Polymeric Coordination Rotaxane

Polymeric Rotaxane Constructed from the Inclusion Complex of β-Cyclodextrin and 4,4′-Dipyridine by Coordination with Nickel(II) Ions**

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Nanometer-sized supramolecular assemblies created by the simple inclusion complexation of host cyclodextrins (CDs) and guest molecules have attracted more and more attention in recent years because of their potential to serve as molecular devices and molecular machines, as well as functional materials.[1–4] Indeed, CDs can be threaded on a polymer chain to form a polyrotaxane and extended to molecular tubes through the cross-linking of adjacent CD units in a polyrotaxane.[5] Furthermore, β- and γ-cyclodextrins can also be constructed into nanometer-sized molecular tubes linked by diphenylhexatrienes,[6] and conjugated polyrotaxanes can be used as building blocks to form insulated molecular wires on which α- or β-CDs are threaded.[7] We recently showed that the resulting complex formed from an organoselenium-bridged β-CD dimer and a platinum ion could be fabricated into bis(molecular tube)s through formation of a pesudorotaxane with poly(propylene glycol), and the bridged bis(β-cyclodextrin)s and calix[4]arene derivatives could also form nanometer-sized linear aggregations by simple host–guest inclusion complexation.[8–10] Molecular semiconductors can also be exploited for organic electronics and single molecules can be manipulated and incorporated into nano-engineered devices at a supramolecular level by threading a charge-transport macromolecule.[11–15] However, higher order polymeric rotaxanes fabricated by metal-ion binding to the inclusion complexes formed between CDs and aromatic molecules have not been investigated so far. Dipyridine–metal complexes have very interesting photochemical and other properties, and therefore many studies have been devoted to this topic.[16] Herein we report our investigations on two uncommon supramolecular aggregations: assembly **1**, formed from the reaction of β-CD with 4,4′-dipyridine (DPD), and polymeric rotaxane **2**, which was synthesized by coordination of **1** with Ni^{II} ions. The binding behavior of **1** and **2** was examined, both in solution and in the solid state, by ^1H NMR

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spectroscopy, X-ray crystallography, induced circular dichroism, powder X-ray diffraction studies, thermogravimetric (TG) and differential thermal analysis (DTA), scanning tunneling microscopy (STM), and transmission electron microscopy (TEM). The binding behavior of the supramolecular assembly formed by the molecular recognition of the host and guest in solution and in the solid state is of particular interest, since the inclusion complex and the polymeric rotaxane display different photophysical behavior. The present investigations have revealed that the resulting complex of CDs with guest molecules is the first step in the formation of a polymeric rotaxane, which provides access to coordination polymeric supramolecules with CDs, and will serve to further our understanding of this developing, but less investigated, area of electroactive organic materials that contain CDs and a coordination linkage.

The polymeric rotaxane **2** was prepared according to the procedures shown in Figure 1. The 1:1 **1**:Ni^{II} coordination in **2** was confirmed by the results of elemental analyses and UV/Vis titration experiments. Direct evidence for the formation of the supramolecular assembly **1** from β-CD and DPD was

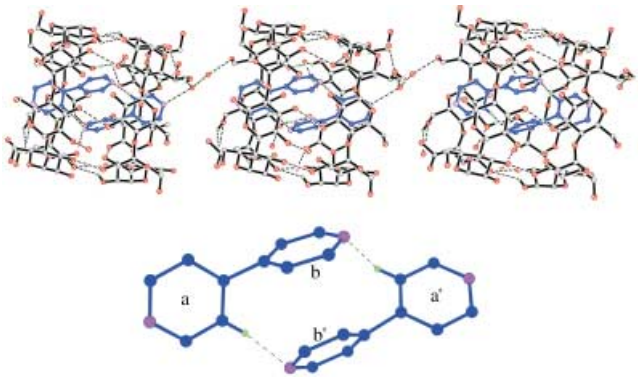

Figure 2. X-ray crystal structure showing the head-to-head channel structure of **1** (top) and the DPD backbones (bottom). The dihedral angles between the plane of the DPD molecular axis and the heptagons composed of seven O atoms of the β-CD are 71.1° and 63.3°, respectively. The DPD molecules are colored by atom type: blue: carbon atoms, pink: nitrogen atoms, and blue: chemical bonds. The CD dimers are also colored by atom type: gray: carbon atoms, red: oxygen atoms, and green: hydrogen atoms involved in hydrogen-bonding interactions.

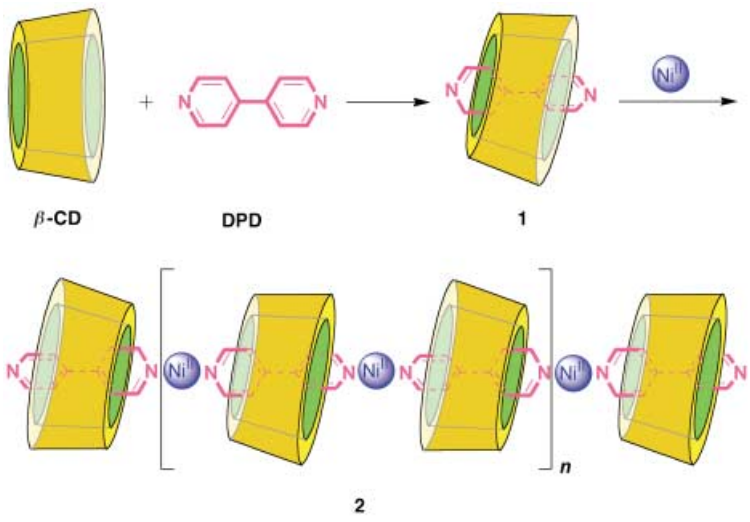

Figure 1. Schematic representation of the formation of **1** and **2**.

obtained in the solid state.[17] As shown in Figure 2, two DPD molecules are embedded into two β-CD cavities in different directions to form a head-to-head dimer arrangement (space group $P\bar{1}$), which is entirely different from the general inclusion complexes formed with β-CD in the solid state.[18] The aromatic ring *a* (or *a*′) of every DPD molecule in the self-assembled dimers is deeply included in a β-CD cavity and another aromatic ring *b* (or *b*′) is only shallowly embedded into the cavity, with a dihedral angel of 94.5° (or 75.6°) between rings *a* (or *a*′) and *b* (or *b*′). This unique assembly behavior is attributed to the cooperative interactions of 13 hydrogen bonds (11 of them come from the hydroxy groups on the secondary sides of the β-CDs and two of them involve a nitrogen atom in the *b* (and *b*′) ring and a *meta*-hydrogen atom in the *a*′ (and *a*) ring) and π-π stacking of two aromatic rings in a face-to-face arrangement (dihedral angel: 42.2°, centroid separation between *b* and *b*′: 3.634 Å) which fix the orientation of the DPD molecules and makes dimer aggregation possible. Interestingly, the head-to-head dimers can further self-assemble to form polymeric supramolecules through formation of hydrogen bonds between dimers using the nitrogen atom in the *a*′ ring.

The binding behavior of **1** and **2** in solution was examined by ^{1}H NMR spectroscopy carried out at 25 °C in D_2O. A change in the chemical shift of all the protons of the DPD molecule is observed in the presence of β-CD relative to a free molecule: the *meta* protons shift upfield (ca. 0.02 ppm) and the *ortho* protons shift downfield (ca. 0.09 ppm), which indicates that a complex has formed between DPD and β-CD. Relative to complex **1**, the *meta* protons in **2** were deshielded by about 0.09 ppm and the *ortho* protons were shielded by about 0.02 ppm in the presence of Ni^{II} ions, thus suggesting that the nitrogen atoms must coordinate to the Ni^{II} ions.[19] The IR spectra of **1** and **2** showed that the C=N stretching vibration in DPD is shifted from 1595 to 1608 cm^{-1}, which could also be ascribed to the coordination of $NiCl_2$.

The induced circular dichroism (ICD) spectra[20] of **1** and **2** were also measured. As can be seen from Figure 3, the circular dichroism spectrum of **1** showed a strong positive Cotton effect, which corresponds to the ^1L_a band at 241 nm ($\Delta\varepsilon = 0.70\ dm^{-3}mol^{-1}cm^{-1}$) and a negative Cotton effect for the ^1L_b band at 269 nm ($\Delta\varepsilon = -0.23\ dm^{-3}mol^{-1}cm^{-1}$). According to the pioneering studies of Kajtár et al.[21] and Harata and Uedaira[22] on the ICD phenomena of cyclodextrin complexes, we can deduce that the DPD moiety of **1** has entered into the β-CD cavity with a slightly acclivitous orientation, which is consistent with that seen in the crystal structure of **1**. Interestingly, the DPD molecule in the β-CD cavity tethered by a Ni^{II} ion gives an opposite ICD signal: a major negative Cotton effect at 232 nm ($\Delta\varepsilon =$

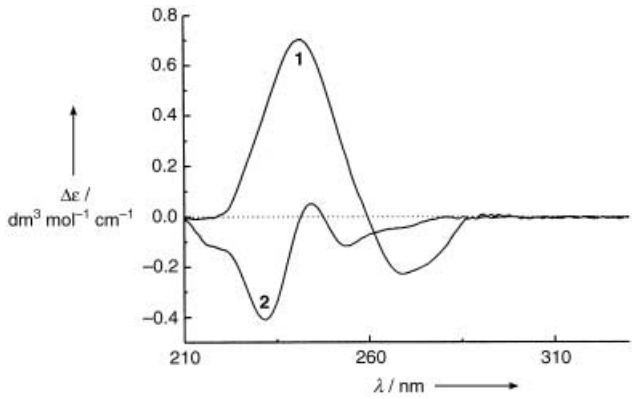

Figure 3. Circular dichroism spectra of **1** (7.9×10^{-5} mol dm^{-3}) and **2** (5.9×10^{-5} mol dm^{-3}) in aqueous solution at 25 °C.

-0.41 dm^{-3}mol^{-1}cm^{-1}) and a moderate negative Cotton effect at 254 nm ($\Delta\varepsilon = -0.12$ dm^{-3}mol^{-1}cm^{-1}) is observed. The opposite ICD signals observed between **1** and **2** indicate that not only do the DPD molecules still lie in the cavity of β-CDs after the formation of **2**, but also that the DPD moiety of **2** may become more acclivitous in the cavity of β-CDs after coordination of Ni^{II} ions.

The powder X-ray diffraction patterns[8,23] of β-CD, DPD, **1**, and **2** were obtained using a Rigaku D/max-2500 diffractometer with CuKα radiation. The diffractogram of β-CDs shows a characteristic reflection at $2\theta = 12.4°$($d = 7.13$ Å) and that of DPD shows a characteristic reflection at $2\theta = 12.5°$($d = 7.06$ Å; see Supporting Information). However, these reflections are changed to $2\theta = 11.8°$ ($d = 7.49$ Å) and $2\theta = 12.1°$ ($d = 7.30$ Å) in the diffractogram of complex **1,** thus indicating that the arrangement of the cyclodextrin in **1** is changed by introduction of DPD. This result is consistent with the arrangement found in the crystal structure. Interestingly, the same characteristic reflection at $2\theta = 12.4°$ ($d = 7.11$ Å) appears again in the diffractogram of **2**, which shows that the coordination of Ni^{II} ions makes the cyclodextrin and DPD reorient upon construction of the polymeric rotaxane **2**.

The thermal stabilities of **1** and **2** were measured by TG and DTA. The TG results showed that the decomposition point of polymeric rotaxane **2** is higher than that of complex **1**. The decomposing temperatures of **1** and **2** are about 244 and 253 °C, respectively, which may be ascribed to the dissociation of β-CD and DPD. The DTA analyses showed an endothermic peak at about 333 °C for **1** and an exothermic peak at about 355 °C for **2**, which represent the temperatures of decomposition of the β-CD. Therefore, these higher thermal dissociation temperatures clearly indicated that the coordination of Ni^{II} ions played a stabilizing role in the molecular aggregation of **2**.

Scanning tunneling microscopy (STM) has become a convenient and widely employed method for the elucidation of the microstructures of supramolecular aggregates.[6,9,10,24,25] The STM image of **2** (Figure 4)[26] shows a regular arrangement of chains of supramolecules on a graphite substrate, which indicates that the polymeric rotaxanes are formed through the coordination of β-CD–DPD complexes with Ni^{II} ions. From the size and shape of the patterns, one bright

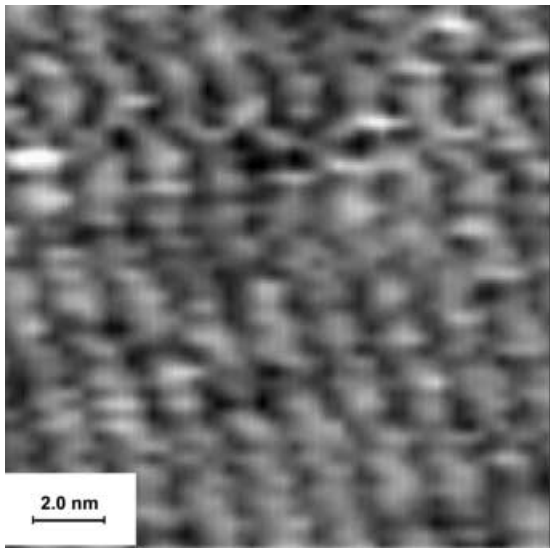

Figure 4. STM image of polymeric rotaxane **2**.

dot corresponds to a β-CD unit, which lies with its longitudinal axis parallel to the surface. The average distance between two adjacent cyclodextrin units in a polymeric rotaxane is about 0.9 nm, while the distance between two adjacent polymeric rotaxanes is roughly 1.9 nm, which results in noticeable topologies.

Transmission electron microscopy (TEM) has also been performed to provide further insight into the size and shape of the aggregates on drying. For visualization by TEM, a sample was prepared by placing one drop of the solution of the polymeric rotaxane **2** onto a carbon-coated copper grid, and then a palladium–iridium alloy was added to thicken the drop and make the images clearer. Thus, the TEM micrographs have only been used to measure the length of the molecular assembly. The detailed TEM micrograph shown in Figure 5 illustrates one of the polymeric rotaxanes **2** with a length of approximately 450 nm.

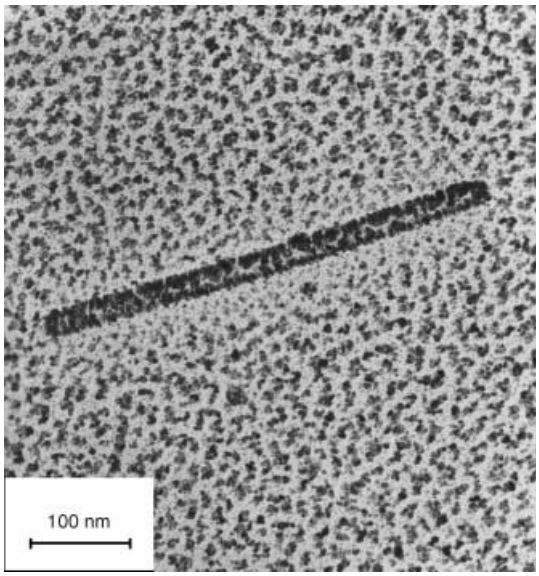

Figure 5. TEM image of polymeric rotaxane **2**.

In summary, two novel polymeric supramolecules have been synthesized by the inclusion complexation of DPD in β-CD and the subsequent coordination of the complex with nickel ions in aqueous solution. The results obtained further suggested that β-CDs could provide a simple means for linking organic molecules into linear-shaped aggregates, which could be used as connectors for designing novel functional materials and which could possess the potential to serve as molecular devices and molecular machines. Endeavors to explore the application of chain supramolecules are currently in progress.

Experimental Section

1: A mixture of β-cyclodextrin (1 mmol) and 4,4′-dipyridine (DPD, 1 mmol) was allowed to react in aqueous solution (60 mL) with stirring at 30 °C for 5 h. The precipitate formed was filtrated to give a white powder. The crude product was then dissolved in hot water to make a saturated solution, which was cooled to room temperature. After removing the precipitates by filtration, a small amount of water was added to the filtrate. The resultant solution was kept at room temperature for a week. The colorless crystal of **1** that formed was collected along with its mother liquor for X-ray crystallographic analysis; yield 78 %. FTIR (KBr): $\tilde{\nu}$ = 3341, 2929, 1595, 1534, 1414, 1365, 1332, 1299, 1241, 1155, 1080, 1032, 944, 851, 805, 756, 611, 578, 528 cm^{-1}; ^1H NMR (300 MHz, D_2O, tetramethylsilane (TMS)): δ = 3.37–3.69 (m, 42H), 4.88–4.90 (d, 7H), 7.53–7.55 (d, 4H), 8.52–8.54 ppm (d, 4H); elemental analysis calcd for $C_{52}H_{78}O_{35}N_2 \cdot 7H_2O$: C 44.07, H 6.54; N 1.98 %; found: C 43.73, H 6.04, N 2.37 %.

2: An aqueous solution (10 mL) of nickel chloride ($NiCl_2 \cdot 6H_2O$, 0.1 mmol) was added dropwise to an aqueous solution (20 mL) of **1** (0.1 mmol). The resultant mixture was then stirred at 40 °C for 7 h. The solvent was evaporated under a reduced pressure, and the precipitate formed was filtered off to give a green powder. The crude product was recrystallized and purified from water and dried in vacuo to give sample **2**; yield 35 %. FTIR (KBr): $\tilde{\nu}$ = 3358, 2930, 1608, 1535, 1491, 1415, 1332, 1221, 1156, 1079, 1031, 945, 855, 809, 756, 707, 577, 531 cm^{-1}; ^1H NMR (300 MHz, D_2O, TMS): δ = 3.39–3.81 (m, 42H), 4.90–4.91 (d, 7H), 7.62–7.64 (d, 4H), 8.50–8.52 ppm (d, 4H); elemental analysis calcd for $(C_{52}H_{78}O_{35}N_2NiCl_2 \cdot 10H_2O)_n$: C 39.01, H 6.17, N 1.75 %; found: C 39.27, H 6.00, N 1.51 %.

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[17] The X-ray intensity data of **1** were collected on a standard Siemens SMART CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monchromator at T = 298 K. Crystal data for **1**: $C_{104}H_{194}N_4O_{89}$: M_r = 2924.63 (including water molecules); dimensions = 0.36 × 0.34 × 0.30 mm; triclinic; space group: $P\bar{1}$; unit cell dimensions: a = 15.364(3), b = 15.497(3), c = 18.115(3) Å, V = 3705.0(11) $Å^3$; Z = 1; ρ_{calcd} = 1.311 $g\,cm^{-3}$; data/restraints/parameters 15431/39/1649. Final R indices $R1$ = 0.0907, $wR2$ = 0.2432. The structures were solved by using direct methods and refined by employing full-matrix least squares on F^2 (Siemens, SHELXTL, version 5.04). CCDC-203243 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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[26] STM experiments were performed by using a DS-89S instrument with a W tip, and were carried out with a sample bias voltage of +300 mV. All images were recorded in the constant-current mode at 2.10 nA. An aqueous solution of sample **2** was prepared at a concentration of 5.5×10^{-5} M and dripped onto a freshly prepared highly ordered pyrolytic graphite surface at room temperature. The sample was then dried in a vacuum for 30 minutes.

