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# Triptycene-scaffolded tetraphenylethylenes with irregular temperaturedependence AIE



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#### ABSTRACT

A series of new tetraphenylethylene monomer, dimer and three-dimensional trimer based triptycenebridged triphenylethenes has been constructed. Their structures were clearly confirmed and the irregular fluorescent behaviors at different temperatures and solvents were investigated. Results showed the new tetraphenylethylenes performed remarkable aggregation-induced emission (AIE) properties and the emission intensities are dependent on temperature and viscosity. Compared with the model tetraphenylethylene without connecting triphenylethylene, the fluorescence quantum yields of the titled triptycenescaffolded tetraphenylethylenes in aggregation are greater than tetraphenylethylene and increased as the increasing of the triphenylethylene units.

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## Introduction

Since aggregation-induced emission (AIE) phenomenon was reported originally in 2001 by Tang and coworkers [1], AIE behaviors have attracted intense interest in many researchers, as the finding provided a promising method to overcome the limit in the development of luminogenic devices caused by aggregationcaused quenching (ACQ) [2]. Tetraphenylethylene is one of the prototypical AIE molecules. Its excellent emission property in aggregate state and solid state in contrast to fluorescence quenching in dilute solution is attributed to the restriction of intramolecular rotation in solid and aggregate state. tetraphenylethylene derivatives has aroused more and more attention due to the versatile abilities to be conveniently incorporated into various multicomponent assemblies [3]. Nowadays, they have been broadly applied in the self-organization, biosensors [4,5], cellular imaging [6], bioprobes [7,8], and so on. Similarly, another representative phenyl building block, triptycene, is a propeller-shaped molecule composed of three 120°-oriented phenylene blades, owning a unique three-dimensional rigid structure [9]. It provides a large free volume around the aromatic skeleton. Due to the arene subunits of triptycene are easy to be further functionalized, triptycene and its derivatives have been studied systematically in the fields of molecular machines [10,11], material chemistry [12–14], and supramolecular chemistry [15]. However, their applications in fluorescent materials are confined because of the non-fluorescent characteristics whether in solvents or in solid state.

In view of the above consideration, we manage to graft different amount of triphenylethylene units into the molecular scaffold of triptycene, in which triphenylethylenes share the benzene rings of the triptycene to construct a series of novel tetraphenylethylene monomer, dimer and three-dimensional trimer. This design considers the atomic economy and the complimentary characteristics of the two blocks, including that the rigid structure of triptycene, which can make intramolecular rotation blocked and enhance AIE performance of triphenylethylenes. Our results show that the triptycene-bonded triphenylethylene presents significant AIE phenomenon and the fluorescence intensities depend on temperature and viscosity. Besides, the fluorescence quantum yields of the new tetraphenylethylene derivatives increase with the increasing of triphenylethylene blocks and are all greater than tetraphenylethylene in aggregation. We hope this design could provide a new choice in the application of solid fluorescent materials based triptycene.

## **Results and discussion**

## Synthesis

The synthetic routes of the three target compounds were shown in Scheme 1. Starting from 1-bromo-1,2,2-triphenylethylene, **4** was prepared according to modified literature procedures [16]. 2lodonetriptycene,2,6-diiodotriptycene and 2,6,14-triiodotrip-



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**Scheme1.** Reagents and conditions: (a) bis(pinacolato)diboron, (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>, PPh<sub>3</sub>, KOPh, toluene, 70 °C, 13 h; (b) 2-iodotriptycene [17], Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF, H<sub>2</sub>O; (c) 2,6-diiodotriptycene [17], Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF, H<sub>2</sub>O, (d) 2,6,14-triiodotriptycene [17], Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF, H<sub>2</sub>O.

tycene were prepared according to previous work [17]. Model tetraphenylethylene without any substituents (**0**) was obtained as the method reported previously [18]. Target compounds **1**, **2** and **3** were prepared via Suzuki coupling reaction, respectively (Supporting Information).

#### Aggregation-induced emission properties

We first investigated the AIE properties of compound 1, 2 and 3 in the H<sub>2</sub>O/THF mixed solution, respectively. Results indicated that all the three compounds exhibited typical aggregation-induced emission (AIE) properties, as shown in Fig. 1. The schematic diagram of the aggregation-induced emission is shown in Scheme 2. Their fluorescent emission could not be observed in pure THF solvent ( $\lambda_{ex}$  = 320 nm), but gradually increased with the increasing of the water fraction because of the heavy aggregation in the aqueous medium which restricting the intramolecular rotation [19]. Here we choose compound **1** as an example to show their fluorescent performances. In Fig. 1a, we can see that the fluorescence emission intensity of compound **1** ( $\sim$ 2.5 × 10<sup>-5</sup> M) in pure THF was close to 0 ( $\lambda_{ex}$  = 320 nm), but increased slowly with the increasing of the water fraction. When the water fraction increased from 20 vol% to 80 vol%, the fluorescence intensity increased, accordingly. Once it reached 90 vol%, the fluorescence intensity increased observably. The other two compounds exhibited the similar emission phenomenon in H<sub>2</sub>O/THF mixed solution (Fig. 1b and c).

The AIE phenomenon can be clearly observed by the fluorescent images of the three compounds in H<sub>2</sub>O/THF mixed solution with different water fractions, as shown in the insert of Fig. 1. The compound 1 was non-fluorescence when it was dissolved in THF solution excited by 320 nm light. Its emission was turned on when the water fraction reached to 80 vol%. The fluorescence increased observably when the water fraction reached to 90 vol% and accompanied by blue fluorescence, as a result of heavy aggregation in the aqueous medium [19]. The test results of laser light scattering showed that the radius of aggregate particles is around 100 nm, and the particle size distribution is very narrow, which indicates that the solution is stable and no insoluble particles are precipitated out directly (Fig. S11). The other two compounds exhibited the similar performances (Fig. 1b and c). Scanning electron microscopy (SEM) image of compound 3 in H<sub>2</sub>O/THF mixtures (90% and 80% water content) was performed to provide further evidence for the aggregate formation, as shown in Fig. 2 and S12. It can be seen that stacked state has been formed in the mixed solvents and the size of aggregates in 90 vol% H<sub>2</sub>O is larger than that in 80 vol% H<sub>2</sub>O.

The absolute fluorescence quantum yields ( $\Phi_f$ ) of compounds **1**, **2**, **3** and the model compound **0** were determined to be 38.7%, 41.3%, 43.8% and 13.9% in H<sub>2</sub>O/THF (90:10) mixed solution, respectively. It indicated that the fluorescence quantum yields of



**Fig. 1.** (a, b, c) Fluorescence emission spectra and images of compounds **1**, **2** and **3** in H<sub>2</sub>O/THF mixed solution with different water fractions.



Scheme 2. Schematic diagram of aggregation-induced emission.



Fig. 2. SEM image of compound 3 in H<sub>2</sub>O/THF mixtures (90% water content).

the target compounds increased as the increasing of triphenylethylene units and were all greater than model compound tetraphenylethylene ( $\mathbf{0}$ ) without triptycenes (Table 1). This is mainly because the triptycene and tetraphenylethylene are both rigid. As the number of triphenylethylenes increases, rigid structure increases and the molecular size becomes larger. Intramolecular rotation is more restricted; thus, the fluorescence intensity becomes stronger in the order of compound  $\mathbf{0}$ - $\mathbf{3}$ .

The solid fluorescence images of compound **1**, **2** and **3** were showed in Fig. 3. In general, triptycene itself has no fluorescence in solution, aggregation and solid. The fluorescence of triphenylethylene is also relatively weak. However, these tetraphenylethylene derivatives based triptycene and triphenylethylene

#### Table 1

Photophysical properties of compounds  $1{-}3$  and the model compound tetrapheny-lethylene (0) (T: 25  $^\circ\text{C}$ ).

Compound	$\lambda_{ex}/nm$	$\lambda_{\max}^{em}/nm$	$\Phi_{\mathrm{f}}$ (%)
1	320	482	38.7
2	320	479	41.3
3	320	478	43.8
0	320	481	13.9

( $\lambda_{ex}$ : excitation wavelength;  $\lambda_{max}^{em}$ : maximum emission wavelength).



Fig. 3. Solid fluorescence images of compounds 1, 2 and 3 before and after excitation of UV light (320 nm).

presented strong blue fluorescence in solid under the irradiation of UV light ( $\lambda_{ex}$  = 320 nm).

It is noteworthy that the fluorescence emission changes irregularly at different temperatures. The 90 vol% H<sub>2</sub>O/THF mixed solutions of the three compounds  $(2.0 \times 10^{-5} \text{ M})$  were chosen to investigate the temperature effects, respectively (Fig. 4). In general, the lower the temperature, the stronger the fluorescence for tetraphenylethylene [20]. Fig. 4 shows that their emission intensities below room temperature are stronger overall than those at 25 °C, owning to the fact that the intramolecular rotation is limited at low temperature [19]. However, the changes fluctuated as the temperature further drops. From Fig. 4 we can see that the emission intensity first increases gradually with the decreasing of the temperature from 25 °C to 0 °C until it reaches the maximum intensity at 0 °C. After that, their fluorescence intensities decrease dramatically when the temperature below zero and finally keep constant below -5 °C. This irregular temperature-dependence phenomenon was rarely reported in the performance of AIE. There might be several reasons: first is attributed to the reduction of solubility and the



Fig. 4. The fluorescence emission spectra of 90% (V/V)  $H_2O/THF$  mixed solution of compounds 1, 2 and 3 at different temperature.

further limitation of intramolecular rotation as the temperature drops, which makes the fluorescence intensity increases; second is that the relative content of the good solvent, THF increases while the poor solvent, H<sub>2</sub>O decreases gradually in the mixed solution due to the formation of solid "ice", which increases solubility and decreases the fluorescent intensity. In addition, the formation of "ice" may lead to scattering, which make the determining fluorescence intensity decreases, too. Finally, these effects achieve a relative equilibrium and the fluorescence intensity remains unchanged

#### Table 2

The fluorescence emission intensities of compounds **1**, **2**, **3** and tetraphenylethylene (**0**) under different temperature (25 °C, 0 °C) in 90% (V/V)  $H_2O/THF$  mixed solution.

Compound	F (25 °C)	F (0 °C)
0	50	130
1	400	630
2	430	740
3	480	920



Fig. 5. Fluorescence emission spectra and images of compounds 1, 2 and 3, respectively, in glycerol/methanol mixed solution with different glycerol fractions.

Table J
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The fluorescence emission inten-
sities of compounds 1, 2, 3 and 0
under different viscosity (glycerol
fractions = 80%, 90%).

Compound	F <sub>1</sub>	$F_2$
0	45	95
1	290	490
2	350	580
3	440	690

 $F_1$  (glycerol fractions = 80%),  $F_2$  (glycerol fractions = 90%).

at a certain temperature [21]. The fluorescence emission intensities (F) of the three target compounds and the model tetraphenylethylene (**0**) with the same concentration under different temperature in 90% (V/V) H<sub>2</sub>O/THF mixed solution were further compared (Table 2). On the whole, the fluorescence emission intensities of the three target compounds increased as the increasing of the triphenylethylene units under the same temperature and were stronger than that of monomer **0**.

The viscosity effect on emission in the glycerol/methanol (V/V) mixed solution was further checked (Fig. 5). Results showed the emissions of the three target compounds became stronger upon increasing the solution viscosity (glycerol fraction). Their fluorescence emissions  $(3.0 \times 10^{-5} \text{ M})$  first increased gradually with the increasing of the glycerol fraction from 10 vol% to 50 vol%, then increased dramatically from 50 vol% to 60 vol%, and finally reached the most fluorescence emissions at around 90 vol% of glycerol fractions ( $\lambda_{ex}$  = 320 nm). The fluorescent images of the three compounds in glycerol/methanol mixed solution with different glycerol fractions were shown in the inserts of Fig. 5. Their fluorescence intensities were very weak when the glycerol fraction was less than 50 vol% but presented obvious blue fluorescence when the glycerol fraction exceeded 50 vol% under the excitation of UV light ( $\lambda_{ex}$  = 320 nm). Besides, we further studied the fluorescence emission intensities of target compounds and tetraphenylethylene (**0**) with the same concentration under different viscosity in glycerol/methanol (V/V) mixed solution (Table 3). It is also found that the fluorescence emission intensities of target compounds increased as the increasing of the triphenylethylene units under the same viscosity and were all higher than that of monomer **0**.

#### Conclusions

In summary, we have designed and constructed a series of new tetraphenylethylene monomer, dimer and 3D trimer based propeller-shaped triptycene and triphenylethenes. Their various fluorescence performances in solutions, solid state and aggregation were investigated. Results showed that they presented remarkable fluorescence in solid but no fluorescence in THF solvent. Their emissions were turned on when added aqueous medium in the solution, which exhibited the significant AIE characteristics. Their irregular fluorescence behaviors at different temperatures were further examined. The fluorescence quantum yields in aggregation increased as the increasing of the triphenylethylene blocks and were all greater than model compound tetraphenylethylene; the fluorescence emission intensities in solutions became stronger upon increasing the solution viscosity. We hope this research could provide a new choice in the application of solid fluorescent materials based triptycene and triphenylethenes.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2018.12.069.

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