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Host-guest complexation induced emission: a pillar[6]arene-based complex with intense fluorescence in dilute solution

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A host-guest inclusion complex was constructed from a water-soluble pillar[6]arene and a tetraphenylethene derivative in water and it exhibited strong fluorescence in 10 dilute solution.

Many organic luminophores exhibit high fluorescence efficiency in dilute solution but suffer from an aggregation-caused quenching (ACQ)¹ effect in the condensed phase. The concentration-quenching effect was caused by the formation of 15 sandwich-shaped excimers and exciplexes aided by the collisional interactions between the aromatic molecules in the excited and ground states. To temper the ACQ effect, many efforts have been made to study the aggregation effect on the optical properties of organic dyes.

- In 2001, a phenomenon of aggregation-induced emission $(AIE)^2$ was observed by Tang *et al* in some propeller-like molecules, such as tetraphenylethene $(TPE)^3$ and hexaphenylsilole. These luminogens are nonemissive in good solvents, but become highly luminescent in the aggregated state.
- ²⁵ Restriction of intramolecular rotation (RIR) in the aggregates has been identified as a main cause for the AIE effect. In solution, the active intramolecular rotation of the phenyl rings of AIE molecules consumes energy. However, in the aggregated state, such motion is restricted, which blocks the nonradiative pathway ³⁰ and activates radiative decay. Besides, the emission intensities of
- AIE luminogens increased *via* RIR methodologies, such as increasing the solvent viscosity, lowering the temperature, applying high pressure, *etc.*² The essence of RIR mechanism is conformational planarity and structural rigidity of AIE molecules.
- ³⁵ Many new AIE luminogens have been developed based on the RIR mechanism, and applied as functional materials, especially as chemosensors, bioprobes, and solid-state emitters.²
- AIE is exactly opposite to the ACQ effect. In comparison to the AIE effect which permits the use of concentrated solutions of ⁴⁰ luminogens and their aggregate suspensions in aqueous media for sensing applications, the traditional sensors work based on the ACQ effect of dilute solutions of conventional luminophores. How to make AIE molecules more emissive in dilute solution so that AIE molecules can act as chemosensors not only in the ⁴⁵ aggregated state but also in dilute solution? This is a challenging
- mission for chemists. A supramolecular approach based on host– guest chemistry can be a unique one to resolve this problem. To

achieve this goal, two prerequisites are usually demanded: one is that the available TPE substances exhibit no fluorescence in ⁵⁰ dilute solution, and the other is that a host with suitable binding sites and cavity can capture the TPE molecules.

Pillararenes^{4,5} are a new generation of macrocyclic hosts for supramolecular chemistry after crown ethers, cyclodextrins, calixarenes, and cucurbiturils.^{6,7} Their repeating units are ⁵⁵ connected by methylene bridges at the *para*-positions, forming a special rigid pillar-like architecture. The unique structures and easy functionalization of pillararenes have endowed them with outstanding abilities to selectively bind different kinds of guests and provided a useful platform for the construction of various ⁶⁰ interesting supramolecular systems.^{4,5}



Scheme 1. Compounds used in this study and the cartoon representation of the formation of the luminescent supramolecular inclusion complex and its application in the detection of paraquat.

- ⁶⁵ On the basis of the above analyses, the utilization of the recognition of water-soluble pillar[6]arene **WP6**⁸ to TPE derivatives can be a good method to investigate host–guest complexation induced emission (Scheme 1). Herein, we report a simple strategy, based on the host–guest complexation between
- 70 WP6 and a TPE derivative 1, to tune the emission behaviour of 1 in dilute aqueous solution. The spontaneously formed [2]pseudorotaxane units efficiently restricted the intramolecular rotation and the non-radiative relaxation channel, thereby resulting in the strong emission of 1 in dilute solution.
- ⁷⁵ Furthermore, the complex between **WP6** and **1** served as a fluorescence "turn-off" probe to detect paraquat because of the competitive binding between **WP6** and two guest molecules (Scheme 1).

WP6 was prepared according to our previous work.^{8a} 80 Compound 1 was prepared according to a previously reported

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method9 and characterized by NMR and electrospray ionization mass spectrometry (Figs. S1-S3, ESI⁺). Similarly, model compound 2 was also prepared.

- Firstly, ¹H NMR spectroscopy was carried out to investigate 5 the host-guest complexation between WP6 and 1 (Fig. S9, ESI⁺). The proton NMR spectra of 1, WP6, and an equimolar mixture of WP6 and 1 showed that this complexation system is fast exchange on the proton NMR time scale. Significant chemical shift changes were observed for some protons on 1 and WP6 10 after complexation (Fig. S9, spectra a-c, ESI⁺). Upfield shifts
- were observed for H_1-H_4 and H_9 of 1. Downfield shifts of the aromatic protons H_a of WP6 were observed. From the 2D NOESY spectrum of a mixture of 10.0 mM WP6 and 1 in D₂O, correlations were observed between protons H₁-H₄ and H₉ of 1
- 15 and proton H_a on WP6, suggesting that alkyl group of 1 was threaded into the cavity of WP6. Therefore, we concluded the formation of the inclusion complex between WP6 and 1 in water (Fig. S10, ESI[†]). The proton NMR spectrum of an equimolar (10.0 mM) D₂O solution of WP6 with 2 was also investigated 20 and similar complexation-induced chemical shift changes were observed. The ability of 2 to form a 1:1 complex with WP6 was assessed by ¹H NMR titration of 2 into WP6 in water and the association constant (K_a) of WP6 \supset 2 was calculated to be (3.22 ± $0.26) \times 10^3 \text{ M}^{-1}$ in water using a nonlinear curve-fitting analysis 25 (Figs. S13-S15, ESI[†]).

Encouraged by the above-mentioned results, we envisioned that 1 might exhibit the strong emission by the addition of WP6, because the intramolecular rotation of the phenyl rings of 1 will be inhibited by the formation of [2]pseudorotaxane units. The $_{30}$ fluorescence properties of 2.00 μ M 1 in the absence or presence of WP6 in water were investigated (Fig. 1). The intramolecular rotation of phenyl rings of 1 may induce the efficient nonradiative annihilation process and thus 1 is nearly nonemissive in water. However, upon the addition of WP6, the rotation of phenyl rings 35 of 1 is restricted. Therefore, the fluorescence intensity increased remarkably. The change of the emission intensities nearly became constant when 32.0 µM WP6 were added, and an approximate 20-fold fluorescence enhancement was observed. In addition, such WP6-induced large fluorescence change of 1 was clearly

40 perceived by naked eye. When 1 was excited at 365 nm using a UV lamp in the presence of 32.0 µM WP6, a strong cyan fluorescence appeared, further supporting the proposed mechanism.

On account of the much higher binding constant of 45 WP6 \supset paraquat $(1.02 \times 10^8 \text{ M}^{-1})^{8a}$ than that of WP6 \supset 2, we further investigate the fluorescence sensing of the inclusion complex between WP6 and 1 for paraquat. Fluorescence titration of the inclusion complex with paraquat was carried out at room temperature in water. As shown in Fig. 2, the significant

- 50 quenching of the fluorescence intensity was found upon the gradual addition of paraquat. It means that in the presence of paraquat, compound 1 slipped out of the cavity of WP6 and WP6 was rethreaded by paraquat. The underlying optical change was ascribed to the formation of a more stable complex
- 55 WP6 paraquat. Therefore, compound 1 became nearly nonemissive again, which is a typical phenomenon of AIE in dilute solution. Moreover, the "turn-off" fluorescence change produced by the addition of paraquat was easily visualized by the

naked eye using a simple UV-lamp.



Fig. 1 Fluorescence spectral changes of 1 (2.00 µM) upon addition of **WP6** (0.00–16.0 equiv) in water ($\lambda_{ex} = 330$ nm, $\lambda_{em} = 490$ nm; slits, 5 nm/5 nm). The inset photographs shows the corresponding fluorescence changes (left: 2.00 µM 1; right: 2.00 µM 1 and 32.0 µM WP6) upon 65 excitation at 365 nm using a UV lamp at 298 K.



Fig. 2 The quench of the fluorescence of a solution of WP6 (32.0 μ M) and 1 (2.00 μ M) upon the titration with paraquat (0.00–160 μ M) in water ($\lambda_{ex} = 330$ nm, $\lambda_{em} = 490$ nm; slits, 5 nm/5 nm). The inset photographs 70 shows the corresponding fluorescence changes (left: 2.00 µM 1 and 32.0 μM WP6; right: 2.00 μM 1, 32.0 μM WP6, and 160 μM paraquat) upon excitation at 365 nm using a UV lamp at 298 K.



Fig. 3 TEM images: (a) TEM image of 1; (b) enlarged TEM image of (a); 75 (c) cartoon representation of the structure of micelles formed by 1; (d) TEM image of the inclusion complex between WP6 and 1; (e) enlarged TEM image of (d); (f) cartoon representation of the formation of the superstructure from 1 and WP6.

After establishing the new host-guest recognition motif in ⁸⁰ water, we further investigate the self-assembly behaviors of 1 and the complex between WP6 and 1. Compound 1 is an amphiphilic molecule which contains the tetraphenylethene unit as the hydrophobic part and four *n*-butyltrimethyl ammonium bromide units as the hydrophilic part. An aqueous solution of 1 was s prepared with a concentration of 1.00×10^{-4} M. According to transmission electron microscopy (TEM), spherical micelles were

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observed with a diameter of \sim 300 nm (Figs. 3a and 3b). These micelles have a regular spherical morphology. Interestingly, upon addition of 4.00 equiv of **WP6**, wheel-like structures with a diameter of \sim 200 nm were observed (Figs. 3d and 3e), drastically

- s different from the micelles formed by 1 alone. The self-assembly process might be that WP6 binds 1 to form a host-guest complex, which is considered as a new amphiphilic supramolecule. The aromatic stacking between the complexes and electrostatic interactions between the quaternary ammonium groups and ¹⁰ carboxylate groups contribute to the generation of wheel-like structures and account for the stability of the resulting
- architectures (Fig. 3f).

In summary, we prepared a host–guest complex between water-soluble pillar[6]arene **WP6** and tetraphenylethene ¹⁵ derivative **1**. The intramolecular rotation of the phenyl rings of **1** were hampered upon the addition of **WP6**, so the complex emits strong fluorescence in dilute solution. This host–guest complex was used as a novel detecting material to probe paraquat because of the competitive host–guest complexation. In addition, the

²⁰ complex between WP6 and 1 self-assembled into interesting wheel-like structures in water, which were different from the small spherical micelles formed by the amphiphilic molecule 1 alone. We expect that this design strategy of host-guest complexation induced emission will provide a sophisticated ²⁵ pathway for guiding the future design of supramolecular functional materials.

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Notes and references

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5 Text:

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