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Construction of Polypseudorotaxane from Low-Molecular Weight Monomers via Dual Noncovalent Interactions

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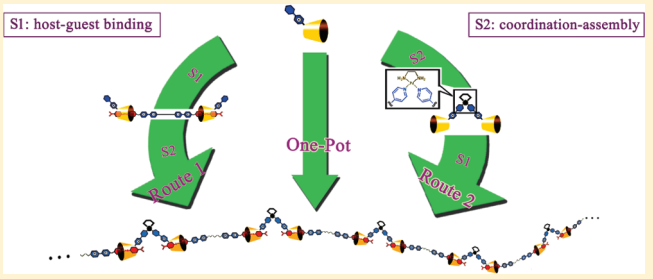
Supporting Information

ABSTRACT: The design and construction of polypseudorotaxanes via noncovalent interactions from low-molecular weight monomers (LMWMs) is playing an important role in the field of supramolecular polymers. In this work, we synthesized three low-molecular weight compounds for supramolecular polymerizations and attempted to employ the metal−ligand interaction between the pyridine nitrogen and Pd (II), for cooperating with the host−guest binding between azobenzene and β-cyclodextrin (β-CD), to complete the end-to-end connection of the polymer chains. Routes for stepwise introduction of two of the self-assembly behaviors as well as a one-pot preparation were investigated by ^{1}H NMR and 2D nuclear Overhauser enhancement spectroscopy (NOESY) ^{1}H NMR spectroscopy. The self-assembly strategies based on the full orthogonality of both noncovalent interactions will allow for a smart and rapid synthesis of precise structural controlled supramolecular polymeric assemblies.



INTRODUCTION

Over the past 2 decades, chemists have focused on developments in construction of polypseudorotaxanes using versatile self-assembly strategies, as these charming macromolecular objects have great potential for applications in energy and biological materials.[1] Conventional polypseudorotaxanes were usually prepared with several macrocyclic components surrounding a long-chain backbone via the host−guest interaction.[2] Their precision was somewhat limited as incomplete inclusion remained in these polymer chains. Conversely, supramolecular polymerization by host−guest binding from low-molecular weight monomers (LMWMs)[3] is becoming a more preferable method for the relative precise construction of the polypseudorotaxanes. Nowadays, in addition to study their precise structures, researchers are also concerned about the synthesis strategies to develop the polypseudorotaxanes with easy, rapid, and spontaneous processes for natural fitness.[4]

Construction of supramolecular polymers, where LMWMs are brought together by a series of noncovalent interactions instead of the conventional covalent polymerization, allows for the spontaneous and selective formation of stable and specific supramolecular backbones and is emerging as a smart design principle for soft materials capable of stimuli-responding[5] and self-healing.[6] Thus far, this methodology has been utilized for fabrication of many supramolecular alternating bipolymer-based polypseudorotaxanes.[3a,b] However, the establishment of precise structural controlled terpolymer-based polypseudorotaxanes using three LMWMs, two noncovalent interactions, has rarely been reported yet. As compared to those bipolymer architectures, the presence of terpolymer-based supramolecular assemblies allows for the incorporation of a greater variety of functionalities. Inspired by these opportunities, we attempt to design and prepare three low-molecular weight compounds with different self-assembly sites for construction of terpolymer-based polypseudorotaxanes. Of course, realizing the morphology transformations of such novel polypseudorotaxanes in a controlled manner is also needed.

Ethylenediamine palladium(II) nitrate (enPd) is prone to generate a strong and quantitative bis-coordination[7] with two equiv of pyridine derivatives in water so that this metal center would be quite suitable to be applied in the combination of cyclodextrin-based supramolecular polymers, a sort of important polypseudorotaxane prototype. In addition, such bis-coordination can quickly and spontaneously lead to a rigid bis-branched complex at room temperature. To employ this metal−ligand interaction for the linkage of the polypseudorotaxane, 4,4′-bipyridine moiety was covalently grafted to the 6-position of the β-cyclodextrin (β-CD) to form an active ligand (CDP, shown in Figure 1). Next, to complete the end-to-end connection of the anticipated copolymer chain, we designed a rodlike guest compound AVVA containing two azobenzene groups in the two ends linked by viologen units as hydrophilic electropositive barriers[8] (Figure 1). Azobenzene is an essential functional unit that can be well encapsulated by the β-CD ring through the spontaneous host−guest bindings.[9]

Since AVVA and enPd can be associated noncovalently with CDP, respectively, at the certain moieties as the above-mentioned

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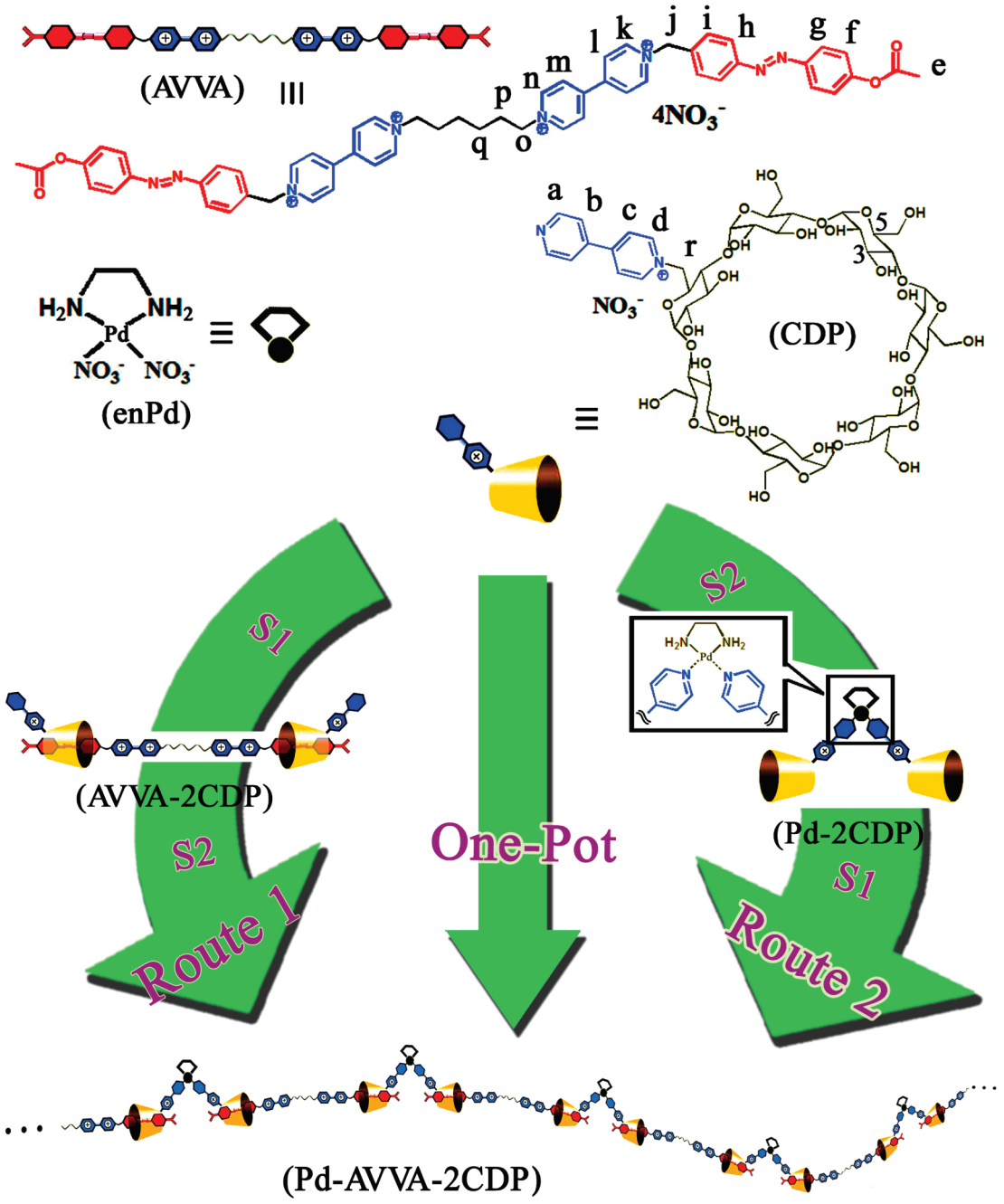

Figure 1. Illustration of the stepwise and one-pot construction processes with two different self-assembly behaviors for the functional polypseudorotaxane Pd-AVVA-2CDP. (Self-assembly behaviors: S1, host−guest binding by introducing 0.5 equiv of AVVA; S2, coordination-assembly by adding 0.5 equiv of enPd).

design, both of the self-assembly processes are orthogonal in this system.[10] In this way, two routes for stepwise self-assemblies need to be discussed: one beginning with the host−guest binding between AVVA and CDP followed by the metal−ligand interaction with enPd, the other following the reverse sequence of the two self-assembly behaviors. In addition, a one-pot route by directly mixing three of the LMWMs could also be extracted. All of these routes for construction of the supramolecular polypseudorotaxanes Pd-AVVA-2CDP can be followed by monitoring characteristic changes in the chemical shifts using ^{1}H NMR spectroscopy, and such construction strategies are outlined in Figure 1.

EXPERIMENTAL SECTION

Instruments. ^{1}H NMR spectra and the ^{13}C NMR were measured on a Brüker AV-400 spectrometer, and the 2D-NOESY NMR spectra were recorded on a Brüker AV-500 or AV-600 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a HP5989 mass spectrometer. Absorption spectra were done on a Varian Cary 500 UV−vis spectrophotometer (1 mm quartz cell used). The photoirradiation was carried on a CHF-XM 500 W high-pressure mercury lamp with a filter for 365 nm in a sealed Ar-saturated 1 mm quartz cell. The distance between the lamp and the sample cell was 20 cm. Melting points were determined by using an X-6 micromelting

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point apparatus. Viscosity measurements were carried out with Ubbelohde microdilution viscometers (Shanghai Liangjing Glass Instrument Factory, 0.50 mm inner diameter) at 25 °C in water. The thermogravimetric analysis (TGA) was conducted on a TGA/SDTA/851e analyzer. Atomic force microscopy (AFM) was performed using an NS-3a AFM microscope at room temperature, and samples were prepared by spin coating an aqueous solution on mica.

Materials. β-Cyclodextrin (β-CD), 1,6-dibromohexane, silver nitrate, 4,4′-bipyridine, and the inorganic reagents were commercially available and used as received. Ethylene diamine palladium chloride was purchased from Alfa Aesar and used as received. Acetonitrile and DMF were dried by a 4A molecular sieve and distilled under reduced pressure before use.

Synthesis of the Monomers. *AVVA.* Compound **B**[11] (0.712 g, 1.29 mmol) was dissolved in DMF (50 mL) at 70 °C. Compound **A**[11] (6.0 g, 18 mmol) was added into the solution, and the mixture was stirred at 80 °C for 12 h. The precipitate was filtered out when it was hot. Then the solid was washed with hot acetonitrile and gave a yellow compound ($AVVA \cdot 4Br^-$) ~0.93 g (59.2%). $AgNO_3$ (100 mg, 0.588 mmol) was added to an aqueous solution (20 mL) containing $AVVA \cdot 4Br^-$ (180 mg, 0.147 mmol), and the mixture was stirred for 10 min at 75 °C in the dark. AgBr formed was removed by filtration while it was hot. Evaporating the filtrate and washing with a little water yielded AVVA as a yellow solid (125 mg, 74%). Mp 196−198 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS): δ = 9.55 (d, J = 6.4 Hz, 4H), 9.38 (d, J = 6.4 Hz, 4H), 8.80 (d, J = 6.8 Hz, 4H), 8.77 (d, J = 6.4 Hz, 4H), 7.98 (d, J = 7.6 Hz, 4H), 7.96 (d, J = 8.4 Hz, 4H), 7.82 (d, J = 8.4 Hz, 4H), 7.39 (d, J = 8.8 Hz, 4H), 4.69 (m, 4H), 2.39 (s, 6H), 1.99 (m, 4H), 1.39 (m, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, 298 K, TMS): δ = 168.99, 153.05, 152.18, 149.42, 148.64, 145.91, 145.86, 145.75, 137.03, 130.18, 127.16, 126.69, 123.96, 123.19, 123.03, 62.93, 60.74, 30.39, 24.79, 20.87. HRMS (ESI): m/z, 1088.3917 $[M - NO_3]^+$

CDP. To a solution of DMF (60 mL) containing mono-(6-*O*-*p*-toluenesulfonyl)-β-cyclodextrin (3 g, 2.38 mmol) was added 4,4′-bipyridine (4.264 g, 16.66 mmol). The resultant mixture was stirred at 90 °C for 4 days under argon. The solution was poured into 200 mL of THF, and the precipitate was collected by filtration to give a crude powder. This product was then applied to silica gel chromatography (*n*-butanol−ethanol− water = 5:4:3) to give a pure sample (371 g). This sample was also ion-exchanged with 1 equiv of $AgNO_3$ at room temperature to give CDP as a white solid. Mp >250 °C. ^{1}H NMR (400 MHz, D_2O, 298 K): δ = 8.87 (d, J = 6.0 Hz, 2H), 8.64 (d, J = 6.0 Hz, 2H), 8.33 (d, J = 6.0 Hz, 2H), 7.76 (d, J = 6.0 Hz, 2H), 4.76−5.20 (m, 14H), 3.22−4.05 (m, 33H), 2.65 (m, 2H). ^{13}C NMR (400 MHz, D_2O, 298 K, TMS): 154.92, 150.10, 145.80, 142.40, 126.03, 122.49, 101.81, 101.67, 81.14, 73.06, 72.99, 72.39, 71.99, 71.91, 71.86, 71.68, 60.31. HRMS (ESI): m/z, 1273.4358 $[M - NO_3]^+$

Ethylene Diamine Palladium Nitrate (enPd). Ethylene diamine palladium chloride (73.6 mg, 0.31 mmol) was suspended in 20 mL water at room temperature. $AgNO_3$ (105.3 mg, 0.62 mmol) was added to the suspension, and the mixture stirred for 0.5 h. A white solid of AgCl formed and was filtered off. The filtrate was evaporated in vacuo, and the pale-yellow solid was directly used for the next step.

RESULTS AND DISCUSSION

Construction of Polypseudorotaxane. The LMWMs compounds AVVA and CDP were fully characterized by ^{1}H NMR, ^{13}C NMR, and HR-MS. All the anions were exchanged to NO_3^- because the nitrate ion is hydrophilic and can hardly compete with the pyridine ligand for the coordination. The first step for constructing the polypseudorotaxane in route 1 is to create an intermediate complex AVVA-2CDP (shown in Figure 1). It was prepared from AVVA by cogrinding of the guest with 2 equiv of solid CDP for ~10 min. The uniformity of the well mixed sample can help enhance the inclusion rate of the host−guest structure in the aqueous solution. As shown in Figure 2B, it clearly reveals one group of proton signals of the guest component in AVVA-2CDP. It is totally different from that of AVVA (shown in Figure 2A) and indicates a complete complexation with 2 equiv of CDP at the test concentration (~5.0 mM). The inclusion of the β-CD ring caused an upfield shift of the protons $H_{g,h}$ and a downfield shift of $H_{i,f}$. These chemical shifts indicate that protons $H_{g,h}$ are located in the center of the β-CD cavity while $H_{i,f}$ stay around the rims of the cavity, respectively. The complex AVVA-2CDP was also well evidenced by ESI-MS. In the mass spectrum of AVVA−2CDP, a peak at m/z = 1272.9, corresponding to $[M]^{3+}$, is observed (Figure S3C, Supporting Information).

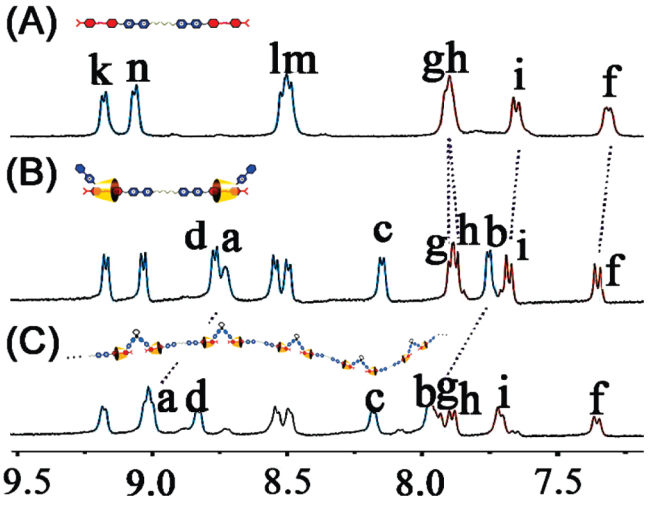

Figure 2. Parts of ^{1}H NMR spectra (400 MHz in D_2O at 298 K) of (A) AVVA, (B) AVVA-2CDP, (C) Pd-AVVA-2CDP (AVVA-2CDP + 1.0 equiv of enPd).

AVVA-2CDP can quickly react with enPd at room temperature as described in the second step of route 1. When a total of 1.0 equiv of enPd was added, and a vast majority of the complexes participated in the bis-coordination. As shown in Figure 2C, it reveals well-assigned new proton signals, which are different from those of AVVA-2CDP (Figure 2B). It is suggested that such bis-coordination brings in extremely high assembly efficiency *in situ*. Protons H_a and H_b display great downfield shifts (from δ = 8.73 to 9.05 for H_a and from δ = 7.75 to 7.95 for H_b) because of the Pd(II) coordination with the ligands via the pyridine nitrogen atoms. A new peak at δ = 2.88 is assigned to the proton signals of the symmetric methylene in the ethylene diamine group. In this way, both the self-assembly behavior have participated in the association of the LMWMs to form the polypseudorotaxane Pd-AVVA-2CDP. Of course, the slow exchange phenomena and minor equilibrium components will be present inevitably in the solution system, but the main component is indeed attributed to the polypseudorotaxane Pd-AVVA-2CDP according to the NMR spectroscopy.

Next, we exchanged the self-assembly sequence and also studied this point by NMR spectrometers. The construction for Pd-AVVA-2CDP via route 2 should undergo another intermediate Pd-2CDP (shown in Figure 1). It is a bis-coordinated complex formed quickly by reaction of CDP with 0.5 equiv of enPd. Protons H_a and H_b of Pd-2CDP still reveal great downfield shifts (from δ = 8.72 to 8.99 for H_a and from δ = 7.84 to 8.07 for H_b), compared with those of CDP, because of the Pd(II) coordination

(see Figure 3A,B). The complex Pd-2CDP was also well evidenced by ESI-MS (Figure S3D in the Supporting Information). The peak at 1405.4 is assigned to $[M - 3NO_3 + 2H_2O]^{2+}$. Then, AVVA was introduced into the system. Accompanied with encapsulating both ends of the azobenzene moieties, a group of clear proton signals of the guest component was generated (Figure 3C). The polypseudorotaxane can be also formed by route 2 from these LMWMs.

In addition to the chemical shifts of the protons in Pd-AVVA-2CDP that can be well assigned in the ^{1}H NMR spectra, the fine structures of the polypseudorotaxane prepared both from route 1

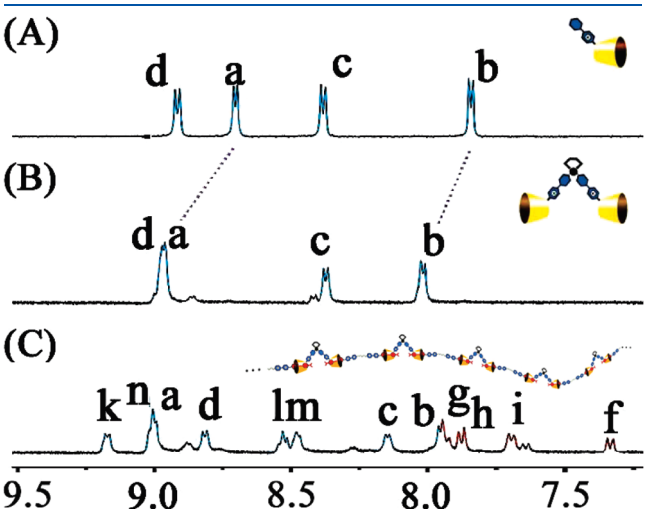

Figure 3. Parts of ^{1}H NMR spectra (400 MHz in D_2O at 298 K) of (A) CDP, (B) Pd-2CDP, (C) Pd-AVVA-2CDP (Pd-2CDP + 1.0 equiv of AVVA).

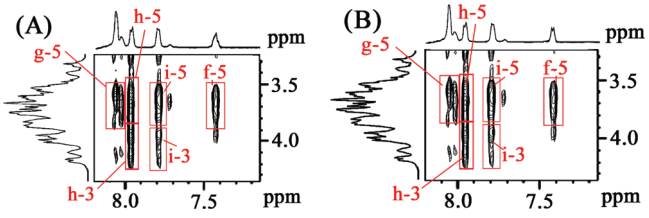

Figure 4. Parts of 2D NOESY ^{1}H NMR spectrum (600 MHz in D_2O at 298 K) of Pd-AVVA-2CDP prepared by route 1 and 2.

and 2 are also satisfactory by investigation of 2D NOESY ^{1}H NMR spectroscopy. As shown in Figure 4A,B, strong NOE signals are observed from H_g, H_f to the internal protons H_5 of the β-CD cavity but almost not from H_g, H_f to H_3 of the β-CD cavity,[12] which proves that a good unidirectional threading of the guest to the β-CD cavity has taken place both from routes 1 and 2 in this supramolecular system. Despite, slight NOE patterns will emerge from H_g, H_f to H_3 when prolonging the NMR scanning time, and these signals are not dominant. It is consistent with the geometry of Pd-AVVA-2CDP shown in Figure 1, which leaves the 4,4′-bipyridine moiety on the 6-position of CDP outward to be linked end-to-end with Pd(II) coordination. A rationale for that would be unfavorable electrostatic repulsions between the positive charge on the alkyl pyridinium connected to the β-CD component and the positive charges of the viologen units, which are closer to each other when threading occurs through the secondary side of the β-CD and hence only keep it entering from its primary side. Such precise structural control can be also confirmed by finding a similar group of NOEs in the intermediate complex AVVA-2CDP (Figure S4A in the Supporting Information).

Except for two of the stepwise strategies, we also explored the one-pot fashion for examining the fine structure of Pd-AVVA-2CDP. We mixed the LMWMs at the ratio of 1:1:2 (1 equiv of enPd, 1 equiv of AVVA, and 2 equiv of CDP) together in D_2O at room temperature. The self-assembly results were also expressed by NMR spectroscopes shown in Figure S8 (Supporting Information). Similar to the case of that prepared by the stepwise fashion, as expected, the well-controlled precise structure of the polypseudorotaxane could be still kept while prepared by the one-pot strategy according to its NOE signals. Thus, ^{1}H NMR and 2D NOESY NMR spectroscopy provides strong evidence for the formation of the polypseudorotaxane Pd-AVVA-2CDP via three different routes, mediated by two strong and orthogonal noncovalent interactions between the independent recognition sites.

Morphology of the Polypseudorotaxane. In addition to characterize the precise structure of the polypseudorotaxane, the morphology and performance of Pd-AVVA-2CDP were also studied. Atomic force microscopy (AFM) was performed to provide further insight into the size and shape of Pd-AVVA-2CDP. The nanowires observed from AFM images, which are in the range from 0.3 to 1 μm, should belong to the polymer chains on the substrate (see Figure 5). The average height of the nanowires (less than 2 nm) was also consistent with the outer diameter of β-CD.[13] The thermal

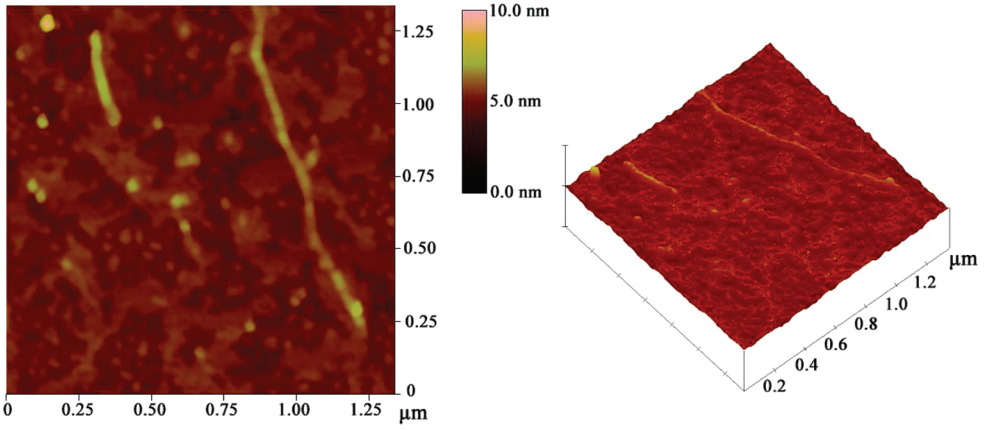

Figure 5. AFM images of the polypseudorotaxane Pd-AVVA-2CDP on a mica surface. The samples for AFM images were prepared by spin-coating a water solution (comprising 0.01 mM AVVA) onto a freshly cleaned mica surface.

property of this supramolecular copolymer was evaluated by TGA under nitrogen atmosphere. It still has a good thermal stability and lost little weight at high temperature (265 °C).

Functional supramolecular copolymers that can response to external stimuli[5] have recently attracted significant attention because of their promising applications in the field of materials capable of controllable delivery and release. The introduction of host−guest interaction between azobenzenyl moiety and a β-CD ring to the main-chain in this system is also considered for construction of polypseudorotaxanes with photoinduced assembly/disassembly behaviors. As the specific viscosity measurement is a reflection of the polymerization degree[14] of the polypseudorotaxanes, we have investigated the specific viscosity change of Pd-AVVA-2CDP along with the 365 nm UV irradiation time.[15] As shown in Figure S10 (Supporting Information), the specific viscosity of the polypseudorotaxane Pd-AVVA-2CDP prepared decreases with prolonging the irradiation time. This result shows that the shrinkage of the polymerization degree is originated from the light-driven β-CD disassembly process. This interconversion process can be even distinguished by the naked eyes (Figure S11, Supporting Information). This stimuli-responsiveness could be recovered to some extent by the irradiation of visible light.

CONCLUSIONS

In summary, this work developed routes for preparation of polypseudorotaxane with well-organized precise structures based on introduction of dual noncovalent interactions: metal−ligand interaction and host−guest binding. The stepwise and one-pot strategies can all result in the formation of the functional polypseudorotaxane by the spontaneous and orthogonal self-assembly behaviors from three LMWMs. Such a novel polypseudorotaxane is based on supramolecular terpolymer architectures, which might lay the foundation of loading a greater variety of functionalities. Assembly/disassembly behavior with photoisomerization on the main-chain was also observed in this system. This work provides a synthesis methodology for smart design and construction of new-type responsive supramolecular copolymers, which may hold important potentials to fabricate versatile drug or gene delivery systems for biomedical applications.

ASSOCIATED CONTENT

Supporting Information. Synthetic procedures of the precursors; ^{1}H NMR, HRMS (ESI) spectra of AVVA, CDP, AVVA-2CDP, and Pd-2CDP; some supplementary data of 2D ROESY NMR; full spectra of ^{1}H NMR spectra; ^{1}H NMR spectra of the photostationary states; and characterizations of the photoinduced assembly/disassembly behaviors. This material is available free of charge via the Internet at http://pubs.acs.org.

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