

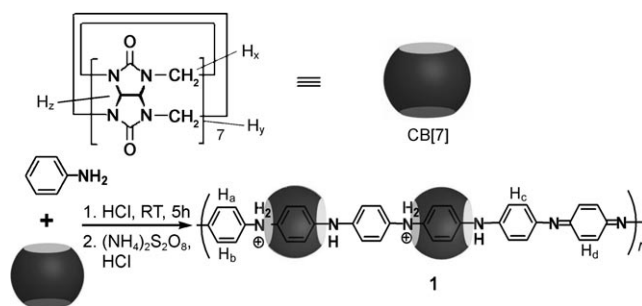
A Polymeric Pseudorotaxane Constructed from Cucurbituril and Aniline, and Stabilization of Its Radical Cation**

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Polymeric (pseudo)rotaxanes constructed through the encapsulation of covalent polymers, especially π -conjugated polymers, by macrocyclic molecules have attracted increasing interest in the fields of both supramolecular chemistry and polymer chemistry because of their fascinating properties, which are different from those of the original covalent polymers.^[1] The early investigations on such polymeric (pseudo)rotaxanes usually involved cyclodextrins^[2] or crown ethers.^[3] The corresponding cucurbit[*n*]uril (CB[*n*], *n* is usually 6–8) systems have also recently been investigated^[4,5a] as a consequence of their considerable binding abilities towards many cationic guests.^[6,7] The first attempts to construct main-chain cucurbituril-threaded polymers were performed by Kim and co-workers^[4c] as well as by Tuncel and Steinke.^[4d,e] Recently, Garcia and co-workers^[5b] synthesized a polypseudorotaxane consisting of the conjugated polymer poly(phenylene vinylene) threaded through multiple cucurbit[7]uril (CB[7]) molecules, and investigated its enhanced luminescence properties. However, many studies have been performed on conducting polymers^[8] to explore their potential applications in material chemistry and electrochemistry.^[9] Among the wide variety of conducting polymers known, polyaniline (PANI) is widely regarded as one of the eminent species because of its high conductivity (up to 1000 S cm^{-1})^[10] and its wide applications in electronic and optical materials.^[11] In general, numerous radical cations exist in the emeraldine state, that is, the conductive doped form, of PANI, and the stabilization of these radical cations is very important to the stability and conductivity of PANI.^[12] The research groups of Goux,^[13] Han,^[14] and Dawn^[15] reported, respectively, the stabilization of PANI radical cations by modulation of the pH value, modification with propylthiosulfonate groups, and complexation with DNA. Recently, Anderson and co-workers^[16] reported the stabilization of a radical cation in a cucurbituril/oligoaniline rotaxane: they found that complexation of an oligoaniline with CB[7] could stabilize its radical cation. However, studies on the threading of CB[7]s on long PANI chains and the resulting stabilization of the radical

cation have so far not been reported to the best of our knowledge. Herein, we report the construction of a polypseudorotaxane **1** by threading a PANI chain through numerous CB[7] cavities. We have also used microscopy, EPR, and cyclic voltammetry to investigate the morphology and stabilization of PANI radical cations. The results showed that, compared with free PANI, the CB[7]/PANI polypseudorotaxane had higher water solubility and the radical cation had greater stability as a result of the complexation with CB[7]. These effects will allow the further application of PANI-based supramolecular assemblies in many fields of material chemistry.

The good host–guest complexation ability of cucurbiturils with aniline derivatives^[7] enabled polypseudorotaxane **1** to be conveniently prepared by a polycondensation reaction of aniline in the presence of CB[7] (Scheme 1) by using a



Scheme 1. Preparation of polypseudorotaxane **1**.

method similar to that used for the preparation of PANI. Analysis of the product after centrifugation showed the approximate molecular weight of **1** to be $1.56 \times 10^5 \text{ g mol}^{-1}$. Integration of the proton signals in the ^1H NMR spectrum of **1** in D_2O indicated that the ratio between the doped phenyl units (a phenyl unit containing two H_a protons ($\delta = 7.20 \text{ ppm}$) and two H_b protons ($\delta = 7.10 \text{ ppm}$)) and CB[7] units (a CB[7] unit containing 14 H_y protons ($\delta = 4.12 \text{ ppm}$)) was 8.16:14.0. From these data, we calculated that two doped phenyl units could thread through a CB[7] unit, which was consistent with the elemental analysis. Moreover, the use of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard showed that the signals assigned to the doped phenyl protons (H_a and H_b) of PANI were clearly shifted upfield ($\Delta\delta = 0.10\text{--}0.09 \text{ ppm}$), while those assigned to the undoped phenyl protons (H_c) showed a slight downfield shift ($\Delta\delta = 0.05 \text{ ppm}$) after treatment with CB[7]. Furthermore, clear upfield shifts of the CB[7] protons ($\Delta\delta = 0.78, 0.87$, and 0.81 ppm for H_x, H_y and H_z , respectively) were also observed in the ^1H NMR spectrum of **1**. These phenomena, along with

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[**] We thank the 973 Program (2006CB932900), the NNSFC (No. 20421202, 20572052, and 20772062), and the Tianjin Natural Science Foundation (07QTPTJC29600) for financial support.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200802805>.

the FTIR and NOESY results (see the Supporting Information), indicated that the CB[7] units were mainly complexed to the doped units of the PANI chain (Scheme 1).

The morphology of the polypseudorotaxane **1** was investigated by TEM and AFM experiments. The TEM image gave a rough insight into the size and shape of **1**. From the TEM images recorded at a relative high concentration (1.05×10^{-4} M calculated on the basis of the repeat unit containing three aniline units and one CB[7]), we could find a number of linear structures that were located side by side to form a straight array (Figure 1). The observed width of a linear structure (ca. 1.5 nm) was consistent with the outer diameter of CB[7] (1.6 nm).^[17] Moreover, the length of the linear arrays could reach approximately 500 nm, being formed by the joining together of approximately 880 aniline units.

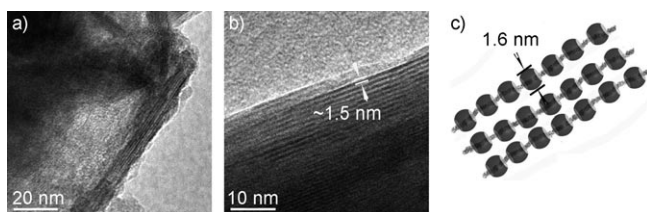


Figure 1. a) TEM image of polypseudorotaxane **1**, b) magnified TEM image, and c) possible aggregation mode of polypseudorotaxane **1**.

The AFM images showed the fine structure of **1**. A highly dilute solution of **1** (1.13×10^{-7} M calculated from the repeat units) was used for the preparation of samples for AFM experiments so as to avoid aggregation of individual assemblies into fibers. As can be seen in Figure 2c, diluting the solution of **1** to a lower concentration resulted in the originally straight fibers shown in the TEM images changing to curved structures; the average height of the linear structures (ca. 1.5 nm) was also consistent with the outer diameter of CB[7]. In the control experiment, the AFM image of PANI showed many small particles (Figure 2a), which is distinctly different from the structural features of **1**.

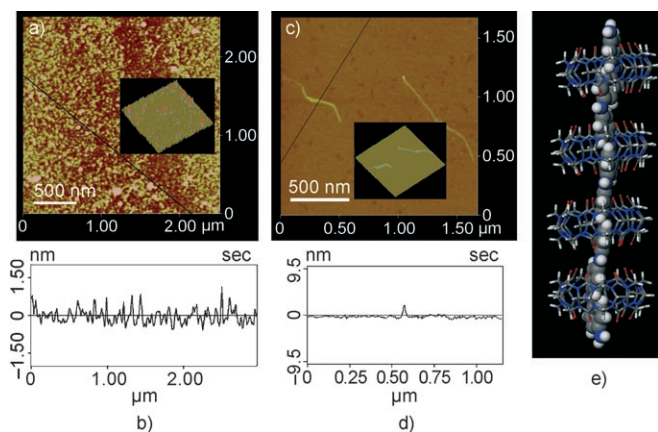


Figure 2. a) AFM image of PANI; b) section analysis of the black line in (a); c) AFM image of **1**; d) section analysis of the black line in (c); and e) possible structure of **1**.

From the TEM and AFM results we could deduce the possible structure of **1** as that shown in Figure 2e.

Interestingly, the introduction of CB[7] greatly increased the water solubility of PANI. To study the solubility, equivalent amounts of polypseudorotaxane **1** and PANI (**1**: 12.0 mg, PANI: 2.3 mg, calculated from the results of the ^1H NMR spectroscopic and elemental analysis) were dissolved in 5 mL of water. After sonication for 2 minutes, the samples were left to stand and then analyzed after 5 minutes, 1 hour, and 10 hours. The results showed that polypseudorotaxane **1** was not only clearly more soluble in water than was PANI, but also remained soluble for more than 10 hours (see the Supporting Information). Furthermore, after removing the insoluble substance by filtration, the filtrate was evaporated under reduced pressure to dryness and the residue was dosed by the weighing method. The results showed that the water solubility of **1** could reach approximately 1.4 mg mL^{-1} , compared to 0.3 mg mL^{-1} for PANI. This result subsequently confirmed the improved water solubility of PANI by complexation with CB[7].

The UV/Vis/NIR spectra of pseudopolyrotaxane **1** at various pH values were recorded to investigate the reversible redox behavior of polypseudorotaxane **1**. Figure 3 shows the

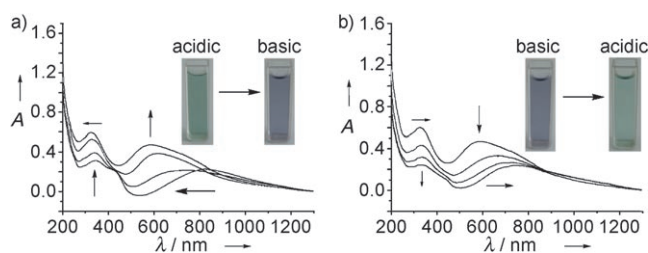


Figure 3. UV/Vis/NIR spectra of **1** ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$ based on the repeat units in water) on addition of a) 1 M NaOH, followed by b) 1 M HCl (0.5 μL per injection).

change in the UV/Vis/NIR spectrum of polypseudorotaxane **1** on addition of 1 M NaOH (Figure 3a) and 1 M HCl (Figure 3b). The UV/Vis/NIR spectrum of polypseudorotaxane **1** showed two characteristic bands at 345 and 828 nm, which were assigned to the polaron band transition of the PANI chain^[18] and indicated that the PANI chain in **1** was mostly in its doped conductive form (emeraldine salt state).^[16] The gradual addition of NaOH resulted in the solution changing from green to blue. Meanwhile, the characteristic UV/Vis/NIR bands shifted to 323 nm (assigned to the π - π^* transition of the PANI chain) and 585 nm (aromatic quinoid transition of the PANI chain),^[19] accompanied by a clear enhancement in the intensity of the adsorption. This phenomenon indicated the conversion of the doped form of the PANI chain into the undoped form. Interestingly, this conversion could be reversed by the addition of HCl (Figure 3b). These results demonstrate that the PANI chain maintained its reversible redox ability upon complexation with CB[7]. Furthermore, by comparing the change in the absorption intensity of **1** at 585 nm with that of parent PANI (Figure 3b) at various pH values (see the Supporting Information), we found that polypseudorotaxane **1** exhibited a slow change from its doped

to undoped form whereas PANI exhibited a sharp change. Moreover, a larger quantity of base (or acid) was needed for polypseudorotaxane **1** to reach its greatest undoped (or doped) state than did PANI. This phenomenon indicated that, after complexation with CB[7], the PANI chain maintained its radical cation stoichiometry as one radical cation per two aniline monomers, but displayed a pronounced delay in its redox process. This result is consistent with the delayed redox process of some other PANI composites, such as PANI complexed with sulfonated polystyrene (SPS).^[20]

Further information on the stabilization of the radical cation by complexation with CB[7] came from the EPR experiments (see the Supporting Information). As compared with that of free PANI, the EPR spectrum of polypseudorotaxane **1** showed a clear broadening of the signals. Moreover, the EPR signals of polypseudorotaxane **1** also exhibited a slower attenuation rate and a smaller attenuation ratio of the signal intensity than PANI. These results demonstrate the improved stability of the radical cation of PANI after complexation with CB[7].

Cyclic voltammetry experiments also confirmed the stabilization of PANI radical cations by CB[7] (see the Supporting Information). In the potential range of -0.15 to 1.0 V versus Ag/AgCl, free PANI showed the two typical oxidation processes at 0.23 and 0.80 V of chemically prepared PANI which correspond to oxidation from the fully reduced poly(*p*-phenylamine) form to emeraldine and the second oxidation from emeraldine to pernigraniline.^[21] However, these two anodic peaks shifted to 0.20 and 0.82 V in the cyclic voltammogram of polypseudorotaxane **1**. The first more negative anodic peak of **1** indicated that the formation of radical cations in **1** was easier than in free PANI. This phenomenon is consistent with the electrochemistry of the CB[7]/oligoaniline system reported by Anderson and co-workers, but the shift in the first oxidation potential for **1** was smaller than that for CB[7]/oligoaniline.^[16] Moreover, the more negative cathodic peak of **1** (at 0.04 V) compared with that of free PANI (at 0.07 V) demonstrated that the one-electron reduction of radical cations in **1** was more difficult than that in PANI. These phenomena also confirmed the effective stabilization of radical cations of PANI on complexation with CB[7].

In conclusion, a PANI/cucurbituril polypseudorotaxane was successfully constructed with a regular one-dimensional linear structure in satisfactory yield. Spectrophotometric and electrochemical studies demonstrated that the introduction of many cucurbituril macrocycles onto a long PANI chain effectively stabilizes the radical cation form, that is, the conductive doped form, of PANI through complexation of the cucurbituril macrocycles with the cationic units of PANI. This complexation leads to a slower attenuation rate and a smaller attenuation ratio of the radical cation, as well as lower first oxidation and reduction potentials compared to those of free PANI. These findings will enable the potential application of the PANI/cucurbituril polypseudorotaxane as insulated molecular wires.

Experimental Section

Synthesis of polypseudorotaxane **1**: Aniline (93 mg, 1.0 mmol) was added to a solution of cucurbit[7]tril (1.43 g, 1.0 mmol) in aqueous HCl (1.0 M, 100 mL). After stirring the mixture at room temperature for 5 h, ammonium persulfate (228 mg, 1.0 mmol) was added, and the mixture was further stirred at room temperature for 10 h. The precipitate was collected by filtration, washed with water, and dried in vacuum to give **1** (318 mg, yield 65% calculated on the basis of aniline) as a dark green powder. UV/Vis/NIR λ_{max} (H₂O): 345 nm ($\epsilon = 3.12 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ based on repeat units) 828 nm ($\epsilon = 2.25 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ based on the repeat units); ¹H NMR (300 MHz, D₂O, DSS): $\delta = 7.20$ (s, 4H, ArH), 7.09 (s, 4H, ArH), 6.61 (s, 2H, ArH), 5.59 (d, $J = 15.6$ Hz, 14H), 5.43 (s, 14H), 5.25 (s, 2H, ArH), 4.12 ppm (d, $J = 15.6$ Hz, 14H); FTIR (KBr): $\tilde{\nu} = 3747, 2990, 2885, 2794, 1734, 1558, 1475, 1420, 1313, 1236, 1150, 967, 805, 589, 504, 469, 417 \text{ cm}^{-1}$. Elemental analysis calcd for C₄₂H₄₂O₁₄·3C₆H₄N·HCl·5H₂O: C 46.16, H 4.25, N 27.97; found: C 46.20, H 4.20, N 27.84.

Received: June 13, 2008

Published online: August 8, 2008

Keywords: cucurbiturils · inclusion compounds · rotaxanes · self-assembly · supramolecular chemistry

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