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ARTICLE

High Yield Synthesis of Polyrotaxane Constructed from Pillar[5]arene and Viologen Polymer and Stabilization of Its Radical Cation

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ABSTRACT: New polyrotaxane composed of pillar[5]arene and viologen polymer was successfully prepared with extremely high yield by capping the chain ends with adamantyl moieties. Pillar[5]arene and viologen polymer are soluble in various solvents such as acetone, acetonitrile, methanol, DMF, and DMSO, while the polyrotaxane was soluble in DMF and DMSO and insoluble in the other organic solvents. Formation of *inter*-molecular hydrogen bonds between the OH moieties of pillar[5]arenes stabilized the structure and reduced the solubility. The polyrotaxane exhibited a thermally induced color change from yellow to violet. On heating, the *inter*-molecular hydrogen bond became weakened, and the shuttling motion of pillar[5]arenes on the polymer axis was fast. Thus, efficient electron transfer from the electron donors of pillar[5]arenes to the electron acceptor of viologen polymer occurred in the whole polymer chain and the radical cation species were stabilized.

Introduction

Polyrotaxanes have attracted much attention as new polymeric materials in which many cyclic molecules are mechanically incorporated onto a polymer chain.[1−6] Cyclodextrins (CDs)[7−14] and crown ethers[15−20] were initially utilized as the macrocyclic components for construction of polyrotaxanes. Harada et al. first reported the formation of CD-based polyrotaxanes.[7−9] Polypseudorotaxanes in which many α-CDs are threaded onto a polymer chain have been prepared, starting from poly(ethylene glycol) and α-CDs. The CD-based polyrotaxanes were prepared by capping the chain ends of the polypseudorotaxanes with bulky stoppers. Since these polyrotaxanes have many reactive OH groups from the CDs, they have been applied to topological gels and multivalent scaffolds.[21−24] Since cucurbiturils can also form very stable host−guest complexes with positively charged molecules in aqueous media, polypseudorotaxanes and polyrotaxanes consisting of cucurbiturils and positively charged polymers have been prepared.[25−28]

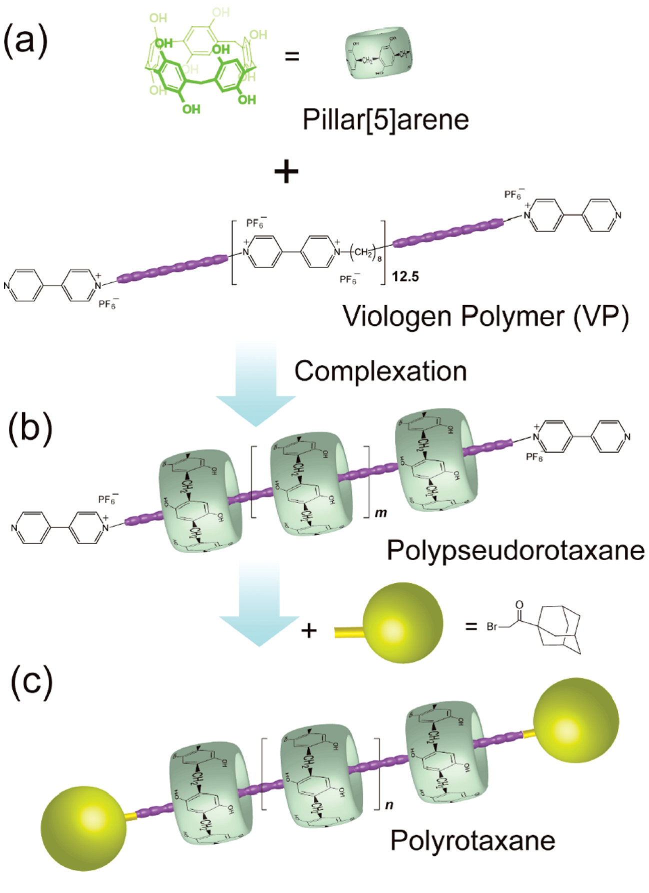

Figure 1. Preparation of pillar[5]arene-based polyrotaxane.

Recently, we synthesized a new type of host molecule for the first time and named it “pillar[5]arene” (Figure 1a).[29−35] The composition of pillar[5]arene is almost the same as that of typical calixarenes[36−41] and noria.[42−45] However, because its repeating units are connected by methylene bridges at the *para*-position, pillar[5]arene has a unique symmetrical pillar architecture, which is different from the basket-shaped structure of the *meta*-bridged calixarenes. Since pillar[5]arene is composed of the electron donor hydroquinone, it exhibits very interesting host−guest properties with electron accepting molecules such as viologen and pyridinium derivatives.[29] On the basis of the host−guest complexation between pillar[5]arene and viologen derivatives, we successfully synthesized a novel polypseudorotaxane constructed from pillar[5]arene as the cyclic rings and viologen polymer (Figure 1a, VP) as the polymeric chain.[35] When VP was mixed with pillar[5]arene, formation of the polypseudorotaxane took place (Figure 1b). However, VP with adamantyl groups at both ends did not form complexes with pillar[5]arene: due to the bulkiness of the adamantyl groups pillar[5]arene does not slip over the end group of the adamantyl moieties. Thus, the adamantyl group is a suitable stopper for synthesis of the polyrotaxane from pillar[5]arene and VP. In this study, we report new polyrotaxanes constructed

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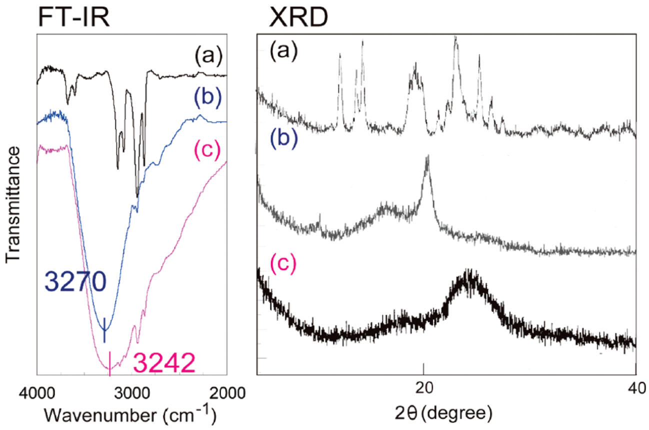

Figure 2. Partial FT-IR spectra and X-ray diffraction patterns of (a) VP, (b) pillar[5]arene, and (c) polyrotaxane.

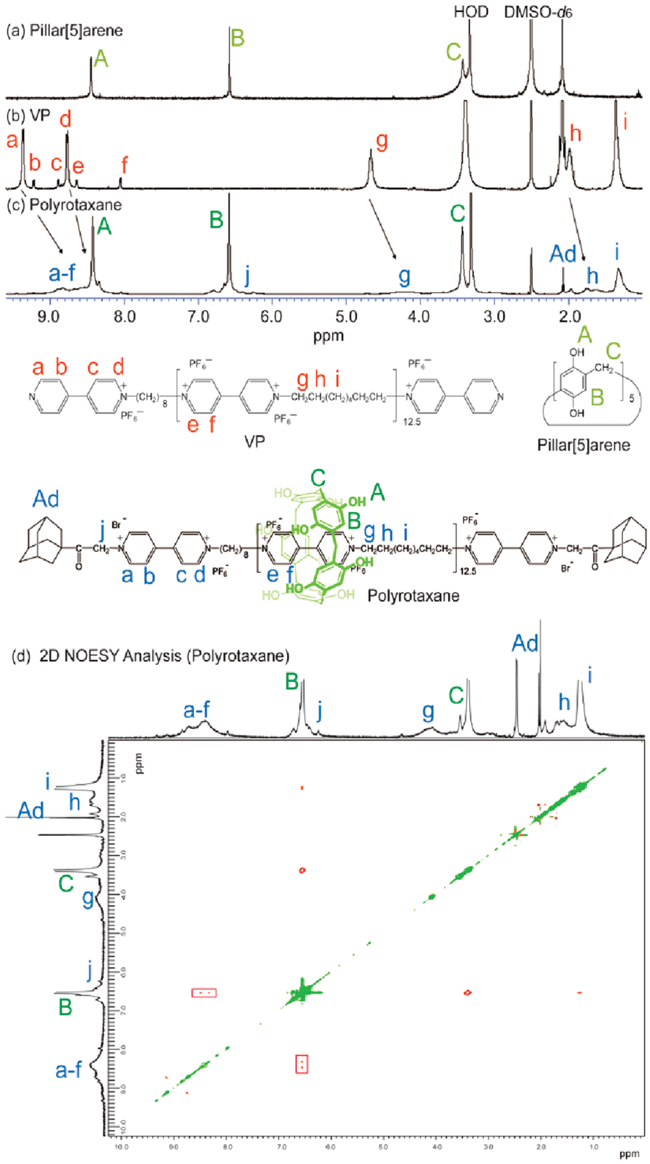

Figure 3. ^{1}H NMR spectra of (a) pillar[5]arene (1.0 mM), (b) VP (1.6 mM), and (c) polyrotaxane (5.0 mM) in DMSO-d_6 at 25 °C. (d) 2D NOESY analysis of polyrotaxane (5.0 mM) in DMSO-d_6 at 25 °C.

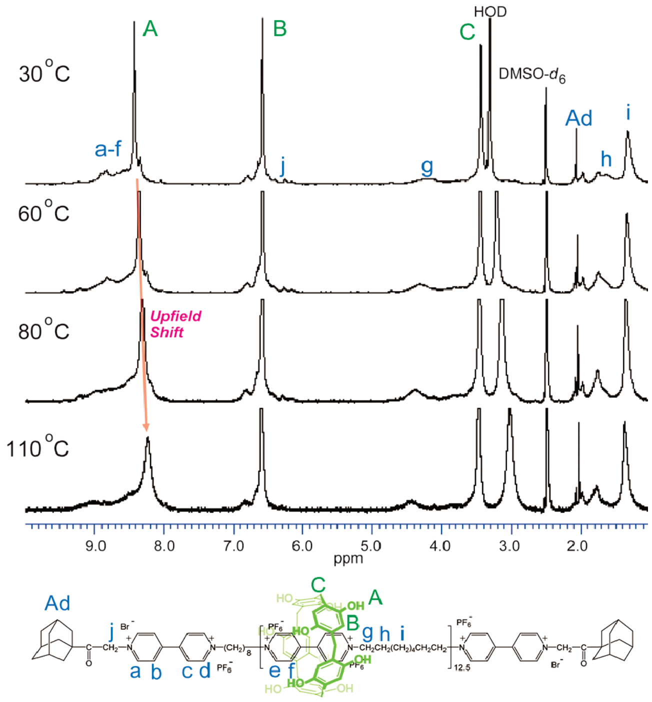

Figure 4. Variable-temperature ^{1}H NMR spectra of polyrotaxane (5.0 mM) in DMSO-d_6.

from pillar[5]arene and VP by capping the chain ends with adamantyl moieties (Figure 1c). Interesting thermally induced color changes of the pillar[5]arene-based polyrotaxanes are also reported.

Results and Discussion

We prepared the polyrotaxane by facile one-pot synthesis. VP and excess pillar[5]arene (25 equiv to VP) were dissolved in a mixed solvent (DMF:acetonitrile = 1:4 v/v). Because of low solubility of pillar[5]arene in acetonitrile, we used DMF as cosolvent. Then, the reaction mixture was stirred for 10 min at 25 °C. Complexation between VP and pillar[5]arenes quickly took place, thus the incubation time is enough. Then, excess amount of 1-adamantyl bromomethyl ketone (59.7 equiv to VP) was added to the mixture. The reaction mixture was heated at 100 °C for 6 h, and precipitate was observed to be formed during the reaction. The reaction mixture was evaporated to dryness. The residue was insoluble in acetonitrile, while pillar[5]arene, 1-adamantyl bromomethyl ketone and VP are soluble in acetonitrile. Thus, the residue was washed several times with acetonitrile to give the polyrotaxane. Interestingly, the pillar[5]arene-based polyrotaxane was isolated in extremely high yield (93.2%), due to the high stability of the complexes between pillar[5]arene and VP even in organic media, which is quite different from the behavior of the widely studied CD-based polypseudorotaxanes. Generally, formation of the CD-based polypseudorotaxanes hardly occurs in DMSO and DMF due to their amphiphilicity.[46,47] However, when pillar[5]arene was mixed with VP in DMSO, formation of the polypseudorotaxane took place.[35] High stability of the pillar[5]arene-VP complex led to the high yield synthesis of the pillar[5]arene-based polyrotaxane. The easy purification procedure (washing with acetonitrile) also facilitated the high yield synthesis.

Pillar[5]arene and VP are soluble in various solvents such as acetone, acetonitrile, methanol, DMF and DMSO, while the polyrotaxane was soluble in DMF and DMSO and insoluble in the other organic solvents. Formation of *inter*-molecular hydrogen bonds between the OH moieties of pillar[5]arenes stabilized the structure and reduced the solubility. The *inter*-molecular hydrogen bond was confirmed by FT-IR measurements (Figure 2, left). The OH stretching band of the pristine pillar[5]arene that was originally positioned at 3270 cm^{-1} (Figure 2b) shifted to 3242 cm^{-1} in the polyrotaxane (Figure 2c), strongly suggesting formation of the *inter*-molecular hydrogen bonding between OH moieties of pillar[5]arene molecules on the polymer axis. X-ray diffraction (XRD) patterns are shown in the right column of Figure 2. The patterns show that the polyrotaxane (Figure 2c) was crystalline, with crystal structure different from those of the constituents VP (Figure 2a) and pillar[5]arene (Figure 2b). The results indicate that the pillar[5]arene molecules on the polymer chain exhibit packing that is different from that of free pillar[5]arene; formation of the polyrotaxane structure changes the stacking structure of pillar[5]arene. The same trends are also observed in CD-based polyrotaxanes.[7−9]

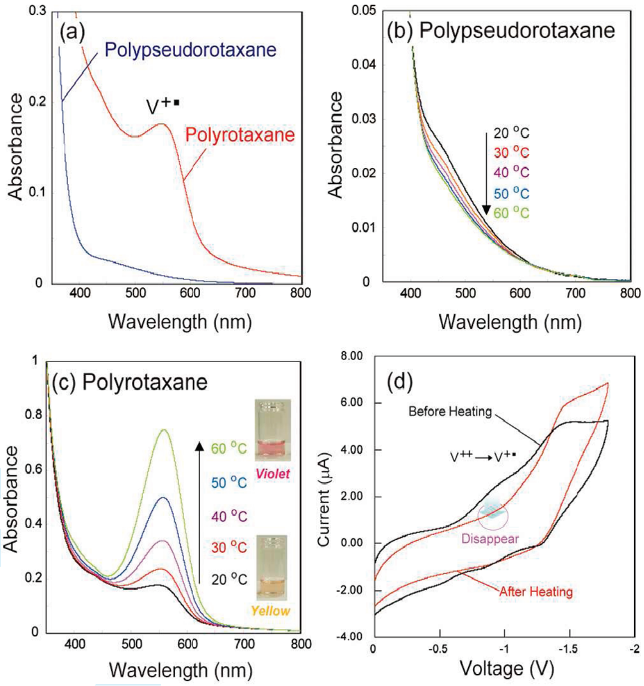

Figure 5. (a) UV−vis spectra of polypseudorotaxane [VP; 50.7 μM, pillar[5]arene; 963 μM (19 equiv to VP), blue line] and polyrotaxane (50.7 μM, red line) in DMSO. Variable-temperature UV−vis spectra of (b) polypseudorotaxane [VP; 50.7 μM, pillar[5]arene; 963 μM (19 equiv to VP)], and (c) polyrotaxane (50.7 μM) in DMSO. (d) Cyclic voltammogram of polyrotaxane (5.0 mM) before heating (black line) and after heating (red line) in DMF with 0.5 M Bu_4NPF_6.

Figure 3c shows ^{1}H NMR spectra of the polyrotaxane at 25 °C. The peaks from pillar[5]arene (peaks A-C), VP (peaks a−i) and adamantyl stopper (peaks j and Ad) were clearly observed. Compared to pristine VP (Figure 3b), the proton signals from the viologen and the methylene moieties (peaks a−f, g, h) clearly shifted upfield and broadened, whereas the resonance bands from the methylene linker (peak i) hardly changed. From 2D NOESY analysis (Figure 3d), NOE correlations were observed between the phenyl protons of pillar[5]arene and the protons of viologen moieties (red rectangles). These observations indicate that the viologen moieties are included in the cavity of pillar[5]arene.

Variable-temperature ^{1}H NMR spectra of the polyrotaxane are shown in Figure 4. Even on heating, the peaks from VP segments were hardly changed, indicating that pillar[5]arene molecules did not dethread from the viologen polymer chain. On the other hand, in the polypseudorotaxane between VP and pillar[5]arene, pillar[5]arenes dethreaded from the polymer axis at 110 °C.[35] Thus, the adamantyl moieties at both ends mechanically prevent pillar[5]arene molecules from dethreading. The OH proton peak (peak A) shifted upfield on heating. The chemical shift of the OH protons reflects the strength of the hydrogen bonding interactions,[48] and as the hydrogen bond interaction weakened, the chemical shift of the OH protons shifted upfield. Consequently, the *inter*-molecular hydrogen bond between pillar[5]arenes became weakened by heating, and the shuttling motion of pillar[5]arenes on the polymer axis should freely occur. Figure 5a shows UV−vis absorption spectra of the polypseudorotaxane and polyrotaxane. In the polypseudorotaxane (the mixture of VP and pillar[5]arene), a broad absorption band around 400−600 nm was observed. The band increased in intensity with increase in the concentration of pillar[5]arene (Supporting Information). Thus, the band is ascribed to the charge-transfer complex between VP and pillar[5]arene. The absorption spectrum of the polyrotaxane was

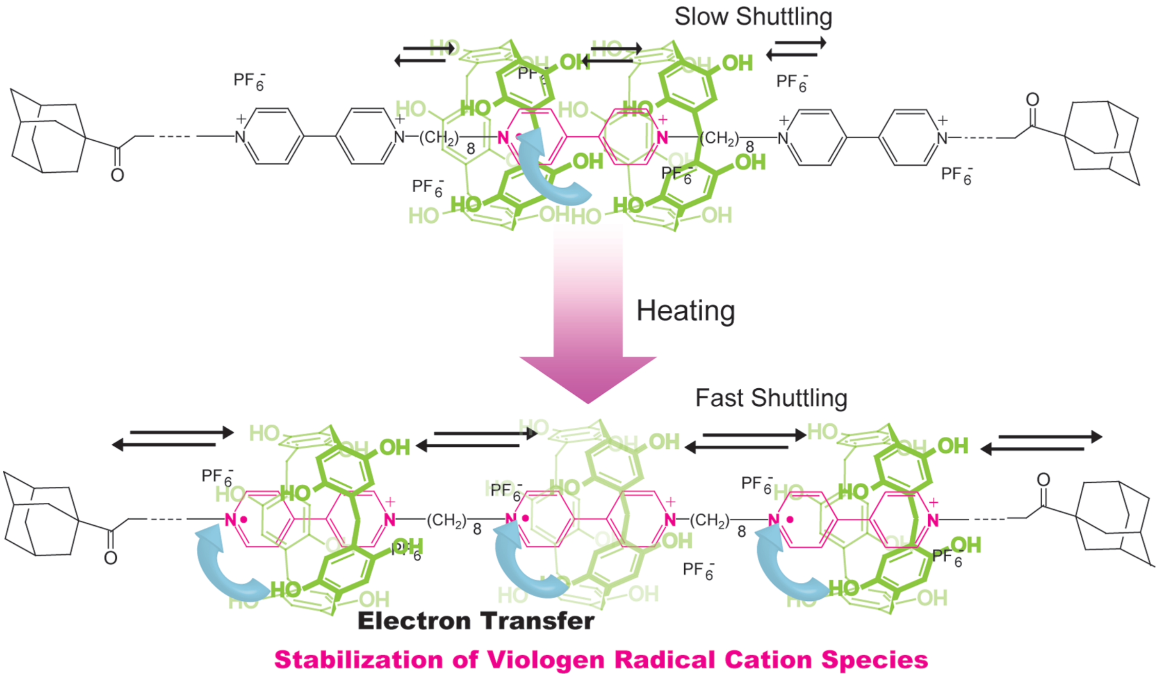

Figure 6. Proposed mechanism of thermally induced electron transfer from pillar[5]arene-based polyrotaxane.

quite different from that of the polypseudorotaxane. A clear absorption band was observed at 540 nm, which was ascribed to the viologen radical cation species.[49−52] In general, the viologen radical cation species are stabilized in the presence of excess electron donors. Since the electron donors of pillar[5]arene molecules were mechanically interlocked on the electron accepting polymeric chain of VP, the viologen radical cations were efficiently covered by electron donors of pillar[5]arenes. Thus, formation of the polyrotaxane led to stabilization of the viologen radical cation species. Figure 5b shows variable-temperature UV−vis spectra of the polypseudorotaxane. On heating, the shoulder from the charge-transfer complexes around 400−600 nm decreased. The data indicate that the charge-transfer complexation between pillar[5]arene and VP decreased on heating, due to dethreading of pillar[5]arenes from the VP chain. By contrast, when the polyrotaxane in DMSO was heated, the absorption peak at 540 nm dramatically increased (Figure 5c), which is the converse phenomenon compared with polypseudorotaxane. On heating, the solution color changed from yellow to violet (Figure 5c). The thermally induced color change was not observed in the polypseudorotaxane, thus, the phenomenon is specific to the polyrotaxane. Figure 6 shows the proposed mechanism of the thermally induced color change for the polyrotaxane. Since the electron donors of pillar[5]arenes covered the VP chain, viologen radical cation was generated. However, due to the *inter*-molecular hydrogen bonds at 20 °C, the shuttling motion of pillar[5]arene should not be fast. Thus, the viologen radical cation species was partially formed. By contrast, on heating, the *inter*-molecular hydrogen bond became weakened, and the shuttling motion of pillar[5]arenes on the polymer axis was fast. Thus, efficient electron transfer from the electron donors of pillar[5]arenes to the electron acceptor VP occurred in the whole polymer chain and the radical cation species were stabilized.

Cyclic voltammetry experiments also confirmed stabilization of the viologen radical cations by heating (Figure 5d). Before heating, in the potential range 0 to −1.8 V vs Ag/AgCl the polyrotaxane showed two typical reduction peaks at −0.99 and −1.4 V. The first and second peaks are associated with the conversion of V^{+2} (dication) to $V^{+\bullet}$ and $V^{+\bullet}$ to V (neutral state), respectively.[53] On heating the first reduction peak disappeared, indicating that V^{+2} species were completely reduced to $V^{+\bullet}$ by heating.

Conclusions

We synthesized new pillar[5]arene-based polyrotaxane by capping the chain ends. The yield of the pillar[5]arene-based polyrotaxane was extremely high (93.2%) compared with CD-, crown ether- and cucurbituril-based polyrotaxanes.[7−9,11,12,14−28] Variable-temperature ^{1}H NMR measurements confirmed that pillar[5]arene molecules did not dethread from the polymer axis. Formation of the polyrotaxane generated the radical cation species, and on heating the radical cation species became stabilized. While photosensitive electron transfer based on supramolecular structures were reported,[49,50] to the best of our knowledge, this is the first example of thermally sensitive electron transfer based on polyrotaxane. It is very interesting that the shuttling behavior of the pillar[5]arene molecules affects the electron transfer. The polyrotaxane constructed from pillar[5]arene has many reactive phenol groups. Consequently, as with the CD-based polyrotaxanes the polyrotaxanes containing pillar[5]arenes will be applicable to topological gels and multivalent scaffolds. This is now under investigation.

Experimental Section

Materials. All solvents and reagents were used as supplied except the following. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Kanto Reagents, Chemicals & Biologicals. Milli-Q water was used for preparation of aqueous solutions.

Measurements. The ^{1}H NMR spectra were recorded at 500 and 400 MHz and ^{13}C NMR spectra were recorded at 125 and 100 MHz with a JEOL-ECA 500 and JEOL-JNM EX400 spectrometers, respectively. UV−vis absorption spectra were recorded with a JASCO V-670. For UV−vis measurements, one centimeter quartz cuvets were used. Cyclic voltammetry was carried out using BAS CV-1200A voltammetric analyzer with a 0.5 M DMF solution containing Bu_4NPF_6 as an electrolyte. The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer.

Synthesis of Viologen Polymer (VP). Viologen polymer (VP) was prepared according to the previous paper.[54] The average number of repeating units (*n*) determined from the peak integration ratio of the viologen proton peak to the proton peak from the end-group using ^{1}H NMR measurement was found to be 12.5.

Synthesis of Polyrotaxane. To a solution of pillar[5]arene (0.60 g, 0.98 mmol) in a mixture of acetonitrile (40 mL) and DMF (10 mL) was added VP (0.30 g, 0.039 mmol), and the reaction was stirred for 10 min at 25 °C. Then, 1-adamantyl bromomethyl ketone (0.60 g, 2.33 mmol) was added to the solution, and the mixture was heated at 100 °C for 6 h. The solution was evaporated to dryness. The residue was washed several times with acetonitrile to give polyrotaxane (0.36 g, yield 93.2%). ^{1}H NMR (DMSO-d_6, 400 MHz, 25 °C, TMS): $\delta =$ 9.50−7.80 (protons from viologen and OH of pillar[5]arene), 7.00−6.10 (phenyl protons of pillar[5]arene and adamantyl moieties), 4.80−4.00 (N−CH_2−), 3.80−3.40 (protons of methylene bridge), 2.20−1.80 (protons from adamantyl moieties), 1.80−1.20 (protons from octyl moieties. ^{13}C NMR (DMSO-d_6, 100 MHz, 25 °C, TMS): δ = 175.2, 173.9, 171.9, 148.7, 147.9, 137.2 (C of phenyl, C=O and viologen moieties), 66.5 (C of C=O), 37.1, 28.9, 27.0, 26.0, 24.6, 22.5 (C of methylene bridge and octyl moieties).

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Supporting Information Available: Figures showing UV−vis spectra of VP by adding pillar[5]arene and full XRD patterns of VP, pillar[5]arene, and polyrotaxane. This material is available free of charge via the Internet at http://pubs.acs.org.

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