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# Water-soluble host-guest fluorescent systems based on fluorophores and cucurbiturils with AIE or ACQ effects



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## ABSTRACT

Tetraphenylethene (TPE) and pyrene as typical aggregation induced emission (AIE) and aggregation caused emission quenching (ACQ) functional groups were utilized to design and synthesize water-soluble fluorescent molecules. Through a self-assembly process with cucurbituril hosts, a completed opposite fluorescence response was observed for TPE and pyrene based fluorescent molecules. The assembly processes were verified by <sup>1</sup>H NMR, UV–Vis, fluorescence spectroscopy. The mechanism was then studied and the aggregation-induced fluorescence change was concluded. These new host-guest supramolecular fluorescence systems can be used as fluorescence sensors or switches, expanding the application of fluorescence systems in biological imaging.

# 1. Introduction

The development of luminescent materials with advanced properties is of great importance to satisfy the need of modern society and technology. The fluorescent molecules in the concentrated solution or aggregated state, are inclined to aggregate to minimize the contact of the environmental medium through strong hydrophobic-hydrophobic or  $\pi$ - $\pi$ stacking interactions [1]. These interactions promote the formation of closed packed excimers or exciplexes, through which the excitation energy is relaxed non-radiatively [2]. This notorious and harmful phenomenon is known as aggregation-caused quenching (ACQ) of light emission in the condensed phase [3-11]. In the past decades, great efforts have been made to tackle the ubiquitous ACQ effect to utilize fluorophores as a molecularly dissolved or dispersed state in dilute solution. Different chemical, physical or engineering methods have been applied to isolate the molecules from each other, and thus minimize the ACQ effect [12–16]. In 2001, Tang group discovered such a system, in which luminogen aggregation played a constructive, instead of destructive, role in the light-emitting process [17]. A series of molecules such as tetraphenylethene (TPE) and hexaphenylsilole (HPS) were found non-luminescent in the solution state but emissive in the aggregate state. They coined "aggregation induced emission" (AIE) for this novel

phenomenon [18-22]. The novel AIE effect is exactly opposite to the traditional ACQ effect. It permits the use of dye solutions with any concentrations for bioassays and enables the development of "turn on" or "light up" nanosensors by taking advantage of luminogenic aggregation, thus exploring their technological applications as chemosensors, bio-probes and solid-state emitters [23-34]. Since the concept of AIE was proposed, AIE luminogens have been judiciously utilized as sensitive and selective chemosensors and bio-probes of turn-on type by incorporating them into chemical and biological systems as labels via chemical bonding or physical mixing. Attracted by the intriguing phenomenon and its fascinating perspectives, several mechanisms have been proposed for the AIE effects. The restriction of intramolecular rotation (RIR) of the peripheral phenyl rings in the aggregate state is the main cause of the AIE effect [35-40]. When the rotation of the phenyl ring in the molecule is limited, the energy in the excited state can only be dissipated through radiation, that is, fluorescence is generated. Thus, it can be naturally associated with the supramolecular self-assembly strategy especially the supramolecular host and guest chemistry which could be taken advantage of to affect the aggregate state and the rotation of the molecular moieties [41].

Herein, we designed and synthesized two organic luminescence molecules that have totally different fluorescence behaviors. One is a

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Fig. 1. Chemical structures of the guest molecule T1, P1 and the host CB[*n*], and schematic representation of the formation of T1\_CB[*n*], P1\_CB[*n*] supramolecular assembly structures and fluorescence enhancement and reduction. The images inserted are the fluorescence changes at endpoints of T1 and P1 in cucurbit [7]uril titration under 365 nm UV-light.



**Fig. 2.** Synthesis of **T1** and **P1**. a: CH<sub>2</sub>Cl<sub>2</sub>, Br<sub>2</sub>, room temperature (r.t.),12 h; b: methyl acrylate, Pd(OAc)<sub>2</sub>, 1,3-Bis(diphenylphosphino)propane, Et<sub>3</sub>N, *N*,*N*-Dime-thylformamide (DMF), 110 °C, 72 h; c: trifluoroacetic acid, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 1 h; d: NaOH, r.t.; e: methyl acrylate, Pd(OAc)<sub>2</sub>, 1,3-Bis(diphenylphosphino)propane, Et<sub>3</sub>N, DMF, 110 °C, 72 h; f: trifluoroacetic acid, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 1 h; g: NaOH, r.t.

TPE based molecule modified by hydrophilic carboxylate groups (**T1**) which is a typical AIE fluorescent molecule. The other one is a pyrene based molecule containing carboxylate groups (**P1**) which is a typical ACQ fluorescent molecule. Both of these two fluorescent molecules are water-soluble. Then the cucurbit[*n*]uril (CB[*n*]) as a host was utilized to assemble with **T1** and **P1**. The supramolecular assembly strategy is used to combine the fluorescent guest molecules with different host molecules and obtain different luminescent assemblies through non-covalent interactions. The photophysical properties of these assemblies were then studied. Very interestingly, the **T1** and **P1** show totally different fluorescence behaviors after assembly with CB[*n*] (Fig. 1). **T1** shows significant fluorescence enhancement while **P1** shows a fluorescence reduction. It is of great significance to study the mechanisms of aggregation-induced luminescence properties.

### 2. Experimental section

#### 2.1. Materials

1,3-Bis(diphenylphosphino)propane, 1,3,6,8-tetrabromopyrene, Pd  $(OAc)_2$  and other chemicals were all purchased from Energy Chemical Company and used as received without further purification. Reagents for synthesis were purchased commercially from Adamas Reagent and used without further purification. Cucurbit [7]uril and cucurbit [8]uril were purchased from Sigma. Unless otherwise specified, all aqueous solutions were prepared with Milli-Q water.

# 2.2. Instruments and methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were performed on 400 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. Unless otherwise indicated, column chromatography was carried out on silica gel (200–300 mesh). The UV–vis absorbance was measured by UV spectrometer (HITACHI, 3900). Fluorescence spectra were recorded on fluorescence spectrometer (HITACHI, F-2700).

#### 2.3. Synthesis

The synthesis of **T1** and **P1** was presented in Fig. 2. **T1** and **P1** were obtained through simple quantitative neutralization of compounds **4** or **7**. The deprotonation of the carboxylic acid groups leads to carboxylate groups which bring good water-solubility of **T1** and **P1**. The synthesis detailed experimental procedure was presented below:

**Compound 2** was synthesized from TPE following the reported literature procedure [42]. TPE (5.0 g, 15.2 mmol) was dissolved in 300 mL CH<sub>2</sub>Cl<sub>2</sub>. 10 mL Br<sub>2</sub> was added dropwise at room temperature. The mixture was stirred at room temperature for 12 h, then the reaction was quenched by ethanol and saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. After neutralized by NaOH to pH = 7, the mixture was washed by CH<sub>2</sub>Cl<sub>2</sub>, the organic layer was dried by sodium sulfate. After filtered and concentrated, the product was purified by column chromatography (pure petroleum) to yield a white powder (9.3 g, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.25 (d, *J* = 8 Hz, 8H), 6.84 (d, *J* = 8 Hz, 8H).

**Compound 3:** Compound **2** (1.0 g, 1.6 mmol), methyl acrylate (2.0 g, 15.6 mmol), Pd(OAc)<sub>2</sub> (75.0 mg, 0.3 mmol), 1,3-bis(diphenylphosphino)propane (**DPPP**) (260.0 mg, 0.6 mmol) and Et<sub>3</sub>N (1.0 mL, 6.2 mmol) were added into 5 mL of dry DMF. The mixture was stirred at 110 °C under N<sub>2</sub> atmosphere for 72 h. When the reaction was complete as determined by the disappearance of the **2**, 20 mL of water was charged. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The organic phases were then dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate and petroleum ether as eluent (1:10 by volume) [43]. A yellow



Fig. 3. Absorption and fluorescence spectral changes of (a), (b) T1 (0.01 mM) and (c), (d) P1 (0.01 mM) upon gradual addition of CB [7] in H<sub>2</sub>O.

solid was obtained in a yield of 45%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (d, *J* = 15.9 Hz, 4H), 7.01 (s, 8H), 6.99 (s, 8H), 6.28 (d, *J* = 15.6 Hz, 4H), 1.51 (s, 36H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.25, 144.65, 142.87, 141.09, 133.41, 131.76, 127.60, 120.29, 80.48, 28.19. HRMS (MALDI) *m/z*: [M<sup>+</sup>] calcd. for C<sub>54</sub>H<sub>60</sub>O<sub>8</sub> 836.4288; found 836.4286.

**Compound 4**: Compound **3** (100.0 mg) was dissolved in 2 mL CH<sub>2</sub>Cl<sub>2</sub>. Trifluoroacetic acid (TFA) (2 mL) was added dropwise. The mixture was then stirred at room temperature for 30 min. After removing the excess acid by evaporation, the mixture was washed by CH<sub>2</sub>Cl<sub>2</sub> to yield a yellow powder (99%).<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.34 (s, 4H), 7.50 (s, 4H), 7.47 (d, *J* = 8.8 Hz, 8H), 7.02 (d, *J* = 8 Hz, 8H), 6.45 (d, *J* = 16 Hz, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.95, 144.98, 143.74, 141.19, 133.36, 131.80, 128.45, 119.79. HRMS (MALDI) *m/z*: [M<sup>+</sup>] calcd. for C<sub>38</sub>H<sub>28</sub>O<sub>8</sub> 612.1784; found 612.1787.

Compound 6: Compound 5 (1.0 g, 1.9 mmol), methyl acrylate (2.5 g, 19.3 mmol), Pd(OAc)<sub>2</sub> (90.0 mg, 0.4 mmol), 1,3-bis(diphenylphosphino)propane (DPPP) (320.0 mg, 0.8 mmol) and Et<sub>3</sub>N (1.1 mL, 7.7 mmol) were added into 8 mL of dry dimethylformamide (DMF). The mixture was stirred for 72 h at 110 °C under N2 atmosphere. When the reaction was complete as determined by the disappearance of 5, 20 mL of water was charged, and the solution was extracted with  $CH_2Cl_2$  (3  $\times$ 20 mL). The organic phases were then dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200-300 mesh) with a mixture of ethyl acetate and petroleum ether as eluent (1:10 by volume). An orange-red solid was obtained with a yield of 48%. <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{CDCl}_3)$ :  $\delta$  8.69 (d, J = 16 Hz, 4H), 8.56 (s, 4H), 8.50 (s, 2H), 6.69 (d, J = 16 Hz, 4H), 1.63 (s, 36H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 165.98, 139.69, 130.26, 130.14, 125.49, 124.21, 124.14, 123.37, 81.06, 28.29. HRMS (MALDI) *m/z*: [M<sup>+</sup>] calcd. for C<sub>44</sub>H<sub>50</sub>O<sub>8</sub> 706.3506; found 706.3507.

**Compound 7**: Compound 6 (100.0 mg) was dissolved in 2 mL  $CH_2Cl_2$ , TFA (2 mL) was added dropwise. The mixture was stirred at room temperature for 30 min. After removing excess acid by evaporation, the mixture was washed by  $CH_2Cl_2$  to yield a red powder (99%).<sup>1</sup>H

NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.94 (s, 4H), 8.69 (d, J = 3.6 Hz, 4H), 8.65 (s, 4H), 7.16 (s, 2H), 7.12 (s, 4H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  175.58, 164.55, 137.23, 129.41, 128.67, 128.03, 126.39, 122.51. HRMS (EI) m/z: [M<sup>+</sup>] calcd. for C<sub>28</sub>H<sub>18</sub>O<sub>8</sub> 482.1002; found 482.1003.

# 3. Results and discussion

Considering the good water solubility and the intrinsic fluorescent characteristic of T1 and P1. The photophysical properties of the fluorescent molecules themselves and the self-assemblies would be very interesting. UV-vis and fluorescence spectroscopy were then employed to investigate the photophysical properties of the guest molecules and the as-formed self-assembled structures. T1 is a typical AIE fluorescent molecule, while P1 is a typical ACQ fluorescent molecule. T1 showed a maximum absorption wavelength of 300 nm and a fluorescence wavelength of 540 nm. A titration experiment was then employed to study the change of the photophysical properties of the self-assembled structures. As shown in Fig. 3a, the addition of CB [7] induced a remarkable blue shift and hypochromism of the absorption. Besides, an obvious enhancement of the fluorescence (10 times increase) was observed (Fig. 3b). The quantum yield increased from 0.7% to 8.5%. This indicated that the addition of CB [7] led to an aggregation of T1. The hydrophilic carboxylate groups were encapsulated into the cavity of the CB [7] in  $H_2O$ . As a result, the aggregation of T1 containing TPE as the classical AIE moiety occurred which led to the fluorescence enhancement. Besides, the self-assembly between the CB [7] and T1 limits the intramolecular motion of the "arms" of T1, and the energy in the excited state can only be dissipated in the form of fluorescence. For P1 which is a classic ACQ molecule with a maximum absorption wavelength of 440 nm and fluorescence wavelength of 480 nm, the variation tendency of UV-vis spectra is similar. A remarkable blue shift and hypochromism of the absorption occurred with the addition of CB [7] (Fig. 3c). However, an obvious quenching in the fluorescence was observed (Fig. 3d) which is in sharp contrast with T1. The quantum yield dramatically reduced with the addition of CB [7], from 37.7% to 0.3%. As an ACQ molecule,



Fig. 4. Absorption and fluorescence spectral changes of (a), (b) T1 (0.01 mM) and (c), (d) P1 (0.01 mM) upon gradual addition of CB [8] in H<sub>2</sub>O.



Fig. 5. <sup>1</sup>H NMR spectra: (a) T1 (3.0 mM) in D<sub>2</sub>O in the presence of 0, 2.0, 4.0, 10.0 equiv. of CB [7] at 25 °C; (b) P1 (1.0 mM) in D<sub>2</sub>O in the presence of 0, 2.0, 4.0, 10.0 equiv. of CB [7] at 25 °C.

the aggregation caused by the self-assembly of the CB [7] quenched the fluorescence of **P1** in H<sub>2</sub>O. To further confirmed this speculation, the larger CB [8] as a host molecule was also tested. The CB [8] shows very similar influence to **T1** or **P1** compared with CB [7]. As shown in Fig. 4, the introduction of CB [8] led to an increase in the fluorescence of **T1** and a decrease of **P1**. The changes in the UV–vis spectra are also similar to the CB [7]. These results indicated that the self-assembly modes of CB

[7] and CB [8] to the **T1** and **P1** are similar. The CB [7] and CB [8] could form host-guest self-assembly structures with the carboxylate in **T1** and **P1**. The hydrophobic peripheries of CB [7] and CB [8] induced the aggregation of these fluorescent molecules. Since the well-known AIE phenomenon of **TPE** and ACQ effect of pyrene, the aggregation brings a completely opposite tendency in the fluorescence.

To clarify the self-assembly modes of the CB[n] and the fluorescent

guests, we also performed the <sup>1</sup>H NMR titration. As shown in Fig. 5, with the increase of the CB [7], the proton signals of **T1** and **P1** decreased gradually and disappeared in the end. No obvious chemical shift changes were observed both for **T1** and **P1**. Above all, these results indicated that the CB[n] as hosts encapsulated only the carboxylate ending parts and inhibited the contact of hydrophilic carboxylate groups to the H<sub>2</sub>O and then induced the aggregation. The opposite fluorescence characteristic of AIE for **T1** and ACQ for **P1** led to totally different fluorescence response.

## 4. Conclusions

Two water-soluble fluorescent molecules containing **TPE** as a typical AIE functional group (**T1**) and pyrene as ACQ functional group (**P1**) were synthesized. The self-assembly process between the CB[*n*] as hosts and the fluorescent molecules as guests were then studied. Interestingly, the **T1** and **P1** showed a completed opposite fluorescence response to the CB[*n*]. The mechanism was then studied and the aggregation-induced fluorescence change was concluded. These novel host-guest supramolecular fluorescent systems may act as fluorescence sensors or switches. The different fluorescence response and the different luminous mechanism may open up a new way for the design of the fluorescent probes and extend the application of these fluorescent systems in bio-imaging.

#### Author statement

We declare that this manuscript entitled "Water-Soluble Host-Guest Fluorescent Systems Based on Fluorophores and Cucurbiturils with AIE or ACQ Effects" is original, has not been published before and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We understand that the Corresponding Author is the sole contact for the Editorial process. He is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

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