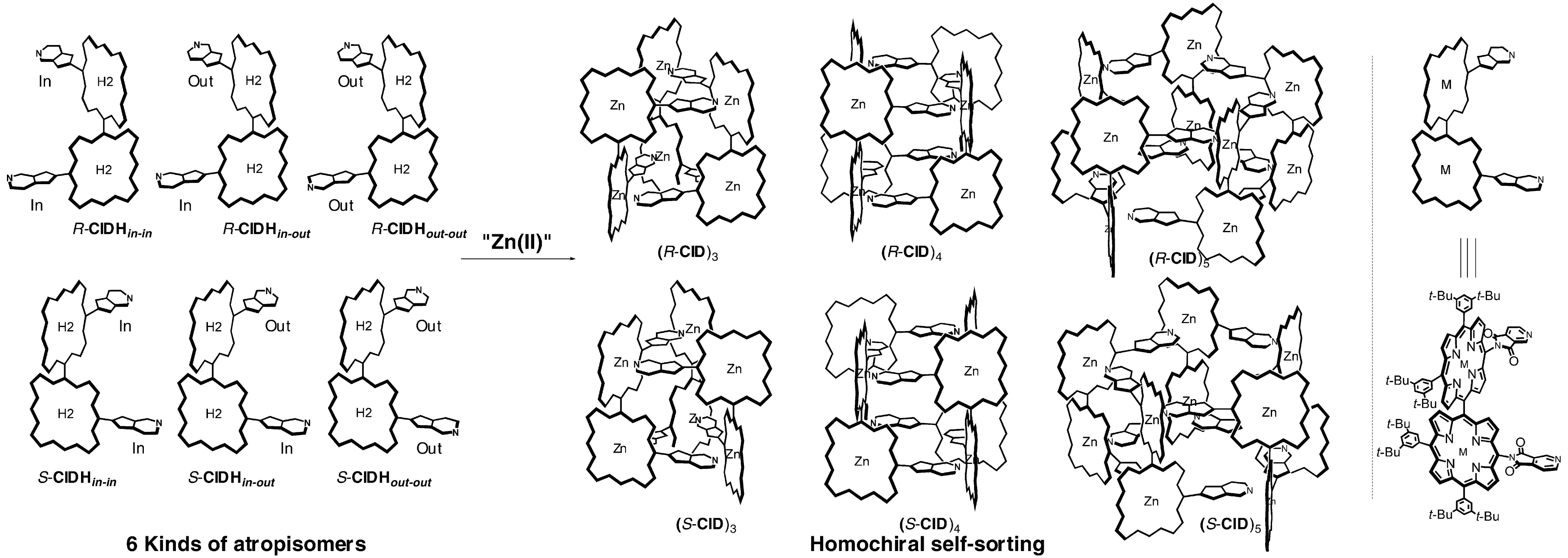


Fig. 4. Crystal structure of *R*-$\mathbf{CID}_{\text{in–in}}$ [31].



Scheme 8. Construction of self-assembled diporphyrin **CID** [31].

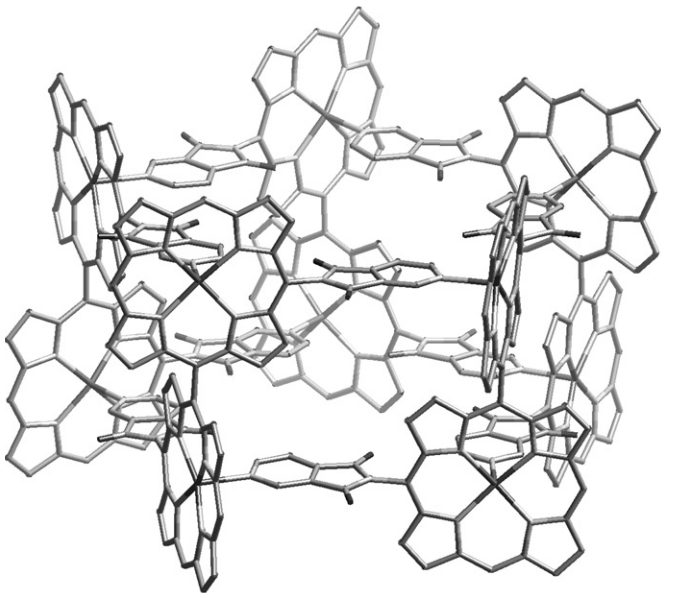


Fig. 5. Crystal structure of *R*-**CID**$_{\text{out–out}}$ [31]. *meso*-Aryl groups are omitted.

a C_5 symmetric pentagonal cylindrical structure with sides of ca. 11.5 Å and internal angles of ca. 108°. In the crystal, the aggregates (*R*-**CID**$_{\text{out–out}}$)$_5$ are stacked in a tubular manner to form an infinite channel of ca. 10 Å diameter. Each pentagonal channel unit contacts through CH–π interactions between 3,5-di-*tert*-butylphenyl groups and Zn(II) porphyrin planes to form a linear zigzag network. Then, the fraction II has been rationally assigned as a tetrameric aggregate (**CID**$_{\text{in–out}}$)$_4$ composed of four molecules of an *in–out* conformer on the basis of its GPC retention time that indicated its molecular size to be larger than (**CID**$_{\text{in–in}}$)$_3$ and smaller than (**CID**$_{\text{out–out}}$)$_5$.

8. Conclusions

In the perspective of metal-mediated assembly, the zinc porphyrins appending pyridine moieties are attractive building blocks, because of relatively large association and a favorable tendency not to spoil the fluorescence of porphyrins. The discrete self-assemblies can be promising molecular architectures for the application of molecular photonic and electronic devises, since they have well-defined rigid structures and ample electronic interactions. We reviewed the self-assemblies of *meso–meso* linked Zn porphyrin having 4-pyridyl group and cinchomeronimide group at *meso* positions. Their assemblies have chirality and show self-discriminating nature. The porphyrin boxes have been shown to serve as a platform to enable very efficient EET processes along the ring circuit with rates that rival those of natural cyclic photosynthetic antenna. We have also demonstrated that the *meso*-cinchomeronimide appended Zn(II) porphyrin **CID** exhibit high-fidelty self-sorting assembling to form discrete cyclic trimer, tetramer, and pentamer with large association constants through perfect discrimination of enantiomeric and conformational differences of the *meso*-cinchomeronimide substituents. Exclusive formation of the discrete cyclic aggregates without appreciable amount of polymeric aggregate is also notable, which is probably driven by favorable entropic factors for formation of cyclic aggregates. Future studies will focus on incorporation of these functional units into more elaborate model systems and exploration of larger cyclic porphyrin arrays.

Acknowledgement

This work was supported by Grant-in-Aid for Scientific Research on Priority Area (No. 18033028, Coordination Space) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] (a) R. van Grondelle, J.P. Dekker, T. Gillbro, V. Sundström, Biochim. Biophys. Acta 1187 (1994) 1;
(b) T. Pullerits, V. Sundström, Acc. Chem. Res. 29 (1996) 381.

[2] (a) R.E. Blankenship, J.M. Olson, M. Miller, in: R.E. Blankenship, M.T. Madigan, C.E. Bauer (Eds.), Anoxygenic Photosynthetic Bacteria, Kluwer Academic Publishers, The Netherlands, 1995, p. 399;
(b) A.R. Holzwarth, K. Griebenow, K. Shaffner, J. Photochem. Photobiol. A: Chem. 65 (1992) 61;
(c) P. Hildebrandt, H. Tamiaki, A.R. Holzwarth, K. Shaffner, J. Phys. Chem. 98 (1994) 2192.

[3] (a) S. Karrasch, P.A. Bullough, R. Ghosh, EMBO J. 14 (1995) 631.

[4] (a) G. McDermott, S.M. Prince, A.A. Freer, A.M. Hawthornthwaite-Lawless, M.Z. Papiz, R.J. Cogdell, N.W. Isaacs, Nature 374 (1995) 517;
(b) J. Koepke, X. Hu, C. Muenke, K. Schulten, H. Michel, Structure 4 (1996) 581.

[5] (a) M.R. Wasielewski, Chem. Rev. 92 (1992) 435;
(b) D. Gust, T.A. Moore, A.L. Moore, Acc. Chem. Res. 26 (1993) 198;
(c) D. Gust, T.A. Moore, A.L. Moore, Acc. Chem. Res. 34 (2001) 40;
(d) D. Holten, D.F. Bocian, J.S. Lindsey, Acc. Chem. Res. 35 (2002) 57;
(e) N. Aratani, A. Osuka, H.S. Cho, D. Kim, J. Photochem. Photobiol. C 3 (2002) 25;
(f) D. Kim, A. Osuka, Acc. Chem. Res. 37 (2004) 735;
(g) T. Hori, Y. Nakamura, N. Aratani, A. Osuka, J. Organometal. Chem. 692 (2007) 148;
(h) Y. Kobuke, K. Ogawa, Bull. Chem. Soc. Jpn. 76 (2003) 689;
(i) A. Satake, Y. Kobuke, Tetrahedron 61 (2005) 13;
(j) H. Imahori, J. Phys. Chem. B 108 (2004) 6130;
(k) T.S. Balaban, Acc. Chem. Res. 38 (2005) 612;
(l) E. Iengo, E. Zangrando, E. Alessio, Acc. Chem. Res. 39 (2006) 841.

[6] (a) G.M. Dubowchik, A.D. Hamilton, J. Chem. Soc., Chem. Commun. (1987) 293;
(b) A. Osuka, K. Maruyama, I. Yamazaki, N. Tamai, Chem. Phys. Lett. 165 (1990) 392;
(c) J.L. Sessler, V.L. Capuano, A. Harriman, J. Am. Chem. Soc. 115 (1993) 4618;
(d) R.W. Wagner, J.S. Lindsey, J. Am. Chem. Soc. 116 (1994) 9759;
(e) A. Osuka, N. Tanabe, S. Kawabata, I. Yamazaki, Y. Nishimura, J. Org. Chem. 60 (1995) 7177;
(f) D.L. Officer, A.K. Burrell, D.C.W. Reid, Chem. Commun. (1996) 1657;
(g) A. Osuka, N. Tanabe, S. Nakajima, K. Maruyama, J. Chem. Soc., Perkin Trans. 2 (1996) 199;
(h) K.K. Jensen, S.B. van Berlekom, J. Kajanus, J. Martensson, B. Albinsson, J. Phys. Chem. A 101 (1997) 2218;
(i) P.L. Taylor, A.P. Wylie, J. Huuskonen, H.L. Anderson, Angew. Chem., Int. Ed. 37 (1998) 986;
(j) O. Mongin, C. Papamicaël, N. Hoyler, A. Gossauer, J. Org. Chem. 63 (1998) 5568;
(k) H.A.M. Biemans, A.E. Rowan, A. Verhoeven, P. Vanoppen, L. Latterini, J. Foekema, A.P.H.J. Schenning, E.W. Meijer, F.C. De Schryver, R.J.M. Nolte, J. Am. Chem. Soc. 120 (1998) 11054;
(l) K. Sugiura, H. Tanaka, T. Matsumoto, T. Kawai, Y. Sakata, Chem. Lett. (1999) 1193;

(m) E.K.L. Yeow, K.P. Ghiggino, J.N.H. Reek, M.J. Crossley, A.W. Bosman, A.P.H.J. Schenning, E.W. Meijer, J. Phys. Chem. B 104 (2000) 2596;
(n) M.R. Benites, T.E. Johnson, S. Weghorn, L. Yu, P.D. Rao, J.R. Diers, S.I. Yang, C. Kirmaier, D.F. Bocian, D. Holten, J.S. Lindsey, J. Mater. Chem. 12 (2001) 65;
(o) M.-S. Choi, T. Aida, T. Yamazaki, I. : Yamazaki, Chem. Eur. J. 8 (2002) 668;
(p) H. Luo, M.S. Choi, Y. Araki, O. Ito, T. Aida, Bull. Chem. Soc. Jpn. 78 (2005) 405;
(q) K. Tashiro, A. Sato, T. Yuzawa, T. Aida, K.-I. Yamanaka, M. Fujitsuka, O. Ito, Chem. Lett. 35 (2006) 518;
(r) R.F. Kelley, M.J. Tauber, M.R. Wasielewski, Angew. Chem., Int. Ed. 45 (2006) 7979;
(s) T. Hasobe, H. Imahori, P.V. Kamat, T.K. Ahn, S.K. Kim, D. Kim, A. Fujimoto, T. Hirakawa, S. Fukuzumi, J. Am. Chem. Soc. 127 (2005) 1216.

[7] (a) J.-M. Lehn, Science 295 (2002) 2400;
(b) M.D. Hollingsworth, Science 295 (2002) 2410.

[8] (a) T. Hayashi, H. Ogoshi, Chem. Soc. Rev. 26 (1997) 355;
(b) T. Imamura, K. Fukushima, Coord. Chem. Rev. 198 (2000) 133;
(c) J. Wojaczynski, L. Latos-Grazynski, Coord. Chem. Rev. 204 (2000) 113;
(d) A.V. Chernook, U. Rempel, C. van Borczyskowski, A.M. Shulga, E.I. Zenkevich, Chem. Phys. Lett. 254 (1996) 229;
(e) L. Flamigni, M.R. Johnson, New J. Chem. 25 (2001) 1368;
(f) R.D. Hartnell, D.P. Arnold, Organometallics 23 (2004) 391.

[9] (a) C.A. Hunter, J.K.M. Sanders, G.S. Beddard, S. Evans, J. Chem. Soc., Chem. Commun. 1989 (1765);
(b) S. Anderson, H.L. Anderson, J.K.M. Sanders, Acc. Chem. Res. 26 (1993) 469;
(c) P. Ballester, A.I. Oliva, A. Costa, P.M. Deya, A. Frontera, R.M. Gomila, C.A. Hunter, J. Am. Chem. Soc. 128 (2006) 5560;
(d) H. Shinmori, T.K. Ahn, H.S. Cho, D. Kim, N. Yoshida, A. Osuka, Angew. Chem., Int. Ed. 42 (2003) 2754;
(e) A. Tsuda, H. Hu, R. Tanaka, T. Aida, Angew. Chem., Int. Ed. 44 (2005) 4884.

[10] (a) G.S. Wilson, H.L. Anderson, Chem. Commun. (1999) 1539;
(b) P.N. Taylor, H.L. Anderson, J. Am. Chem. Soc. 121 (1999) 11538;
(c) T.E. Screen, J.R.G. Thorne, R.G. Denning, D.G. Bucknall, H.L. Anderson, J. Am. Chem. Soc. 124 (2002) 9712;
(d) T.E. Screen, J.R.G. Thorne, R.G. Denning, D.G. Bucknall, H.L. Anderson, J. Mater. Chem. 13 (2003) 2796.

[11] (a) C.A. Hunter, R.K. Hyde, Angew. Chem., Int. Ed. Engl. 35 (1996) 1936;
(b) R.A. Haycock, A. Yartsev, U. Michelsen, V. Sundström, C.A. Hunter, Angew. Chem., Int. Ed. 39 (2000) 3616.

[12] (a) K. Ogawa, Y. Kobuke, Angew. Chem., Int. Ed. 39 (2000) 4070;
(b) K. Ogawa, T. Zhang, K. Yoshihara, Y. Kobuke, J. Am. Chem. Soc. 124 (2002) 22;
(c) R. Takahashi, Y. Kobuke, J. Am. Chem. Soc. 125 (2003) 2372.

[13] N. Fujita, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, Angew. Chem., Int. Ed. 40 (2001) 1718.

[14] A. Tsuda, S. Sakamoto, K. Yamaguchi, T. Aida, J. Am. Chem. Soc. 125 (2003) 15722.

[15] (a) E.B. Fleischer, A.M. Shachter, Inorg. Chem. 30 (1991) 3763;
(b) B.F. Abrahams, B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 113 (1991) 3606;
(c) Y. Diskin-Posner, S. Dahal, I. Goldberg, Angew. Chem., Int. Ed. 39 (2000) 1288;
(d) I. Goldberg, Chem. Commun. (2005) 1243;
(e) D.W. Smithenry, S.R. Wilson, K.S. Suslick, Inorg. Chem. 42 (2003) 7719;
(f) T. Ohmura, A. Usuki, K. Fukumori, T. Ohta, M. Ito, K. Tatsumi, Inorg. Chem. 45 (2006) 7988.

[16] R.T. Stibrany, J. Vasudevan, S. Knapp, J.A. Potenza, T. Emge, H.J. Schugar, J. Am. Chem. Soc. 118 (1996) 3980.

[17] R.A. Haycock, C.A. Hunter, D.A. James, U. Michelsen, L.R. Sutton, Org. Lett. 2 (2000) 2435.

[18] (a) A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki, Y. Nishimura, Angew. Chem., Int. Ed. 37 (1998) 3023;
(b) A. Nakano, A. Osuka, T. Yamazaki, Y. Nishimura, S. Akimoto, I. Yamazaki, A. Itaya, M. Murakami, H. Miyasaka, Chem. Eur. J. 7 (2001) 3134;
(c) A. Nakano, T. Yamazaki, Y. Nishimura, I. Yamazaki, A. Osuka, Chem. Eur. J. 6 (2000) 3254.

[19] (a) A. Osuka, H. Shimidzu, Angew. Chem., Int. Ed. Engl. 36 (1997) 135;
(b) N. Aratani, A. Osuka, Y.H. Kim, D.H. Jeong, D. Kim, Angew. Chem., Int. Ed. 39 (2000) 1458;
(c) Y.H. Kim, D.H. Jeong, D. Kim, S.C. Jeoung, H.S. Cho, S.K. Kim, N. Aratani, A. Osuka, J. Am. Chem. Soc. 123 (2001) 76;
(d) N. Aratani, A. Takagi, Y. Yanagawa, T. Matsumoto, T. Kawai, Z.S. Yoon, D. Kim, A. Osuka, Chem. Eur. J. 11 (2005) 3389;
(e) N. Yoshida, T. Ishizuka, A. Osuka, D.H. Jeong, H.S. Cho, D. Kim, Y. Matsuzaki, A. Nogami, K. Tanaka, Chem. Eur. J. 9 (2003) 58.

[20] (a) X. Peng, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, I.-W. Hwang, T.K. Ahn, D. Kim, A. Osuka, J. Am. Chem. Soc. 126 (2004) 4468;
(b) Y. Nakamura, I.-W. Hwang, N. Aratani, T.K. Ahn, D.M. Ko, A. Takagi, T. Kawai, T. Matsumoto, D. Kim, A. Osuka, J. Am. Chem. Soc. 127 (2005) 236;
(c) T. Hori, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, M.-C. Yoon, Z.S. Yoon, S. Cho, D. Kim, A. Osuka, Chem. Eur. J. 12 (2006) 1319.

[21] (a) A. Tsuda, A. Osuka, Science 293 (2001) 79;
(b) A. Tsuda, A. Osuka, Adv. Mater. 14 (2002) 75;
(c) A. Tsuda, H. Furuta, A. Osuka, J. Am. Chem. Soc. 123 (2001) 10304;
(d) D.Y. Kim, T.K. Ahn, J.H. Kwon, D. Kim, T. Ikeue, N. Aratani, A. Osuka, M. Shigeiwa, S. Maeda, J. Phys. Chem. A 109 (2005) 2996;
(e) T.K. Ahn, K.S. Kim, D.Y. Kim, S.B. Noh, N. Aratani, C. Ikeda, A. Osuka, D. Kim, J. Am. Chem. Soc. 128 (2006) 1700.

[22] L. Stryer, Biochemistry, 4th ed., W.H. Freeman, New York, 1995.

[23] R. Krämer, J.-M. Lehn, A. Marquis-Rigault, Proc. Natl. Acad. Sci. U.S.A. 90 (1993) 5394.

[24] (a) A. Wu, A. Chakraborty, J.C. Fettinger, R.A. Flowers II, L. Isaacs, Angew. Chem., Int. Ed. 41 (2002) 4028;
(b) A. Wu, L. Isaacs, J. Am. Chem. Soc. 125 (2003) 4831;
(c) P. Mukhopadhyay, A. Wu, L. Isaacs, J. Org. Chem. 69 (2004) 6157.

[25] (a) M. Cai, A.L. Marlow, J.C. Fettinger, D. Fabris, T.J. Haverlock, B.A. Moyer, J.T. Davis, Angew. Chem., Int. Ed. 39 (2000) 1283;
(b) X. Shi, J.C. Fettinger, M. Cai, J.T. Davis, Angew. Chem., Int. Ed. 39 (2000) 3124;
(c) M. Cai, X. Shi, V. Sidorov, D. Fabris, Y. Lam, J.T. Davis, Tetrahedron 58 (2002) 661;
(d) X. Shi, J.C. Fettinger, J.T. Davis, J. Am. Chem. Soc. 123 (2001) 6738.

[26] (a) F.H. Beijer, R.P. Sijbesma, H. Kooijman, A.L. Spek, E.W. Meijer, J. Am. Chem. Soc. 120 (1998) 6761;
(b) K.A. Jolliffe, P. Timmerman, D.N. Reinhoudt, Angew. Chem., Int. Ed. 38 (1999) 933;
(c) R.K. Castellano, C. Nuckolls, J. Rebek Jr., J. Am. Chem. Soc. 121 (1999) 11156;
(d) A. Shivanyuk, J. Rebek Jr., J. Am. Chem. Soc. 124 (2002) 12074;
(e) P.S. Corbin, L.J. Lawless, Z. Li, Y. Ma, M.J. Witmer, S.C. Zimmerman, Proc. Natl. Acad. Sci. U.S.A. 99 (2002) 5099;
(f) Y. Ma, S.V. Kolotuchin, S.C. Zimmerman, J. Am. Chem. Soc. 124 (2002) 13757.

[27] A. Tsuda, T. Nakamura, S. Sakamoto, K. Yamaguchi, A. Osuka, Angew. Chem., Int. Ed. 41 (2002) 2817.

[28] I.-W. Hwang, T. Kamada, T.K. Ahn, D.M. Ko, T. Nakamura, A. Tsuda, A. Osuka, D. Kim, J. Am. Chem. Soc. 126 (2004) 16187.

[29] I.-W. Hwang, H.S. Cho, D.H. Jeong, D. Kim, A. Tsuda, T. Nakamura, A. Osuka, J. Phys. Chem. B 107 (2003) 9977.

[30] N. Yoshida, A. Osuka, Tetrahedron Lett. 41 (2000) 9287.

[31] T. Kamada, N. Aratani, T. Ikeda, N. Shibata, Y. Higuchi, A. Wakamiya, S. Yamaguchi, K.S. Kim, Z.S. Yoon, D. Kim, A. Osuka, J. Am. Chem. Soc. 128 (2006) 7670.