

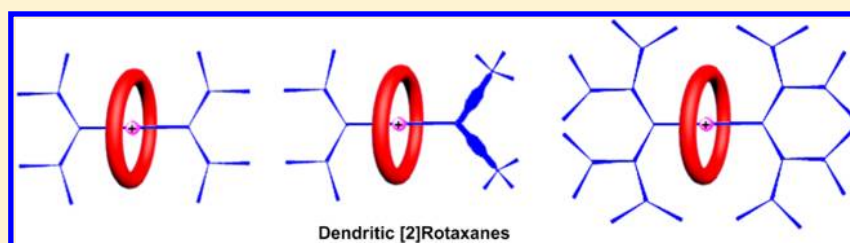
Dendritic [2]Rotaxanes: Synthesis, Characterization, and Properties

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Supporting Information



Dendritic [2]Rotaxanes

ABSTRACT: A series of dendritic ammonium salts have been designed and synthesized. Subsequently, they were used to construct the corresponding [2]rotaxanes by a template-directed clipping approach. Unusually, two unsymmetrical dendritic [2]rotaxanes containing fluorophore (pyrene units) were also obtained; their optical properties, such as UV/vis absorption and fluorescence, were measured. The results indicate that these two rotaxanes possess stronger intermolecular interaction in the solid state than in solution. As a result, solutions of high concentration readily formed the excimer. These special rotaxanes might be applied in dynamic fluorescence-responsive materials, and the rotaxane structure will also be used as a strategy to adjust the aggregated behaviors of fluorescent molecules.

1. INTRODUCTION

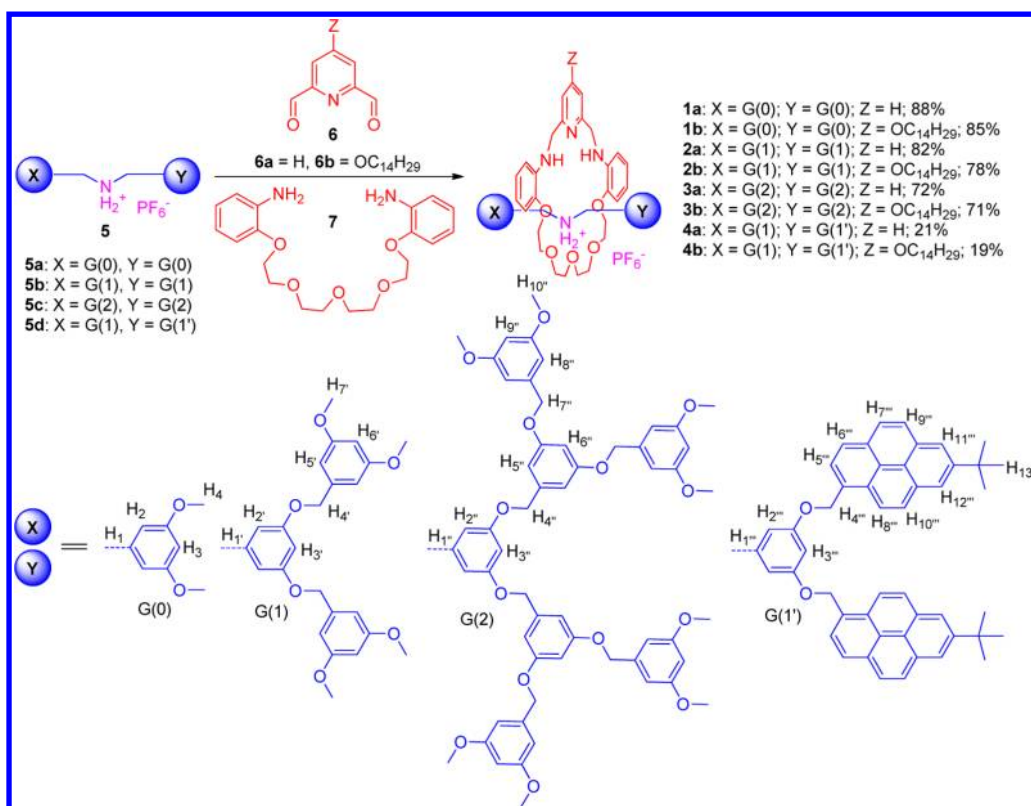
Mechanically interlocked rotaxanes have attracted increasing attention as a result of their potential application in nanoelectronics,¹ artificial muscles,² macroscopic liquid transport,³ and mesoporous silica-mounted nanovalves.⁴ In the meantime, this intensive study of rotaxanes has promoted increased understanding of design strategies and more complex systems such as rotaxane-based polymers.⁵ Dendrimers, for instance, contain highly branched and regularly repeating molecular architectures. They have emerged as one of the most striking areas of modern supramolecular chemistry since the middle 1980s.⁶ During the past few decades, many applications have been found for dendrimers, such as in the areas of encapsulation and delivery, catalysis, and materials science.⁷ Recently, some dendritic rotaxanes have been reported. For example, Stoddart et al. (1996) reported a series of dendritic rotaxanes, prepared by using the dendritic groups as a stopper.⁸ Subsequently, they utilized the “threading-followed-by-stoppering” strategy to construct a rotaxane-based dendrimer in which the two bis-dendrons acted as stoppers.⁹ Recently, Smith’s group made a similar report.¹⁰ Yang et al. reported the synthesis of [6]pseudorotaxanes through the coordinative-driven self-assembly of tris(crown ether)hexagons, dendritic dibenzylammonium and platinum cations.¹¹ On the basis of the above structural characteristics by which the dendritic groups were installed on the guest template, the Stoddart group developed a pseudorotaxane-based dendrimer by using a dendritic crown ether and dendritic ammonium.¹²

Usually, the template-directed clipping reaction based on 2,6-pyridinedicarboxaldehyde and tetraethylene glycol bis(2-aminophenyl)ether is considered an efficient strategy for the synthesis, in high yields, of all types of rotaxanes, such as linear [2]rotaxanes and oligomers,¹³ rectangular [4]rotaxanes,¹⁴ pH-induced switchable rotaxanes,¹⁵ daisy chains,¹⁶ and heterorotaxanes.¹⁷ Recently, we also utilized this approach to efficiently synthesize a series of catenanes.¹⁸ The examples presented above suggested to us that the dynamic clipping reaction for the construction of mechanically interlocked molecules would be highly efficient. In addition, the success of the template-directed clipping reaction is clearly an integral part of the construction of rotaxane-based dendrimers. Stoddart et al. reported the preparation of a series of dendritic rotaxanes by taking advantage of dendritic group-substituted 2,6-pyridinedicarboxaldehyde with tetraethylene glycol bis(2-aminophenyl)ether.¹⁹ This work reports the design and synthesis of a series of dendritic rotaxanes in which the dendritic stoppers were installed on the two sides of dialkylammonium by implementation of a dynamic covalent chemical process (Scheme 1). An important point to realize is that the fluorophore (pyrene units) was introduced to the stoppering sites to afford fluorescent rotaxane-based dendrimers. Their photophysical properties in solution and thin film states and their self-assembly properties as a function of concentration in solution were investigated.

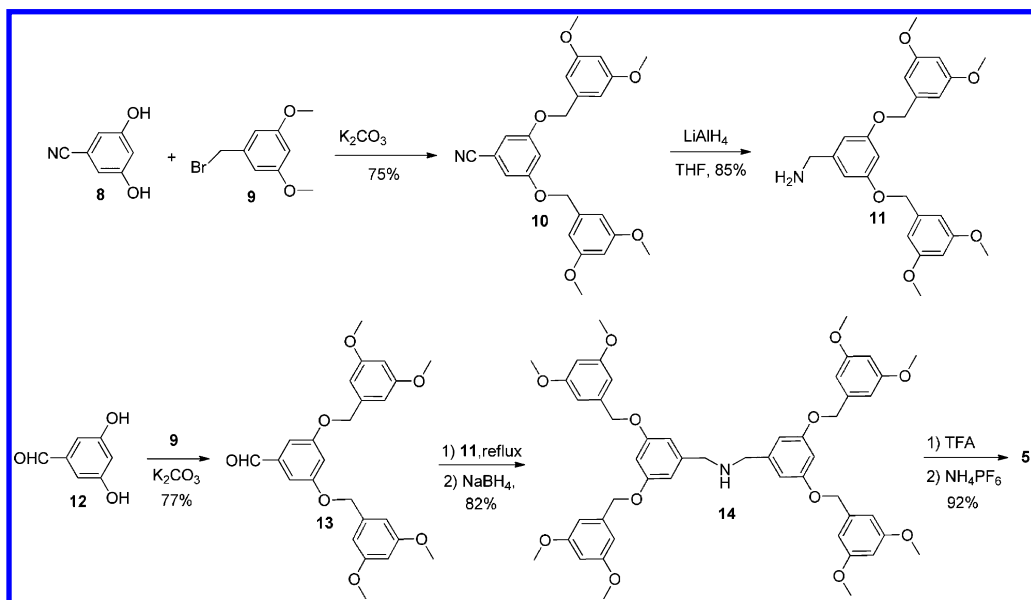
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Scheme 1. Schematic Representation of the “Template-Directed Clipping” Approach for the Construction of the Dendritic [2]Rotaxanes



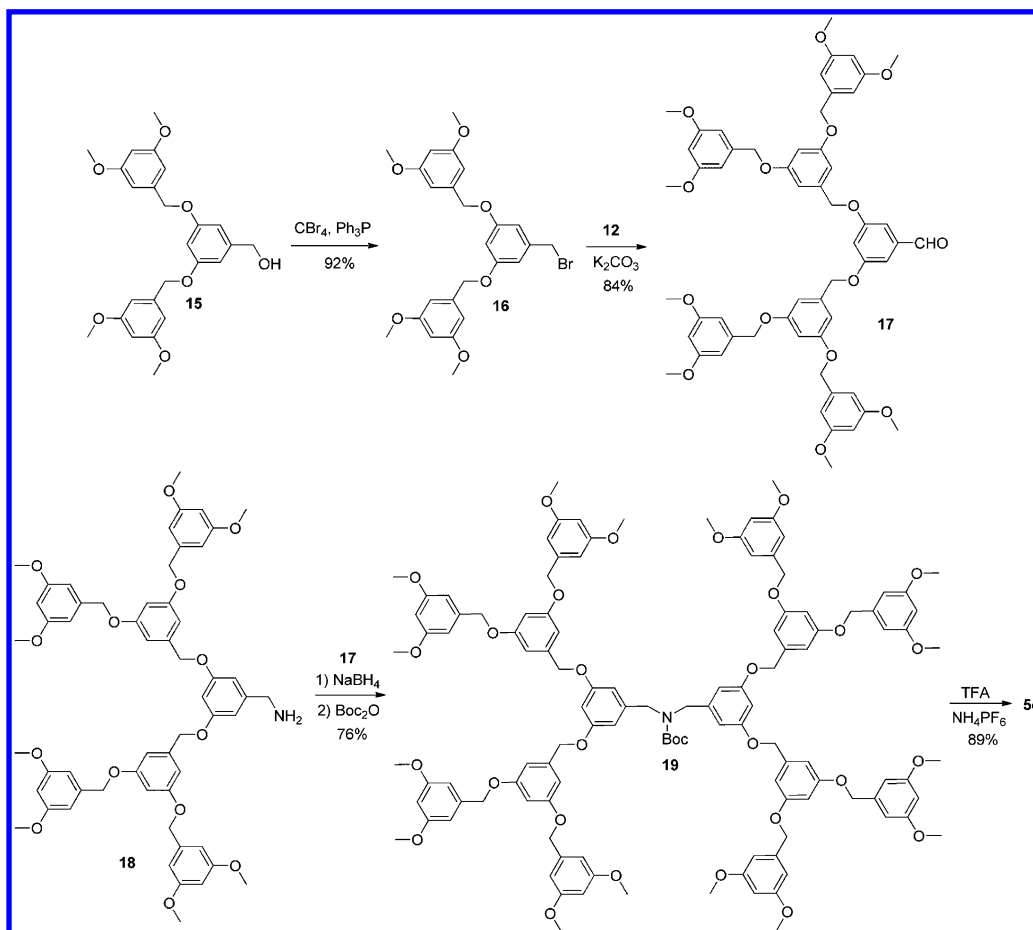
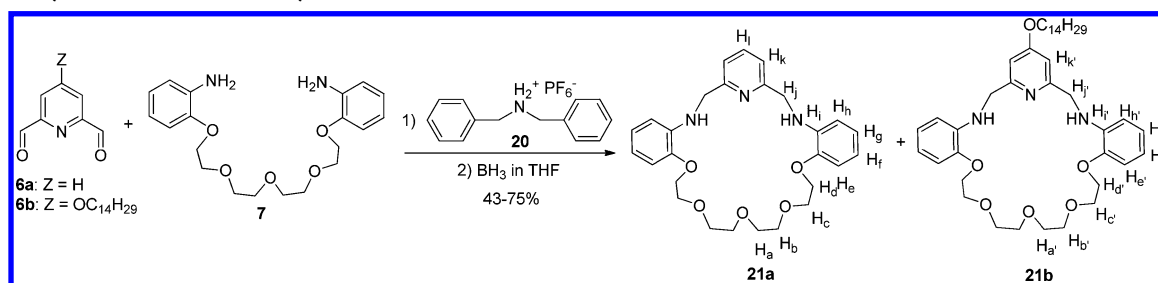
Scheme 2. Synthesis of the Dendritic Dialkylammoniums Salt 5b



2. RESULTS AND DISCUSSION

The synthesis of the dendritic dialkylammonium salts **5b** and **5c** is outlined in Schemes 2 and 3. The G0 dendritic dialkylammonium salt **5a** was prepared using a method reported previously.²⁰ As shown in Scheme 2, the treatment of 3,5-dihydroxybenzonitrile **8** and 3,5-dihydroxybenzaldehyde **12** with **9** in DMF in the presence of K₂CO₃ afforded compounds **10** and **13** in 75% and 77% yields, respectively. Subsequently, the reduction of compound **10** with LiAlH₄ in

THF gave the corresponding amine **11**, which was used for the next step without further purification. Condensation of benzylamine **11** with aldehyde **13** then produced the corresponding reversible dynamic imine, which was reduced by NaBH₄ in the solution of THF and MeOH to give the kinetically stable amine **14**, in 82% yield. Protonation of the free amine with excess trifluoroacetic acid (TFA) and subsequent counterion exchange with saturated NH₄PF₆

Scheme 3. Synthesis of the Dendritic Dialkylammonium Salt **5c**Scheme 4. Synthesis of the Macrocycles **21**

solution afforded the G1 dialkylammonium salt **5b** in 92% yield for the two steps.

Similarly, the synthesis of the G2 dialkylammonium salt **5c** is outlined in Scheme 3. First, the benzyl alcohol **15** was reacted with CBr_4 and Ph_3P to get the requisite intermediate **16**. Subsequently, 3,5-dihydroxybenzaldehyde **12** was treated with **16** in DMF in the presence of K_2CO_3 to afford compound **17** in 84% yield. Then, condensation of benzylamine **18** with the aldehyde **17** produced the corresponding reversible dynamic imine which was reduced by NaBH_4 in a solution of THF and MeOH to give the kinetically stable amine in a yield of 88%. In spite of the high yield, convenient purification was possible since the NH of the free amines could be protected by the Boc_2O . Subsequently, the Boc-protected alkylamines **19** were obtained in overall yields of 76% for the two steps. The Boc protective group was removed with excess trifluoroacetic acid (TFA) in dry dichloromethane, and the amine produced was

simultaneously protonated. Subsequent counterion exchange with saturated NH_4PF_6 solution afforded the G2 dialkylammonium salt **5c** in an 89% yield. In addition, one group of substances was needed to aid spectroscopic analysis of the processes involved in the dendritic [2]rotaxane formation; this included the *N*-hetero crown ethers **21a**^{14a} and **21b**.¹⁸ These were synthesized in 43–75% yields by the condensation of 2,6-pyridinedicarboxaldehyde **6a**, 4-(tetradecyloxy)pyridine-2,6-dicarboxaldehyde **6b**, and tetra(ethylene glycol)-bis(2-aminophenyl)ether **7**, respectively, followed by reduction with BH_3 /THF under the template effect of dibenzylammonium **20**, as outlined in Scheme 4.^{14a} The chemical structures of all the new compounds were confirmed by standard spectroscopic characterizations, such as NMR, mass spectrometry, and elemental analyses (see Supporting Information [SI]).

Next, the G0–G3 dialkylammonium salts were subjected to the dynamic covalent chemistry. First, **5a** was used to

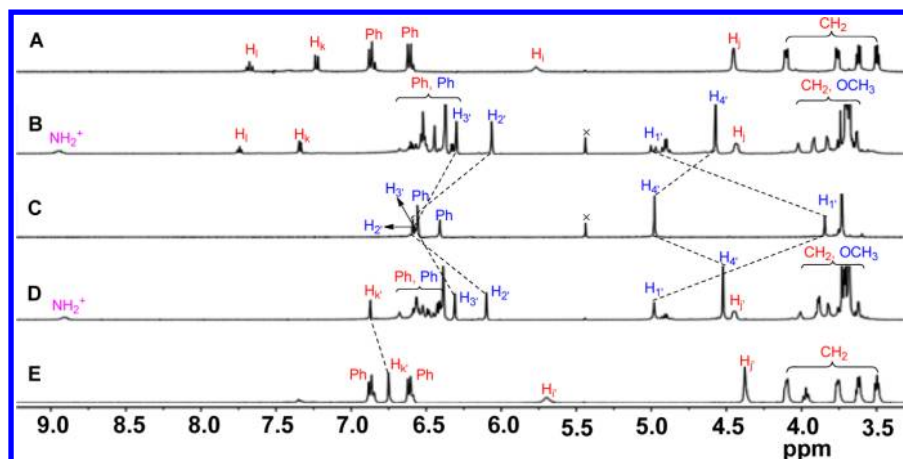


Figure 1. Partial ^1H NMR spectra (600 MHz in CD_3CN at rt) of **21a** (A), **2a** (B), **5b** (C), **2b** (D), and **21b** (E).

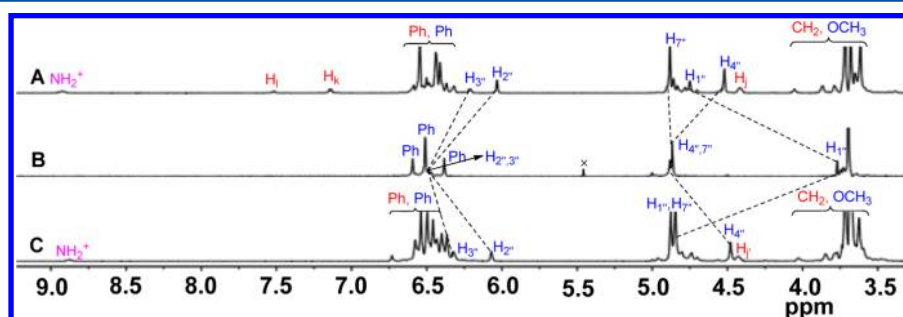
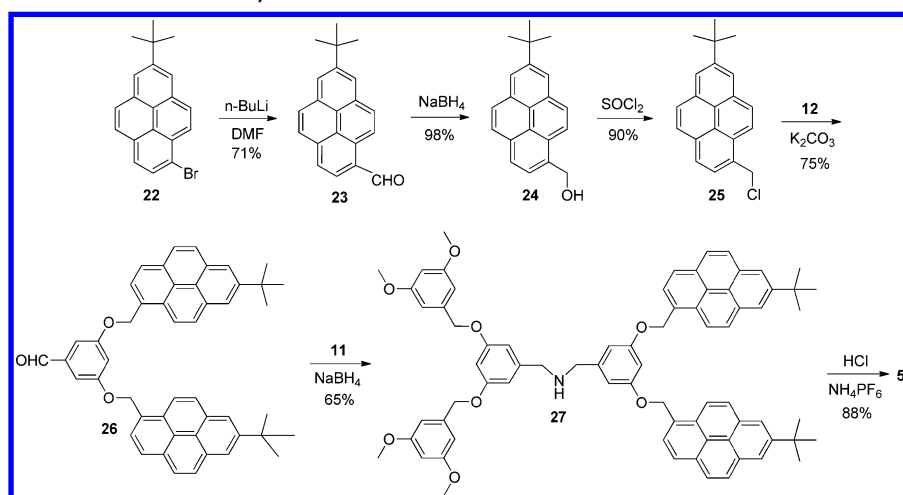


Figure 2. Partial ^1H NMR spectra (600 MHz in CD_3CN at rt) of **3a** (A), **5c** (B), and **3b** (C).

Scheme 5. Synthesis of the Dendritic Dialkylammonium Salt **5d**



synthesize the [2]rotaxanes **1a** and **1b**; [2]rotaxane **1a** has been reported in the literature.^{13a} Meanwhile, the substituted dialdehyde **6b** has also been used by our group to construct catenanes.¹⁸ Here, the ammonium salt **5a** was also used to perform the dynamic clipping reaction with **6b** and **7** in anhydrous CH_3CN . The mixture was then treated with $\text{BH}_3 \cdot \text{THF}$ to afford [2]rotaxanes **1b** in 85% yield. The simple [2]rotaxanes have been well characterized by ^1H NMR spectroscopy. From the ^1H NMR (as shown in Figure S1, SI), [2]rotaxane **1b** displayed some shifts similar to those of [2]rotaxane **1a**. For example, the resonance of the protons on the stopper units (H_2 and H_3) showed an obvious upfield shift, due to the shielding effect of the encircling crown ethers. In

addition, the resonances for the central methylene (H_1) were shifted downfield. Next, the first-generation dendritic [2]-rotaxanes **2a** and **2b** were synthesized using the same method, in 82% and 78% yields, respectively. Evidence for the formation of **2a** and **2b** in this process comes from analysis of their ^1H NMR spectra. As shown in Figure 1, an obvious downfield shift of the resonance for the methylene protons ($\text{H}_{1'}$) and upfield shifts for the benzene ring protons ($\text{H}_{2'}$ and $\text{H}_{3'}$) on the stopper units of **5b**, as revealed by a comparison of the spectra of **2a** and **2b**, show that the crown ether unit in the former substance is threaded by the ammonium template. Meanwhile, other methylene protons ($\text{H}_{4'}$) displayed obvious upfield shifts. It is notable that the protons of NH_2^+ in the template of

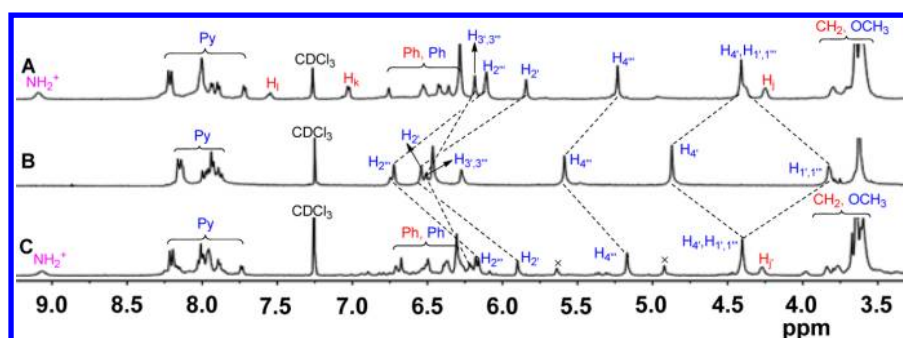


Figure 3. Partial ^1H NMR spectra (600 MHz in CDCl_3 at rt) of **4a** (A), **5d** (B), and **4b** (C).

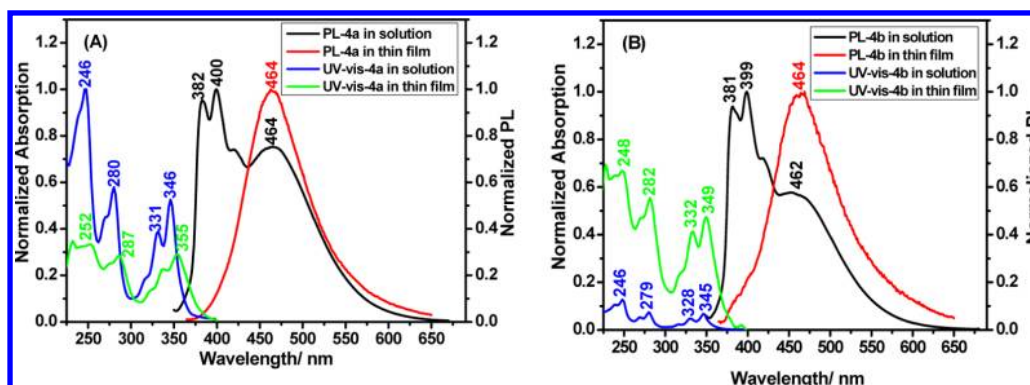


Figure 4. UV-vis absorption and photoluminescence spectra of **4a** and **4b** in CH_2Cl_2 solution (1.0×10^{-5} M) and in thin film.

rotaxane **2a** were detected at 8.97 ppm because of the stabilizing effect of the hydrogen-bonding interactions of the oxygens on the N-hetero crown ether **21a** with the ammonium hydrogen atoms. Moreover, similar chemical shift changes for the characteristic protons on [2]rotaxane **2b** were observed. These results are in good agreement with published literature.^{13–19} Subsequently, a similar method was used to construct the second-generation dendritic [2]rotaxanes. As a result of steric hindrance, the mixture used for the clipping reaction had to be stirred for 7 days to afford the target molecules **3a** and **3b**, in yields of 72% and 71%, respectively. An investigation of the ^1H NMR indicated that the second-generation dendritic [2]rotaxanes had shifts similar to those of the resonances of some other protons, such as the two neighboring methylene protons ($\text{H}_{1'}$) of ammonium, other methylene protons ($\text{H}_{4'}$) and benzene ring protons ($\text{H}_{2'}$ and $\text{H}_{3'}$). This is made clear by a comparison of the spectra of **2a** and **2b**, as shown in Figure 2. These results indicate that the N-hetero crown ether encircled the ammonium site. Further proof was provided by the ESI-MS or MALDI-MS in acetonitrile. For example, the peaks at m/z 1009.9, 1342.4, 1555.5, 2430.3, and 2642.4 can be assigned to the $[\text{M} - \text{PF}_6]^-$ species, in which M represents the [2]rotaxanes **1b**, **2a**, **2b**, **3a** and **3b**, respectively (see SI).

The success of our synthesis of the dendritic rotaxanes inspired us to investigate further the functional dendritic rotaxanes. Subsequent work has focused on the dendritic [2]rotaxane containing a fluorophore. For this work, we selected pyrene as the fluorescent unit. The dialkylammonium salt **5d**, which has an asymmetrical structure consisting of different dendritic stopper units G1 and G1', was synthesized according to the synthetic route described by Scheme 5. First, compound **22** was reacted with $n\text{-BuLi}$ in anhydrous THF at -78°C for 3 h, then dry DMF was added to obtain the

corresponding aldehyde **23**. Subsequently, **23** was reduced by NaBH_4 in a solution of THF and MeOH to give the desired alcohol **24**. The alcohol was chlorized by SOCl_2 to obtain benzyl chloride **25**, subsequently used without further purification. Then, 3,5-dihydroxybenzaldehyde **12** with the benzyl chloride **25** in DMF in the presence of K_2CO_3 afforded the ester **26**, in 75% yield. The amine **27** was synthesized using a similar condensation reaction. Subsequent protonation of the free amine with an excess of 1 M HCl in acetone, followed by counterion exchange with saturated NH_4PF_6 solution, afforded the ammonium salt **5d**.

A similar clipping reaction was performed by mixing the ammonium salt **5d** with **6** and **7**. The process of self-assembly could be followed using ^1H NMR. The ^1H NMR spectrum of the [2]rotaxane **4a** is shown in Figure 3A. Compared with the spectrum of the template **5d** (Figure 3B), the resonance of the protons ($\text{H}_{1'}$ and $\text{H}_{1''}$) in the two side methylene groups, adjacent to the ammonium, showed obvious downfield shifts, while the resonance of the protons ($\text{H}_{4'}$ and $\text{H}_{4''}$) on the stopper groups also showed contrary shifts, owing to the shielding effect of the encircling N-hetero crown ether ring system. Furthermore, as depicted in Figure 3A, upfield shifts of the resonances for the benzene ring protons ($\text{H}_{2'}$, $\text{H}_{2''}$ and $\text{H}_{3'}$, $\text{H}_{3''}$) were observed, in comparison to the spectrum of the template **5d**, as shown in Figure 3B. Similar changes of signal resonances are also reflected in the ^1H NMR of [2]rotaxane **4b**, as shown in Figure 3C. The observed shifts in the proton resonances, which are in good agreement with those described above for the first- and second-generation dendritic [2]rotaxanes, suggest that the newly installed crown ether ring system in the dendritic [2]rotaxanes **4a** and **4b** encircled the ammonium moiety of **5d**. In addition, there is an obvious change, in that the overlapping peaks on the pyrene units of **5d** are split, possibly due to the introduction of N-hetero crown

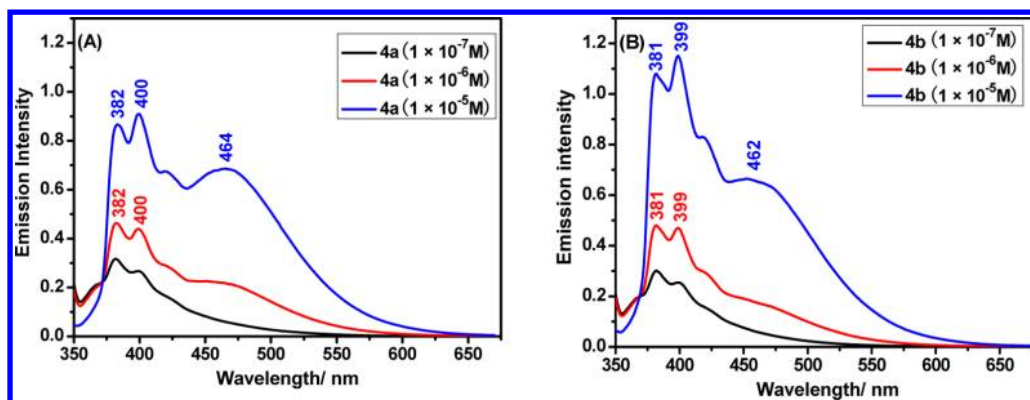


Figure 5. Photoluminescence spectra of **4a** and **4b** in CH_2Cl_2 solution at different concentrations.

ether weakening the stacking between the pyrene units. Additional evidence supporting this conclusion comes from analysis of the MALDI mass spectrum (SI), which contains peaks at m/z 1581.6, and 1793.9 that correspond to the $-\text{PF}_6$ salts of [2]rotaxanes **4a** and **4b**, respectively.

Following the introduction of the fluorescent pyrene units, an investigation was performed of the optical properties of **4a** and **4b**. The UV–vis absorption and fluorescence spectra of **4a** and **4b**, in solution and in the solid state, are presented in Figure 4. The UV–vis absorption spectrum of **4a** in dichloromethane (1.0×10^{-5} M) shows four main absorptions, at 246 nm, 280 nm, 331 and 346 nm. A similar spectrum is also observed in the UV–vis absorption spectra of **4b** in Figure 4B. Compared with the absorption in solution, the thin films of **4a** and **4b** display 5–9 nm red shifts, which implies that there is stronger intermolecular interaction in the solid state. Subsequently, the photoluminescence spectra were also investigated. As can be seen in Figure 4A and B, the spectra of [2]rotaxane **4a** and **4b** have a broad emission from 350 to 650 nm in solution. Usually, pyrene is easy to form an excimer (dimer) in an electronic excited state, and the emission band associated with the excimer will occur at a longer wavelength that is significantly different, often a rather broad featureless transition over a wide range of wavelengths. Furthermore, the excimer emission generally locates between 410 and 480 nm, while monomer emission typically shows three or four transitions, between 390 and 420 nm.²¹ The views are well reflected in our experiment by investigating photoluminescence spectra of different concentration. The emission spectra in Figure 5A,B show that the intensity of the emission bands decreased significantly with decreasing concentration. The fluorescence spectra of **4a** and **4b** show broader emission bands, with three main peaks around at 382, 400, and 464 nm, when the concentration in dichloromethane solution was 1.0×10^{-5} M. Additionally, the intensity of the fluorescence bands clearly decreased by diluting the solution to 1.0×10^{-6} M. In addition, the bands in the visible region for **4a** and **4b** became weak emission bands. The intensity of emission continued to decrease upon further dilution from 1.0×10^{-6} M to 1.0×10^{-7} M, resulting in the complete disappearance of the fluorescence bands in the visible region (470–550 nm). Therefore, the emission bands of **4a** and **4b** from 350 to 420 nm can be ascribed to the emission of the monomer of pyrene-based rotaxanes, while another broader emission band from 430 to 600 nm is assigned to the formation of excimer. Additionally, the films of **4a** and **4b** only show a peak around at 464 nm. These results indicated that [2]rotaxanes **4a** and **4b** had a

stronger intermolecular interaction in such a mechanically interlocked system and tended to form the excimer at higher concentration, while the excimer will be decreased at low concentration. In consideration of the fact that pyrene-based fluorescent [2]rotaxanes **4a** and **4b** possess optical character similar to that of pyrene, it thus provides a reference to construct the fluorescent, mechanically interlocked molecules and to adjust the aggregated behaviors.

3. CONCLUSION

We have successfully synthesized a series of dendritic dialkylammonium salts, from G0 to G2, using a template-directed clipping approach to efficiently self-assemble a series of [2]rotaxane-based dendrimers. This has proved possible even though some bigger dendritic groups were introduced. Subsequently, the pyrene fluorophore was successfully introduced to the stopper group, and two unsymmetrical dendritic [2]rotaxanes were synthesized. Their optical properties indicate that they possess stronger intermolecular interaction in the solid state than in solution, and readily form the excimer in solutions of higher concentration. Further work will focus on their functionalization and application, such as preparing dynamic self-assembling fluorescent materials, adjusting the aggregated behaviors and constructing multi-fluorophore molecules.

4. EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under argon atmosphere from sodium-benzophenone. 1-(Bromomethyl)-3,5-dimethoxybenzene **9**,²³ **11**,²⁴ **13**,²⁵ **14**,²⁵ **15**,²⁶ **16**,²⁷ **17**,²⁶ **18**,²⁴ and 1-bromo-7-(*tert*-butyl)pyrene **22**²⁸ were prepared by literature methods or modified literature methods. All other starting materials were obtained commercially as analytical-grade and used without further purification. ¹H NMR spectra were collected with 400 MHz or 600 MHz spectrometer, while ¹³C NMR spectra were collected with a 400 MHz spectrometer. Mass spectra were measured in the ESI or MALDI mode. UV–vis spectra were obtained on a UV spectrophotometer, and fluorescence spectra were taken on a luminescence spectrometer.

Synthesis of 10. Into a 250-mL, two-necked, round-bottom flask equipped with a magnetic stirrer was placed a mixture of **8** (1.35 g, 10.0 mmol), 1-(bromomethyl)-3,5-dimethoxybenzene **9** (4.60 g, 20.0 mmol), and potassium carbonate (4.20 g, 30.0 mmol); then 200 mL DMF was added. The reaction was stirred for 24 h at 50 °C under argon atmosphere. The resulting mixture was allowed to cool to room temperature and was filtered. After that, the solvents were removed under vacuum, and the residue was extracted by ethyl acetate and then dried over anhydrous Na_2SO_4 , removed of solvent under reduced

pressure, and purified on a silica gel column using dichloromethane/petroleum ether (2:1) as the eluent to obtain **10** as a white solid. Yield: 3.26 g, 75%. Compound **10**: ^1H NMR (600 MHz, CDCl_3): δ ppm = 6.83 (d, J = 2.4 Hz, 2H), 6.79 (s, 1H), 6.54 (d, J = 1.8 Hz, 4H), 6.43 (t, J = 1.8 Hz, 2H), 4.98 (s, 4H), 3.80 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 161.0, 159.8, 138.0, 118.6, 113.3, 110.9, 107.2, 105.1, 99.9, 70.3, 55.3. ESI MS: m/z = 458.10 $[\text{M} + \text{Na}^+]$, 475.40 $[\text{M} + \text{K}^+]$; calculated exact mass: 435.20. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_6$: C, 68.95; H, 5.79; N, 3.22. Found: C, 68.81; H, 5.68; N, 3.29.

Synthesis of 5b. To a solution of the amine **14** (0.86 g, 1.0 mmol) in dry CH_2Cl_2 (20 mL), was added TFA (0.32 mL, 5.0 mmol) at room temperature. After the solution stirred for 2 h under argon atmosphere, the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and MeOH, and then saturated NH_4PF_6 (20 mL, aq) was added and stirred for several minutes to yield a white creamy solid. The residue was extracted by CH_2Cl_2 . The organic layer was washed by H_2O for three times and dried over anhydrous Na_2SO_4 , and the solvent was removed under vacuum to give the compound **5b**. Yield: 0.93 g, 92%. Compound **5b**: ^1H NMR (600 MHz, CD_3CN): δ ppm = 6.62 (d, J = 1.8 Hz, 4H), 6.60 (d, J = 1.8 Hz, 2H), 6.58 (d, J = 1.8 Hz, 8H), 6.43 (t, J = 1.8 Hz, 4H), 5.00 (s, 8H), 3.87 (s, 4H), 3.75 (s, 24H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 161.6, 160.5, 140.0, 138.1, 108.6, 105.9, 102.3, 99.8, 70.1, 55.5, 52.2. ESI MS: m/z = 862.70 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 1007.30. Anal. Calcd for $\text{C}_{50}\text{H}_{56}\text{F}_6\text{NO}_{12}\text{P}$: C, 59.58; H, 5.60; N, 1.62. Found: C, 59.50; H, 5.48; N, 1.67.

Synthesis of 19. A mixture of **18** (0.98 g, 1.0 mmol) and **17** (0.98 g, 1.0 mmol) in dry toluene (80 mL) was placed into a 100 mL round-bottom flask and refluxed for 24 h under argon atmosphere. The solvent was removed under vacuum, and the residue was dissolved in THF (50 mL) and MeOH (50 mL), and then NaBH_4 (0.38 g, 10.0 mmol) was added in portions. After stirring overnight, the solvents were removed under vacuum, and the residue was extracted by dichloromethane. The organic layer was washed by brine until clear, dried over anhydrous Na_2SO_4 , and concentrated in vacuo to give a kinetically stable amine as a light-yellowish oil in the yield of 88%. The unpurified amine was dissolved in dry chloroform (20 mL), and then Boc_2O (0.44 g, 2.0 mmol) and triethylamine (0.43 mL) were added. The mixture was stirred at room temperature for 24 h. Removal of solvent under reduced pressure and purification on a silica gel column using petroleum ether/ethyl acetate (1:1) as the eluent obtained the Boc-protected **19** as a white solid. Yield: 1.37 g, 76%. Compound **19**: ^1H NMR (600 MHz, CDCl_3): δ ppm = 6.64 (s, 4H), 6.57–6.53 (m, 24H), 6.49–6.48 (m, 2H), 6.41–6.39 (m, 12H), 4.98 (s, 4H), 4.92–4.89 (m, 24H), 3.76 (s, 48H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 160.8, 159.9, 139.0, 138.6, 106.8, 106.2, 105.1, 101.4, 100.7, 99.8, 80.1, 69.8, 60.3, 55.2, 28.3, 14.1. ESI MS: m/z = 2072.98 $[\text{M} + \text{Na}^+]$, 2088.94 $[\text{M} + \text{K}^+]$; calculated exact mass: 2049.84. Anal. Calcd for $\text{C}_{115}\text{H}_{127}\text{NO}_{30}$: C, 69.68; H, 6.24; N, 0.68. Found: C, 69.75; H, 6.33; N, 0.61.

Synthesis of 5c. To a solution of the Boc-protected amine **19** (1.03 g, 0.5 mmol) in dry CH_2Cl_2 (20 mL) was added TFA (0.16 mL, 2.5 mmol) at room temperature. After stirring for 2 h under argon atmosphere, the solvent was removed under a vacuum. The residue was dissolved in CH_2Cl_2 and MeOH, and then saturated NH_4PF_6 (10 mL, aq) was added and stirred for several minutes to yield a white creamy solid. The residue was extracted by CH_2Cl_2 , and the organic layer was washed by H_2O three times and dried over anhydrous Na_2SO_4 , and the solvents were removed under vacuum to give the compound **5c**. Yield: 0.93 g, 89%. Compound **5c**: ^1H NMR (600 MHz, CD_3CN): δ ppm = 6.60 (s, 8H), 6.52 (d, J = 1.2 Hz, 20H), 6.49 (s, 4H), 6.48 (s, 2H), 6.39 (s, 8H), 4.89–4.87 (m, 24H), 3.78 (s, 4H), 3.70 (s, 48H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 161.6, 160.6, 140.2, 108.4, 107.1, 106.0, 105.1, 102.3, 102.0, 100.0, 70.1, 55.6, 52.4. ESI MS: m/z = 1950.710 $[\text{M} - \text{PF}_6^-]$, 1972.66 $[\text{M} - \text{HPF}_6 + \text{Na}^+]$, 1988.64 $[\text{M} - \text{HPF}_6 + \text{K}^+]$; calculated exact mass: 2095.76. Anal. Calcd for $\text{C}_{50}\text{H}_{56}\text{F}_6\text{NO}_{12}\text{P}$: C, 65.29; H, 5.77; N, 0.72. Found: C, 65.39; H, 5.89; N, 0.76.

Synthesis of 23. Bromopyrene derivative **22** (2.50 g, 7.5 mmol) was placed in a 250 mL two-necked round-bottomed flask and mixed

with dry THF (120 mL) and then cooled to -78°C . After $n\text{-BuLi}$ (1.6 M in hexane, 5.6 mL, 9.0 mmol) was added to this mixture, the reaction mixture was stirred at -78°C for 3 h. DMF (0.6 mL, 7.8 mmol) was added to this reaction mixture at one portion at -78°C . The reaction mixture was stirred at -78°C for 40 min and then poured into a saturated aqueous NH_4Cl solution. The resulting solid was obtained by filtration, and the organic filtrates were separated. The aqueous layer was extracted with CH_2Cl_2 , and then the combined organic extracts were washed with a saturated aqueous NaHCO_3 solution and a saturated aqueous NaCl solution, successively. The organic extracts were dried over anhydrous Na_2SO_4 and then filtered and concentrated under reduced pressure; purification on a silica gel column using petroleum ether/ethyl acetate (8:1) as the eluent obtained compound **23** as a yellow solid. Yield: 1.52 g, 71%. Compound **23**: ^1H NMR (600 MHz, CDCl_3): δ ppm = 10.76 (s, 1H), 9.38 (d, J = 9.0 Hz, 1H), 8.39 (d, J = 12 Hz, 1H), 8.34 (d, J = 7.8 Hz, 2H), 8.29 (d, J = 9.6 Hz, 1H), 8.21–8.20 (m, 2H), 8.06 (d, J = 6 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 193.1, 149.7, 135.2, 131.0, 130.9, 130.8, 130.7, 130.1, 127.0, 126.9, 124.3, 124.2, 124.0, 122.7, 122.1, 35.2, 31.8. EI MS: m/z = 286.04; calculated exact mass: 286.14. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}$: C, 88.08; H, 6.34. Found: C, 88.15; H, 6.29.

Synthesis of 24. In a round-bottom flask charged with a stir bar was stirred compound **23** (0.63 g, 2.2 mmol) at 0°C in THF. A solution of NaBH_4 (0.25 g, 6.5 mmol) in 95% ethanol (15 mL) was prepared along with 10 drops of 1 M NaOH. This solution was added to the aldehyde and stirred at 0°C for 15 min; the mixture changed from a yellow-green color to milky white. The mixture was quenched with 10% HCl, diluted with water (50 mL), and extracted with CH_2Cl_2 (3×30 mL). The combined organic fractions were washed with NaHCO_3 solution and water successively and then dried with anhydrous Na_2SO_4 . Filtration and evaporation afforded the desired alcohol **24**. Yield: 0.62 g, 98%. Compound **24**: ^1H NMR (600 MHz, CDCl_3): δ ppm = 8.32 (d, J = 6.0 Hz, 1H), 8.23 (d, J = 6.0 Hz, 2H), 8.11 (t, J = 12.0 Hz, 2H), 8.04–8.01 (m, 2H), 7.98 (d, J = 6.0 Hz, 1H), 5.38 (s, 2H), 1.59 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 149.0, 133.4, 131.0, 130.5, 128.4, 128.0, 127.5, 127.2, 125.5, 124.7, 124.4, 122.9, 122.8, 122.5, 122.4, 63.6, 35.2, 31.9. EI MS: m/z = 288.06; calculated exact mass: 288.15. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}$: C, 87.45; H, 6.99. Found: C, 87.33; H, 6.89.

Synthesis of 26. To a solution of pyrenemethanol **24** (2.50 g, 8.6 mmol) in CH_2Cl_2 (50 mL) was added pyridine (1.00 g, 12.6 mmol), and then SOCl_2 (4 mL, 6.53 g, 54.8 mmol) was added dropwise via a dropping funnel. After the solution was stirred overnight at room temperature, ice (50 g) was added. The CH_2Cl_2 phase was collected and dried with anhydrous Na_2SO_4 . Upon the removal of solvent, **25** was obtained as yellow powders in 90% yield without further purification because of instability. In a 250 mL two-necked, round-bottom flask equipped with a magnetic stirrer was placed a mixture of **12** (0.21 g, 1.5 mmol), **25** (0.92 g, 3.0 mmol), and potassium carbonate (0.62 g, 4.5 mmol); then 150 mL DMF was added. The reaction was stirred for 24 h at 50°C under an argon atmosphere. The resulting mixture was allowed to cool to room temperature and filtered. After that, the solvent was removed under vacuum, and the residue was extracted by ethyl acetate, then dried over anhydrous Na_2SO_4 , and then removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether/ethyl acetate (5:1) as the eluent to obtain the compound **26** as a light-yellow solid. Yield: 4.38 g, 75%. Compound **26**: ^1H NMR (400 MHz, CDCl_3): δ ppm = 9.94 (s, 1H), 8.24–8.22 (m, 6H), 8.12 (d, J = 8.0 Hz, 4H), 8.07–8.01 (m, 6H), 7.30 (s, 2H), 7.09 (s, 1H), 5.75 (s, 4H), 1.58 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 191.8, 160.5, 149.2, 131.5, 131.0, 130.5, 129.0, 128.7, 127.1, 124.4, 122.8, 122.6, 108.8, 108.5, 69.1, 35.2, 31.9. ESI MS: m/z = 701.40 $[\text{M} + \text{Na}^+]$, 717.30 $[\text{M} + \text{K}^+]$; calculated exact mass: 678.31. Anal. Calcd for $\text{C}_{49}\text{H}_{42}\text{O}_3$: C, 86.69; H, 6.24. Found: C, 86.77; H, 6.19.

Synthesis of 27. A mixture of **26** (0.68 g, 1.0 mmol) and **11** (0.44 g, 1.0 mmol) in dry toluene (80 mL) in a 100 mL round-bottom flask was refluxed for 24 h under argon atmosphere. The solvent was removed under vacuum, and the residue was dissolved in THF (30

mL) and MeOH (30 mL), and then NaBH_4 (0.38 g, 10.0 mmol) was added in portions. After stirring overnight, the solvents were removed under vacuum, and the residue was extracted by CH_2Cl_2 . The organic layer was washed by brine until clear, dried over anhydrous Na_2SO_4 , removed of solvent under reduced pressure, and purified on a silica gel column using petroleum ether/ethyl acetate (2:1) as the eluent to obtain the compound 27 as a light-yellow solid. Yield: 0.72 g, 65%. Compound 27: ^1H NMR (400 MHz, CDCl_3): δ ppm = 8.26–8.22 (m, 6H), 8.10–8.08 (m, 4H), 8.05–7.99 (m, 6H), 6.80 (s, 3H), 6.63 (s, 2H), 6.54 (s, 3H), 6.51 (s, 2H), 6.36 (s, 2H), 5.71 (s, 4H), 4.95 (s, 4H), 3.80–3.78 (m, 4H), 3.72 (s, 12H), 1.58 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 161.0, 160.9, 160.3, 160.0, 159.9, 149.1, 139.3, 139.2, 131.3, 129.0, 127.1, 122.8, 122.5, 122.5, 107.6, 107.4, 107.2, 105.3, 105.2, 100.0, 70.1, 68.9, 55.2, 53.2, 35.1, 31.8. ESI MS: m/z = 1102.50 $[\text{M} + \text{H}^+]$; calculated exact mass: 1101.52. Anal. Calcd for $\text{C}_{74}\text{H}_{71}\text{NO}_8$: C, 80.63; H, 6.49; N, 1.27. Found: C, 80.50; H, 6.42; N, 1.36.

Synthesis of 5d. 27 (1.10 g, 1.0 mmol) was dissolved in acetone (200 mL) and treated sequentially with HCl (aq) (1 M, 2 mL) and saturated NH_4PF_6 (aq) (20 mL). The organic solvent was evaporated under reduced pressure; the precipitate was filtered off and washed with water (10 mL) for several times to afford 5d as a yellow solid. Yield: 1.10 g, 88%. Compound 5d: ^1H NMR (400 MHz, CDCl_3): δ ppm = 8.15 (d, J = 8.8 Hz, 6H), 8.00–7.87 (m, 10H), 6.75–6.73 (m, 2H), 6.54 (s, 2H), 6.51 (s, 2H), 6.47 (s, 4H), 6.28 (s, 2H), 5.59 (s, 4H), 4.88 (s, 4H), 3.83 (s, 4H), 3.63 (s, 12H), 1.55 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm = 160.8, 160.5, 160.2, 149.0, 138.8, 138.7, 131.1, 130.9, 130.4, 128.9, 128.8, 122.7, 122.5, 108.6, 108.3, 105.1, 99.8, 69.8, 68.7, 55.1, 35.1, 31.8, 29.7. ESI MS: m/z = 1102.80 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 1247.50. Anal. Calcd for $\text{C}_{74}\text{H}_{72}\text{F}_6\text{N}_4\text{O}_8\text{P}$: C, 71.20; H, 5.81; N, 1.12. Found: C, 71.09; H, 5.73; N, 1.21.

Synthesis of 1b. A mixture of salt 5a (93 mg, 0.2 mmol), tetraethylene glycol bis(2-aminophenyl)ether 7 (75 mg, 0.2 mmol), and 2,6-pyridinedicarboxaldehyde derivative 6b (69 mg, 0.2 mmol) was stirred for 24 h in dry CH_3CN (10 mL) under argon atmosphere at room temperature. Then 1 M $\text{BH}_3\cdot\text{THF}$ solution (1.6 mL) was added, and the mixture was further stirred overnight. The solvents were removed under vacuum, and the residue was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeCN}/\text{MeOH}$ = 100:0:0–75:25:1) to give the [2]rotaxane 1b. Yield: 0.20 g, 85%. Compound 1b: ^1H NMR (600 MHz, CD_3CN): δ ppm = 8.80 (s, 2H), 6.95 (s, 2H), 6.70–6.64 (m, 4H), 6.61–6.60 (m, 2H), 6.45 (d, J = 7.2 Hz, 2H), 6.27 (s, 2H), 6.14 (s, 4H), 4.52 (br, 4H), 4.41 (s, 2H), 4.15–4.13 (m, 2H), 4.04 (s, 4H), 3.92 (d, J = 3.0 Hz, 4H), 3.83 (s, 4H), 3.77 (s, 2H), 3.75 (s, 4H), 3.42 (s, 12H), 1.82 (t, J = 5.4 Hz, 2H), 1.49 (br, 2H), 1.40 (br, 2H), 1.29 (br, 18H), 0.89 (m, 3H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 161.5, 147.2, 137.6, 134.7, 122.0, 120.0, 112.9, 110.8, 109.4, 108.4, 108.1, 107.3, 101.4, 71.6, 71.0, 70.7, 69.9, 68.1, 55.6, 53.2, 50.1, 32.3, 30.0, 29.7, 29.1, 26.2, 23.0, 14.1. ESI MS: m/z = 1009.90 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 1154.59. Anal. Calcd for $\text{C}_{59}\text{H}_{85}\text{F}_6\text{N}_4\text{O}_{10}\text{P}$: C, 61.34; H, 7.42; N, 4.85. Found: C, 61.22; H, 7.51; N, 4.80.

Synthesis of 2a. The synthesis procedure of 2a was similar to the synthesis of 1b. Yield: 0.12 g, 82%. Compound 2a: ^1H NMR (600 MHz, CD_3CN): δ ppm = 8.97 (s, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 2H), 6.63–6.61 (m, 3H), 6.55–6.51 (m, 7H), 6.46–6.45 (m, 3H), 6.40–6.39 (m, 7H), 6.35–6.34 (m, 2H), 6.32–6.31 (m, 2H), 6.08 (d, J = 1.8 Hz, 2H), 5.02–4.99 (m, 2H), 4.92 (d, J = 6.6 Hz, 2H), 4.59 (s, 5H), 4.45 (br, 3H), 4.04 (s, 2H), 3.94–3.93 (m, 3H), 3.85–3.84 (m, 3H), 3.76 (s, 2H), 3.73–3.68 (m, 31H), 3.65 (d, J = 3.6 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 161.5, 160.2, 147.5, 139.9, 137.2, 135.0, 122.8, 121.8, 120.2, 112.9, 110.6, 108.3, 105.9, 105.5, 103.9, 99.9, 99.2, 71.6, 71.0, 70.1, 69.5, 67.9, 55.5, 53.0, 49.9. ESI MS: m/z = 1342.40 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 1486.59. Anal. Calcd for $\text{C}_{77}\text{H}_{85}\text{F}_6\text{N}_4\text{O}_{17}\text{P}$: C, 62.17; H, 6.03; N, 3.77. Found: C, 62.09; H, 6.17; N, 3.82.

Synthesis of 2b. The synthesis procedure of 2b was similar to the synthesis of 1b. Yield: 0.13 g, 78%. Compound 2b: ^1H NMR (600 MHz, CD_3CN): δ ppm = 8.92 (s, 2H), 6.88 (s, 2H), 6.59–6.58 (m,

5H), 6.54 (d, J = 1.8 Hz, 2H), 6.50 (d, J = 7.8 Hz, 2H), 6.46 (s, 1H), 6.44 (s, 2H), 6.42 (s, 2H), 6.40 (d, J = 1.8 Hz, 6H), 6.32 (br, 3H), 6.11 (d, J = 1.8 Hz, 3H), 5.00 (s, 2H), 4.54 (br, 5H), 4.46 (br, 3H), 4.02 (s, 2H), 3.92–3.90 (m, 6H), 3.84–3.83 (m, 3H), 3.75 (br, 7H), 3.73 (br, 5H), 3.72 (s, 4H), 3.70 (s, 18H), 3.64–3.63 (m, 3H), 1.68 (t, J = 7.2, 2H), 1.30 (br, 22H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 161.6, 160.2, 147.3, 139.8, 137.3, 135.0, 121.8, 112.7, 110.5, 109.2, 108.8, 108.1, 105.9, 105.5, 104.1, 99.9, 99.2, 71.7, 71.0, 70.1, 69.5, 67.9, 55.5, 53.0, 50.1, 32.3, 30.0, 29.7, 29.1, 26.1, 23.0, 14.1. ESI MS: m/z = 1555.50 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 1698.80. Anal. Calcd for $\text{C}_{91}\text{H}_{117}\text{F}_6\text{N}_4\text{O}_{18}\text{P}$: C, 64.30; H, 6.94; N, 3.30. Found: C, 64.39; H, 6.87; N, 3.23.

Synthesis of 3a. The synthesis procedure of 3a was similar to the synthesis of 1b. Yield: 0.19 g, 72%. Compound 3a: ^1H NMR (600 MHz, CD_3CN): δ ppm = 8.92 (s, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 2H), 6.59 (br, 3H), 6.54 (br, 11H), 6.52 (s, 2H), 6.50 (s, 2H), 6.48 (s, 3H), 6.46 (s, 1H), 6.44 (br, 11H), 6.41–6.40 (m, 7H), 6.37 (s, 2H), 6.32 (br, 3H), 6.21 (d, J = 7.2 Hz, 2H), 6.03 (br, 3H), 4.90 (s, 1H), 4.88 (br, 9H), 4.86 (br, 3H), 4.83 (s, 1H), 4.78 (s, 2H), 4.75 (s, 3H), 4.70 (s, 1H), 4.52 (br, 5H), 4.41 (br, 3H), 4.05 (s, 2H), 3.86 (br, 3H), 3.79 (br, 3H), 3.71 (br, 28H), 3.68 (br, 12H), 3.65 (br, 5H), 3.61 (br, 14H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 161.9, 161.8, 160.7, 160.6, 147.6, 140.3, 140.2, 137.4, 135.1, 122.1, 110.9, 110.0, 108.6, 107.3, 107.2, 107.1, 106.2, 104.1, 102.2, 101.7, 100.1, 70.3, 69.9, 55.8, 55.7, 32.0, 23.1, 14.1. MALDI MS: m/z = 2430.25 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 2575.01. Anal. Calcd for $\text{C}_{141}\text{H}_{153}\text{F}_6\text{N}_4\text{O}_{33}\text{P}$: C, 65.72; H, 5.98; N, 2.17. Found: C, 65.66; H, 5.84; N, 2.25.

Synthesis of 3b. The synthesis procedure of 3b was similar to the synthesis of 1b. Yield: 0.20 g, 71%. Compound 3b: ^1H NMR (600 MHz, CD_3CN): δ ppm = 8.88 (s, 2H), 6.73 (s, 1H), 6.57 (br, 4H), 6.53 (br, 9H), 6.49 (br, 9H), 6.45 (br, 7H), 6.43 (br, 5H), 6.40 (br, 6H), 6.36 (br, 5H), 6.32 (br, 3H), 6.06 (s, 3H), 4.87 (br, 8H), 4.84 (br, 10H), 4.73 (s, 3H), 4.47 (s, 4H), 4.42 (br, 3H), 4.02 (s, 2H), 3.84 (s, 2H), 3.78–3.76 (m, 3H), 3.71–3.70 (m, 22H), 3.67–3.66 (m, 32H), 3.61 (d, J = 1.8 Hz, 9H), 1.44 (s, 2H), 1.24–0.89 (m, 22H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 161.8, 161.8, 161.4, 160.7, 160.5, 147.5, 140.5, 140.3, 140.3, 140.1, 137.5, 135.2, 113.0, 108.5, 107.3, 107.0, 106.1, 102.2, 101.7, 100.2, 100.1, 71.9, 71.1, 71.0, 70.3, 69.9, 69.3, 68.2, 55.7, 55.7, 53.2, 52.8, 50.4, 32.4, 30.2, 29.8, 26.3, 23.1, 14.2. MALDI MS: m/z = 2642.39 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 2787.22. Anal. Calcd for $\text{C}_{153}\text{H}_{181}\text{F}_6\text{N}_4\text{O}_{34}\text{P}$: C, 66.75; H, 6.54; N, 2.01. Found: C, 66.65; H, 6.59; N, 2.12.

Synthesis of 4a. A mixture of 5d (125 mg, 0.1 mmol), tetraethylene glycol bis(2-aminophenyl)ether 7 (38 mg, 0.1 mmol), and 2,6-pyridinedicarboxaldehyde 6a (14 mg, 0.1 mmol) were stirred for 24 h in dry CH_3NO_2 (20 mL) under argon atmosphere at room temperature. Then 1 M $\text{BH}_3\cdot\text{THF}$ solution (0.8 mL) was added, and the mixture was further stirred overnight. The solvents were removed under vacuum, and the residue was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeCN}/\text{MeOH}$ = 100:0:0–75:25:1) to give the [2]rotaxane 4a. Yield: 36 mg, 21%. Compound 4a: ^1H NMR (600 MHz, CDCl_3): δ ppm = 9.08 (s, 2H), 8.20 (d, J = 12.6 Hz, 4H), 7.99 (s, 6H), 7.92 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 7.2 Hz, 2H), 6.75 (s, 1H), 6.52 (t, J = 6.6 Hz, 3H), 6.41 (d, J = 7.2 Hz, 2H), 6.35 (s, 1H), 6.27 (s, 6H), 6.17 (s, 2H), 6.10 (br, 3H), 5.83 (s, 2H), 5.22 (s, 4H), 4.40 (br, 5H), 4.24 (br, 2H), 3.78 (br, 3H), 3.70–3.60 (m, 26H), 3.20–3.05 (m, 4H), 1.59 (s, 18H). The ^{13}C NMR spectrum could not be collected due to the poor solubility of 4a. MALDI MS: m/z = 1581.62 $[\text{M} - \text{PF}_6^-]$; calculated exact mass: 1726.73. Anal. Calcd for $\text{C}_{101}\text{H}_{105}\text{F}_6\text{N}_4\text{O}_{13}\text{P}$: C, 70.21; H, 6.12; N, 3.24. Found: C, 70.29; H, 6.01; N, 3.29.

Synthesis of 4b. The synthesis procedure of 4b was similar to that of 4a. Yield: 37 mg, 19%. Compound 4b: ^1H NMR (600 MHz, CDCl_3): δ ppm = 9.07 (s, 2H), 8.21 (d, J = 12.6 Hz, 4H), 8.03–8.00 (m, 6H), 7.96 (t, J = 4.8 Hz, 2H), 7.90–7.89 (m, 2H), 7.74 (d, J = 7.8 Hz, 2H), 6.72 (s, 1H), 6.68 (s, 1H), 6.52–6.50 (m, 4H), 6.40–6.37 (m, 4H), 6.31 (br, 5H), 6.22–6.21 (m, 2H), 6.17 (d, J = 10.8 Hz, 3H),

5.91 (s, 2H), 5.18 (s, 3H), 4.41 (br, 5H), 4.28 (s, 2H), 3.98 (s, 1H), 3.84–3.77 (m, 4H), 3.68 (s, 2H), 3.65 (br, 13H), 3.62–3.60 (m, 12H), 3.30 (d, $J = 15.6$ Hz, 2H), 3.18 (d, $J = 15.6$ Hz, 2H), 1.76 (s, 2H), 1.59 (s, 18H), 1.26 (br, 22H), 0.89 (s, 3H). The ^{13}C NMR spectrum could not be collected due to the poor solubility of **4b**. MALDI MS: $m/z = 1793.95$ [$\text{M} - \text{PF}_6^-$]; calculated exact mass: 1938.95. Anal. Calcd for $\text{C}_{115}\text{H}_{133}\text{F}_6\text{N}_4\text{O}_{14}\text{P}$: C, 71.19; H, 6.91; N, 2.89. Found: C, 71.10; H, 6.84; N, 2.92.

■ ASSOCIATED CONTENT

■ Supporting Information

Partial ^1H NMR spectra of [2]rotaxanes **1a–b**; UV spectra of **4a,b** and NMR, MS spectra of all the interminates and dendritic [2]rotaxanes. 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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■ REFERENCES

- (1) (a) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, 289, 1172. (b) Yu, H.; Luo, Y.; Beverly, K.; Stoddart, J. F.; Tseng, H.-R.; Heath, J. R. *Angew. Chem., Int. Ed.* **2003**, 42, 5706. (c) Choi, J. W.; Flood, A. H.; Steuerman, D. W.; Nygaard, S.; Braunschweig, A. B.; Moonen, N. N. P.; Laursen, B. W.; Luo, Y.; Delonno, E.; Peters, A. J.; Jeppesen, J. O.; Xu, K.; Stoddart, J. F.; Heath, J. R. *Chem.—Eur. J.* **2006**, 12, 261. (d) Green, J. E.; Choi, J. W.; Boukai, A.; Bunimovich, Y.; Johnston-Halperin, E.; Delonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shin, Y. S.; Tseng, H.-R.; Stoddart, J. F.; Heath, J. R. *Nature* **2007**, 445, 414.
- (2) (a) Jiménez-Molero, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P.; De Cian, A. *Angew. Chem., Int. Ed.* **2000**, 39, 1295. (b) Collin, J.-P.; Dietrich-Buchecker, C.; Gaviña, P.; Jiménez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, 34, 477. (c) Huang, T. J.; Brough, B.; Ho, C.-M.; Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Tseng, H.-R.; Stoddart, J. F.; Baller, M.; Magonov, S. *Appl. Phys. Lett.* **2004**, 85, 5391. (d) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C.-M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, 127, 9745. (e) Wu, J.; Leung, K. C. F.; Benítez, D.; Han, J. Y.; Cantrill, S. J.; Fang, L.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2008**, 47, 7470.
- (3) Berná, J.; Leigh, D. A.; Lubomska, M.; Mendoza, S. M.; Pérez, E. M.; Rudolf, P.; Teobaldi, G.; Zerbetto, F. *Nat. Mater.* **2005**, 4, 704.
- (4) (a) Hernandez, R.; Tseng, H.-R.; Wong, J. W.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2004**, 126, 3370. (b) Nguyen, T. D.; Tseng, H.-R.; Celestre, P. C.; Flood, A. H.; Liu, Y.; Stoddart, J. F.; Zink, J. I. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, 102, 10029. (c) Nguyen, T. D.; Liu, Y.; Saha, S.; Leung, K. C. F.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2007**, 129, 626. (d) Saha, S.; Leung, K. C. F.; Nguyen, T. D.; Stoddart, J. F.; Zink, J. I. *Adv. Funct. Mater.* **2007**, 17, 685.
- (5) (a) Fyfe, M. C. T.; Stoddart, J. F. *Coord. Chem. Rev.* **1999**, 183, 139. (b) Harada, A.; Hashidzume, A.; Yamaguchi, H.; Takashima, Y. *Chem. Rev.* **2009**, 109, 5974. (c) Harada, A.; Takashima, Y.; Yamaguchi, H. *Chem. Soc. Rev.* **2009**, 38, 875. (d) Zheng, B.; Wang, F.; Dong, S.; Huang, F. *Chem. Soc. Rev.* **2012**, 41, 1621. (e) Avestro, A.-J.; Belowich, M. E.; Stoddart, J. F. *Chem. Soc. Rev.* **2012**, 41, 5881. (f) Vukotic, V. N.; Loeb, S. J. *Chem. Soc. Rev.* **2012**, 41, 5896. (g) Li, S.-L.; Xiao, T.; Lin, C.; Wang, L. *Chem. Soc. Rev.* **2012**, 41, 5950. (h) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, 41, 6042. (i) Yan, X.; Zheng, B.; Huang, F. *Polym. Chem.* **2013**, 4, 2395.
- (6) (a) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*; VCH-Wiley: New York, NY, 2000; (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Synthesis, Perspectives*; Wiley-VCH: Weinheim, 2001; (c) Zimmerman, S. C.; Lawless, L. J. *Supramolecular Chemistry of Dendrimers*; Topics in Current Chemistry, Vol. 217; Springer: Berlin, 2001; pp 95–120; (d) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, 101, 3819. (e) Newkome, G. R.; Shreiner, C. D. *Polymer* **2008**, 49, 1. (f) Newkome, G. R.; Shreiner, C. D. *Chem. Rev.* **2010**, 110, 6338. (g) Astruc, D.; Ruiz, J. *Tetrahedron* **2010**, 66, 1769. (h) Smith, D. K. *Tetrahedron* **2003**, 59, 3797.
- (7) (a) Gorman, C. B.; Smith, J. C. *J. Am. Chem. Soc.* **2000**, 122, 9342. (b) Wang, P.; Moorefield, C. N.; Newkome, G. R. *Org. Lett.* **2004**, 6, 1197. (c) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, 101, 2991. (d) Li, W.-S.; Jiang, D.-L.; Suna, Y.; Aida, T. *J. Am. Chem. Soc.* **2005**, 127, 7700. (e) Weener, J.-W.; Meijer, E. W. *Adv. Mater.* **2000**, 12, 741. (f) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, 122, 12385. (g) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, 110, 1857. (h) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, 109, 6275. (i) Kozaki, M.; Tujimura, H.; Suzuki, S.; Okada, K. *Tetrahedron Lett.* **2008**, 49, 2931. (j) Dykes, G. M.; Smith, D. K. *Tetrahedron* **2003**, 59, 3999. (k) Drouet, S.; Paul-Roth, C. O. *Tetrahedron* **2009**, 65, 10693. (l) Lee, J. W.; Kim, J. H.; Kim, B.-K.; Shin, W. S.; Jin, S.-H. *Tetrahedron* **2006**, 62, 894.
- (8) Amabilino, D. B.; Ashton, P. R.; Balzani, V.; Brown, C. L.; Credi, A.; Fréchet, J. M. J.; Leon, J. W.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; Venturi, M. *J. Am. Chem. Soc.* **1996**, 118, 12012.
- (9) Elizarov, A. M.; Chiu, S.-H.; Glink, P. T.; Stoddart, J. F. *Org. Lett.* **2002**, 4, 679.
- (10) Xiao, S.; Fu, N.; Peckham, K.; Smith, B. D. *Org. Lett.* **2010**, 12, 140.
- (11) Xu, X.-D.; Ou-Yang, J.-K.; Zhang, J.; Zhang, Y.-Y.; Gong, H.-Y.; Yu, Y.-h.; Yang, H.-B. *Tetrahedron* **2013**, 69, 1086.
- (12) Elizarov, A. M.; Chang, T.; Chiu, S.-H.; Stoddart, J. F. *Org. Lett.* **2002**, 4, 3565.
- (13) (a) Glink, P. T.; Oliva, A. I.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, 40, 1870. (b) Horn, M.; Ihringer, J.; Glink, P. T.; Stoddart, J. F. *Chem.—Eur. J.* **2003**, 9, 4046. (c) Leung, K. C.-F.; Wong, W.-Y.; Aricó, F.; Haussmann, P. C.; Stoddart, J. F. *Org. Biomol. Chem.* **2010**, 8, 83. (d) Wong, W.-Y.; Leung, K. C.-F.; Stoddart, J. F. *Org. Biomol. Chem.* **2010**, 8, 2332. (e) Belowich, M. E.; Valente, C.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2010**, 49, 7208. (f) Belowich, M. E.; Valente, C.; Smaldone, R. A.; Friedman, D. C.; Thiel, J.; Cronin, L.; Stoddart, J. F. *J. Am. Chem. Soc.* **2012**, 134, 5243. (g) Chen, S.; Do, J. T.; Zhang, Q.; Yao, S.; Yan, F.; Peters, E. C.; Schöler, H. R.; Schultz, P. G.; Ding, S. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, 104, 17266.
- (14) (a) Aricó, F.; Chang, T.; Cantrill, S. J.; Khan, S. I.; Stoddart, J. F. *Chem.—Eur. J.* **2005**, 11, 4655. (b) Yin, J.; Dasgupta, S.; Wu, J. *Org. Lett.* **2010**, 12, 1712.
- (15) Zhou, W.; Li, J.; He, X.; Li, C.; Lv, J.; Li, Y.; Wang, S.; Liu, H.; Zhu, D. *Chem.—Eur. J.* **2008**, 14, 754.
- (16) Bozdemir, O. A.; Barin, G.; Belowich, M. E.; Basuray, A. N.; Beuerlea, F.; Stoddart, J. F. *Chem. Commun.* **2012**, 48, 10401.
- (17) Yin, J.; Chi, C.; Wu, J. *Org. Biomol. Chem.* **2010**, 8, 2594.

- (18) Li, Z.; Liu, W.; Wu, J.; Liu, S. H.; Yin, J. *J. Org. Chem.* **2012**, *77*, 7129.
- (19) (a) Leung, K. C.-F.; Aricó, F.; Cantrill, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5808. (b) Leung, K. C.-F.; Aric, F.; Cantrill, S. J.; Stoddart, J. F. *Macromolecules* **2007**, *40*, 3951.
- (20) Glink, P. T.; Oliva, A. I.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1870.
- (21) (a) Luo, J.; Qu, H.; Yin, J.; Zhang, X.; Huang, K.-W.; Chi, C. J. *Mater. Chem.* **2009**, *19*, 8202. (b) Liu, X.; Yang, X.; Fu, Y.; Zhu, C.; Cheng, Y. *Tetrahedron* **2011**, *67*, 3181. (c) Manandhar, E.; Wallace, K. J. *Inorg. Chim. Acta* **2012**, *381*, 15. (d) Ingale, S. A.; Seela, F. J. *Org. Chem.* **2012**, *77*, 9352. (e) Hwang, J.; Choi, M. G.; Eor, S.; Chang, S.-K. *Inorg. Chem.* **2012**, *51*, 1634. (f) Nishimura, T.; Xu, S.-Y.; Jiang, Y.-B.; Fossey, J. S.; Sakurai, K.; Bull, S. D.; James, T. D. *Chem. Commun.* **2013**, *49*, 478.
- (22) (a) Gadde, S.; Batchelor, E. K.; Weiss, J. P.; Ling, Y.; Kaifer, A. E. *J. Am. Chem. Soc.* **2008**, *130*, 17114. (b) Biedermann, F.; Elmalem, E.; Ghosh, I.; Nau, W. M.; Scherman, O. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 7739.
- (23) Lu, C.; Guo, Y.; Li, J.; Yao, M.; Liao, Q.; Xie, Z.; Li, X. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 7683.
- (24) Kim, J.-H.; Lee, E.; Jeong, Y.-H.; Jang, W.-D. *Chem. Mater.* **2012**, *24*, 2356.
- (25) Han, S. C.; Lee, J. W.; Jin, S.-H. *Macromol. Res.* **2012**, *20*, 1083.
- (26) Han, S. C.; Jin, S.-H.; Lee, J. W. *Bull. Korean Chem. Soc.* **2011**, *32*, 3624.
- (27) Fujimoto, Y.; Ubukata, T.; Yokoyama, Y. *Chem. Commun.* **2008**, 5755.
- (28) Figueira-Duarte, T. M.; Simon, S. C.; Wagner, M.; Druzhinin, S. I.; Zachariasse, K. A.; Müllen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 10175.