

Construction and Efficient Radical Cation Stabilization of Cyclodextrin/Aniline Polypseudorotaxane and Its Conjugate with Carbon Nanotubes

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Dedicated to Professor Yoshihisa Inoue on the occasion of his 60th birthday.

In recent years, developments of conducting polymers for their significant potential applications have attracted increased attentions in material chemistry and electrochemistry.^[1] Among a wide variety of conducting polymers, polyaniline (PANI) is very eminent due to its simple synthesis,^[2] environment stability,^[3] optical activity,^[4] and controllability.^[5] For example, PANI were widely used as the chain molecule in the construction of various polymetric (pseudo)rotaxanes involving cyclodextrins (CDs),^[6] crown ethers,^[7] and cucurbiturils (CBs),^[8,9] most of which showed charming properties that were different from those of PANI backbone. It is well known that there existed numerous radical cations in the emeraldine state, i.e., the conductive doped form, of PANI, and the stabilization of these radical cations is very important to the stability and conductivity of PANI.^[10] In previous reports, PANI could be stabilized by pH modulate,^[11] propylthio-sulfonated modification,^[12] and complexation with DNA.^[13] Recently, Anderson and coworkers^[14] reported the radical cation stabilization in a CB[7]/oligoaniline rotaxane. More recently, we also reported that the threading of CB[7] could enhance the stability of radical cations in PANI chain.^[9] On the other hand, carbon nanotubes (CNTs), as one of the most interesting carbon materials, are of great interests over the past years due to their exceptional electrical, chemical, and mechanical properties that make them an ideal candidate for diverse applications in nanoelectronics, biosensors, and so on.^[15,16] Furthermore, the combination of conducting polymers, especially PANI, with CNTs into composite materials were found able to offer the enticing prospect of materials with enhanced functionality compared to polymers.^[17] Recently, we constructed a CNT-polypseudorotaxane conjugate by wrapping anthrylcyclodextrin-based polypseudorotaxane on CNT, showing good abilities of wrapping and cleaving the double-stranded DNA.^[18] Herein, we successfully constructed a polypseudorotaxane **1** by capsulizing a PANI chain with numerous per-methylated- β -CD (PM- β -CD) cavities as well as its triad conjugate **2** with multi-walled carbon nanotube (MWCNT)

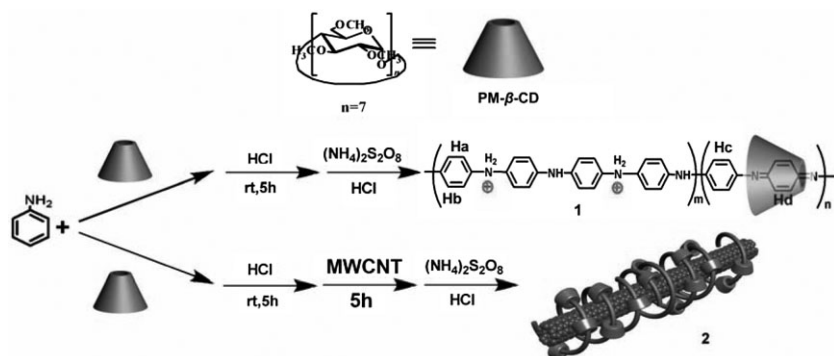
by wrapping polypseudorotaxane **1** on MWCNT (Scheme 1). Moreover, their morphology, water solubility, and stabilization effect to PANI radical cations were sufficiently investigated. The results showed that both polypseudorotaxane **1** and triad **2**, with a satisfactory water solubility, presented the fairly high stabilization abilities to the radical cation form, i.e., the conductive doped form, of PANI. These results will serve us to further explore the application of PANI-based supramolecular assemblies in many fields of material chemistry.

Using a method similar to that in our previous report,^[9] polypseudorotaxane **1** was conveniently obtained in 76% yield by a polycondensation reaction of aniline in the presence of PM- β -CD, and the centrifugation experiment gave an approximate molecular weight of **1** as $1.49 \times 10^5 \text{ g mol}^{-1}$. A comparison of the integration area of the ¹H NMR signals of **1** (see Supporting information) indicated that the ratio between the aromatic protons of PANI chain (including Ha protons ($\delta = 7.30 \text{ ppm}$) and Hb protons ($\delta = 7.16 \text{ ppm}$) in doped phenyl units, Hc protons ($\delta = 6.58 \text{ ppm}$) and Hd protons ($\delta = 5.39 \text{ ppm}$) in quinoid units) and the H1 protons of PM- β -CD units (a PM- β -CD unit containing 7 H1 protons ($\delta = 5.12 \text{ ppm}$)) was 22.3:7.4. These data indicated that ca. 5 phenyl units of PANI chain could thread a PM- β -CD unit, which was consistent with the result of element analyses. As compared with the corresponding signals of free PANI, the protons signals assigned to the doped phenyl protons (Ha and Hb) of PANI chain in **1** showed no obvious chemical shifts, but those assigned to the quinoid protons (Hd) of PANI in **1** gave a considerable downfield shift ($\Delta\delta = 0.14 \text{ ppm}$). Moreover, the inner protons (H3, H5) of PM- β -CD cavity turned more complicated in the ¹H NMR spectrum of **1**, accompanied by the slight downfield shifts. These phenomena, along with the FT-IR results, jointly indicated that PM- β -CD units mainly complexed the undoped aromatic rings of PANI.

Similar to the preparation of **1**, triad **2** was also successfully constructed by the polycondensation reaction of aniline in the presence of both PM- β -CD and MWCNT. The Raman spectrum (see Supporting Information) of MWCNT showed two characteristic peaks, where the one at 1587 cm^{-1} (G band) was assigned to the Raman-allowed phonon high-frequency E_{2g} first-order mode, and the other at 1350 cm^{-1} (D band) was assigned to the defects in the curved graphene sheets, tube ends, and turbostratic structure.^[19] The Raman spectrum of **1** showed four characteristic peaks at 1183, 1228, 1486, and 1617 cm^{-1} assigned to the

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Scheme 1. Preparation of polypseudorotaxane 1 and triad 2.

C–H bending of the quinoid ring, C–H bending of the benzenoid ring, C–C stretching of the quinoid ring, and C–C stretching of the benzene ring, respectively. Interestingly, the G band of MWCNT in 2 shifted to 1598 cm^{-1} , but the shift of D band was insignificant. The obvious up-shift of the G band peak indicated the strong attachment of 1 to MWCNT due to an increase in the elastic constant of the harmonic oscillator of the 1-coated MWCNT, and the insignificant shift of the D band implied that 1 did not covalently attach to MWCNT.^[20] As a reference, the physical mixture of 1 with MWCNT showed a Raman spectrum that could be characterized as a superimposition of 1 and MWCNT. Besides Raman spectroscopy, XPS experiments were also employed to give the detailed surface information of triad 2. The XPS spectrum of triad 2 (see Supporting Information) showed all of the expected peaks of the associated elements. In a further analysis, the C1s spectrum of triad 2 presented two peaks at 284.6 and 286.1 eV assigned to $-\text{C}=\text{C}-$ and $-\text{C}-\text{O}/-\text{C}-\text{H}/-\text{C}-\text{N}$ groups, respectively. In a control experiment, the C1s spectrum of triad 2 strongly resembled that of polypseudorotaxane 1, but somewhat differed from that of PANI, showing the disappearance of the peak at 288.7 eV assigned to $-\text{C}=\text{N}$ of the quinoid rings due to the inclusion complexation of PM- β -CD units with the undoped aromatic rings of PANI. In addition, the disappearance of the $\pi^* \leftarrow \pi$ shakeup (291.4 eV) of MWCNT in the C1s spectrum of triad 2 also indicated the association of 1 on the surface of the MWCNT, leading to the appreciable influence over the chemical environment of MWCNT surface.^[21] On the other hand, the N1s spectrum of 2 also resemble to that of 1, exhibiting two peaks at 399.6 and 400.9 eV assigned to $-\text{NH}-$ and $-\text{NH}_2^+-$ groups.^[22] Through a calculation based on the results of XPS, elemental analysis, and NMR experiments, the ratio between 1 and MWCNT in triad 2 was found as one repeated unit of 1 per 70 carbon atoms of MWCNT.

The morphological information was obtained from atomic force microscopic (AFM) and transmission electron microscopic (TEM) experiments. As a reference, the AFM image of PANI showed many small spherical particles. However, the morphology of the

resultant polypseudorotaxane 1 and triad 2 presented distinctly different features. As seen in Figure 1a, the image of polypseudorotaxane 1 showed the curving strand-like structures, and the average height of the strand (ca. 1.7 nm) was basically consistent with the outer diameter of PM- β -CD cavity (1.65 nm).^[23] Interestingly, Figure 1e clearly illustrated the wrapping of polypseudorotaxane 1 on MWCNT, and the measured height of triad 2 was ca. 70 nm. Considering the measured height of polypseudorotaxane 1 (ca. 2.0 nm) and the diameter of selected MWCNT (30–40 nm), we deduced that several polypseudorotaxane 1 may wrap on MWCNT rather than only one. TEM images further

validated the different morphology of polypseudorotaxane 1 and triad 2. Figure 2a showed a typical TEM image of polypseudorotaxane 1, which indicated that the curving strand-like structures observed in AFM images were consisted of many small aggregates. In a TEM image of triad 2 (Fig. 2b), most of the MWCNT surface was covered, accompanied by the clear broadening of MWCNT, and the average width of triad 2 (ca. 70 nm) was basically consistent with its measured height by AFM. These results jointly confirmed that the polypseudorotaxane 1 was wrapped on MWCNT.

Interestingly, the introduction of PM- β -CDs lead to a considerably increased water solubility of either PANI or MWCNT. The results of the solubilization experiments (see Supporting Information) showed that either polypseudorotaxane 1 or triad 2 not only presented the obviously higher water solubility (the measured water solubility could reach ca. 1.7 mg mL^{-1} for 1 and 1.0 mg mL^{-1} for 2) than PANI or MWCNT but also could keep soluble for more than 10 h. This result subsequently confirmed the reliability of the improved water solubility of PANI and MWCNT.

The direct information about the radical cation stabilization effect of polypseudorotaxane 1 and triad 2 came from the EPR experiments. As can be seen in Figure 3, the EPR spectrum of either polypseudorotaxane 1 or triad 2 showed the obvious broadening of signal peaks as compared with that of free PANI. Interestingly, the EPR signals of polypseudorotaxane 1 exhibited

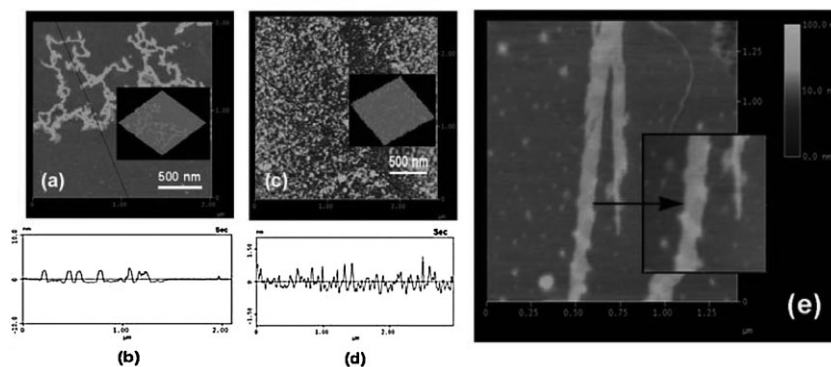


Figure 1. (a) AFM image of 1 (Insert: AFM topographic image) and (b) height profile; (c) AFM image of PANI (Insert: AFM topographic image) and (d) height profile; (e) AFM image of 2.

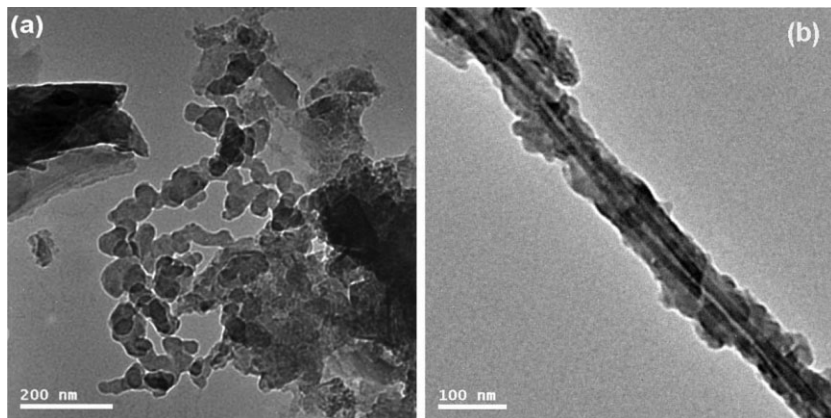


Figure 2. TEM images of (a) polypseudorotaxane **1** and (b) triad **2**.

the much slower attenuation speed and the much smaller attenuation ratio of the signal intensity than those of PANI, and the stabilization effect of **1** was found to be even better than the previously reported cucurbit[7]uril/PANI system.^[9] These results demonstrated the improved radical cation stability of PANI after the complexation with PM- β -CD. This phenomenon was similar to the reported ones on the radical cation stabilization by the complexation of β -CD or polysaccharide, where the restricted mobility of the supramolecular system may play an important role.^[24] More interestingly, after wrapping the polypseudorotaxane **1** on MWCNT, the EPR signals of triad **2** showed the further decreased attenuation speed and the attenuation ratio of the signal intensity as compared with that of polypseudorotaxane **1**. A possible reason may be that the introduction of MWCNT as a good electron acceptor enabled the donor-acceptor interactions between PANI and MWCNT,^[25] which consequently led to the improved radical cation stability. It should be noted that the introduction of MWCNT not only enhanced the radical cation stabilization effect of polypseudorotaxane **1** to some extent but also increased the thermal stability and the conductivity of **1**. TGA analysis (see Supporting Information) showed that the decomposition temperature of triad **2** (370 °C) was 40 °C higher than

that of polypseudorotaxane **1**, which indicated the high thermal stability of triad **2** as a composite material as compared with polypseudorotaxane **1**. In addition, the conductivity of polypseudorotaxane **1** was measured to be $5.27 \times 10^{-2} \text{ S m}^{-1}$. Significantly, after associating the polypseudorotaxane **1** with MWCNT, the resultant triad **2** showed the conductivity up to 1.29 S m^{-1} , which was 25 times as high as that of **1**.

The cyclic voltammetry (CV) experiments also confirmed the improved radical cation stability of **1** and **2** (see Supporting Information). In a potential range between -0.12 and 1.0 V versus Ag/AgCl, PANI showed two anodic peaks at 0.23 and 0.77 V , which should be attributed to two typical oxidation processes of chemically prepared

PANI, including the oxidation from the fully reduced poly(*p*-phenylamine) form to emeraldine and the second oxidation from emeraldine to pernigraniline.^[26] However, the first anodic peak of either polypseudorotaxane **1** or triad **2** shifted to 0.20 V . The more negative first anodic peak of **1** or **2** indicated that the formation of radical cations in **1** or **2** was easier than in free PANI. This phenomenon was consistent with the electrochemistry of the reported cucurbit[7]uril/oligoaniline^[8] and cucurbit[7]uril/PANI^[9] systems and also confirmed the effective stabilization of radical cations of PANI by **1** and **2**.

In conclusion, a PM- β -CD/PANI polypseudorotaxane and its conjugate with MWCNT were synthesized successfully from PM- β -CD, aniline, and MWCNT in >70% yield by using the simple chemical polymerization method, and their structure and morphology were sufficiently characterized. Significantly, the formation of PM- β -CD/PANI polypseudorotaxane and its MWCNT conjugate with improved water solubilities, dramatically stabilized the radical cation form, i.e., the conductive doped form, of PANI. These results may explore a novel way to construct conductive composite material through a supramolecular chemistry approach and enable the potential application of the PANI-based supramolecules as insulated molecular wires.

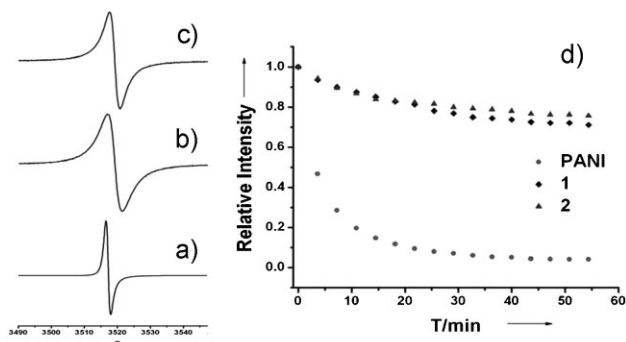


Figure 3. EPR spectra of (a) PANI ($1.87 \times 10^{-4} \text{ mol dm}^{-3}$ based on repeat units), (b) polypseudorotaxane **1** ($2.16 \times 10^{-4} \text{ mol dm}^{-3}$ based on repeat units), and (c) triad **2** ($2.03 \times 10^{-4} \text{ mol dm}^{-3}$ based on repeat units of **1** in aqueous solution. For PANI, $g = 2.0036$; polypseudorotaxane **1**, $g = 2.0038$; triad **2**, $g = 2.0038$). (d) EPR signal decay of polypseudorotaxane **1**, triad **2**, and PANI in aqueous solution (\blacklozenge : **1**, \blacktriangle : **2**, and \bullet : PANI).

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