

Polymer Chemistry

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An Acid/Base Switchable and Reversibly Cross-Linkable Polyrotaxane†

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5 A main chain-type polyrotaxane was fabricated by employing a one-pot synthesis strategy from a pseudorotaxane monomer and an end-capping agent. Based on this polyrotaxane, a controllable molecular machine was furnished upon the external acid/base stimuli, and a reversible transition between linear and cross-linked polyrotaxane was achieved by the successive addition of [PdCl₂(PhCN)₂] and PPh₃.

Introduction

10 Mechanically interlocked polymers (MIPs), a class of polymers with mechanical bonds incorporated into the structures, have attracted much attention not only because of their intriguing architectures and topologies but also as a result of their interesting physical properties and potential applications in
15 molecular devices, nanomaterials, and biomaterials.¹ Owing to the existence of mechanical bonds, MIPs are expected to have more flexibility, mobility, and controllability compared to conventional polymers that are constructed only by covalent bonds, which make it possible to conveniently provide smart and
20 stimuli-responsive materials.^{1–8} Since the pioneering work in 1990s by Harada,² Gibson,³ and other groups,^{4–7} a variety of MIPs, including polyrotaxanes^{1c} and polycatenanes^{1f}, have been widely synthesized and studied. Among them, main-chain-type polyrotaxanes, in which cyclic molecules are threaded onto linear
25 polymer chains and mechanically interlocked by bulky end groups, have become one of the most intensively investigated MIP structures.^{1e,8} Main-chain-type polyrotaxanes have shown a few of distinctive physical and mechanical properties. Since the cyclic molecules are not covalently bound to the polymer
30 segment, they can slide and rotate on the linear component of the polyrotaxanes. This feature could be utilized to make fascinating molecular materials, such as a tubular polymer formed by cross-linking macrocycles in a single polyrotaxane,^{2a} insulated
35 swellable polyrotaxane gels,⁸ⁱ gene delivery^{8a–c,8k,9} and drug delivery systems.^{8l,10}

The chemical synthesis and assembly of artificial molecular machines (AMMs) have become of central interest in chemistry and material science with the aim of engineering dynamic
40 microscopic devices and functional materials via bottom-up approaches.¹¹ A number of charming examples of AMMs have been reported based on mechanically interlocked structures. The combination of AMMs into MIPs also emerged with unlimited future prospects for the integration of individual AMMs to
45 nanoscale devices. Among the growing collection of molecular systems under consideration for material applications, stimuli-responsive MIPs have shown great promise.¹² Stoddart et al.^{12b} and Grubbs et al.^{12c} respectively reported the covalent

incorporation of bistable [c2]daisy chains into polymers to form
50 switchable poly[c2]daisy chains. More recently, Buhler and Giuseppone et al.^{12d} achieved pH-switchable poly[c2]daisy chains via coordinative polymerization from a [c2]daisy chain monomer. These switchable poly[c2]daisy chains scaled up of individual mechanical motions to obtain biomimetic molecular muscles. Yui
55 and co-workers succeeded in synthesizing a series of pH-responsive¹³ or thermoresponsive¹⁴ polyrotaxanes consisting of cyclodextrins and linear polymers. Other stimuli-responsive molecular devices and molecular machines with MIPs were also fabricated and operated via the change of pH or temperature,¹⁵ the
60 addition of chemical reagents,¹⁶ electrochemical oxidation-reduction,¹⁷ or photoirradiation.¹⁸ These systems demonstrated reversible and dynamic movements between their components, such as shuttling, enabling them to serve as the stimuli-responsive materials. Nevertheless, there are only a few examples involving
65 the combined use of two or more stimuli in responsive MIPs. Herein, we report a unique dual-action main chain-type polyrotaxane, in which the host, dipyrido[24]crown-8 (DP24C8)¹⁹, not only can be controllably shuttled on the axle of the polyrotaxane by adding acid/base stimuli but also can be
70 reversibly cross-linked via Pd coordination and decoordination.

Experimental section

Materials and Methods

NaH, 3,5-dimethylphenol, 5-bromo-1-pentene, and the 2nd generation Grubbs catalyst were reagent grade and used as
75 received. DP24C8¹⁹ and dialkylammonium **3**²⁰ were synthesized according to the literature procedures. THF and dichloromethane were dried according to the typical procedures described in the literature. The other solvents were employed as purchased.

NMR spectra were collected on a Bruker AVANCE DMX-400
80 spectrometer with the residual solvent or TMS as the internal standard. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Molecular weight distributions were measured on a
85 conventional gel permeation chromatography (GPC) system equipped with a Waters 1525 Isocratic HPLC pump, a Waters

2414 refractive index detector, and a set of Waters Styragel columns (HR1, HR2 and HR4, 7.80 mm × 300 mm). GPC measurements were carried out at 35 °C using a DMF solution as the eluent with a flow rate of 1.00 mL/min. The system was calibrated with linear polystyrene standards. Thermogravimetric analysis (TGA) of the polymer was recorded on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 20 °C/min from 20 °C to 600 °C. The thermal property of the sample was characterized by a differential scanning calorimetry (TA Q2000, USA) under nitrogen atmosphere. The sample was first heated from -50 °C to 150 °C, followed by cooling to -50 °C, and finally reheated to 150 °C to obtain the glass transition temperature of the polymer. All the process was at the same rate, 10 °C/min.

The linear polyrotaxane **4** sample for AFM was prepared using the following procedure: A solution of the polymer in acetone (50 µM/L) was precipitated into H₂O of a Si wafer, which was cleaned subsequently in ultrasonic bath and dried in a stream of nitrogen finally. Meanwhile, the cross-linked supramolecular polymer sample for AFM was obtained by mixing polyrotaxane **4** and [PdCl₂(PhCN)₂] in chloroform and the precipitation was dissolved in DMF (5 µM/L), the solution was added to H₂O of a Si wafer, which was cleaned subsequently in ultrasonic bath and dried in a stream of nitrogen finally. The samples were dried in a vacuum oven at room temperature overnight before AFM measurements. A scanning probe microscope (SPM), MultiMode Nanoscope IVa, equipped with a J-scanner was used for tapping mode AFM. Images were obtained under ambient conditions at a resolution of 512 × 512 pixels/line, and at scan rates ranging from 0.5 to 1 Hz, using etched silicon probes (Veeco Instruments) with a cantilever length of 125 µm, a resonant frequency of ~300 kHz, and a spring constant of ~40 N/m. Scanning electron microscope (SEM) was used to view the surface of the polymer films with a JSM-6390LV. Image analyses were performed using the corresponding commercial software.

Synthesis of compound **1**

3,5-Dimethylphenol (1.20 g, 10.0 mmol) in THF (20.0 mL) was cooled to 0 °C, NaH (0.480 g, 20.0 mmol) was added in batches in 5 min. The mixture was stirred for 10 min at room temperature and 5-bromo-1-pentene (22.9 g, 120 mmol) was added dropwise. The mixture was refluxed overnight before being quenched with MeOH/H₂O. The solvent was evaporated under vacuum and the residue partitioned between ethyl acetate and brine. The organic layer was dried with anhydrous Na₂SO₄ and then concentrated under vacuum to give a residue. The crude product was purified by column chromatography (SiO₂:petroleum ether/ethyl acetate = 20:1) to afford compound **1** as a colorless liquid (1.25 g, 66.0%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.60 (s, 1H), 6.54 (s, 2H), 5.81–5.91 (m, 1H), 4.99–5.09 (m, 2H), 3.94 (t, *J* = 6.0 Hz, 2H), 2.29 (s, 6H), 2.24 (q, *J* = 8.0 Hz, 2H), 1.87 (qt, *J* = 6.0 Hz, 8.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 159.17, 139.24, 138.03, 122.41, 115.23, 112.31, 66.98, 30.27, 28.61, 21.56. HRMS: *m/z* calcd for C₁₃H₁₈O ([M + H]⁺), 190.1358; found, 190.1359, error 0.5 ppm.

Synthesis of polyrotaxane **4**

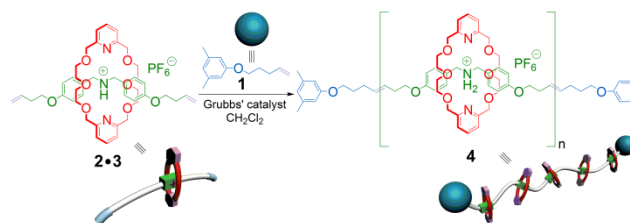
DP24C8 (**2**, 139 mg, 0.332 mmol) and ammonium diene

monomer (**3**, 130 mg, 0.269 mmol) were dissolved in CH₂Cl₂ and the solution was stirred for 10 min. The solvent was removed under reduced pressure to afford a mixture containing the pseudorotaxane monomer **2•3** as a white solid. Compound **1** (25.4 mg, 0.133 mmol) and the prepared pseudorotaxane monomer **2•3** were then dissolved in dry CH₂Cl₂ (0.2 mL) and frozen to -78 °C under the argon atmosphere. After the 2nd generation Grubbs catalyst (2.50 mol%, 5.00 mg) was quickly added, the reaction was allowed to warm to room temperature and then to 35 °C. After 30 minutes, the solvent was removed under reduced pressure, and dry CH₂Cl₂ (0.2 mL) was added. This “cycling” process was repeated at 1 h, 2 h, and 12 h. After 24 h, the reaction mixture was diluted with CH₂Cl₂ (0.2 mL) and added dropwise into 1:1 hexanes/diethyl ether (60 mL) to afford the desired polymer. The solid was collected via vacuum filtration, rinsed with cold hexanes/diethyl ether (1:1 v/v) and dried under vacuum to afford polyrotaxane polymer **4** as a solid (88.0 mg, 29.0%).

Results and discussion

Design and synthesis

There are several different methods to produce main-chain-type polyrotaxanes. Two typical strategies are: (1) threading cyclic molecules onto linear polymer axis molecules then ending with bulky substituents, and (2) polymerization of pseudorotaxanes or rotaxanes.¹⁶ The former strategy is frequently used when the linear polymer axis is conveniently available, while the latter is more suitable as the linear axis is difficult to be obtained. We adopted the latter strategy to prepare a new main-chain-type polyrotaxane from a pseudorotaxane based on the well-studied dipyrido[24]crown-8 (DP24C8, **2**)/dialkylammonium recognition motif established by Stoddart et al.¹⁹ The polyrotaxane **4** was synthesized from the *in situ* generated pseudorotaxane **2•3** and the end-capping group **1** by one-pot²¹ olefins metathesis polymerization.²² With this convenient method developed by Grubbs et al, efficient complexation, polymerization, and end-capping were accomplished in a single operation to yield the main-chain-type polyrotaxane **4** (Scheme 1). The unreacted monomers and side products were removed simply by the precipitation from dichloromethane into a mixture of hexanes and diethyl ether.



Scheme 1 Synthesis of main-chain-type polyrotaxane **4** by one-pot olefins metathesis polymerization (shown as an idealized state, fully threaded polyrotaxane).

NMR characterization

The complexation between **2** and dialkylammonium derivative **3** was firstly investigated as a recognition model. As shown in Figure 1, the proton NMR spectrum of an equimolar solution of **2** and **3** exhibited two sets of peaks, indicating slow-exchange complexation on the proton NMR time scale.¹⁹ After

complexation, peaks corresponding to H_b, H_c, H_d and H_e on **2** and H₆ and H₇ on **3** moved upfield, while H_a on **2** and H₅ on **3** moved downfield. All of these chemical shift changes indicated that DP24C8 ring bound **3** on the dibenzylammonium position. By integrations of the peaks from **2** and **3** (Figure S4, Supporting Information), the stoichiometry of this complexation model was determined to be 1:1; the association constants (K_a) of 1:1 complex **2**·**3** in CDCl₃ at 10.0 mM concentration was calculated to be $7.20 \times 10^3 \text{ M}^{-1}$ using the single-point method.¹⁹ The synthesis of the polyrotaxane **4** was carried out at a much higher concentration to increase the complexation percentage of **2** and **3**.

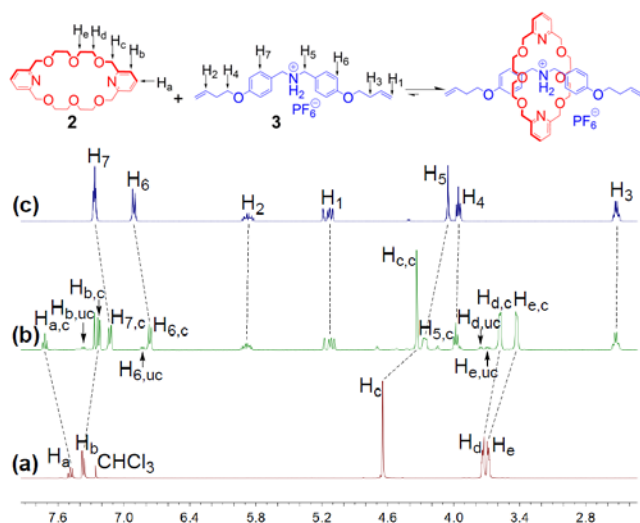


Figure 1 Partial proton NMR spectra (400 MHz, CDCl₃, 22 °C): (a) **2**, (b) an equimolar mixture of **2** and **3** (10.0 mM), and (c) **3**. Complexed and uncomplexed species are denoted by “c” and “uc”, respectively.

Proton NMR spectra of polyrotaxane **4** and its starting materials in CDCl₃ and DMSO-*d*₆ are shown in Figure 2 and Figure 3, respectively. The broad peaks of polyrotaxane **4** are typical characteristics of polymers. The peak representing terminal olefinic protons disappeared, which indicated the completion of the polymerization reaction. Chemical shift changes of polyrotaxane **4** in CDCl₃ (Figure 2) were similar to those changes after mixing equimolar **2** and **3** (Figure 1). The signals of methylene protons H_c on **2** and phenylic protons H₆ on dibenzylammonium moieties separated into two sets (Figure 2), corresponding to the complexed and uncomplexed species or moieties. After polymerization, pyridinic protons H_b, methylene protons H_c, ethyleneoxy protons H_d and H_e, and phenylic protons H₆ and H₇ moved upfield, while pyridinic protons H_a and benzylic protons H₅ shifted downfield. These evidences proved the formation of main-chain-type polyrotaxane and the existence of strong interactions between the host and dibenzylammonium moieties in CDCl₃. By comparing the integration of H_{6,c} with H_{6,uc} on the dibenzylammonium, we found that about 70% of dibenzylammonium moieties on the axis were bound with DP24C8 (Figure S5, Supporting Information). Moreover, the average degree of polymerization (DP) was determined to be around 5.0 by comparing the integration of H₆ on dibenzylammonium with that of H₁₃ or H₁₅ on the dimethylphenylene end-cap (Figure S5, Supporting Information).

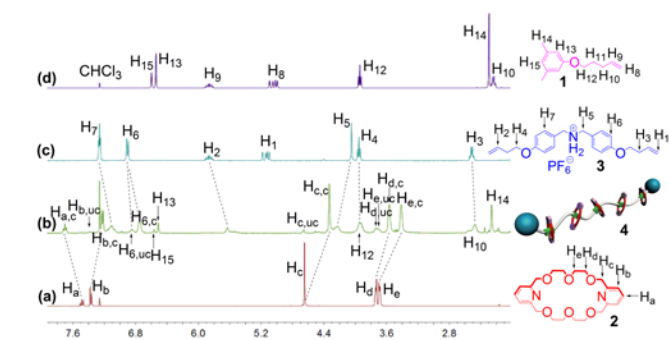


Figure 2 Partial proton NMR spectra (400 MHz, CDCl₃, 22 °C) of (a) **2**, (b) polyrotaxane **4**, (c) **3**, and (d) **1**. Complexed and uncomplexed species or moieties are denoted by “c” and “uc”, respectively.

In CD₃SOCD₃ (Figure 3), the peaks assignable to the protons on **2** and axis also separated into two sets, corresponding to the complexed and uncomplexed species or moieties. Compared to the proton NMR spectrum of polyrotaxane **4** in CDCl₃ (Figure 2b), the uncomplexed **2** and uncomplexed dibenzylammonium moieties increased, which was probably owing to that pseudorotaxane species and side interactions existing between the host and dumbbell-shaped/unstopped axis in CDCl₃ were destroyed in CD₃SOCD₃, a strong hydrogen bonding competitive solvent. By comparing both the integration of complexed **2** with uncomplexed **2** and the integration of complexed dibenzylammonium moieties with uncomplexed dibenzylammonium moieties, it was found that about 70% of **2** was mechanically interlocked into the dumbbell-shaped axis to occupy about 70% of dibenzylammonium moieties (Figure S6, Supporting Information). Correspondingly, there were obvious chemical shift changes of protons H_a, H_c, H_d, and H_e on the threaded **2** and protons H₅, H₆, and H₇ on the threaded dibenzylammonium moieties (Figure 3). These evidences indicated that mechanically interlocked polymer **4** formed although a small part of unlocked DP24C8 and uncomplexed dibenzylammonium moieties existed meanwhile.

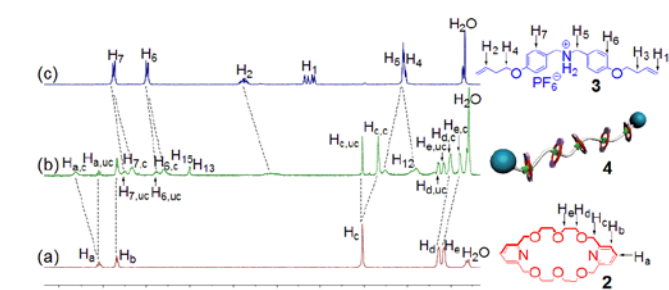


Figure 3 Partial proton NMR spectra (400 MHz, CD₃SOCD₃, 22 °C) of (a) **2**, (b) polyrotaxane **4**, and (c) **3**. Complexed and uncomplexed species or moieties are denoted by “c” and “uc”, respectively.

2-D NOESY NMR spectrum of polyrotaxane **4** in CDCl₃ (Figure 4) showed that the aromatic protons H₇ on the dialkylammonium moieties was correlated with the pyridinic protons H_{a,c} and ethyleneoxy protons H_{d,c} and H_{e,c} of **2**, while H_{6,c} on the dialkylammonium moieties was correlated with methylene protons H_{c,c}. NOE correlation signals were also observed for the aromatic protons H_{7,c} and ethyleneoxy protons H_{d,c} and H_{e,c} in CD₃SOCD₃ (Figure 5), confirming the existence of threaded structure in the main-chain-type polyrotaxane backbone.

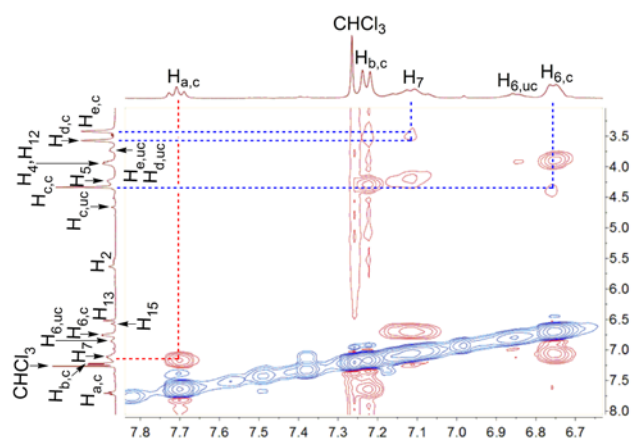


Figure 4 Partial NOESY spectrum of polyrotaxane **4** in CDCl_3 .

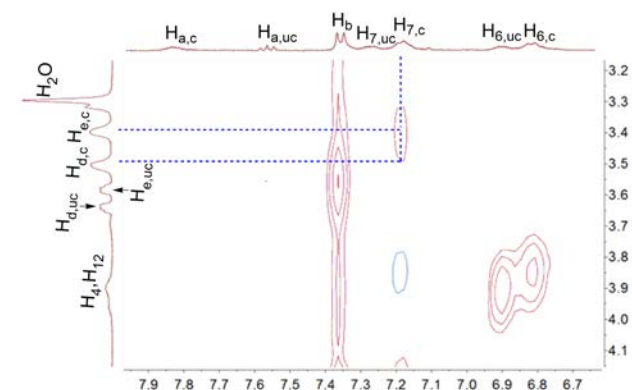


Figure 5 Partial NOESY spectrum of polyrotaxane **4** in CD_3SOCD_3 .

Polymer Characterization

The polyrotaxane **4** was further characterized by gel permeation chromatography (GPC) analysis. Using conventional calculations, polystyrene as the standard and DMF as the solvent, M_n and polydispersity of polyrotaxane **4** from GPC analysis (Figure S7, Supporting Information) were estimated to be 4.77 kDa and 1.42, respectively. This measured M_n value corresponded to about 5 rotaxane repeating units in a single polymer chain (Scheme 1), which was consistent with the average DP value calculated from the NMR integration.

The polymer behavior of polyrotaxane **4** was further confirmed by DSC from the second heating run (Figure S8, Supporting Information). As shown in the DSC curve, the heat absorption peak at 34.7 °C was obvious, which was attributed mainly to the glass transition temperature. The thermal stability of polyrotaxane **4** as investigated by thermogravimetric analysis (TGA) (Figure S9, Supporting Information) was good. About 5% weight loss was found up to 100 °C, which corresponded to the decomposition of PF_6 to HF. Upon heating to 200 °C, only slight decomposition was observed. After further heating to 400 °C, the weight for the linked alkyl groups and ethers in polyrotaxane **4** was successively lost, corresponding to about 55% of weight. At last the aromatic units and the counterions were left after 500 °C, which accounted for about 35% weight of **4**.

The atomic force microscopy (AFM) images (Figure 6a) of

polyrotaxane **4**, prepared by precipitation of an acetone solution into water, showed linear aggregation on the silica surface. Nonetheless, the scanning electron microscopy (SEM) images (Figure 6b), which were prepared by precipitation of a dichloromethane solution of **4** into water, exhibited nanoparticle aggregation with an average diameter of 200–500 nm. These microscopic characterizations provided further supports for the formation of polyrotaxane. The difference of morphologies exhibited by SEM and AFM is possibly due to the different solvents used for the preparation of the samples.

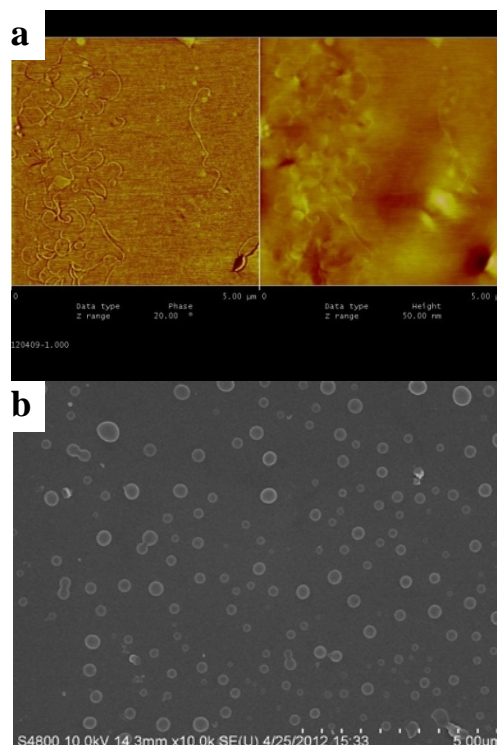


Figure 6 AFM (a) and SEM (b) images of polyrotaxane **4**.

Acid/base controllable molecular machine based on polyrotaxane **4**

The operation of polyrotaxane **4** as an acid/base controllable molecular machine took place upon the external stimuli, via adding trifluoroacetic acid (TFA)/triethylamine (TEA), owing to the basicity of pyridyls on DP24C8 (Figure 7). After the addition of TFA into a solution of polyrotaxane **4** in CDCl_3 , pyridyls on DP24C8 were protonated and the crown ether moieties moved from dibenzylammonium units to long-chain alkyl units due to the charge repulsion. When it was neutralized with equivalent TEA, DP24C8 spontaneously moved back to the secondary ammonium units promoted by the recovery of the host-guest recognition.

^1H NMR studies provided clear evidences for movements of the acid/base controllable molecular shuttle based on polyrotaxane **4** (Figure 8). After 13.6 equivalent of TFA was added to a 3.30 mM solution of **4**, the protons H_a , H_c , H_d , and H_e , on DP24C8, exhibited downfield shifts (Figure 8b vs Figure 8a). Most of the alkenyl protons H_2 simultaneously moved upfield to the position of $\text{H}_{2,c}$, while a small part of H_2 remained as $\text{H}_{2,uc}$, indicating that most of DP24C8 shuttled to the alkenyl or alkyl

units after acidification. After 13.6 equivalent of TEA was then introduced, the protons on both the host and axle of polyrotaxane **4** shifted back to the original state before TFA was added (Figure 8c vs Figure 8a), indicative of that the protonated DP24C8 was neutralized and the host moved back to the secondary ammonium units. Nonetheless, DP24C8 still stayed on the secondary ammonium units after 27.2 equivalent of TEA was further added (Figure 8d), which implied that the presence of excess TEA could not neutralize the secondary ammoniums on the axle of **4**.

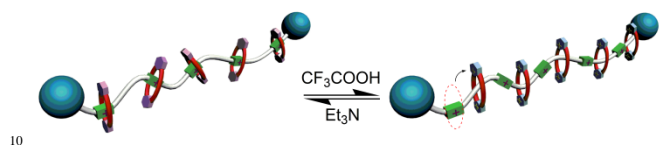


Figure 7 Cartoon illustration of acid/base controllable molecular machine based on polyrotaxane **4** (shown as an idealized state, fully threaded polyrotaxane).

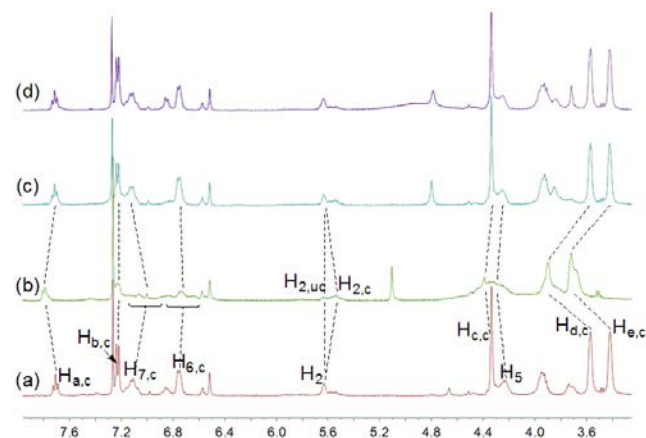


Figure 8 Partial proton NMR spectra of (400 MHz, CDCl_3 , 22 °C) (a) 3.30 mM **4**, (b) 3.30 mM **4** + 45.0 mM TFA, (c) 3.30 mM **4** + 45.0 mM TFA + 45.0 mM TEA, and (d) 3.30 mM **4** + 45.0 mM TFA + 90.0 mM TEA. Complexed and uncomplexed species or moieties are denoted by “c” and “uc”, respectively.

20 Reversible cross-linking of polyrotaxane **4**

The two pyridyls on DP24C8 could be further utilized as ligands for metal coordination to fabricate the metallic cross-linked polyrotaxane. When $[\text{PdCl}_2(\text{PhCN})_2]$ was added as a metal precursor, palladium(II) complexes could be formed with the pyridyl ligands on the hosts to cross-link the linear polyrotaxane **4** as illustrated in Figure 9. To investigate the feasibility of this approach, we studied the feed-ratio effect of $[\text{PdCl}_2(\text{PhCN})_2]$ on the formation of the cross-linked polyrotaxane (Figure 10). Upon progressive addition of $[\text{PdCl}_2(\text{PhCN})_2]$, the intensity of all protons on **4** subsequently decreased (Figure 10b–f vs Figure 10a) because the cross-linked polyrotaxane was produced and precipitated from the solution. Increasing the amount of $[\text{PdCl}_2(\text{PhCN})_2]$ favored the cross-linking process. The original signals of polyrotaxane **4** were almost disappeared when 10.0 equivalent of $[\text{PdCl}_2(\text{PhCN})_2]$ was added to the solution of **4**, which was an obvious evidence for the complete conversion from the linear polyrotaxane to the cross-linked polyrotaxane.

Deconstruction of the cross-linked polyrotaxane networks was triggered by the addition of a competitive ligand, PPh_3 . The

competition reaction for coordination at the metal center, to form the $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ complex and retrieve the linear polyrotaxane, was confirmed by the restoration of the protons' signals of **4**. When 2.00 equivalent (to the amount of $[\text{PdCl}_2(\text{PhCN})_2]$) of PPh_3 was added to the solution, the original linear polyrotaxane was almost entirely restored (Figure 10i vs Figure 10a). Therefore, the successive addition of the metal cross-linker $[\text{PdCl}_2(\text{PhCN})_2]$ and the use of the competitive ligand PPh_3 provide a convenient method for the reversible transition between linear and cross-linked polyrotaxane (Figure 9).

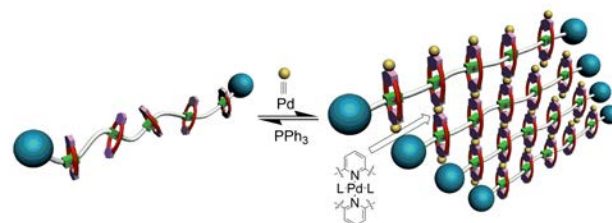


Figure 9 Cartoon illustration of the reversible cross-linking of polyrotaxane **4** (shown as an idealized state, fully threaded polyrotaxane).

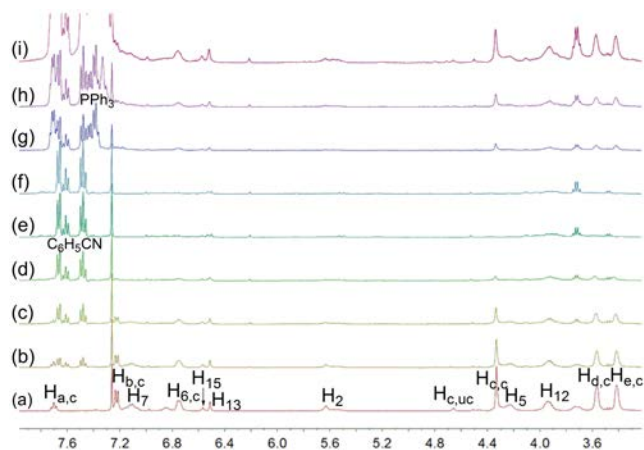


Figure 10 Partial proton NMR spectra of (400 MHz, CDCl_3 , 22 °C) (a) 3.30 mM **4**, (b) 3.30 mM **4** + 6.60 mM $[\text{PdCl}_2(\text{PhCN})_2]$, (c) 3.30 mM **4** + 13.2 mM $[\text{PdCl}_2(\text{PhCN})_2]$, (d) 3.30 mM **4** + 19.8 mM $[\text{PdCl}_2(\text{PhCN})_2]$, (e) 3.30 mM **4** + 26.4 mM $[\text{PdCl}_2(\text{PhCN})_2]$, (f) 3.30 mM **4** + 33.0 mM $[\text{PdCl}_2(\text{PhCN})_2]$, (g) 3.30 mM **4** + 33.0 mM $[\text{PdCl}_2(\text{PhCN})_2]$ + 26.4 mM PPh_3 , (h) 3.30 mM **4** + 33.0 mM $[\text{PdCl}_2(\text{PhCN})_2]$ + 33.0 mM PPh_3 , (i) 3.30 mM **4** + 33.0 mM $[\text{PdCl}_2(\text{PhCN})_2]$ + 66.0 mM PPh_3 . Complexed and uncomplexed species or moieties are denoted by “c” and “uc”, respectively.

The formation of the cross-linked polyrotaxane was also confirmed by AFM and SEM images (Figure 11). After **4** was cross-linked via Pd coordination, the morphology in AFM images changed from linear pattern to cross-linked nanoparticle aggregation (Figure 11a vs Figure 6a). The cross-linked morphology in SEM images (Figure 11b vs Figure 6b), which were prepared by precipitation of a chloroform solution of **4** into a solution of $[\text{PdCl}_2(\text{PhCN})_2]$, further provides a visible evidence for the formation of cross-linked polyrotaxane.

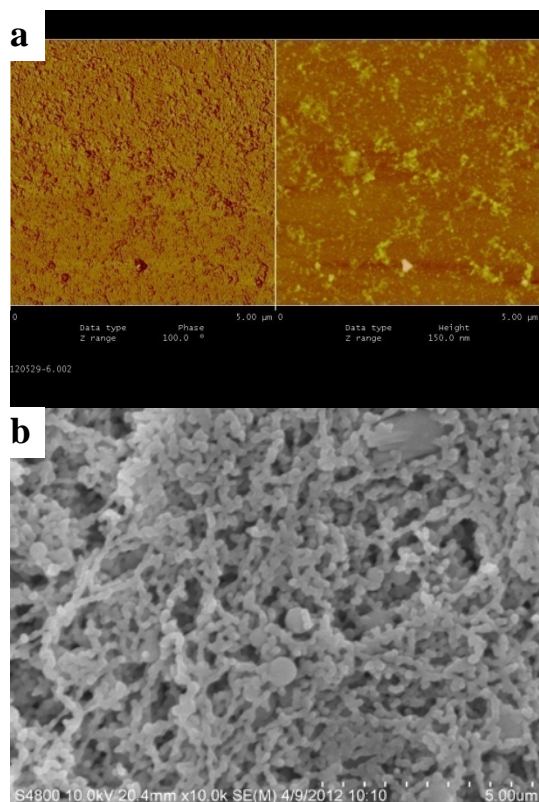


Figure 11 AFM (a) and SEM (b) images of the cross-linked polyrotaxane.

Conclusions

In summary, we have prepared a unique main chain-type polyrotaxane by using a one-pot synthesis strategy based on the dipyrido[24]crown-8/dialkylammonium recognition motif. The obtained polyrotaxane was characterized by various techniques including ^1H NMR, NOESY, GPC, TGA, DSC, SEM, and AFM. Its molecular weight M_n reached 4.77 kDa with polydispersity of 1.42 as determined by GPC, indicating 5 repeating units existed in a single polymer chain. It is another example to demonstrate that dynamic supramolecular monomers can be used to construct mechanically interlocked polymers efficiently and conveniently. Furthermore, based on this main chain-type polyrotaxane, a controllable molecular machine was furnished upon the external acid/base stimuli, and the reversible transition between linear and cross-linked polyrotaxane was achieved via successively adding a metal cross-linker $[\text{PdCl}_2(\text{PhCN})_2]$ and a competitive ligand PPH_3 . These studies not only provided a convenient method to fabricate main chain-type polyrotaxanes and therefore avoided the tedious synthesis of rotaxane monomers, but also furnished an alternative tool for the topological control and stimuli responsiveness of macromolecules, which benefits the construction of smart materials.

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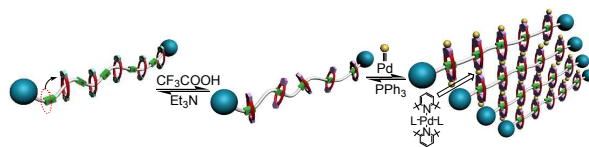
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Notes and references

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- † Electronic Supplementary Information (ESI) available: Complementary data for compound **1**, pseudorotaxane **2•3**, and polyrotaxane **4**. See DOI: 10.1039/b000000x/
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TOC Graphic:



- 5 A main chain-type polyrotaxane was fabricated based on the DP24C8/dialkylammonium recognition motif, in which the host could be controllably shuttled on the axle of the polyrotaxane upon acid/base stimuli and reversibly cross-linked via Pd coordination and decoordination.