Hydrophobic Assembling of a Coordination Nanobowl into a Dimeric Capsule Which Can Accommodate up to Six Large Organic Molecules

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Dimerization of bowl-shaped molecules is an attractive approach to molecular capsules which are capable of accommodating organic molecules within their interior space. Both covalent and noncovalent dimers of bowl-shaped molecules have been studied continuously during the past decade.[1−4]

Bowl-shaped coordination compound **1** in Figure 1, which was reported recently,[5] can be a unique component for a dimeric capsule because of the following novel aspects of this compound. First, the bowl itself assembles spontaneously from 10 small components: six (en)Pd^{2+} units and four pyridine-functionalized ligands. Second, the bowl has a dimension of ~3 nm, and thus the cavity in the dimeric structure is extraordinarily large in comparison to those of previously reported capsules. Third, the nature of the bowl is amphiphilic: that is, the open cavity of **1** is surrounded by 16 aromatic rings and thus is hydrophobic, whereas the outside surface of the bowl is hydrophilic due to the exposure of six charged Pd(II) centers. Here we show that bowl **1** assembles in the solid state into a dimeric capsule and accommodates as many as six neutral organic molecules within a large hydrophobic pocket.

We first observed high binding ability of **1** in aqueous solution toward neutral organic molecules. For example, when *m*-terphenyl (**2**) was suspended in aqueous solution of **1** (50 mM) at 80 °C, this water immiscible guest was gradually dissolved in the aqueous phase within a few hours, forming a host−guest complex. The host−guest ratio was saturated at 1:2 when excess amount of **2** was employed, showing that two molecules of **2** were accommodated by nanobowl **1**. ^{1}H NMR showed broad peaks at room temperature, which, however, became sharp at elevated temperatures.[6] Thus, the guest motion is relatively slow on the NMR time scale at room temperature. The signals of **2** were highly upfield shifted ($\Delta\delta$ −1.0 to −2.5 ppm, compared to free guest in $CDCl_3$). After the removal of the excess guest by filtration, the host−guest complex was precipitated by adding ethanol and, after filtration, isolated in 68% yield. Elemental analysis agreed with the 1:2 host−guest ratio.[6]

The solid-state structure of the host−guest complex was particularly interesting because it showed a dimeric capsule structure of **1** accommodating four molecules of **2** (Figure 2).[6] The whole structure cannot be divided into a couple of simple 1:2 complexes because each guest is hosted by two nanobowls. Concerning orange-colored **2** in Figure 2, for example, two benzene rings bind to the upper-rim of one bowl, while the third one binds to the upper-rim of another bowl (π stacking ~3.5−4.0 Å). Similarly, two benzene rings of pink-colored **2** are trapped inside one bowl, and the remaining third one is linked by the upper rim of another bowl. Therefore, this 2:4 aggregate is a spherical capsule-like entity with 24 positive charges and dimension of ~3 × 4 nm.

To study the shape specificity in the complexation within the nanobowl cavity, we also examined *o*- and *p*-terphenyl guests (**3** and **4**, respectively) which have the same volume as **2**. Single crystals were obtained for the complex from **1** and **3** (1:2 ratio) and successfully analyzed by X-ray crystallography. Again, we observed the formation of a hydrophobic dimer of bowl **1**, encapsulating four molecules of **3**.[7] In this case, however, each bowl nicely accommodates two guest molecules in the cavity through face-to-face interaction, and hence, the whole solid structure is a hydrophobic pair of 1:2 complexes rather than a 2:4 complex. Although the solid structure showed the 1:2 complexation, the host−guest ratio in solution was saturated at 1:1.5. This result demonstrates that $\mathbf{1}\bullet(\mathbf{3})_2$ complex is less stable than $\mathbf{1}\bullet(\mathbf{2})_2$ (which might be dimeric $(\mathbf{1})_2\bullet(\mathbf{2})_4$ even in solution) and there exists rapid equilibration among $\mathbf{1}\bullet(\mathbf{3})_n$ species ($n = 0$, 1, 2; averaged $n = 1.5$). Linear guest **4** was obviously not favored for the complexation with **1** because the maximum host−guest ratio was only 1:0.2. No single crystals have been obtained for the complex from **1** and **4**.

More surprisingly, nanobowl **1** was shown to bind as many as six molecules of *cis*-stilbene (**5**) within its dimerized capsule structure (Figure 3). By letting the 100 mM solution of the host−guest complex stand overnight at room temperature, single crystals of $(\mathbf{1})_2\bullet(\mathbf{5})_6$ were obtained in 70% yield, and the crystal structure was solved (Figure 3).[8] To fill the inner cavity efficiently, six guests self-assemble into an organic cluster through aromatic interactions (π−π and CH−π interactions ~3.5−4.0 Å). Two of them obviously exist between two hosts interacting with the rims of the two bowls.

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(6) Crystal data of $[(\mathbf{1})_2\bullet(\mathbf{2})_4]^{24+}(NO_3)_{24}$: $C_{120}H_{124}N_{48}O_{36}Pd_6$, $M = 3453.07$, monoclinic, space group $P2_1/c$, $a = 19.579(3)$ Å, $b = 20.880(4)$ Å, $c = 40.705(8)$ Å, $\beta = 103.673(9)°$, $V = 16169(5)$ Å^3, $Z = 4$. Final R indices ($I > 2\sigma(I)$): $R_1 = 0.1127$, $wR_2 = 0.2368$. GOF on $F^2 = 1.025$. X-ray crystallographic details, NMR data, and elemental analysis are provided in Supporting Information.

(7) Crystal data of $[\mathbf{1}\bullet(\mathbf{3})_2]^{12+}(NO_3)_{12}$: $C_{120}H_{124}N_{48}O_{36}Pd_6$, $M = 3453.07$, triclinic, space group $P\bar{1}$, $a = 21.048(1)$ Å, $b = 21.2230(11)$ Å, $c = 24.507(1)$ Å, $\alpha = 83.098(1)$, $\beta = 73.547(1)°$, $\gamma = 74.542(1)°$, $V = 10110(1)$ Å^3, $Z = 2$. Final R indices ($I > 2\sigma(I)$): $R_1 = 0.1180$, $wR_2 = 0.3134$. GOF on $F^2 = 1.378$. X-ray crystallographic details (including structural drawings), NMR data, and elemental analysis are provided in Supporting Information.

(8) Crystal data of $[(\mathbf{1})_2\bullet(\mathbf{5})_6]^{24+}(NO_3)_{24}$: $C_{126}H_{132}N_{48}O_{36}Pd_6$, $M = 3533.20$, monoclinic, space group $P2_1/c$, $a = 20.182(7)$ Å, $b = 36.508(13)$ Å, $c = 25.441(9)$ Å, $\beta = 100.079(7)°$, $V = 18456(11)$ Å^3, $Z = 4$. Final R indices ($I > 2\sigma(I)$): $R_1 = 0.1471$, $wR_2 = 0.3220$. GOF on $F^2 = 1.558$. X-ray crystallographic details, NMR data, and elemental analysis are provided in Supporting Information.

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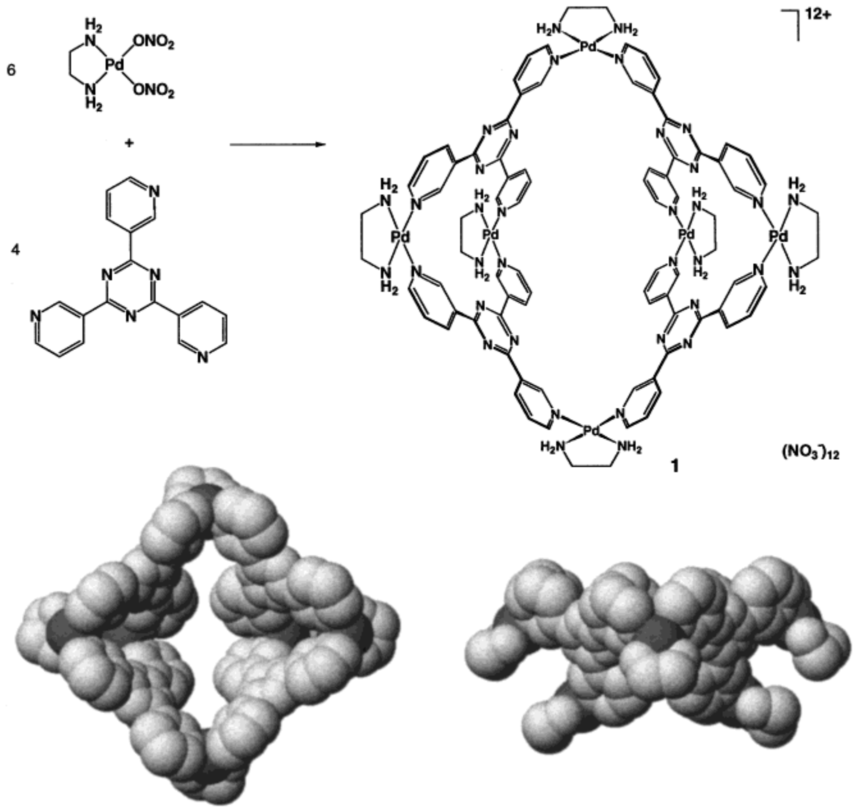

Figure 1. Self-assembly of coordination nanobowl **1**.[5] (b) X-ray structure of **1**. Left: a top view; right: a side view.

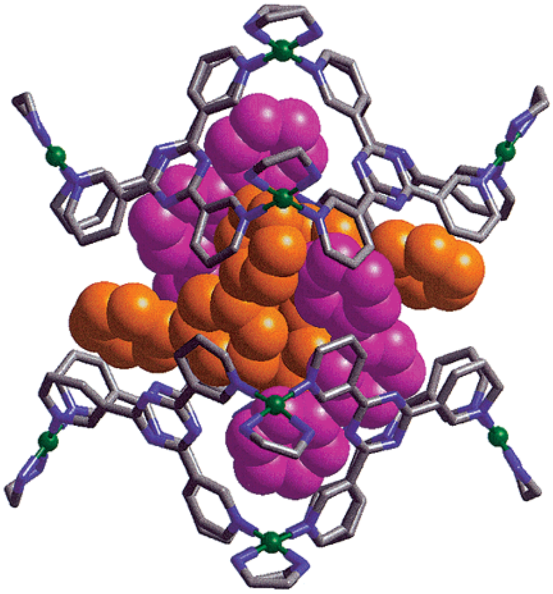

Figure 2. Crystal structure of the dimer capsule $(\mathbf{1})_2\bullet(\mathbf{2})_4$ complex.

In solution, 1:3 host−guest ratio was observed when excess **5** was suspended in a 100 mM aqueous solution of **1**. This ratio was, however, decreased at lower concentrations: that is, 1:2 at 50 mM and 1:1 at 20 mM.[8] Most probably, the stable dimeric $(\mathbf{1})_2\bullet(\mathbf{5})_6$ structure exists at high concentrations but dissociates into less stable monomers which can accommodate only one or two guest molecules. Complexation of nanobowl **1** with small organic molecules such as benzene or toluene was also observed. However, host−guest ratio was 1:1 to 1:2 at any concentrations (10−100 mM). Probably, a stable capsule-like entity does not assemble with these guests, and only monomeric 1:1 or 1:2 host−guest complexes are formed in solution.

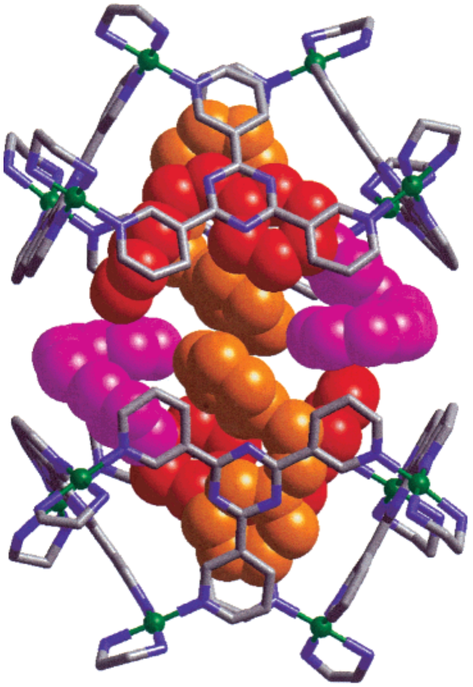

Figure 3. Crystal structure of the dimer capsule $(\mathbf{1})_2\bullet(\mathbf{5})_6$ complex.

Supporting Information Available: X-ray crystallographic details, NMR data, and elemental analysis for host−guest complexes $(\mathbf{1})_2\bullet(\mathbf{2})_4$, $(\mathbf{1})\bullet(\mathbf{3})_2$, and $(\mathbf{1})_2\bullet(\mathbf{5})_6$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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