

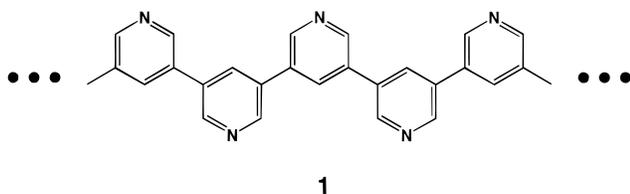
Quantitative Formation of Coordination Nanotubes Templated by Rodlike Guests

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Molecular-based tubular structures have attracted considerable current interest because of their potential abilities for selective inclusion and transportation of ions and molecules and catalysis for specific chemical transformations, by exploiting the interior space of the tubes.^{1–5} For constructing nanotube structures, noncovalent syntheses using hydrophobic interaction^{2,5} and hydrogen bonding^{3,4} have been shown to be quite effective, although the precise control of tube lengths remains unrealized yet. Herein reported is a coordination approach to nanotubes possessing very stable, discrete frameworks. We designed the assembly of oligo(3,5-pyridine)s (**1**) into tubular structures by linking them with transition metal components.



Our strategy is summarized in Scheme 1. Pentakis(3,5-pyridine) ligand **1a**,⁶ for example, should take a planar conformation due to the dipole repulsion among pyridine nuclei. Thus, when this ligand is linked together with Pd(II) building block **2** which provides 90 degree turn into the assembled structure,⁷ coordination nanotube **3a**²⁰⁺ is expected to assemble from 4 molecules of **1a** and 10 molecules of **2**. Similar coordination tubes **3b**¹⁶⁺ and **3c**¹²⁺ are also designed.

In fact, the quantitative assembly of coordination nanotube **3a**²⁰⁺ was achieved, following Scheme 1, with the aid of the remarkable template effect of a rodlike template molecule.^{8–10}

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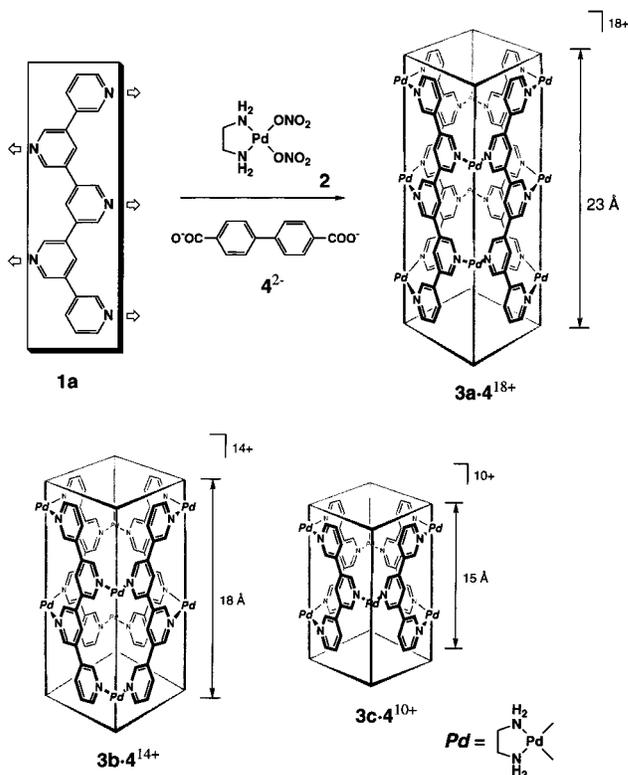
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Scheme 1



Thus, the reaction of **1a** with **2** in D₂O first resulted in the formation of uncharacterized products (Figure 1a). Surprisingly, the addition of disodium 4,4'-biphenylenedicarboxylate (Na₂·**4**) to the solution induced the assembly of a single product (Figure 1b), which smoothly turned into a sole product after the solution was heated at 60 °C for 1 h (Figure 1c). The NMR spectrum showed nine proton signals which stemmed from half the framework of **1a** in the product. Furthermore, a NOESY experiment supported the planar conformation of the ligand framework.¹¹ From these observations, the product was assigned as coordination nanotube **3a**²⁰⁺ including template **4**²⁻ in the tube. Actually, the formula of **3a**·**4**·(NO₃)₁₈ was confirmed by ESI-MS measurement (*m/z* 699 [M - 6(NO₃)]⁶⁺; 852 [M - 5(NO₃)]⁵⁺; 1080 [M - 4(NO₃)]⁴⁺). From the aqueous solution, the host-guest complex (**3a**·**4**·(NO₃)₁₈) was isolated as a colorless precipitate in 81% yield by adding large amount of acetone. Elemental analysis was consistent with the formula of **3a**·**4**·(NO₃)₁₈·(H₂O)₂₅.¹²

The template effect of **4**²⁻ for the assembly of tube **3a**²⁰⁺ has been obviously revealed by the following results. First, the protons of guest **4**²⁻ were highly upfield-shifted in ¹H NMR by 2.6 ppm

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(9) Metal-ion templating: (a) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P. *Tetrahedron Lett.* **1983**, *24*, 5095 (b) For a review, see: Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795.

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(11) NOE cross-peaks were observed between H_c-H_e, H_d-H_f, H_i-H_h, and H_g-H_i in **3a**, indicating the coplanar, zigzag conformation of ligand **1a**.

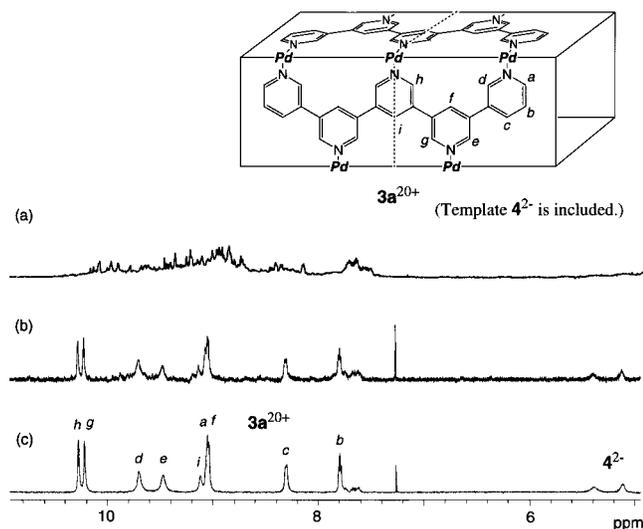


Figure 1. The ^1H NMR observation of the guest-templated formation of $3\mathbf{a}\cdot\mathbf{4}^{18+}$ (500 MHz, D_2O , 25 $^\circ\text{C}$, TMS as an external standard). Spectra were obtained after the following procedures. (a) Ligand $\mathbf{1a}$ (0.01 mmol) was treated with $\mathbf{2}$ (0.025 mmol, 1 mL) in D_2O (1 mL) for 5 min at 60 $^\circ\text{C}$. (b) To this solution was added a D_2O solution of $\text{Na}_2\cdot\mathbf{4}$ (25 mM, 0.12 mL) and the mixture was stirred for 1 h at room temperature. (c) Then, the mixture was stirred for additional 1 h at 60 $^\circ\text{C}$.

indicating the accommodation of the guest in the nanotube. Second, other rodlike molecules such as unsubstituted biphenyl and *p*-terphenyl were effective, whereas large molecules such as adamantane carboxylate did not show any template effect. Third, in the absence of $\mathbf{4}^{2-}$, tube $\mathbf{3a}^{20+}$ was not assembled effectively even after one week at 60 $^\circ\text{C}$.

The template molecule was strongly bound within the interior of the tube and even unsubstituted biphenyl could not be extracted with CHCl_3 from an aqueous solution of $\mathbf{3a}^{20+}\cdot\text{biphenyl}$ at room temperature. Only at high temperatures (>70 $^\circ\text{C}$), biphenyl was slowly extracted with CHCl_3 from the aqueous solution. Interestingly, the guest-templated assembly of tube $\mathbf{3a}^{20+}$ is a complete reversible process: i.e., when the guest biphenyl was extracted into the CHCl_3 phase at 70 $^\circ\text{C}$, once assembled $\mathbf{3a}^{20+}$ easily turned into an oligomer mixture, which regenerated tube $\mathbf{3a}^{20+}$ upon the addition of the template molecule to the mixture again.

The tubular structure enclathrating the template molecule was confirmed by the X-ray crystallographic analysis of complex $\mathbf{3c}\cdot\mathbf{4}\cdot(\text{NO}_3)_{10}$ assembled from tris(3,5-pyridine) ligand $\mathbf{1c}$, Pd(II) complex $\mathbf{2}$, and template $\mathbf{4}^{2-}$. Again, the treatment of $\mathbf{1c}$ with $\mathbf{2}$ afforded a complex mixture, which, however turned into $\mathbf{3c}\cdot\mathbf{4}^{10+}$ upon addition of $\mathbf{4}^{2-}$ and heating at 70 $^\circ\text{C}$.¹³ Single crystals were obtained by diffusing isopropyl alcohol into an aqueous solution of $\mathbf{3c}^{12+}$ and $\mathbf{4}^{2-}$ (1:2) at room temperature for 2 d. The crystal structure (Figure 2a) displays the tubular structure of $\mathbf{3c}^{12+}$ which is efficiently assembled around template $\mathbf{4}^{2-}$.¹⁴ As expected, each ligand takes almost planar conformation, and dihedral angles between adjacent pyridine rings are less than 28 $^\circ$. The top view

(12) Preparation and physical properties of $\mathbf{3a}\cdot\mathbf{4}\cdot(\text{NO}_3)_{18}$: $\mathbf{1a}$ (0.04 mmol) and $\mathbf{2}$ (0.1 mmol) were combined in H_2O (1.5 mL) and stirred for 5 h at 70 $^\circ\text{C}$. To this solution, an aqueous solution (0.5 mL) of $\text{Na}_2\cdot\mathbf{4}$ (0.01 mmol) was added, and the mixture was stirred at 70 $^\circ\text{C}$ for 9 h. After filtration, addition of acetone (10 mL) to the solution precipitated a colorless powder which was collected and dried under reduced pressure to give $\mathbf{3a}\cdot\mathbf{4}\cdot(\text{NO}_3)_{18}$ in 81% yield: mp 256–258 $^\circ\text{C}$ dec; ^1H NMR (500 MHz, D_2O , 60 $^\circ\text{C}$, TMS as an external standard) δ = 10.12 (s, 8H, PyH α), 10.06 (s, 8H, PyH α), 9.55 (brs, 8H, PyH α), 9.34 (brs, 8H, PyH α), 8.98 (s, 4H, PyH γ), 8.94 (d, J = 6.4 Hz, 8H, PyH α), 8.91 (s, 8H, PyH γ), 8.21 (d, J = 7.7 Hz, 8H, PyH γ), 7.70 (t, J = 6.4 Hz, 8H, PyH β), 5.32 (brs, 4H, ArH), 4.99 (brs, 4H, ArH), 3.0–2.8 (m, 40H, CH $_2$); ^{13}C NMR (125 MHz, D_2O , 60 $^\circ\text{C}$, TMS) δ = 153.2 (CH), 151.5 (CH), 151.3 (CH), 151.2 (CH), 150.0 (CH), 139.4 (CH), 135.6 (CH and Cq), 134.2 (Cq), 133.7 (Cq), 133.5 (CH), 133.3 (Cq), 129.1 (CH), 128.2 (CH), 122.7 (CH), 48.1 (CH $_2$), 48.0 (CH $_2$), 47.9 (CH $_2$). IR (KBr, cm^{-1}) 1589, 1385, 1509, 704. Elemental analysis: Calcd for $\text{C}_{134}\text{H}_{156}\text{N}_{58}\text{O}_{38}\text{Pd}_{10}\cdot 25\text{H}_2\text{O}$: C, 32.05; H, 4.13; N, 16.18. Found: C, 32.24; H, 3.98; N, 15.97.

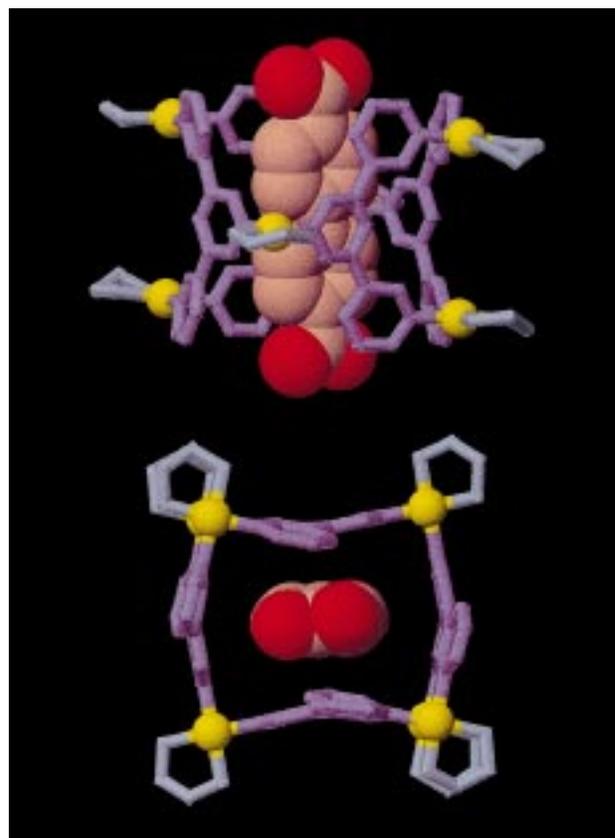


Figure 2. (a) Crystal structure of $\mathbf{3c}\cdot(\mathbf{4})_2\cdot(\text{NO}_3)_8$. (b) Top view. For clarity, H atoms are omitted.

of this complex (Figure 2b) shows strong π – π and CH– π interactions between $\mathbf{3c}^{12+}$ and $\mathbf{4}^{2-}$. Namely, the shape from the top view, which should be square ideally, is significantly distorted in such a way that two ligands are stacked on the π -face of $\mathbf{4}^{2-}$ with π – π interaction distances (3.5–3.6 \AA) and two other ligands are orthogonally interacted with $\mathbf{4}^{2-}$ in CH– π interaction distances (2.9–3.0 \AA). Interestingly, another biphenyldicarboxylate is located outside and stacked between the tubes, though it is omitted for clarity.

Supporting Information Available: Preparation and physical properties of $\mathbf{1a}$ – \mathbf{c} and $\mathbf{3b}\cdot\mathbf{4}\cdot(\text{NO}_3)_{14}$, NMR spectra of $\mathbf{3}\cdot\mathbf{4}$ complexes (^1H , ^{13}C , HH-COSY, NOESY, CH-COSY, and HMBC), crystallographic data of $\mathbf{3c}\cdot(\mathbf{4})_2\cdot(\text{NO}_3)_8$, and VT- ^1H NMR observation of $\mathbf{3a}\cdot\mathbf{4}^{18+}$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Complex $\mathbf{3c}\cdot\mathbf{4}^{10+}$ for NMR measurement was prepared by reaction of $\mathbf{1c}$, $\mathbf{2}$, and $\text{Na}_2\cdot\mathbf{4}$ in D_2O in ratio of 4:6:1. ^1H NMR (500 MHz, D_2O , 25 $^\circ\text{C}$, TMS as external standard) δ = 9.88 (d, J = 2.0 Hz, 8H, PyH α), 9.56 (d, J = 1.5 Hz, 8H, PyH α), 9.06 (dd, J = 5.8, 1.0 Hz, 8H, PyH α), 8.92 (s, 4H, PyH γ), 8.21 (d, J = 8.2 Hz, 4H, PyH γ), 7.68 (dd, J = 8.2, 5.8 Hz, 8H, PyH β), 5.57 (d, J = 8.2 Hz, 4H, ArH), 5.01 (d, J = 8.2 Hz, 4H, ArH), 3.0–2.9 (m, 24H, CH $_2$); ^{13}C NMR (125 MHz, D_2O , 25 $^\circ\text{C}$, TMS) δ = 170.4 (Cq), 153.4 (CH), 150.2 (CH), 149.8 (CH), 138.5 (CH), 137.6 (Cq), 137.5 (Cq), 135.4 (CH), 134.7 (Cq), 132.9 (Cq), 129.5 (CH), 128.3 (CH), 122.2 (CH), 47.8 (CH $_2$), 47.7 (CH $_2$). Although the formation of 1:1 complex ($\mathbf{3c}\cdot\mathbf{4}^{10+}$) was confirmed by NMR, crystallization always gave 1:2 complex $\mathbf{3c}\cdot(\mathbf{4})_2\cdot(\text{NO}_3)_8$ including one molecule of $\mathbf{4}$ in the tube and another molecule of $\mathbf{4}$ outside the tube (see X-ray result in Supporting Information). Isolation and physical properties of $\mathbf{3c}\cdot(\mathbf{4})_2\cdot(\text{NO}_3)_8$: compound $\text{Na}_2\cdot\mathbf{4}$ (0.018 mmol) was added to a solution of $\mathbf{1c}$ (0.035 mmol) and $\mathbf{2}$ (0.052 mmol) in H_2O (0.5 mL). The mixture was heated at 70 $^\circ\text{C}$ for 1 d and filtered. Slow diffusion of ethanol into the solution for 4 d precipitated a colorless powder, which was collected and dried under reduced pressure to give $\mathbf{3c}\cdot(\mathbf{4})_2\cdot(\text{NO}_3)_8$ in 95% yield (based on $\mathbf{4}^{2-}$): mp 226–227 $^\circ\text{C}$ dec; IR (KBr, cm^{-1}) 1583, 1539, 1385, 1507, 702. Elemental analysis: Calcd for $\text{C}_{100}\text{H}_{108}\text{N}_{32}\text{O}_{32}\text{Pd}_6\cdot 15\text{H}_2\text{O}$: C, 37.78; H, 4.38; N, 14.10. Found: C, 37.74; H, 4.26; N, 14.16. ESI-MS: m/z 469 [$M - 6(\text{NO}_3)$] $^{6+}$; 639 [$M - 5(\text{NO}_3)$] $^{5+}$; 868 [$M - 4(\text{NO}_3)$] $^{4+}$.

(14) X-ray data for $\text{C}_{100}\text{H}_{108}\text{N}_{32}\text{O}_{32}\text{Pd}_6\cdot 26\text{H}_2\text{O}$: M = 3377.58, monoclinic, space group $P2_1/n$; a = 17.429(3) \AA , b = 14.785(3) \AA , c = 27.061(5) \AA , β = 101.555(4), V = 6832(2) \AA^3 ; ρ_{calc} = 1.642 g/cm^3 , Z = 2; $F(000)$ = 3448; $\mu(\text{Mo K}\alpha)$ = 0.876 mm^{-1} ; temp. 293 $^\circ\text{C}$; 28290 reflections collected, 11995 ($I > 2\sigma(I)$) reflections observed; $R1$ = 0.0812; $wR2$ = 0.2110.