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A Self-Assembled Porphyrin-Based Dimeric Capsule Constructed by a Pd(II)–Pyridine Interaction Which Shows Efficient Guest Inclusion

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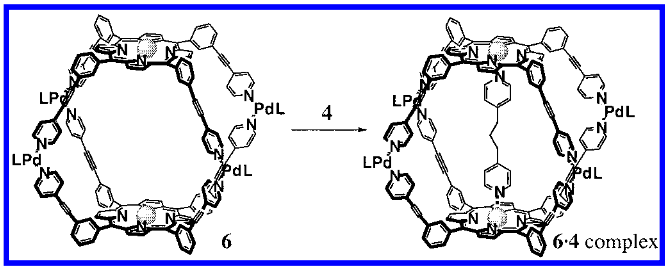
ABSTRACT



Novel self-assembled molecular capsules were constructed from two moles of pyridine-containing porphyrin derivatives and four moles of Pd(II) complexes utilizing a pyridine–Pd(II) interaction. The ^{1}H NMR spectral studies established that these self-assembled molecular capsules 5 and 6 have a highly symmetrical D_{4h} structure as well as a large inside cavity. It was shown that molecular capsule 6 can include a large bipyridine guest by a two-point simultaneous pyridine–Zn(II) interaction.

A great deal of effort has been devoted toward multiporphyrin arrays such as molecular wires,[1] molecular switches,[2] photosynthetic systems,[3] photosensitizers for DNA cleavage,[4] and photocurrent generation.[5] A combination of these excellent devices with host−guest chemistry has a large future potential but is much less developed so far. A few cyclic host compounds composed of covalently linked multiporphyrins have been synthesized, and some of them can include guest molecules such as pyridine derivatives[6,7] and fullerenes.[8] The findings suggest that molecular capsules with a three-dimensional cavity would have larger association constants and kinetically slower exchange rates for specific guest molecules than cyclic compounds with a two-dimensional cavity, but the syntheses of such molecular capsules are

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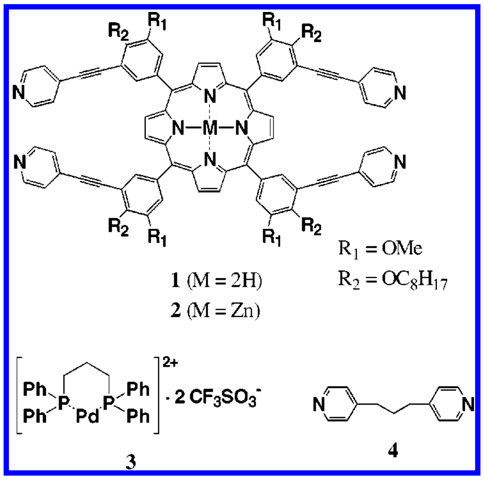
frequently very troublesome. Here, it occurred to us that the utilization of coordination bonds has been somewhat neglected, given that Fujita et al.[9] and Stang et al.[10] have shown a number of attractive examples in which coordination bonds are employed for the construction of self-assembled supramolecular architectures.[11] We previously found that two homooxacalix[3]arenes dimerize with three *cis*-Pd(II) complexes into a molecular capsule according to a self-assembled manner.[12,13] The spectroscopic studies have shown that the molecular capsule thus formed can specifically include [60]-fullerene, the selectivity of [60]fullerene vs [70]fullerene being nearly "perfect".[12,14] Utilizing this class of concept, several self-assembled multiporphyrin arrays were recently reported in organic solvents.[15] However, most of the preceding examples are two-dimensional macrocycles without a sufficient inclusion cavity, whereas the examples for three-demensional molecular capsules have been very limited.[16,17] If such a novel molecular capsule with "porphyrin walls" is successfully constructed, it follows that a guest is shielded inside the cavity while electrons are injected only via these "porphyrin walls". With this object in mind, we here report novel self-assembled molecular capsules constructed from porphyrin **1** or **2** through the pyridyl−Pd(II) interaction. Very interestingly, we have found that these molecular capsules can include bipyridine derivatives with relatively large association constants.



1 (M = 2H)

2 (M = Zn)

3

4

Compound **1** was obtained[18] in 22% yield by the reaction of 3-methoxy-4-*n*-octyloxy-5-pyridin-4-ylethynyl benzaldehyde with pyrrole in propionic acid. Compound **2** was obtained in 99% yield by the reaction of **1** with $Zn(OAc)_2$. These compounds were identified by IR, ^{1}H NMR, and MALDI-TOF mass ($[M + H]^+$ = 1651.9 and 1713.8 for **1** and **2**, respectively) spectral evidence and elemental analyses.

As shown in Figure 1b, the simple ^{1}H NMR splitting pattern was obtained when **1** and **3** were mixed in a 1:2 ratio in $CDCl_3$. When the ratio was higher or lower than this value, the ^{1}H NMR spectra gave additional peaks and became very complicated. Careful examination of Figure 1b and the ^{1}H-^{1}H COSY spectrum reveals that all peaks of **1·3** complex can be assigned to one kind of signals, supporting the 2:4 **1**/**3** complex (**5**) with a D_{4h} symmetrical structure but not the 1:2 complex with a C_{2v} symmetrical structure ais inconceivable because the rigid tetraphenylporphyrin skeleton of **1** suppresses the pyridyl groups to get close to each other and thus prevents **1** from the formation of the intramolecular bonds with two *cis*-Pd(II) complexes. Meanwhile, a solution of **2** in $CDCl_3$ gave a very complicated and very broadened ^{1}H NMR spectrum, suggesting that the pyridyl groups act as axial ligands to bind Zn(II) intermolecularly.[19] When **3** was added, **2** gave a ^{1}H NMR spectral splitting pattern very

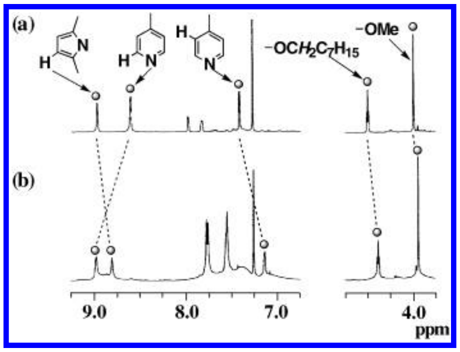


Figure 1. Partial ^{1}H NMR spectra of (a) **1** (2.2 mM) and (b) [**1**]:[**3**] = 1:2 (2.2 mM/4.4 mM): $CDCl_3$, 27 °C, 600 MHz.

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(18) Synthetic details and characterization data relating to **1** and **2** can be found in the Supporting Information.

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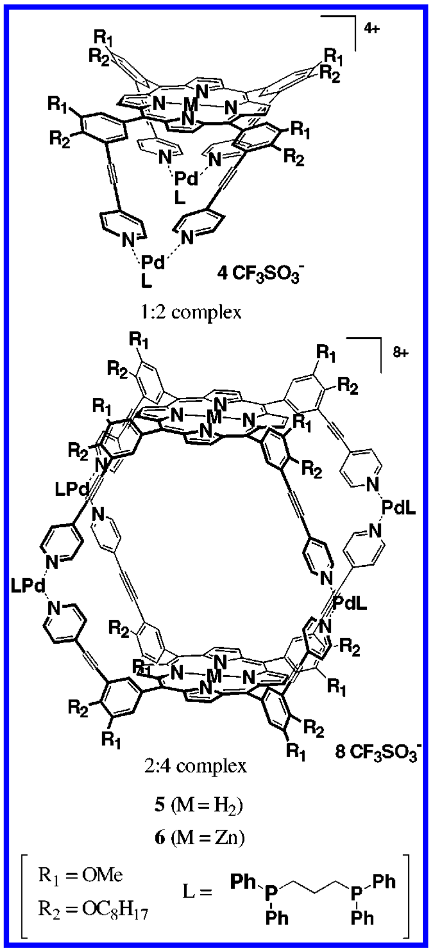

Figure 2. Schematic illustration of 1:2 and 2:4 complexes.

similar to that of 2:4 **1**/**3** complex (Figure 3b), which can be also assigned to the molecular capsule **6**.

The formation of molecular capsule **6** was also supported by coldspray ionization mass spectrometery (CIS-MS).[20] When a CH_2Cl_2 solution containing **2** and **3** in a 1:2 ratio was subjected to the CIS-MS measurement, strong peaks appeared at 967, 1190, and 1525, which are assignable to [**6** − $6CF_3SO_3^-$]$^{6+}$, [**6** − $5CF_3SO_3^-$]$^{5+}$, and [**6** − $4CF_3SO_3^-$]$^{4+}$, respectively.

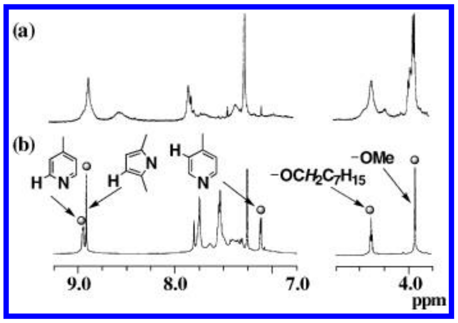

Figure 3. Partial ^{1}H NMR spectra of (a) **2** (1.5 mM) and (b) [**2**]:[**3**] = 1:2 (1.5 mM/3.0 mM): $CDCl_3$, 27 °C, 600 MHz.

Here, we evaluated whether these novel molecular capsules are capable of including some guest molecules. NMR spectroscopic studies have provided clear evidence that **6** can form complex with 4,4′-trimethylenedipyridine (**4**). The ^{1}H NMR spectrum of **6** in the presence of **4** is shown in Figure 4. The proton signals for free **6** and **6·4** complex appear separately. The peak separation implies that the complexation−decomplexation exchange rate is slower than the ^{1}H NMR time-scale. The stoichiometry of **6·4** complex was estimated to be 1:1 from the peak intensities. These results consistently support the view that **4** resides in the cavity of **6**.[21] Large upfield shift is observed for the α- and β-protons in the pyridyl groups of **4** (1.91 and 4.69 ppm, respectively). These changes are ascribed to the strong shielding effect of the porphyrin π-systems on the α- and β-protons of the included **4**.

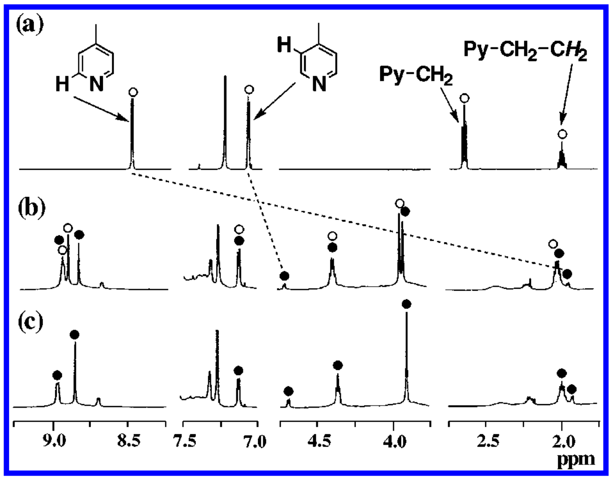

Figure 4. Partial ^{1}H NMR spectra of (a) **4** (0.8 mM), (b) [**6**]:[**4**] = 2:1 (0.8 mM/0.4 mM), and (c) [**6**]:[**4**] = 1:1 (0.8 mM/0.8 mM): $CDCl_3$, 27 °C, 600 MHz. Open and filled circles denote the signals for free **4** and **6** and those for **6·4** complex, respectively.

Figure 5 shows the influence of added **4** on the absorption spectral change in **6** (25 °C, $CHCl_3$). It is seen from Figure

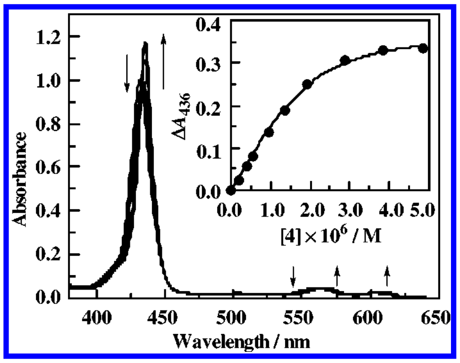

Figure 5. Absorption spectral change in **6** (2.0×10^{-6} M): [**4**] = 0−5.0×10^{-6} M. Insert: ΔA_{436} vs [**4**] plot in $CHCl_3$ at 25 °C.

5 that the λ_{max} for the Soret band (431 nm) shifts to longer wavelength (436 nm) with a tight isosbestic point (433 nm in the Soret band region). The result supports the view that two pyridine units in **4** simultaneously coordinate to Zn(II) in **6**. From a plot of ΔA_{436} vs [**4**] (inserted in Figure 5), one can obtain $K = 2.6 \times 10^6$ M^{-1} for the formation of the 1:1 complex from **4** and **6** (the formation of **6·4** complex is 65% at [**4**] = [**6**] = 2.0×10^{-6} M). Since the K for the formation of the 1:1 complex from pyridine and ZnTPP (TPP = tetraphenylporphyrin) (estimated under the similar measurement conditions) is 1.1×10^3 M^{-1}, one can regard that the two-point simultaneous binding dramatically enhances the K value. Moreover, the formation of **6·4** complex was also supported by coldspray ionization mass spectrometry. When a CH_2Cl_2 solution containing **4** and **6** in a 1:1 ratio was subjected to the CIS-MS measurement, strong peaks appeared at 1000, 1223, and 1574, which are assignable to [**6·4** − 6 $CF_3SO_3^-$]$^{6+}$, [**6·4** − 5 $CF_3SO_3^-$]$^{5+}$, and [**6·4** − 4 $CF_3SO_3^-$]$^{4+}$, respectively.

In conclusion, two porphyrin-based building blocks (**1** or **2**) intermolecularly bind four *cis*-Pd(II) complexes, resulting in a novel molecular capsule according to a self-assembled manner. Owing to rigid acetylene spacers between *meso*-phenyl moieties and pyridyl moieties in **2**, molecular capsule **6** can hold an unusually large cavity enough to bind large bipyridine guest **4**. These results show that porphyrins can act as powerful building blocks for constructing molecular capsules in a self-assembled manner. The further applications of these systems to porphyrin-mediated molecular recognition, redox reactions, photochemical reactions, etc. are currently under investigation in these laboratories.

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Supporting Information Available: Synthetic scheme and assignment of the ^{1}H NMR spectra of **1**, **2**, **5**, **6**, and **6·4** complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Although **4** is capable of coordination to Pd(II) to decomposed the capsular structure, it favorably interacts with porphyrin−Zn(II) for the steric suitability.