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Polypseudorotaxane Constructed from Pillar[5]arene and Viologen Polymer

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Introduction. Polypseudorotaxanes and polyrotaxanes constructed through complexation of covalent polymers with macrocyclic molecules have attracted tremendous interest in the fields of supramolecular, material and biomedical chemistry because the macrocyclic rings move freely and rotate on the polymer axis.[1] For construction of polypseudorotaxanes and polyrotaxanes, cyclodextrins[2–4] and crown ethers[5] were initially utilized as the macrocyclic components. Harada et al. first reported the formation of polypseudorotaxanes consisting of cyclodextrins and linear polymers such as poly(ethylene glycol) and poly(propylene glycol).[2] Cyclodextrin molecules are spontaneously threaded onto the polymer chain in water due to hydrophobic interactions between the linear polymer chain and the inner cavity of the cyclodextrin. Moreover, by addition of bulky end-capping groups to the polypseudorotaxanes, cyclodextrin-based polyrotaxanes were successfully synthesized.[3] 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.[6]

We recently synthesized a new type of host molecule and named it "pillar[5]arene" (Figure 1a).[7,8] The composition of pillar[5]arene is almost the same as that of typical calixarenes.[9] 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 an electron donor of hydroquinone, it exhibits very interesting host−guest properties with electron accepting molecules such as viologen and pyridinium derivatives.[7] Therefore, in the present communication we report a novel polypseudorotaxane constructed from pillar[5]arene as the cyclic rings and viologen polymer as the polymeric chain (Figure 1b). We investigated the effects of the end-group and the length of the linker between the viologen moieties on complexation of the viologen polymers with pillar[5]arene. Moreover, intriguing solvent-dependent shuttling behavior of pillar[5]arene along the polymer axis is reported.

Results and Discussion. We prepared viologen polymers containing linkers with different lengths between the viologen moieties [Figure 1b, VP-3 (m = 3), VP-8 (m = 8)]. In addition, by using VP-8 as a starting material, the adamantane-capped viologen polymer (Figure 1b, VP-8-Ad) was prepared. By using ^{1}H NMR measurements, the average number of repeating units (n) was determined from the peak integration ratio of the viologen proton peak to the proton peak from the end-group.

Figure 2a shows the ^{1}H NMR spectra of VP-8 upon addition of pillar[5]arene in acetone-d_6/acetonitrile-d_3 (1:1 v/v). The proton signals from the viologen (peak i) and the methylene moieties (peaks b and c) clearly shifted upfield, whereas the resonance bands from the methylene linker (peak a) hardly changed. The peaks of pillar[5]arene slightly shifted downfield and became broadening by mixing pillar[5]arene with VP-8. These trends were also observed in the host−guest complex between pillar[5]arene and octyl viologen salt, which was constituent unit model of VP-8.[7] From 2D ROESY analysis, ROE correlations were observed between the phenyl protons of pillar[5]arene and the viologen moieties of VP-8 (Supporting Information). These observations indicate that the viologen and the methylene moieties adjacent to the N atoms were included in the cavity of pillar[5]arene. The peaks of the viologen and the methylene moieties showed a shift, thus the shuttling movement of pillar[5]arene along the polymer axis was fast on the NMR time scale (Figure 3a). By contrast, when pillar[5]arene was mixed with VP-8 in DMSO-d_6, the peaks from the viologen (peak (i) and the methylene moieties (peaks b and c) became split (Figure 2b). In DMSO-d_6, pillar[5]arene interacted with VP-8, as occurred in acetone-d_6/acetonitorile-d_3 (1:1 v/v). However, the situation is unlike the case of acetone-d_6/acetonitorile-d_3 (1:1 v/v). In DMSO-d_6, a new set of split peaks from complexed and free species of VP-8 was observed; thus, the shuttling movement of pillar[5]arene in DMSO-d_6 was slow on the NMR time scale (Figure 3b). In DMSO-d_6, at temperatures above 60 °C, the shuttling movement of pillar[5]arene was fast on the NMR time scale, and pillar[5]arene molecules dethreaded from the viologen polymer chain at temperatures above 110 °C (Supporting Information). Generally, formation of host−guest complexes hardly occurs in DMSO due to the amphiphilicity of DMSO.[10] Thus, the formation of the polypseudorotaxane in DMSO is interesting, and the pillar[5]arene-based polypseudorotaxane should be quite different from widely studied cyclodextrin-based polyrotaxanes. Formation of the host−guest complex between pillar[5]arene and VP-8 was also examined by UV−vis measurements (Supporting Information). The broad absorption band that was observed from 700 nm increased in intensity with increase in the concentration of pillar[5]arene. The band is ascribed to the charge-transfer complex between VP-8 and pillar[5]arene.

When VP-8-Ad was mixed with pillar[5]arene in DMSO-d_6, changes in the peaks were not observed (Supporting Information). Pillar[5]arene did not slip over the end group of the adamantyl moieties due to the bulkiness of the adamantyl stopper (Figure 3c). The observation implies that pillar[5]arene threaded onto the polymer axis of

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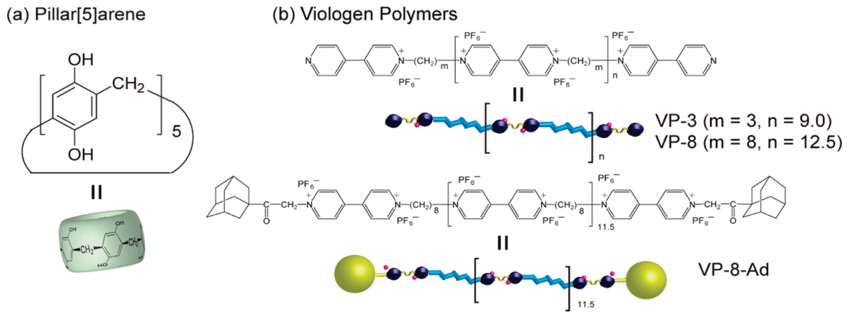

Figure 1. (a) Pillar[5]arene used as ring and (b) viologen polymers used as polymeric chain in this work.

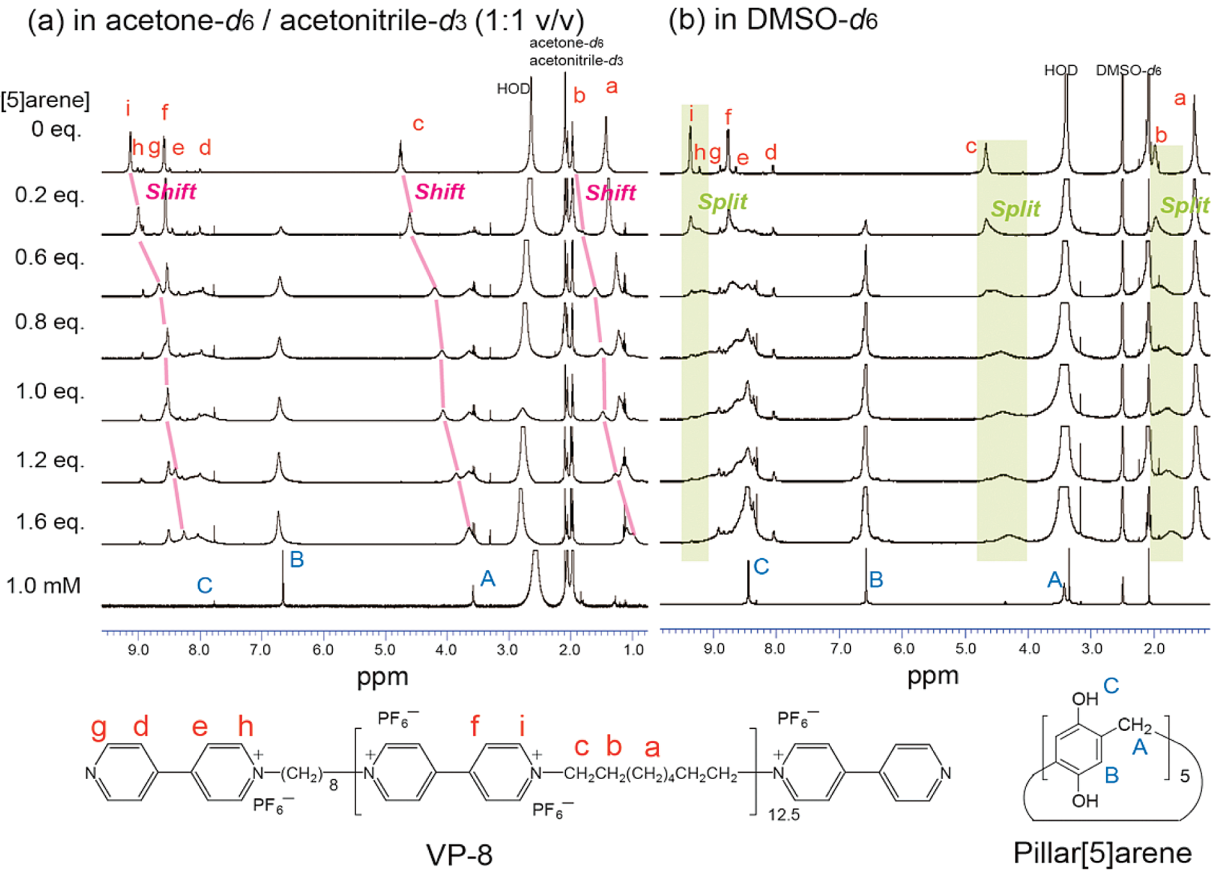

Figure 2. ^{1}H NMR spectra of VP-8 (1.6 mM) upon addition of pillar[5]arene (0−1.6 equiv to viologen unit) in (a) acetone-d_6/acetonitrile-d_3 (1:1 v/v) and (b) DMSO-d_6 at 25 °C. At the bottom, ^{1}H NMR spectra of pillar[5]arene (1.0 mM) in (a) acetone-d_6/acetonitrile-d_3 (1:1 v/v) and (b) DMSO-d_6 at 25 °C are shown.

VP-8 from both ends. By using VP-3 as the polymer axis, small peak shifts from the viologen and the methylene moieties around the N atoms were observed. The values of the peak shifts of the methylene protons adjacent to the N atoms resulting from adding pillar[5]arene are shown in Figure 4. In case of VP-8, even with small amount of pillar[5]arene, large peak shift was quickly observed. On the other hand, in VP-3, the values of the peak shift were gradually increased with pillar[5]arene. These data indicate that the interaction of pillar[5]arene with VP-8 is stronger than with VP-3. Because of the bulkiness of pillar[5]arene, the length between the viologen moieties in VP-3 may be too short to form stable complexes.

Conclusions. We successfully synthesized a new polypseudorotaxane from pillar[5]arene and viologen polymer. The shuttling movement of pillar[5]arene in acetone-d_6/acetonitrile-d_3 (1:1 v/v) was fast on the NMR time scale, whereas in DMSO-d_6 the shuttling motion of pillar[5]arene along the polymer axis was slow on the NMR time scale. Formation of the host−guest complex depended on the length of the linker between viologen moieties. The host−guest interaction of pillar[5]arene with VP-8 is stronger than with VP-3. Since the adamantyl moiety is large enough to prevent the threading of pillar[5]arene, VP-8-Ad did not form a complex with pillar[5]arene. Thus, the adamantyl group is a suitable stoppers for synthesis of the polyrotaxane from pillar[5]arene and VP-8. We are preparing the polyrotaxane by attaching adamantane stoppers to both ends of the polypseudorotaxane between pillar[5]arene and VP-8.

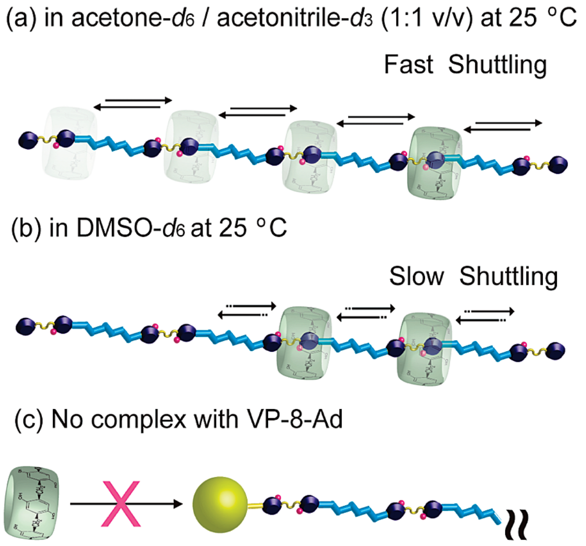

Figure 3. Complexation behaviors of pillar[5]arene with (a) VP-8 in acetone-d_6/acetonitrile-d_3 (1:1 v/v), (b) VP-8 in DMSO-d_6, and (c) VP-8-Ad in DMSO-d_6.

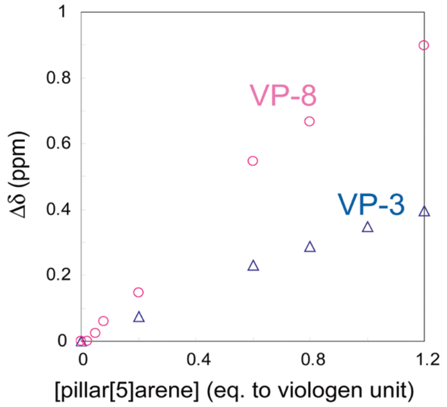

Figure 4. Peak shift of the resonance band attributed to methylene proton adjacent to the N atoms of VP-8 (pink square) and VP-3 (blue triangle) with varying concentration of pillar[5]arene in acetone-d_6/acetonitrile-d_3 (1:1 v/v).

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Supporting Information Available: Experimental section, UV−vis spectra of VP-8 by adding pillar[5]arene, variable-temperature ^{1}H NMR spectra of VP-8 with pillar[5]arene in DMSO-d_6, and ^{1}H NMR spectra of VP-8-Ad with pillar[5]arene. This material is available free of charge via the Internet at http://pubs.acs.org.

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