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Cucurbit[10]uril-based [2]Rotaxane: Preparation and Supramolecular Assembly-Induced Fluorescence Enhancement

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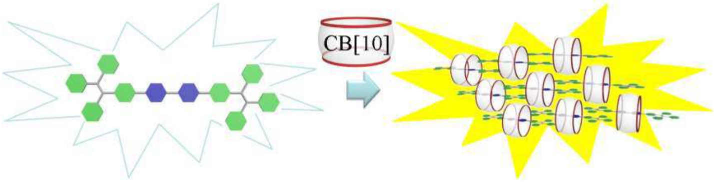


Abstract

As the cucurbit[n]uril (CB[n]) homologue with the largest cavity size, cucurbit[10]uril (CB[10]) can encapsulate big guests to form interesting host-guest complexes/assemblies. Herein, we report the preparation and fluorescence properties of CB[10]-based [2]rotaxane (CB[10]•**1**) formed from cucurbit[10]uril and dumbbell-like guest **1**. This [2]rotaxane (CB[10]•**1**) is assembled by C=O•••N^+ ion-dipole interactions between oxygen atoms of the carbonyl fringed portals of CB[10] and the positively charged pyridinium units of **1** via the slipping method under heating at 95 °C in DMSO. In contrast, other cucurbit[n]uril (CB[n], n = 6-8) homologues can't form rotaxanes with **1** due to their smaller cavities. The dumbbell-like guest **1** is a poor emitter in DMSO. Interestingly, the formation of CB[10]•**1** renders the restriction of intramolecular

rotation of TPE, which features a strong fluorescent intensity, long lifetime and high quantum yield. Furthermore, CB[10]•**1** is shown to aggregate plate-like structures with various sizes in different solvents (DMSO, THF or $CHCl_3$), resulting in a stepwise aggregation-induced emission enhancement effect. This kind of CB[10]-based [2]rotaxane may be used to fabricate luminescent systems with unique emission properties.

Introduction

Luminescent molecules or systems have attracted increasing interest due to their applications as optical devices,[1] photo-induced materials,[2] biological applications (imaging,[3] sensor,[4] and probes[5]), photodynamic therapy,[6] and molecular machines,[7] among other applications. The self-assembly of luminescent molecules[8] through non-covalent forces cause the change of luminescent properties, including excimer formation,[9] fluorescence resonance energy transfer (FRET),[10] aggregation-caused quench (ACQ),[11] aggregation-induced emission (AIE)/aggregation-induced emission enhancement (AIEE),[12] and J-/H-aggregation.[13] Inspired by these phenomena, supramolecular scientists, especially those who are interested in host-guest chemistry and material chemistry, have developed a series of new design strategies for tuning emission properties via host-guest recognitions to achieve functional systems, such as near-infrared materials[14] and energy transfer systems.[15]

Cucurbit[n]urils (CB[n]s),[16] a family of pumpkin-shaped macrocyclic molecules bearing a rigid hydrophobic cavity and two identical carbonyl fringed portals, are of great interest because of their excellent recognition property in water and wide applications in molecular recognition,[17] self-assembly,[18] catalysis,[19] bio-sensor,[20] drug delivery,[21] supramolecular polymer,[22] molecular machine,[23] and other supramolecular systems.[24] In particular, CB[n]s are also well known to form complexes with a range of organic fluorophores, which cause profound changes in increasing fluorescent intensity, lifetime and quantum yield,[25] enhancing photothermal conversion[6] and tuning fluorescent color[26] through host-guest interaction with their hydrophobic cavities in water. For examples, Kaifer and co-workers discovered that CB[7] could form stable host-guest complexes with cyanine dyes to achieve the emission off-on switch between the H-aggregation and J-aggregation.[27]

Galoppini and co-workers described an unprecedented fluorescence enhancement of viologen derivative bound with two CB[7].[25c] Ni and co-workers reported a CB[8] across-linked supramolecular luminescent system with tunable and dynamical photophysical properties.[26]

As the CB[n] homologue with the largest cavity size, cucurbit[10]uril (CB[10]) is unique because of its ability to bind large guests within its cavity (Figure 1a).[28] For examples, Day, Isaacs, Collins, Wallace and Liu found that CB[10] could encapsulate cucurbit[5]uril,[28a] calix[4]arene,[28b] triazene-arylene oligomer,[28c] metalloporhyrin,[28d] platinum/ruthenium/iridium polypyridyl complexes,[28e-g] and blue box,[28h] respectively. However, few reports were involved with the construction of supramolecular luminescent system from CB[10] as a host in the solution.[28g] In this paper, we report the preparation and supramolecular assembly-induced fluorescence enhancement of rotaxane CB[10]•**1** formed from CB[10] and a dumbbell-like guest, 1,1'-ditetraphenylethenyl-4,4'-bipyridine-1,1'-diium dichloride (**1**), in DMSO. In this case, CB[10] imposes a structural confinement of guest **1**, resulting in the restriction of intramolecular rotation (RIR) of tetraphenylethylene (TPE) in CB[10]•**1** and increasing their electron density by ion-dipole interactions. These effects together improve fluorescent emission properties of this rotaxane system. At the same time, CB[10]•**1** further exhibits a stepwise aggregation-induced emission enhancement (AIEE) effect in different solvents (THF or $CHCl_3$).

Results and discussion

Design and synthesis of dumbbell-like guests

As a mechanically interlocked molecule, a rotaxane must have a dumbbell-like molecule as axle which is threaded through a macrocyclic molecule.[29] Recently, cucurbit[n]uril-based rotaxanes as supramolecular building blocks have been synthesized and used for the construction of sophisticated supramolecular architectures, such as infinite 1D lines,[30] 2D networks,[31] 3D frameworks,[32] and discrete molecular necklaces.[33] To prepare CB[10]-based rotaxane, a dumbbell-like molecule with a suitable recognition site for anchoring CB[10] and two large enough stoppers is required.

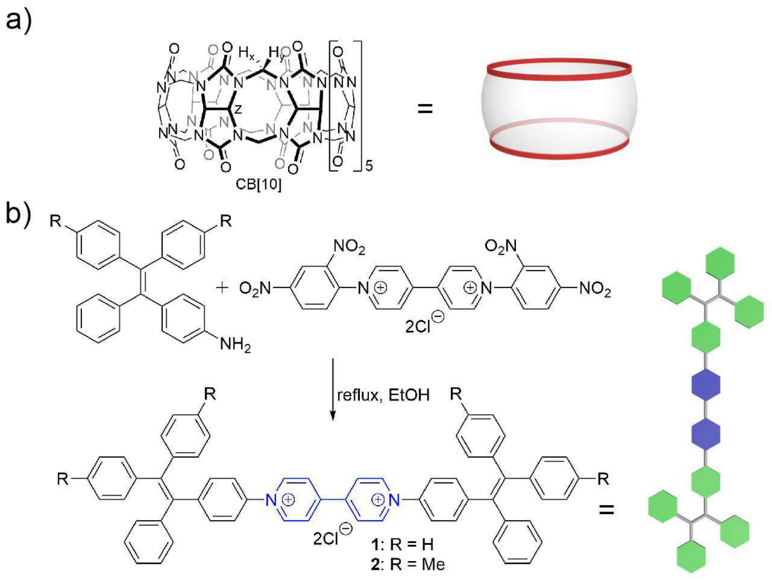


Figure 1. a) Chemical structure of CB[10]; b) Synthesis of dumbbell-like guests **1-2**.

Viologen derivatives as the bis-cationic and aromatic guests are suitable recognition units for fabricating a mechanically interlocked complex with cucurbit[n]uril, which has a hydrophobic cavity for aromatic residues and two cyclic carbonyl portals for positively charged pyridinium units.[34] Tetraphenylethylene (TPE) moiety was incorporated for its AIE effect and also acts as stopper. Therefore, we designed and synthesized two dumbbell-like guest, 1,1'-ditetraphenylethenyl-4,4'-bipyridine-1,1'-diium dichloride derivatives (**1-2**), containing a viologen unit in the middle for binding CB[10] and two TPE units at both terminals as stopper and fluorophore. As shown in Figure 1b, guests **1-2** were synthesized by the reaction of corresponding mono-amino TPE with *N,N*'-bis(2,4-dinitrophenyl) 4,4'-bipyridine-1,1'-diium chloride salt by the Zincke reaction, in 96% yield (See supporting information). We envision that guests **1-2** would undergo host-guest interaction with CB[n] to generate CB[n]-based rotaxane, resulting in the change of aggregation and the restriction of intramolecular rotation (RIR) of TPE to realize fluorescence enhancement.

The preparation of rotaxane CB[10]•1

CB[n] compounds are slightly soluble in water and almost insoluble in common organic solvents, but solvent-soluble guests that are encapsulated in the cavities of CB[n]s usually can promote the solubility of CB[n]-based complexes. We found that the dumbbell-like guest **1** (chloride salt) was insoluble in water, but soluble in DMSO or MeOH. Therefore, we decided to investigate the host-guest recognition of **1** with CB[n] (n = 6-8, 10) by ^{1}H NMR in DMSO-d_6, even though CB[n]s had extremely poor solubility in DMSO-d_6. It is known that the diameter at the portal of CB[n] (n = 6-8) is 3.9, 5.4, and 6.9 Å, respectively.[16] Because the size of TPE unit is about 7.4-9.0 Å, which is bigger than the size of CB[n] (n = 6-8),[35] they can't encapsulate **1** even under heating at high temperature for several weeks. As a result, we failed to gain the rotaxanes from **1** and CB[n] (n = 6-8) via the slipping method (Figure S5).

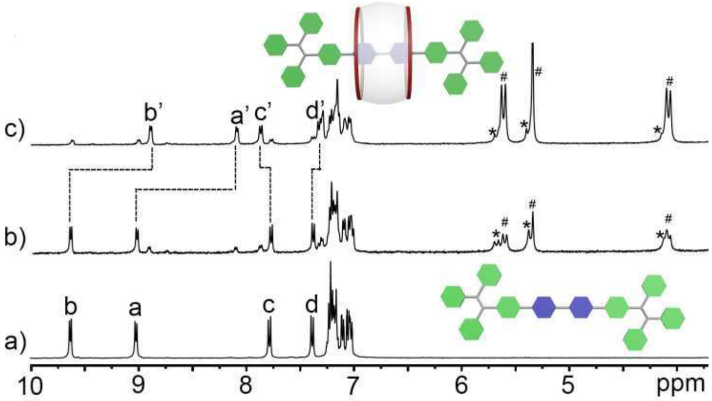


Figure 2. ^{1}H NMR spectra (400 MHz, DMSO-d_6, rt) for: a) **1**; b) **1** (0.5 mM) and CB[10] (0.5 mM) at 95 °C for 2 days, c) **1** (0.5 mM) and CB[10] (0.5 mM) for 17 days at 95 °C. *Free CB[10] and $^{\#}$bound CB[10]. Here primed (') denote protons binding with host.

Unlike smaller CB[n] (n = 6-8), CB[10] with the portal diameter of 9.5-10.6 Å and volume of ~870 Å^{3} could be threaded with the TPE unit to form a rotaxane via the slipping method. We observed a slowly-slipping formation process of rotaxane CB[10]•**1** by ^{1}H NMR in DMSO-d_6. Figure 2 shows the ^{1}H NMR spectra recorded for guest **1** alone, as an initial mixture of **1** with CB[10], and as rotaxane CB[10]•**1**. Initially, the resonance peaks of free **1** didn't change at all when 1 equiv of CB[10] was added into the solution of **1** in DMSO-d_6 at room temperature. Surprisingly, however, some tiny peaks belonging to bound **1** were observed when the mixture was heated at 95 °C for 2 days. At the same time, the resonance peaks of free and bound CB[10] became much clearer, indicating that the host-guest complex was coming up (Figure 2b). This phenomenon suggested that the unsubstituted TPE units of guest **1** were able to reversibly thread through CB[10] at higher temperature, and then the dynamic complex became kinetically trapped as a rotaxane at the lower temperature. The positive result encouraged us to continue this experiment. Under heating at 95 °C for 17 days, it was showed that the resonance peaks of both free **1** and free CB[10] nearly disappeared and the resonance peaks of host-guest complex grew up, which was a strong evidence for the formation of rotaxane CB[10]•**1** in 81% yield (Figure 2c and S6). It also illustrated that the formation of rotaxane CB[10]•**1** promoted the solubility of CB[10] in DMSO. While the resonance peaks (H_a and H_b) of 4,4'-bipyridine-1,1'-diium unit were shifted upfield of 0.93 and 0.74 ppm, the resonance peaks (H_c and H_d) of TPE units near 4,4'-bipyridine-1,1'-diium unit slightly shifted downfield of 0.09 ppm and upfield of 0.08 ppm, respectively. Compared with free CB[10], all the resonance peaks of bound CB[10] showed slight upfield shift (0.04~0.08 ppm). Based on these NMR shifts, 4,4'-bipyridine-1,1'-diium unit of **1** is exactly anchored inside the cavity of CB[10]. Figure S7 shows side views of the electrostatic potential energy mapped onto the van der Waals surface of **1** and CB[10]•**1** complex. Obviously, the formation of CB[10]•**1** complex results in substantial reduction in the electrostatic potential at the N atoms on the 4,4'-bipyridine-1,1'-ium unit as a consequence of the C=O•••N^+ ion-dipole interactions.[17a]

In addition, the COSY and NOESY spectra also revealed the supramolecular assembled structure of rotaxane CB[10]•**1** in the solution (Figure S8-S9). ESI-MS spectrum further showed that a double-charged peak of rotaxane CB[10]•**1** (m/z = 1239.9350) was consistent with the simulated peak of $[CB[10]\cdot\mathbf{1}]^{2+}$ (m/z 1239.9292, Figure S10). All evidences of NMR and ESI-MS confirm that CB[10] can slip into the middle of dumbbell-like guest **1** under heating situation in DMSO, and bind with 4,4'-bipyridine-1,1'-diium unit by the C=O•••N^+ ion-dipole interactions to form a stable CB[10]-based [2]rotaxane. However, guest **2** can't thread through CB[10] to form the rotaxane under the same condition, due to the appropriate size of the dimethyl TPE units (Figure S11).

Aggregation-induced emission enhancement of CB[10]•1

TPE derivatives with unique AIE property have been widely used as building block for fabricating fluorescent materials.[12] Furthermore, the host-guest recognitions have been demonstrated to be an efficient tool to realize RIR of TPE unit in the limited cavity of host.[35-46] Therefore, we decided to investigate the fluorescent emission properties of rotaxane CB[10]•**1** by fluorescence experiments. Interestingly, **1** exhibits highly selective fluorescence enhancement with CB[10] in DMSO solution due to the formation of [2]rotaxane CB[10]•**1**. As shown in Figure 3a, **1** is non-fluorescent in DMSO. Meanwhile CB[n] (n = 6-8) have almost no effect on the fluorescence emission because these hosts can not encapsulate **1**. When CB[10] slipped to the middle of **1** with binding 4,4'-bipyridine-1,1'-diium unit to form [2]rotaxane CB[10]•**1**, however, the fluorescent emission was obviously turned on with yellow color (λ_{em} = 558 nm) (Figure 3a). This fluorescence turn-on phenomenon could be attributed to the formation of CB[10]•**1,** which resulted in the restriction of intramolecular rotation of TPE (First step in Scheme 1). Furthermore, quantum yields and fluorescence lifetime for CB[10]•**1** were measured in DMSO, as shown in Table S1. The quantum yield of CB[10]•**1** increased up to Φ = 0.50 in DMSO, while CB[10]•**1** displayed only one decay kinetics with contribution from a lifetime of 3.33 ns in DMSO (Figure S12). UV-vis spectra also showed that only CB[10] can bind **1** to form rotaxane, resulting in a blue shift (Δλ = 32 nm) of the absorption maximun (Figure 3b).

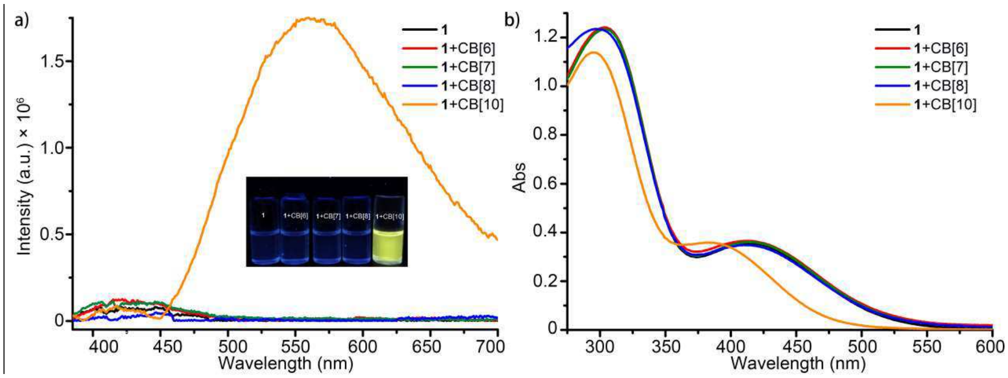


Figure 3. a) Fluorescence spectra of **1** (10 μM) and b) UV-vis spectra of **1** (50 μM) without and with 1 equiv of CB[n] (n = 6-8, 10) in DMSO, under heating at 95 ˚C for 17 days; insert photo: pictures of **1**, **1**+CB[6], **1**+CB[7], **1**+CB[8], and **1**+CB[10] in DMSO under a 365 nm lamp. λ_{ex} = 365 nm; Ex/Em slits = 5/5 nm.

Due to the AIE property of TPE unit, we envisioned that the concentration of CB[10]•**1** and the addition of other solvents with low or high polarity should control the aggregation of CB[10]•**1** in the solution phase to exhibit stronger emission properties. The fluorescence intensity of CB[10]•**1** in DMSO increased linearly as the concentration of CB[10]•**1** was gradually increased from 2.0 to 28.8 μM, and then showed little changes up to 100 μM, which implies that critical aggregate concentration of CB[10]•**1** in DMSO is around 28.8 μM (Figure S13). Furthermore, fluorescent emission of **1** and CB[10]•**1** were recorded by adding 10 different solvents including polar and non-polar solvents (Figure 4). **1** showed the best fluorescence enhancement in 1,4-dioxane while CB[10]•**1** has the strongest fluorescent emission in $CHCl_3$ (Figure S14-S15). The quantum yield and lifetime of CB[10]•**1** in $CHCl_3$ are $\Phi = 0.78$ and 2.50 ns (Figure S12). It is worthy to note that the fluorescent intensity of CB[10]•**1** is always stronger than that of **1** in different solvents, because these relaxation processes of TPE units are severely hindered by the hydrophobic cavity of CB[10] which enhances the AIE effect. It also indicated that the formation of CB[10]•**1** decrease the solubility in all solvents. Specifically, the fluorescent intensity of CB[10]•**1** in THF or $CHCl_3$ is obviously stronger than that in DMSO, which shows a stepwise aggregation-induced emission enhancement (Second step in Scheme 1). In order to investigate the AIE property of CB[10]•**1**, further tests of the fluorescence were carried out in the mixed solvent of DMSO/H_2O. Figure S16 showed that when increasing the DMSO contents from 10 to 100%, fluorescent intensity with the emission maximum at 558 nm was increased gradually, which suggested that CB[10]•**1** had strong AIE property. Compared with organic TPE deriveratives, both **1** and CB[10]•**1** showed weak fluorescence in water, probably because the H_2O molecules tend to bipyridine-1,1’-diium cations, resulting in disassembly of CH•••π stacking between **1** molecules (Figure S17).

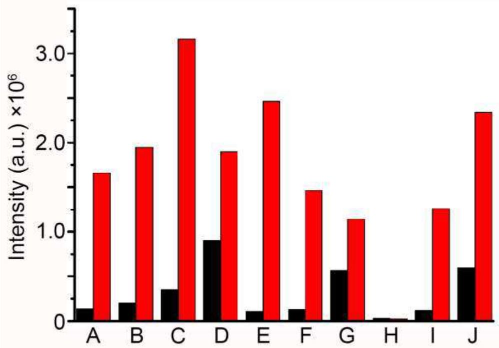
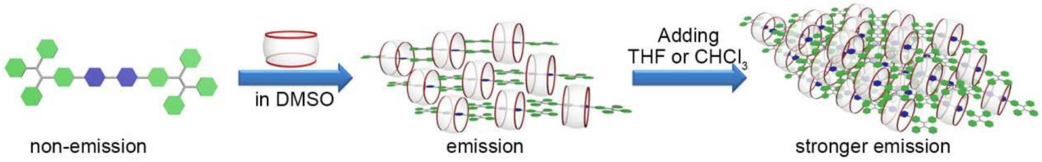


Figure 4. Fluorescence intensity at 600 nm of **1** (10 μM, black column) and CB[10]•**1** (10 μM, red column) in different solvents including 1% DMSO (A = acetone; B = CH_2Cl_2; C = $CHCl_3$; D = 1,4-dioxane; E = DMF; F = DMSO; G = EA; H = H_2O; I = MeOH; J = THF). λ_{ex} = 365 nm; Ex/Em slits = 5/5 nm.



Scheme 1. Cartoon illustrations of a stepwise aggregation-induced emission enhancement of CB[10]•**1**.

Aggregation morphology of 1 and CB[10]•1

In order to further understand the aggregation behaviors of **1** and CB[10]•**1**, the dynamic light scattering (DLS) and the scanning electron microscopy (SEM) experiments were utilized. The aggregation transformation between **1** and CB[10]•**1** was evidenced by DLS experiments which revealed that the diameter (*D*) of aggregates of CB[10]•**1** in DMSO was ~396.1 nm at 0.10 mM and ~295.3 nm at 0.01 mM, respectively (Figure 5 and S18). These values are ~53 and ~39 times larger than that of **1** alone (~7.5 nm) which is consistent with the size of **1**. The DLS study confirmed again the aggregation of CB[10]•**1** in THF or $CHCl_3$ by demonstrating a huge increase of the hydrodynamic diameter of the species (~955.4 nm in THF; ~1106.0 nm in $CHCl_3$) in the solution of CB[10]•**1** at the same concentration (Figure 5 and S19a). Therefore, the florescence enhancement of CB[10]•**1** after addition of THF or $CHCl_3$ could be attributed to more aggregation of CB[10]•**1**, which resulted in further inhibition of the rotation of TPE units in the stacked structures (Scheme 1).

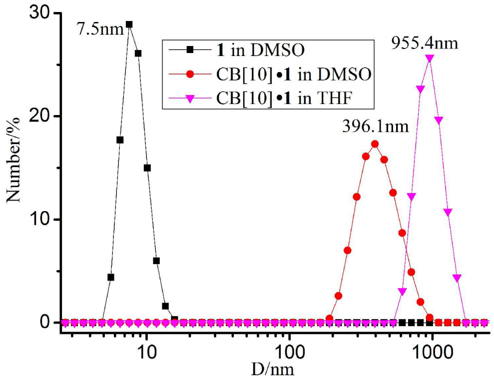


Figure 5. DLS profiles of **1** (0.10 mM) in DMSO and CB[10]•**1** (0.10 mM) in DMSO or THF including 10% DMSO.

The morphology of the aggregates formed from the solution of **1** or CB[10]•**1** were observed by SEM (Figure 6). The SEM images in Figure 6a-b show monodispersed spherical structures with a diameter ranging from 160 nm to 598 nm, probably due to the self-assembly between **1** molecules. As shown in Figure 6c-d, well dispersed plate-like structure of CB[10]•**1** instead of the spherical structure of **1** was observed. It indicated that the formation of [2] rotaxane CB[10]•**1** could turn the spherical self-assembled structure of **1** into the plate-like self-assembled structure of CB[10]•**1**, companying with fluorescence enhancement. Interestingly, the dispersed plate-like structures were combined with each other to form larger stacked structures in THF (Figure 6e-f) or $CHCl_3$ (Figure S19b-c).

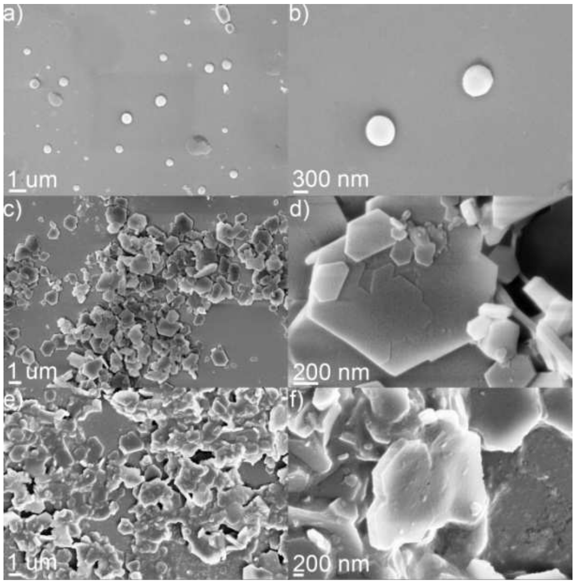


Figure 6. SEM images of the samples from a) and b) **1** (0.10 mM) in DMSO; c) and d) CB[10]•**1** (0.10 mM) in DMSO; e) and f) CB[10]•**1** (0.10 mM) in THF including 10% DMSO.

X-ray crystal structure of 1

To understand the relationship between fluorescence enhancement and aggregation, we turned to X-ray experiment. We were fortunate to obtain X-ray quality crystals of **1** as red plates from 4:1 (v/v) MeOH/DMF solution by slow vapor diffusion of *i*Pr_2O at room temperature. Firstly, Figure 7a-b illustrate the dimerization of **1** to yield a bimolecular structure **1**•**1** by CH•••π interactions between tetraphenylethylene units (Table S2). The dihedral angle of two pyridine rings in 4,4’-bipyridine-1,1’-diium units of **1** are about 33.1^o. Although the 4,4’-bipyridine-1,1’-diium units in two different molecules are not parallel, the face-to-face stacking of **1•1** is stabilized by four CH•••π interactions among tetraphenylethylene units. Subsequently, as shown in Figure 7c-d, the dimer **1•1** engages other **1•1** dimers through CH•••π interactions among tetraphenylethylene units along with *b* axis (Figure S20a) and *c* axis (Figure S20b), respectively, to form a 3D network-like arrangement. Therefore, the X-ray structure of **1** further confirms that the aggregation of CB[10]•**1** could be stabilized by multiple CH•••π interactions between tetraphenylethylene stoppers of CB[10]•**1**, and exhibit a stepwise AIEE effect in THF or $CHCl_3$.

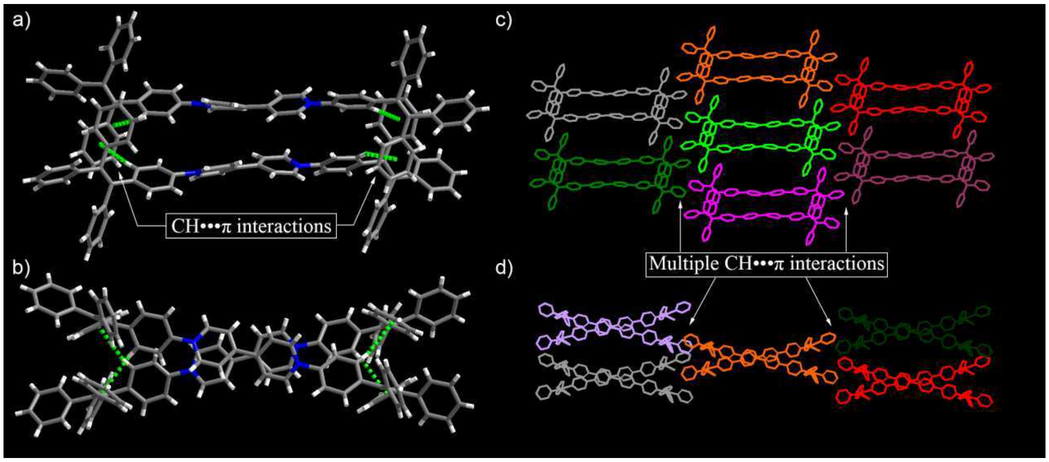


Figure 7. The crystal structure of **1**: a) side view and b) top view of face-to-face stacking dimer **1•1**; c) side view and d) top view of stacking networks between **1•1** dimers Color code: N, blue; O, red; C, gray; H, white. CH•••π interactions: green dot line. Chloride ions to balance the charge are omitted.

Conclusions

In summary, we have designed and synthesized a dumbbell-like guest **1** which is non-fluorescent but becomes a highly fluorescent [2]rotaxane CB[10]•**1** upon host-guest interaction with CB[10] via the slipping method under heating at 95 ^{o}C in DMSO. The photophysical properties and aggregation structures of **1** and CB[10]•**1** were unambiguously elucidated by fluorescence, UV-vis, DLS, SEM, and X-ray experiments. We are able to demonstrate that the formation of CB[10]•**1** is companied with strong fluorescent intensity, long lifetime and high quantum yield. Compared with **1**, CB[10]•**1** also exhibits a stepwise aggregation-induced emission enhancement property in THF or $CHCl_3$. Therefore, supramolecular assembly strategy to prepare luminescent systems, which are easily endowed with multiple emission properties, may find useful application not only in luminescent materials but also in stimuli-responsive systems and molecular machines.

Experimental Section

General Experimental Methods. Starting materials were purchased from commercial suppliers were used without further purification. CB[n] (n = 6,[47] 7,[48] 8,[48] 10[28b]) was prepared according to the published procedure. Melting points were determined using XT-4 apparatus. IR spectra were recorded on a Bruker IFS 120HR spectrometer and were reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were done on a Bruker ascend spectrometer at 400 MHz. Electron Spray Ionization (ESI) mass spectra were acquired by using a Bruker micrOTOF-Q II electrospray instrument. Fluorescence spectra were recorded on a Horiba Fluorolog-3 spectrometer equipped with a xenon discharge lamp using 1 cm quartz cells. DLS data was recorded on a Malvern Zetasizer nano ZS90 spectrometer using a monochromatic coherent He-Ne laser (633 nm) as the light source and a detector that detected the scattered light at an angle of 90º. SEM images were obtained on Carl Zeiss SIGMA.

Fluorescence measurement. Fluorescence spectra were obtained with a solution of **1** (3 mL, 10 μM) or CB[10]•**1** (3 mL, 10 μM) in a quartz cell. The solution of CB[10]•**1** (1.0 mM) in DMSO was prepared after being heated at 95 ^{o}C for 17 days. The different solvents were added to the DMSO solution of CB[10]•**1** (1.0 mM) to make the ratio of DMSO into 1%.

Scanning Electron Microscope measurement. One drop of the solution of **1** (0.10 mM) or CB[10]•**1** (0.10 mM) was placed on the silicon wafer, dried for 1 day under heating at 50 oC. And the samples were then coated with Au in the ion coater for 90 s. The solution of CB[10]•**1** (1.0 mM)in DMSO was prepared after being heated at 95 ^{o}C for 17 days. The different solvents were added to the DMSO solution of CB[10]•**1** (1.0 mM) to make the ratio of DMSO into 10%.

Dynamic light scattering measurement. DLS data were obtained with a solution of **1** (1 mL, 0.10 mM) or CB[10]•**1** (1 mL, 0.10 mM or 0.01 mM) in a quartz cell. The solution of CB[10]•**1** (1.0 mM) in DMSO was prepared after being heated at 95 ^{o}C for 17 days. The different solvents were added to the DMSO solution of CB[10]•**1** (1.0 mM) to make the ratio of DMSO into 10%.

Synthetic Procedures. *Compound 1*. A mixture of 4-(1,2,2-triphenylvinyl)aniline (384 mg, 1.10 mmol) and 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (281.8 mg, 0.50

mmol) in ethanol (25 mL) was heated at reflux for 3 days. After cooling down to room temperature, the product was precipitated with diethyl ether, and washed with diethyl ether and acetone to yield **1** as a red solid (427 mg, 0.48 mmol, 96%). M.p. 248-249 ˚C. IR (KBr, cm^{-1}): 3401s, 3108m, 3052m, 3020m, 1630s, 1485m, 1436m, 761w, 698s. ^{1}H NMR (400 MHz, DMSO-d_6): 9.62 (d, J = 6.8 Hz, 4H), 9.01 (d, J = 6.8 Hz, 4H), 7.77 (d, J = 8.6 Hz, 4H), 7.38 (d, J = 8.6 Hz, 4H), 7.25-7.00 (m, 30H). ^{13}C NMR (100 MHz, DMSO-d_6): 148.6, 146.7, 145.5, 142.7, 142.5, 142.5, 140.1, 138.7, 132.3, 130.7, 130.5, 128.2, 128.1, 127.9, 127.2, 127.0, 126.6, 124.2 (only 18 of the 21 resonances expected were observed). HRMS (ESI-TOF) m/z: [**1**-2Cl$^-$]$^{2+}$ Calcd for $C_{62}H_{46}N_2$ 409.1825; Found 409.1819.

Compound ***2***. A mixture of compound 4-(1-phenyl-2,2-di-p-tolylvinyl)aniline (100 mg, 0.27 mmol) and 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (67.9 mg, 0.12 mmol) in ethanol (10 mL) was heated at reflux for 3 days. After cooling down to room temperature, the solvent was reduced, and the product was dissolved in acetone and then precipitated with diethyl ether, and washed with diethyl ether to yield **2** as a red solid (90 mg, 0.10 mmol, 83.3%). M.p. 200-201 ˚C. IR (KBr, cm^{-1}): 3409s, 3021m, 2917m, 1604s, 1499m, 1443m, 1306m, 822w, 668w. ^{1}H NMR (400 MHz, DMSO-d_6): 9.63 (d, J = 6.8, 4H), 9.01 (d, J = 6.8, 4H), 7.77 (d, J = 8.6, 4H), 7.35 (d, J = 8.6, 4H), 7.25-6.85 (m, 26H), 2.23 (s, 6H), 2.21 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 147.0, 145.5, 142.9, 142.4, 139.9, 139.7, 137.8, 136.3, 136.1, 132.3, 130.7, 130.6, 128.8, 128.5, 128.1, 126.8, 126.6, 124.2, 20.8, 20.7. HRMS (ESI-TOF) m/z: [**2**-2Cl$^-$]$^{2+}$ Calcd for $C_{66}H_{54}N_2$ 437.2138; Found 437.2144.

Associated Content

Supporting Information

NMR data, ESI-MS data, fluorescent spectra, UV-vis spectra, SEM, DLS, and X-ray data (PDF)

Crystallographic data for CCDC-1511208 (**1**) (CIF)

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