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Cucurbit[7]uril–tetraphenylethene host–guest system induced emission activity†

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A host–guest complex was successfully constructed from cucurbit[7]uril (Q[7]) and quaternary ammonium-modified tetraphenylethene derivative, 1,1,2,2-tetrakis{2-[2-(*N*,*N*,*N*-trimethylammonium)ethyoxyl]phenyl}-tetraphenylethene bromide (TAPET), and characterized by a wide range of techniques. This host–guest complex exhibits an AIE nature, resulting in strong fluorescence in dilute solution due to the restriction of the intramolecular rotation of the phenyl moieties of TAPET upon the addition of Q[7]. Moreover, addition of competitive guest 1-adamantanamine hydrochloride (Ada) leads to effective dissociation of the host–guest complex Q[7]–TATPE and turns the fluorescence emission off.

Molecular compounds with aggregation-induced emission (AIE)[1] or aggregation induced enhanced emission (AIEE)[2] characteristics have provided a promising platform for the design and creation of efficient light emitters ranging from optical materials to sensors.[3] Since the first AIE molecular compound reported by Tang *et al.* in 2001,[1a] a wide variety of AIE molecular materials have been synthesized based on the mechanism of restricting the intramolecular motions (RIM).[3b,4a] Among various AIE molecular compounds, tetraphenylethene (TPE) and its functionalized derivatives can be readily obtained *via* facile synthetic transformation, and are non-emissive in the molecularly dissolved state but show enhanced fluorescence emission in both the aggregated form and the solid state.[4] In contrast to the conventional organic luminophores with aggregation-caused quenching (ACQ) effect, TPE derivatives with AIE-activity have demonstrated improved efficiency and sensitivity as chemosensors, bio-probes, and solid-state emitters with great application potentials.[5]

Actually many methodologies including increasing the solvent viscosity, lowering the temperature, and applying high pressure[1b,6] have been developed to fabricate TPE-based AIE-active materials.[1b,4b] In particular, host–guest recognition was proved efficient to restrict the intramolecular motions of TPE molecules in recently years, resulting in the turn-on of fluorescence emission of TPE derivatives *via* the AIE mechanism.[7] Quite a number of macrocyclic hosts such as crown ethers, calixarenes, cyclodextrins, and pillararenes have been employed to include the TPE molecule inside their cavities to induce the in AIE-activity.[8] In 2014, Tang demonstrated that when the phenyl moieties of TPE were included in the cavity of β-cyclodextrins through host–guest interaction, the neutral TPE derivative then showed an enhanced fluorescence emission.[7b] Also in 2014, Li reported the self-assembled fluorescent organic nanoparticles fabricated from *p*-sulfonatocalix[4]arene and quaternary ammonium-modified TPE in water.[8f] Recently, Huang and co-workers constructed a host–guest inclusion complex from water-soluble pillar[6]arene and tetraphenylethene derivative, which exhibited strong fluorescence in dilute solution.[8h]

Cucurbit[*n*]urils (Q[*n*]),[9] as a new class of macrocyclic hosts, exhibit exceptional molecular recognition properties due to their high binding affinities and tunable association and dissociation properties and have been widely utilized in developing supramolecular switches, supramolecular polymers, supramolecular nanoparticles, and other supramolecular systems with fascinating properties and application potentials.[10] However, there still exists no AIE-active supramolecular system that is constructed between cucurbit[*n*]uril and TPE derivative depending on the host–guest interactions, to the best of our knowledge. Herein we describe the construction of the cucurbit[7]uril (Q[7])-based host–guest system with 1,1,2,2-tetrakis{2-[2-(*N*,*N*,*N*-trimethylammonium)ethyoxyl]-phenyl}-tetraphenylethene bromide (TAPET), Scheme 1, representing the first Q[*n*]-involved host–guest complex constructed with TPE. In particular, in this host–guest system the phenyl moieties of TAPET were included in the cavity of Q[7], resulting in the strong emission of TAPET in dilute solution. The present result therefore represents the first host–guest system constructed between cucurbit[*n*]uril and TPE with AIE-activity.

Host Q[7] was prepared according to the published procedure.[9a] The target guest together with corresponding intermediary compounds was synthesized in a facile route as shown in Scheme S1 (ESI†). At the very beginning, the intermediate compound tetrahydroxyl TPE (**1**) was synthesized by McMurry coupling reaction between two bis(4-hydroxyphenyl)-methanones. Then reaction of

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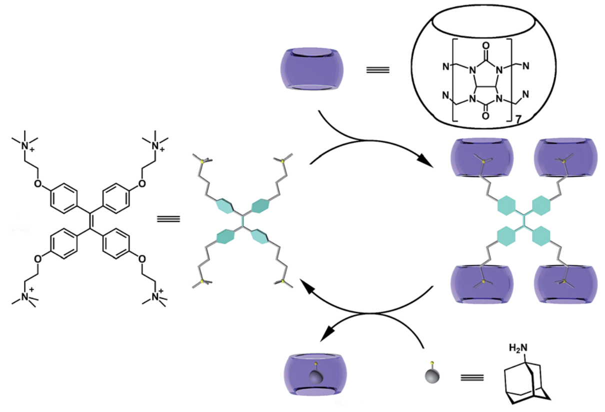
† Electronic supplementary information (ESI) available: Synthesis procedure, NMR, MALDI-TOF mass spectrum, electronic absorption and fluorescence spectra, DLS and AFM results. See DOI: 10.1039/c5ra24264a



Scheme 1 Schematic representation of the formation of the AIE-active host–guest complex between Q[7] and 1,1,2,2-tetrakis{2-[2-(*N*,*N*,*N*-trimethylammonium)ethyoxyl]phenyl}-tetraphenylethene bromide (TAPET).

tetrahydroxyl TPE with 1,2-dibromoethane promoted by K_2CO_3 and KI in DMF led to the formation of compound 1,1,2,2-tetrakis[4-(2-bromoethoxy)phenyl]ethane (**2**),[8g,h] which further reacted with trimethylamine in ethanol afforded the target guest compound TATPE (**3**). It is worth noting that the quaternary ammonium cation moieties incorporated in this guest compound lend this compound good water-solubility, rendering the reaction with water soluble Q[7] to be able to occur in aqueous solution. By simply mixing Q[7] and TATPE in aqueous solution, strong host–guest interactions between the two species of molecules led to the formation of pseudorotaxane Q[7]–TATPE. All the key intermediate and target compounds have been characterized by ^1H and ^{13}C NMR spectroscopy, Fig. S1 and S2 (ESI†).

In order to investigate the complexation of Q[7] with TATPE in solution, ^1H NMR titration experiments were first performed by adding increasing amount of Q[7] into the solution of TATPE in D_2O. As clearly shown in Fig. 1, the proton H_1 and H_2 attributed to the methyl proton and methylene proton experience significantly upfield shift from 3.09 and 3.66 ppm to 2.88 and 3.48 ppm, respectively. Furthermore, the methylene protons H_3 and aromatic protons H_4 exhibit obviously downfield shift from 4.31 and 6.69 ppm to 4.39 and 6.83 ppm, respectively. These shifts in their direction and magnitude suggest that the methyl group and methylene linked with the quaternised N^+ of the guest TATPE are located within the interior cavity of Q[7] due to the formation of the inclusion complex Q[7]–TATPE. This is further confirmed by the NOESY cross-signals between the methyl proton H_1 of TATPE and the methylene proton of Q[7] in the NOESY spectrum of the mixture between TATPE and Q[7] in D_2O, Fig. S3 (ESI†).

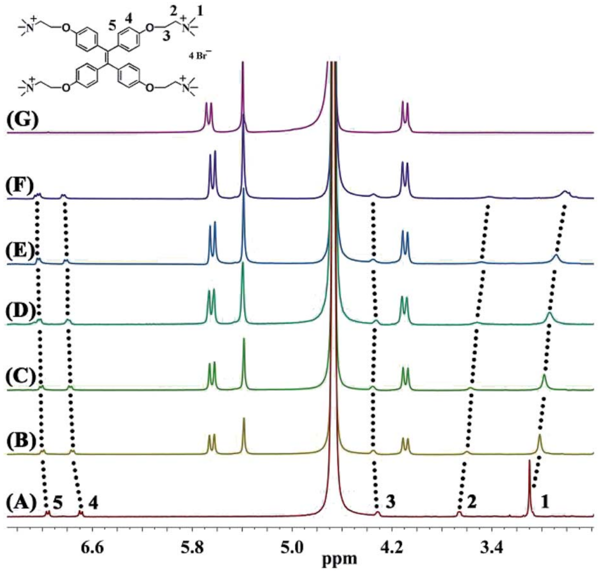


Fig. 1 ^1H NMR spectra of TATPE (A) as well as Q[7] and TATPE in the molar ratio of 2 : 1 (B), 2.5 : 1 (C), 3 : 1 (D), 3.5 : 1 (E), 4 : 1 (F), and Q[7] (G) recorded in D_2O at 25 °C.

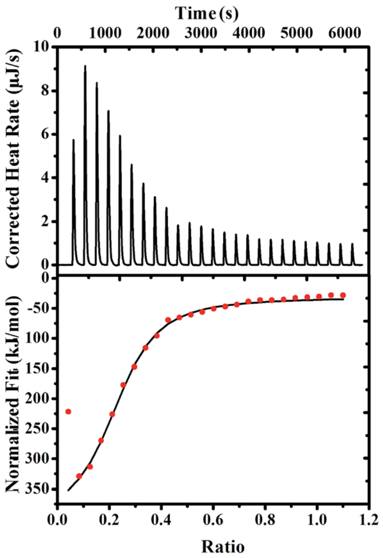


Fig. 2 ITC data for the binding of Q[7] with TATPE in H_2O at 25 °C.

Isothermal titration calorimetry (ITC) measurements are able to afford quantitative information for the host–guest complexation including both the binding affinity and thermodynamic origin. As a consequence, a solution of TATPE was consecutively injected into the solution of Q[7] at 25 °C to record the exothermic binding isotherm, Fig. 2, resulting in the resolution of the binding molar ratio value of $N = 0.243$. This result is very close to the expected value of 0.25, suggesting the binding stoichiometry of Q[7] to TATPE is 4 : 1. This is also in accordance with the MALDI-TOF mass spectroscopic result, Fig. S4 (ESI†). In addition, the association constant of $K_a = (3.06 \pm 0.16) \times 10^5\ M^{-4}$ for Q[7] with TATPE was also derived on the basis of corresponding experimental result. Such a high binding constant suggests the relatively strong host–guest interaction between Q[7] and TATPE, indicating the formation of stable inclusion complex in aqueous solution. Meanwhile, the relatively large negative enthalpy value of Q[7]–TATPE system deduced reveals that the assembly process of inclusion complex of Q[7] with TATPE is typically driven by a favorable enthalpy change, Table S1 (ESI†).

As described above, both ^{1}H NMR and ITC measurements indicate the formation of pseudorotaxane unit between Q[7] and TATPE in aqueous solvent, which might be able to inhibit the intramolecular rotation of the phenyl moieties of TATPE, inducing TATPE to exhibit strong emission. As a consequence, the fluorescence properties of 2.0 μM TATPE in the absence or presence of Q[7] in water were comparatively investigated. As shown in Fig. 3, TATPE is nearly nonemissive in water due to the efficient nonradiative annihilation process induced by the intramolecular rotation of phenyl moieties of TATPE. However, upon addition of Q[7], the rotation of phenyl moieties of TATPE is restricted, leading to the remarkably increased fluorescence intensity. The emission intensity gradually got increased along with the increase in the Q[7] added, which became nearly constant when 140.0 μM Q[7] was added, resulting in the observation of approximately 16-fold fluorescence enhancement. In addition, such a Q[7]-induced significant fluorescence enhancement of TATPE is even to be clearly observed by naked eye: When TATPE was excited at 365 nm using a UV lamp in the presence of 35.0 equiv. of Q[7], a strong cyan fluorescence appeared. This gives additional support for the AIE mechanism as proposed.

Further investigation of the binding stoichiometry between Q[7] and TATPE was carried out by Job's plot method. As shown in Fig. S5 (ESI†), the maximum peak appeared at the molar fraction of 0.20, corresponding to 1 : 4 binding stoichiometry of TATPE to Q[7]. This is consistent with that deduced from the ITC analysis as detailed above.

Furthermore, transmission electron microscopy (TEM) was used to provide further insight into the size and morphology of the supramolecular aggregates formed from Q[7] and TATPE. After evaporating the solution of Q[7] and TATPE on copper grid, spherical micelles with a diameter of ~40 nm were observed by TEM image, and the spherical micelles showed multilamellar stacks, Fig. S6 (ESI†). Most probably, self-assembly between Q[7] and TATPE led to the formation of a host–guest supramolecular complex with amphiphilicity depending on the electrostatic interactions between the quaternary ammonium groups of TATPE and oxygen atoms at the portals of Q[7]. With the Q[7]–TATPE host–guest system as starting material, further self-assembly depending on the π–π interactions between the phenyl moieties of neighboring TATPE in the host–guest system, with the help of the C–H⋯π interactions between the methylene group of Q[7] and the phenyl moieties of TATPE in neighboring host–guest system, results in the formation of spherical-like nano-structures.

Due to the stronger binding ability of Q[7] with 1-adamantanamine hydrochloride (Ada),[11] Ada was added into the Q[7]–TATPE system as a competitive guest. As shown in Fig. S7 (ESI†), upon adding Ada into the Q[7]–TATPE supramolecular complex in D_2O, all of the proton resonances of Ada exhibited obviously upfield shifts, with H_I, H_{II}, and H_{III} having chemical shift differences of 0.63, 0.61 and 0.67 ppm in comparison with the free guest Ada. At the same time, all the signals of TATPE in the complex Q[7]–TATPE system returned to the original state of the free TATPE molecule, indicating the dissociation of the original supramolecular system Q[7]–TATPE and concomitant formation of a new inclusion complex between Q[7] and Ada.

As expected, along with the addition of increasing amount of competitive guest Ada into the Q[7]–TATPE system at a fixed concentration of 2.0×10^{-6} M in H_2O, the fluorescence intensity got gradually decreased at 464 nm while the emission significantly increased at 396 nm, Fig. 4 and S8 (ESI†), with a clear isoemissive point appearing at 420 nm, indicating the dissociation of the Q[7]–TATPE complex and the formation of a new complex between Ada and Q[7]. These results reveal that in the presence of Ada, TATPE slipped out of the cavity of Q[7] and Ada was included by Q[7]. The underlying optical change was ascribed to the formation of a more stable complex Q[7]–Ada. This results in the nonemissive TATPE molecules again in

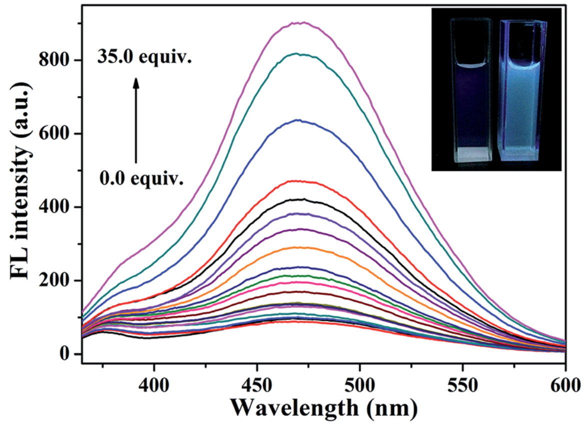


Fig. 3 Fluorescence spectra of TATPE (2×10^{-6} mol L^{-1}) upon addition of Q[7] at 470 nm in H_2O with excitation of 330 nm (the TATPE/Q[7] molar ratio changing from 0 to 35). The inset photographs show the corresponding fluorescence change (left: 2.0 μM TATPE; right: 2.0 μM TATPE and 70.0 μM Q[7]) illuminated at 365 nm using a UV lamp at 25 °C.

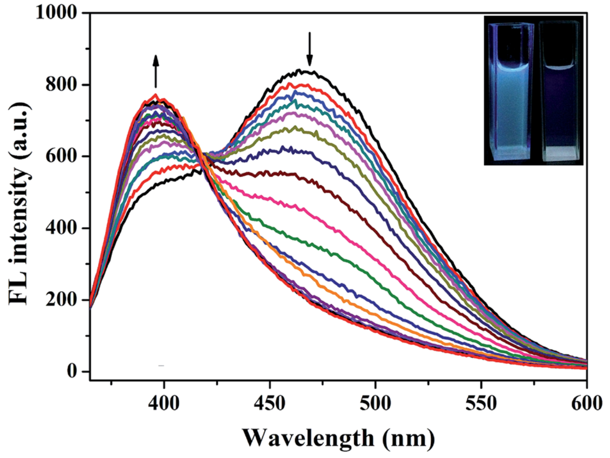


Fig. 4 Fluorescence spectra of a solution of TATPE (2.0 μM) and Q[7] (70.0 μM) upon addition of Ada in H_2O at 25 °C with excitation of 330 nm (the Ada/Q[7] molar ratio changing from 0 to 38). The inset photographs show the corresponding fluorescence change (left: 2.0 μM TATPE and 70.0 μM Q[7]; right: 2.0 μM TATPE, 70.0 μM Q[7], and 70.0 μM Ada) illuminated at 365 nm using a UV lamp at 25 °C.

solution. Moreover, the fluorescence change yielded by the addition of Ada could also be visualized by the naked eye under a 365 nm lamp, Fig. 4.

In summary, an AIE-active host–guest system was successfully constructed between Q[7] and quaternary ammonium-modified tetraphenylethene derivative TATPE, representing the first example of AIE-active host–guest complex formed between Q[7] and TATPE. This host–guest complex exhibits AIE nature, resulting in strong fluorescence in dilute solution due to the restriction of the intramolecular rotation of the phenyl moieties of TAPET upon the addition of Q[7]. Moreover, addition of competitive guest 1-adamantanamine hydrochloride leads to effective dissociation of the host–guest complex Q[7]–TATPE and turns the fluorescence emission off. The present result is helpful for the future design and construction of host–guest systems with AIE activity with application potentials.

Experimental section

General remarks

All reagents and solvents were obtained from commercial sources without further purification. The compounds of **1–3** were prepared according to the literature procedure.[8g,12]

Measurements

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer in D_2O and DMSO-d_6. Steady-state fluorescence spectroscopic studies were performed on an F4500 (Hitachi). MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analysis was performed on an Elementar Vavio El III. Titration experiments were carried out on a NANO ITC SV from Ta Inc. at 25 °C. TEM images were taken on a JEM-100CX II (JEOL Ltd., Japan) electron microscope operated at 100 kV.

Synthetic procedures

Preparation of 4,4′,4″,4‴-(ethene-1,1,2,2-tetrayl)tetraphenol (1). Under a nitrogen atmosphere, Zn powder (1.6 g, 25.0 mmol) was dispersed in dry tetrahydrofuran (40.0 mL). The mixture was cooled to 0 °C and $TiCl_4$ (1.7 mL, 15.0 mmol) was slowly added while maintaining the temperature below 10 °C. The mixture was warmed to room temperature for 0.5 h. After cooling the mixture to 0 °C, the solution of *p*-hydroxyl diphenyl ketone (0.50 g, 2.5 mmol) in dry tetrahydrofuran (15.0 mL) was added slowly. The reaction mixture was heated to reflux for 10 h and quenched with 10% K_2CO_3 aqueous solution, then extracted with CH_2Cl_2. The organic layer was collected and concentrated. The residue was purified by flash column chromatography on silica gel using *n*-hexane/CH_2Cl_2/acetone = 20 : 5 : 1 as eluent, affording 0.31 g of target compound as a white solid, 31%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ (ppm): 8.93 (s, 4H), 7.06 (d, 8H), 6.47 (d, 8H).

Preparation of 1,1,2,2-tetrakis[4-(2-bromoethoxy)phenyl]-ethene (2). To a 250 mL flask containing anhydrous potassium carbonate (0.14 g, 1.0 mmol), compound **1** (0.20 g, 0.50 mmol) in dry DMF (100.0 mL) together with 1,2-dibromoethane (3.7 g, 20.0 mmol) was added at 50 °C. The reaction mixture was stirred for 48 h. After the solid was filtered off, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 as eluent to afford 0.35 g of product as a purple solid, 85%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ (ppm): 6.87 (d, $J = 8.0$ Hz, 8H), 6.72 (d, $J = 8.0$ Hz, 8H), 4.23 (t, $J = 12.0$ Hz, 8H), 3.75 (t, $J = 12.0$ Hz, 8H).

Preparation of 1,1,2,2-tetrakis{2-[2-(*N*,*N*,*N*-trimethylammonium)-ethyoxyl]phenyl}-tetraphenylethene bromide (3). Compound **2** (0.25 g, 0.30 mmol) and trimethylamine (33% in ethanol, 6.50 mL, 25.1 mmol) were added to ethanol (50.0 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation and deionized water (20.0 mL) was added. After filtration, a clear solution was obtained. Then water was removed by evaporation. The residue was washed thoroughly with diethyl ether, giving the water soluble product **3** with the yield of 0.28 g, 88%. ^{1}H NMR (400 MHz, D_2O, 25 °C) δ (ppm): 6.96 (d, $J = 8.0$ Hz, 8H), 6.69 (d, $J = 8.0$ Hz, 8H), 4.31 (t, $J = 12.0$ Hz, 8H), 3.66 (t, $J = 12.0$ Hz, 8H), 3.10 (s, 36H). MS calcd for $C_{60}H_{58}N_4O_4Br_4$: 1218.74; found: *m*/*z* 1219.53. Anal. calcd for $C_{46}H_{68}N_4O_4Br_4$: C, 52.09; H, 6.46; N, 5.28; found C, 53.14; H, 6.38; N, 5.19.

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