Stabilization of a Self-assembled Coordination Nanotube by Covalent Link

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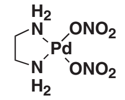
A newly designed oligopyridine ligand in which two tris(3,5-pyridine) units are linked by an alkyl spacer is complexed with (en)Pd$(NO_3)_2$ leading to the self-assembly of a coordination nanotube with an empty cavity. The covalent link in the ligand considerably stabilizes the tube because the tube framework without the covalent link does not assemble unless a template is employed. Size-discriminated alkane inclusion by the tube is also disclosed.

Nanotube structures have attracted considerable current interest both in chemistry and physics. In particular, molecular-based nanotubes with well-defined structures have been efficiently constructed through molecular self-assembly exploiting hydrogen bond as well as coordination bond.[1–4] We have recently shown that Pd(II) block **1** and tris(3,5-pyridine) ligand **2** self-assemble into coordination nanotube $\mathbf{4}^{12+}$ with the aid of the template effect of rod-like guests.[5] However, $\mathbf{4}^{12+}$ immediately collapses when the template molecule is removed. This fact suggests that the stability of the tube is attributed not only to the cooperation of the Pd–N bonds but also to the non-bonded interactions between the tube and the template. The construction of more stable tubes which do not collapse even in the absence of guests is particularly important to develop functional tubes that work via reversible host–guest complexation/decomplexation. We have therefore designed new ligand **3** in which two units of **2** are covalently linked by an alkyl (butyl) spacer to make the tube structure more stable. Here, we report the efficient self-assembly of ligand **3** into tubular structure $\mathbf{5}^{12+}$ without using any template molecules. Tube $\mathbf{5}^{12+}$ can encapsulate aliphatic guests such as hexane that was ineffective to induce the assembly of $\mathbf{4}^{12+}$ in our previous study.



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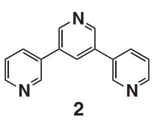

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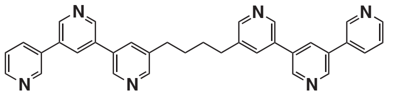

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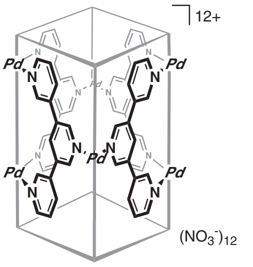
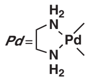
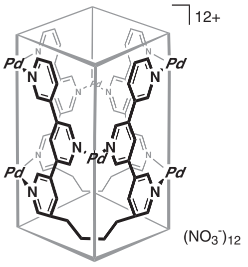


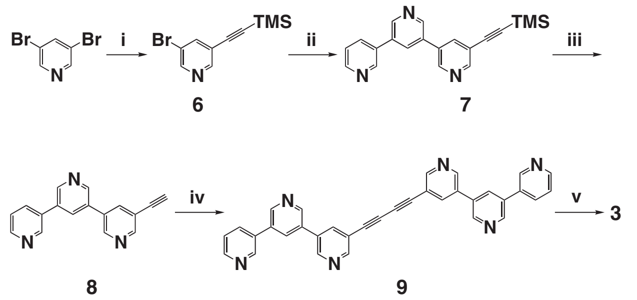
$\mathbf{4}^{12+}$





$\mathbf{5}^{12+}$

Ligand **3** was synthesized according to Scheme 1. The coupling reaction of 3,5-dibromopyridine with (trimethylsilyl)acetylene gave **6** (88%), which was subsequently treated with stannylbipyridine under the Stille coupling condition to give terpyridine **7** in 45% yield. Desilylation (71%) followed by the Hay acetylene coupling provided diterpyridine **9** (78%), which was then converted into **3** in 82% yield by hydrogenation.



Scheme 1. Reagents and conditions: (i) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, NEt_3, rt; (ii) 5-tributylstannyl-3,3′-bipyridine, $Pd(PPh_3)_4$, toluene, reflux; (iii) KF, THF/MeOH, rt; (iv) CuCl, TMEDA, O_2, CH_2Cl_2, rt; (v) Pd/C, H_2, H_3O^+, rt.

The assembly of coordination nanotube $\mathbf{5}^{12+}$ without a template molecule was accomplished by simply mixing ligand **3** and **1**. Thus, ligand **3** (0.014 mmol) and **1** (0.042 mmol) were dissolved in D_2O (0.7 mL) and the mixture was stirred for 2 h at 70 °C to give mainly a single product in a high yield (Figure 1a).[6] The NMR spectrum displayed ten proton signals in the aromatic region suggesting the formation of a highly symmetric single component. CSI-MS (coldspray-ionization mass spectrometry) evidenced the stoichiometry of $\mathbf{5}^{12+}$ with prominent $[M–(NO_3)_n]^{n+}$ peaks (e.g., m/z 1330.0 $[M–(NO_3)_2]^{2+}$ and 865.8 $[M–(NO_3)_3]^{3+}$).[7] The product was isolated as a colorless precipitate in 79% yield by adding a large amount of acetone to the reaction mixture.

From the symmetry and stoichiometry shown by NMR and CSI-MS, respectively, the product can be assigned to either expected $\mathbf{5}^{12+}$ or its structural isomer $\mathbf{10}^{12+}$, whose symmetries are dictated as C_{2v} or C_{2h}, respectively. To distinguish these two structures, we examined the complexation with a symmetric guest, anthracene (**11**), which should be desymmetrized in C_{2v} host $\mathbf{5}^{12+}$ but not in C_{2h} host $\mathbf{10}^{12+}$. Thus, **11** was suspended in the solution. After 2 h at 70 °C, ^1H NMR clearly showed the

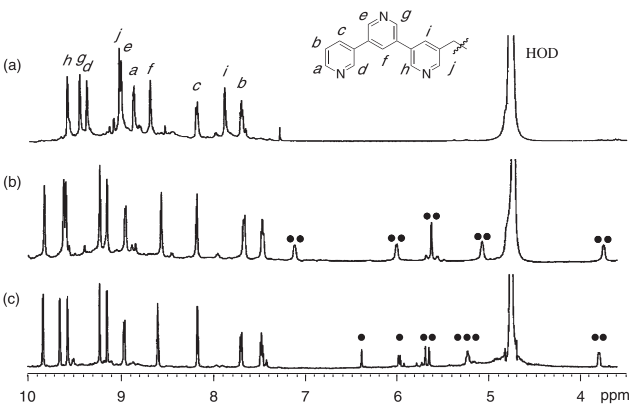
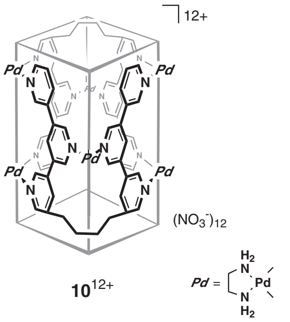


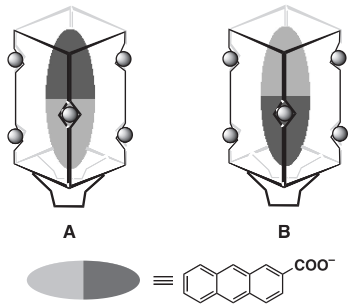
Figure 1. The ^{1}H NMR observations of the formation of nanotube complexes (500 MHz, D_2O, 25 °C, TMS as an external standard). (a) Complex $\mathbf{5}^{12+}$ assembled from treating ligand **3** with **1** in D_2O for 2 h at 70 °C. (b) Complex $\mathbf{5}\cdot\mathbf{11}^{12+}$ assembled upon the addition of **11**. (c) Complex $\mathbf{5}\cdot\mathbf{12}^{11+}$ assembled upon the addition of $Na^+\cdot\mathbf{12}^-$. Circles indicate guest signals.

desymmetrization of **11** (Figure 1b); five aromatic signals of **11** appeared at δ 7.1–3.7. Thus we concluded that ligand **3** was assembled into C_{2v} host $\mathbf{5}^{12+}$.[8]



$\mathbf{10}^{12+}$

An asymmetric guest like sodium 2-anthracenecarboxylate ($Na^+\cdot\mathbf{12}^-$) can be accommodated in two ways to give isomers **A** or **B**. However, when $\mathbf{12}^-$ was added to the solution of $\mathbf{5}^{12+}$, the formation of a single isomer was observed (Figure 1c). Most probably, the complex is assigned as isomer **A** where alkyl spacers make one end of the tube more hydrophobic and suitable for accommodating the hydrophobic site of the guest.



The size and the shape of coordination nanotube $\mathbf{5}^{12+}$ are almost the same as those of $\mathbf{4}^{12+}$. However, the striking feature of $\mathbf{5}^{12+}$ is the stability of the tube framework. In addition to aromatic guests, nanotube $\mathbf{5}^{12+}$ encapsulates aliphatic guests, which did not induce the assembly of $\mathbf{4}^{12+}$ because of insufficient stabilization. Thus, hexane was enclathrated by suspending it in a solution of $\mathbf{5}^{12+}$ in D_2O at room temperature. The proton signals of enclathrated hexane were observed at δ −1.4 to −1.7 in the ^{1}H NMR spectrum. The 1:1 host–guest ratio was clearly confirmed by NMR spectroscopy. Guest encapsulation was also observed with similar aliphatic molecules such as cyclohexane and octane. Thus, tube $\mathbf{5}^{12+}$ should have considerable flexibility to accommodate such guests. The lengths of host and guest should be compatible since decane and dodecane were not accommodated. This result shows that nanotube $\mathbf{5}^{12+}$ can discriminate the chain length of linear alkanes.

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6 Coordination nanotube $\mathbf{5}^{12+}$: A mixture of **1** (12.2 mg, 0.042 mmol) and **3** (7.3 mg 0.014 mmol) was stirred for 2 h at 70 °C in H_2O (0.7 mL) and cooled to room temperature. After filtration, the complex **5** was isolated as a colorless precipitate in 79% yield by adding a large amount of acetone. mp 289 °C (decomp); ^{1}H NMR (500 MHz, D_2O, 25 °C, TMS as an external standard) δ 9.58 (s, 4H; Py*H*), 9.45 (s, 4H; Py*H*), 9.37 (s, 4H; Py*H*), 9.05 (s, 4H; Py*H*), 8.99 (s, 4H; Py*H*), 8.86 (d, $J = 5.7$ Hz, 4H; Py*H*), 8.68 (s, 4H; Py*H*), 8.17 (d, $J = 8.0$ Hz, 4H; Py*H*), 7.86 (s, 4H; Py*H*), 7.68 (m, 4H; Py*H*), 3.00–2.64 (m, 32H; $NH_2CH_2CH_2NH_2$ and CH_2), 1.75 (s, 8H; CH_2); ^{13}C NMR (125 MHz, D_2O, 25 °C, TMS as an external standard) δ 151.48 (*C*H), 151.06 (*C*H), 150.69 (*C*H), 149.97 (*C*H), 147.90 (*C*H), 147.78 (*C*H), 141.72 (C_q), 138.60 (*C*H), 137.52 (*C*H), 136.60 (*C*H), 134.58 (C_q), 134.29 (C_q), 134.03 (C_q), 132.99 (C_q), 126.95 (*C*H), 47.31–45.84 ($NH_2CH_2CH_2NH_2$), 32.18 (CH_2), 28.23 (CH_2); IR (KBr, cm^{-1}) 1609, 1375, 1029, 703; Anal. Calcd. for $C_{80}H_{104}N_{36}O_{36}Pd_6\cdot13H_2O$: C, 31.83; H, 4.34; N, 16.70%. Found: C, 31.81; H, 4.42; N, 16.48%.

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8 Two alkyl spacers in $\mathbf{5}^{12+}$ are closer to each other than those in $\mathbf{10}^{12+}$. Probably, this makes $\mathbf{5}^{12+}$ more stable.

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