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A 3.5-nm Coordination Nanotube

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Molecular self-assembly has been providing quite efficient approaches to well-defined tubular structures, which attract considerable current interest in broad scientific areas.[1−5] One of the most efficient approaches to molecular-based tubes is to link tape-like molecules into cylindrical shapes (Scheme 1). According to this strategy, we have previously synthesized 2-nm sized coordination nanotubes from pentapyridine, Py-Py′-Py′-Py′-Py (Py = 3-pyridyl, Py′ = 3,5-pyridylene), and enPd$(NO_3)_2$.[5] In this molecular design, the tube can be, in principle, elongated by simply increasing the number of pyridine rings of the ligand. However, the assembly of a tube from hexapyridine, Py-Py′-Py′-Py′-Py′-Py, was unsuccessful because of very poor solubility of this ligand. Accordingly, we have designed flexible molecular tape **1** in which two Py-Py′-Py units are connected by a biphenyl linker. The length of this ligand in its extended form is 3.5 nm, which should be directly transferred to that of the tube. We report here that the self-assembly of a 3.5-nm coordination nanotube $\mathbf{2}^{24+}$ is accomplished by using a 3.0-nm strand molecule as a template.[6] Facile preparation as well as the stability of the tube even after the template removal makes possible the discrete assembly of tubes that potentially interpenetrate biological membranes whose thickness is comparable to the length of the present coordination nanotube.

The key to the assembly of a long coordination tube is the selection of a linker that connects two tape-shaped units. When a flexible alkyl linker (−$(CH_2)_4$−) was used, the ligand adopted a U-shaped conformation that leads to unfavorable intramolecular coordination with enPd$(NO_3)_2$. To avoid the U-shaped orientation, we designed ligand **1** that possesses a rigid biphenylene spacer. This ligand was prepared in a good yield in two steps from 4,4′-biphenol (alkylation with 3-Br-C_6H_3N-CH_2Cl followed by cross-coupling with 3-tributylstannyl-3,3′-bipyridine).

For the assembly of **1** into the 3.5-nm coordination tube $\mathbf{2}^{24+}$, we also designed ca. 3.0-nm strand molecule **3** as a template. In **3**, two anthracenecarbonyl moieties are linked by a diethylene glycol unit, being ideal to fit within tube $\mathbf{2}^{24+}$. In fact, we observed the remarkable template effect of **3** for the smooth assembly of $\mathbf{2}^{24+}$. When the complexation of ligand **1** with enPd$(NO_3)_2$ was examined in the absence of the template, the formation of a very complex mixture resulted in (Figure 1a). However, the addition of **3** to the solution induced the conversion of the complex mixture into a single product within 6 h at 70 °C (Figure 1b). The NMR spectrum was consistent with the formation of tube $\mathbf{2}\bullet\mathbf{3}^{24+}$. Twelve proton signals (H_a−H_l) that stemmed from half the framework of $\mathbf{2}^{24+}$ were clearly observed. Template **3** was also observed symmetrically with outstanding upfield-shifting that indicated the accommodation of **3** in the tube. The methylene protons are diastereotopic and thus observed as an AB quartet. In addition to satisfactory NMR

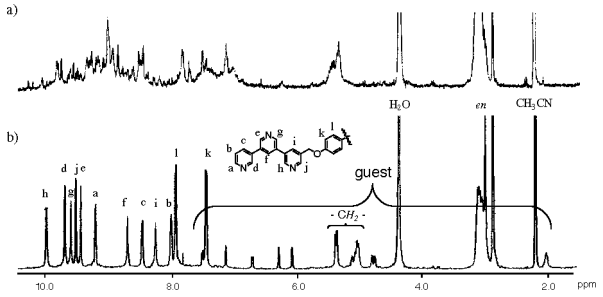
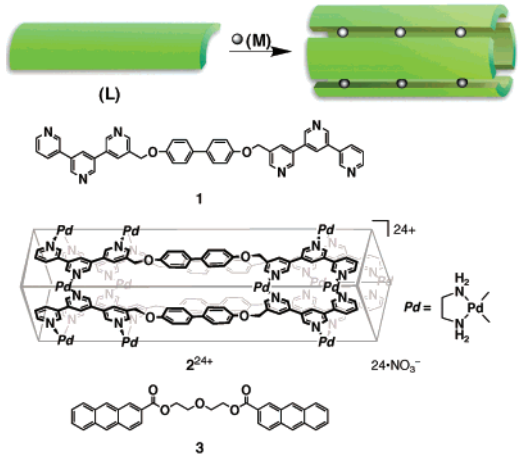


Figure 1. ^{1}H NMR observation of the templated formation of $\mathbf{2}\bullet\mathbf{3}^{24+}$ (500 MHz, D_2O−CD_3CN). (a) An oligomeric mixture obtained from **1** and enPd$(NO_3)_2$. (b) The $\mathbf{2}\bullet\mathbf{3}^{24+}$ complex assembled after the addition of **3**.

Scheme 1



spectroscopic results, the formula of $\mathbf{2}\bullet\mathbf{3}\bullet(NO_3)_{24}$ was confirmed by coldspray ionization mass spectrometry (CSI-MS) with a series of prominent peaks of $[M - (NO_3^-)_n]^{n+}$.[7]

The structure of $\mathbf{2}\bullet\mathbf{3}^{24+}$ complex (see Figure 2) was unambiguously determined by a single-crystal X-ray analysis. Single crystals were obtained by the slow evaporation of the solution of $\mathbf{2}\bullet\mathbf{3}^{24+}$ over one month. Despite the severe disorder of solvent molecules and the poor resolution of spots due to an extraordinarily long *b* axis (122 Å), synchrotron X-ray irradiation with high flux and low divergence afforded high-quality diffraction data, from which the tubular structure of $\mathbf{2}^{24+}$ with the length of 3.5-nm was revealed, which is, to our knowledge, the longest tubular host compound among those crystallographically defined.[5c,8,9] Each ligand adopted the most extended conformation, while the tube framework was slightly helicated.

Guest **3** is also the longest among those revealed thus far by an X-ray analysis. Within the cavity of $\mathbf{2}^{24+}$, two anthracene moieties of **3** are gripped by four tris(3,5-pyridine) units that are held together

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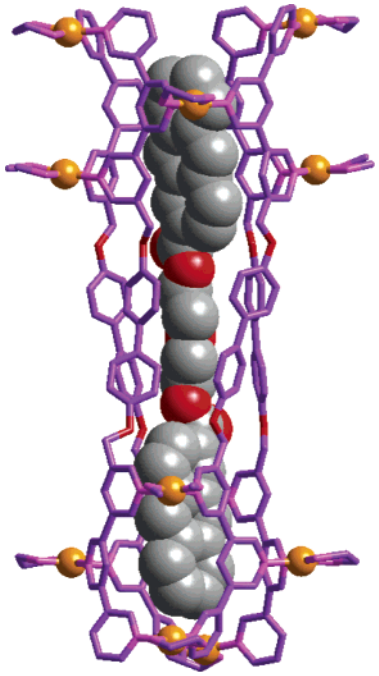

Figure 2. Crystal structure of **2•3**$^{24+}$. For clarity, H atoms, solvent molecules, and anions are omitted.

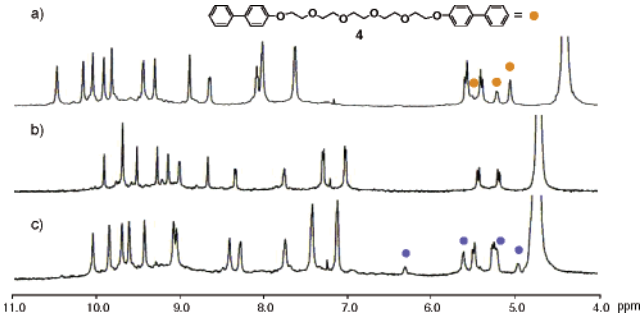

Figure 3. ^{1}H NMR observation of guest removal/reinclusion in tube **2**$^{24+}$ (500 MHz, D_2O-CD_3CN). (a) **2•4**$^{24+}$ complex. (b) Empty **2**$^{24+}$ after extraction of template **4** with $CDCl_3$. (c) **2•(5)**$_2^{22+}$ obtained by reinclusion of Na•**5** into the empty tube. Circles indicate guest signals.

by six Pd(II) ions via $\pi-\pi$ stacking and CH$-\pi$ contact. The diethylene glycol linker is essential because the tube did not assemble efficiently when anthracene or anthracenecarboxylate was employed as a template. Probably, Pd(II)-linked frameworks at both ends of **2**$^{24+}$ are simultaneously assembled by dual templating at the two anthracene moieties of **3**.

In the presence of another linear molecule **4** (in Figure 3), the high-yield formation of **2•4**$^{24+}$ was also observed (Figure 3a). Guest **4** seems, however, less effectively bound than **3** because **4** was easily replaced by **3** in 1 h at room temperature when **3** (1.0 equiv) was added to the solution of **2•4**$^{24+}$. This result is remarkable because the guest exchange requires the movement of **3** and **4** by more than 3 nm within the tubular cavity of **2**$^{24+}$. The guest exchange probably takes place by an S_N2-like mechanism, as previously discussed.[5b]

Template molecule **4** could be removed by extracting it with $CHCl_3$ (Figure 3b). After removal of the guest, the framework remained unchanged at room temperature, in sharp contrast to the behavior of previously reported shorter tubes that immediately collapsed when the template was removed.[5a] This fact indicates that, being cooperatively sustained by 24 Pd(II)−pyridine interactions, empty tube **2**$^{24+}$ possesses considerable kinetic stability.[5c,10] The empty tube is, of course, capable of binding other molecules in the cavity. Guests **3** and **4** reentered the tube within 1 h at room temperature when they were suspended in the solution of **2**$^{24+}$.[11] A small rodlike guest, sodium biphenylcarboxylate (Na•**5**), was also included, giving **2•(5)**$_2^{22+}$ complex (Figure 3c). The two guest molecules were equivalently observed by ^{1}H NMR spectroscopy, indicating symmetrical inclusion, in which COO^- groups are exposed outside at both ends of the tube. Particularly interesting is that the **2•(5)**$_2^{22+}$ complex can be efficiently formed only via **2•4**$^{24+}$ complex. This fact clearly demonstrates the "chaperoning effect" of **4** in the self-assembly of kinetically stabilized **2**$^{24+}$ and **2•(5)**$_2^{22+}$ complexes.[12]

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Note Added after ASAP Posting. After this paper was posted ASAP on August 17, 2004, an error in the compound numbers in the first sentence of the third paragraph was corrected. The corrected version was posted August 18, 2004.

Supporting Information Available: Preparation and physical properties of **1**, **3**, **5**, **2**$^{24+}$, **2•3**$^{24+}$, **2•4**$^{24+}$, and **2•(5)**$_2^{22+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) X-ray crystallographic measurement was performed on PF-AR NW2 beamline at High Energy Accelerator Research Organization (KEK), Japan. Crystal data for **2•3**$^{24+}$: orthorhombic, space group *Fdd*2, λ(synchrotron) = 0.68900 Å, T = 88(2) K, a = 49.2540(12) Å, b = 122.86(4) Å, c = 27.6620(5) Å, V = 167395(55) Å^3, Z = 16, d_{calcd} = 1.138 Mg/m^3. The detailed crystallographic information was described in a CIF file deposited in CCDC 238715.

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