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Efficient enhancement of fluorescence emission *via* TPE functionalized cationic pillar[5]arene-based host–guest recognition-mediated supramolecular self-assembly

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ABSTRACT

A tetraphenylethene (TPE) functionalized cationic pillar[5]arene (**CWP5-TPE**) was successfully synthesized, and the intramolecular rotation of the TPE motif was restricted *via* cationic pillar[5]arene-based host–guest recognition-mediated supramolecular self-assembly in water, resulting in the efficient enhancement of fluorescence emission based on the aggregation induced emission (AIE) mechanism. **CWP5-TPE** self-assembled into nanoribbons while the host–guest inclusion complex formed into supramolecular amphiphile nanoparticles in water.

Pillar[*n*]arenes, whose repeating units are connected by methylene bridges at the *para*-positions of 2,5-dialkoxybenzene rings, mainly including pillar[5]arenes,[1] pillar[6]arenes[2] and other high-level pillar[*n*]arenes ($n \geq 7$),[3–6] have stimulated a tremendous upsurge of interest since their first report in 2008.[7] Due to their unique symmetric pillar-shaped structures, facile tunable functionality, as well as intriguing host–guest binding abilities,[1–7,8] pillararenes have been defined as a new generation of macrocyclic host molecules in supramolecular chemistry after cyclodextrins,[9] crown ethers,[10] cucurbiturils[11] and calixarenes.[12] In recent years, the host–guest properties of pillararenes have been investigated intensively and also been explored widely in the construction of numerous supramolecular systems, such as supramolecular polymers,[1k,1p,1s] drug-release systems,[1r,2a,2c,2g,2h] transmembrane channels[1e,1v,1w] and other advanced functional materials.[13] Among them, pillararene-based fluorescent materials have attracted considerable attention owing to their promising applications in cell imaging,[1t] drug delivery[1r,2c,2g] and chemosensors.[1o,2e,14]

However, the conventional organic fluorophores have a fatal drawback that the luminescence in aqueous solution is usually quenched due to aggregation-caused quenching (ACQ) effect. Obviously, ACQ effect limits the applications of the conventional organic fluorophores in practice to a great extent.[11e,15] In 2001, Tang *et al* discovered the phenomenon named aggregation induced emission (AIE),[16] which is completely opposite to ACQ effect. Many scholars have made great efforts to the development of materials with AIE in recent years.[17] Among them, as a typical AIE luminogen, tetraphenylethene (TPE) has been extensively studied. Upon restriction of intramolecular rotation of the phenyl rings by increasing the solvent viscosity, lowering the temperature or applying high pressure, the luminous efficiency of TPE can be greatly enhanced due to the obstruction of the nonradiative pathway and activation of radiative decay.[17] Moreover, TPE-based florescence nanoparticles were also widely constructed to improve their luminous efficiency recently.[17f,17j,17k,18] Although there are a few literatures being reported to modify the TPE moieties onto neutral pillararenes to construct supramolecular polymers,[17b,17c] to the best of our knowledge, the research of modifying TPE moieties onto water-soluble pillararenes and further using them to construct fluorescence nanoparticles has not been reported so far.

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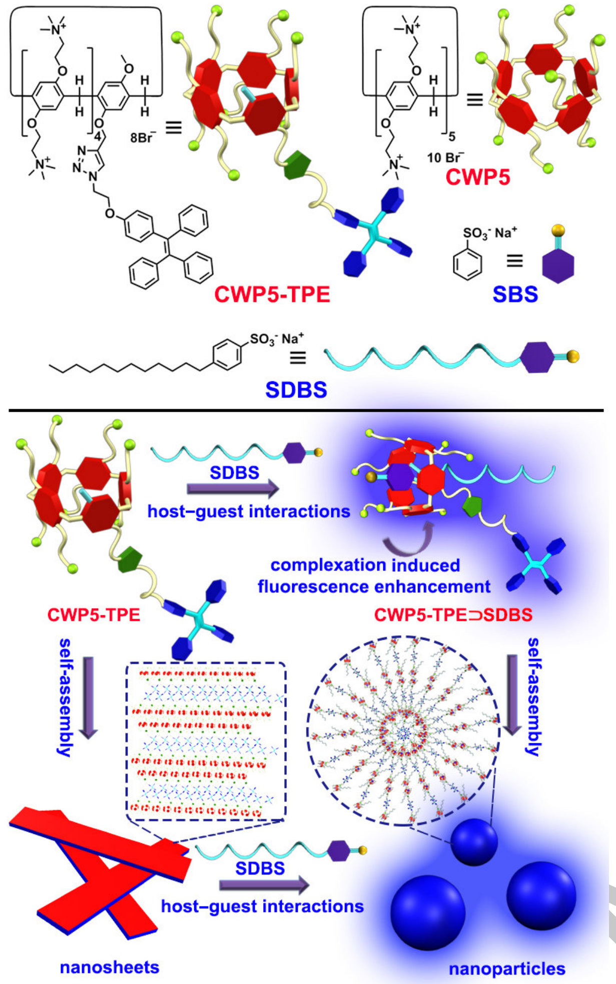

Scheme 1. Top: structures and cartoon representations of **CWP5-TPE**, **SDBS**, **CWP5** and **SBS**; bottom: cartoon representation of the self-assemblies of **CWP5-TPE** and **CWP5-TPE⊃SDBS**.

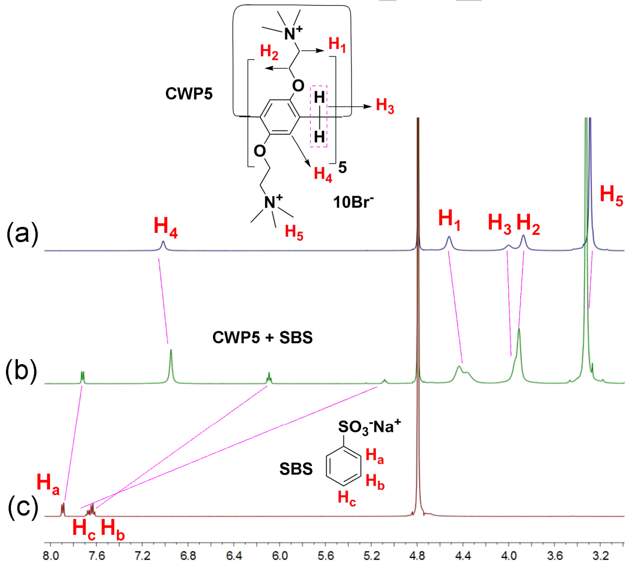

Figure 1. Partial ^{1}H NMR (400 MHz, D_2O, 298.15 K) spectra: (a) **CWP5** (5.0 mM); (b) **CWP5** (5.0 mM) and **SBS** (5.0 mM); (c) **SBS** (5.0 mM).

Herein we designed and synthesized a novel functionalized cationic pillar[5]arene which was modified with **TPE**. A click reaction was adopted to conjugate the **TPE** moiety to the cationic water-soluble pillar[5]arene. All the compounds were obtained under moderate reaction conditions with satisfactory yields. Based on the host−guest interactions between the functionalized cationic pillar[5]arene (**CWP5-TPE**) and sodium dodecyl benzene sulfonate (**SDBS**), we presented a novel strategy to restrict the intramolecular rotation of the benzene rings of **TPE**, resulting in a significant fluorescence emission enhancement (Scheme 1).

To ensure the formation of a host−guest complex between **CWP5-TPE** and **SDBS**, ^{1}H NMR spectroscopy in D_2O was firstly utilized by using cationic water-soluble pillar[5]arene **CWP5** and sodium benzenesulfonate **SBS** as model compounds. Figure 1 shows the ^{1}H NMR spectra of **SBS** in D_2O recorded in the absence and presence of approximately 1.0 equiv. of **CWP5**. Only one set of the peaks was observed, indicating the fast-exchange complexation on the NMR time scale. Compared with the spectrum of free **SBS**, the peaks of protons $H_{a\text{-}c}$ on **SBS** shifted upfield significantly ($\Delta\delta = -0.17$, -1.54 and -2.61 ppm for H_a, H_b and H_c, respectively, Figure 1) after complexation with **CWP5**. Meanwhile, the peaks of protons $H_{1\text{-}5}$ on **CWP5** shifted downfield or upfield slightly ($\Delta\delta = -0.09$, 0.04, -0.09, -0.07 and 0.03 ppm for H_1, H_2, H_3, H_4 and H_5, respectively, Figure 1). The reason is that these protons on the guest located in the cavity of the pillararene to form an inclusion complex and were shielded by the electron-rich cavity of pillararene. Moreover, H_1 was split into two separated peaks as a result of the asymmetric structure of **SBS** whose anionic sulfonate head group was close to the cationic quaternary ammonium groups at one end of the **CWP5** and formed into a 1:1 inclusion complex.[19] 2D NOESY NMR spectrum of the solution of **CWP5** and **SBS** in D_2O was also carried out to prove the formation of host−guest complex (Figure S13). Nuclear overhauser effect (NOE) correlations were observed between protons H_a and H_1, H_2, H_3, H_4 (A, B, C points, Figure S13), H_b and H_2, H_3, H_4 (D, E points, Figure S13), H_c and H_1, H_4 (F, G points, Figure S13). These results proved that the negatively charged benzene sulfonate **SBS** threaded into the positively charged **CWP5** and formed into an inclusion complex.[19]

Isothermal titration calorimetry (ITC) is a useful method to study the association constant (K_a) and stoichiometry of a host–guest complex and its thermo-dynamic parameters (enthalpy change $\Delta H°$ and entropy change $\Delta S°$). From ITC experiments (Figure S14), the K_a value of **CWP5⊃SBS** was calculated to be $(8.83 \pm 1.05) \times 10^{4}$ M^{-1}. The titration data were well fitted by computer simulation by using the "one set of binding site" model, demonstrating 1:1 complexation between **CWP5** and **SBS** (Figure S14). Moreover, according to the thermodynamic data listed in Figure S14, the complexation was driven by both enthalpy and entropy changes ($\Delta H° = -15.27$ KJ mol^{-1}; $T\Delta S° = 13.02$ KJ mol^{-1}, $|\Delta H°| > |T\Delta S°|$).[19] In addition, from the UV-vis absorption titration spectra (Figure S15), Job plot of complex **CWP5-TPE⊃SDBS** showed a 1:1 stoichiometry between **CWP5-TPE** and **SDBS** which was in accordance with the ITC results of demonstrating 1:1 complexation between **CWP5** and **SBS** (Figure S14) by plotting the absorbance difference at 291 nm (a characteristic absorption peak of **CWP5-TPE**) against the mole fraction of **CWP5-TPE** (Figure S15).

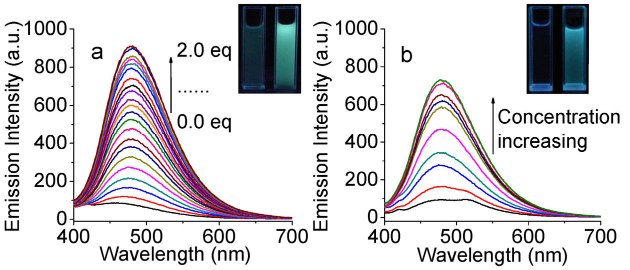

Figure 2. (a) Fluorescence emission spectra of **CWP5-TPE** (1.0×10^{-4} M) in the presence of **SDBS** from 0.0 equiv to 2.0 equiv in water. The inset photograph shows the corresponding fluorescence of **CWP5-TPE** alone (left) and **CWP5-TPE⊃SDBS** (right, molar ratio 1:2) in water upon excitation at 365 nm using a UV lamp at 298.15 K. (b) Fluorescence emission spectra of **CWP5-TPE⊃SDBS** (molar ratio 1:1) aqueous solution at different concentrations (from 1.0×10^{-5} M to 1.0×10^{-4}M). The inset photograph shows the corresponding fluorescence of **CWP5-TPE⊃SDBS** (molar ratio 1:1) in water at the concentrations of 1.0×10^{-5} M (left) and 1.0×10^{-4} M (right), respectively, upon excitation at 365 nm using a UV lamp at 298.15 K.

Then, we utilized fluorescence titration experiments to confirm the formation of host–guest complex between **CWP5-TPE** and **SDBS**. As shown in Figure 2a, a very weak fluorescence emission of **CWP5-TPE** was observed at 461 nm, while upon addition of **SDBS** from 0.1 equiv to 2.0 equiv, the emission intensity of the supramolecular aggregates increased significantly and a new emission band centered at 477 nm appeared in the fluorescent spectra as a result of the host–guest interactions between **CWP5-TPE** and **SDBS**. The fluorescence emission intensity of **CWP5-TPE** increased approximately 11-fold by addition of 2.0 equiv of **SDBS**. Furthermore, concentration-dependent fluorescent emission spectra of **CWP5-TPE⊃SDBS** (molar ratio 1:1, Figure 2b) was conducted. As a result of the stoichiometry of host–guest complex was 1:1 according to the ITC experiments (Figure S14) and the UV-vis absorption titration experiments (Figure S15), additionally, in order to keep in line with the molar ratio of host-guest in critical aggregation concentration (CAC) experiments (Figure S17), we adopted the same molar ratio of host-guest (1:1) in the investigation of concentration-dependent fluorescent emission spectra. At low concentration (1.0×10^{-5} M), **CWP5-TPE⊃SDBS** had very weak emission, while with the concentration increasing, the luminescence intensity increased gradually. When the concentration of **CWP5-TPE⊃SDBS** increased to be 9.0×10^{-5} M, which is approximately in accordance with the CAC value of **CWP5-TPE⊃SDBS** (8.0×10^{-5} M, Figure S17), the fluorescence intensity reached the highest value, which is approximately 8-fold of that at 1.0×10^{-5} M. Notably, the fluorescence emission of **CWP5-TPE⊃SDBS** could be clearly visualized under UV light (excited at 365 nm) by naked eyes (the inset photographs in Figure 2). We speculated that the reason for the fluorescence intensity enhancement may be that the negatively charged **SDBS** threaded into the cavity of **CWP5-TPE** to form a supramolecular amphiphile and further self-assembled in solution which made **TPE** moiety stack more tightly so that the intramolecular rotation of the benzene rings of **TPE** was further restricted.

Finally, in order to verify the self-assembly behaviours of **CWP5-TPE** and **CWP5-TPE⊃SDBS**. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) were investigated (Figure 3 and Figure S21). The TEM images revealed that the aggregates of **CWP5-TPE** were ribbon-like assemblies (Figure 3a) while the aggregates of **CWP5-TPE⊃SDBS** were spherical assemblies (Figure 3b and Figure 3c).

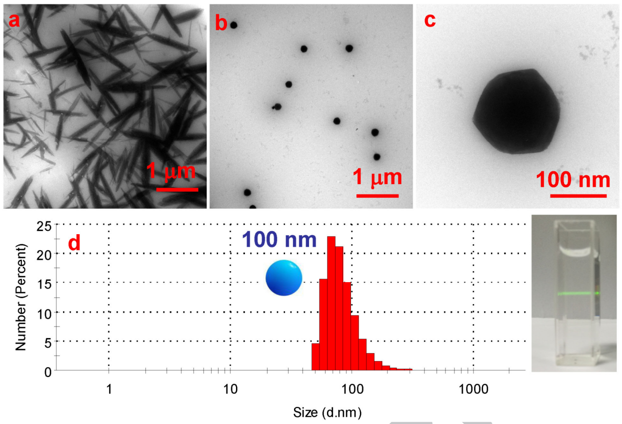

Figure 3. TEM images: (a) **CWP5-TPE** (1.0×10^{-3} M) and (b) **CWP5-TPE⊃SDBS** (1.0×10^{-3} M). (c) Amplified TEM image of **CWP5-TPE⊃SDBS** (1.0×10^{-3} M). (d) DLS study and Tyndall effect of the host–guest complex **CWP5-TPE⊃SDBS** (1.0×10^{-3} M).

Although the average diameter of **CWP5-TPE⊃SDBS** increased slightly upon its concentration increasing, the average diameter of **CWP5-TPE⊃SDBS** was still approximately 100 nm (Figure S21),[1t] which was consistent with the TEM results (Figure 3b and Figure 3c) as a result of the nanoparticles composed of multiple layers structures self-assembled by **CWP5-TPE⊃SDBS** (Scheme 1). **CWP5-TPE** self-assembled into nanoribbons driven by hydrophobic interactions and π–π interactions of the **TPE** moieties with very weak emission in water (Figure 2a) and its fluorescence quantum yield (Φ_F) was 1.23 % (Table S1), therefore, it can be acted as a macrocycle amphiphile molecule. However, after adding **SDBS**, the nanoribbons transformed into nanoparticles as a result of the formation of suprarmolecular amphiphile between **CWP5-TPE** and **SDBS** driven by hydrophobic interactions, π–π interactions and electrostatic interactions of the **CWP5-TPE** and **SDBS**. The rotation of the benzene rings of **TPE** was further restricted in the amphiphile nanoparticles formed by **CWP5-TPE⊃SDBS** so that the nonradiative pathway was obstructed and the radiative decay was activated, therefore the emission intensity of the suprarmolecular amphiphile nanoparticles (Φ_F was 11.84 %, Table S1) was more stronger than the nanoribbon formed by **CWP5-TPE** alone (Figure 2a). Additionally, the solution of **CWP5-TPE⊃SDBS** exhibited a clear Tyndall effect (Figure 3d), indicating the formation of regular aggregates of nanopaiticles.

In summary, novel AIE-active nanoparticles were fabricated by utilizing **CWP5-TPE⊃SDBS** as the self-assembly building block. In contrast to the nanoribbons self-assembled from **CWP5-TPE** alone, **CWP5-TPE⊃SDBS** self-assembled into nanoparticles and the average diameter of the nanoparticles was approximately 100 nm. The nanoribbons showed very weak fluorescence emission, while the nanoparticles showed much more stronger fluorescence emission at the same concentrations because the intramolecular rotation of the benzene rings of the **TPE** group was restricted significantly and the nonradiative decay pathway was blocked by the formation of a supramolecular amphiphile. Therefore, we developed a new strategy for fabricating the AIE-emissive nanoparticles based on host–guest chemistry of **CWP5-TPE** and **SDBS**. These research results indicated that functionalized cationic pillar[5]arene-based host–guest complexes will be significant for the development of many fields such as biological and pharmaceutical fields, including cell imaging, drug delivery and biosensors, *etc*.

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Supplementary Material

Supplementary data (Synthetic procedures, characterization, determination of association constants and other materials.) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/

Referencess

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Graphical Abstract

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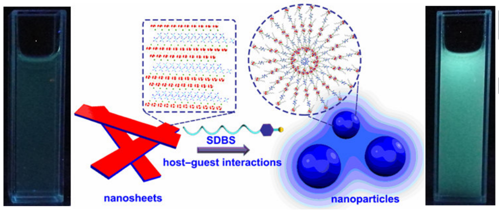
Efficient enhancement of fluorescence emission *via* TPE functionalized cationic pillar[5]arene-based host–guest recognition-mediated supramolecular self-assembly

Jifu Sun*, Li Shao, Jiong Zhou, Bin Hua, Zhihua Zhang, Qing Li and Jie Yang*



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Research highlights

- Cationic pillar[5]arene modified with **TPE** was synthesized for the first time.
- Host−guest interactions were confirmed by NMR, UV−vis absorption spectra and ITC.
- The fluorescence emission was efficiently enhanced by host−guest complexion.
- The self-assemblies of host−guest complexes were verified by TEM and DLS.