# Construction of a Long Cyclodextrin-Based Bis(molecular tube) from Bis(polypseudorotaxane) and Its Capture of $C_{60}$

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**ABSTRACT** The preorganized bis(polypseudorotaxane) (~20 nm long) formed by the multiple metallo-bridged poly($\beta$-cyclodextrin)s has been successfully converted to the lengthened bis(molecular tube) (~200 nm long) through the intermolecular joining of ~10 discrete bis(polypseudorotaxane) units and the subsequent removal of the polymer templates. The obtained bis(molecular tube), which is quite soluble in water, dimethylformamide, and dimethyl sulfoxide, has been comprehensively characterized by NMR, gel permeation chromatography, static light scattering, X-ray powder diffraction, thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, and scanning tunneling microscopy. Further investigations demonstrate that this bis(molecular tube) can capture $C_{60}$ through interaction with its many $\pi$-electron-rich biquinolino groups.

**KEYWORDS:** bis(polypseudorotaxane) · organic nanotube · fullerene · cyclodextrin · synthesis

In recent years, the construction of organic nanotubes represents a very active area of research due to its potential applications in the one-dimensional transport of energy, charge, and ions.[1−19] Among the constructed organic nanotubes, those formed by the covalent linkage of cyclodextrins have attracted more and more attention. For example, Harada *et al.* reported the construction of open-ended hollow mononanotubes from polymer-threaded cyclodextrin polyrotaxanes.[20,21] Yui *et al.* prepared a $\beta$-cyclodextrin-based nanotube and investigated its inclusion complexation thermodynamics with sodium alkyl sulfonates, demonstrating that the nanotubular structure is preferable for supramolecular interactions with longer alkyl chains.[22] Ito *et al.* reported a dendritic supramolecular structure with three branches formed by cyclodextrins-based molecular nanotubes and star polymers.[23] Using a method similar to that reported by Harada,[20,21] we threaded metallobis($\beta$-cyclodextrin)s on two poly(propylene glycol) (PPG) chains to generate the bis(polyrotaxane) and then converted it to the nanometer-scaled bis(molecular tube) possessing many coordinated metal centers.[24] In these reports, the general method applied for the construction of a cyclodextrin-based nanotube is the cross-linkage of adjacent cyclodextrin units in a polymer-threaded polyrotaxane *via* covalent bonds, followed by removal of the polymer templates. However, a disadvantage of this method is that the length of the cyclodextrin nanotube thus formed is mainly dependent on the length of the polymer template. This dependence makes the construcion of long nanotubes difficult. To address this limitation, we constructed a preorganized bis(polypseudorotaxane) possessing many $\pi$-electron-rich biquinolino groups[25] and successfully converted it to a lengthened bis(molecular tube) through intrapolypseudorotaxane and interpolypseudorotaxane linkages. Static light scattering and transmission electron microscopy (TEM) studies show that roughly 10 units of bis(polypseudorotaxane) are connected together to form the bis(molecular tube). Significantly, through the interactions between the biquinolino groups and fullerenes, the obtained bis(molecular tube) can efficiently capture $C_{60}$. These results may open a new channel in the design and preparation of long cyclodextrin-based nanotubes.

## RESULTS AND DISCUSSION

The bis(molecular tube) **4** was prepared according to the procedures shown in Scheme 1. First, the preorganized bis(polypseudorotaxane) **3** was prepared by threading the 2,4-dinitrofluorobenzene-terminated PPG (DFB-PPG) chains through metallobridged bis($\beta$-cyclodextrin)s.[25] Sub-

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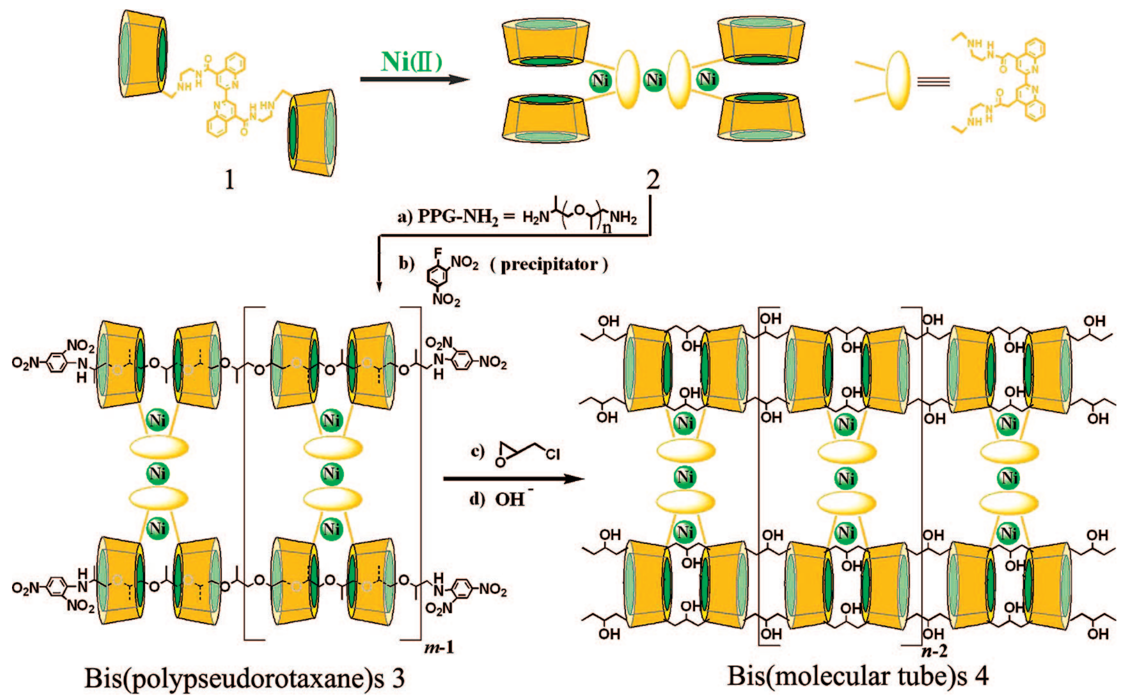

**Scheme 1. Synthesis of bis(molecular tube) 4. The counterion to Ni(II) is $NO_3^-$.**

sequently, the bis(molecular tube) **4** was obtained through the cross-linking reaction of **3** with epichlorohydrin in a basic environment, followed by removal of DFB-PPG chains. During the preparation and purification process, we made several attempts to remove the possible impurities. First, we performed the cross-linking reaction in aqueous solution in order to maintain the hydrophobic interactions between cyclodextrin cavities and DFB-PPG chains and to prevent the dethreading of DFB-PPG chain from bis(polypseudorotaxane). Second, the cross-linked bis(polypseudorotaxane) was washed with acetone to remove the DFB-PPG chains, as the DFB-PPG chain is quite soluble in acetone but the bis(molecular tube) **4** is not. Furthermore, the bis(molecular tube) **4**, which is quite soluble in water, DMF and DMSO, was purified by column chromatography and comprehensively characterized by NMR, static light scattering, gel permeation chromatography (GPC), X-ray powder diffraction (XRD), thermogravimetric (TG), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning tunneling microscopy (STM).

**The Cross-Linking Degree of the Bis(molecular tube).** The degree of cross-linking, $p$, a molar ratio of the cross-linking residue to the block residue ($\beta$-cyclodextrin unit), was determined from the results of the elemental analysis of **4** by using the equation,[24,26]

$$\frac{C(\%)}{1-H_2O(\%)}=\frac{2\times[12.011\times(42\times2+24+3p)]}{2pM_{PPR}+2M_{bCD}+3M_{Ni(NO_3)_2}}$$

where $p$ denotes the degree of cross-linking and $M_{PPR}$, $M_{bCD}$, and $M_{Ni(NO_3)_2}$ indicate the molecular weights of cross-linking 2-propanol residue, bridged cyclodextrins, and $Ni(NO_3)_2$, respectively. From the equation, the value of $p$ was obtained as 4. This indicates that every two adjacent cyclodextrin units are cross-linked by two 2-propanol residues, as shown in Scheme 1.

**$^1$H NMR Spectroscopy.** As compared with that of **3** (Figure 1), the $^1$H NMR spectrum of **4** clearly displays the absence of the methyl protons (at $\delta$ 1.0–1.2 ppm) and dinitrobenzene protons (at $\delta$ 7.4–7.6 and 8.5–8.7 ppm) of DFB-PPG and the presence of methylene and methine protons (at $\delta$ 3.5–3.7 ppm) of 2-propanol residues.

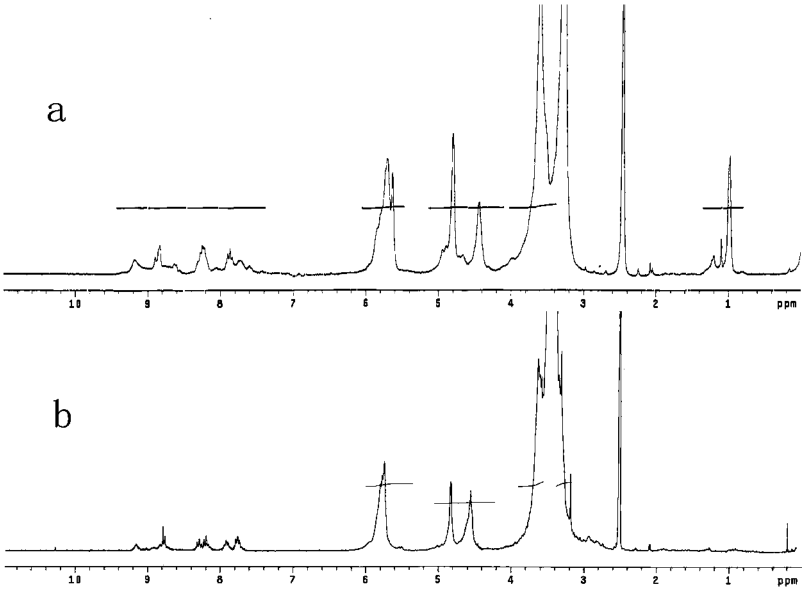

**Figure 1. $^1$H NMR spectra of (a) 3 and (b) 4 in DMSO-$d_6$ at 25 °C.**

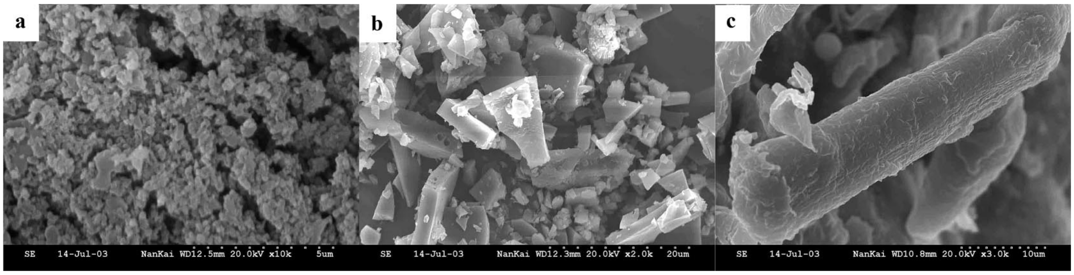

Figure 2. SEM images of (a) **2**, (b) **3**, and (c) **4**.

Moreover, the color of cross-linked bis(polypseudorotaxane) changes from light yellow (the color of the dinitrobenzene groups) to light gray after being washed with acetone. These phenomena support the assumption of the removal of DFB-PPG chains and the cross-linking of cyclodextrin units. In addition, an aqueous solution of **4** can remain transparent at temperatures from 25 to 80 °C. Moreover, the concentration-dependent UV spectra of **4** show that the intensities of the absorption maximum of **4** at 332 nm exhibit the good relationship *versus* concentration in the measured concentration range (0–6.4 mg/mL), indicating that the bis(molecular tube) is not a simple aggregate but possesses homogeneity with a rigid structure.

**Weight-Average Molecular Weight.** From the reported method[25] the weight-average molecular weight of **4** was measured to be $3.2 \times 10^5\ \mathrm{g \cdot mol^{-1}}$ by means of static light scattering experiments (see Supporting Information for the details), which is much larger than that of **3** ($\sim 3.4 \times 10^4\ \mathrm{g \cdot mol^{-1}}$). This result indicates that, in addition to the cross-linking within a bis(polypseudorotaxane), several bis(polypseudorotaxane) are also intermolecularly cross-linked together to form the bis(molecular tube). Through a simple calculation based on the molecular weight of **3**, **4**, 2-propanol residue, and DFB-PPG, we conclude that a bis(molecular tube) **4** is composed of ~10 bis(polypseudorotaxane) units. Moreover, the measured polydispersity of **4** (polydispersity index (PDI) = 1.86) by GPC is higher than that of **3** (PDI = 1.49)[25] indicating an increasing molecular weight distribution after cross-linking. A possible reaction mechanism might be as follows: First, in aqueous solution at a relative high concentration, the 2,4-dinitrophenyl terminal groups of adjacent bis(polypseudorotaxane)s **3** may partly overlapped due to the $\pi-\pi$ interactions to form a longer bis(polypseudorotaxane)s, like the assembly mode of $\beta$-cyclodextrin with diphenylhexatrienes to a nanotube in water.[18] Then, the bis(molecular tube) **4** was obtained through the cross-linking of adjacent $\beta$-cyclodextrin units in the longer bis(polypseudorotaxane) in a basic environment, followed by removal of DFB-PPG chains.

**Morphology.** Microscopy and XRD studies generated more information about the morphology of the bis(molecular tube). A comparison of SEM images reveals that the surface morphologies of **2**, **3**, and **4** are very different. As shown in Figure 2, **2** displays an irregular morphology, while **3** can be characterized as a sheetlike morphology. Interestingly, the image of **4** shows an ordered cylindrical morphology with a larger surface size than that of **3**. Such significant differences in surface morphologies may indicate that the arrangement mode of **3** becomes more ordered after the intra- and especially intermolecular linkage. This deduction can be verified by the XRD data (see Supporting Information). Although bis(polypseudorotaxane) **3** is somewhat amorphous, the XRD pattern of **4** shows several sharp reflections at $2\theta = 18.9°$ (4.7 Å), 27.3° (3.3 Å), 31.6° (2.8 Å), 45.4° (2.0 Å), 53.8° (1.7 Å), 56.4° (1.6 Å), 66.2° (1.4 Å), 72.9° (1.3 Å), and 75.2 (1.3 Å), indicating the crystalline nature of **4**. Moreover, the prominent strong peaks at $2\theta = 13.0°$ and 18.2° in the XRD pattern of **3**, which are characteristic of formation of the inclusion complexes between cyclodextrin channels and PPG chains,[27,28] almost disappear in the XRD pattern of **4**, reflecting the destruction of the bis(polypseudorotaxane) structure. These phenomena, together with SEM results, jointly indicate that bis(polypseudorotaxane) has been converted into a more regular structure, that is, an ordered bis(molecular tube).

TEM and STM were also performed to characterize the fine structure of **4**. TEM images give a rough insight into the size and shape of **4** as a linear assembly with the length of ~200 nm and the width of ~4 nm (Figure 3). From TEM images, we find that the length of **4** is nearly 10 times that of bis(polypseudorotaxane) **3** (~20 nm),[25] which further verifies our previous conclu-

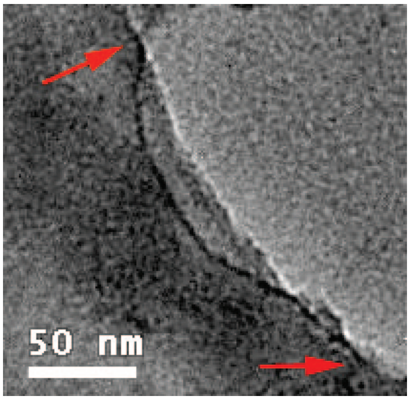

Figure 3. TEM image of **4**.

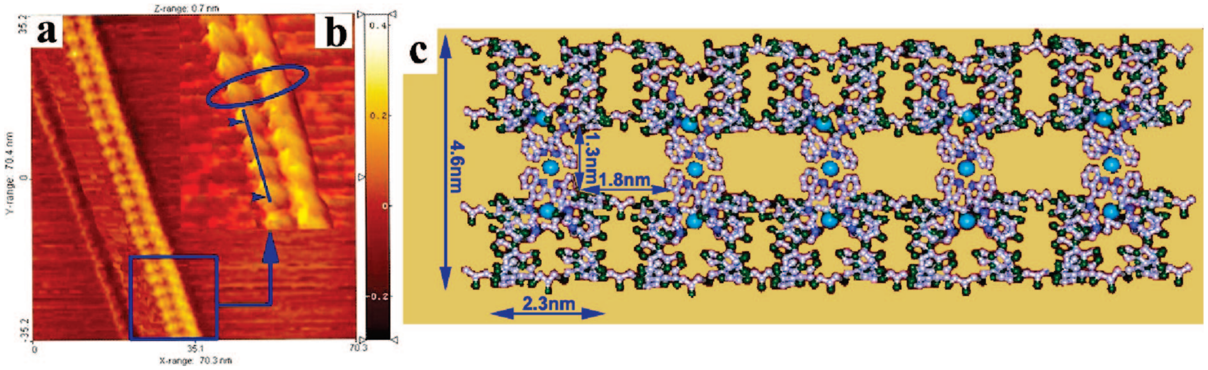

Figure 4. (a) STM image of **4** on the HOPG surface (sample bias voltage +300 mV, tunneling current 1.0 nA, and a Pt−Ir tip). (b) A sectional image in 3D mode. (c) The possible schematic structure of **4**.

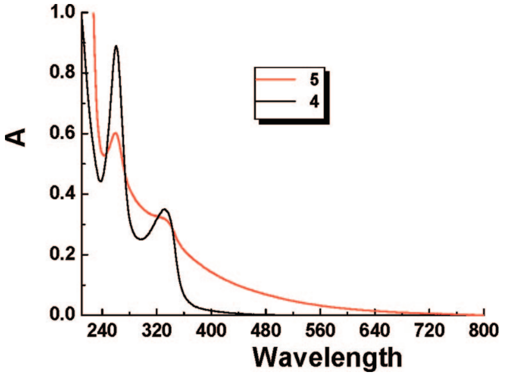

Figure 5. UV–vis spectra of **4** and **5** in a pH 7.2 Tris-HCl buffer solution at 25 °C. [**4**] = 0.6 mg/mL; [**5**] = 0.4 mg/mL.

sion that a bis(molecular tube) **4** is composed of ~10 bis(polypseudorotaxane) units.

Furthermore, a typical STM image of **4** on a graphite substrate (Figure 4a) clearly displays a double-lined structure with a total width of ~4.6 nm, which is basically consistent with the result from the TEM image. To visualize the detailed structure, a sectional picture in three-dimensional (3D) mode is also shown in Figure 2b. It is well-known that the external diameter and the height of the $\beta$-CD cavity are 1.54 and 0.79 nm, respectively.[29] Moreover, the length and width of the biquinolino linker are calculated to be ~1.30 and 0.67 nm, respectively, using a MM2 method. Through a simple calculation based on these data and a Corey−Pauling−Koltun (CPK) molecular model study, the length of a biquinolino-linked bis($\beta$-cyclodextrin) **1** is calculated as ~2.88 nm (2 × $\beta$-cyclodextrin's height + biquinolino's length), its width as ~2.21 nm ($\beta$-cyclodextrin's external diameter + biquinolino's width), and its height as 1.54 nm ($\beta$-cyclodextrin's external diameter). These data are in good agreement with the observed length (~2.9 nm), width (~2.3 nm) and height (~1.6 nm) of each bright dot in Figure 4b. Therefore, we can conclude that one bright dot corresponds to a bis($\beta$-cyclodextrin) unit, and thus two bright dots in transverse direction represent a metallobridged bis($\beta$-cyclodextrin) **2**. On the basis of these observations, we deduce a possible structure of **4** as shown in Figure 4c. According to a CPK molecular model study on this structure, the size of the hole between two adjacent metallobridged bis($\beta$-cyclodextrin) units is calculated to be ~1.3 × 1.8 nm, which is suitable to accommodate a $C_{60}$ (van der Waals diameter ~1.0 nm) or $C_{70}$ (van der Waals diameter ~1.0–1.2 nm) molecule.

**Capturing Fullerenes with the Bis(molecular tube).** With a high water solubility and a good preorganized structure, bis(molecular tube) may possess the capability of capturing fullerenes within the ordered holes formed by two adjacent metallobridged bis($\beta$-cyclodextrin) units through the interactions between multiple biquinolino groups and fullerenes and thus efficiently enhancing the solubility of fullerenes in water. This hypothesis is validated by the following experiments. An excess amount of $C_{60}$ was added to a toluene/DMF solution of **4**. After the reaction mixture was stirred for 3 days, the unreacted materials were removed and the $C_{60}$-contained bis(molecular tube) **5** was obtained in 16% yield, which shows a satisfactory water solubility up to 7 mg · mL$^{-1}$. The UV–vis spectrum of **5** in aqueous solution shows an obvious peak broadening in the wavelength range of 300–700 nm as compared with that of **4** (Figure 5). The typical vibration bands at 523 and 820 cm$^{-1}$ assigned to the $C_{60}$

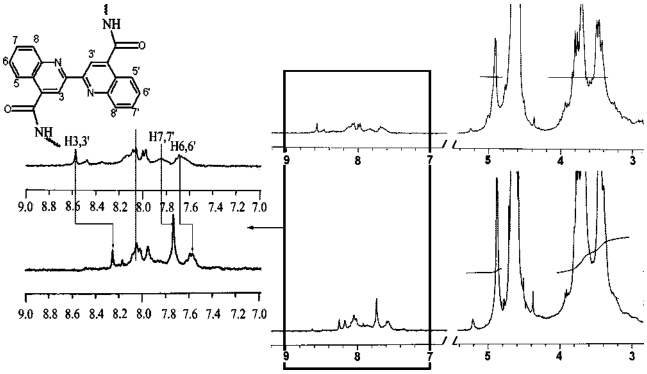

Figure 6. $^1$H NMR spectra of bis(molecular tube) **4** (top) and **5** (bottom) in $D_2O$ at 25 °C.

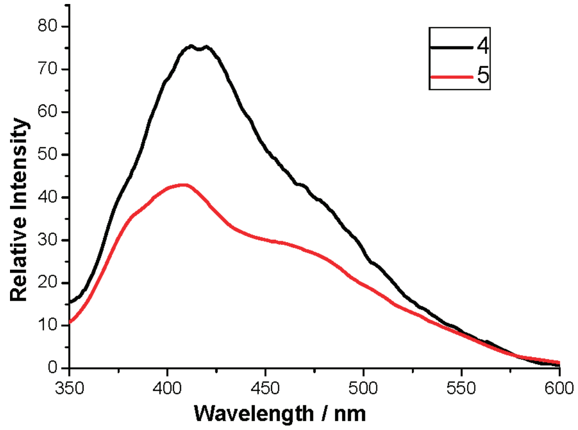

**Figure 7. Fluorescence spectra of 4 (black) and 5 (red) in aqueous solution ([4] = [5] = 3.0 × $10^{-2}$ mg/mL) in phosphate buffer solution (pH 7.20) at 25 °C, $\lambda_{ex}$ = 330 nm.**

unit are also observed in the FT-IR of **5**. The $^1$H NMR signals assigned to the 3,3′-, 7,7′-, and 6,6′-protons of biquinolino groups in **5** display appreciable upfield shifts ($\Delta\delta = 0.34$ ppm for 3,3′-protons, $\Delta\delta = 0.1$ ppm for 7,7′-protons, and $\Delta\delta = 0.11$ ppm for 6,6′-protons) as compared with the corresponding protons in **4** (Figure 6). Moreover, the fluorescence emission maximum of **4** shows a significant decrease after capturing $C_{60}$ (Figure 7), which may be attributed to interactions between the biquinolino group and $C_{60}$. The nature of bonding of $C_{60}$to **4** may be due to the $\pi-\pi$ interactions between the bisquinoline groups and $C_{60}$, like the cases of the noncovalent binding of electron-rich aromatic components such as porphyrins and calixarenes with $C_{60}$.[30−32] In addition, the electropositive central metal ion $Ni^{2+}$ may interact with the electron density of a 6:6 ring juncture of $C_{60}$ (*i.e.*, the "double" bond), like the metal–ligand bond in the complexation of metalloprophyrins to $C_{60}$.[33,34]

The thermogravimetric differential thermal analysis (TG−DTA) curve allowed us to determine the $C_{60}$ content of **5** (Figure 8). Considering the high thermal stability of $C_{60}$ (only decomposes over 850 °C), we deduce that the weight loss below 600 °C (91.8%) in the TG curve of **5** should be assigned to the decomposition of bis(molecular tube) **4**. On the other hand, there is a $T_p$ peak at 224 °C in the DTA curve. Moreover, the TG curve also displays an obvious inflection point around this temperature. Therefore, we deduce that the weight loss (11.6%) before 224 °C should be assigned to the loss of water from the bis(molecular tube) and the residue (8.2%) beyond 600 °C should be assigned to the $C_{60}$ and nickel oxide. In a control experiment, **4** only remained 3.2% of its weight beyond 600 °C (see Supporting Information).

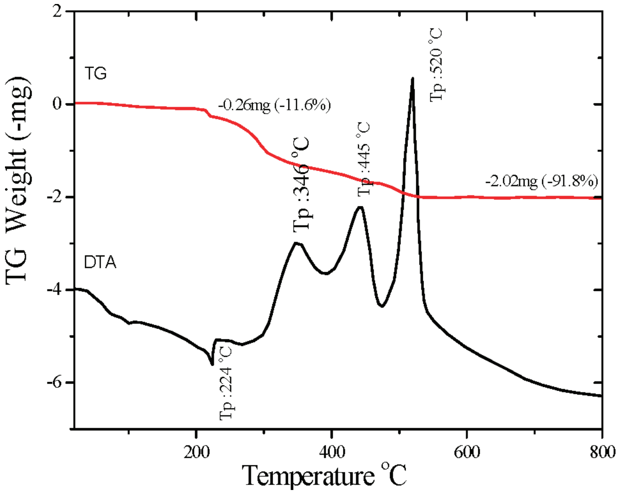

**Figure 8. TG−DTA curve of 5. The sample weight of 5 is 2.2 mg.**

The weight content of $C_{60}$ ($m_{C_{60}-\mathbf{5}}$ %) in **5** was determined from the TG result of **5** by using the simultaneous equations (eqs 1, 2, 3, and 4), where *m* denotes the weight content, and the subscript of *m* denotes the component in **5** or **4**. The $m_{NiO-\mathbf{4}}$ %, $m_{organic-\mathbf{5}}$ %, and $m_{organic-\mathbf{5}}$ % can be calculated from the structural formula of **5** and **4**.

$$m_{H_2O-\mathbf{5}}\% + m_{C_{60}-\mathbf{5}}\% + m_{organic-\mathbf{5}}\% + m_{NiO-\mathbf{5}}\% + m_{background}\% = 100\% \qquad (1)$$

$$m_{C_{60}-\mathbf{5}}\% + m_{NiO-\mathbf{5}}\% = 8.2\% - m_{background}\% \qquad (2)$$

$$m_{H_2O-\mathbf{5}}\% = 11.6\% \qquad (3)$$

$$m_{background}\% = 3.2\% - m_{NiO-\mathbf{4}}\% \qquad (4)$$

Through a simple calculation based on TG data, the weight contents of $C_{60}$ and NiO in **5** are found to be 5% and 3%, which are basically consistent with the corresponding values ($C_{60}$, 5.6%; NiO, 2.9%) calculated from the elemental analysis data. This result means 53% of the ordered holes formed by two adjacent metallobridged bis($\beta$-cyclodextrin) units in **5** associate with $C_{60}$.

## CONCLUSIONS

In summary, we successfully constructed a lengthened bis(molecular tube) through the intramolecular and intermolecular joining of the preorganized bis(polypseudorotaxane). The obtained bis(molecular tube) can efficiently capture fullerenes within the holes formed by adjacent metallobridged bis($\beta$-cyclodextrin) units. Possessing numerous fullerene centers and two free cyclodextrin-based molecular tubes that can selectively include various organic/inorganic/biological substrates, the fullerene-contained bis(molecular tube) may have potential applications in material and biological sciences. Endeavors to explore their applications are currently in progress.

## MATERIALS AND METHODS

**General Information.** $^1$H NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed on a Perkin-Elmer-2400C instrument. Thermogravimetric (TG) and differential thermal analysis (DTA) were recorded with a RIGAKU Standard type instrument. Samples were heated at 20 °C/min from room temperature to 700 °C (**4**) or to 800 °C (**5**) in a dynamic nitrogen atmosphere (flow rate $= 70$ mL/min). Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D/max 2500 diffractometer with Cu K$\alpha$ radiation (40 kV, 100 mA). SEM images were recorded on a HITACHI S-3500N scanning electron microscope. FT-IR spectra were recorded on a Shimadzu Bio-Rad FTS 135 instrument. UV spectra were performed on a Shimadzu UV-2401 spectrophotometer. Luminescence spectra in aqueous solution were measured in a conventional rectangular quartz cell ($10 \times 10 \times 45$ mm) at 25 °C on a JASCO FP-750 spectrometer equipped with a constant-temperature water bath. Deionized–distilled water was used as solvent in all spectral measurements.

STM experiments were performed by using a Nanosurf instrument (Switzerland) with a Pt$-$Ir tip and carried out with a sample bias voltage of $+300$ mV. All images were recorded in the constant-current mode. The samples were dissolved in water at a concentration of $1 \times 10^{-5}$ M, which was sufficiently diluted to enable observation of an isolated structure of the assemblies. A drop of sample was dripped onto the freshly cleaved highly ordered pyrolytic graphite (HOPG) substrate, followed by evaporating the liquid for at least 2 h in air.

The sample examined by a high-resolution transmission electron microscope (TEM) (Philips Tecnai G2 20 S-TWIN microscope) with 200 kV operating voltage was prepared by placing a drop of the aqueous solution of bis(molecular tube) in the concentration of $\sim 1 \times 10^{-6}$ M onto a carbon-coated copper grid.

The static light scattering experiments were performed on a Brookhaven Instruments BI-200SM goniometer and a BI9000AT correlator with vortially polarized light at $\lambda_0 = 514.5$ nm and an (Innova 304) Ar$^+$ ion laser. The experiment is performed at 25 °C in DMF by using toluene as the standard reference. The scattering angle is fixed at 90°.

GPC was performed by a Waters 515 HPLC pump and a Waters 2414 refractive index detector. DMF was used as an eluent at a flow rate of 1.0 mL/min at 50 °C. Polystyrene standards were used for the calibration.

**Materials.** Bis($\beta$-cyclodextrin) **1**, metallobridged bis($\beta$-cyclodextrin) **2**, and bis(polypseudorotaxane) **3** were synthesized according to the reported procedures.[25]

**Preparation of Bis(molecular tube) 4.** Bis(polypseudorotaxane) **3** (35 mg) and epichlorohydrin (6 mg) were added to a 10% aqueous NaOH solution (5 mL), and the mixture was stirred for 36 h at room temperature. The resulting mixture was neutralized with 20% $HNO_3$ to give a light yellow precipitate. After collection by filtration, the precipitate was dissolved in DMF, and poured into a large amount of acetone. The precipitate obtained was collected by centrifugation, washed thoroughly with acetone, purified by column chromatography on Sephadex G-25 with deionized–distilled water as eluant, and dried in vacuo to give **4** (13.8 mg) as a light gray solid. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): $\delta$ 3.19–3.64 (broad, 248H $\times$ $n$; $C_{2-6}$ H of $\beta$-CD, $CH_2$ of ethylene group and CH, $CH_2$ of 2-propanol residues, N$-$H), $\delta$ 4.51–4.72 (s, 24H $\times$ $n$; O-6H of $\beta$-CD, and O$-$H of 2-propanol residues), $\delta$ 4.84 (s, 28H $\times$ $n$; C-1 H of $\beta$-CD), $\delta$ 5.63–5.90(m, 44H $\times$ $n$; O-2,3 H of $\beta$-CD), $\delta$ 7.6–9.2 (broad, 24H $\times$ $n$; biquinolino-H and amide-H). IR (KBr, cm$^{-1}$): $\nu$ 3346, 2929, 1650, 1599, 1425, 1364, 1208, 1155, 1078, 1032, 945, 847, 758, 706, 581, 530, 450. Anal. Calcd (%) for $[C_{240}H_{352}O_{166}N_{18}Ni_3 \cdot 66H_2O]_n$: C, 38.38; H, 6.50; N, 3.36. Found: C, 38.62; H, 6.50; N, 3.21.

**$C_{60}$ Capturing.** Bis(molecular tube) **4** (25.0 mg) was dissolved in a mixture of toluene and DMF (v/v $=$ 4:6, 150 mL), and $C_{60}$ (6.0 mg) in 25 mL of toluene was added to the solution. The resulting mixture was stirred for 1 day at room temperature, during which the light yellow homogeneous solution turned deep brown. Then, 8.0 mg of $C_{60}$ was added in three portions, and the mixture was stirred for another 2 days. After the solvent was removed under vacuum, the residue was dissolved in a minimum amount of water. The unreacted $C_{60}$ was removed by centrifugation, and the water phase was poured into acetone. The precipitate obtained was washed with acetone, purified by column chromatography on Sephadex G-25 with deionized–distilled water as eluant, and dried in vacuo to give **5** (5.1 mg) as a dark brown solid. $^1$H NMR (300 MHz, $D_2O$, ppm): $\delta$ 3.00–4.02 (broad, 244H $\times$ $n$; $C_{2-6}$H of $\beta$-CD, $CH_2$ of ethylene group, and CH, $CH_2$ of 2-propanol residues), $\delta$ 4.87(s, 28H $\times$ $n$; C-1 H of $\beta$-CD), $\delta$ 7.52–8.12 (broad, 20H $\times$ $n$; biquinolino-H). IR (KBr, cm$^{-1}$): $\nu$ 3343, 2921, 2250, 2124, 1651, 1559, 1456, 1364, 1261, 1153, 1031, 820, 765, 666, 523, 486. Anal. Calcd (%) for $[C_{240}H_{352}O_{166}N_{18}Ni_3 \cdot 49H_2O \cdot 0.53C_{60}]_n$: C, 43.03; H, 5.98; N 3.32. Found: C, 43.41; H, 6.10; N, 3.30.

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*Supporting Information Available:* The details of static light scattering experiments of **4**, concentration-dependent UV spectra of **4**, XRD spectra of **3**, **4**, and TG-DTA curves of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

## REFERENCES AND NOTES

1. Ghadiri, M. R.; Granja, J. R.; Buehler, L. K. Artificial Transmembrane Ion Channels from Self-Assembling Peptide Nanotubes. *Nature* **1994**, *369*, 301–304.
2. Nostrum, C. F. S.; Pichen, J.; Schouten, A.-J.; Nolte, R. J. M. Synthesis and Supramolecular Chemistry of Novel Liquid Crystalline Crown Ether-Substituted Phthalocyanines: Toward Molecular Wires and Molecular Ionoelectronics. *J. Am. Chem. Soc.* **1995**, *117*, 9957–9965.
3. Matsui, H.; Holtman, C. Organic Nanotube Bridge Fabrication by Controlling Molecular Self-Assembly Processes between Spherical and Tubular Formations. *Nano Lett.* **2002**, *2*, 887–889.
4. Shenton, W.; Douglas, T.; Young, M.; Stubbs, G.; Mann, S. Inorganic-Organic Nanotube Composites from Template Mineralization of Tobacco Mosaic Virus. *Adv. Mater.* **1999**, *11*, 253–256.
5. Kohli, P.; Harrell, C. C.; Cao, Z.-H.; Gasparac, R.; Tan, W.-H.; Martin, C. R. DNA-Functionalized Nanotube Membranes with Single-Base Mismatch Selectivity. *Science* **2004**, *305*, 984–989.
6. Mitchell, D. T.; Trofin, L.; Nevanen, T. K.; Soderlund, H.; Martin, C. R. Antibody-Based Bio-Nanotube Membranes for Enantiomeric Drug Separations. *Science* **2002**, *296*, 2198–2200.
7. Shimizu, T.; Masuda, M.; Minamikawa, H. Supramolecular Nanotube Architectures Based on Amphiphilic Molecules. *Chem. Rev.* **2005**, *105*, 1401–1444.
8. Aleshin, A. N. Polymer Nanofibers and Nanotubes: Charge Transport and Device Applications. *Adv. Mater.* **2006**, *18*, 17–27.
9. Gao, X.-Y.; Matsui, H. Peptide-Based Nanotubes and Their Applications in Bionanotechnology. *Adv. Mater.* **2005**, *17*, 2037–2050.
10. Kameta, N.; Masuda, M.; Minamikawa, H.; Goutev, N. V.; Rim, J. A.; Jung, J. H.; Shimizu, T. Selective Construction of Supramolecular Nanotube Hosts with Cationic Inner Surfaces. *Adv. Mater.* **2005**, *17*, 2732–2736.
11. Vauthey, S.; Santoso, S.; Gong, H.; Watson, N.; Zhang, S.-G. Molecular Self-Assembly of Surfactant-Like Peptides to Form Nanotubes and Nanovesicles. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5355–5360.
12. Kim, S.-Y.; Lee, J.-W.; Jung, J.-H.; Kang, J.-K. Hydrogen Storage Property on Nickel-Atom-Dispersed Organosilica Nanotubes. *Chem. Mater.* **2007**, *19*, 135–137.
13. Fenniri, H.; Deng, B.-L.; Ribbe, A. E.; Hallenga, K. ; Jacob, J.; Thiyagarajan, P. Entropically Driven Self-Assembly of Multichannel Rosette Nanotubes. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 6487–6492.

14. Couet, J; Biesalski, M. Conjugating Self-Assembling Rigid Rings to Flexible Polymer Coils for the Design of Organic Nanotubes. *Soft Matter* **2006**, *2*, 1005–1014.
15. Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. Self-Assembling Organic Nanotubes. *Angew. Chem., Int. Ed.* **2001**, *40*, 988–1011.
16. Pantos, G. D.; Pengo, P.; Sanders, J. K. M. Hydrogen-Bonded Helical Organic Nanotubes. *Angew. Chem., Int. Ed.* **2007**, *46*, 194–197.
17. Dalgarno, S. J.; Cave, G. W. V.; Atwood, J. L. Toward the Isolation of Functional Organic Nanotubes. *Angew. Chem., Int. Ed.* **2006**, *45*, 570–574.
18. Li, G.; McGown, L. B. Molecular Nanotube Aggregates of $\beta$- and $\gamma$-Cyclodextrins Linked by Diphenylhexatrienes. *Science* **1994**, *264*, 249–251.
19. Liu, Y.; Chen, G.-S.; Yong, C.; Zhang, N.; Chen, J.; Zhao, Y.-L. Bundle-Shaped Cyclodextrin-Tb Nano-Supramolecular Assembly Mediated by C60: Intramolecular Energy Transfer. *Nano Lett.* **2006**, *6*, 2196–2200.
20. Harada, A.; Li, J.; Kamachi, M. The Molecular Necklace: A Rotaxane Containing Many Threaded $\alpha$-Cyclodextrins. *Nature* **1992**, *356*, 325–327.
21. Harada, A.; Li, J.; Kamachi, M. Synthesis of a Tubular Polymer from Threaded Cyclodextrins. *Nature* **1993**, *364*, 516–518.
22. Ikeda, T.; Hirota, E.; Ooya, T.; Yui, N. Thermodynamic Analysis of Inclusion Complexation between $\alpha$-Cyclodextrin-Based Molecular Tube and Sodium Alkyl Sulfonate. *Langmuir* **2001**, *17*, 234–238.
23. Okumura, Y.; Ito, K.; Hayakawa, R.; Nishi, T. Self-Assembling Dendritic Supramolecule of Molecular Nanotubes and Starpolymers. *Langmuir* **2000**, *16*, 10278–10280.
24. Liu, Y.; You, C.-C.; Zhang, H.-Y.; Kang, S.-Z.; Zhu, C.-F.; Wang, C. Bis(molecular tube)s: Supramolecular Assembly of Complexes of Organoselenium-Bridged $\beta$-Cyclodextrins with Platinum(IV). *Nano Lett.* **2001**, *1*, 613–616.
25. Liu, Y.; Song, Y.; Wang, H.; Zhang, H.-Y.; Li, X.-Q. Bis(polypseudorotaxane)s Formed by Multiple Metallo-Bridged $\beta$-cyclodextrins and the Thermodynamic Origin of Their Molecular Aggregation. *Macromolecules* **2004**, *37*, 6370–6375.
26. Sugiura, I.; Komiyama, M.; Toshima, N.; Hirai, H. Immobilized $\beta$-cyclodextrins. Preparation with Various Crosslinking Reagents and the Guest Binding Properities. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1643–1651.
27. Huang, L.; Tonelli, A. E. Polymer Inclusion Compounds. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1998**, *C38*, 781–837.
28. Liu, Y.; Li, L.; Zhang, H.-Y.; Zhao, Y.-L;.; Wu, X. (pseudopolyrotaxane)s Possessing Copper(II) Ions Formed by Different Polymer Chains and Bis($\beta$-cyclodextrin)s Bridge with a 2,2′-Bipyridine-4,4′-dicarboxy Tether. *Macromolecules* **2002**, *35*, 9934–9938.
29. Saenger, W.; Jacob, J.; Gessler, K.; Steiner, T.; Hoffmann, D.; Sanbe, H.; Koizumi, K.; Smith, S. M.; Takaha, T. Structures of the Common Cyclodextrins and Their Larger Analogues−Beyond the Doughnut. *Chem. Rev.* **1998**, *98*, 1787–1802.
30. Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Boyd, P. D. W. Supramolecular Fullerene-Porphyrin Chemistry. Fullerene Complexation by Metalated "Jaws Porphyrin" Hosts. *J. Am. Chem. Soc.* **2002**, *124*, 6604–6612.
31. Boyd, P. D. W.; Reed, C. A. Fullerene-Porphyrin Constructs. *Acc. Chem. Res.* **2005**, *38*, 235–242.
32. Haino, T.; Matsumoto, Y.; Fukazawa, Y. Supramolecular Nano Networks Formed by Molecular-Recognition-Directed Self-Assembly of Ditopic Calix[5]arene and Dumbbell [60]Fullerene. *J. Am. Chem. Soc.* **2005**, *127*, 8936–8937.
33. Yamaguchi, T.; Ishii, N.; Tashiro, K.; Aida, T. Supramolecular Peapods Composed of a Metalloporphyrin Nanotube and Fullerenes. *J. Am. Chem. Soc.* **2003**, *125*, 13934–13935.
34. Tashiro, K.; Aida, T. Metalloporphyrin Hosts for Supramolecular Chemistry of Fullerenes. *Chem. Soc. Res.* **2007**, *36*, 189–197.