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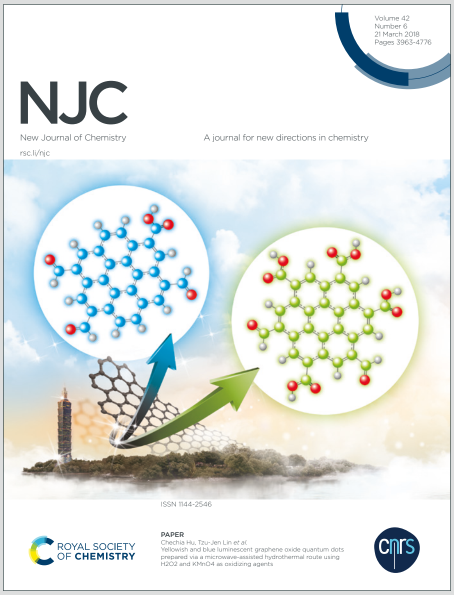

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PAPER
Chechia Hu, Tzu-Jen Lin *et al.*
Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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COMMUNICATION

Emission enhancement of cationic tetraphenylethylene derivatives by encapsulation in cucurbit[10]uril host in water

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Binding of a series of cationic tetraphenylethylene (TPE) derivatives with cucurbit[10]uril (CB[10]) host has been investigated. Compared to the free forms, all guests exhibit fluorescence enhancement upon encapsulation by CB[10]. Thus, by restricting intramolecular rotation through host-guest encapsulation instead of aggregation, fluorescence enhancement of TPE derivatives can be realized in water.

Luminescent molecules have attracted considerable research interests, owing to their broad applications in photoluminescent probes, biological applications, light-harvesting systems, white-light emission systems, and so on.[1-5] However, most of the luminophores are weakly emissive or non-emissive in the aggregated and solid states because of aggregation-caused quenching (ACQ) effect.[6] In 2001, Tang's group defined the aggregation-induced emission (AIE) effect and disclosed the mechanism called restriction of intramolecular rotation (RIR).[7] Tetraphenylethylene (TPE) molecules, a typical aggregation-induced emission luminogens (AIEgens), has been widely used in many fields such as chemical sensors, biological probes, cell Imaging and so on.[8-11] Therefore, activating the RIR process of TPE is a key factor to realize the strong fluorescence of TPE derivatives.[12] Up to now, many efficient methods such as intermolecular network[13,14] and rigid metal–organic framework,[15] have been used to achieve this goal.

Recently, host–guest complexation has attracted considerable attention for its wide applications in modulating the photophysical properties of fluorescent molecules.[16] What's more, host-guest interactions can be used as physical processes to restrict the intramolecular rotation of TPE unit, and construct functional TPE supramolecular assemblies.[17] For examples, Wang and co-workers synthesized a TPE- functionalized pillar[5]arene which exhibits the ''turn-on'' of fluorescence emission based on host–guest recognition-mediated cross-linking.[18] Yang *et al.* demonstrated that TPE decorated pillar[5]arene units could be used to construct AIE supramolecular polymer gels with multiple stimuli-responsive behaviours.[19]

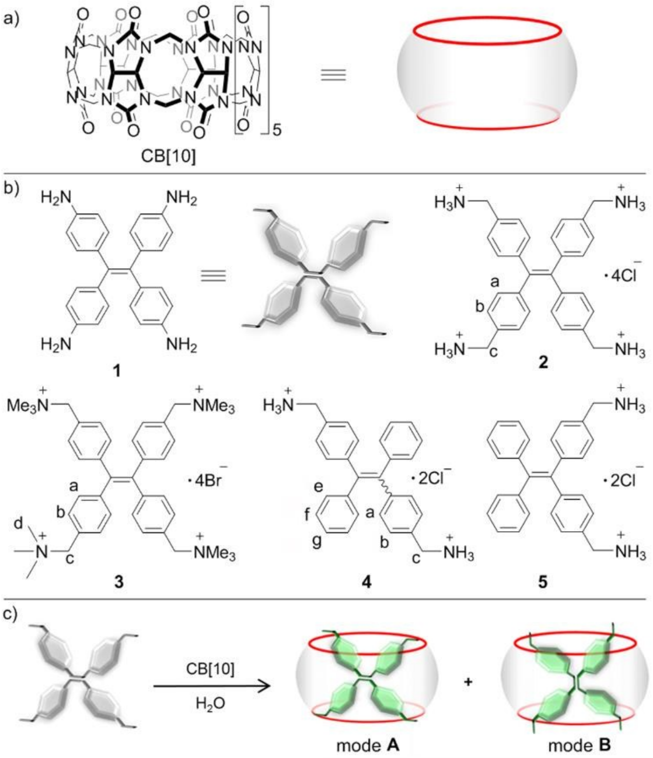

Fig. 1 Structures of host and guest compounds (a, b), and schematic illustration of the formation of two plausible inclusion complexes between TPE guest and CB[10] (c).

Cucurbit[*n*]uril (CB[*n*], *n* = 5–8, 10) is a kind of rigid macrocyclic host with various sized hydrophobic cavity, and has been found many applications.[20-22] Recently, CB[*n*] was also

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used as "linker" to fabricate supramolecular functional AIE materials containing TPE units.[23-29] In these cases, substituted groups on TPE cores bind internally or externally to CB[*n*] to limit the intramolecular rotation, causing the assembling-induced emission enhancement.[30]

Among the CB[*n*] family, CB[10] possesses the largest cavity with a volume of ~870 Å^3 and the portal diameter of ~10 Å.[31] Therefore, bigger or multiple guests, such as Blue Box, metal–terpyridyl complexes, could be selectively encapsulated by CB[10].[32-38] Herein, we report another supramolecular host–guest strategy to activate the RIR process of TPE units through encapsulation of TPE core in CB[10]. The results show all selected TPE guests can form 1:1 inclusion complexes with CB[10] in aqueous solution, arousing an increased molecular emission enhancement. Two binding modes of host–guest complexation in which the vinyl group of TPE is perpendicular or parallel to the port of CB[10] were observed.

CB[10] is extremely insoluble in aqueous solution unlike other CB[*n*]s, but it could be dissolved in water phase after forming inclusion complexes with a water-soluble guest.[32] So we relied on water-soluble cationic TPE derivatives as much as possible. And binding studies of TPE derivatives with CB[10] were investigated according to ^{1}H NMR titration which has been utilized to characterize host-guest binding behaviours.[39]

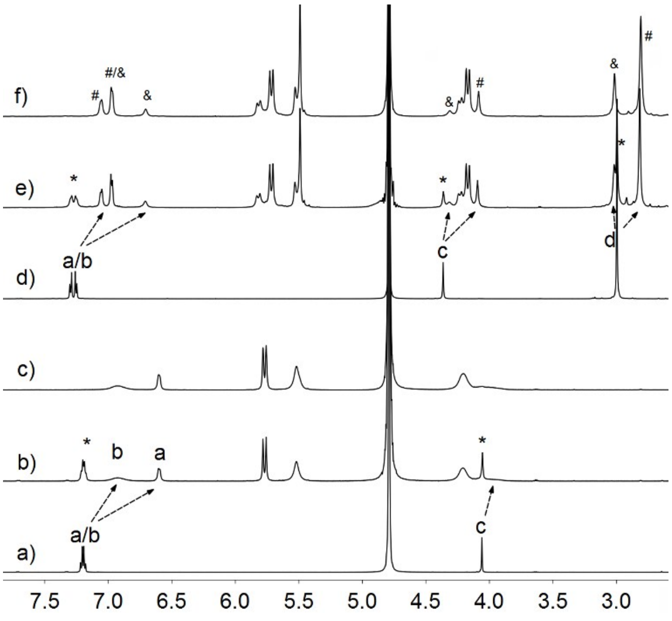
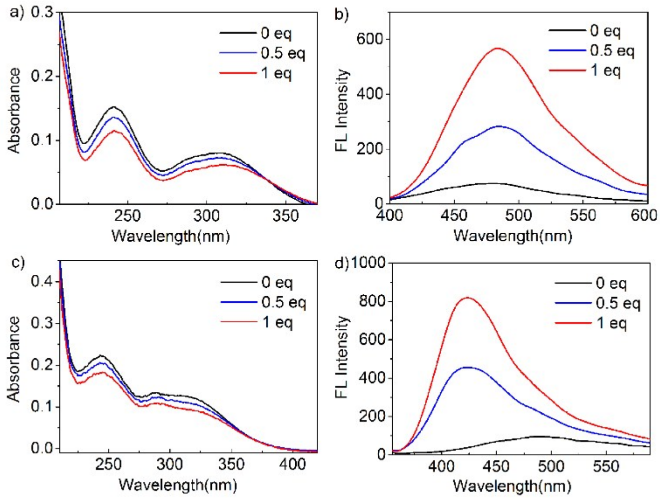


Fig. 2 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of: a) free **2** (1.0 mM); b) 2:1 mixture of **2** and CB[10]; c) CB[10]·**2** (1.0 mM); d) free **3** (1.0 mM); e) 2:1 mixture of **3** and CB[10]; f) CB[10]·**3** (1.0 mM) (resonances of free **2** and **3** are marked with *; resonances representing two binding modes for CB[10]·**3** are marked with $^\#$ and $^\&$).

Dissolution of CB[10] was observed when it was added to an acidic aqueous solution of TPE guest **1**, implying the complexation of **1** with CB[10]. ^{1}H NMR titration in D_2O/DCl showed that all signals of aromatic proton shifted upfield, suggesting the encapsulation of whole TPE core inside the cavity of CB[10] (Fig. S4, ESI†). Slow exchange kinetics on the ^{1}H NMR time scale allowed us to calculate the binding ratio between host and guest as 1:1, based on the integrals of the corresponding proton resonances.[39] Unfortunately, when further studying the fluorescence change of guest **1** upon addition of CB[10], we found that the fluorescence intensity of complex CB[10]·**1** is not enhanced as expected (Fig. S5, ESI†). It seems that CB[10] could not efficiently limit the intramolecular rotation of guest **1**. Another possibility is that high pH may not be good for the fluorescence of guest **1**. So we synthesized other two molecules **2** and **3**.

By taking advantage of good solubilities of **2** and **3** in neutral pH, we investigated the binding interactions between them and CB[10] via ^{1}H NMR spectroscopy in D_2O. As seen in Fig. 2a and 2b, the signals for H_a and H_b proton on the aromatic rings of **2** significantly shifted upfield. And overlapping signals for H_a and H_b proton (Fig. 2a) can be differentiated in the presence of CB[10] (Fig. 2b), which is because H_a proton is located deeper in the cavity of CB[10] than H_b proton. Although the binding between **2** and CB[10] exhibits slow exchange kinetics on ^{1}H NMR time scale, observation of broadening of all proton signals implies that interesting kinetic binding happened. Like guest **2**, the binding of **3** with CB[10] also shows slow exchange kinetics (Fig. 2d-2f). Difference is that more host and guest peaks were observed. Integration for host and guest protons (Fig. S6) and COSY NMR (Fig. S7) show: 1) the binding ratio of host-guest is 1:1; the ratio of two bound methyl group (& and # at 3.01 and 2.80 ppm in Fig 2f) is ~ 1:2 (same ratio for bound CB[10] peaks at 5.82 and 5.71 ppm). All results suggest that two binding modes exist in the complex CB[10]·**3** and the ratio of them is 1:2. Considering all results and the structure of **3**, we highly believe that the vinyl group of TPE is parallel to the port of CB[10] in one mode (mode **A** in Fig 1c) and perpendicular in the other (mode **B** in Fig 1c). So broadening of signals for all protons of CB[10]·**2** in Fig. 2c could be the results of fast switching between mode **A** and **B**. Additionally, the ESI-MS test further proves the 1:1 complexation of CB[10] and **3** (m/z = 787.29) (Fig. S8, ESI†).

Fig. 3 UV/vis spectra (a) and fluorescence spectra (b) of **2** with addition of



CB[10] (0, 0.5 equiv., 1.0 equiv.) ([**2**] = 10 μM, λ_{ex} =320 nm); UV/vis spectra (c) and fluorescence spectra (d) of **3** with addition of CB[10] ([**3**] = 10 μM, λ_{ex} = 310 nm, slit = 5 X 5 nm).

UV/vis and fluorescence spectroscopies were employed to further investigate the complexation of CB[10] with **2**/**3** and the

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influence of CB[10] on the emission property of guest **2**/**3**.[40] As illustrated in Fig. 3a, the characteristic absorption peak of TPE moiety at about 320 nm decreased with addition of CB[10] to the aqueous solution of guest **2**. Fluorescence spectroscopy showed that free guest **2** exhibits weak fluorescence emission at 480 nm. However with addition of CB[10], the increase of emission intensity with 7 times stronger than that of free **2** was observed when 1 equivalent of CB[10] was added (Fig. 3b). And for the CB[10]·**3** complex, the UV/vis spectrum showed similar tendency of the decreased absorptions due to the host-guest complexaion (Fig. 3c). Similar to guest **2**, emission intensity of **3** increased 8 times in the presence of CB[10], compared to the free **3** in water (Fig. 3d). Interestingly, in this case about 60 nm blue-shift was observed with addition of 1 equivalent of CB[10], which could be caused by the enhancement of conformational planarization.[41] Both of the UV/vis and fluorescence spectra titration clearly demonstrated the complexation of **2**, **3** with CB[10]. Although all guests **1**-**3** can be encapsulated by CB[10], emission intensity of **2**/**3** increased more than **1**. This fluorescence turn-on phenomenon could be explained by efficient restriction of intramolecular rotation resulted from the formation of CB[10]·**2** and CB[10]·**3** complexes, as well as other factors.[16]

With above results in hand, we wondered whether two-substituted TPE derivatives (**4** and **5** in Fig. 1b) show the similar emission enhancement, since these guests could be further used in designing functional materials with CB[10]. Instead, if four big (or long) groups attached on phenyl groups of guest **2** or **3**, we doubt CB[10] could cover the TPE core.

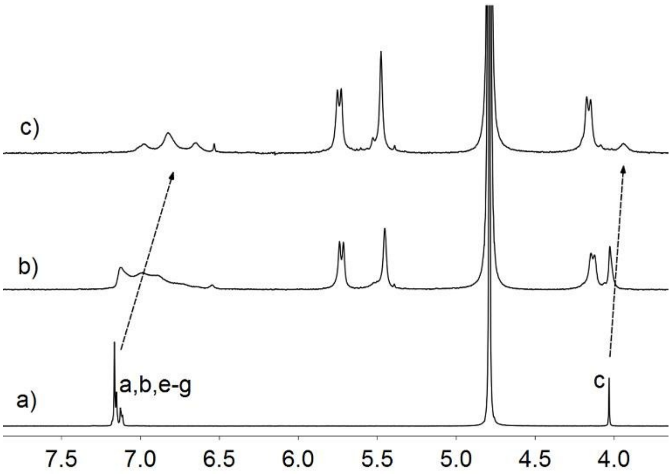

Fig. 4 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of: a) free **4** (1.0 mM); b) 2:1 mixture of **4** and CB[10]; c) CB[10]·**4** (1.0 mM) (resonances of free **4** are marked with *).

From Fig. 4, we can see that the binding between guest **4** and CB[10] exhibits fast exchange kinetics on NMR time scale, possibly resulting from the less binding sites compared to guests **1**-**3**. Integration suggests the formation of 1:1 complex CB[10]·**4**. Furthermore, the complexation could also be confirmed by UV/vis spectroscopy (Fig. S9, ESI†). The average decrease of absorption intensity implies the 1:1 complexation. As expected, the fluorescence intensity of **4** was increased in the presence of CB[10] (Fig. S9, ESI†) but with up to 3 times which are much less compared to that of **2**/**3**. This may be attributed to that the benzene ring without substituent binding sites can rotate freely in the cavity of CB[10]. Meanwhile, when CB[10] was added into the aqueous solution of **5**, we saw CB[10] dissolved first then precipitate formed. Peaks representing guest **5** and CB[10] can not be observed in the ^{1}H NMR spectra (Fig. S10, ESI†), implying the formation of insoluble complex CB[10]·**5**.

In conclusion, based on the host-guest interaction, we reported for the first time that cationic TPE derivatives showed an enhanced molecular emission when they were encapsulated in the cavity of CB[10] in an aqueous solution. Guests **2** and **3** exhibit fluorescence enhancement when 1 equivalent of CB[10] existed. As the binding sites decrease, the time of emission enhancement of guests **4** are less than the former. All results prove that encapsulation in host CB[10] dramatically limit the intramolecular rotation of TPE guests. Our strategy does not request the aggregation of TPE molecules, suggesting that much lower concentration might be adopted for AIEgens broad application.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Emission enhancement of cationic tetraphenylethylene derivatives by encapsulation in cucurbit[10]uril host in water

Chang Liu, Yong Wu, Xie Han and Simin Liu*

Encapsulation of cationic tetraphenylethylene guests in cucurbit[10]uril host in water results in strong emission enhancement of these guests due to the host-guest interaction caused restriction of intramolecular rotation.