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Tetraphenylethene-containing supramolecular hyperbranched polymers: aggregation-induced emission by supramolecular polymerization in aqueous solution

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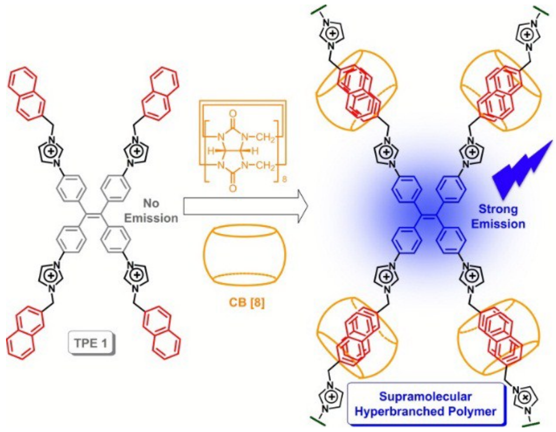
Supramolecular hyperbranched polymers have been successfully constructed by using host-enhanced π-π interaction between CB[8] and a naphthyl-substituted tetraphenylethene derivative, which exhibited a strong fluorescence in aqeuous solution due to aggregation-induced emission.

Emerged from the elegant combination of supramolecular chemistry and polymer science, supramolecular polymers have been rapidly developing as a popular and independent research area, which are defined as polymeric arrays of monomeric units that are held together by highly directional and reversible noncovalent interactions, resulting in polymeric properties in solution and bulk.[1-7] The obtained supramolecular polymers not only show traditional polymeric properties, but also possess new structures and functions, making them unique candidates for supramolecular materials. Different noncovalent interactions have been utilized to construct supramolecular polymers, such as multiple hydrogen-bonding,[8-15] metal-coordination interactions,[16-24] host-guest interactions,[2-3,25-44] donor-acceptor interactions,[45-49] van der Waals forces[50] and so on.

As an important branch of supramolecular polymers, fluorescent supramolecular polymers have attracted extensive attention by introducing the fluorescent moieties.[51-54] However, many fluorescent moieties exhibit high fluorescence efficiency in dilute solution but suffer from an aggregation-caused quenching (ACQ) effect in the condensed phase,[55] which limits the luminescence ability of supramolecular polymers and their further application as highly fluorescent materials. Aggregation-induced emission (AIE), which was a remarkable phenomenon first reported and intensively studied by Tang since 2001,[56-58] was used as a new approach to diminish ACQ. By introducing the tetraphenylethylene (TPE) derivatives into the building blocks, Ma, Liu and Huang constructed supramolecular polymers with host-guest complexation induced emission through bis-*p*-sulfonatocalixarene,[54] *p*-sulfonatocalix[4]arene,[59] and pillar[6]arene.[60]

In order to further investigate supramolecular polymers with AIE properties, herein, we report a simple strategy, based on the host-guest complexation between CB[8] and a TPE derivative **1**, to construct supramolecular hyperbranched polymers. Such monomer with four naphthyl-substituted arms and a TPE core formed supramolecular hyperbranched polymers through host-enhanced π-π interaction (Scheme 1).[37-38] The host-guest interactions between CB[8] and **1** efficiently restricted the intramolecular rotation and the non-radiative relaxation channel, thereby resulting in the strong emission of **1** in dilute solution.



Scheme 1 Illustration of the formation of supramolecular hyperbranched polymers through self-assembly of TPE derivative **1** and CB[8].

The synthesis of TPE derivative **1** was carried out by a one-step reaction as shown in Scheme 2. After reaction at 90 °C for 48 h, the product can be obtained as a yellow-green powder by adding dropwise of 400 mL of diethyl ether and filtered in a

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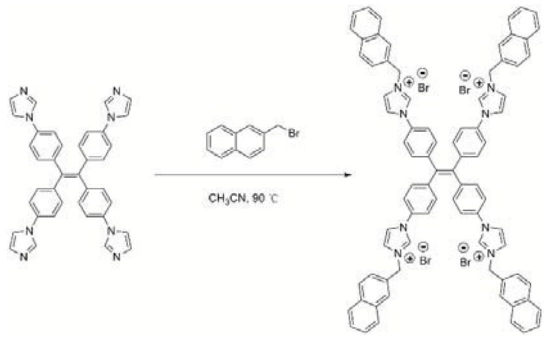
yield of 85%. The identity was confirmed by ^{1}H NMR, and HRESI MS. As expected, TPE derivative **1** is very soluble both in organic solvents and in water.



Scheme 2 Synthesis route of TPE derivative **1**.

In order to demonstrate the host-guest interaction between **1** and CB[8], ^{1}H NMR spectra of **1** before and after addition of CB[8] were studied. After adding CB[8] into the aqueous solution of **1**, the proton peaks of naphthalene groups and TPE core moved to the high field and broadened (Fig. S1), indicating that the naphthalene moieties are efficiently encapsulated by CB[8] to form hyperbranched supramolecular polymers. To further confirm the host-guest complexation between them, a Job's plot was used to confirm the binding stoichiometry between **1** and CB[8] (Fig. 1). Both **1** and CB[8] solutions were prepared in aqueous solution. The total concentration of **1** and CB[8] was fixed at 80 μM, while the molar ratio of **1** was increased from 0 to 1. The intensity of the fluorescence emission at 460 nm (the maximum emission peak of **1**) was recorded when the molar ratio of **1** was changed, so that the dependence of the intensity on the molar ratio of **1** could be determined. The change in the emission reached a maximum at a ratio of ~0.33 in Job's plot, confirming the 1:2 stoichiometry between **1** and CB[8] in water.

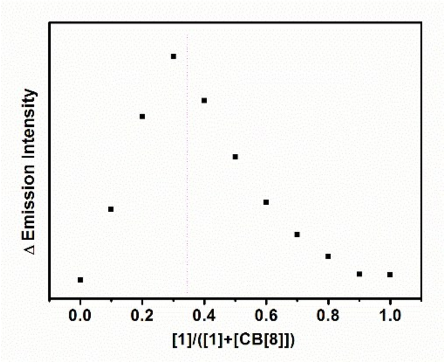


Fig. 1 Job's plot of the change in emission spectra at 460 nm; excitation wavelength was 330 nm; the total concentration of **1** and CB[8] was fixed at 80 μM.

In order to characterize the formation of supramolecular polymers, diffusion-ordered NMR spectroscopy (DOSY) was employed to determine the diffusion coefficients before and after supramolecular polymerization. The average diffusion coefficients of **1** and CB[8] were measured to be 8.17×10^{-10} m^{2}s^{-1} and 8.12×10^{-10} m^{2}s^{-1}, respectively. After formation of supramolecular polymers, it gives an independent and relatively low diffusion coefficient with a value of 3.01×10^{-10} m^2 s^{-1}. The significant decrease of the diffusion coefficient implies that large polymeric species have formed.

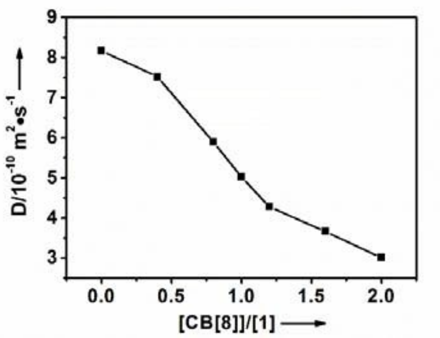


Fig. 2 Diffusion coefficient of 67.6 μM **1** with different ratios of CB[8].

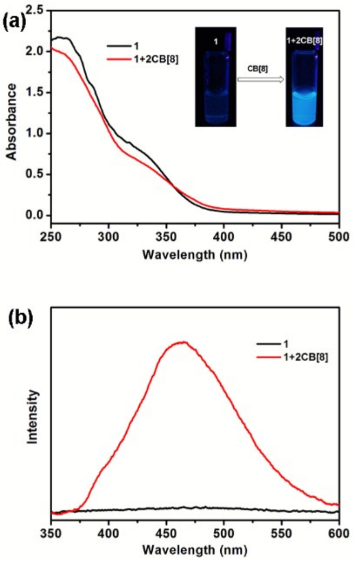


Fig. 3 (a) UV/vis spectra of **1** (33.8 μM, black) and **1**-2CB[8] (33.8 μM, red). (b) Fluorescence spectra of **1** (33.8 μM, black) and **1**-2CB[8] (33.8 μM, red).

UV-vis spectroscopy and fluorescence spectroscopy were employed to further confirm the formation of supramolecular polymers and the attractive aggregation-induced emission property. From UV-vis spectra (Fig. 3a), the absorption of the naphthalene moieties at about 275 nm decreased after addition of CB[8] into the aqueous solution of TPE derivative **1**, indicating that naphthalene moieties are encapsulated in the cavity of CB[8]. Meanwhile, the absorption of 330 nm attributed to the TPE core decreased and red-shifted. The fluorescence properties of TPE derivative **1** in the absence or presence of CB[8] in water were also investigated as shown in Fig. 3b. The intramolecular rotation of phenyl rings of **1** may induce the efficient nonradiative annihilation process and thus **1** is nearly nonemissive in water. However, in sharp contrast to the little changes in absorption spectra, upon the addition of CB[8], the rotation of phenyl rings of **1** is restricted. Therefore, the fluorescence intensity with a max λ_{em} at 460 nm increased remarkably. The fluroresncent quantum yield was significantly increased from 0.19% to 14.7% after formation of supramolecular polymers. On the other hand, the increase of emission intensity with increasing addition of CB[8] gives no obvious changes when two equiv. of CB[8] was introduced, suggesting their strong binding affinity and the formation of a 1 : 2 inclusion complex, which was in good agreement with that confirmed by Job's plot (Fig. 1). In addition, such CB[8]-induced large fluorescence change of **1** was clearly observed by naked eyes. When **1** was excited at 365 nm using a UV lamp in the presence of CB[8], a strong blue fluorescence appeared, further supporting the proposed mechanism above.

After establishing the host-guest induced supramolecular hyperbranched polymers in water, we further investigate the self-assembly behaviors the complex between CB[8] and **1**. The aggregated species of the supramolecular polymers in aqueous solution was corroborated by dynamic light scattering (DLS) experiments (Fig. S2). CONTIN analysis of the DLS autocorrelation function of the supramolecular polymers shows a main distribution of hydrodynamic diameter (D_h) of the aggregates centered at ~300 nm in aqueous solution. Transmission electron microscopy (TEM) was performed to gain a direct visualization of the size and morphology. As shown in Fig.S3, individual spherical aggregates were clearly observed with the diameter in the range of 300 nm, in a good agreement with that obtained by DLS.

Conclusions

In summary, we constructed supramolecular hyperbranched polymers by using host-enhanced π-π interaction between CB[8] and a naphthyl-substituted TPE derivative **1**. The intramolecular rotation of the phenyl rings of **1** was hampered upon the addition of CB[8], so the complex emits strong fluorescence in dilute solution. In addition, the supramolecular hyperbranched polymers between CB[8] and **1** self-assembled into spherical structures in water. We expect that this design strategy to construct supramolecular polymers by using host-guest complexation induced emission will enrich the field of supramolecular polymerization with new building blocks and architectures for guiding the future design of supramolecular functional materials.

Acknowledgements

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Tetraphenylethene-containing supramolecular hyperbranched polymers: aggregation-induced emission by supramolecular polymerization in aqueous solution

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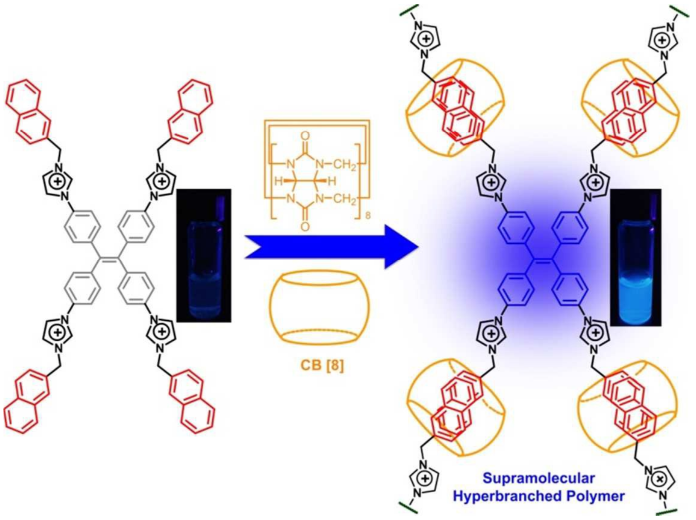

Supramolecular hyperbranched polymers have been constructed by using host-enhanced π-π interaction between CB[8] and a TPE derivative with aggregation-induced emission.