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Light-Controllable Cucurbit[7]uril-Based Molecular Shuttle

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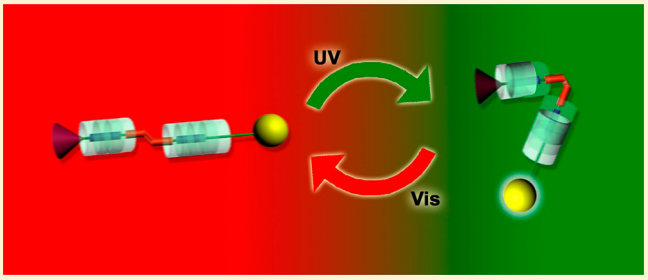
Supporting Information

ABSTRACT: The design and construction of novel artificial molecular machines can be categorized as a currently important field of modern chemistry. In the present work, a novel photoresponsive [3]rotaxane containing two cucurbit[7]uril (CB[7]) rings and a dumbbell component consisting of one *trans*-azobenzene unit along with two viologen units was developed. Each viologen group was encircled by a CB[7] ring with a rapid shuttling equilibration distribution extended to the *trans*-azobenzene unit located in the middle of the dumbbell component. Upon the *trans*-to-*cis* photoisomerization of the azobenzene unit under UV light irradiation, a shuttling restriction of the CB[7] rings along the dumbbell component was observed. The equilibration distribution of the macrocycles on the dumbbell component can be recovered by the *cis*-to-*trans* photoisomerization of the azobenzene unit under visible light irradiation. Such a controllable shuttling process was fully characterized by ^{1}H NMR spectroscopy and was easily indicated by fluorescent changes of the [3]rotaxane.



INTRODUCTION

Mechanically interlocked molecules (MIMs) that bear a controlled relative motion pattern between components have been studied extensively because these fascinating prototypes present great potentials for applications in artificial molecular switches and machines.[1] Among these MIMs, light-driven molecular shuttles or motors are of considerable interest because their response to a photochemical process is usually rapid and precise and can be operated remotely without generating any chemical waste.[2] In particular, dynamically driven shuttling via photoisomerization is more popular, as such a process can be easily conducted in situ.[3] Cucurbit[*n*]urils (CBs) are an important class of macrocyclic molecules which stand out among molecular hosts on account of their water solubility, structural symmetry, and selective recognition toward positively charged species with extremely high binding constants (up to 10^{15} M^{-1} in water).[4] Due to these features, the CB rings have been employed to fabricate robust host–guest architectures or networks for a variety of applications.[5] Research on CB-based molecular shuttles directly driven by the photoisomerization is, however, still scarce, and only a few of research groups have demonstrated CB-based host–guest complexes with a light-driven association/dissociation process to the best of our knowledge.[6] Constructing light-controllable CB-based rotaxanes remains a challenge, simply because the binding abilities of the CB rings with light-active groups (e.g., azobenzene and stilbene) are relatively low.

In order to overcome this obstacle, a model MIM with a shuttling equilibrium distribution of the CB ring along the axle was taken into consideration. Viologen unit can be effectively complexed by the CB[7] ring with a high binding affinity (10^5 to 10^6 M^{-1}), and this host–guest inclusion process can be extended to the nearby groups via an equilibrating distribution of the ring at room temperature.[7] Herein, a [3]rotaxane (**R1** in Figure 1) containing two CB[7] rings and a dumbbell component comprising an azobenzene group directly linked by two viologen units was synthesized. Since the shuttling equilibrium distribution of the CB[7] rings in the [3]rotaxane was extended from the viologen units to the azobenzene one, the shuttling process was affected by the *trans*–*cis* photoisomerization of the azobenzene unit. The isophthalate group was introduced as one stopper of the CB[7]-based [3]rotaxane **R1** that was prepared by a slippage approach,[9] while the naphthalimide moiety was chosen as the other stopper as well as a fluorescence indicator. Because the dumbbell compound (**1** in Figure 1) is unsymmetrical and relatively complicated, we also prepared two simplified dumbbell-like compounds (**2** and **3**) for the constructions of CB[7]-based [2]rotaxanes (**R2** and **R3**) as references.

The synthetic route and details for the preparation of the dumbbell compounds **1**–**3** and the rotaxanes **R1**–**R3** are presented in the Experimental Section. An improved slippage approach[8] was employed to prepare these CB[7]-based rotaxanes. Taking advantage of the annular diameter (5.4–7.3 Å)[4c,d] of the CB[7] ring that closes to the size of the stopper isophthalic acid (7.0 Å), in our study, the CB[7] rings were threaded onto the dumbbell components in boiling water at

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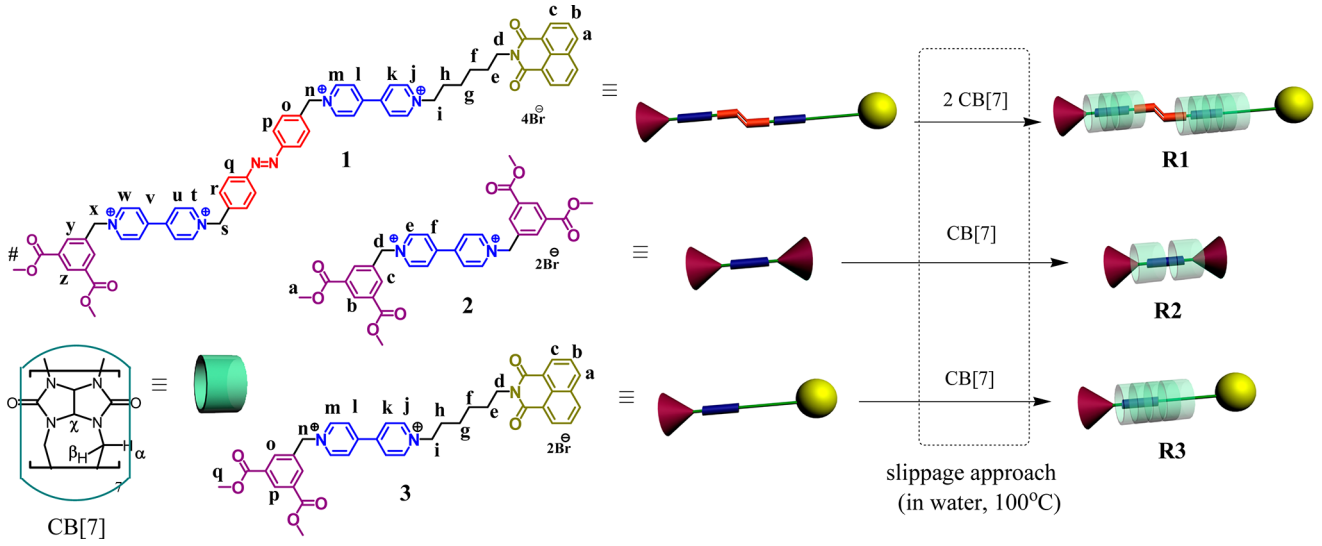

Figure 1. Schematic representations of dumbbell molecules **1**–**3** and the corresponding rotaxanes **R1**–**R3**. The protons are defined alongside the structural formula.

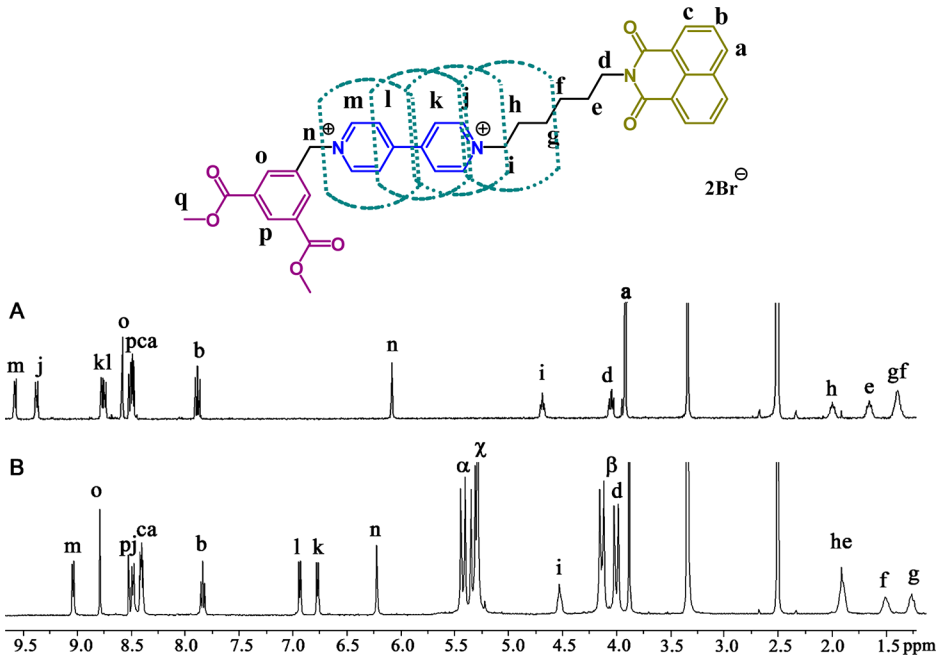

Figure 2. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) of (A) dumbbell molecule **3** and (B) [2]rotaxane **R3** along with a conformational representation of the CB[7] shuttling distribution.

100 °C, a temperature when the CB[7] ring was expanded. Once the solution was cooled to room temperature, the rings were shrinked back and were prevented by the isophthalate stopper from dethreading, resulting in the formations of the corresponding rotaxanes in a relatively high yield without the purification by column chromatography. This synthetic methodology was clearly evidenced by the NMR and MS spectra of the rotaxanes **R1**–**R3**. As 1-adamantanamine hydrochloride presents a high binding affinity of over 10^{12} M^{-1} with CB[7] at room temperature, it would competitively bind with the CB[7] ring if **R1** is a complex. In a control experiment, there was no ^{1}H NMR spectral change observed when mixing an excess amount of 1-adamantanamine hydrochloride with **R1**, confirming the formation of the rotaxane architecture (Figure S1 in the Supporting Information). The CB[7] ring cannot be threaded by the dumbbell molecule at room temperature because there was no proton shift observed from the dumbbell molecule in the presence of the CB[7] ring at room temperature in either water or dimethyl sulfoxide (DMSO) (Figures S2 and S3 in the Supporting Information). Since the rotaxanes show relatively low water solubility, we performed the experiments in DMSO.

RESULTS AND DISCUSSION

Shuttling of CB[7] in Rotaxanes. Although the NOE patterns in ^{1}H NOESY spectra were employed to assist the characterizations (Figures S4–S7 in the Supporting Information), it was still not easy to assign all the proton resonances in [3]rotaxane **R1**. Therefore, two reference rotaxanes **R2** and **R3** with relatively simple structures were investigated first. It is

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well-known that the proton resonances of a guest molecule exhibit upfield shifts when it is located in the CB cavity on account of the shielding effect, while the resonances will undergo downfield shifts when the guest molecule is outside the cavity and near the portal of the CB ring owing to a deshielding effect.[9] The resonances of the protons $H_{g\text{-}m}$ in the ^{1}H NMR spectrum (Figure 2) of [2]rotaxane **R3** shift upfield, whereas those of the protons H_f and H_n shift downfield, as compared with the corresponding protons in the dumbbell molecule **3**. These results clearly indicate that the protons $H_{g\text{-}m}$ are inside the CB[7] cavity, and the CB[7] ring shuttles around the viologen unit within the range between the protons H_f and H_n on the NMR time scale at room temperature. Other protons in the dumbbell component are far away from the CB[7] ring and are scarcely affected by the ring. As compared to the ^{1}H NMR spectrum of the dumbbell compound **2**, the resonance shifts of some protons can be observed in the spectrum of [2]rotaxane **R2** (Figure 3). There was no new proton peak

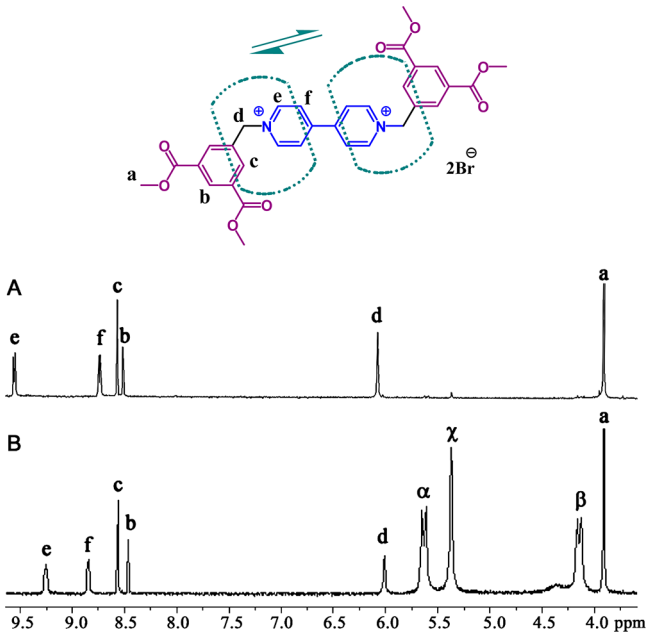

Figure 3. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) of (A) dumbbell molecule **2** and (B) [2]rotaxane **R2** along with a conformational representation of the CB[7] shuttling distribution.

observed, indicating that [2]rotaxane **R2** remains a symmetric conformation on the NMR time scale. The resonances of the protons H_d and H_e on the dumbbell shift upfield, whereas that of H_f shift downfield in the ^{1}H NMR spectrum of [2]rotaxane **R2**, demonstrating that the protons H_d and H_e are inside the CB[7] cavity while the protons H_f are around the rim of the ring. According to the fact that these proton signals are still coalesced, it can be concluded that the CB[7] ring in [2]rotaxane **R2** shuttles rapidly along the axle with a main distribution on two pyridinium units of the viologen moiety in order to include the protons H_d and H_e.

The formation of [3]rotaxane **R1** was confirmed by the ^{1}H NMR and ESI-MS studies, indicating a 2:1 host−guest architecture. It was not easy to prepare a CB[7]-based [2]rotaxane from dumbbell molecule **1**. Even an equal amount of the CB[7] ring and dumbbell molecule **1** was added, the product was still the [3]rotaxane where one dumbbell was encircled by two CB[7] rings, simply because of the coexistence of two viologen binding sites on the dumbbell component for the encirclement of two CB[7] rings. With the assistance from the control studies of [2]rotaxanes **R2** and **R3**, all of the proton signals in [3]rotaxane **R1** can be assigned. As seen from Figures 4 and 5, the resonances of the protons $H_{g\text{-}o}$ and $H_{r\text{-}w}$ in [3]rotaxane **R1** reveal upfield shifts, while only the protons H_e, H_f, H_p, H_q, and H_x show downfield shifts. These observations indicate that the two CB[7] rings shuttle separately around each viologen unit. Their shuttling ranges are along the axle from H_f to H_p and from H_q to H_x, respectively, demonstrating that the shuttling equilibrium distributions of the two CB[7] rings are extended from the viologen units to the phenyl groups of the azobenzene unit. The thermal stability of the [3]rotaxane was also investigated. Heating the temperature to 90 °C followed by cooling to room temperature can enable the [3]rotaxane to change back to the initial state (Figure S8 in the Supporting Information).

Restriction of Shuttling Equilibration Distribution upon Photoisomerization. Upon UV light irradiation, the ^{1}H NMR spectra of both dumbbell molecule **1** and [3]rotaxane **R1** show a group of upfield shifts for the protons $H_{o\text{-}r}$ in the aromatic region, corresponding to the azobenzenyl unit turning from the *trans* form to its *cis* form. The maximum photoisomerization efficiency is 40−50% according to the NMR integral studies of these protons. In contrast, the resonances of the protons H_j, H_m, H_t, and H_w on the viologen units as well as other protons on the dumbbell component did not show obvious shifts (Figure 5A,D for comparison). Similar to the case in the initial *trans* form of [3]rotaxane **R1**, two CB[7] rings can still shuttle around the viologen units in the *cis* form of [3]rotaxane **R1**, evidenced by the upfield shifts of the protons $H_{j'}$, $H_{m'}$, $H_{o'}$, $H_{r'}$, $H_{t'}$, and $H_{w'}$ as well as the downfield shifts of the protons $H_{p'}$ and $H_{q'}$ (Figure 5C,D for comparison). However, the extent of these resonance shifts in the *cis* form is different as compared with the corresponding resonance shifts in the *trans* form. Each of those protons $H_{j'}$, $H_{m'}$, $H_{t'}$, and $H_{w'}$ on the viologen units exhibits bigger upfield shift ($\Delta\delta H_{j'}$ = −0.78 ppm, $\Delta\delta H_{m'}$ = −0.67 ppm, $\Delta\delta H_{t'}$ = −0.84 ppm, and $\Delta\delta H_{w'}$ = −0.53 ppm, the resonance peaks labeled in blue in Figure 5C,D) than corresponding protons in the *trans* form ($\Delta\delta H_j$ = −0.73 ppm, $\Delta\delta H_m$ = −0.61 ppm, $\Delta\delta H_t$ = −0.72 ppm, and $\Delta\delta H_w$ = −0.50 ppm, the resonance peaks labeled in blue in Figure 5A,B). On the contrary, the protons $H_{o'/r'}$ and $H_{p'/q'}$ on the azobenzene unit show less upfield and downfield shifts, respectively ($\Delta\delta H_{o'}$ = −0.10 ppm, $\Delta\delta H_{r'}$ = −0.30 ppm, $\Delta\delta H_{p'}$ = +0.08 ppm, and $\Delta\delta H_{q'}$ = +0.14 ppm, the resonance peaks labeled in red in Figure 5C,D) than corresponding protons ($\Delta\delta H_o$ = −0.30 ppm, $\Delta\delta H_r$ = −0.51 ppm, $\Delta\delta H_p$ = +0.09 ppm, and $\Delta\delta H_q$ = +0.16 ppm, the resonance peaks labeled in red in Figure 5A,B). These observations indicate a compensation mechanism; that is, the shuttling equilibrium distribution of the CB[7] rings was partly diverted from the azobenzene unit to the viologen units on account of structural restriction after the *trans*-to-*cis* photoisomerization (Figure 6). The distribution of the CB[7] rings on the alkyl chain was not significantly affected by the photoisomerization because there were no proton shifts observed in ^{1}H NMR spectra. Thus, a light-controlled ring shuttling mechanism that relied on the equilibrium distribution change was demonstrated for the [3]rotaxane.

Shuttling Equilibrium Distribution Change Indicated by Spectra. The fluorescent band at ∼385 nm basically originates from the emission of the 1,8-naphthalimide group. The *trans*-to-*cis* photoisomerization of the dumbbell molecule **1**

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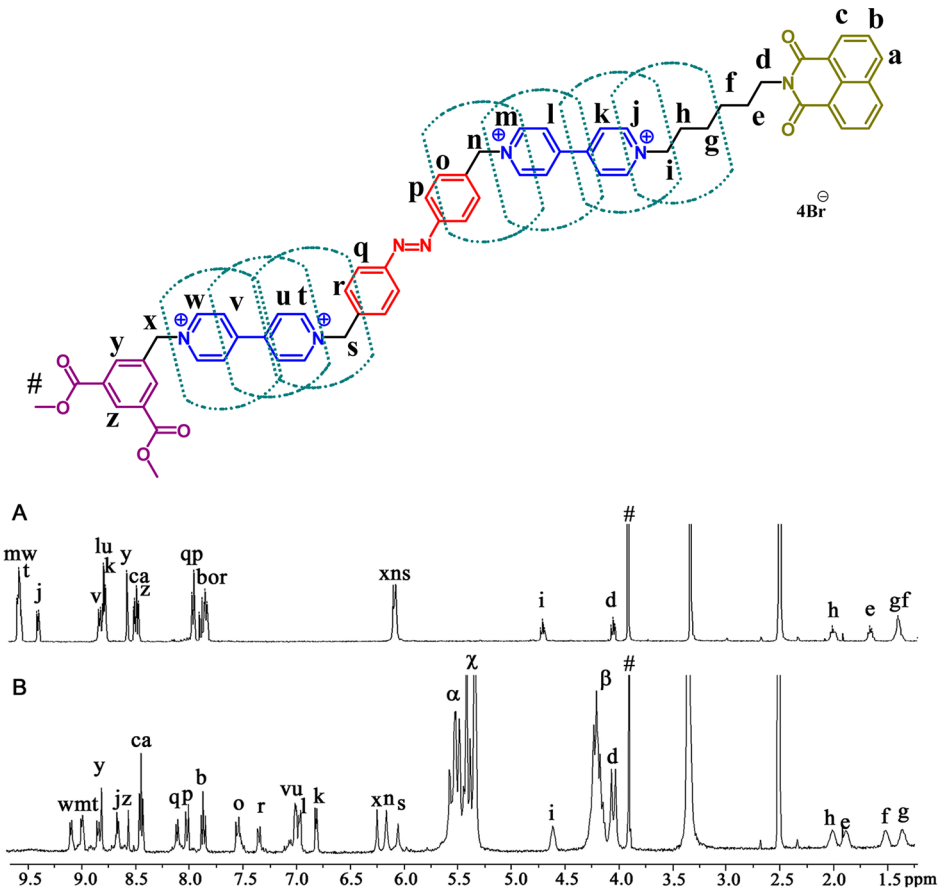

Figure 4. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) of (A) dumbbell molecule **1** and (B) [3]rotaxane **R1** along with a conformational representation of the CB[7] shuttling distribution.

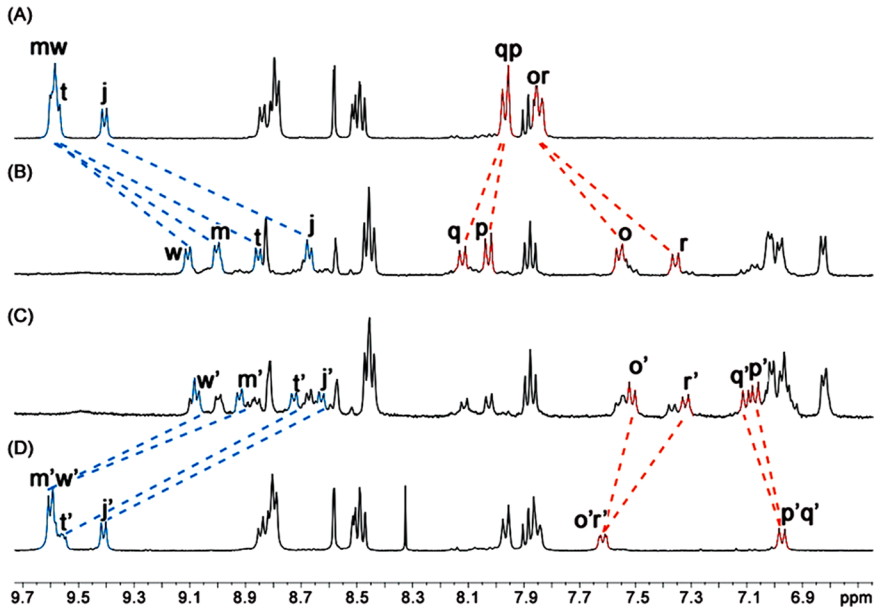

Figure 5. Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) of (A) dumbbell molecule **1**, (B) [3]rotaxane **R1**, (C) [3]rotaxane **R1** after sufficient photoirradiation at 365 nm, and (D) dumbbell molecule **1** after sufficient photoirradiation at 365 nm.

did not cause any obvious emission intensity change before and after UV light irradiation (curves a and b in Figure 7). In contrast, the emission intensity of [3]rotaxane **R1** increases by about 33% after the *trans*-to-*cis* photoisomerization (curves c and d in Figure 7). Clearly, the fluorescent change is the result of the shuttling equilibrium distribution change of the CB[7] rings along the dumbbell component. The fluorescent enhancement may be attributed to the conformational modulation effect of the rigid CB[7] ring.[10] The flexible dumbbell molecule **1** may adopt a bent conformation where the

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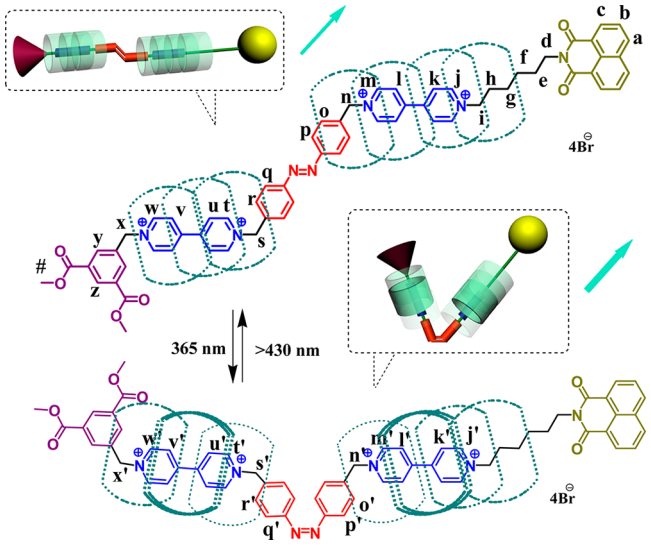

Figure 6. Schematic representation for light-controlled CB[7] ring shuttling equilibrium distribution in [3]rotaxane **R1**.

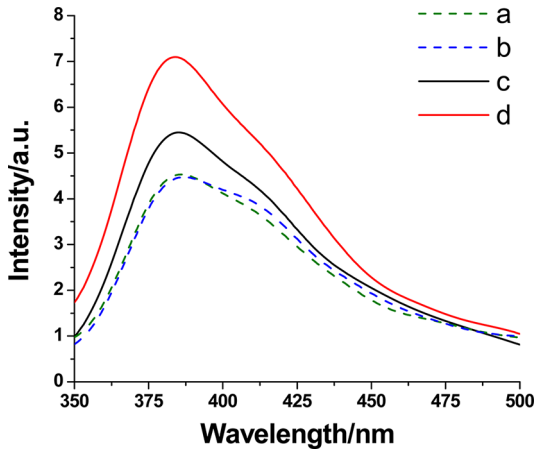

Figure 7. Emission spectra (λ_{ex} = 340 nm) of dumbbell molecule **1** (0.021 mM in DMSO, 295 K) (a) before and (b) after irradiation at 365 nm for 300 s, when compared with significant emission change for [3]rotaxane **R1** (0.021 mM in DMSO, 295 K) (c) before and (d) after irradiation at 365 nm for 300 s.

viologen and 1,8-naphthalimide units are close to each other, resulting in fluorescence quenching on account of intramolecular charge transfer between the viologen unit and 1,8-naphthalimide unit. In the [3]rotaxane, UV-light-induced equilibrium distribution change makes the CB[7] rings more concentrated on the viologen units. The encirclements of the CB[7] rings on the viologen units protect the viologen units from the potential charge transfer, restoring the fluorescence.[10]

In addition, time-dependent absorption changes of the [3]rotaxane were recorded upon the photoirradiation (Figures S9–S11 in the Supporting Information). Similar light-controllable shuttling behavior of the [3]rotaxane in aqueous solution and on the [3]rotaxane-doped poly(methyl methacrylate) (PMMA) film was also explored (Figures S12 and S13 in the Supporting Information). The observations indicate that the light-triggered shuttling equilibrium distribution change of the ring can be easily distinguished by spectral variations.

CONCLUSION

A new cucurbit[7]uril-based [3]rotaxane with light-controllable shuttling distribution change of the macrocycles along the dumbbell component has been developed. The key step in the synthetic process is to incorporate the azobenzene unit with two viologen groups in the dumbbell component, resulting in a rapidly equilibrating distribution for the cucurbit[7]uril rings; that is, the cucurbit[7]uril rings encircle the viologen units with a shuttling extension to the azobenzene unit. The *trans*-to-*cis* photoisomerization of the azobenzene unit leads to the restriction of the shuttling distribution to a certain extent and makes the rings more concentrated on the viologen units. This [3]rotaxane with alterable shuttling equilibrium distribution has been effectively characterized by ^{1}H NMR spectroscopy and easily indicated by spectral variations. The fabrication and investigation of such kind of molecular shuttle could be valuable for enhancing the performance of cucurbituril-based molecular machines.

EXPERIMENTAL SECTION

Instruments. ^{1}H NMR, ^{13}C NMR, and ^{1}H NOESY NMR spectra were recorded on an NMR spectrometer. The electronic spray ionization mass spectra (ESI-MS) were recorded on a quadrupole ion trap mass spectrometer. The high-resolution mass spectra (HR-MS) were obtained on a Q-TOF mass spectrometer. Absorption spectra were recorded on a UV–vis–NIR spectrophotometer, while the emission spectra were recorded on a fluorescence spectrophotometer. Melting points were determined using an automated melting point system. The photoirradiation was carried out on a UV lamp (15 W) with an irradiation wavelength of 365 nm in a sealed Ar-saturated 1 cm quartz cell.

Materials. Benzoyl peroxide, 4,4′-bipyridine, *N*-bromosuccinimide, cucurbit[7]uril (CB[7]), 1,6-dibromohexane, 5-methylisophthalic acid, 1,8-naphthalimide, sodium methoxide, and *p*-toluidine were purchased commercially and used as received. All of the solvents and inorganic reagents were commercially available. Synthetic routes for the preparations of the dumbbell compounds **1**, **2**, and **3** are shown in Figure 8.

Compound ***1a***. This compound was prepared according to the literature report.[11]

Compound ***1b***. 1,8-Naphthalimide (0.86 g, 4.36 mmol) was suspended in a mixture of *N*,*N*-dimethylformamide (DMF) (20 mL) and DMSO (20 mL), and then sodium methoxide (0.224 g, 4.14 mmol) was added to the solution with stirring at room temperature. The suspension turned to a clear solution after several minutes. Then, 1,6-dibromohexane (3.02 g, 12.4 mmol) was added into the solution, and the solution mixture was kept stirring for 6 h. The mixture solution was poured into water (250 mL), and solid crude product was slowly precipitated. The crude product was filtered and recrystallized by ethanol to afford **1b** (1.25 g, 85.6%): mp 95–96 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 8.49 (m, 4H), 7.88 (t, J = 8.0 Hz, 2H), 4.05 (t, J = 8.0 Hz, 2H), 3.54 (t, J = 8.0 Hz, 2H), 1.82 (dd, J_1 = J_2 = 8.0 Hz, 2H), 1.65 (dd, J_1 = J_2 = 8.0 Hz, 2H), 1.43 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 163.9, 134.8, 131.8, 131.2, 127.8, 127.7, 122.6, 35.6, 32.6, 27.8, 27.8, 26.1. HR-MS (ESI): calcd for $C_{18}H_{19}NO_2{}^{79}Br$ $[M + H]^+$ m/z = 360.0599, found m/z 360.0594.

Compound ***1c***. A solution of **1b** (1.2 g, 3.3 mmol) and 4,4′-bipyridine (3.6 g, 23.1 mmol) in acetonitrile (35 mL) was stirred at 80 °C for 1 day. After cooling to room temperature, the mixture was filtered. The solid was washed with acetonitrile to provide a white compound **1c** (1.36 g, 79.9%): mp 226–227 °C (decomp.). ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.25 (d, J = 4.0 Hz, 2H), 8.88 (d, J = 4.0 Hz, 2H), 8.65 (d, J = 8.0 Hz, 2H), 8.50 (m, 4H), 8.06 (d, J = 8.0 Hz, 2H), 7.89 (t, J = 8.0 Hz, 2H), 4.66 (t, J = 8.0 Hz, 2H), 4.06 (t, J = 8.0 Hz, 2H), 1.99 (br, 2H), 1.67 (br, 2H), 1.41 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 163.9, 152.6,

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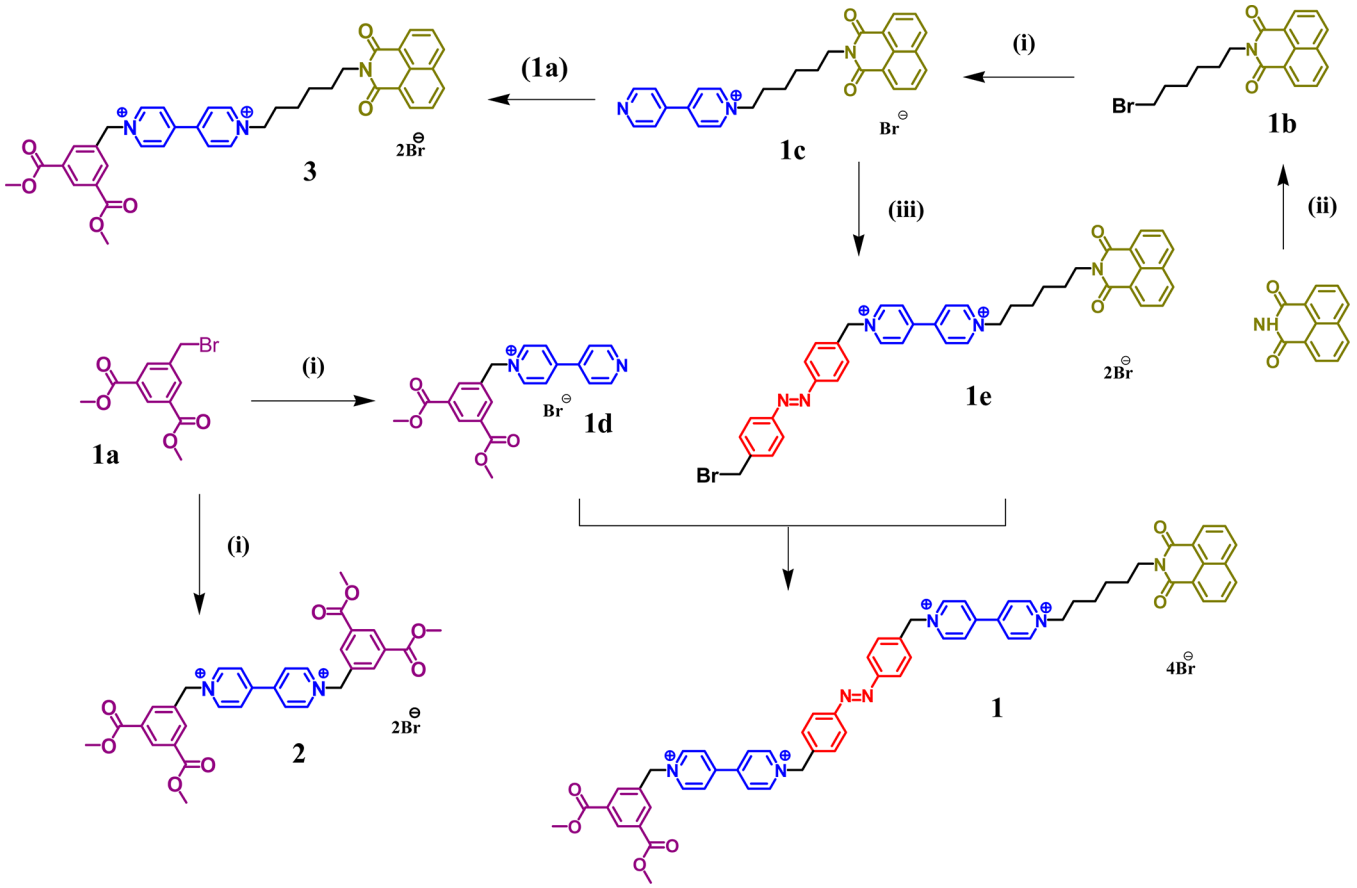

Figure 8. Synthetic routes for the preparations of the dumbbell compounds **1**, **2**, and **3**. Reagents and conditions: (i) 4,4′-bipyridine, (ii) 1,6-dibromohexane and sodium methoxide, (iii) bis(4-bromomethylphenyl)diazene.

151.5, 145.8, 134.9, 132.6, 131.2, 127.8, 127.6, 125.9, 122.5, 122.4, 60.3, 31.0, 27.8, 26.4, 25.6. HR-MS (ESI): calcd for $C_{28}H_{26}N_3O_2$ $[M - Br]^+$ m/z = 436.2025, found m/z 436.2025.

Compound ***1d***. A solution of **1a** (0.94 g, 3.3 mmol) and 4,4′-bipyridine (3.6 g, 23.1 mmol) in acetonitrile (55 mL) was stirred at 80 °C for 1 day. After cooling to room temperature, the mixture was filtered. The solid was washed with acetonitrile to give a pale yellow compound **1d** (1.1 g, 75.7%): mp 222−223 °C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6, 295 K, TMS): δ = 9.43 (d, J = 9.0 Hz, 2H), 8.87 (d, J = 6.0 Hz, 2H), 8.65 (d, J = 6.0 Hz, 2H), 8.56 (s, 2H), 8.51 (s, 1H), 8.01 (d, J = 6.0 Hz, 2H), 6.04 (s, 2H), 3.92 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 165.7, 153.7, 151.1, 145.6, 141.6, 135.3, 134.8, 131.7, 131.0, 126.4, 122.6, 62.6, 53.3. HR-MS (ESI): calcd for $C_{21}H_{19}N_2O_4$ $[M - Br]^+$ m/z = 363.1345, found m/z 363.1346.

Compound ***1e***. Bis(4-bromomethylphenyl)diazene[12] (4.0 g, 10.9 mmol) was dissolved in DMF (75 mL) at 100 °C. The solution was then added with compound **1c** (0.8 g, 1.56 mmol) and stirred at 100 °C for 7 h. The mixture solution was filtered while it was hot. The filtrate was then poured into toluene (300 mL) to precipitate some orange solid. The mixture was kept overnight and then filtered. The solid was washed with hot chloroform (50 mL) and acetonitrile (40 mL) and dried in vacuo, affording pure orange compound **1e** (997 mg, 72.3%): mp >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.56 (d, J = 8.0 Hz, 2H), 9.39 (d, J = 8.0 Hz, 2H), 8.81 (d, J = 8.0 Hz, 2H), 8.77 (d, J = 8.0 Hz, 2H), 8.49 (m, 4H), 7.98 (d, J = 8.0 Hz, 2H), 7.88 (m, 4H), 7.83 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 6.06 (s, 2H), 4.82 (s, 2H), 4.70 (t, J = 8.0 Hz, 2H), 4.05 (t, J = 8.0 Hz, 2H), 2.00 (br, 2H), 1.65 (br, 2H), 1.40 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 163.9, 151.9, 149.8, 149.0, 146.4, 146.2, 134.9, 131.8, 131.2, 131.0, 130.7, 127.8, 127.8, 127.7, 127.6, 127.2, 123.7, 123.6, 123.5, 123.1, 122.5, 63.2, 62.8, 61.3, 34.0, 31.1, 27.8, 26.4, 25.6. HR-MS (ESI): calcd for $C_{42}H_{38}N_5O_2{}^{79}Br^{81}Br$ $[M - Br]^+$ m/z = 804.1372, found m/z 804.1377.

Dumbbell Compound ***1***. A suspension of compound **1e** (650 mg, 0.74 mmol) in DMF (20 mL) was heated to 90 °C, and then compound **1d** (326 mg, 0.74 mmol) was added into the solution. The mixture solution was kept stirring at 90 °C for 6 h. Some precipitates were observed. The mixture solution was filtered while it was hot. The solid was washed with a small amount of cool DMF to give orange product **1** (383 mg, 39%): mp >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.59 (m, 6H), 9.41 (d, J = 8.0 Hz, 2H), 8.84 (d, J = 8.0 Hz, 2H), 8.80 (m, 6H), 8.58 (s, 2H), 8.47 (m, 5H), 7.94 (m, 4H), 7.87 (m, 6H), 6.09 (m, 6H), 4.71 (t, J = 8.0 Hz, 2H), 4.05 (t, J = 8.0 Hz, 2H), 3.92 (s, 6H), 2.00 (br, 2H), 1.65 (br, 2H), 1.40 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 165.4, 163.9, 152.6, 149.7, 149.7, 149.7, 149.0, 146.4, 146.4, 146.3, 146.2, 138.0, 137.9, 135.9, 135.2, 134.9, 131.8, 131.6, 131.2, 131.0, 130.8, 127.8, 127.8, 127.8, 127.7, 127.2, 123.8, 122.5, 63.2, 62.7, 61.3, 53.2, 31.1, 27.8, 26.4, 25.6. MS (ESI): calcd for $[M - 3Br]^{3+}$ m/z = 363.12, found m/z 363.27; $[M - 4Br]^{4+}$ m/z = 251.85, found m/z 251.95. HR-MS (ESI): calcd for $C_{63}H_{57}N_7O_6{}^{79}Br^{81}Br_2$ $[M - Br]^+$ m/z = 1248.1879, found m/z 1248.1898.

[3]Rotaxane ***R1***. Compound **1** (13.2 mg, 0.01 mmol) and CB[7] (23.3 mg, 0.02 mmol) were dissolved in deionized water (5 mL), and the solution was heated to 100 °C. The solution was kept stirring at the temperature for 10 h and was quickly cooled using an ice bath. Then, the aqueous solution was poured into ethanol (30 mL), and the product was precipitated. The product **R1** (15.6 mg, 42.7%) was collected by centrifugation (6000 rps, 20 min): mp >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.10 (d, J = 4.0 Hz, 2H), 9.00 (d, J = 4.0 Hz, 2H), 8.85 (d, J = 4.0 Hz, 2H), 8.83 (s, 2H), 8.66 (d, J = 8.0 Hz, 2H), 8.58 (s, 1H), 8.46 (m, 4H), 8.12 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.87 (m, 2H), 7.56 (d, J = 8.0 Hz, 2H),

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7.36 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 4.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 4.0 Hz, 2H), 6.26 (s, 2H), 6.17 (s, 2H), 6.06 (s, 2H), 5.58−5.34 (m, 56H), 4.62 (br, 2H), 4.24−4.04 (m, 30H), 3.91 (s, 6H), 2.02 (br, 2H), 1.90 (br, 2H), 1.52 (br, 2H), 1.37 (br, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 165.9, 164.1, 155.5, 155.3, 155.3, 155.1, 152.1, 148.5, 148.4, 148.0, 147.2, 137.3, 134.5, 134.0, 133.3, 131.6, 131.5, 130.8, 129.1, 128.3, 127.8, 127.5, 124.5, 123.9, 123.8, 123.8, 123.5, 123.1, 122.8, 122.6, 70.4, 70.3, 63.4, 63.0, 62.4, 52.9, 52.2, 52.0, 48.6, 30.8, 28.2, 27.2, 25.5, 21.1, 13.7. MS (ESI): calcd for $[M - 4Br]^{4+}$ m/z = 833.52, found m/z 833.60. HR-MS (ESI): calcd for $C_{37}H_{37}N_{16}O_8$ $[M - 4Br]^{4+}$ m/z = 833.2980, found m/z 833.2969.

Dumbbell Compound **2**. A solution of **1a** (3.76 g, 13.2 mmol) and 4,4′-bipyridine (147 mg, 0.94 mmol) in acetonitrile (70 mL) was stirred at 80 °C for 1 day. After cooling to room temperature, the mixture solution was filtered. The solid was washed with acetonitrile to give a pale yellow compound **2** (452 mg, 65.9%): mp >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.56 (d, J = 8.0 Hz, 4H), 8.74 (d, J = 8.0 Hz, 4H), 8.57 (s, 4H), 8.52 (s, 2H), 6.08 (s, 4H), 3.92 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 165.4, 149.8, 146.3, 135.9, 135.2, 131.6, 131.0, 127.8, 62.7, 53.2. HR-MS (ESI): calcd for $C_{32}H_{30}N_2O_8{}^{81}Br$ $[M - Br]^+$ m/z = 651.1165, found m/z 651.1171.

[2]Rotaxane ***R2***. Compound **2** (14.5 mg, 0.02 mmol) and CB[7] (23.3 mg, 0.02 mmol) were dissolved in deionized water (5 mL), and the solution was heated to 100 °C. The solution was kept stirring at the temperature for 10 h and was quickly cooled using an ice bath. Then, the aqueous solution was poured into ethanol (30 mL), and the product was precipitated. The product **R2** (14.4 mg, 38.1%) was collected by centrifugation (6000 rps, 20 min): mp >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.25 (br, 4H), 8.85 (d, J = 8.0 Hz, 4H), 8.57 (s, 4H), 8.47 (s, 2H), 6.02 (s, 4H), 5.65−5.62 (m, 14H), 5.38 (br, 14H), 4.15 (m, 14H), 3.91 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 165.7, 155.1, 150.4, 145.2, 138.3, 134.9, 131.1, 128.5, 125.3, 70.5, 59.8, 54.1, 52.8. MS (ESI): calcd for $[M - 2Br]^{2+}$ m/z = 866.78, found m/z 866.92. HR-MS (ESI): calcd for $C_{37}H_{36}N_{15}O_{11}$ $[M - 2Br]^{2+}$ m/z = 866.2719, found m/z 866.2641.

Dumbbell Compound **3**. A solution of **1c** (516 mg, 1.0 mmol) and **1a** (574 mg, 2.0 mmol) in a mixture solution of DMF (5 mL) and acetonitrile (30 mL) was stirred at 90 °C for 1 day. After cooling to room temperature, the mixture solution was filtered. The solid was washed with acetonitrile to provide a pale yellow compound **2** (497 mg, 61.9%): mp >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.57 (d, J = 8.0 Hz, 2H), 9.38 (d, J = 8.0 Hz, 2H), 8.78 (d, J = 8.0 Hz, 2H), 8.74 (d, J = 8.0 Hz, 2H), 8.58 (s, 2H), 8.49 (m, 5H), 7.89 (m, 2H), 6.08 (s, 2H), 4.69 (t, J = 8.0 Hz, 2H), 4.05 (t, J = 8.0 Hz, 2H), 3.92(s, 6H), 2.00 (br, 2H), 1.66 (br, 2H), 1.39 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 165.4, 163.9, 149.8, 149.1, 146.3, 146.2, 135.9, 135.2, 134.9, 131.8, 131.6, 131.2, 131.0, 127.8, 127.8, 127.7, 127.2, 122.5, 62.7, 61.3, 53.2, 31.1, 27.8, 26.4, 25.6. HR-MS (ESI): calcd for $C_{39}H_{37}N_3O_6{}^{81}Br$ $[M - Br]^+$ m/z = 724.1854, found m/z 724.1845.

[2]Rotaxane ***R3***. Compound **3** (16.1 mg, 0.02 mmol) and CB[7] (23.3 mg, 0.02 mmol) were dissolved in deionized water (5 mL), and the solution was heated to 100 °C. The solution was kept stirring at the temperature for 10 h and was quickly cooled using an ice bath. Then, the aqueous solution was poured into ethanol (30 mL), and the product was precipitated. The product **R3** (12.1 mg, 30.7%) was collected by centrifugation (6000 rps, 20 min): mp >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K, TMS): δ = 9.05 (d, J = 4.0 Hz, 2H), 8.80 (s, 2H), 8.53 (s, 1H), 8.49 (d, J = 8.0 Hz, 2H), 8.42 (m, 4H), 7.84 (m, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.23 (s, 2H), 5.44−5.29 (m, 28H), 4.53 (br, 2H), 4.16−3.98 (m, 16H), 4.69 (t, J = 8.0 Hz, 2H), 4.05 (t, J = 8.0 Hz, 2H), 3.92(s, 6H), 1.91 (br, 4H), 1.50 (br, 2H), 1.26 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K, TMS): δ = 165.7, 164.0, 155.1, 150.1, 148.3, 147.7, 146.6, 137.1, 134.5, 133.6, 131.5, 131.4, 131.0, 130.7, 127.8, 127.4, 124.0, 122.9, 122.6, 70.2, 63.4, 63.0, 56.6, 52.9, 30.5, 28.1, 27.2, 25.6, 19.1. MS (ESI): calcd for $[M - 2Br]^{2+}$ m/z = 903.35, found m/z 903.37. HR-MS (ESI): calcd for $C_{40}H_{39}N_{16}O_{10}$ $[M - 2Br]^{2+}$ m/z = 903.3035, found m/z 903.3031.

Preparations of ***1***- *and* ***R1***-*Doped Poly(methyl methacrylate) Solid Films*. Compound **1** or [3]rotaxane **R1** was dispersed into an anisole solution containing 10 wt % of PMMA in order to form a solution with the concentration of 1 μM. Then, the solid film was obtained by spin-coating this solution on one side of 1 mm quartz cuvette. The cuvette was inserted into the cuvette holder at an angle about 45° to the incident light for the fluorescence test.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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