Polyrotaxane with Cyclodextrins as Stoppers and Its Assembly Behavior

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Introduction

In recent years, nanometer-scaled supramolecular assemblies constructed by the simple inclusion complexation of cyclodextrins (CDs) with organic molecules represent a very active topic of science and technology due to their potential to serve as molecular devices, molecular machines, and functional materials.[1−5] Among them, CD-based polyrotaxanes (PRs) as new polymeric materials have attracted more and more attention. Harada et al. prepared tens of CD-based PRs by threading many CD units onto a polymer chain and then capping the resultant polypseudorotaxane (PPRs) using naphthyl, dinitrobenzoyl, dinitrophenyl, trinitrophenyl, anthryl, and trityl groups as stoppers.[6] Stoddart et al. also prepared some CD-threaded PRs and reviewed a number of CD-containing PRs using various organic molecules as stoppers, which exhibited significant chemical and biological functions.[1,7] However, using these organic molecules as stoppers also brings some disadvantages. For example, the introduction of these bulk hydrophobic molecules not only obviously decreases the water solubility of resultant PRs but also prevents the further assembly of PRs to larger aggregates. Recently, we successfully prepared some nanometer-scaled suparmolecular assembles possessing metal centers through the intermolecular coordination or inclusion complexation.[8] On the basis of preliminary work, we wish to report herein a convenient and efficient method for the termination of PRs using CDs as stoppers. Possessing two free CD cavities at the terminals, the resultant CD-capped PRs can be further assembled to larger aggregates by the 2:1 inclusion complexation between these free CD cavities and a wide variety of hydrophobic guests/substrates including C_{60}.[9] In addition, the employment of CDs as stoppers also enables a satisfactory water solubility of PR. Therefore, this approach may open a new direction in the design and preparation of functional materials, especially PRs at the nanometer scale.

Experimental Section

Syntheses. As shown in Scheme 1, PPR **1** was prepared by reacting β-CD and poly(propylene glycol)bis(2-aminopropyl ether) (PPG-NH_2, MW $\approx$ 2000) according to a reported method.[10] 6-Deoxy-6-formyl-β-CD was synthesized according to literature procedure.[11] PPR **1** (300 mg) and 6-deoxy-6-formyl-β-CD (60 mg) were dissolved in dry DMF (20 mL). The resultant mixture was refluxed for 7 h under stirring and then poured into acetone (200 mL). The precipitate was dissolved in a minimum amount of hot water and then poured into 150 mL acetone. The precipitate formed was collected by filtration to obtain a light yellow powder, which was washed with a small amount of cold water to give PR **2** as a light yellow powder in 50% yield. Then, PR **2** (200 mg) was dissolved in water and C_{60} (22 mg) was added under stirring at 30 °C. The resultant mixture was stirred for 24 h, and the solution became brown. The unreacted C_{60} was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure to give aggregate **3** in 78% yield as a dark brown powder.

Microscopy Measurements. Scanning tunneling microscopy (STM) experiments were performed by using a Nanosurf instrument (Switzerland) with a Pt−Ir tip and were carried out with a sample bias voltage of +300 mV. All images were recorded in the constant-current mode. An aqueous solution of sample **3** were prepared at a diluted concentration of 5×10^{-6} M and dripped onto a freshly prepared highly ordered pyrolytic graphite surface at room temperature. The sample was then dried in a vacuum for 2 h. All measurements were performed in air at room temperature. The transmission electron microscope (TEM) micrographs were obtained in a top-entry Philips EM300 microscope, operated at an accelerating voltage of 80 keV.

Results and Discussion

Characterization of PPR 1 and PR 2. A ^{1}H NMR spectrum of **1** shows that the integral area ratio between PPG-NH_2's methyl protons (a molecule of PPG-NH_2 2000 contains ca. 102 methyl protons, $\delta = 1.03-1.05$ ppm) and CD's C_1−H protons (a molecule of CD contains 7 C_1−H protons, $\delta = 4.83$ ppm) is 8.1:7.0. In the case of **2**, this ratio decreases to 6.8:7.0. According to these ^{1}H NMR data, we can calculate that there are ca. 13 CD units in **1** and ca. 15 CD units in **2**. Moreover, the signals assigned to the protons ($-C\mathbf{H}{=}N-$, $\delta = 7.95$ ppm) and carbons ($-\mathbf{C}H{=}N-$, $\delta = 163$ ppm) of imine groups in **2** are also observed in the NMR spectra of **2**. These results clearly indicate that two CD cavities are successfully introduced at the amino terminals of PPR **1**. The water solubility of **2** is assessed by the preparation of its saturated solution. An excess amount of **2** is put into 2 mL of water, and the mixture is stirred for 1 h. After removing the insoluble substance by filtration, the filtrate is evaporated under reduced pressure to dryness, and the residue is dosed by a weighing method. The results show that the water solubility of **2** is 15.5 mg/mL, which is similar to that of natural β-CD (18 mg/mL). In the control experiment, a clear solution is obtained by dissolving 15.5 mg of **2** in 1 mL of water.

After obtaining the desired PR **2**, we further examine its application potential in the construction of larger aggregates. A reaction of **2** with C_{60} in an aqueous solution gives aggregate **3** in 78% yield as a dark brown powder, which has a moderate water solubility up to 1 mg/mL at 25 °C and can remain stable for several weeks when stored in a refrigerator (4 °C). Besides the obvious color change, the appearance of two absorption maxima at 339 and 283 nm in the UV/vis spectrum of **3** as well as the typical FT-IR bands at 527 and 810 cm^{-1} assigned to the C_{60} units in **3** verify an effective association of **2** with C_{60}. Moreover, the solid-state CPMAS/DD ^{13}C NMR of **3** displays two characteristic signals at 141.2 and 127.1 ppm assigned to the C_{60} groups, which also confirms the presence of C_{60} in **3**.

STM and TEM. STM and TEM experiments give direct evidence for the formation of **3**. The STM image of **3** (Figure 3) shows a linear array composed of several

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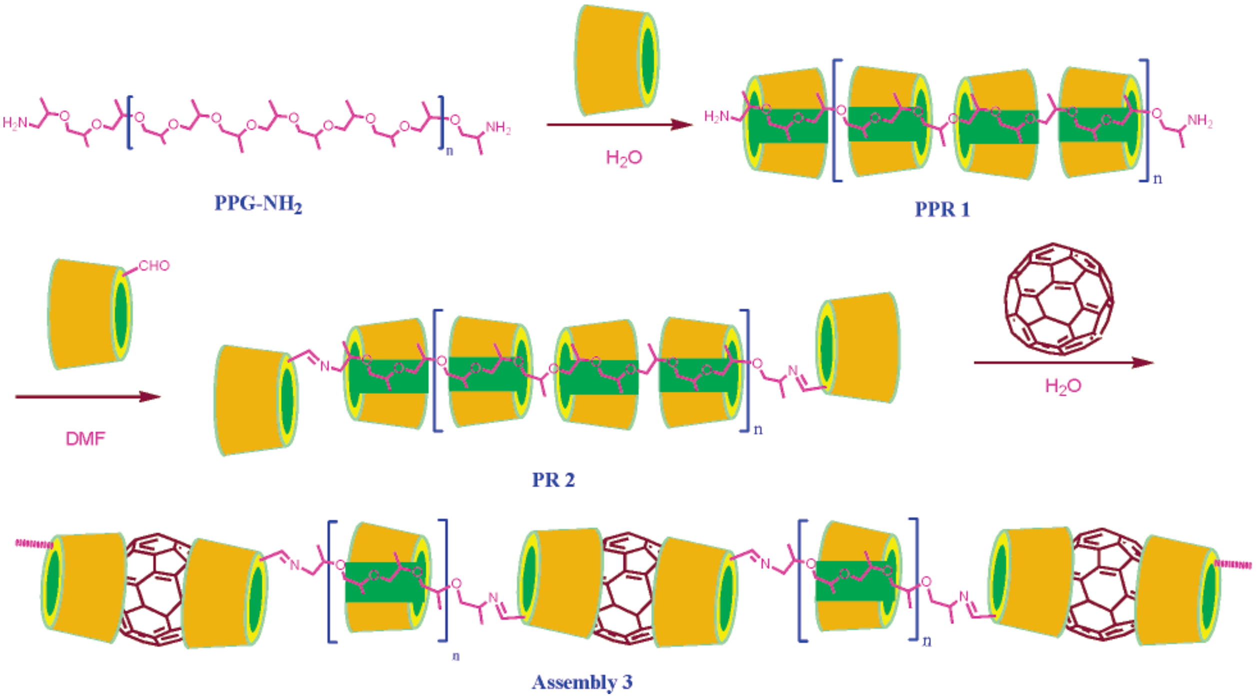
Scheme 1. Preparation of PPR 1, PR2, and Aggregate 3



white lines separated by dark dots (marked by arrows). On the basis of our preliminary STM experiments of C_{60}-containing aggregates,[8b] we can deduce that these white lines should represent CD-threaded PRs **2**, and the dark dots should be C_{60}. Through a Corey–Pauling–Koltun molecular model study, we calculate the length of PR **2** as ca. 14.5 nm, which is basically consistent with the measured length of the white lines (15.2 ± 0.7 nm) in Figure 2. Moreover, the width (1.8 nm) and height (1.7 nm) of these white lines are also consistent with the outer diameter (1.54 nm) of β-CD. In addition to STM images, TEM images also give a rough insight into the size and shape of **3**. For visualization by TEM, a sample was prepared from one drop of the solution of assembly **3** brought onto carbon-coated copper grid and then was shaded with palladium–iridium alloy to thicken and make the images more clear. Therefore, the TEM micrographs only have been used to measure the length of the supramolecular assembly. From the TEM images, we can find that there exist many linear structures in different lengths, and the longest line is in the range of 600–700 nm (Figure 3). On the other hand, the GPC

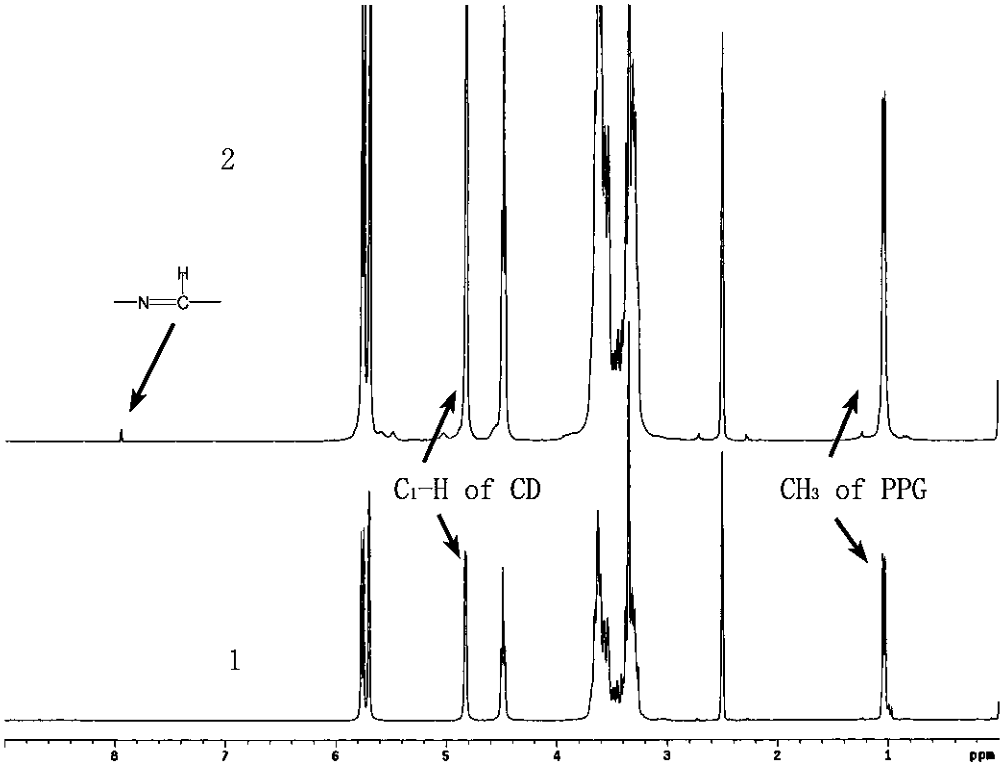


Figure 1. ^{1}H NMR spectra of (a) PPR **1** and (b) PR **2** in DMSO-d_6.

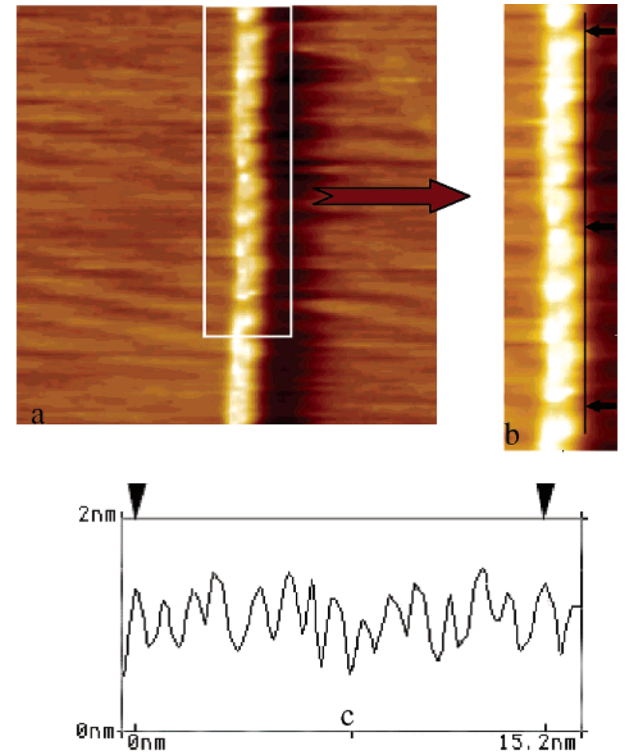


Figure 2. STM image of (a) **3**, (b) enlarged image on a HOPG surface (tunneling current 2.0 nA), and (c) line profile of image shown in (b).

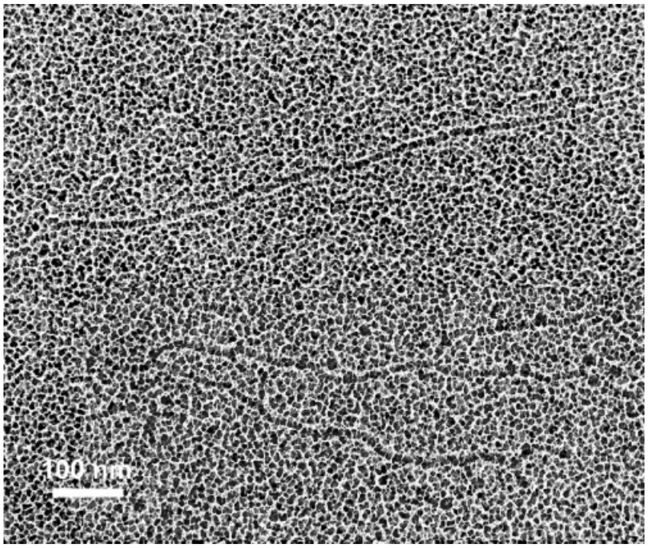


Figure 3. TEM image of **3**.

spectrum of **3** in water solution shows a unimodal elution pattern and a polydispersity of ca. 1.07. According to the GPC data, the average molecular weight of **3** is calculated to be 235 kg/mol. Therefore, we can deduce that the polyrotaxane composed of ca. 13 units of **2** is the major species contained in the reaction mixture.

In conclusion, we present a convenient and efficient method for the preparation of CD-capped polyrotaxanes. On the basis of this method, we can obtain the CD-capped polyrotaxanes with special lengths by selecting polymer chains with appropriate molecular weights. Furthermore, these polyrotaxanes can be assembled to larger aggregates through the noncovalent linkage of organic molecules. This observation will significantly extend the possible length of the resultant supramolecular aggregate. Further studies employing PPGs with different molecular weights as thread reagents, CDs with different cavity sizes as stoppers and different molecules as organic bridges are still in progress.

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Supporting Information Available: UV–vis spectra, FT-IR spectra, GPC spectrum, and CPMAS/DD ^{13}C NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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