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Tetraphenylethene Modified [n]Rotaxanes: Synthesis, Characterization and Aggregation-Induced Emission Behaviors

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A series of novel [n]rotaxanes based on tetraphenylethene (TPE) backbone were constructed by a template-directed clipping approach and their structures were well-characterized. Investigation on optical properties showed that these rotaxanes and their corresponding ammoniums had aggregation-induced emission (AIE) behaviors. However, there were obvious differences as following: 1) rotaxanes occurred the aggregation state under the amount of less water compared with the corresponding ammonium; 2) the rotaxanes with long alkoxyl chain on the pyridine unit of crown ether formed the aggregation state under the amount of less water than that of no alkoxyl-substituted rotaxanes and 3) nearer distance between TPE unit and N-hetero crown ether component resulted in the aggregation state more easily than that of farther distance. The result suggested that the mechanically interlocked structures can adjust the aggregate state of AIE molecules.

Introduction

Studies on the mechanically interlocked molecules (MIMs) have become one of the popular topics of supramolecular chemistry.[1] Rotaxanes, one of the most important classes of mechanically interlocked molecules, have deserved increasing interest owing to their beautiful architectures, topological importance and great applications in the fields of materials science, nanotechnology, and biological science.[2] Recently, functional [n]rotaxanes possessing fluorescence have attracted considerable attention.[3]

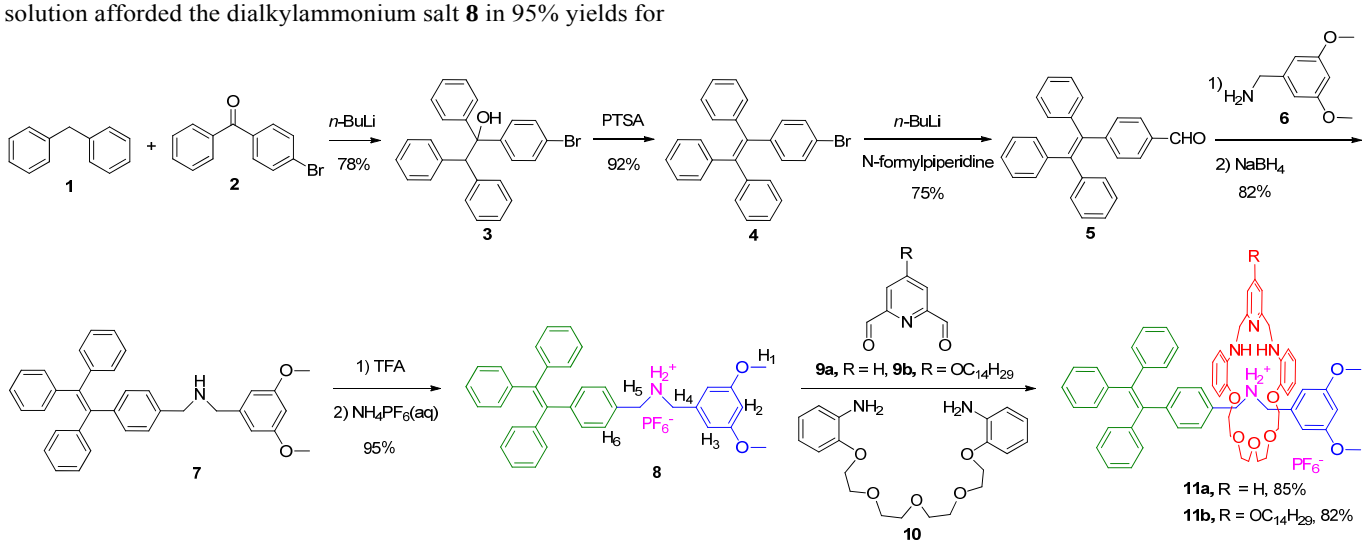
Since Tang's group observed a novel phenomenon of aggregation-induced emission (AIE) in 2001 [4] and elaborated the cause for the AIE phenomenon that was restriction of intramolecular rotation (RIR).[5] Lately, some fluorogens with an AIE effect have attracted increasing interest ascribing to the unique emission characterization.[6] As a classic backbone, tetraphenylethylene (TPE) is a typical AIE-active material. Over the past several years, an abundant amount of researches have been contributed to design and synthesize functional TPE-based molecules with attractive optical properties. The unique luminescence behaviour of TPE has been harnessed for the development of solid state lighting materials,[7] biological sensors,[8] chemosensors,[9] explosive detection,[10] latent finger print[11] and luminescent polymers.[12]

In our recent works, we have confirmed the mechanical interaction can be used as an efficient strategy to adjust the properties of photochromic materials owing to the formation of pseudorotaxanes.[13] For the TPE derivatives, we also want to know if such mechanical interaction can modify the AIE behavior. It is well known that TPE can induce the AIE property due to the inhibition of bonds rotation of benzene rings.[7-12] Exactly, rotaxane with mechanical interaction can form a shielding host-guest complex. As a consequence, the AIE property will be influenced by mechanical interaction. Herein, we design and synthesize three TPE molecules with an ammonium moiety, in which the ammonium is employed as a template to efficiently generate the mechanically interlocked rotaxanes. Their photophysical properties indicated that the target rotaxanes exhibited excellent aggregation-induced emission effect, which make them act promising candidates as AIE supermolecule materials with potential technological applications. While this work was in progress, a closely-related paper was published by Tang.[14]

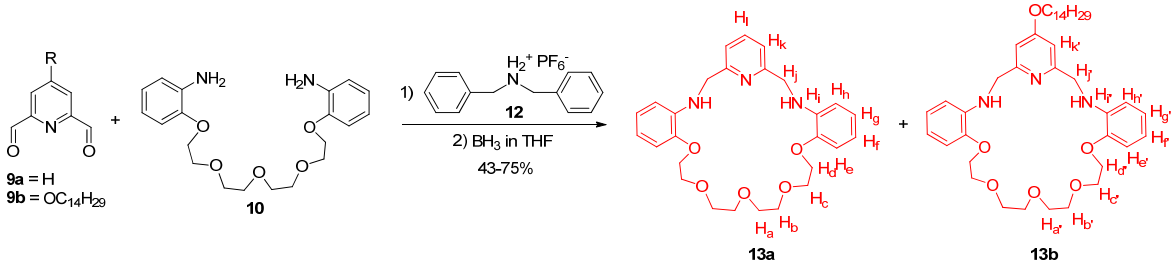
Results and discussion

To study impact of N-hetero crown ring on AIE behavior of dialkylammonium salts based tetraphenylethene (TPE), [2]rotaxanes **11a** and **11b** with N-hetero crown ether ring adjacent to TPE stopper were designed and synthesized. The synthetic protocol for rotaxanes **11** is outlined in Scheme 1. Firstly, diphenylmethane **1** as starting material was reacted with *n*-BuLi in anhydrous THF at 0 °C for 1 h, then 4-bromobenzophenone **2** was added and further stirred for 6 h to obtain the alcohol **3**. Subsequently, **3** was refluxed in toluene in the presence of p-toluene sulphonic acid to give the desired **4**.[15] Compound **4** was reacted with *n*-BuLi in anhydrous THF at -78 °C for 2 h, and then N-formylpiperidine was added to obtain the corresponding aldehyde **5**.[16] Then, condensation of aldehyde **5** with (3,5-dimethoxyphenyl)methanamine **6** produced the corresponding reversible dynamic imine, which was reduced by $NaBH_4$ in the solution of THF and MeOH, to give the kinetically stable amine **7** in 82% yield. Protonation of the free amine with excess trifluoroacetic acid (TFA) and

subsequent counter-ion exchange with saturated NH_4PF_6 solution afforded the dialkylammonium salt **8** in 95% yields for



Scheme 1. Synthesis of Rotaxanes **11**.



Scheme 2. Synthesis of the macrocycles **13**.

the two steps. Afterwards, the dynamic covalent chemistry approach was adopted to bring about three-component self-assembly processes to afford [2]rotaxane **11**. Compounds **9a** and substituted dialdehyde **9b** had been utilized to construct [2]catenanes,[17] hetero[n]rotaxanes,[18] dendritic rotaxanes,[19] rotacatenanes,[20] and others [13, 21] in our previous works. Herein, ammonium salt **8** was also subjected to perform the dynamic clipping reaction with **9** and **10** [22] in anhydrous CH_3CN, and then the mixture was treated with BH_3·THF to afford [2]rotaxanes **11a-b** in 85% and 82% yields, respectively. Furthermore, for comparison, *N*-hetero crown ethers **13a** [22] and **13b** [17] was synthesized to aid spectroscopic analysis of the assembly processes, as outlined in Scheme 2. [2]rotaxane **11a** was well depicted by ^{1}H NMR spectra. From the ^{1}H NMR (Figure 1), an obvious upfield shift was observed for the resonance of the protons on the stopper units (H_2, H_3, H_6 and H_1) due to the shielding effect of the encircling crown ethers. Furthermore, the resonances for the central methylene (H_4 and H_5) shifted downfield. It was notable that protons NH_2^+ in the template of rotaxane **11a** could be detected at 8.85 ppm because of the stabilizing effect of the hydrogen bonding interactions of the oxygen atoms on N-hetero crown ether **13a** with the ammonium hydrogen atoms. In addition, [2]rotaxane **11b** displayed some similar shifts with [2]rotaxane **11a**. Further proof was proved by MALDI-MS in acetonitrile. The peak at *m/z* 991.61 and 1203.76 can be assigned to the $[M\text{-}PF_6^-]^+$ species, in which M was [2]rotaxanes **11a** and **11b**, respectively. 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).

Following introduction of AIE-active tetraphenylethylene (TPE) units, the photoluminescence (PL) spectra and UV spectra were studied in acetonitrile / water mixtures with various water contents, to evaluate the AIE behaviors of salt **8** and rotaxanes **11a-b**. As shown in Figure 2A, the solutions of salt **8** are not obviously emissive until *fw* was up to 80%. However, when the water fraction exceeds 85%, the PL intensity rapidly increases. A dramatic enhancement in luminescence is observed when the water fraction reaches 90%. As the compound is insoluble in water, increasing the water fraction in the mixed solvent might change the form of the compound from a dissolved or well-dispersed state in pure acetonitrile to aggregated particles in the mixtures with high water content. The emission of salt **8** is thus caused by aggregation, which is typically AIE active. In the acetonitrile solution, the multiple phenyls of TPE undergo active twisting motions against the 3, 5-dimethoxy phenyl units linked by the dimethylammonium NH_2^+ axis. In the aggregates, the intramolecular rotations are restricted, thus turning on the emission of the dialkylammonium salt **11**. It is known that the molecular size and effect of steric hindrance influence their rotation, and a larger molecule should have lower freedom of rotation.[23] Subsequently, the photolumminescence of [2]rotaxanes **11a** and **11b** were also investigated. As shown in Figure 2B and 2C, when the water fraction reaches 80% and 70%, respectively, the fluorescence intensity of **11a-b** is found

to rapidly get enhanced, which implies [2]rotaxanes **11a-b** arise aggregation state more easily in acetonitrile in comparison to

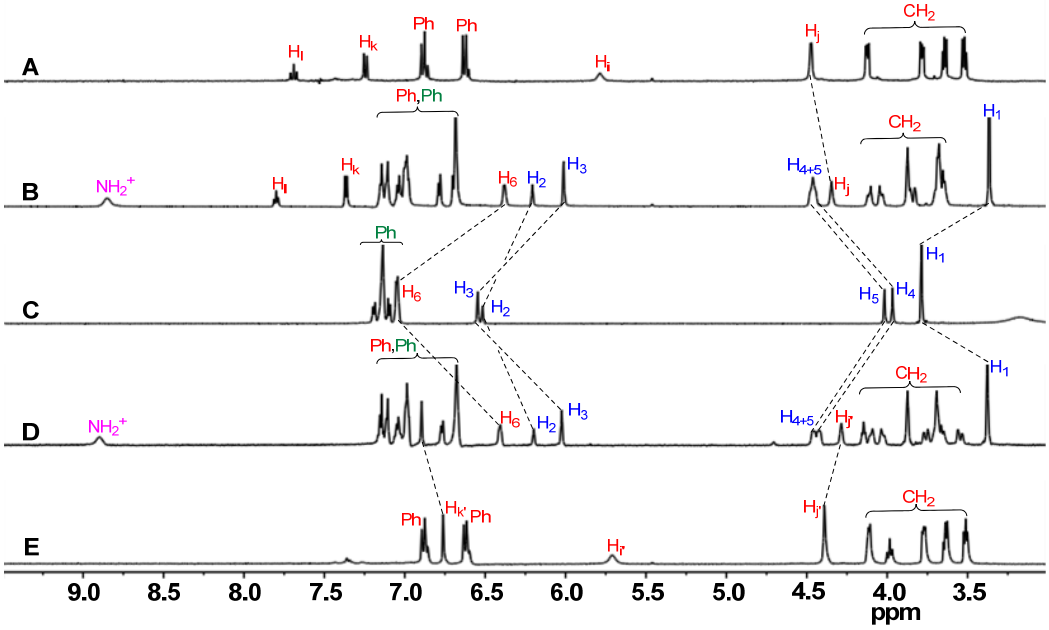


Figure 1. ^{1}H NMR spectra (600 MHz in CD_3CN at rt) of **13a** (A); **11a** (B); **8** (C); **11b** (D) and **13b** (E).

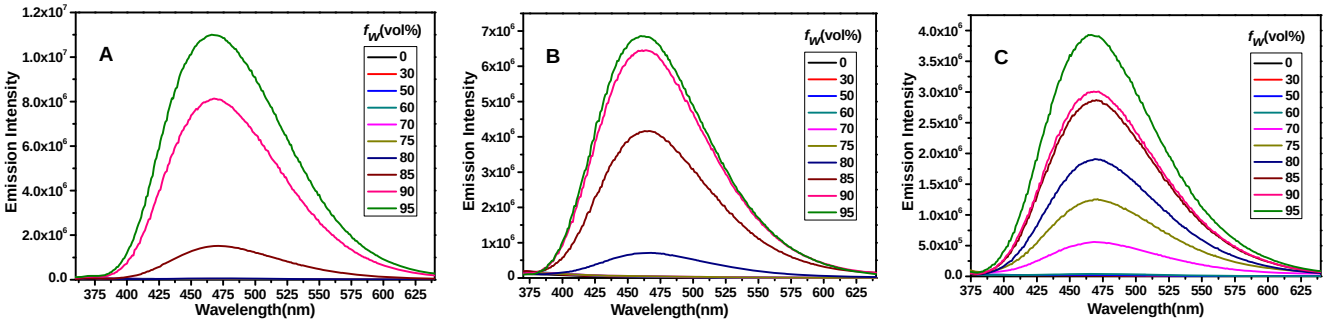


Figure 2. PL spectra of **8** (A), **11a** (B) and **11b** (C) in CH_3CN / water mixtures with different water fractions.

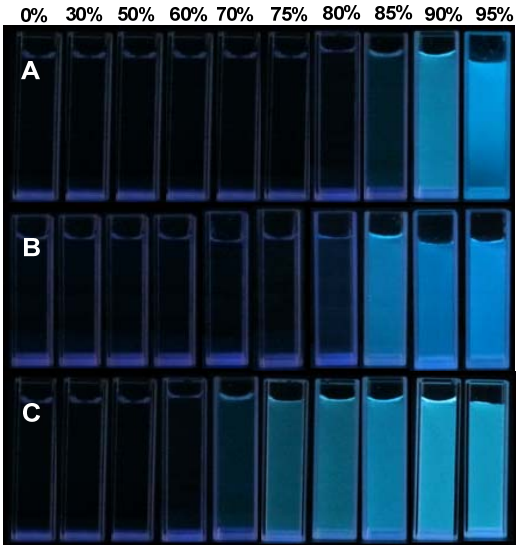
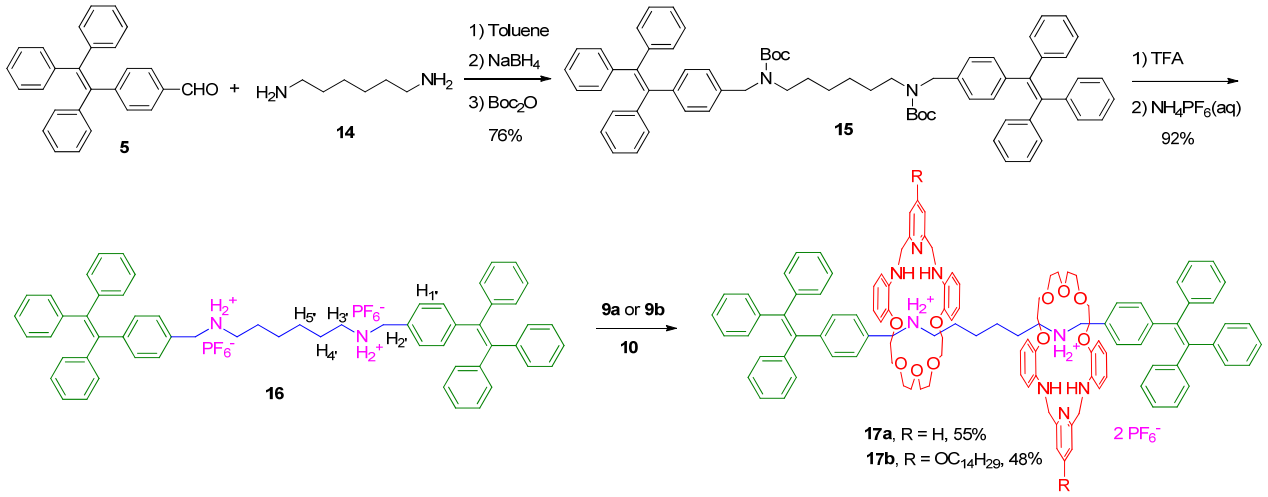


Figure 3. Photographs of **8**(A), **11a**(B) and **11b**(C) in CH_3CN / water mixtures with different fractions of water (f_w) taken under UV illumination.

corresponding ammonium. Moreover, rotaxane **11b** with long alkyl chain displays more significant compared with **11a**. Further proofs were supplied by UV-vis absorption spectra of **8**, **11a** and **11b** in different water fraction. The level-off tails are found at the longer wavelength region when water fraction up to 70%. Such tails are commonly observed in nanoparticle suspensions and are attributed to the light scattering effect of the aggregates. (Figure S1) As shown in Figure 3A-C, photographs of them in different water fraction furnish further critical evidence to manifest their different levels of AIE behavior. In view of the effect of molecular structures towards AIE behavior, we consult a theoretical DFT calculation by using Gaussian 09 programs at the B3LYP/6-31G* level. As shown in Figure S2, the host macrocycles have a large overlap with TPE group in **11a-b**. The introduce of long alkyl chain in **11b** made the host macrocycles have a larger overlap with TPE group than that of **11a** which result in the AIE phenomena of **11b** came early than that of **11a**. In all, the AIE phenomena of

11a-b came early than that of ammonium salt **8** due to the introducing of host macrocycles.

To further confirm the results described above, a symmetrical [3]rotaxane **17** with similar molecular feature as [2]rotaxanes **11** that host macrocycle adjacent to TPE unit was



Scheme 3. Synthesis of Rotaxanes **17**.

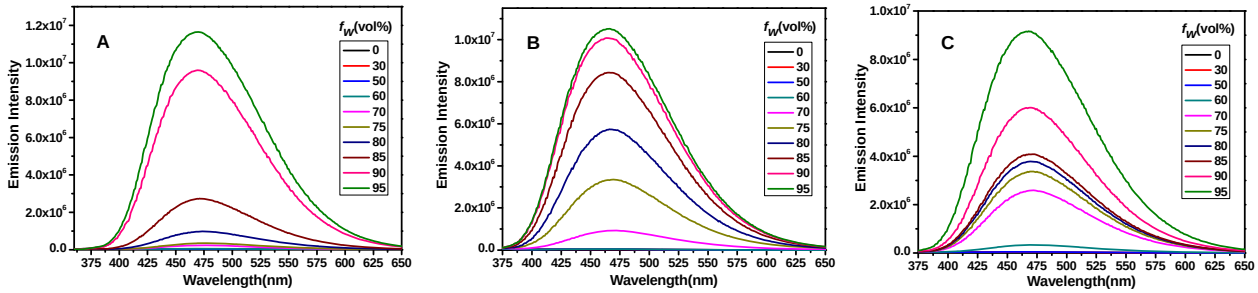


Figure 4. PL spectra of **16** (A), **17a** (B) and **17b** (C) in CH_3CN / water mixtures with different water fractions.

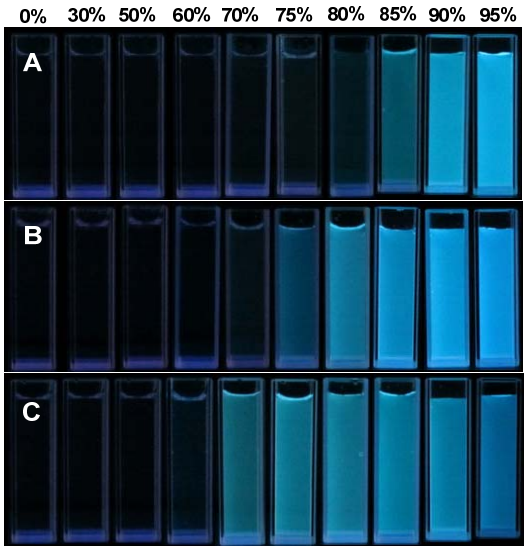
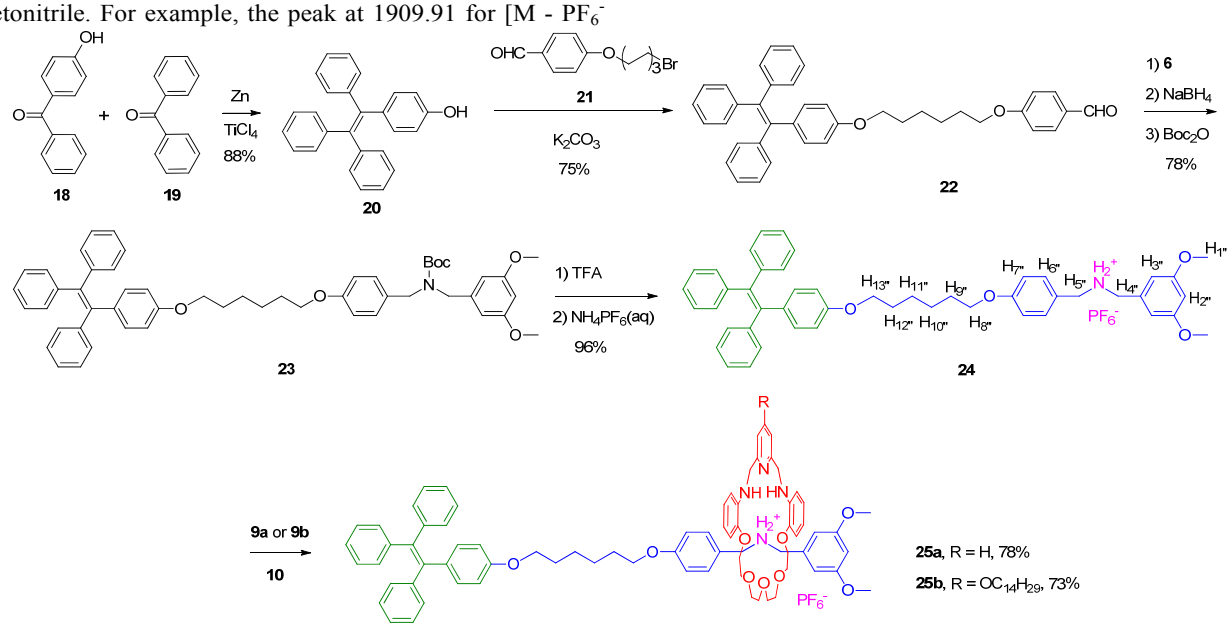


Figure 5. Photographs of **16**(A), **17a**(B) and **17b**(C) in CH_3CN / water mixtures with different fractions of water (f_w) taken under UV illumination.

designed and synthesized. Similarly, the synthesis of [3]rotaxanes **17a** and **17b** is outlined in Scheme 3, condensation of aldehyde **5** with hexane-1, 6-diamine **14** produced the corresponding reversible dynamic imine, which was reduced by $NaBH_4$, to afford the kinetically stable amine. In consideration of convenient purification, the NH of free amines was protected by the Boc_2O before purification. Then, the Boc-protected alkylamines **15** were obtained in overall yield of 76% for the two steps. The Boc protective group was removed with excess trifluoroacetic acid (TFA) in dry dichloromethane, and the amine generated was simultaneously protonated. Subsequent counterion exchange with saturated NH_4PF_6 solution afforded ammonium salt **16** in 92% yield. Then ammonium salt **16** was also subjected to perform the dynamic clipping reaction with **9** and **10** in anhydrous CH_3CN, and then the mixture was treated with BH_3•THF to afford [3]rotaxanes **17a** and **17b** were prepared by using same method in 55% and 48% yields, respectively. Evidence for the formation of **17a** and **17b** in this process came from analysis of their ^1H NMR spectrum. [3]rotaxane **17a** is shown in Figure S3-A, and compared with the spectrum of template **16** (Figure S3-B), the resonance of the methylene protons ($H_{2'}$) displayed a downfield shift while the protons on the stopper units ($H_{1'}$) showed an obvious upfield shift. Moreover notably, the ammonium (NH_2^+) is detected at 8.66 ppm. These results indicated that the N-hetero crown ether

encircled the site of ammonium. The investigation on the ^{1}H NMR indicated that [3]rotaxane **17b** had similar shifts in comparison to **17a**. Further proof was proved by MALDI-MS in acetonitrile. For example, the peak at 1909.91 for [M - PF_6^-]$^+$, 1763.98 for [M - HPF_6 - PF_6^-]$^+$ and 2188.52 for [M - HPF_6 - PF_6^-]$^+$ could be detected, which further confirmed the formation of [3]rotaxanes **17a-b** successfully. (see supporting information).



Scheme 4. Synthesis of Rotaxanes **25.**

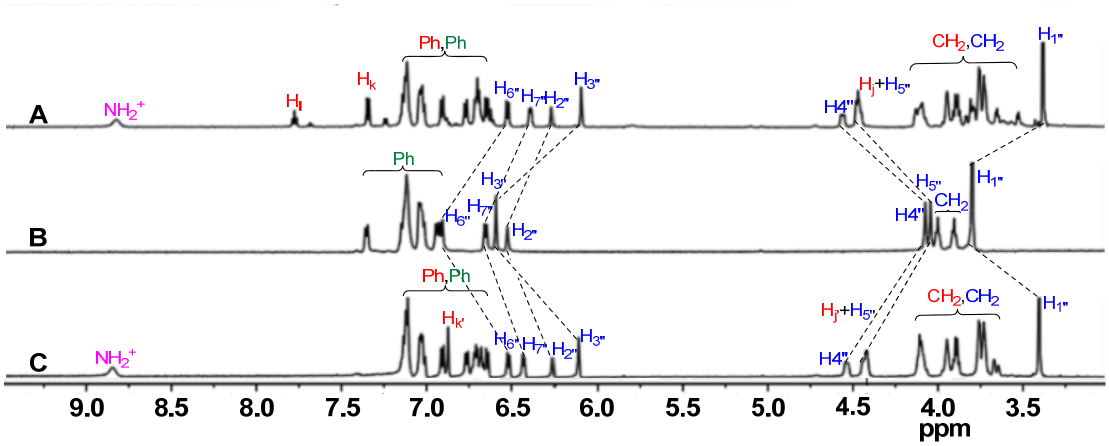


Figure 6. ^{1}H NMR spectra (600 MHz in CD_3CN at rt) of **25a** (A); **24** (B) and **25b** (C).

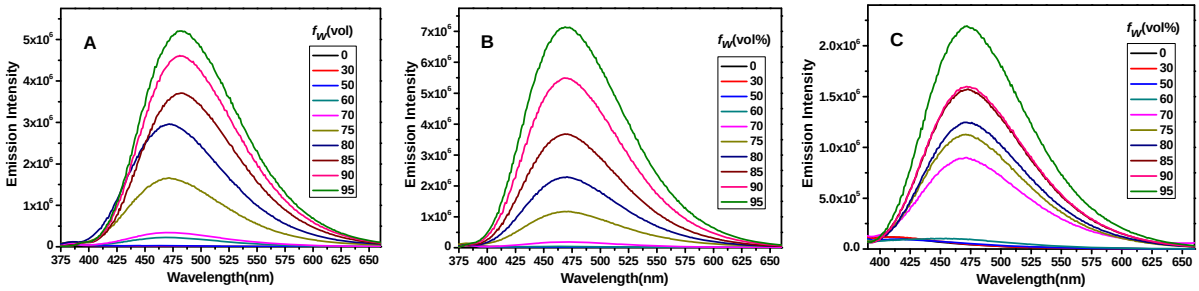


Figure 7. PL spectra of **24**(A), **25a** (B) and **25b** (C) in CH_3CN / water mixtures with different water fractions.

Then, [3]rotaxanes **17a-b** and the corresponding ammonium **16** were also studied in the photoluminescence spectra and UV spectra. As shown in Figure 4A-C, the emission from the

acetonitrile solution of the ammonium **16** was so weak that almost no photoluminescence signal was observed. However, a dramatic enhancement of luminescence could be observed when the water fraction in the acetonitrile solution exceeded 85%. Meanwhile, with regard to [3]rotaxanes **17a-b**, the PL intensity of them was observed to get significantly enhanced, when water fraction reached 75% and 70%, respectively. Further, we found that [3]rotaxanes **17a-b** arise aggregation state more easily by a comparison of salt **16**.(Figure 5A-C). Similar to [2]rotaxanes **11a-b**, these [n]rotaxanes with molecular feature that N-hetero crown ether ring adjacent to TPE stopper arise aggregation state more easily than corresponding ammonium salts. Accordingly, it is concluded that the non-covalent mechanical interaction can affect molecular AIE behavior, despite they possess similar UV/vis absorption spectra (Figure S1). For ammonium and rotaxanes, the existence of host macrocycles in rotaxanes will affect the rotation of TPE moiety due to near distance between the template ammonium and TPE unit. The rotaxanes **11b** and **17b** with long alkoxyl chain on the pyridine unit of crown ether arise aggregation state more easily than no alkoxyl-substituted rotaxanes **11a** and **17a**, which was possibly attributed to the effect of longer alkoxyl chains for TPE moiety. The theoretical DFT calculation results were record (ESI in Figure S2), the results were similar to that of **8**, **11a-b**. According to the optimized structures, we find that the crown ether components of **17a** and **17b** wrap a benzene ring of TPE moiety, which will affect the rotation of TPE. As a hydrophobic group, the introduction of long alkoxyl chain on host crown ether component of **17b** makes the crown ether components have a larger shielding than that of **17a**, resulting in the aggregation state more easily.

For confirming the effect of alkoxyl chain on the pyridine, we deign and synthesize another ammonium, in which, the ammonium template lies in far position from TPE moiety. The stepwise synthesis of rotaxanes **25a-b** is depicted in Scheme 4. Firstly, the intermediate 1-(4-hydroxyphenyl)-1,2,2-triphenylethene **20** was prepared by cross-coupling of 4-hydroxyl-phenylbenzophenone **18** and benzophenone **19** using Zn powder as the catalyst.[24] Subsequently, the alcohol **20** was converted to compound **22** upon treatment with **21** in DMF in the presence of K_2CO_3 in 75% yield. Similarly, the ammonium **24** was prepared by condensation of aldehyde **22** and **6** followed by reduction, protonation, and counterion exchange. Afterwards, the similar clipping reaction was further performed to synthesize [2]rotaxanes **25a** and **25b** in yields of 78% and 73%, respectively. Evidence for the formation of **25a** and **25b** in this process came from analysis of their ^{1}H NMR spectrum. As shown in Figure 6, an investigation of the ^{1}H NMR manifested that an obvious downfield shifts for the methylene protons ($H_{4''}$ and $H_{5''}$) and upfield shifts for benzene ring protons ($H_{2''}$, $H_{3''}$, $H_{6''}$, $H_{7''}$) on benzene rings of **25a** and **25b** by a comparison of the spectra of **24**, which indicated that the crown ether unit encircled the site of ammonium template. Meanwhile, methyl protons ($H_{1''}$) on the stopper unit displayed obvious upfield shifts. In addition, protons NH_2^+ in the template of rotaxane **25a** could be observed at 8.83 ppm due to the same reason as [2]rotaxanes **11a** and **11b**. Moreover the similar chemical shift changes for characteristic protons on [2]rotaxane **25b** were detected. These results described above were in good agreement with a wealth of published literature.[13, 17-20, 25] Additional evidence supporting this conclusion comes from analysis of the MALDI mass spectrum, which contains peaks at m/z 1328.58 and 1395.92 that correspond to - PF_6 salts of [2]rotaxanes **25a** and **25b**, respectively.

Subsequently, we studied the AIE behaviors of salt **24** and [2]rotaxanes **25a-b**. As could be observed in Figure 7A-C, the three compounds arise aggregation state nearly simultaneously that the PL curves of them are basically flat lines paralleled to the abscissa with water fraction of acetonitrile/water mixture increased from 0% to 60% and that notably the PL intensity of them all dramatically jumps with the increase in water fraction up to 70%. The PL spectra of them all indicate similar AIE behaviors (Figure S4). And they also revealed similar UV-vis absorption (Figure S1). The optimized structures of 25a-b showed that there was no obvious overlap between the host macrocycles and TPE groups as shown in Figure S2. These investigations suggest that the mechanical interaction can change the AIE behavior when the host macrocycle is nearby the TPE moiety. Moreover, the functional group such as alkoxyl group on the pyridine unit of macrocycle component also has influence on the AIE behavior and this may due to the hydrophilic character of the alkoxyl group.

From the above, [2]rotaxanes **11a-b** and [3]rotaxanes **17a-b** with the molecular feature that N-hetero crown ether ring adjacent to TPE unit arise aggregation state more easily in comparison to the corresponding ammonium, respectively. However, [2]rotaxanes **25a** and **25b** in which host macrocycle located at the far position of TPE have similar AIE behavior as template **24**. In other words, N-hetero crown ether ring has great influence on AIE behavior of the template based on TPE, as the ring is close to TPE; On the contrary, if the ring is far from TPE, there is little influence on AIE behavior of ammonium salt.

Conclusions

In summary, a series of novel AIE-active [n]rotaxanes have been successfully developed in this work. Owing to introduction of tetraphenylethene (TPE) units, it endows [n]rotaxanes predominant photophysical properties. Photoluminescence and UV-vis properties of the rotaxanes and their templates were investigated. To our excitement, these [n]rotaxanes express perfect aggregation-induce emission (AIE) effect. Meanwhile, It is noteworthy that [n]rotaxanes with characteristic of N-hetero crown ether ring adjacent to TPE stopper arise aggregation state more easily than their corresponding ammonium salts; [n]rotaxanes with host macrocircle distant to TPE stopper show same AIE behavior as corresponding ammonium salt. The present results may provide a novel perspective for the design and construct of AIE-active mechanically interlocked molecules. Further work will focus on their functionalization and application, such as preparing

dynamic AIE-active supramolecular materials, AIE-active fluorescent supramolecular biosensor.

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. Compound **21** was prepared by literature methods.[26] All other starting materials were obtained commercially as analytical-grade and used without further purification. ^{1}H NMR spectra were collected with Varian Mercury Plus 400 MHz or 600 MHz spectrometer, while ^{13}C NMR spectra were collected with a 400 MHz spectrometer. Mass spectra were all measured with the ultrafleXtreme MALDI-TOF-TOF. UV−vis spectra were obtained on a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer, and fluorescence spectra were taken on a Hitachi Model F-4500 fluorescent spectrophotometer. The elemental analyses were obtained on Vario ELIII CHNSO.

Synthesis of 7. A mixture of **5** (0.36 g, 1.0 mmol) and **6** (0.17 g, 1.0 mmol) in dry toluene (50 mL) into 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 for overnight, the solvents were removed under vacuum, and the residue was extracted by dichloromethane (DCM). The organic layer was washed by brine till clear, dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure and purification on a silicagel column using petroleum ether / ethyl acetate (4 : 1) as the eluent give a kinetically stable amine **7** as a low yellowish solid, rf=0.54. Yield: 0.42 g, 82%. Compound **7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.09 – 6.97 (m, 19H), 6.48 (d, *J* = 2.0 Hz, 2H), 6.36 (t, *J* = 2.0 Hz, 1H), 3.78 (s, 6H), 3.70 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 160.8, 143.7, 143.7, 142.4, 140.8, 140.7, 138.0, 131.3, 131.3, 127.6, 127.5, 126.3, 106.0, 99.0, 55.3, 53.0, 52.6. MALDI MS: *m/z* = 512.21 [M + H$^+$]; calculated exact mass: 511.25. Anal. Calcd for $C_{36}H_{33}NO_2$: C, 84.51; H, 6.50; N, 2.74. Found: C, 84.58; H, 6.61; N, 2.68.

Synthesis of 8. To a solution of the amine **7** (0.51 g, 1.0 mmol) in dry DCM (20 mL), TFA (0.32 mL, 5.0 mmol) was added at room temperature. After stirring for 2 h under argon atmosphere, the solvent was removed under vacuum. The residue was dissolved in MeOH (5.0 mL), and then saturated NH_4PF_6 (20.0 mL, aq) was added to yield a off-white precipitate. After filtering, washing with H_2O and dry under vacuum, the title compound **8** was obtained as an off-white solid, rf=0.66. Yield: 0.62 g, 95%. Compound **8**: ^{1}H NMR (600 MHz, CD_3CN): δ 7.19 (d, *J* = 7.8 Hz, 2H), 7.14 (s, 9H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 6.0 Hz, 6H), 6.55 (s, 2H), 6.52 (s, 1H), 4.01 (s, 2H), 3.96 (s, 2H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 145.3, 143.3, 143.1, 142.9, 141.9, 139.8, 133.1, 132.1, 131.1, 128.9, 128.9, 128.8, 127.7, 127.6, 126.6, 107.0, 101.5, 55.4, 50.7, 50.5. MALDI MS: *m/z* = 512.31[M – PF_6^-]; calculated exact mass: 657.22. Anal. Calcd for $C_{36}H_{34}F_6NO_2P$: C, 65.75; H, 5.21; N, 2.13. Found: C, 65.69; H, 5.11; N, 2.22.

Synthesis of [2]rotaxane 11a. A mixture of salt **8** (131 mg, 0.2 mmol), tetraethyleneglycol bis(2-aminophenyl)ether **10** (75 mg, 0.2 mmol) and 2,6-pyridinedicarboxaldehyde **9a** (27 mg, 0.2 mmol) were stirred for 48 h in dry CH_3CN (10 mL) under argon atmosphere at room temperature. Then 1M BH_3·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, DCM / MeCN / MeOH = 100 : 0 : 0 ~ 75 : 25 : 1) to give the [2]rotaxane **11a**, rf=0.67. Yield: 193 mg, 85%. Compound of **11a:** ^{1}H NMR (600 MHz, CD_3CN). δ 8.85 (s, 2H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.15 - 7.14 (m, 2H), 7.12 - 7.11 (m, 3H), 7.05 - 7.02 (m, 3H), 7.00 - 6.97 (m, 6H), 6.78 (d, *J* = 7.8 Hz, 2H), 6.70 – 6.68 (m, 8H), 6.38 (d, *J* = 4.8 Hz, 2H), 6.21 (s, 1H), 6.01 (s, 2H), 4.46 (s, 4H), 4.34 (s, 2H), 4.12 – 4.10 (m, 2H), 4.03 (d, *J* = 11.4 Hz, 2H), 3.87 – 3.85 (m, 4H), 3.82 (d, *J* = 3.0 Hz, 1H), 3.70 – 3.67 (m, 6H), 3.64 (d, *J* = 6.6 Hz, 3H), 3.36 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN) δ 161.5, 159.3, 147.5, 145.1, 144.0, 143.9, 143.9, 137.5, 134.9, 132.0, 131.4, 131.3, 131.2, 129.4, 128.5, 128.4, 127.3, 127.3, 122.7, 121.9, 120.3, 119.2, 113.3, 110.8, 107.1, 101.4, 71.9, 71.6, 71.0, 68.1, 55.5, 53.0, 52.8, 50.4. MALDI MS: *m/z* = 991.61 [M – PF_6^-]; calculated exact mass: 1136.47. Anal. Calcd for $C_{63}H_{67}F_6N_4O_7P$: C, 66.54; H, 5.94; N, 4.93. Found: C, 66.65; H, 5.84; N, 4.88.

Synthesis of [2]rotaxane 11b. A mixture of salt **8** (131 mg, 0.20 mmol), tetraethyleneglycol bis(2-aminophenyl)ether **10** (75 mg, 0.20 mmol) and 2,6-pyridinedicarboxaldehyde derivative **9b** (70 mg, 0.20 mmol) were stirred for 48 h in dry CH_3CN (10 mL) under argon atmosphere at room temperature. Then 1M BH_3·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, DCM / MeCN / MeOH = 100 : 0 : 0 ~ 75 : 25 : 1) to give the [2]rotaxane **11b**, rf=0.48. Yield: 221 mg, 82%**.** Compound of **11b:** ^{1}H NMR (600 MHz, CD_3CN) δ 8.90 (s, 2H), 7.15 (d, *J* = 7.2 Hz, 3H), 7.11 (br, 3H), 7.04 (d, *J* = 7.2 Hz, 3H), 6.99 – 6.97 (m, 6H), 6.89 (s, 2H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.68 (s, 8H), 6.41(t, *J* = 3.6 Hz, 2H), 6.20 (s, 1H), 6.02 (s, 2H), 4.46 – 4.41 (m, 4H), 4.28 (s, 2H), 4.14 (t, *J* = 6.0 Hz, 2H), 4.09 (br, 2H), 4.02 (d, *J* = 10.8 Hz, 2H), 3.87 (br, 4H), 3.76 (d, *J* = 13.8 Hz, 2H), 3.69 (br, 6H), 3.54 (d, *J* = 16.8 Hz, 2H), 3.37 (s, 6H), 1.84 – 1.82 (m, 2H), 1.52 – 1.48 (m, 2H), 1.42 – 1.40 (m, 2H), 1.29 (br, 18H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 167.2, 161.5, 161.1, 147.4, 145.0, 144.0, 143.9, 143.9, 142.5, 140.7, 137.6, 134.9, 131.9, 131.4, 131.3, 131.2, 129.4, 128.5, 128.3, 127.2, 121.9, 120.2, 113.2, 110.8, 108.9, 107.2, 101.4, 71.9, 71.6, 70.9, 68.1, 68.1, 55.5, 53.0, 52.8, 50.4, 32.3, 30.0, 29.7, 29.7, 29.2, 26.3, 23.0, 14.1. MALDI MS: *m/z* = 1203.76 [M – PF_6^-]; calculated exact mass: 1348.68. Anal. Calcd for $C_{77}H_{95}F_6N_4O_8P$: C, 68.53; H, 7.10; N, 4.15. Found: C, 68.61; H, 7.19; N, 4.10.

Synthesis of 15. A mixture of **5** (0.72 g, 2.0 mmol) and **14** (0.12 g, 1.0 mmol) in dry toluene (60 mL) into a 100 mL round-bottom flask was refuxed 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 $NaBH_4$ (0.31 g, 8.0 mmol) was added in portions. After stirring for overnight, the solvents were removed under vacuum, and the residue was extracted by dichloromethane (DCM). The organic layer was washed by brine till clear, dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a kinetically stable amine as a low yellowish oil. The unpurified amine was dissolved in dry chloroform (20 mL), and then Boc_2O (1.76 g, 8.0 mmol) and triethylamine (0.86 mL) were added. The mixture was stirred at room temperature for 24 h. Removal of solvent under reduced pressure and purification on

a silicagel column using petroleum ether / ethyl acetate (4 : 1) as the eluent obtained the Boc-protected **15** as a white solid, rf=0.76. Yield: 0.76 g, 76%. Compound **15**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 - 7.01 (m, 38H), 4.30 (d, *J* = 28.4 Hz, 4H), 3.10 (d, *J* = 49.2 Hz, 4H), 1.45 (s, 9H), 1.37 (s, 9H), 1.21 (br, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.5, 140.9, 140.6, 131.3, 127.6, 126.4, 79.4, 28.4, 28.1, 26.6. MALDI MS: *m/z* = 1028.01[M + Na^+]; calculated exact mass: 1004.55. Anal. Calcd for $C_{70}H_{72}N_2O_4$: C, 83.63; H, 7.22; N, 2.79. Found: C, 83.71; H, 7.26; N, 2.69.

Synthesis of 16. To a solution of the Boc-protected amine **15** (1.00 g, 1.0 mmol) in dry DCM (20 mL), TFA (0.64 mL, 10.0 mmol) was added at room tempeature. After stirring for 2 h under argon atmosphere, the solvent was removed under vacuum. The residue was dissolved in MeOH (5.0 mL), and then saturated NH_4PF_6 (30.0 mL, aq) was added to yield a off-white precipitate. After filtering, washing with H_2O and dry under vacuum, the title compound **16** was obtained as an off-white solid, rf=0.65. Yield: 1.01 g, 92%. Compound of **16**. ^{1}H NMR (600 MHz, CD_3CN) δ 7.19 (br, 2H), 7.14 (br, 17H), 7.10 (br, 5H), 7.04 (br, 14H), 3.97 (s, 4H), 2.85 (br, 4H), 1.60 (br, 4H), 1.32 (br, 4H). ^{13}C NMR (100 MHz, CD_3CN) δ 145.2, 144.0, 142.3, 140.8, 131.4, 128.4, 127.2, 51.7, 47.9, 26.3, 25.9. MALDI MS: *m/z* = 805.55[M - HPF_6 - PF_6^-]; calculated exact mass: 1096.39. Anal. Calcd for $C_{60}H_{58}F_{12}N_2P_2$: C, 65.69; H, 5.33; N, 2.55. Found: C, 65.59; H, 5.25; N, 2.63.

Synthesis of [3]rotaxane 17a. A mixture of salt **16** (110 mg, 0.1 mmol), tetraethyleneglycol bis(2-aminophenyl)ether **10** (75 mg, 0.2 mmol) and 2,6-pyridinedicarboxaldehyde **9a** (27 mg, 0.2 mmol) were stirred for 72 h in dry CH_3CN (10 mL) under argon atmosphere at room temperature. Then 1M BH_3·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, DCM / MeCN / MeOH = 100 : 0 : 0 ~ 75 : 25 : 1) to give the [3]rotaxane **17a**, rf=0.56. Yield: 113 mg, 55%. Compound of **17a:** ^{1}H NMR (600 MHz, CD_3CN) δ 8.66 (s, 4H), 7.83 (t, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 4H), 7.14 – 7.13 (m, 12H), 7.12 (s, 4H), 7.08 (s, 2H), 7.05 (br, 2H), 7.03 (d, *J* = 4.2 Hz, 6H), 7.00 (br, 10H), 6.97 – 6.96 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 3.0 Hz, 2H), 6.70 (d, *J* = 7.2 Hz, 2H), 6.45 (d, *J* = 7.8 Hz, 4H), 4.74 (s, 4H), 4.35 – 4.33 (m, 3H), 4.23 (t, *J* = 8.4 Hz, 4H), 4.09 – 4.07 (m, 7H), 3.97 – 3.93 (m, 3H), 3.86 – 3.84 (m, 4H), 3.77 – 3.74 (m, 4H), 3.65 – 3.58 (m, 12H), 3.57 – 3.53 (m, 7H), 1.29 (br, 4H), 0.91 – 0.89 (m, 4H). ^{13}C NMR (100 MHz, CD_3CN) δ 182.3, 159.2, 147.8, 145.0, 144.1, 144.1, 142.5, 140.9, 138.9, 137.8, 132.0, 131.5, 131.5, 131.3, 129.6, 128.5, 128.5, 127.3, 122.7, 122.0, 120.6, 120.4, 113.6, 113.5, 111.1, 111.0, 71.9, 71.5, 70.9, 70.1, 69.4, 68.4, 50.8, 26.3. MALDI MS: *m/z* = 1909.91 [M – PF_6^-], 1763.98 [M - HPF_6 - PF_6^-]; calculated exact mass: 2054.87. Anal. Calcd for $C_{114}H_{124}F_{12}N_8O_{10}P_2$: C, 66.59; H, 6.08; N, 5.45. Found: C, 66.51; H, 6.00; N, 5.57.

Synthesis of [3]rotaxane 17b. A mixture of salt **16** (110 mg, 0.1 mmol), tetraethyleneglycol bis(2-aminophenyl)ether **10** (75 mg, 0.2 mmol) and 2,6-pyridinedicarboxaldehyde derivative **9b** (75 mg, 0.2 mmol) were stirred for 72 h in dry CH_3CN (10 mL) under argon atmosphere at room temperature. Then 1M BH_3·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, DCM / MeCN / MeOH = 100 : 0 : 0 ~ 75 : 25 : 1) to give the [3]rotaxane 2**b**, rf=0.56. Yield:119 mg, 48%. Compound of **17b:** ^{1}H NMR (600 MHz, CD_3CN) δ 8.65 (s, 4H), 7.14 - 7.13 (m, 21H), 7.10 (br, 3H), 7.06 (d, *J* = 8.4 Hz, 5H), 7.02 (br, 8H), 6.99 (br, 5H), 6.91 (br, 4H), 6.85 (d, *J* = 6.6 Hz, 2H), 6.78(br, 2), 6.73 (br, 4H), 6.48 (s, 4H), 4.68 (br, 2H), 4.57 (s, 1H), 4.31 (t, *J* = 6.6 Hz, 3H), 4.21 (br, 15H), 4.07 (s, 2H), 3.91 (br, 9H), 3.73 (s, 1H), 3.64 – 3.58 (m, 12H), 3.43 (br, 7H), 1.87 (br, 4H), 1.53 – 1.48 (m, 4H), 1.42 – 1.38 (m, 4H), 1.29 (br, 40H), 0.90 – 0.88 (m, 10H). ^{13}C NMR (100 MHz, CD_3CN) δ 147.6, 145.4, 144.5, 144.2, 144.1, 144.1, 142.6, 141.2, 140.9, 138.2, 133.7, 132.1, 131.6, 131.4, 130.0, 128.7, 128.6, 128.5, 127.4, 122.6, 120.7, 113.9, 105.1, 71.7, 71.3, 71.1, 70.7, 49.2, 32.4, 30.1, 29.8, 29.7, 26.3, 23.2, 14.2. MALDI MS: *m/z* = 2188.52 [M - HPF_6 - PF_6^-]; calculated exact mass: 2479.30. Anal. Calcd for $C_{142}H_{180}F_{12}N_8O_{12}P_2$: C, 68.75; H, 7.31; N, 4.52. Found: C, 68.71; H, 7.39; N, 4.45.

Synthesis of 22. In a 250 mL two-necked, round-bottom flask equipped with a magnetic stirrer a mixture of **20** (0.70 g, 2.0 mmol), **21** (0.57 g, 2.0 mmol) and potassium carbonate (0.55 g, 4.0 mmol) was placed, 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 were removed under vacuum, and the residue was extracted by ethyl acetate, and then dried over anhydrous Na_2SO_4. Upon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether / ethyl acetate (4 : 1) as the eluent to obtain the compound **22** as a low yellow oil, rf=0.69. Yield: 0.83 g, 75%. Compound of **22:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.08 – 6.97 (m, 17H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.05 (s, 2H), 3.89 (s, 2H), 1.81 (d, *J* = 25.2 Hz, 4H), 1.53 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 164.1, 157.5, 143.9, 140.5, 140.0, 135.9, 132.5, 132.0, 131.3, 129.7, 127.7, 127.5, 126.3, 126.2, 114.7, 113.5, 68.2, 67.5, 29.2, 29.0, 25.8. MALDI MS: *m/z* = 552.31 [M]; calculated exact mass: 552.27. Anal. Calcd for $C_{39}H_{36}O_3$: C, 84.75; H, 6.57. Found: C, 84.68; H, 6.68.

Synthesis of 23. A mixture of **22** (0.55 g, 1.0 mmol) and **6** (0.17 g, 1.0 mmol) in dry toluene (50 mL) into 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 $NaBH_4$ (0.19 g, 5.0 mmol) was added in portions. After stirring for overnight, the solvents were removed under vacuum, and the residue was extracted by dichloromethane (DCM). The organic layer was washed by brine till clear, dried over anhydrous Na_2SO_4 and concentrated in vacuum to give a kinetically stable amine as low yellowish oil. The unpurified amine was dissolved in dry chloroform (20 mL), and then Boc_2O (0.88 g, 4.0 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 (4 : 1) as the eluent obtained the Boc-protected **23** as a low yellowish oil, rf=0.72. Yield: 0.63 g, 78%. Compound of **23:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 6.99 (m, 15H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.43 (s, 1H), 6.36 (t, *J* = 11.2 Hz, 4H), 4.34 (d, *J* = 10.0 Hz, 2H), 4.26 (d, *J* = 7.6 Hz, 2H), 3.95 (t, *J* = 6.0 Hz, 2H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.79 – 3.77 (m, 8H), 1.80 – 1.77 (m, 4H), 1.59 (s, 2H), 1.50 (s, 9H), 1.46 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 158.3, 157.5, 143.9, 140.5, 139.9, 135.9, 132.5, 131.3, 129.8, 127.6, 127.5, 126.3, 126.1, 114.4, 113.5, 105.7, 105.2,

99.0, 79.9, 67.8, 67.5, 55.2, 49.0, 48.7, 29.2, 28.4, 25.9. MALDI MS: *m/z* = 803.29 [M], 826.29 [M + Na^+], 842.24 [M + K^+]; calculated exact mass: 803.42. Anal. Calcd for $C_{53}H_{57}NO_6$: C, 79.17; H, 7.15; N, 1.74. Found: C, 79.24; H, 7.26; N, 1.71.

Synthesis of 24. To a solution of the Boc-protected amine **23** (0.80 g, 1.0 mmol) in dry DCM (20 mL), TFA (0.32 mL, 5.0 mmol) was added at room temperature. After stirring for 2 h under argon atmosphere, the solvent was removed under vacuum. The residue was dissolved in MeOH (5.0 mL), and then saturated NH_4PF_6 (20.0 mL, aq) was added to yield an off-white precipitate. After filtering, washing with H_2O and dry under vacuum, the title compound **24** was obtained as an off-white solid, rf=0.65. Yield: 0.82 g, 96%. Compound of **24**: ^{1}H NMR (600 MHz, CD_3CN) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.15-7.12 (m, 9H), 7.04 – 7.01 (m, 6H), 6.94-6.90 (m, 4H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.59 (s, 2H), 6.52 (s, 1H), 4.06 (s, 2H), 4.03 (s, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 3.78 (s, 6H), 1.78-1.72 (m, 4H), 1.49 (s, 4H). ^{13}C NMR (100 MHz, CD_3CN) δ 161.8, 160.5, 158.3, 144.6, 141.3, 132.8, 132.2, 131.6, 128.3 , 127.0, 115.3, 114.2, 108.2, 55.8, 51.5, 51.4, 41.5, 41.2, 29.5, 26.1. MALDI MS: *m/z* = 704.42 [M – PF_6^-]; calculated exact mass: 849.34. Anal. Calcd for $C_{48}H_{50}F_6NO_4P$: C, 67.83; H, 5.93; N, 1.65. Found: C, 67.80; H, 5.85; N, 1.72.

Synthesis of [2]rotaxane 25a. The synthesis procedure of **25a** was similar to the synthesis of **11a**. Yield: 155 mg, 78%. Compound of **25a:** ^{1}H NMR (600 MHz, CD_3CN) δ 8.83 (s, 2H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.10 (m, 9H), 7.04 – 7.01 (m, 6H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.71 – 6.99 (m 6H), 6.65 – 6.63 (m, 2H), 6.52 (d, *J* = 8.4 Hz, 2H), 6.39 (t, *J* = 4.8 Hz, 2H), 6.26 (s, 1H), 6.09 (d, *J* = 2.4 Hz, 2H), 4.55 (t, *J* = 7.2 Hz, 2H), 4.47 – 4.44 (m, 4H), 4.11 – 4.08 (m, 4H), 3.93 (br, 3H), 3.89 – 3.87 (m, 2H), 3.79 – 3.78 (m, 2H), 3.75 - 3.74 (m, 5H), 3.72 (br, 4H), 3.64 (t, *J* = 4.8 Hz, 2H), 3.37 (s, 6H), 1.73 – 1.70 (m, 4H), 1.46 (br, 4H). ^{13}C NMR (100 MHz, CD_3CN) δ 161.6, 160.1, 159.4, 158.3, 147.4, 144.6, 141.3, 140.8, 138.8, 137.6, 136.4, 135.3, 132.8, 131.6, 131.3, 128.4, 128.3, 127.1, 127.0, 124.2, 122.7, 121.9, 120.2, 115.2, 114.2, 113.1, 110.8, 107.0, 101.4, 71.9, 71.6, 71.0, 68.2, 68.1, 55.6, 52.8, 50.2, 29.5, 29.3, 26.1. MALDI MS: *m/z* = 1183.75 [M – PF_6^-]; calculated exact mass: 1328.58. Anal. Calcd for $C_{75}H_{83}F_6N_4O_9P$: C, 67.76; H, 6.29; N, 4.21. Found: C, 67.82; H, 6.21; N, 4.10.

Synthesis of [2]rotaxane 25b. The synthesis procedure of **25b** was similar to the synthesis of **11b.** Yield: 169 mg, 73%. Compound of **25b:** ^{1}H NMR (600 MHz, CD_3CN) δ 8.85 (s, 2H), 7.14 – 7.11 (m, 10H), 7.04 – 7.01 (m, 5H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.72 – 6.69 (m, 4H), 6.68 – 6.66 (m, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 7.2 Hz, 2H), 6.26 (s, 1H), 6.11 (s, 2H), 4.53 (br, 2H), 4.40 (br, 4H), 4.10 – 4.08 (m, 4H), 3.93 (s, 4H), 3.90 – 3.86 (m, 4H), 3.74 (d, *J* = 3.0 Hz, 5H), 3.72 (br, 5H), 3.64 (d, *J* = 15.6 Hz, 2H), 3.39 (s, 6H), 1.81 – 1.78 (m, 2H), 1.72 – 1.71 (m, 4H), 1.46 (br, 6H), 1.38 (br, 2H), 1.29 (br, 18H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 167.3, 161.7, 161.3, 160.2, 158.5, 147.5, 144.8, 144.7, 141.5, 141.0, 137.8, 136.5, 135.4, 132.9, 131.7, 131.7, 131.4, 128.5, 128.4, 127.1, 127.1, 124.4, 122.0, 120.2, 115.3, 114.3, 113.2, 110.9, 109.0, 107.3, 101.5, 72.1, 71.8, 71.1, 69.1, 68.4, 68.2, 55.7, 52.9, 50.5, 32.4, 30.2, 30.2, 30.1, 30.1, 29.9, 29.8, 29.6, 29.4, 29.4, 26.4, 26.2, 23.2, 14.3. MALDI MS: *m/z* = 1395.92 [M – PF_6^-]; calculated exact mass: 1540.79. Anal. Calcd for $C_{89}H_{111}F_6N_4O_{10}P$: C, 69.33; H, 7.26; N, 3.63. Found: C, 69.25; H, 7.17; N, 3.60.

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† Electronic Supplementary Information (ESI) available: [UV-vis spectra of **8**, **11**, **16**, **17**, **24** and **25** and Photographs of **24** and **25** in CH_3CN/water mixtures with different fractions of water (f_w) taken under UV illumination ; optomized structures, NMR, MS spectra of all the interminates and AIE-active [n]rotaxanes.]. See DOI: 10.1039/b000000x/

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