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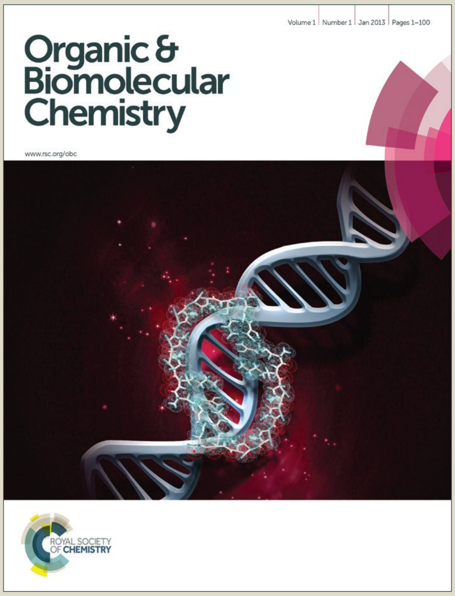

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Aggregation-induced emission behavior of pH-controlled molecular shuttle based on tetraphenylethene moiety

Xie Han, Meijiao Cao, Zhiqiang Xu, Di Wu, Zhao Chen, Anxin Wu, Sheng Hua Liu, Jun Yin*[a]

Tetraphenylethene (TPE) with aggregation-induced emission (AIE) behavior as a popular backbone is applied widely in the construction of functional supramolecular system. In this work, a TPE-based linear molecule having amide and amine units is synthesized. Its ammonium as template is used to construct the N-hetero crown ether-based [2]rotaxane by the template-directed clipping approach. Their structures are well-characterized by NMR, MALDI-TOF-MS and elemental analysis. Owing to the existence of amide unit, the [2]rotaxane possesses the function of molecular shuttle. The shuttling motion of the macrocycle component between ammonium station and amide station can be driven by external acid-base stimuli in solution, accompanied by visual behavior changes. Investigation on AIE behavior of them shows that (1) ammonium reaches the aggregation state almost in the presence of same water with its deprotonated form; (2) the [2]rotaxane that the macrocycle component locates in the site of ammonium forms the aggregation state in the presence of less water than [2]rotaxane that macrocycle component locates in the site of amide, attributing to stronger interaction between crown ether component and TPE unit of template component when the distance between each other is shorter. The result indicates that the shuttling motion of macrocycle component can adjust the aggregation state of AIE molecules.

Introduction

Mechanically interlocked molecules such as rotaxanes and catenanes have become typical candidates in constructing artificial molecular machines such as molecular muscles, molecular elevators, molecular shuttles.[1] The shuttling motion of ring component endows these artificial molecular machines with unique function and the movement can be driven by different kinds of external stimuli such as illumination,[2] electrochemical potential,[2d,3] ions [4] and pH changes.[5] Nowadays, molecular shuttle has been widely used in the design of functional supermolecules by taking advantage of the reversible ring component motion between different states, which may vary the intercomponent interactions such as energy transfer,[6] electron transfer [7] and charge transfer.[5i,8] And usually, these interactions lead to the electronic or photophysical property changes of molecules.[9]

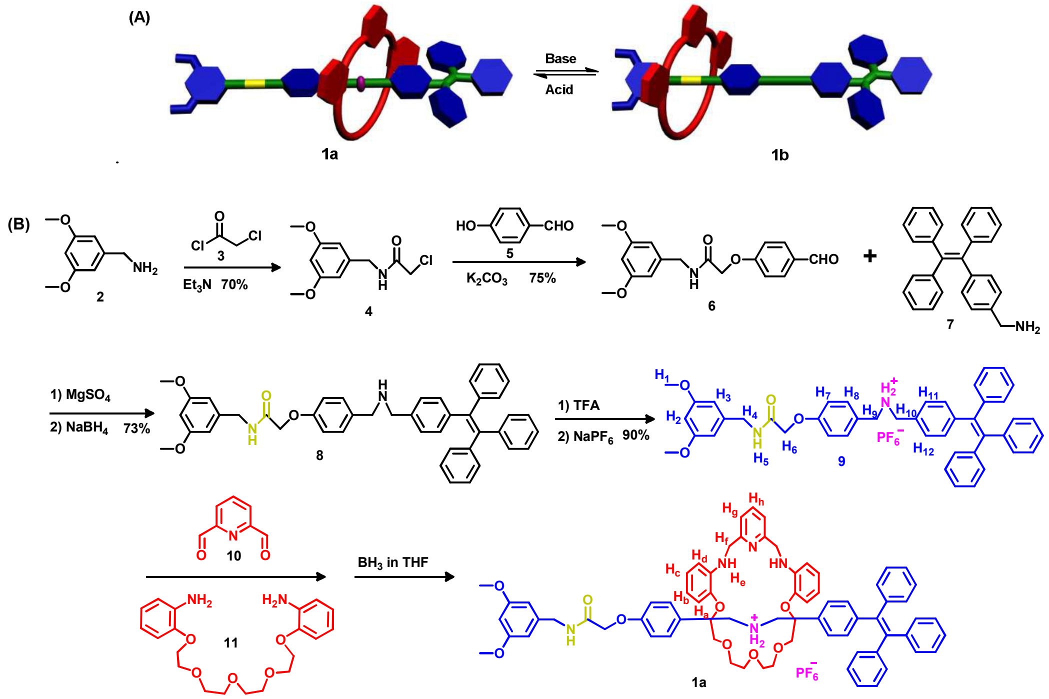
Aggregation induced emission (AIE) was firstly defined by Tang in 2001.[10] Since then numerous compounds with AIE feature have been synthesized and widely applied in optoelectronic materials,[11] biological sensors,[12] chemosensors,[13] explosive detection,[14] luminescent polymers,[15] mechanofluorochromism [16] and gels.[17] Conventionally, restriction of intramolecular rotation of phenyl on TPE unit is the main reason caused AIE phenomenon. Recently, Tang's group reported a TPE complex based on β-cyclodextrin macrocycle, in which β-cyclodextrin could restrict the rotation of TPE as a result of host-guest interaction.[18] Zheng et al. also found that the AIE characteristic of a amphiphilic TPE derivative could be changed by the inclusion interaction with γ-cyclodextrin.[19] More, Lin et al. constructed a functional [2]catenane base on TPE and studied its AIE behavior.[20] These investigations confirm that host-gust interaction may play an important role for the AIE behavior of TPE.

In our recent work, we have reported a series of N-hetero crown ether-based [n]rotaxanes containing TPE unit on the template component.[21] Investigation on the AIE property showed that a smaller distance resulted in the aggregation state being reached more easily than when there was a longer distance between the TPE unit and N-hetero crown ether component. In view of the fact that rotaxane molecules having the function of shuttling motion can be used a molecular shuttle under the external stimuli, the model of molecular shuttle can achieve the reversible linear motion and avoid a longer synthesis for studying the interaction of macrocycle with TPE-based template. Herein, we design and synthesize a bistable [2]rotaxane containing a TPE-based ammonium moiety, which can be used as a molecular shuttle to achieve the linear motion by adjusting the acid-base balance. Studies on AIE behavior indicate that the shuttling motion of macrocycle component can change the aggregation state of AIE molecules.

RESULTS AND DISCUSSION

The designed molecular shuttle has [2]rotaxane backbone, composed of N-hetero crown ether component and ammonium template. In which, the linear template contains two different recognition sites, namely, amide and ammonium (-NH_2^+-). In the protonation state, the macrocycle component locates in the ammonium site closed to the TPE unit while the N-hetero crown ether may glide to the amide site stayed away the TPE unit after neutralizing ammonium, as presented in Scheme 1(A). The synthetic route of molecular shuttle **1a** is outlined in Scheme 1(B). The 3, 5-dimethoxybenzylamine **2** as starting material was treated with 2-chloroacetyl chloride **3** in the presence of Et_3N at 0℃ to afford amide **4**.[22] Subsequently, compound **4** was reacted with aldehyde **5** to form the corresponding aldehyde **6**. Then, the condensation of **6** with TPE **7** that was synthesized according to the previous literature [23] led to the formation of corresponding reversible dynamic imine, which was reduced by $NaBH_4$ to obtain the desired kinetically stable amine **8** in 73% yield. Treatment of **8** with excess trifluoroacetic acid (TFA) led to the protonation of the amine group in **8** and subsequent counter-ion exchange with saturated NH_4PF_6 solution produced the key substance **9**, which was subjected to perform the template-directed clipping reaction with **10** and **11**,[24] affording the corresponding [2]rotaxane **1a** after reduction with $BH_3 \cdot THF$. Deprotonation of the [2]rotaxane **1a** with NaOH aqueous solution (pH 13.0) produces the desired [2]rotaxane **1b** in 95% yield.

These key intermediates have been well-defined by standard spectroscopic techniques such as NMR spectroscopy and mass spectrometry (In ESI). Subsequently, the process of clipping reaction was monitored by ^1H NMR. A broad singlet at δ = 9.9 ppm for ammonium NH_2^+ protons as well as a signal at δ = 8.34 ppm due to the imine (CH=N) were observed (In Fig. S1), which indicated the formation of dynamic [2]rotaxane. Treating the mixture with $BH_3 \cdot THF$ reduced the dynamic imine bond into the kinetically stable C−NH bonds. And then the pure form of [2]rotaxane **1a** was obtained by column chromatography in 65% yield. As expected for complexation, the signals assigned to H_9 and H_{10} adjacent to NH_2^+ experienced a significant downfield shift with respect to those in salt **8**.[25] Under the shielding effect of the macrocycle, obvious upfield shifts (H_{11}, H_{12} and H_7, H_8) were observed. In the ^1H NMR spectra, the resonance of NH_2^+ protons in the kinetically stable [2]rotaxane **1a** exhibited an obvious upfield shift compared with the dynamic [2]rotaxane and they could be detected at 8.86 ppm due to the effect of the hydrogen bonding of the oxygen atoms on the macrocycle component with the ammonium hydrogen atoms (Fig. 1C). Thus, the ^1H NMR spectra gave an evidence of the formation [2]rotaxane **1a** and the selective binding of N-hetero crown ether with NH_2^+ center. Additional evidence supporting the formation of [2]rotaxane **1a** was provided by analysis of MALDI-MS, which featured a peak at m/z 1154.438, attributable to the respective $[M - PF_6^-]^+$species, in which M was the [2]rotaxane **1a** (In ESI).



Scheme 1 (A) The models of [2]rotaxanes **1a** and **1b**; (B) Synthesis of [2]rotaxane **1a**.

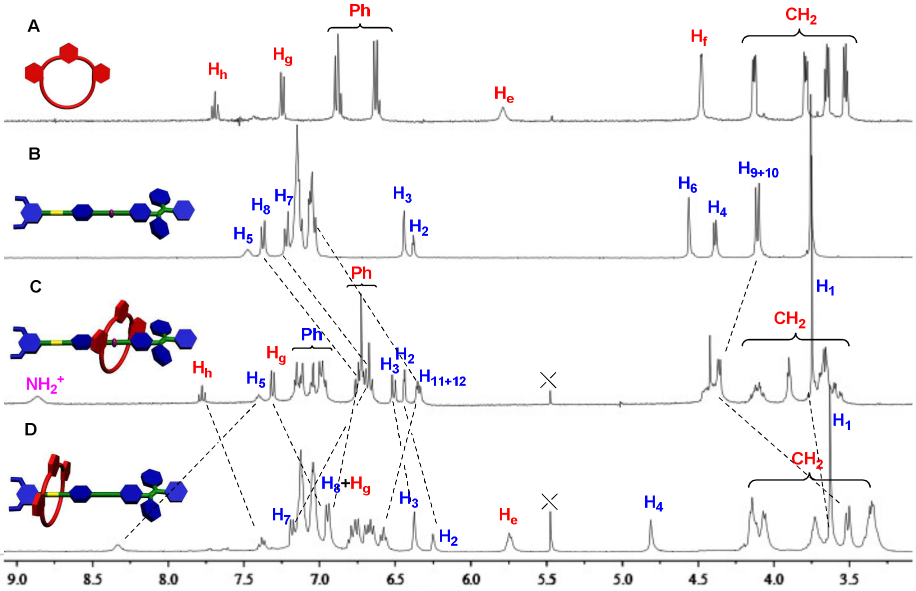


Fig. 1. Partial ^1H NMR spectra (400 MHz in CD_3CN at rt) of macrocycle component (A); **9** (B); **1a** (C) and **1b** (D)

In previous report, neutralizing the ammonium on the template component resulted in the motion of macrocycle component from ammonium site to amide site.[4b] Next, [2]rotaxane **1a** was neutralized by NaOH to produce [2]rotaxane **1b**. Similarly, the process of shuttling motion was recorded by ^1H NMR spectrometry. As shown in Fig. 1D, the signals for H_9 and H_{10} displayed an upfield shift of 0.85 ppm upon treatment of NaOH solution, which clearly indicated that the addition of base induced the deprotonation of dialkylammonium center and the breaking of the C–H•••O hydrogen bonds. Additionally, the signal corresponding to the protons on the stopper units (H_1) exhibited an upfield shift due to the shielding effect of the macrocycle. Simultaneously, the signal of NH proton (H_5) on the amide group shifted downfield from δ = 7.40 to 8.33 ppm, which could be attribute to the formation of hydrogen bond between N-hetero crown ether and amide. These characteristic resonances implied that deprotonation of the dialkylammonium center prompted the motion of macrocycle component from the NH_2^+ center to the amide recognition site. Similarly, the MALDI-MS proved the formation of [2]rotaxane **1b**, the peak at m/z 1154.495 was assigned to the [M + H$^+$], in which M was the [2]rotaxane **1b**.

Introduction of tetraphenylethylene (TPE) units authorizes it possesses the AIE property. Subsequent investigation focused on the AIE behaviors of [2]rotaxanes and their corresponding guests by adjusting various water fractions (f_W) of acetonitrile–water mixtures. Firstly, we investigated the AIE behavior of compounds **8** and **9**. As shown in Fig. 2A, ammonium **9** was almost nonfluorescent when the f_W was below 80%. A remarkable fluorescence enhancement was observed when the f_W was up to 90%. This can be attributed to the aggregation of compound **9** in acetonitrile–water solution with a higher amount of water. And the aggregation induced restriction of intramolecular rotations of the TPE unit was considered to be the reason that turns on the emission of **9**. While compound **8** showed an emission band at 460 nm when the f_W reached 80%, it was clear that deprotonation of ammonium salt **9** could promote the aggregation state easier in Fig. 2C. This may be attribute to the ammonium salt **9** possesses better solubility compared to compound **8** in high water fraction solution.[26] For the UV-vis absorption spectra of compounds **8** and **9** (Fig. S2 in ESI), no obvious changes were observed.

Subsequently, we investigated the AIE behavior of [2]rotaxanes **1a** and **1b** for exploring the effect when the macrocycle component located in the different binding site. As shown in Fig 3A, the fluorescence intensity was found to be rapidly enhanced as soon as the f_W reached 80%, which indicated that [2]rotaxane **1a** had an advantage in getting the aggregation state more easily with the increase of f_W compared with the corresponding ammonium **9**. This result was consistent with our report in previous work.[21] As described above, our purpose is to investigate the effect of shuttling motion towards AIE behavior. Subsequent investigation was performed via similar method. The N-hetero crown ether component of [2]rotanxane **1b** was located far away from the AIE-active TPE unit in comparison to [2]rotanxane **1a**. From their optical properties, it was found that [2]rotanxanes **1a** and **1b** had similar UV-vis absorption (Fig. S2 in ESI), but they exhibited different AIE behaviors. As shown in Fig. 3C, the solution of [2]rotanxane **1b** didn't exhibit any fluorescence until the water fraction reached 90%. The photographs of **1a** and **1b** (Fig. 3B and 3D) in different water fractions provided further evidence for their different AIE behavior. These results suggested that **1a** was easier to reach the aggregation state in comparison to its deprotonated product, which was possibly attributed to the different inclusion effect of N-hetero crown ether towards the AIE-active TPE unit. Further, we investigated the effect of different viscosity for the optical behavior of **1a** and **1b** by varying the ratio of methanol and glycerol. The result indicated that increasing the fraction of glycerol led to the enhancement of emission intensity owing to the rotation inhibition of TPE unit (Fig. S3 in ESI). This result was well in agreement with the mechanism described the aggregation induced restriction of intramolecular rotations of TPE units in acetonitrile-water.

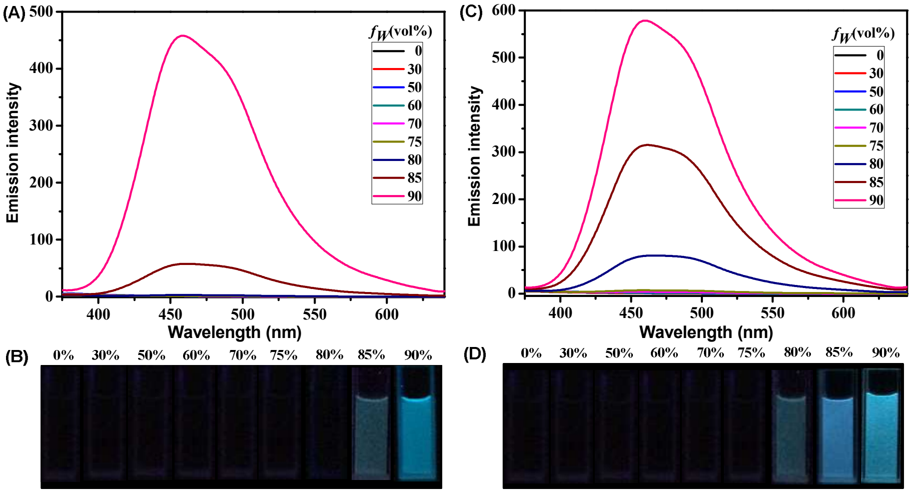


Fig. 2. Fluorescent spectra and photographs of **8** and **9** in CH_3CN–water mixtures with different water fractions (λ_{ex} = 340 nm). (A) Spectra changes of **9**; (B) photographs of **9** taken under UV illumination; (C) spectra changes of **8**; (D) photographs of **8** taken under UV illumination.

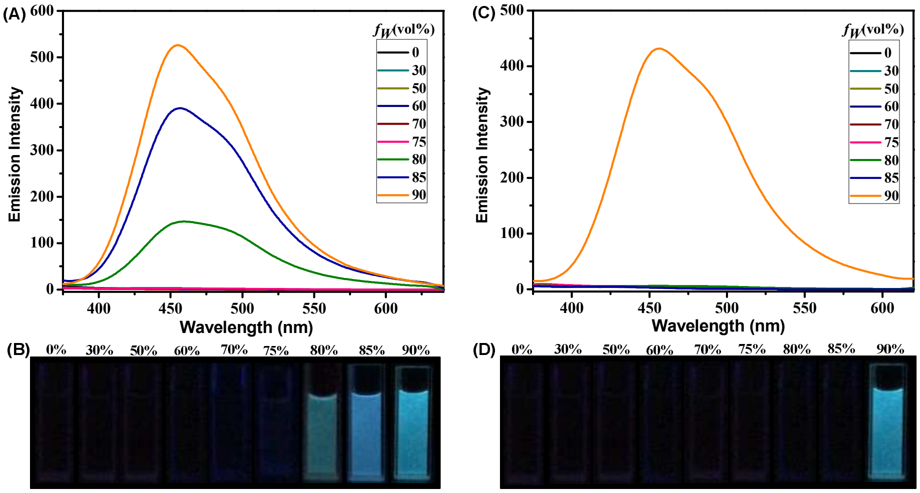


Fig. 3. Fluorescent spectra and photographs of **1a** and **1b** in CH_3CN–water mixtures with different water fractions (λ_{ex} = 340 nm). (A) Spectra changes of **1a**; (B) photographs of **1a** taken under UV illumination; (C) spectra changes of **1b**; (D) photographs of **1b** taken under UV illumination.

Next, a theoretical DFT calculation by using the Gaussian 09 programs at the B3LYP/6-31G* level was employed to further confirm the inclusion effect of N-hetero crown ether. As shown in Fig. 4, the inclusion of N-hetero crown ether ring for NH_2^+ center led to the overlap of the macrocycle component with TPE unit, which may affect the rotation of the TPE moiety. Upon the treatment of base, the macrocycle component moved to the amide site from ammonium site. According to the optimized structure of [2]rotanxane **1b** in Fig 4, the N-hetero crown ether is far from the TPE unit, which implies that the interaction between the macrocycle and TPE unit is weaker. The result of DFT calculation further confirms the mechanically interlocked interaction can adjust the AIE behavior and the pH-controlled shuttling motion of macrocycle component may change the optical behavior.

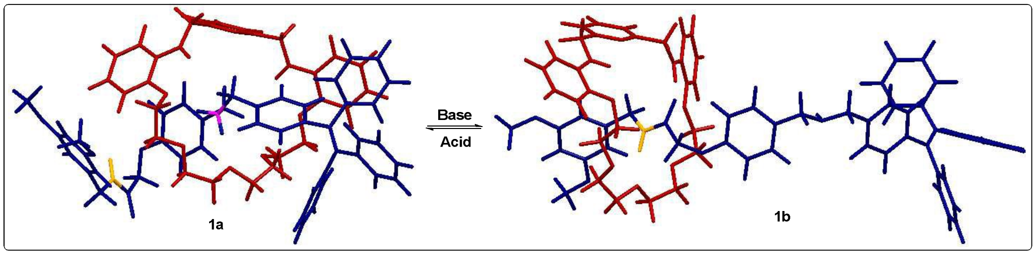


Fig. 4. The energy-minimized structures of [2]rotanxanes **1a** and **1b** based on density functional theory (DFT) calculations at the B3LYP/6-31 G* level using Gaussian 09 programs.

Conclusions

In summary, a TPE-based molecular shuttle having amide and amine units has been synthesized and well-characterized in this work. The introduction of tetraphenylethene(TPE) unit endowed the molecular shuttle with AIE characteristic. As expected, acid-base stimuli can drive the macrocycle component to shuttle between ammonium station and amide station, accompanied by the photophysical properties change. Investigation of the AIE behavior indicates that the macrocycle component located in the site of ammonium forms the aggregation state in the presence of less water than [2]rotaxane that macrocycle component located in the site of amide, attributing to their stronger interaction each other when the distance between TPE and ammonium is shorter. The presented results may establish a novel perspective for the design and construction of AIE-active mechanically interlocked molecules.

Experimental Section

General Methods. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. All starting materials were obtained commercially as analytical-grade and used without further purification. ^{1}H and ^{13}C NMR spectra were collected on an American Varian Mercury Plus 400 spectrometer (400 MHz). Mass spectra were measured with the ultrafleXtreme MALDI-TOF-TOF or EI-MS. UV-Vis spectra were obtained on U-3310 UV spectrophotometer. Fluorescence spectra were taken on Perkin-Elmer, LS-55 fluorescence spectrophotometer. The elemental analyses were obtained on a Vario ELIII CHNSO.

Synthesis of 6: To a solution of 4-hydroxybenzaldehyde (0.1 g, 0.9 mmol) in acetone, 2-Chloro-N-(4-methoxybenzyl)acetamide (0.2 g, 0.8 mmol) and anhydrous potassium carbonate was added. The reaction mixture was refluxed under nitrogen atmosphere for 8 h and cooled to room temperature. The solution was filtered, the filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on SiO_2 with ethyl acetate and petroleum ether to give compound **6** (0.2 g, 74%) as white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.87 (m, 4H), 7.82 (d, J = 8 Hz, 2H), 7.08 (t, J = 8 Hz, 2H), 7.01 (d, J = 8 Hz, 2H), 6.41 (s, 2H), 6.35 (s, 1H), 4.60 (s, 2H), 4.46 (d, J = 8 Hz, 2H), 3.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 190.6, 167.1, 161.0, 140.0, 132.0, 130.9, 115.0, 105.6, 99.2, 67.1, 55.2, 43.0. EI-MS: m/z= 329.00. calculated exact mass: 329.13. Anal. Calcd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.81; N, 4.25. Found: C, 65.77; H, 5.74; N, 4.19.

Synthesis of 8: To a solution of compound **6** (0.5 g, 1.5 mmol) in anhydrous EtOH was added compound **7** (0.25 g, 1.5 mmol), with anhydrous magnesium sulfate acting as drying agent. The mixture was refluxed under nitrogen atmosphere for 24 h. After removing the solvent, the residue was dissolved in MeOH (20 mL) and THF (20 mL). To this solution was added sodium borohydride (0.29 g, 7.6 mmol) in portions. After being stirred overnight, the reaction was quenched with saturated ammonium chloride solution, extracted with DCM, the organic layer was dried over sodium sulfate. The solvents were removed under vacuum and the residue was purified on a silica gel column with ethyl acetate and petroleum ether to give **8** (0.57 g, 92%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.22-7.28 (m, 3H), 6.93-7.07 (m, 18H), 6.84-6.87 (m, 2H), 6.39-6.42 (m, 2H), 6.36 (t, J = 4 Hz, 1H), 4.51 (d, J = 4 Hz, 2H), 4.46 (d, J = 4 Hz, 2H), 3.77 (s, 6H), 3.67 (d, J = 4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.2, 161.1, 156.2, 143.7, 143.6, 142.4, 140.8, 140.7, 140.0, 138.2, 134.0, 131.2, 129.6, 128.7, 127.6, 127.4, 126.3, 114.5, 105.6, 99.5, 67.5, 64.5, 55.3, 52.7, 52.3, 43.0, 31.5. EI-MS: m/z= 674.43. Anal. Calcd for $C_{45}H_{42}N_2O_4$: C, 80.09; H, 6.27; N, 4.15. Found: C, 79.95; H, 6.35; N, 4.09.

Synthesis of 9: To a solution of compound **8** (0.4 g, 1mmol) in dry DCM (20 mL), TFA (0.31 mL, 4.9 mmol) was added slowly at room temperature. After reacting for 2 h under nitrogen atmosphere, the solvent was rotor-evaporated. The residue was dissolved in MeOH (5 mL), and then saturated MH_4PF_6 (20 mL, aq) was added to yield a white power. After filtering, washing with H_2O and drying under vacuum, compound **9** was obtained as a white precipitate. Yield: 0.68 g, 85%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 7.47 (t, J = 6 Hz, 1H), 7.36 (t, J = 8 Hz, 2H), 7.21 (d, J = 8 Hz, 2H), 7.11-7.15 (m, 11H), 7.02-7.07 (m, 8H), 6.44 (s, 2H), 6.37 (s, 1H), 4.37 (d, J = 8 Hz, 2H), 4.09 (d, J = 8 Hz, 2H), 3.74 (s, 6H). The ^{13}C NMR could not be collected due to the poor solubility of **8**. MALDI MS: m/z = 675.27 [M-PF_6^-]; calculated exact mass: 820.29. Anal. Calcd for $C_{45}H_{43}F_6N_2O_4P$: C, 65.85; H, 5.28; N, 3.41. Found: C, 65.95; H, 5.33; N, 3.37.

Synthesis of [2]rotaxane 1a: A mixture of salt 8 (82 mg, 0.1 mmol), 2,6-pyridinedicarboxaldehyde (14 mg, 0.1 mmol) and tetraethyleneglycol bis(2-aminophenyl)ether (38 mg, 0.1 mmol) was dissolved in anhydrous MeCN, the solution was stirred under nitrogen atmosphere for 36 h. Then 1 M $BH_3 \cdot THF$ was added and the mixture was reacted overnight. The solvents were removed under vacuum and the residue was purified on a silica gel column with DCM and MeOH to give [2]rotaxane **1a** as a white powder. Yield: 69 mg, 65%. [2] rotaxane **1a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (br, 2H), 7.77 (t, J = 8 Hz, 1H), 7.40 (t, J = 8 Hz, 1H), 7.30 (d, J = 8 Hz, 2H), 7.11-7.17 (m, 7H), 7.03-7.05 (m, 3H), 6.95-7.00 (m, 6H), 6.65-6.76 (m, 12H), 6.49 (d, J = 8 Hz, 2H), 6.43 (d, J = 4 Hz, 1H), 6.32-6.36 (m, 3H), 4.34-4.46 (m, 10H), 4.05-4.15 (m, 4H), 3.89 (t, J = 4 Hz, 4H), 3.73 (s, 6H), 3.63-3.69 (m, 8H), 3.54-3.59 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): 173.0, 166.4, 163.8, 163.2, 152.2, 142.3, 136.5, 136.0, 135.9, 135.8, 133.9, 133.1, 133.0, 131.9, 127.1, 126.5, 124.9, 120.0, 118.1, 115.6, 110.7, 104.0, 76.6, 76.2, 75.6, 72.8, 72.4, 60.3, 57.1, 55.1, 47.4. MALDI MS: m/z = 1154.44 [M-PF_6^-]; calculated exact mass: 1299.53. Anal. Calcd for $C_{72}H_{76}F_6N_5O_9P$: C, 66.50; H, 5.89; N, 5.39. Found: C, 66.63; H, 5.81; N, 5.34.

Synthesis of [2]rotaxane 1b: [2]rotaxane **1a** (10 mg) was dissolved in chloroform (2 mL), NaOH solution (0.1 M, 2 mL, aq) was added dropwise, the mixture was stirred at room temperature for 2 h. Then the solution was extracted with chloroform, the organic layer was combined and dried over sodium sulfate. Removal of solvent under reduced pressure give [2]rotaxane **1b** as a light yellow powder. Yield: 8 mg, 90%. [2]rotaxane **1b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (s, 1H), 7.38 (t, J = 8 Hz, 1H), 7.17 (d, J = 8 Hz, 2H), 7.11-7.14 (m, 9H), 7.02-7.06 (m, 8H), 6.93 (d, J = 8 Hz, 4H), 6.74-6.81 (m, 4H), 6.64-6.70 (m, 4H), 6.57 (t, J = 6 Hz, 2H), 6.37 (s, 2H), 6.25 (s, 1H), 5.74 (t, J = 4 Hz, 2H), 4.80 (s, 2H), 4.10-4.14 (m, 6H), 4.04-4.07 (m, 4H), 3.68-3.76 (m, 4H), 3.62 (s, 6H), 3.49 (d, J = 8 Hz, 4H), 3.30-3.39 (m, 8H). ^{13}C NMR (100 MHz, CD_3CN): 160.6, 158.4, 146.3, 143.5, 141.3, 141.0, 131.4, 131.1, 129.5, 127.9, 127.6, 126.4, 126.3, 121.7, 121.4, 114.8, 110.1, 106.1, 99.0, 70.8, 70.4, 67.7, 67.2, 55.2, 53.3, 52.1, 52.0, 49.8, 45.5, 42.9, 31.8, 29.6, 29.3, 22.6, 14.0. MALDI MS: m/z = 1154.50 [M+H$^+$]; calculated exact mass: 1153.56. Anal. Calcd for $C_{72}H_{75}N_5O_9$: C, 74.91; H, 6.55; N, 6.07. Found: C, 74.79; H, 6.62; N, 5.99.

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Notes and references

[a] Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China E-mail: yinj@mail.ccnu.edu.cn

† Electronic Supplementary Information (ESI) available: Partial ^{1}H NMR spectra of **1a**. NMR, MS spectra of all the interminates, fluorescent and UV-vis spectra of **8**, **9**, **1a** and **1b** See DOI: 10.1039/b000000x/

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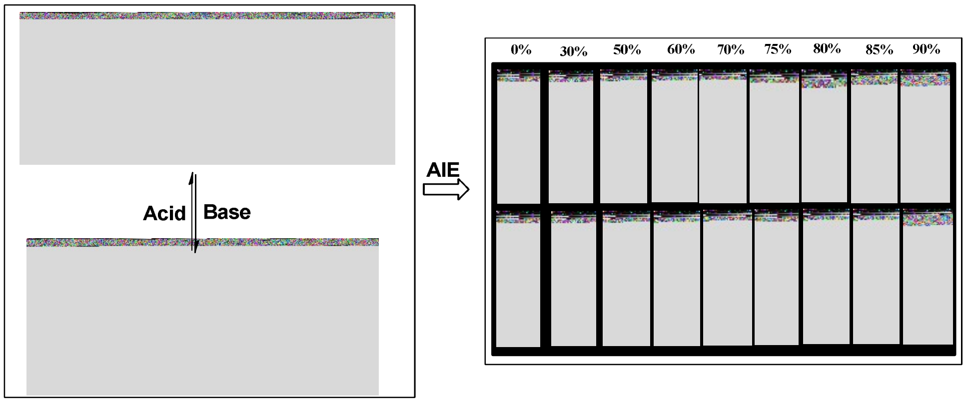
Aggregation-Induced Emission Behavior of pH-controlled Molecular Shuttle Based on Tetraphenylethene Moiety

Xie Han, Meijiao Cao, Zhiqiang Xu, Di Wu, Zhao Chen, Anxin Wu, Sheng Hua Liu,* Jun Yin*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China.



A TPE-based molecular shuttle having amide and amine units has been synthesized. The shuttling motion of the macrocycle component can adjust its AIE behaviour.