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Construction of Monomeric and Polymeric Porphyrin Compartments by a Pd(II)−Pyridine Interaction and Their Chiral Twisting by a BINAP Ligand

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The construction of chirally twisted porphyrin-based molecular capsule **6** and polymeric capsule **8** was investigated by means of scanning electron microscopy (SEM) and ^{1}H NMR, UV−visible, and CD spectroscopic observations. Molecular capsule **6** and polymeric capsule **8** were constructed by the reaction of chiral cis-Pd(II) complex **4** bearing a (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) ligand with porphyrin **1** bearing four pyridyl groups and porphyrin **2** bearing eight pyridyl groups, respectively. The peak-splitting pattern of the β-pyrrole protons in the ^{1}H NMR spectrum and the specific CD spectral pattern bearing an exciton coupling band indicate that both molecular capsule **6** and polymeric capsule **8** are chirally twisted. Moreover, it was found that the CD intensity of the polymeric capsule plotted against [**4**]/([**4**] + [**3**]) shows a sigmoidal curvature, reflecting a unique cooperativity among the ligand groups; that is, the ligand existing in excess over the other dominates the twisting direction. These results consistently demonstrate that "chirality" in these molecular assembly systems is conveniently controlled by the use of chiral ligands.

Introduction

Metal-mediated self-assembly has been proved to be a very effective methodology in constructing two- or three-dimensional supramolecular architectures, such as macrocycles, molecular containers, tubular structures, interlocked and intertwined structures, and helicates, which are useful in molecular or chiral recognition, host−guest chemistry, catalysis, and memory storage.[1] Self-assembly of large supramolecular cages using pyridyl−Pd linkages, contributed mainly by Stang and Fujita, is especially appealing because of their structural variety and functional uniqueness.[2] On the other hand, porphyrin derivatives are widely used for designing molecular receptors, sensors, electron or energy transfer systems, and building blocks for higher order molecular architectures because of their specific optical and electrical properties. Especially, a great deal of effort has been devoted toward multiporphyrin arrays[3] useful for molecular wires,[4] molecular rulers,[5] molecular switches,[6] photosynthetic systems,[7] photosensitizers for DNA cleavage,[8] and photo-

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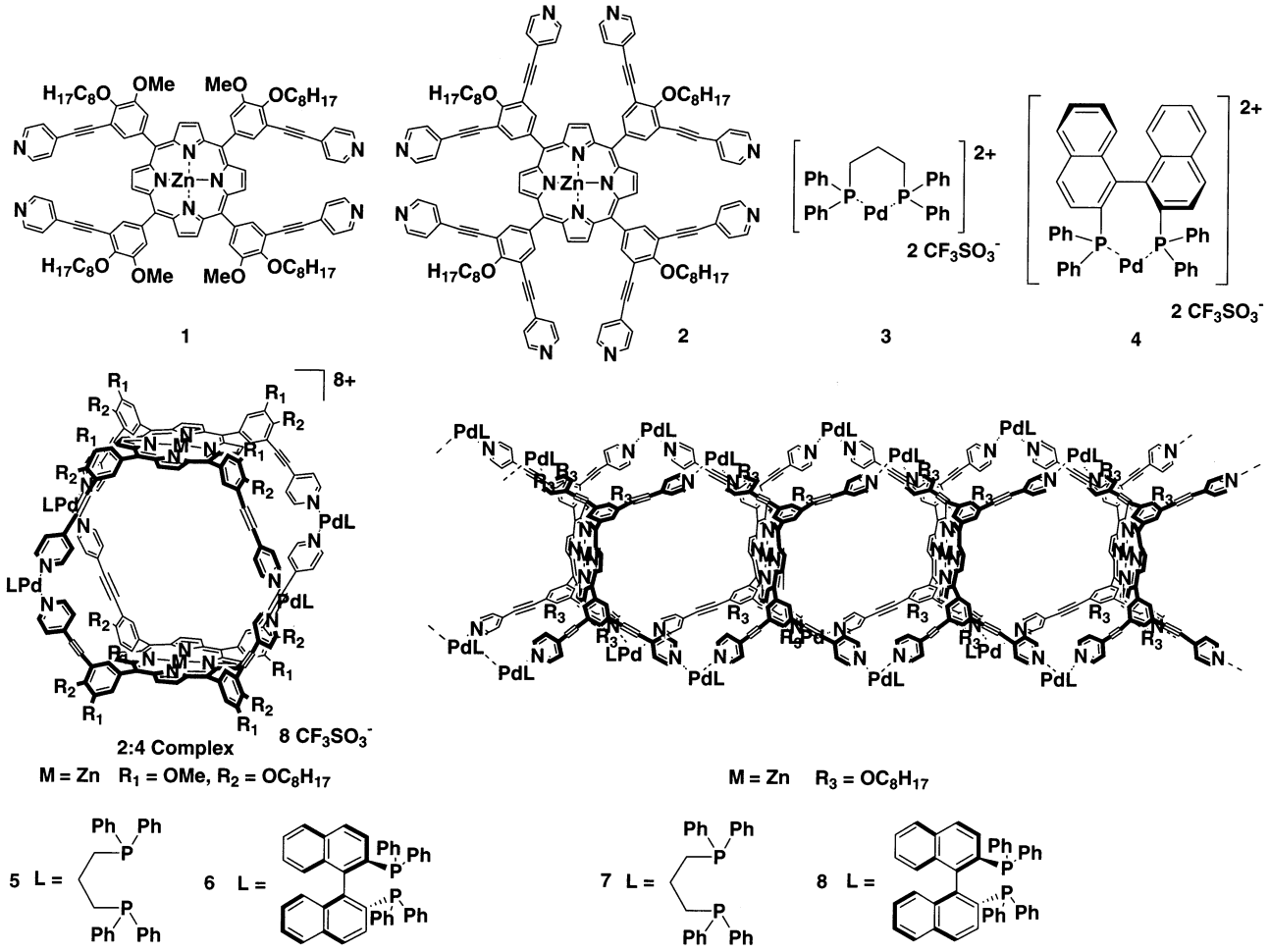
CHART 1



current generation.[9] A number of multiporphyrin arrays that are linked by noncovalent bonds in a self-assembly manner[10] or by covalent bonds in a polymeric fashion[11] have been reported. Covalently linked multiporphyrin arrays have attracted a great deal of attention in the construction of a huge π-conjugation system. Recently, fully conjugated porphyrin tapes that have electronic absorption bands in the infrared region have been reported by Osuka's group.[4f−i] However, the molecular design of such covalently linked multiporphyrin arrays frequently meets very serious synthetic difficulty. On the other hand, the molecular design of multiporphyrin arrays linked by noncovalent bonds in a self-assembly manner has unlimited future potentials for development of novel functional materials. In constructing such self-assembled multiporphyrin arrays, one of the most effective methodologies is to use coordination bonds such as pyridine−Pd(II) interaction or axial ligation.[12] We previously found that porphyrin **1** (Chart 1) bearing four pyridyl groups dimerizes with four *cis*-Pd(II) complexes **3** into a molecular capsule (**5**) according to a self-assembled manner.[13] Moreover, the spectroscopic studies showed that the molecular capsule thus formed can

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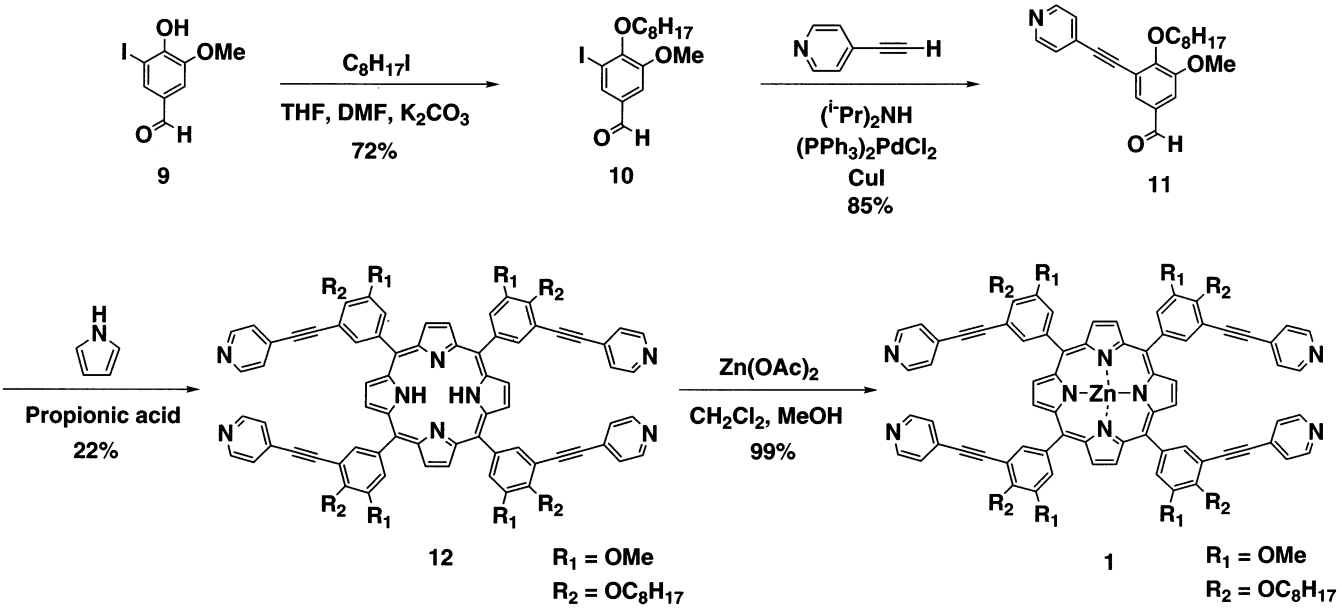
SCHEME 1



specifically include a large bipyridine guest.[13] On the other hand, porphyrin **2** bearing eight pyridyl groups at the upper and lower sides of each porphyrin forms a linear compartmentalized aggregate (**7**) with *cis*-Pd(II) complexes **3**, which can also include a large bipyridine guest.[14] These novel capsular and polymeric assemblies are expected to include various guest molecules and can be further applied to nanowires, redox reactions, photochemical reactions, guest-recognition molecular switches, etc.

In this paper, we have introduced the concept of "chirality" into this class of porphyrin-based molecular assemblies. There are a few precedents in which "chiral" factors are introduced into molecular capsules formed by covalent bonds.[15] To the best of our knowledge, however, there are a limited number of studies on the introduction of "chirality" into molecular capsules or polymeric capsules according to a self-assembled manner.[16] The design of such chiral molecular assembly systems is more difficult and complicated, but if it is achieved, one can expect that the systems would show more important and more interesting inclusion and recognition properties from the viewpoint of practical applications and combinatorial chemistry.[16]

Results and Discussion

Syntheses and Molecular Design. Compounds **1** and **2** were synthesized as shown in Schemes 1 and 2, respectively. These compounds were identified by ^{1}H NMR and MALDI-TOF mass spectral evidence and elemental analyses. In an attempt to introduce a concept of "chirality", we designed molecular capsule **6**, which is composed of two porphyrin derivatives (**1**)[13] bearing four 4-pyridyl substituents and four chiral *cis*-Pd(II) complexes (**4**)[17] bearing a (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) ligand, and polymeric capsule **8**, which is composed of porphyrin derivatives (**2**)[14] bearing eight 4-pyridyl substituents and chiral *cis*-Pd(II) complexes (**4**) bearing a BINAP ligand.

A Novel Self-Assembled Porphyrin Capsule Constructed from Chiral *cis*-Pd(II) Complexes (4) and Porphyrin Derivatives (1). The UV−vis absorption spectra of **1** (9.5×10^{-6} mol dm^{-3}) were measured in CH_2Cl_2 at 25 °C as a function of **4** concentration (Figure 1). The Q-band (560 nm for **1**) shifted to shorter wavelength with increasing **4** concentration. Generally, a Soret band shifts to longer wavelength when a pyridyl group coordinates to Zn(II) as an axial ligand. Therefore, this experimental result suggests that in the absence of **4**, the pyridyl group intermolecularly coordinates to Zn(II) as an axial ligand and the product is a mixture of several species (monomer, Zn(II)-coordinated dimer, trimer, etc.), whereas in the presence of **4**, it is decomplexed from Zn(II) to interact with Pd(II). Eventually, **1** and **4** form a capsular structure using **4** as pillar units. As shown in an inset of Figure 1, a plot of ΔAbs_{560nm} vs [**4**]/[**1**] has an inflection point at [**4**]/[**1**] = 2.0. This value indicates that the complex is formed with a 1:2 **1**/**4** stoichiometry.[18] In the ^{1}H NMR spectrum, the simple splitting pattern was obtained only when **1** (1.0×10^{-3} mol dm^{-3}) and **4** (2.0 ×

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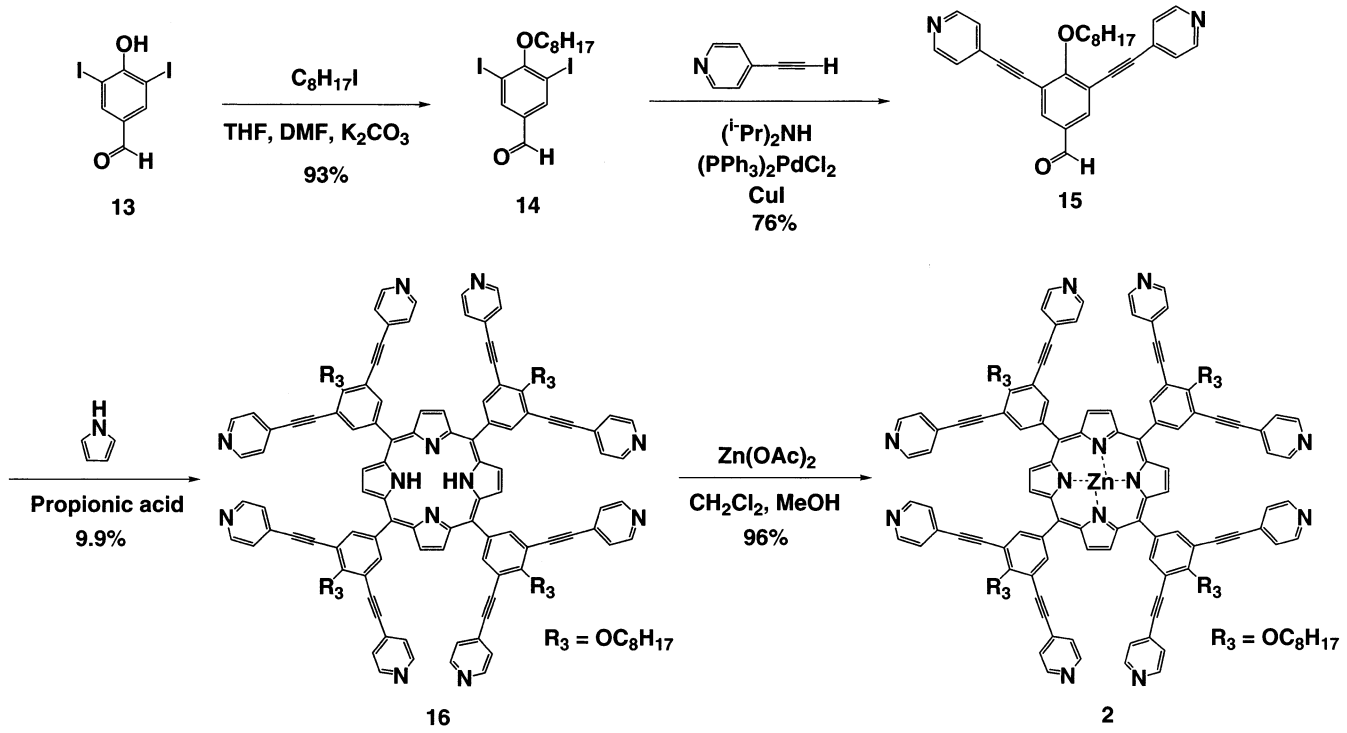
(18) The product is a mixture of several species (monomer, Zn(II)-coordinated dimer, trimer, etc.) in the **4**/**1** < 2.0 region, whereas the spectra are scarcely changed in the **4**/**1** ≥ 2.0 region. Under these conditions, one cannot observe tight isosbestic points but may consider that the stoichiometry is 2:1 in the high **4** concentration region. In Figure 1, although the isosbestic points are not tight, they do exist at 550, 575, and 600 nm. This lack of tight isobestic points is, as mentioned above, due to the mixture in the **4**/**1** < 2.0 region. The similar spectral situation is also adapted to the polymeric **4**/**2** system.

SCHEME 2



10^{-3} mol dm^{-3}) were mixed in a 1:2 molar ratio in CD_2Cl_2 at 25 °C (Figure 2; Figure S1 in Supporting Information). When the ratio was higher or lower than this value, the ^{1}H NMR spectra gave additional peaks and the splitting pattern became very complicated. The results support, as already evidenced for a **1**/**3** complex,[13] the formation of molecular capsule **6** (5.0×10^{-4} mol dm^{-3})

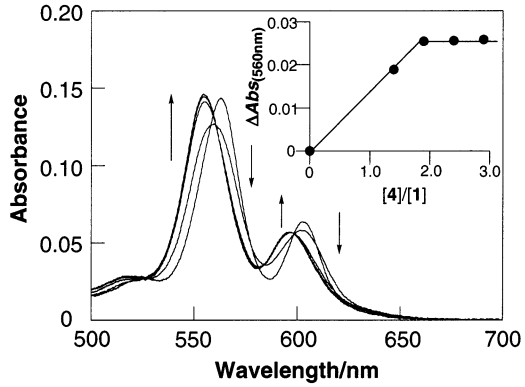


FIGURE 1. Absorption spectral change induced by addition of [**4**] in CH_2Cl_2 at 25 °C: [**1**] = 9.5×10^{-6} M, [**4**] = 0−2.9×10^{-5} M. Inset: molar ratio plot.

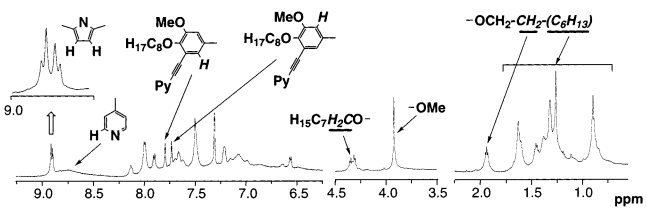


FIGURE 2. Partial ^{1}H NMR spectrum of **6** in CD_2Cl_2 at 25 °C: [**1**] = 1.0 mM, [**4**] = 2.0 mM. The full ^{1}H NMR spectrum is shown in the Supporting Information (Figure S1).

with a 1:2 **1**/**4** stoichiometry. The ^{1}H NMR spectrum of the 1:2 **1**/**4** complex is similar to that of the 1:2 **1**/**3** complex with D_{4h} symmetry. The formation of molecular capsule **6** was further corroborated by cold spray ionization mass spectrometery (CSI-MS).[19] The CSI-MS spectrum of the 1:2 **1**/**4** ([**1**] = 4.8×10^{-4} mol dm^{-3}, [**4**] = 9.6×10^{-4} mol dm^{-3}) mixture showed strong peaks at *m*/*z* 3620.2 and 7388.5, which are assignable to [**6** − $2CF_3SO_3^-]^{2+}$ and [**6** − $CF_3SO_3^-]^+$, respectively (Figure S2 in Supporting Information).

Further details of the molecular structure for **6** were obtained from the ^{1}H NMR spectra. The α- and β-protons in the pyridyl groups of **1** gave very broadened peaks, suggesting that the space between the pyridyl and diphenylphosphino groups is sterically very crowded.[20] It is noteworthy to mention that the β-pyrrole protons appear as double-doublets (Figure 2, inset); that is, molecular capsule **6** has two different kinds of β-pyrrole protons and they couple with each other. This peak-splitting pattern can be explained by the twisting motion of four *meso*-phenyl units around the porphyrin plate (Figure 3); when the four *meso*-phenyl units lean to one side, two different environments are produced in the porphyrin plate, and consequently, two different kinds of β-pyrrole protons (grouped into H_a and H_b) appear in the ^{1}H NMR spectrum. Since this peak-splitting pattern is similar to that of a homooxacalix[3]arene-based dimeric capsule featuring a chiral twisting motion,[16f] we consider that the present peak-splitting is also due to the twisting

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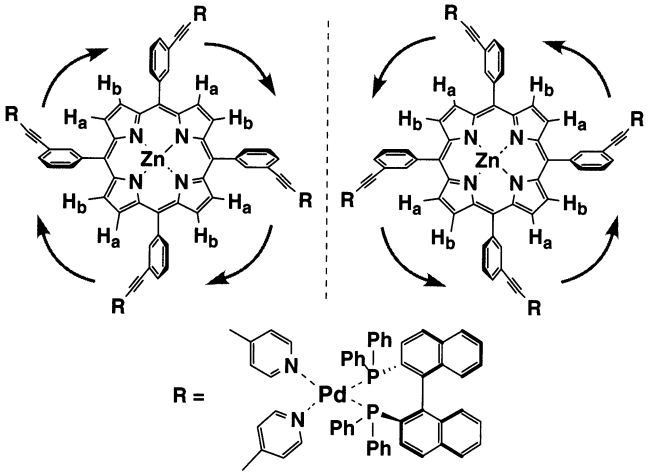


FIGURE 3. Possible twisting motion of four *meso*-phenyl substituents.

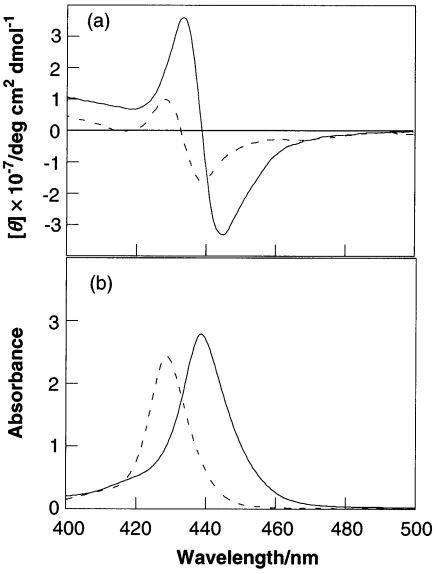


FIGURE 4. (a) CD spectra of **6** ([**1**] = 9.5 × 10^{-6} M, [**4**] = 1.9 × 10^{-5} M) and **8** ([**2**] = 1.3 × 10^{-5} M, [**4**] = 5.2 × 10^{-5} M) in CH_2Cl_2 at 25 °C. (b) Absorption spectra of **6** ([**1**] = 6.4 × 10^{-6} M, [**4**] = 1.3 × 10^{-5} M) and **8** ([**2**] = 8.9 × 10^{-6} M, [**4**] = 3.6 × 10^{-5} M) in CH_2Cl_2 at 25 °C: ···, **6**; −, **8**.

motion of four *meso*-phenyl units around the porphyrin plate. This means that molecular capsule **6** has "chirality" arising from its twisting structure.

We confirmed the helicity of **6** by circular dichroism (CD) spectroscopy (Figure 4a). In CH_2Cl_2 at 25 °C, a split CD band of **6** ([**1**] = 9.5 × 10^{-6} M, [**4**] = 1.9 × 10^{-5} M), which crosses the [θ] = 0 line at 432 nm (same wavelength as the λ_{max} = 430 nm in the Soret band region of the absorption spectrum of **6** ([**1**] = 6.4 × 10^{-6} M, [**4**] = 1.3 × 10^{-5} M)), is ascribed to an exiton coupling. It was suggested from the most stable conformation of **6** calculated by computational methods (Discover 3/Insight II 98.0) that **6** has the left-handed helical twisting structure (Figure S3 in Supporting Information). This conformation is reasonable for the split CD band with a negative first Cotton effect and a positive second Cotton effect.[21] In other words, the CD band is not due to induced CD (ICD) from chiral BINAP ligands but due to molecular chirality

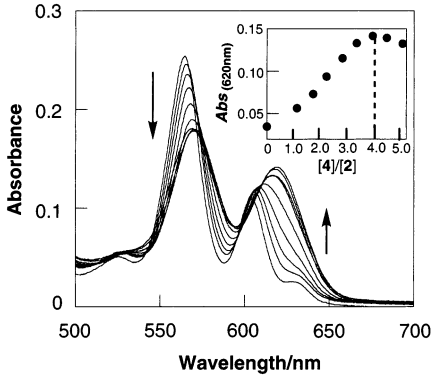


FIGURE 5. Absorption spectral change induced by addition of [**4**] in CH_2Cl_2 at 25 °C: [**2**] = 1.3 × 10^{-5} M, [**4**] = 0−6.8 × 10^{-5} M. Inset: molar ratio plot.

in the porphyrin moieties. This finding clearly reveals that **6** has a chiral twisting structure under the influence of chiral BINAP ligands.

A Novel Self-Assembled Porphyrin Polymer Constructed from Chiral *cis*-Pd(II) Complexes (4) and Porphyrin Derivatives (2). It is already established that porphyrin derivative **2** and *cis*-Pd(II) complex **3** can form a one-dimensional polymeric structure (**7**).[14] It thus occurred to us that when chiral Pd(II) complex **4** is used as a "comonomer", polymer **8** might result in a chirally twisted structure.

First, we determined the stoichiometry of the complex formed from **2** and **4**. The UV−vis absorption spectra of **2** (1.3 × 10^{-5} M) were measured in CH_2Cl_2 at 25 °C as a function of **4** concentration (0−6.8 × 10^{-5} M) (Figure 5). The Q-band (620 nm for **2**) shifted to longer wavelength, in contrast to the shorter wavelength shift observed for a **1** + **4** system (vide supra). Presumably, this longer wavelength shift is related to the polymeric aggregate, but the mechanistic origin is not yet clear at present. As shown in an inset of Figure 5, a plot of $\Delta Abs_{620\ nm}$ vs [**4**]/[**2**] has an inflection point at [**4**]/[**2**] = 4.0. This value supports the view that the complex is formed with a 1:4 **2**/**4** stoichiometry. Since ΔAbs_{620nm} was much less affected above [**4**]/[**2**] = 4.0, one can conclude that the pyridyl groups of **2** scarcely interact with Zn(II) in the [**4**]/[**2**] = 4.0 complex.[18] The absorption spectrum of the 1:4 **2**/**4** complex is similar to that of 1:4 **2**/**3** complex (**7**),[14] supporting the formation of one-dimensional polymeric structure **8**.

Second, to obtain evidence for the formation of a self-assembled polymeric structure, we measured the molecular weight of polymer **8** in solution by a dynamic light-scattering method.[22] In CH_2Cl_2, the average particle size of **8** ([**2**] = 1.3 × 10^{-5} M, [**4**] = 5.2 × 10^{-5} M) was estimated to be ca. 80 nm. The result indicates that the self-assembled polymer is formed in solution. On the other hand, ^{1}H NMR spectroscopy did not give any useful information, because the solution containing polymer **8** in CD_2Cl_2 showed a very peak broadened spectrum. To obtain visual insights into the aggregation mode, we

(21) Sugasaki, A.; Ikeda, M.; Takeuchi, M.; Shinkai, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3839−3842.

(22) Preparation of the sample for dynamic light-scattering: A mixture of **2** (1.3 × 10^{-5} M) and **4** (5.2 × 10^{-5} M) in CH_2Cl_2 was stirred at room temperature for 1 min.

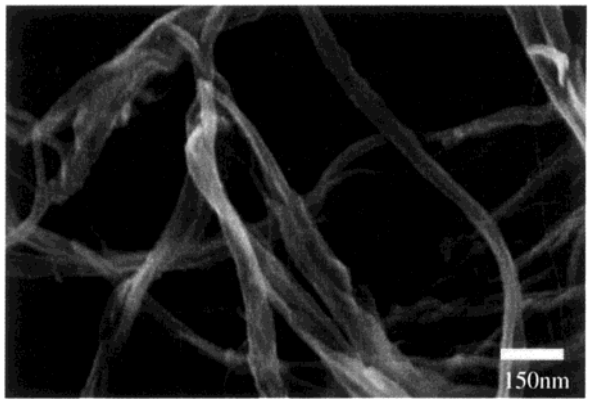


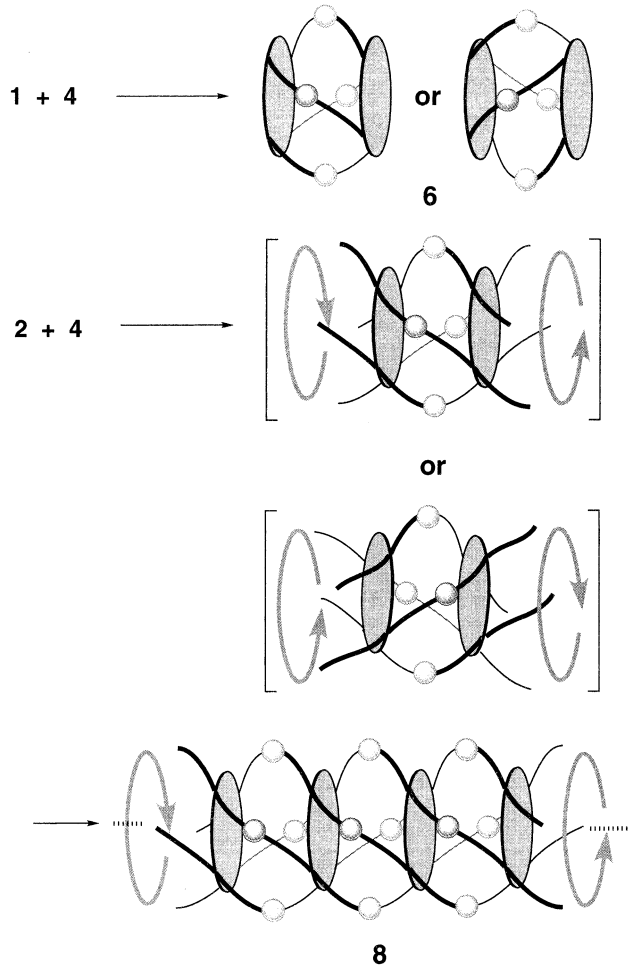
FIGURE 6. SEM image of **8**.

prepared dry samples for scanning electron microscope (SEM) observation.[23] In the SEM picture thus obtained (Figure 6), the well-grown fibrous structures with diameters of ca. 20−40 nm were abundantly observed. The fibers were very long, suggesting that the **2** + **4** mixture tends to grow into a one-dimensional direction and the polymer with porphyrin compartments is stably formed.

Third, we confirmed the presence of the helicity in **8** ([**2**] = 1.3 × 10^{-5} M, [**4**] = 5.2 × 10^{-5} M), by CD spectroscopy (Figure 4a). In CH_2Cl_2 at 25 °C, a split CD band, which crosses the [θ] = 0 line at 439 nm [same as wavelength λ_{max} = 439 nm of the absorption spectrum of **8** ([**2**] = 8.9 × 10^{-6} M, [**4**] = 3.6 × 10^{-5} M)], is ascribed to an exiton coupling. This CD pattern, which consists of a negative first Cotton effect and a positive second Cotton effect, is very similar to that of molecular capsule **6**. This result supports the view that polymer **8** is a one-dimensional polymeric aggregate with a chirally twisting structure. On the other hand, the CD intensity of **8** is stronger than that of **6** (Figure 4). This result suggests that since two pyridyl groups are connected to a *meso*-phenyl moiety by rigid acetylene spacers in **2**, the helicity of polymer **8** is transmitted through the *meso*-phenyl moieties more efficiently to the polymeric chain (Scheme 3).

We have learned from the molecular modeling of **7** and **8** that these polymeric rods are sterically very rigid. This suggests that when one **2** unit is twisted by **4**, its neighboring **2** units are enforced to be twisted cooperatively. This kind of cooperativity is similar to a "sergeant and soldiers" relationship rarely observed in molecular assembly systems and polymeric systems;[24,25] that is, when the CD intensity is plotted against [**4**]/([**4**] + [**3**]) (where the total concentration of [**4**] + [**3**] (5.2 × 10^{-5} M) is maintained constant), the plot may deviate from the 45° linear relationship, because the influence of achiral

SCHEME 3



3 predominates that of **4** at [**4**]/([**4**] + [**3**]) < 0.5, whereas chiral **4** predominates over **3** at [**4**]/([**4**] + [**3**]) > 0.5. The CD measurements on the **3**/**4** mixtures were conducted in CH_2Cl_2 at 25 °C (Method A). Very interestingly, we observed a sigmoidal increase in the CD intensity. As shown in an inset of Figure 7, the CD intensity increases with the increase in the ratio of **4** and crosses the 45° line at [**4**]/([**4**] + [**3**]) = ca. 0.7 ([**4**] = 3.6 × 10^{-5} M, [**3**] = 1.6 × 10^{-5} M). Although two plots at [**4**]/([**4**] + [**3**]) > 0.7 only slightly exceed the 45° line, we have repeatedly confirmed that they are reproducible and higher than the 45° line beyond the error range. The result implies that at low [**4**]/([**4**] + [**3**]) region **2** tends to form achiral polymeric rods, whereas only at very high [**4**]/([**4**] + [**3**]) region can **2** form chirally twisted polymeric rods. The asymmetry in the sigmoidal curvature is explained by the stability difference between the achiral polymeric rod and the chirally twisted polymeric rod. In the achiral structure the *meso*-phenyl substituents can occupy the most stable dihedral angle perpendicular to the porphyrin plane. In contrast, in the chirally twisted structure the *meso*-phenyl substituents must rotate, more or less, to the energetically unfavorable angle.[26] Thus, the region governed by achiral **3** is larger than that governed by chiral **4**. It is important, however, that the region governed by chiral **4** does exist. One can propose, therefore, that one compartment in the polymeric rod

(23) Preparation of the sample for scanning electron microscopy: A mixture of **2** (1.0 × 10^{-4} M) and **4** (4.0 × 10^{-4} M) in CH_2Cl_2 solvent was stirred at room temperature for 1 min. One drop of a **2** + **4** mixture in CH_2Cl_2 was placed on a carbon-coated grid on a filter paper. The drop immediately penetrated into the filter paper, and the grids were allowed to dry in air. This sample was coated with Pt under argon for 30 s.

(24) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452−6454.

(25) (a) Brunsveld, L.; Lohmeijer, B. G. G.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Commun.* **2000**, 2305−2306. (b) Brunsveld, L.; Lohmeijer, B. G. G.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Incl. Phenom. Macro.* **2001**, *41*, 61−64.

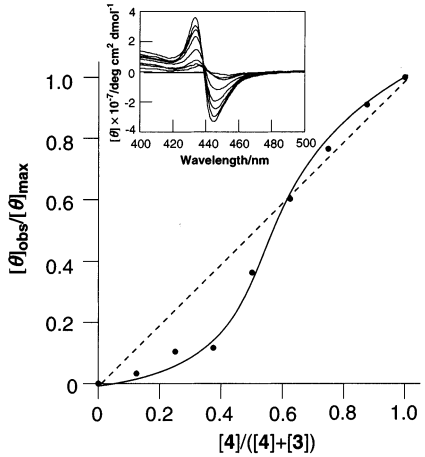


FIGURE 7. Plot of $[\theta]_{obs}/[\theta]_{max}$ at 446 nm vs [**4**]/([**4**] + [**3**]) in CH_2Cl_2 at 25 °C: [**2**] = 1.3×10^{-5} M, [**3**] + [**4**] = 5.2×10^{-5} M (constant). $[\theta]_{max}$ denotes the $[\theta]_{446nm}$ value at [**4**]/([**4**] + [**3**]) = 1.0. The 45° line is shown by a dotted line. Inset: CD spectral change induced by a molar ratio variation.

tends to cooperatively construct the same compartments in its neighboring units.

Conclusions

In conclusion, this paper demonstrates the molecular design of novel chiral porphyrin-based molecular capsular and polymeric structures constructed in a self-assembled manner. This method has a unique feature that the helicity is conveniently introduced by the use of an optically active ligand, BINAP. Reflecting the very rigid polymeric structure, the plot of the CD intensity vs [**4**]/([**4**] + [**3**]) shows a sigmoidal curvature arising from a unique cooperativity occurring along the one-dimensional rod. One may regard this phenomenon as a novel cooperativity attained in a one-dimensional molecular assembly. We are now testing how this rule appears when guest molecules are included in the compartments. Furthermore, we believe that these chiral capsule **6** and polymer **8** would be useful not only as conventional hosts for chiral guest recognition but also as candidates for switch-functionalized assemblies by redox reactions, photochemical reactions, guest inclusion, etc.

Experimental Section

Method A. The CD measurements on the **2** + **3**/**4** (mixture) were conducted in CH_2Cl_2 at 25 °C. The concentration of [**2**] (1.3×10^{-5} M) and the total concentration of [**4**] + [**3**] (5.2×10^{-5} M) are maintained constant. The values of [**4**]/([**4**] + [**3**]), a ratio of chiral factors, were changed from 0 (i.e., [**4**] = 0 M) to 1.0 (i.e., [**4**] = 5.2×10^{-5} M). The CD spectra of mixtures obtained with various chiral factors were measured.

5-Iodo-3-methoxy-4-octyloxybenzaldehyde (10). A mixture of 5-iodovanillin (2.00 g, 7.19 mmol), 1-iodooctane (8.63 g, 35.9 mmol), and K_2CO_3 (5.04 g, 36.5 mmol) in a mixed solution of THF (40 mL) and DMF (10 mL) was stirred at reflux temperature for 24 h. After cooling, the mixture was filtered and the filtrate was concentrated in vacuo. After purification by column chromatography (silica gel, chloroform/hexane = 1:1 v/v), 2.03 g of colorless oil (R_f = 0.40, chloroform/hexane = 1:1 v/v, silica plate) was obtained: yield, 72%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.85 (d, J = 1.9 Hz, 1H), 7.40 (d, J = 1.9 Hz, 1H), 4.09 (t, J = 6.6 Hz, 2H), 3.90 (s, 3H), 1.92−1.76 (m, 2H), 1.58−1.29 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H); MALDI-TOF MS m/z 390.8 (M + H$^+$).

3-Methoxy-4-octyloxy-5-(4-pyridyl)ethynylbenzaldehyde (11). A mixture of **10** (1.45 g, 3.70 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.53 g, 0.75 mmol), and copper(I) iodide (0.14 g, 0.75 mmol) in diisopropylamine (40 mL) was stirred at room temperature under a nitrogen atmosphere. After addition of 4-ethynylpyridine[27] (0.52 g, 5.00 mmol) into the solution, the mixture was stirred at room temperature for 24 h. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in chloroform and the solution was washed twice with water and then dried over anhydrous Na_2SO_4. After evaporation to dryness, the residue was purified by column chromatography (silica gel, ethyl acetate). Thus, 1.15 g of pale yellow oil (R_f = 0.70, ethyl acetate, silica plate) was obtained: yield, 85%;^{1}H NMR (250 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.63 (d, J = 5.8 Hz, 2H), 7.61 (s, 1H), 7.45 (s, 1H), 7.39 (d, J = 5.8 Hz, 2H), 4.26 (t, J = 6.6 Hz, 2H), 3.93 (s, 3H), 1.83−1.73 (m, 2H), 1.50−1.25 (m, 10H), 0.85 (t, J = 6.8 Hz, 3H); MALDI-TOF MS m/z 366.5 (M + H$^+$).

5,10,15,20-Tetrakis[[3-(4-pyridyl)ethynyl-4-octyloxy-5-methoxy]phenyl]porphyrin (12). A mixture of **11** (1.00 g, 2.74 mmol) and pyrrole (0.18 g, 2.68 mmol) in propionic acid (100 mL) was stirred at reflux temperature for 3 h. The solvent was evaporated, and the residue was dissolved in chloroform. The solution was washed with aqueous Na_2CO_3 and water and then dried over anhydrous Na_2SO_4. After evaporation to dryness, the residue was purified by column chromatography (alumina gel, chloroform/hexane = 1:1 v/v) and gel permeation chromatography. Thus, 0.25 g of purple solid (R_f = 0.50, chloroform, alumina plate) was obtained: yield, 22%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 8H), 8.60 (d, J = 5.8 Hz, 8H), 7.97 (d, J = 5.5 Hz, 4H), 7.82 (d, J = 5.5 Hz, 4H), 7.39 (d, J = 5.8 Hz, 8H), 4.48 (t, 8H, J = 6.6 Hz), 3.98 (s, 12H), 2.03−2.01 (m, 8H), 1.80−1.25 (m, 40H), 0.91 (t, J = 6.8 Hz, 12H), −2.81 (s, 2H); MALDI-TOF MS m/z 1651.9 (M + H$^+$). Anal. Calcd for $C_{108}H_{114}N_8O_8 \cdot 3H_2O$: C, 76.03; H, 7.09; N, 6.57. Found: C, 75.96; H, 7.10; N, 6.30.

Zn(II) 5,10,15,20-Tetrakis[[3-(4-pyridyl)ethynyl-4-octyloxy-5-methoxy]phenyl]porphyrin (1). A mixture of **12** (30 mg, 0.018 mmol) and zinc acetate (18 mg, 0.083 mmol) in a mixed solvent of methanol (3 mL) and dichloromethane (3 mL) was stirred at room temperature for 20 min. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, chloroform/methanol = 9:1 v/v). Thus, 31 mg of purple solid (R_f = 0.50, chloroform/methanol = 9:1 v/v, silica plate) was obtained: yield, 99%; ^{1}H NMR (600 MHz, pyridine) δ 9.42 (m, 8H), 8.79 (d, J = 4.3 Hz, 8H), 7.64 (d, J = 4.3 Hz, 8H), 4.67 (t, 8H, J = 6.6 Hz), 4.00 (m, 12H, OMe), 2.17−2.14 (m, 8H), 1.82−1.25 (m, 40H), 0.87 (t, J = 6.8 Hz, 12H); MALDI-TOF MS m/z 1713.8 (M + H$^+$). Anal. Calcd for $C_{108}H_{112}N_8O_8Zn \cdot 3H_2O$: C, 73.31; H, 6.72; N, 6.33. Found: C, 73.52; H, 6.82; N, 6.17.

3,5-Diiodo-4-octyloxybenzaldehyde (14). A mixture of 3,5-diiodo-4-hydroxybenzaldehyde[28] (1.50 g, 4.00 mmol), 1-iodooctane (4.30 g, 18.0 mmol), and K_2CO_3 (2.50 g, 18.0 mmol) in a mixed solvent of THF (40 mL) and DMF (10 mL) was stirred at reflux temperature for 24 h. After cooling, the filtrate was concentrated in vacuo. After purification by column chromatography (silica gel, chloroform/hexane = 1:1 v/v), 1.80 g of colorless solid (R_f = 0.60, chloroform/ hexane = 1:1 v/v, silica

(26) The most stable conformations of **5** and **6** were estimated by computational methods (Discover 3/Insight II 98.0). As a result, we confirmed that the inclination angle of the *meso*-phenyl groups in **6** is larger than that in **5**. Since the most stable conformation adopts 90°, one may consider that **5** is more stable than **6**. The similar situation is also adapted to **7** and **8**.

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(28) Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Kondo, M.; Okamoto, T. *Chem. Lett*. **1987**, 2109−2112.

plate) was obtained: yield, 93%; mp 43.3−44.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.20 (s, 2H), 3.97 (t, J = 6.6 Hz, 2H), 1.92−1.83 (m, 2H), 1.50−1.20 (m, 10H), 0.84 (t, J = 6.8 Hz, 3H); MALDI-TOF MS m/z 487.3 (M + H$^+$).

3,5-Bis(4-pyridyl)ethynyl-4-octyloxybenzaldehyde (15). A mixture of **14** (1.80 g, 3.70 mmol), bis(triphenylphosphine)-palladium(II) dichloride (0.53 g, 0.75 mmol), and copper(I) iodide (0.14 g, 0.75 mmol) in diisopropylamine (40 mL) was stirred at room temperature under a nitrogen atmosphere. After addition of 4-ethynylpyridine[27] (0.82 g, 8.00 mmol) into the solution, the mixture was stirred at room temperature for 24 h. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in chloroform and the solution was washed twice with water and then dried over anhydrous Na_2SO_4. After evaporation to dryness, the residue was purified by column chromatography (silica gel, ethyl acetate). Thus, 1.20 g of pale yellow solid (R_f = 0.60, ethyl acetate, silica plate) was obtained: yield, 76%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.65 (d, J = 5.9 Hz, 4H), 8.04 (s, 2H), 7.40 (d, J = 5.9 Hz, 4H), 4.51 (t, J = 6.6 Hz, 2H), 1.83−1.92 (m, 2H), 1.20−1.50 (m, 10H), 0.84 (t, J = 6.8 Hz, 3H); MALDI-TOF MS m/z 437.5 (M + H$^+$).

5,10,15,20-Tetrakis[[3,5-bis(4-pyridyl)ethynyl-4-octyl-oxy]]phenylporphyrin (16). A mixture of **15** (1.00 g, 2.30 mmol) and pyrrole (0.15 g, 2.30 mmol) in propionic acid (150 mL) was stirred at reflux temperature for 3 h. The solvent was evaporated, and the residue was dissolved in dichloromethane. The solution was washed with aqueous Na_2CO_3 and water and then dried over anhydrous Na_2SO_4. After evaporation to dryness, the residue was purified by column chromatography (silica gel, chloroform/MeOH = 9:1 v/v). Thus, 0.11 g of purple solid (R_f = 0.50, chloroform/methanol = 9:1 v/v, silica plate) was obtained: yield, 9.9%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (s, 8H), 8.60 (d, J = 5.9 Hz, 16H), 8.38 (s, 8H), 7.42 (d, J = 5.9 Hz, 16H), 4.70 (t, 8H, J = 6.6 Hz), 2.09−2.12 (m, 8H), 1.50−1.20 (m, 40H), 0.84 (t, J = 6.8 Hz, 12H), −2.83 (s, 2H); MALDI-TOF MS m/z 1936.5 (M + H$^+$). Anal. Calcd for $C_{132}H_{118}N_{12}O_4 \cdot CH_2Cl_2$: C, 79.03; H, 5.98; N, 8.32. Found: C, 79.16; H, 6.21; N, 8.10.

Zn(II) 5,10,15,20-Tetrakis[[3,5-bis(4-pyridyl)ethynyl-4-octyloxy]]phenylporphyrin (2). A mixture of **16** (60 mg, 0.031 mmol) and zinc acetate (20 mg, 0.093 mmol) in a mixed solvent of methanol (10 mL) and dichloromethane (3 mL) was stirred at room temperature for 20 min. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, chloroform/methanol = 9:1 v/v). Thus, 60 mg of purple solid (R_f = 0.50, chloroform/methanol = 9:1 v/v, silica plate) was obtained: yield, 96%; ^{1}H NMR (600 MHz, pyridine) δ 9.04 (s, 8H), 8.50 (s, 8H), 8.46 (d, J = 5.7 Hz, 16H), 7.28 (d, J = 5.7 Hz, 16H), 4.53 (t, 8H, J = 6.6 Hz), 1.98−1.88 (m, 8H), 1.64−0.86 (m, 40H), 0.51 (t, J = 6.8 Hz, 12H); MALDI-TOF MS m/z 1998.3 (M + H$^+$). Anal. Calcd for $C_{132}H_{116}N_{12}O_4$-Zn·2MeOH: C, 77.98; H, 6.06; N, 8.14. Found: C, 77.76; H, 6.01; N, 7.92.

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Supporting Information Available: ^{1}H NMR (Figure S1) and CSI-MS (Figure S2) spectra of **6** and molecular modeling (Figure S3) of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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