

Multistimuli Sensitive Behavior of Novel Bodipy-Involved Pillar[5]arene-Based Fluorescent [2]Rotaxane and Its Supramolecular Gel

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Fluorescent [2]rotaxane BC12P5 is successfully constructed with 1,4-diethoxypillar[5]arene as wheel over a long alkyl axle with Bodipy chromophore as one stopper for the first time. NMR spectra clearly reveal its molecular shuttle nature triggered by multiple external stimuli including solvent polarity and temperature. In particular, the fluorescence nature introduced into [2]rotaxane BC12P5 renders it a good sensor for the external stimuli. Nevertheless, the supramolecular gel successfully fabricated from this novel rotaxane system via self-assembly in dimethyl sulfoxide (DMSO) also shows reversible gel–sol phase transition upon multiple external stimuli such as heating/cooling, shaking/resting, or the addition of different anions. Interestingly, exposure of the supramolecular gel film to HCl or ammonia vapor induces the change in the film fluorescence intensity, endowing this system with a potential application in gas detecting.

been applied to construct the rotaxane-based molecular motors.^[6] Pillar[*n*]arenes, as the new member of functional macrocyclic family, have also been employed as good building block to create rotaxanes shortly after their first synthesis in 2008.^[7] In 2011, Stoddart and co-worker reported the first pillar[5]arene-based [2]rotaxane formed between a pillar[5]arene and *N,N'*-bis(3,5-di-*tert*-butylbenzyl)octane-1,8-diamine,^[8] which was followed by the construction of different species of [2]rotaxanes^[9] and novel [3]rotaxanes.^[10] However, pillararene-based rotaxanes with multiple external stimuli responsiveness, especially those incorporating fluorogenic functionalities remain rarely explored.

On the other hand, boron dipyrromethene (Bodipy) dyes have constituted one of the most important families of simple organic luminophores due to their special absorption and emission properties.^[11] Their strong absorption and emission in the visible and near-infrared range render them great application potential in chemosensors and probes, biological labels, laser dyes, photodynamic therapy agents, and a plethora of photonic devices.^[12] Bodipy-involved rotaxanes have, however, been rarely reported thus far, limited to several crown ether/cucurbit[*n*]uril-based rotaxanes,^[13] to the best of our knowledge.

In the present paper, we describe the preparation and characterization of a new type of fluorescent [2]rotaxane BC12P5 constructed on the basis of pillar[5]arene wheel and a dumbbell-shaped axle with Bodipy chromophore as one stopper, **Scheme 1**, which appears to represent the first Bodipy-involved pillar[5]arene-based rotaxane. The pillar[5]arene wheel of this novel [2]rotaxane BC12P5 was revealed to move over its dumbbell-shaped alkyl axle under multiple external stimuli including the solvent polarity, temperature, and pH value on the basis of the NMR and fluorescent spectroscopic investigations. Nevertheless, [2]rotaxane BC12P5 is able to self-assemble into supramolecular gel in dimethyl sulfoxide (DMSO), which also shows reversible gel–sol phase transition upon multiple external stimuli like heating/cooling, shaking/resting, or the addition of different anions.

At the end of this section, it is noteworthy that in the past decade supramolecular gels formed by self-assembly of organic molecules into entangled structures to immobilize the solvents have attracted extensive research interests due to their potential applications in chemosensors, optoelectronic devices, drug

1. Introduction

Inspired by naturally occurring biological motors such as the ATPase rotary motor and the kinesin or myosin linear motor systems,^[1] chemists have tried to construct a variety of artificial molecular machines^[2] including the unidirectional rotors, shuttles, scissors, and molecular muscles that can perform diverse molecular motions.^[3] Rotaxanes, with a typical mechanically interlocked structure, have been widely employed as crucial precursor and building blocks for the fabrication of advanced supramolecular architectures^[4] like molecular shuttles and switches with molecular motions upon certain external stimuli.^[5] Thus far a series of macrocyclic compounds including crown ethers, cyclodextrins, and cucurbit[*n*]urils have

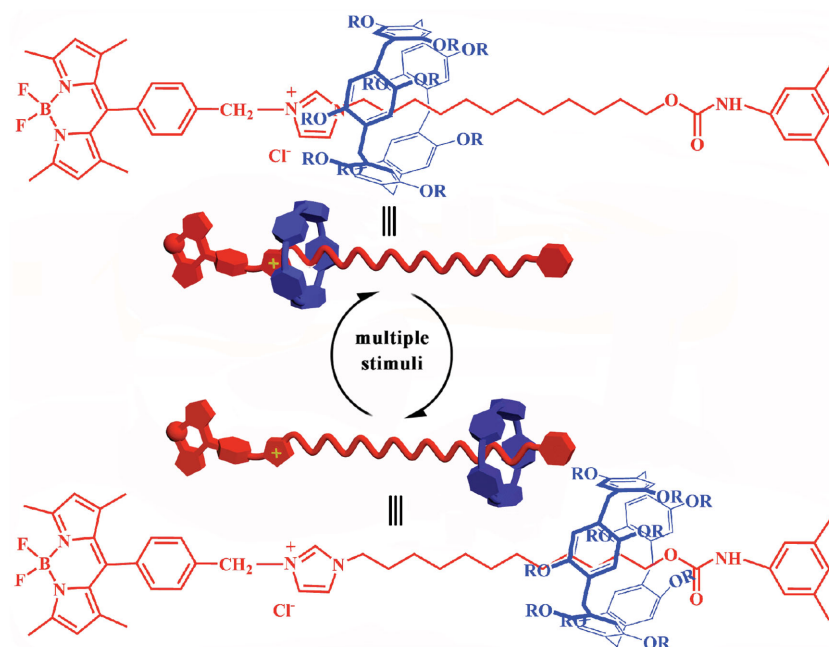
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Scheme 1. Schematic molecular structures of [2]rotaxane BC12P5 under external stimuli.

delivery, tissue engineering, biomaterials, and surface science.^[14] The present Bodipy-containing pillar[5]arene-based fluorescent gel is therefore expected to find applications in related fields.

2. Results and Discussion

2.1. Molecular Design and Synthesis

Generally, rotaxane is constructed by wheel and axle components. In the present case, 1,4-diethoxypillar[5]arene (EtP5) is chosen as the wheel of the target [2]rotaxane BC12P5 with 12-(1H-imidazol-1-yl)dodecanol (1) stopped by a carbamic unit and a meso-chloro-benzyl-Bodipy unit (2) at both ends as an axle, Scheme 1. Interestingly, the Bodipy unit introduced as one stopper of the axle also provides the [2]rotaxane BC12P5 with an effective fluorescence chromophore, enabling the detection of the responsiveness to external stimuli by fluorescence method. Both EtP5 and the semiblocked rod-like Bodipy derivative Bodipy-C12OH (3) were prepared according to the published procedures.^[7d,12b] Reaction of EtP5 with the semiblocked rod-like component Bodipy derivative 3 in CHCl₃ led to the formation of pseudorotaxane structure, which then reacted with 1-isocyanato-3,5-dimethylbenzene in CHCl₃ afforded the target [2]rotaxane BC12P5. Satisfactory elemental analysis result was obtained for the newly prepared [2]

rotaxane BC12P5 after repeated column chromatography followed by recrystallization. The matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrum displayed intense signal at $m/z = 1627.95$, corresponding to the molecular ion $[M-Cl]^+$. Nevertheless, the key intermediate and the target [2]rotaxane BC12P5 were also characterized by ¹H and ¹³C NMR spectroscopies, Figures S1–S6 (Supporting Information).

2.2. NMR Characterization

Figure 1 and **Figure S7** (Supporting Information) show the ¹H NMR and 2D nuclear Overhauser enhancement spectroscopy (NOESY) of [2]rotaxane BC12P5 in CDCl₃. For comparative study, the NMR spectra for the two components, namely the wheel and the axle Bodipy-C12OH-isocyanato (4), in CDCl₃ were also recorded and shown in **Figure 1**. Comparison in the NMR spectrum of these three species reveals that the ¹H NMR spectrum of [2]rotaxane BC12P5 is not a simple superimposition of the spectra of pure compound 4 and EtP5 in the same deuterated solvent, indicating the effective interaction between the host wheel and the guest axle in the supramolecular rotaxane system. As can be seen, **Figure 1** and **Table S1** (Supporting Information), after being fabricated into [2]rotaxane BC12P5, the signals of the methylene protons H₉, H₁₀, H₁₁, and H₁₂ on the axle (which are adjacent to the imidazolium unit in the axle) take obvious upfield shift from 1.31, 1.31, 1.96, 4.29 to 0.39, −0.46, −1.19, and 3.98 ppm, respectively. This is also true

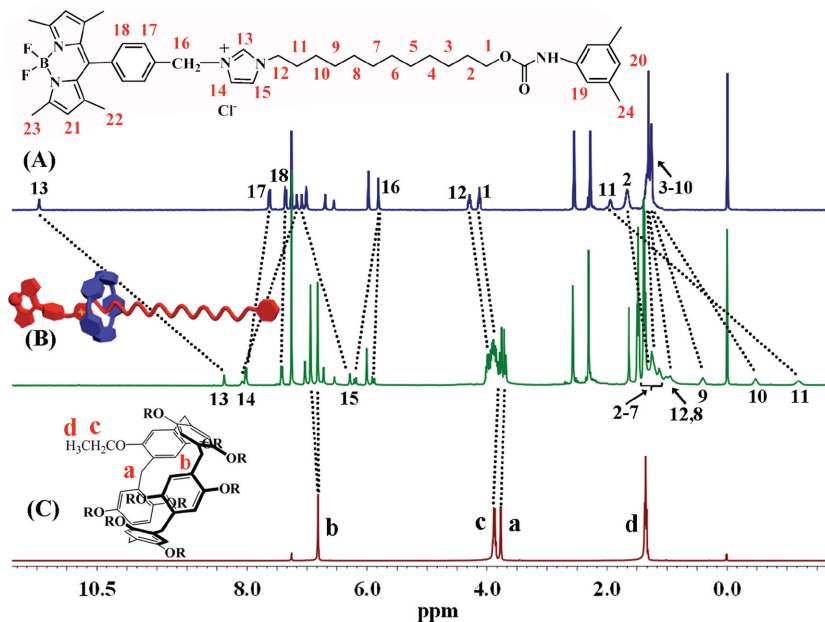


Figure 1. ¹H NMR spectra of A) compound 4, B) [2]rotaxane BC12P5, and C) EtP5 recorded in CDCl₃ at 25 °C.

for the imidazolium protons H_{13} and H_{15} with substantial upfield shift from 11.47 and 7.09 to 8.39 and 6.30 ppm, respectively. These results suggest the encapsulation of the imidazolium moiety and its adjacent methylene groups in the axle by the pillar[5]arene wheel in [2]rotaxane BC12P5 in $CDCl_3$. Additional support for this point comes from the cross-peaks between the aromatic protons H_b of pillar[5]arene ring and the methylene protons H_9 and H_{10} observed in the NOESY spectrum of [2]rotaxane BC12P5, Figure S7 (Supporting Information).

To reveal the solvent polarity effect on the [2]rotaxane BC12P5 conformation, a more polar solvent, $DMSO-d_6$, was utilized for comparative NMR investigations. As shown in Figure S8 and Table S2 (Supporting Information), the signals of the methylene protons H_1 , H_2 , H_3 , H_4 , H_5 , and H_6 that are adjacent to the carbamic stopper in the axle exhibit substantial upfield shift ($\Delta\delta = -0.38$, -0.84 , -1.67 , -2.08 , -1.91 , and -1.47 ppm, respectively) in the rotaxane system in comparison with those for pure compound 4, revealing the shielding effect of the host EtP5 cavity on these protons and in turn suggesting the methylene groups adjacent to the carbamic stopper in the axle threaded into the cavity of the pillar[5]arene ring in [2]rotaxane BC12P5 in $DMSO-d_6$. This is further confirmed by the cross-peaks between the signals of methylene protons H_3 , H_4 , H_5 , and H_6 of the alkyl chain and the phenyl proton H_b of the pillar[5]arene moiety observed in the 2D NOESY spectrum of [2]rotaxane BC12P5 in $DMSO-d_6$, Figure S7 (Supporting Information). Obviously, different conformation was employed by [2]rotaxane BC12P5 in $DMSO-d_6$ from that in $CDCl_3$ due to the difference in the solvent and [2]rotaxane BC12P5 intermolecular interactions, suggesting the possible solvent polarity-driven molecular shuttle nature of this system.

2.3. Solvent Polarity-Driven Molecular Shuttle

As described above, 1H NMR measurements indicate that the solvent polarity change might be able to induce the pillar[5]arene cavity to move on the alkyl chain in [2]rotaxane BC12P5. As a result, systematic studies over the 1H NMR spectra of [2]rotaxane BC12P5 in a series of mixed solvents with different ratio of $CDCl_3/DMSO-d_6$ were carried out. As shown in Figure 2 and Table S3 (Supporting Information), along with the decrease in the solvent polarity due to the stepwise addition of $CDCl_3$ into $DMSO-d_6$, the signals of the methylene protons H_9 , H_{10} , H_{11} , and H_{12} and the imidazolium protons H_{13} in the axle of [2]rotaxane BC12P5 experience substantial upfield shift. However, the signals of the methylene protons (that are adjacent to the carbamic stopper) such as H_2 , H_3 , H_4 , H_5 , and H_6 take obvious downfield shift, demonstrating the gradual movement of the pillar[5]arene moiety on the axle from the methylene groups

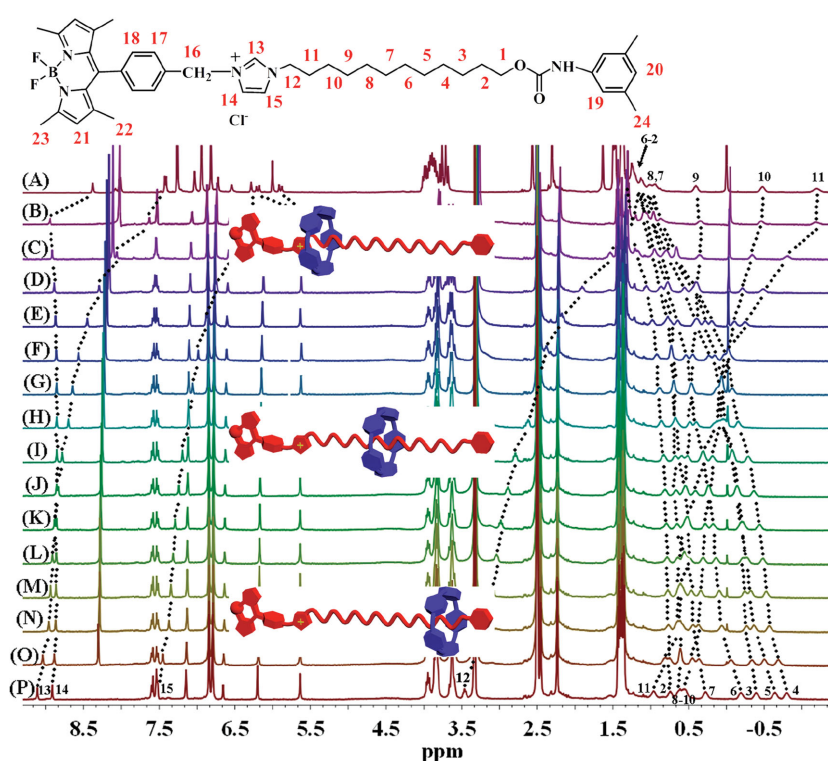


Figure 2. Systematic change in the 1H NMR spectrum of [2]rotaxane BC12P5 along with the change in the ratio of $CDCl_3/DMSO-d_6$ (v/v): A) $CDCl_3$, B) 1:1, C) 1:1.5, D) 1:2, E) 1:2.5, F) 1:3, G) 1:3.5, H) 1:4, I) 1:5, J) 1:6, K) 1:7, L) 1:8, M) 1:9, N) 1:10, O) 1:20, and P) $DMSO-d_6$ recorded at 25 $^{\circ}C$.

adjacent to the carbamic stopper to those adjacent to the imidazolium unit along with the decrease in the solvent polarity, revealing the solvent polarity-driven molecular shuttle nature of [2]rotaxane BC12P5.

2.4. Thermally Driven Molecular Shuttle

In order to try to investigate the molecular motion of [2]rotaxane BC12P5 under temperature stimuli, the temperature-dependent 1H NMR spectra for the rotaxane system were recorded in $DMSO-d_6$. As exhibited in Figure S9 and Table S4 (Supporting Information), along with increasing the temperature, the signals of the methylene protons H_9 , H_{10} , H_{11} , and H_{12} (which are close to the Bodipy stopper) and the imidazolium protons H_{13} , H_{14} , and H_{15} gradually move to upfield direction. For instance, the signal of proton H_{12} shifts from 3.46 to 2.19 ppm along with the temperature change from 25 to 115 $^{\circ}C$. In contrast, the signals of methylene protons H_2 , H_3 , H_4 , H_5 , and H_6 (which are adjacent to the carbamic stopper) gradually move to the downfield direction as the temperature increases as exemplified by the shift of proton H_2 signal from 0.75 ppm at 25 $^{\circ}C$ to 1.10 ppm at 115 $^{\circ}C$, Figure S10 and Table S4 (Supporting Information). These results clearly reveal the temperature-driven molecular shuttle nature of [2]rotaxane BC12P5. Nevertheless, on the basis of the just above section and according to these NMR spectroscopic results, the pillar[5]arene ring[2]rotaxane BC12P5 should locate on the methylene groups of the axle

that are adjacent to the carbamic stopper at low temperature in DMSO- d_6 . Along with increasing the temperature, the pillarene ring gradually slides to the imidazolium unit.

2.5. Fluorescence Properties of [2]rotaxane BC12P5 in Solution

2.5.1. Effects of Solvent Polarity on the Fluorescence Properties

Due to the incorporation of the Bodipy fluorescent chromophore in the present rotaxane system, the fluorescence properties of this system were therefore studied following the solvent polarity change. As displayed in Figure S11 (Supporting Information), with the system concentration being fixed at 1×10^{-5} M, the fluorescence intensity of [2]rotaxane BC12P5 gradually gets decreased along with the addition of CHCl_3 into the solution of DMSO. In pure CHCl_3 , a total decrease by the most of 23% in the fluorescence intensity was achieved in comparison with that in pure DMSO. In good contrast, the fluorescence property of compound 4 was also studied. As shown in Figure S11 (Supporting Information), the fluorescence intensity of 4 gradually gets decreased along with the addition of CHCl_3 into the solution of DMSO. In pure CHCl_3 , the fluorescence intensity of compound 4 decreases for about 37% in comparison with that in pure DMSO. This is in line with that observed for [2]rotaxane BC12P5. However, the decrease in the fluorescence intensity for compound 4 is larger than that of [2]rotaxane BC12P5. This seems to indicate the relatively less effect of the solvent polarity-driven molecular shuttle motion on the fluorescence intensity, suggesting the more effect of the solvent polarity on the fluorescence intensity. In line with previous investigation,^[15] in the present case higher fluorescence intensity for [2]rotaxane BC12P5 in polar solvent is achieved due mainly to the decrease in the nonradiative rate constant (which minimizes the nonradiative energy loss) with the help of the solvent polarity-driven molecular shuttle motion.

2.5.2. Effect of Temperature on the Fluorescence Properties

As can be easily expected, the fluorescence intensity of [2]rotaxane BC12P5 at a fixed concentration of 1×10^{-5} M in DMSO also takes systematic change along with the change in temperature, gradually decreased along with the temperature increase, by the most of 52% at 25 °C in comparison with that at 115 °C, **Figure 3**. This is also true for the reference compound 4. As shown in Figure S12 (Supporting Information), along with increasing the temperature, the fluorescence intensity of 4 gets gradually decreased in a similar manner to that of [2]rotaxane BC12P5, indicating the weaker influence of the thermally driven molecular shuttle movement of [2]rotaxane BC12P5 on the axle to the fluorescence intensity than that due to the consumption of more nonradiative energy at high temperature.^[16]

2.5.3. Effect of Acid/Base Change on the Fluorescence Properties

Acid/base titration experiments were also carried out to reveal the sensor property of [2]rotaxane BC12P5. As can be seen

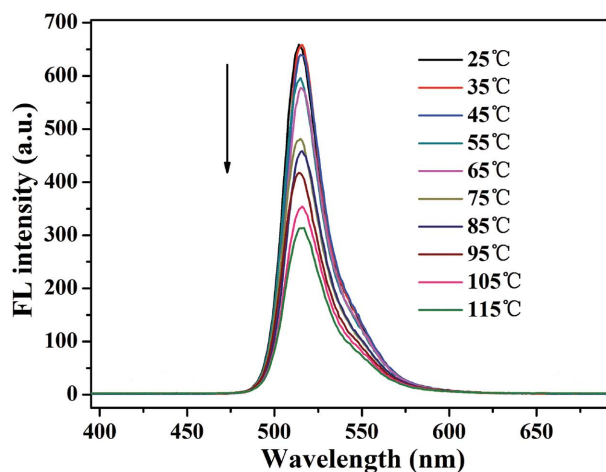


Figure 3. Systematic change in the fluorescence spectrum of [2]rotaxane BC12P5 in DMSO (1×10^{-5} mol L $^{-1}$) along with the temperature change from 25 to 115 °C.

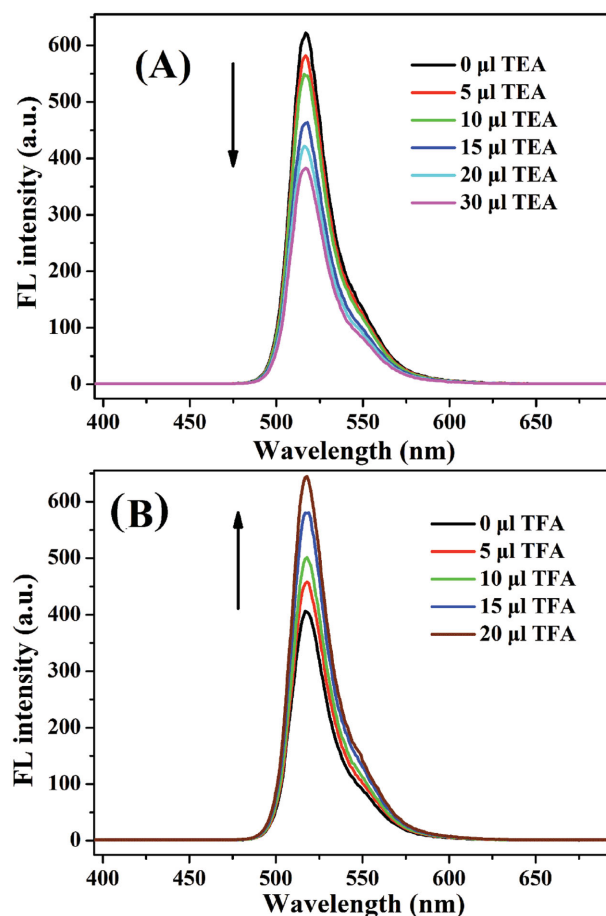
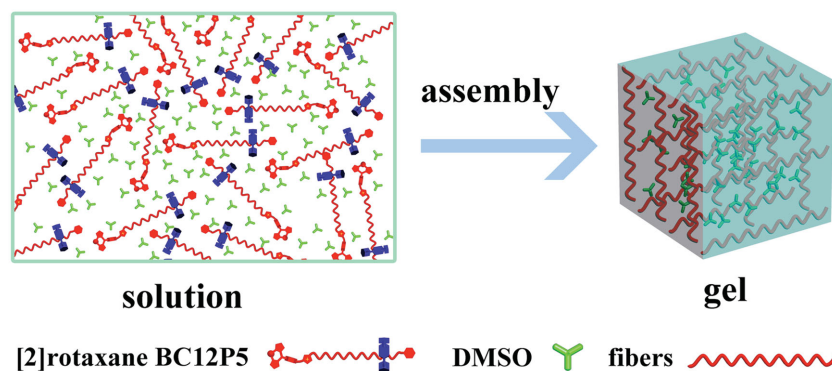


Figure 4. The fluorescence emission spectra of [2]rotaxane BC12P5 (1×10^{-5} mol L $^{-1}$) in CHCl_3 upon addition of increasing amount (0, 5, 10, 15, 20, and 30 μL) of TEA (A) and then of increasing amount (0, 5, 10, 15, and 20 μL) of TFA at 25 °C (B).

in Figure 4, along with the gradual addition of triethylamine (TEA) into the CHCl_3 solution of [2]rotaxane BC12P5 from 0 to 30 μL , the fluorescence intensity at 516 nm undergoes a consecutive decrease of 38%. However, the fluorescence spectrum could completely recover upon addition of trifluoroacetic acid (TFA) into the above-described CHCl_3 solution from 0 to 20 μL , indicating the influence of the pH on the fluorescence intensity. On the basis of previous research result,^[17] the fluorescence-quenching photoinduced electron transfer (PET) between the amine and Bodipy core at the extreme of high pH is able to occur because electron transfer may occur through space, resulting in the recovery of the fluorescence intensity of [2]rotaxane BC12P5 due to the neutralization upon addition of TFA. As can be expected, the fluorescence intensity for **4** upon addition of TEA into the solution also gets decreased in quite a similar manner to that of [2]rotaxane BC12P5, Figure S13 (Supporting Information). Nevertheless, the fluorescence intensity for this system also gets recovered after adding TFA.

2.6. Preparation of [2]rotaxane BC12P5 Supramolecular Gel

Supramolecular gels constructed from low-molecular-weight molecules (LMWMs) simultaneously possessing both toughness and flexibility as gelators depending on reversible noncovalent interactions play important role in the development of soft material science.^[14d] Due to the relatively rigid structure of the host component and the soft structure of the guest component usually employed by the rotaxanes and pseudorotaxanes, either rotaxanes or pseudorotaxanes with a mechanically interlocked structure have been used as suitable gelators to construct supramolecular gels.^[18] In the present case, the π - π interactions between the phenylene moieties of neighboring pillar[5]arene rings of [2]rotaxane BC12P5, as well as between the Bodipy-Bodipy stacking, Bodipy, and imidazolium moieties, with the help of the van der Waals forces between long alkyl chains in the neighboring [2]rotaxane BC12P5 systems result in the formation of 1D supramolecular arrays, which subsequently self-assemble into the cross-linked network depending on the similar intermolecular interactions as mentioned above between neighboring [2]rotaxane BC12P5 systems in different 1D arrays, Scheme 2. This 3D network then entraps the DMSO molecules with its porous structure, leading to the



Scheme 2. Schematic representation of self-assembling [2]rotaxane BC12P5 into the supramolecular gel via 1D aggregate in DMSO.

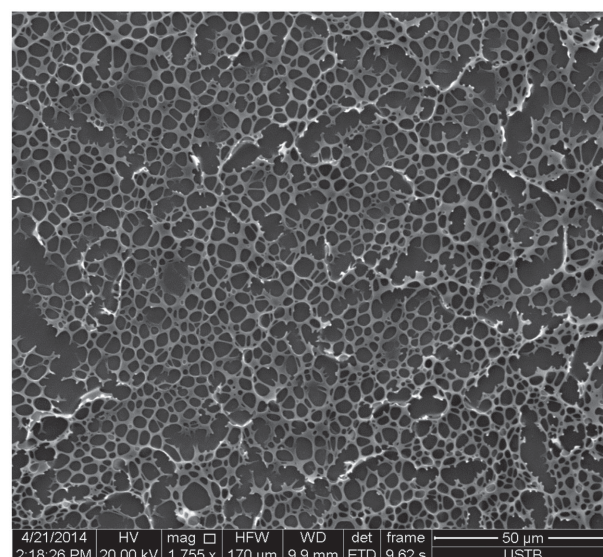


Figure 5. SEM image of the supramolecular gel of [2]rotaxane BC12P5 formed in DMSO by drop casting on the copper grid.

formation of a novel supramolecular gel containing Bodipy fluorescence chromophore depending mainly on the hydrogen bonding interaction between the solvent DMSO molecules and [2]rotaxane BC12P5 systems.^[19] The critical gelation concentration for [2]rotaxane BC12P5/DMSO was about 11.2 wt%. Figure 5 shows the scanning electron microscope (SEM) image of the gel formed from [2]rotaxane BC12P5. The 3D network constructed from nanofibers with an interconnected porous structure observed clearly reveals the gel nature of this system.

2.7. Multiple Stimuli-Responsive Reversible Gel-Sol Transitions of the Supramolecular Gel

Due to the sensitivity of the noncovalent interactions to external stimuli including solvent, temperature, pH, and mechanical stress, supramolecular gels usually exhibit stimuli responsiveness to the environment. As a consequence, multiple stimuli-responsive behaviors of the present supramolecular gels were also investigated. Similar to other gels, a reversible gel-sol transition could be easily achieved by shaking (here through ultrasonic waves) or resting of this gel system. In addition, after adding CF_3COOAg into the supramolecular gel system, the gel gradually collapses and finally becomes a solution after removing the AgCl precipitate. Upon addition of a little excess amount of tetrabutylammonium chloride (TBACl) into the solution, supramolecular gel is reformed.^[5],20] Nevertheless, most probably associated with the temperature-dependent nature of its building block, the supramolecular gel fabricated from [2]rotaxane BC12P5 is also sensitive to temperature. As displayed in Figure 6, along with increasing the temperature, the supramolecular gel gradually becomes a

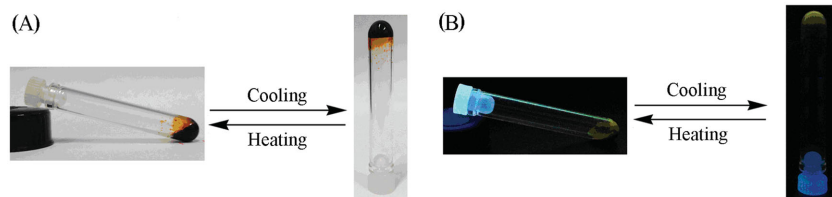


Figure 6. Photographs of reversible sol-gel transition upon cooling/heating under A) ambient light and B) illuminated at 365 nm.

solution with the gel-to-solution phase transition temperature (T_{gel}) of about 338 K. Reversibly, along with decreasing the temperature, the solution formed over 338 K return to the gel phase.

This gel also shows acid/base stimuli-responsiveness. In comparison with [2]rotaxane BC12P5 in DMSO solution, the supramolecular gel thin film prepared by coating onto quartz slide shows a redshifted broadened fluorescence at 534 nm with obviously weakened intensity due to the enhanced intermolecular interactions of [2]rotaxane BC12P5 in the gel state, Figure S14 (Supporting Information). Interestingly, upon being exposed to HCl gas, the thin film gel fluorescence intensity gets significantly decreased, by the most of 50%, accompanied also by a visually clear fluorescence color change from yellow to purplish red under UV light, Figure S15 (Supporting Information). In contrast, when being exposed to the NH_3 gas, the fluorescence intensity of the supramolecular gel thin film gets increased by the most of 100% but without showing the visually color change behavior. These results seem to suggest the potential of this supramolecular gel as the acidic/basic gas sensor.

3. Conclusion

In summary, the first Bodipy-involved fluorescent [2]rotaxane BC12P5 was designed and prepared. This novel [2]rotaxane BC12P5 system exhibits molecular shuttle nature under multiple external stimuli including solvent polarity and temperature according to NMR spectra. In particular, the fluorescent nature introduced into [2]rotaxane BC12P5 renders it a good sensor for these external stimuli. Nevertheless, the self-assembled supramolecular gel formed from this rotaxane system with the help of DMSO also shows multiple external stimuli-induced reversible gel-sol phase transition upon shaking/resting, heating/cooling, or the addition of different anions. In particular, exposure of this supramolecular gel film to the HCl gas leads to obvious decrease in the fluorescence intensity accompanied by a visually clear fluorescence color change under UV light, endowing the system with a application potential in acidic gas detecting.

4. Experimental Section

General Remarks: All reagents were obtained from commercial sources without further purification. The compounds of **1**, **2**, **3**, **4**, and EtP5 were prepared according to the literature procedure.^[7d,12b]

Measurements: NMR spectra were recorded on a Bruker DPX 400 spectrometer in CDCl_3 and $\text{DMSO}-d_6$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Steady-state

fluorescence spectra were performed on an F4500 (Hitachi). MALDI-TOF mass spectra was taken on a Bruker BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometer with α -cyano-4-hydroxycinnamic acid as matrix. Elemental analysis was performed on an Elementar Vavio EI III.

Preparation of 12-(1H-Imidazol-1-yl)dodecanol (1): 1H-imidazole (6.80 g, 0.10 mol), NaOH (4.00 g, 0.10 mol), and 12-bromododecan-1-ol (2.65 g, 0.10 mol) in DMSO (20 mL) were stirred at 70 °C for 24 h. The solvent was poured into water.

After filtration, the residue was dried by air to give **1** as a white solid with 80% yield. ^1H NMR (400 MHz, CDCl_3 , 25 °C, δ): 7.48 (s, 1H), 7.07 (s, 1H), 6.92 (s, 1H), 3.94 (t, J = 12 Hz, 2H), 3.66 (s, J = 12 Hz, 2H), 1.77 (m, 4H), 1.28 (m, 16H); ^{13}C NMR (400 MHz, CDCl_3 , 25 °C, δ): 137.21, 129.52, 118.90, 63.15, 47.18, 36.06, 32.96, 31.19, 29.93, 29.65, 29.56, 29.54, 29.51, 29.49, 29.13, 27.36, 26.64, 25.87, 25.69. MS m/z : $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{15}\text{H}_{28}\text{N}_2\text{O}$, 252.39; found, 291.75. Anal. calcd for $\text{C}_{15}\text{H}_{28}\text{N}_2\text{O}$: C 71.38, H 11.18, N 11.10; found: C 71.29, H 11.23, N 11.21.

Preparation of Meso-chloro-benzyl-Bodipy (2): 4-(Chloromethyl)benzoyl chloride (3.84 g, 20.3 mmol) was added dropwise to a stirred solution of 2,4-dimethyl-1H-pyrrole (3.86 g, 40.6 mmol) in dichloromethane (200 mL) at room temperature under nitrogen, and the mixture was heated at 50 °C with stirring for 2 h. After vacuum evaporation of the solvent, toluene (150 mL), dichloromethane (15 mL), and triethylamine (13 mL) were added to the residual solid. The mixture was stirred at room temperature for 30 min under nitrogen and boron trifluoride diethyl etherate (18 mL) was then added. After heating at 50 °C for 1.5 h, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v) eluent to give **2** with 45% yield. ^1H NMR (400 MHz, CDCl_3 , 25 °C, δ): 7.53 (d, J = 8 Hz, 2H), 7.29 (d, J = 8 Hz, 2H), 5.98 (s, 2H), 7.03 (s, 4H), 4.66 (s, 2H), 2.55 (s, 6H), 1.38 (s, 6H); ^{13}C NMR (400 MHz, CDCl_3 , 25 °C, δ): 155.84, 143.17, 141.09, 138.77, 135.28, 131.49, 129.38, 128.61, 121.49, 45.73, 14.73. MS m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{BClF}_2\text{N}_2$, 372.65; found, 372.15. Anal. calcd for $\text{C}_{20}\text{H}_{20}\text{BClF}_2\text{N}_2$: C 64.46, H 5.41, N 7.52; found: C 64.38, H 5.46, N 7.64.

Preparation of Bodipy-C12OH (3): **1** (0.25 g, 1.0 mmol) and **2** (0.37 g, 1.0 mmol) were refluxed in CH_3CN (100 mL) for 7 d. After filtration and solvent evaporation, the crude product was precipitated by diethyl ether to yield compound **3** as a red solid with 67% yield. ^1H NMR (400 MHz, CDCl_3 , 25 °C, δ): 11.41 (s, 1H), 7.64 (d, J = 8 Hz, 2H), 7.37 (d, J = 8 Hz, 2H), 7.18 (s, 1H), 7.10 (s, 1H), 5.98 (s, 2H), 5.81 (s, 2H), 4.32 (t, J = 16 Hz, 2H), 3.65 (t, J = 16 Hz, 2H), 2.55 (s, 6H), 1.95 (m, 2H), 1.57 (m, 2H), 1.32 (m, 22H); ^{13}C NMR (400 MHz, CDCl_3 , 25 °C, δ): 156.14, 142.81, 140.25, 139.05, 136.64, 134.42, 131.31, 129.94, 129.50, 121.76, 121.65, 121.12, 63.03, 53.17, 50.59, 32.90, 30.29, 29.49, 29.38, 29.34, 29.30, 28.93, 26.34, 25.81, 14.74, 14.60. MS m/z : $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{35}\text{H}_{48}\text{BF}_2\text{N}_4\text{OCl}$, 589.59; found, 589.37. Anal. calcd for $\text{C}_{35}\text{H}_{48}\text{BF}_2\text{N}_4\text{OCl}$: C 67.26, H 7.74, N 8.96; found: C 67.33, H 7.66, N 8.89.

Preparation of Bodipy-C12OH-isocyanato (4): A mixture of **3** (0.31 g, 0.5 mmol), dibutyltin dilaurate (one drop), and 1-isocyanato-3,5-dimethylbenzene (0.22 g, 1.5 mmol) in CHCl_3 (0.3 mL) was stirred at -6 °C for 24 h. After filtration and solvent evaporation, the crude product was purified by flash column chromatography with $(\text{CH}_2\text{Cl}_2/\text{MeOH}, 15:1, \text{v/v})$ as eluent to yield compound **4** as a red solid with 76% yield. ^1H NMR (400 MHz, CDCl_3 , 25 °C, δ): 11.47 (s, 1H), 7.64 (d, J = 8 Hz, 2H), 7.37 (s, J = 8 Hz, 2H), 7.17 (s, 1H), 7.09 (s, 1H), 7.01 (s, 2H), 6.70 (s, 1H), 6.55 (s, 1H), 5.98 (s, 2H), 5.81 (s, 2H), 4.32 (t, J = 16 Hz, 2H), 4.15 (t, J = 16 Hz, 2H), 2.55 (s, 6H), 2.28 (s, 6H), 1.94 (m, 2H), 1.62 (m, 2H), 1.34 (m, 22H); ^{13}C NMR (400 MHz, CDCl_3 , 25 °C, δ): 156.16, 142.80, 140.20, 139.31, 138.89, 137.97, 136.69, 134.32, 131.30, 129.91, 129.52, 125.24, 121.65, 120.92, 116.59, 65.41, 53.18, 50.59, 30.30, 29.55, 29.52, 29.48, 29.40, 29.32, 29.07, 29.02, 26.39, 25.95, 21.52, 14.75, 14.61. MS m/z : $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{44}\text{H}_{57}\text{BF}_2\text{N}_5\text{O}_2\text{Cl}$, 736.76; found, 736.57. Anal. calcd for $\text{C}_{44}\text{H}_{57}\text{BF}_2\text{N}_5\text{O}_2\text{Cl}$: C 68.44, H 7.44, N 9.07; found: C 68.35, H 7.53, N 9.11.

Preparation of EtP5: To a solution of 1-ethoxy-4-methoxybenzene (3.35 g, 20.0 mmol) and paraformaldehyde (0.75 g, 25.0 mmol) in 1,2-dichloroethane (300 mL), boron trifluoride diethyl etherate [BF₃·O(C₂H₅)₂, 2.52 mL, 20.0 mmol] was added under nitrogen atmosphere at 25 °C. Then, the mixture was stirred for 4 h. The solution was washed by saturated sodium chloride solution and dried by anhydrous sodium sulfate. The solvent was removed and the residue was purified by flash column chromatography on silica gel with CH₂Cl₂ as eluent, affording EtP5 as a white solid with 46% yield. ¹H NMR (400 MHz, CDCl₃, 25 °C, δ): 6.81 (s, 10H), 3.89 (m, 20H), 3.77 (s, 10H), 1.36 (m, 30H); ¹³C NMR (400 MHz, CDCl₃, 25 °C, δ): 149.83, 128.54, 114.70, 63.67, 40.24, 31.71, 29.71, 22.77, 15.35, 14.24. MS *m/z*: [M⁺] calcd for C₅₅H₇₀O₁₀, 891.14; found, 890.76. Anal. calcd for C₅₅H₇₀O₁₀: C 74.13, H 7.92; found: C 74.23, H 7.86.

Preparation of [2]Rotaxane BC12P5 (5): A mixture of **3** (62.49 mg, 0.10 mmol) and EtP5 (0.37 g, 0.40 mmol) was stirred in CHCl₃ (0.40 mL) at –6 °C for 2 h. Then dibutylindilaurate (one drop) and 1-isocyanato-3,5-dimethylbenzene (0.20 g, 1.3 mmol) were added. The mixture was further stirred for 3 h. The solvent was removed and the residue was purified by flash column chromatography on silica gel with (CH₂Cl₂/MeOH = 25/1, v/v) eluent to afford **5** as a red solid with 76% yield. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C, δ): 9.12 (s, 1H), 7.93 (s, 1H), 7.60 (d, *J* = 8 Hz, 2H), 7.54 (d, *J* = 8 Hz, 3H), 7.15 (s, 2H), 6.84 (s, 5H), 6.79 (s 5H), 6.65 (s, 1H), 6.20 (s, 2H), 5.63 (s, 2H), 3.97 (m, 3H), 3.86 (m, 16H), 3.63 (m, 13H), 3.49 (m, 2H), 2.45 (s, 6H), 2.24 (s, 6H), 1.44–1.35 (m, 36H), 0.97 (m, 2H), 0.74 (m, 2H), 0.59 (m, 6H), 0.27 (m, 2H), –0.2 (m, 2H), –0.4 (m, 2H), –0.65 (m, 2H), –0.81 (m, 2H); ¹³C NMR (400 MHz, CDCl₃, 25 °C, δ): 156.06, 150.60, 149.47, 142.85, 138.93, 136.10, 135.76, 133.69, 131.47, 130.32, 130.09, 129.15, 125.84, 125.26, 122.89, 121.79, 121.62, 116.90, 116.51, 114.79, 66.22, 65.30, 63.86, 52.07, 48.37, 31.28, 30.78, 30.50, 30.06, 29.85, 29.70, 29.40, 28.93, 28.88, 27.12, 26.57, 25.73, 21.54, 15.74, 15.58, 14.76, 14.69. MS *m/z*: [M–Cl]⁺ calcd for C₉₉H₁₂₇BF₂N₅O₁₂Cl, 1627.90; found, 1627.95. Anal. calcd for C₉₉H₁₂₇BF₂N₅O₁₂Cl: C 71.49, H 7.70, N 4.21; found: C 71.41, H 7.78, N 4.26.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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