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# A new synthesis protocol for photochromic triarylethenes and their multifunctional derivatives

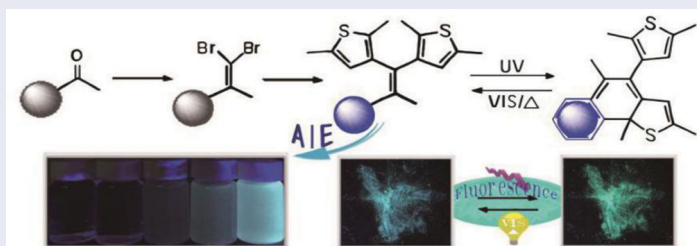
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## ABSTRACT

A synthesis protocol was presented and applied in the preparation of a series of new photochromic triarylethene (TAE) derivatives cherishing bifunctional groups. The titled molecules all perform photochromism in the rare yellow absorption band in both solution and solid. Some of them show classical aggregation-induced emission (AIE) fluorescence properties, and the fluorescence exhibits distinctive photo-controllable performance. The synthesis and design of photochromic triarylethenes could provide a new alternative for achieving solid photochromic and photo-controllable fluorescent materials based on simple structures and convenient synthesis process.

## GRAPHICAL ABSTRACT



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## KEYWORDS

Aggregation-induced emission; fluorescence; photochromism; synthesis; triarylethene

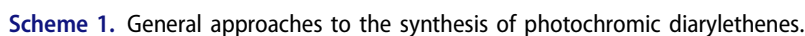
## Introduction

Photochromic diarylethenes play a crucial role in functional materials, which have aroused enormous attention because of their distinctive isomers and unique physical and chemical properties.<sup>[1,2]</sup> Plenty of diarylethene derivatives with high fatigue resistance, good thermal stability, fast response and high quantum efficiency have been extensively studied for versatile applications in information storage, chemical sensors, molecular machines, biological macromolecules, etc.<sup>[3–15]</sup> Masahiro Irie reported the preparation and photochromism of thermally stable diarylethenes in 1988.<sup>[16]</sup> Since then, researchers have developed a variety of preparation methods for different

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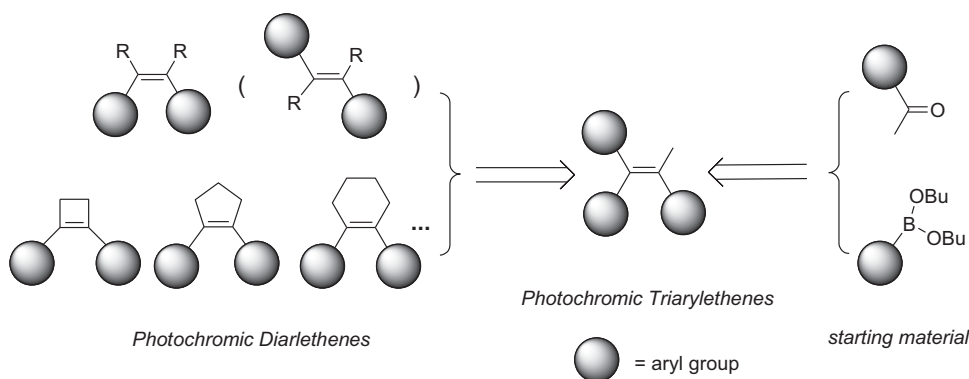
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molecular structures and applications: Fan et al.<sup>[17]</sup> synthesized some analogous cis-trans isomerized diarylethenes from corresponding ketones. Uchida's group used P(OEt)<sub>3</sub> as a catalyst and got the photochromic diarylethenes from thiophene derivatives.<sup>[18]</sup> Apart from these, heterocyclic diarylethenes were obtained by bonding oxamyl with acid chloride,<sup>[19]</sup> and it could be synthesized from acyloin as well.<sup>[20]</sup> It was also an effective way to yield diarylethenes by combining the alkenyl halides and aromatic compounds.<sup>[21–25]</sup> In addition, Lucas and Feringa et al.<sup>[26–30]</sup> developed a series of diarylethenes by McMurry coupling reaction from diketone compounds. Another route to synthesize photochromic diarylethenes was the addition reaction of olefins and alkynes.<sup>[31–34]</sup> Furthermore, Sud<sup>[35]</sup> obtained the diarylethenes through the substitution of the aromatic alkyne compounds, while they were also prepared from ethyl acetoacetate derivatives.<sup>[36–39]</sup> Dehydration of alcohol compounds to obtain olefinic compounds, the diarylethenes were got from pinacol by Dinesh and coworkers in the same way.<sup>[40]</sup> These are, to the best of our knowledge, the most common methods to construct the diarylethene molecules. Thienyl diarylethenes were taken as examples, and the reported synthetic routes of diarylethenes are shown in [Scheme 1](#).

The researches mentioned above have made important contributions in the development and application of photochromic diarylethenes, because they not only constructed a variety of promising functional materials but also were applied in many new fields. However, some molecular designs are defective, for example, there are cis-trans configurations in structural design, which might bring difficulty to the purification of the products. Otherwise, extra rings have to be introduced to fix the ethylene bridges in order to



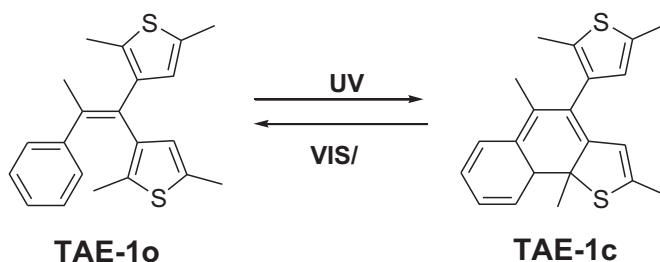
**Scheme 2.** The schematic diagram for the synthesis of triarylethenes.

avoid the unwanted isomers, which will increase extra work in preparation or confining the spatial configuration of the photochromic molecules. These inconveniences in preparation and purification may limit their applications. In view of the above consideration, we manage to design a kind of simple photochromic diarylethene system that fundamentally avoids the production of cis-trans isomers and does not require the extra addition of rings to immobilize ethylene bridge (Scheme 2). Furthermore, considering the practical limitations of fluorescence quenching of common diarylethene in solution and aggregation, diverse functional groups of aggregation-induced emission<sup>[41–51]</sup> have further been introduced to the molecules through the combination of tristyrene (AIE unit) and the diarylethene (photochromic unit) which sharing the same vinyl bridge. Results show that this design is beneficial to the synthesis of asymmetric photochromic molecules. Interestingly, the target compounds perform obvious photochromism and thermal reversibility in both solution and aggregation. Some of them exhibit both optically-controlled fluorescent performance and AIE properties. These compounds are desirable for the applications in solid luminescent materials. This design could provide a new idea for constructing photochromic and fluorescent materials based on simple structures and cyclization mode.

## Results and discussion

### Photochromic behaviors in solution and solid

As expected, all of the three target compounds showed noteworthy photochromic features in both solution and aggregation. Firstly, the photochromic performances of the three heterotriarylethenes (**TAE-1o**, **TAE-2o** and **TAE-3o**) were investigated in solution at room temperature, the photoinduced absorption spectra and corresponding color changes of **TAE-1o** in THF solution were shown in Figure S13(a). The solution of the open-ring isomers is colorless and do not show any optical absorption in the visible light region. While **TAE-1o** turned the rare yellow for photochromic diarylethenes after it was treated with UV light, which was attributed to the formation of the closed-ring isomers by a mechanism of the cyclization<sup>[52]</sup> between the thiophene and benzene at the same side (Scheme 3). The backward reaction took place upon irradiation with more than 400 nm light. **TAE-1o** was chose as an example to show their photochromic



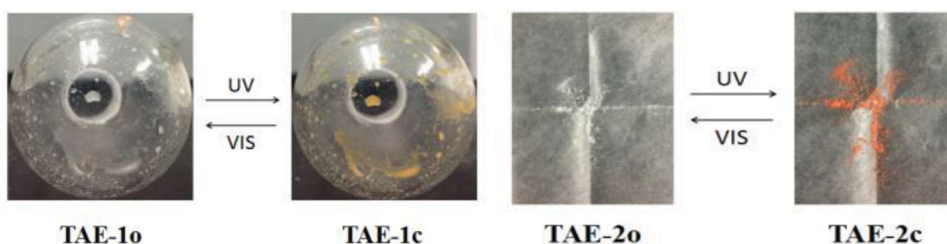
**Scheme 3.** The photochromic reaction of TAE-1.

behaviors. It was clear that upon irradiation with UV light (254 nm), the THF solution of **TAE-1o** turned yellow quickly. Meanwhile, a new absorption peak at 460 nm appeared along with the decrease of the absorption band at around 265 nm, and the photostationary state was achieved after irradiation for 2 min. What's more, a clear isosbestic point was observed at 285 nm, which indicated the reversible two-component photochromic reaction.<sup>[53,54]</sup> Moreover, the yellow solution of the photostationary was bleached entirely when exposed to visible light. The other two compounds exhibited the similar photochromic behaviors (Figure S13(b,c)).

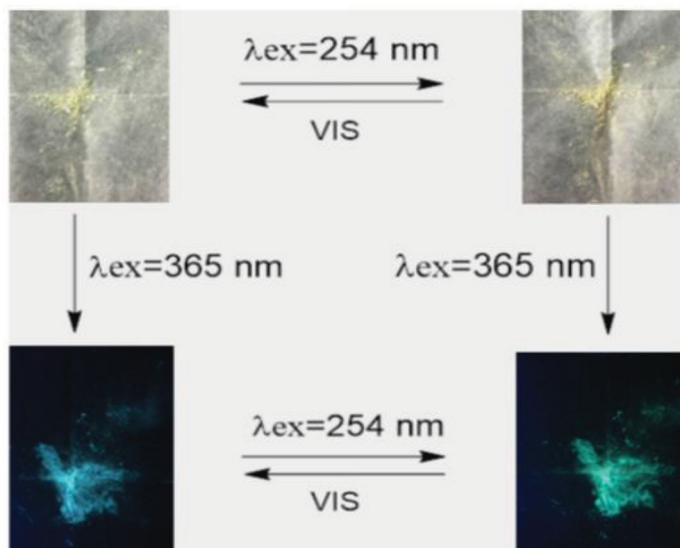
Compounds **TAE-1**, **TAE-2** and **TAE-3** exhibited obvious photochromic properties in the solid powders as well. The color changes of them in solid powders before and after photochromism were illustrated in Figures 1 and 2. Taken **TAE-2** for instance to describe its photochromic behavior (Figure 1). With the irradiation of 254 nm UV light for several minutes, the color of **TAE-2** changed from white (**TAE-2o**) to orange yellow (**TAE-2c**), while upon irradiation with visible light, the orange yellow powders reverted to white gradually. It indicated that the color change of **TAE-2** in solid powders was reversible. **TAE-1** and **TAE-3** performed the similar photochromic behavior in solid powders. It is worth noting that after UV-light irradiation (254 nm), the solid fluorescence emission of **TAE-3o** changed from blue to green, while the green fluorescence returned to blue again when it was exposed with visible light (Figure 2). As shown in the fluorescence emission spectra of **TAE-3** (Figure 3), compound **TAE-3** emitted strong fluorescence at about 405 nm before ultraviolet light irradiation. With the extension of ultraviolet light exposure time, the fluorescence intensity at 405 nm gradually decreased, and new fluorescence emission peak appeared in the range of 460–650 nm. This change could be restored to the original state after irradiation of visible light, which indicated that the compound has undergone reversible photochromism during the illumination process. The change in fluorescence may be caused by the expansion of conjugate range after photochromism. This distinctive photo-controllable fluorescence is desirable for solid fluorescent materials.

### Thermal reversibility

All of the closed-ring isomers, **TAE-1c**, **TAE-2c** and **TAE-3c**, were also thermally reversible, which could transfer to their open forms in dark. Taken **TAE-2c** as an example (Figure S14(b)), the THF solution of **TAE-2c** ( $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) with photostationary state was kept in the dark for about 6 hours, that maximum absorption at



**Figure 1.** Photochromic behaviors of **TAE-1** and **TAE-2** in solid powders.

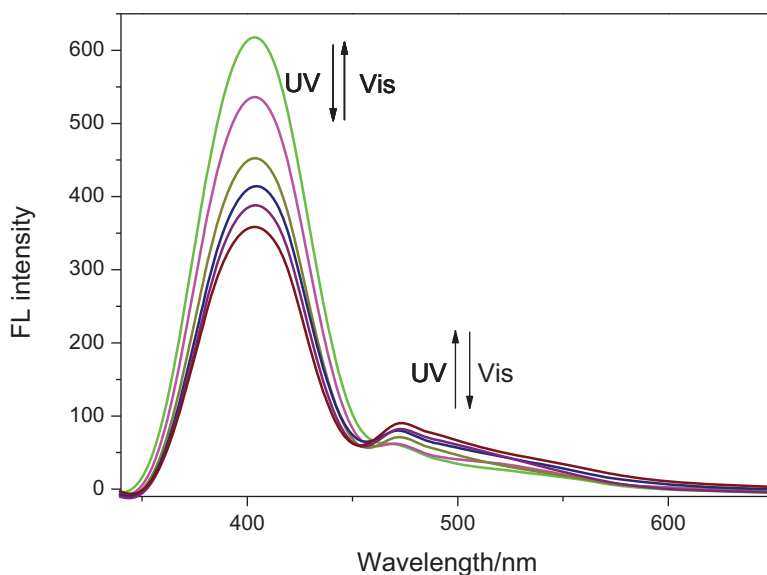


**Figure 2.** Photochromism and photo-controllable fluorescence images of **TAE-3** under 365 nm in solid powders.

468 nm decayed to the original spectra, accompanied by the orange solution fading to colorless. It meant that the closed-ring form, **TAE-2c**, could recover to the open-ring form (**TAE-2o**). Similarly, the maximum absorption at 460 nm and 470 nm of **TAE-1c** and **TAE-3c** in THF ( $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) decayed to the original spectra when kept in dark for 400 min and 350 min respectively with corresponding color changes.

### **Light reversibility and fatigue resistance**

The recycling of the photochromic process of the three target compounds were illustrated as a function of alternate exposure to UV (254 nm) and visible light (500 nm). Taken **TAE-2** as an example (Figure S16), the maximum absorption of photostationary state decayed significantly after it was tested 5 cycles, which indicates that **TAE-2** has a certain photoreversible property but shows obvious fatigue after 5 photocyclization and cycloreversion cycles. **TAE-1** and **TAE-3** showed similar reversibility and fatigue resistance (Figures S15 and S17). The main fatigue process of photochromic compounds are caused by the photostable byproduct formations. While the

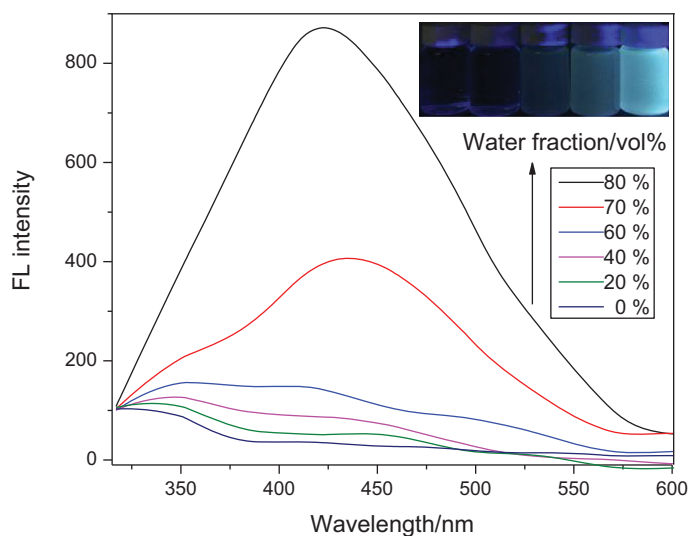


**Figure 3.** Changes in fluorescence spectra of **TAE-3** in THF ( $5.0 \times 10^{-5}$  M) upon irradiation at 254 nm.

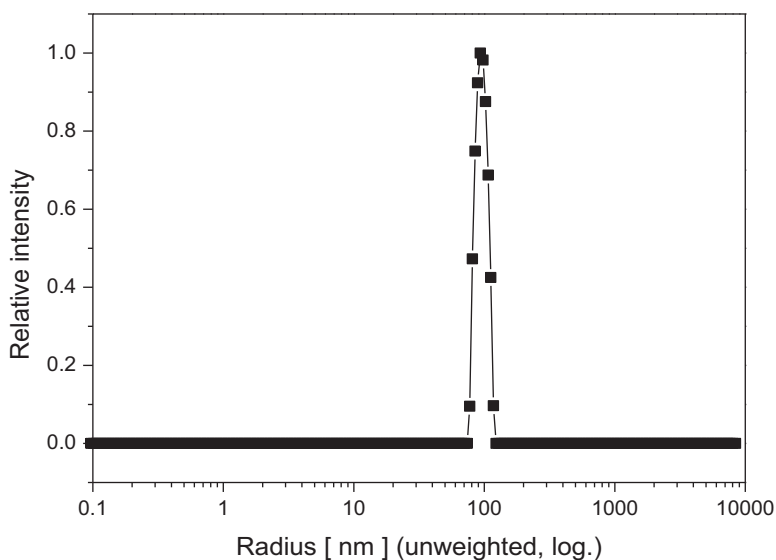
introduction of methyl groups at the 4-positions of the thiophene rings may improve the fatigue resistance of these compounds due to the methyl substituents are considered to prevent rearrangement of the thiophene rings to the six-membered condensed ring.<sup>[1]</sup>

### Aggregation-induced emission properties

In addition to the obvious photochromic behaviors and thermal reversibility in both solution and solid powders, **TAE-3** had excellent AIE properties simultaneously. To investigate the AIE properties of the target compounds, their fluorescence spectra in H<sub>2</sub>O/THF mixture solution with different water fractions were recorded. Given these spectra data observations, **TAE-3** exhibited typical AIE properties, as shown in Figure 4. The fluorescent emission of **TAE-3** could not be observed in pure THF solvent ( $\lambda_{\text{ex}} = 310$  nm), but it was increased gradually with the increasing of the water fraction because of the aggregation in the aqueous medium which restricting the intramolecular rotation.<sup>[46]</sup> As the fluorescence spectra and images (Figure 4) show that the fluorescence emission intensity of **TAE-3** ( $5 \times 10^{-5}$  M) in pure THF was close to 0 ( $\lambda_{\text{ex}} = 310$  nm), but it increased slowly when the water fraction increased from 20 vol% to 60 vol%. The fluorescence emission intensity increased observably when the water fraction reached to 70 vol%, and finally reach the peak when the water fraction is 80 vol%. **TAE-3**'s emission was turned on gradually when the water fraction increased and accompanied by blue fluorescence, as a result of the aggregation in the aqueous medium.<sup>[55]</sup> The test results of laser light scattering showed that the radius of aggregate particle is around 100 nm, and the particle size distribution is narrow enough, which indicates that the solution is stable and no insoluble particles are precipitated out directly (Figure 5).



**Figure 4.** Fluorescence spectra and images of **TAE-3** in  $\text{H}_2\text{O}/\text{THF}$  mixture solution with different water fractions, the inset shows the fluorescence photographs of **TAE-3** with different water fractions.

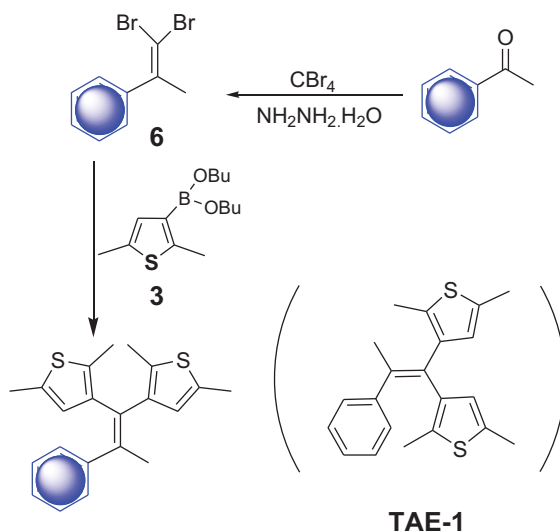


**Figure 5.** Laser light scattering of **TAE-3** in  $\text{H}_2\text{O}/\text{THF}$  mixtures (80% water content).

## Experimental

All reagents were purchased commercially and used without further purification unless otherwise mentioned.  $^1\text{H}$  NMR spectra (400 MHz) and  $^{13}\text{C}$  NMR spectra (101 MHz) were recorded on a Bruker AV400 spectrometer using  $\text{CDCl}_3$  as solvent and tetramethylsilane as internal standard. All HRMS spectrometric analyses were tested on a LCT Premier XE mass spectrometer. The UV light for irradiation was generated by LED sources and the lamp power is 5 W. Absorption and fluorescence spectra were recorded





**Scheme 4.** The synthesis protocol for photochromic triarylethenes.

on Agilent Technologies Cary 60 UV-Vis and Varian Cray Eclipse fluorescence spectrophotometer, respectively.

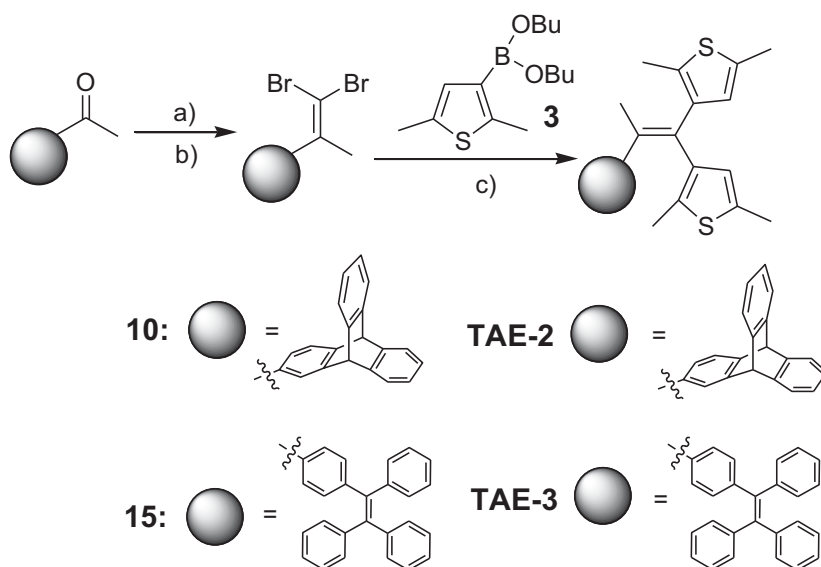
Generally, the photochromic diarylethenes obtained from two ketone molecules need to take the following process: the acylation of aromatic compounds as the first step, followed by a Friedel–Crafts reaction to obtain the precursors, finally, the target compounds were obtained by McMurry coupling reaction. The shortcomings of this method are that the *cis-trans* isomerization of the products are difficult to separate, and the low yield of single product due to *cis-trans* isomers. Moreover, this method is not suitable to the synthesis of asymmetric diarylethenes.<sup>[56]</sup> Another class of diarylethenes needs an extra ring to fix the ethylene bridge, which leads to an increase in synthetic steps and workload.<sup>[26]</sup> The synthetic protocol in this paper circumvented these shortcomings. It mainly included two steps. The commercial aryl ketone was reacted first with hydrazine and carbon tetrabromide respectively to get the key intermediate dibromocarbene. Then the titled triarylethenes could be conveniently obtained by the classic Suzuki coupling reaction (Scheme 4).

The photochromic triarylethene **TAE-1** was obtained firstly as colorless transparent liquid in 66% yield through this method. Furthermore, another two new triarylethene derivatives **TAE-2** and **TAE-3** were achieved successfully by replaced the aryl group of the aryl ketone with more huge functional blocks, triptycene and tetra-arylethene. The synthetic routes are shown in Scheme 5. The intermediate carbene was prepared by revised procedures reported previously.<sup>[57,58]</sup>

Reagents and conditions: (a)  $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$ ,  $\text{HOAc}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ; (b)  $\text{CBr}_4$ ,  $\text{CuI}$ ;  $\text{DMSO-NH}_3$ ; (c)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{THF}$ ,  $\text{H}_2\text{O}$ .

### **Synthesis of 3,3'-(2-phenylprop-1-ene-1,1-diyl)bis(2,5-dimethylthiophene) (TAE-1)**

Compound **6** (450 mg, 1.64 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (1.38 g, 10.00 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (180 mg, 0.16 mmol) were added into a dry 50 mL two-necked flask orderly.



**Scheme 5.** The synthetic routes of the target compounds TAE-2, TAE-3.

5 mL of water and 15 mL of distilled THF were added into the flask subsequently, the argon protection device was installed, and replaced the gas of the flask 3 times with argon. The reaction system gradually warmed up in the oil bath, when the temperature rose to 60 °C, borate **3** was added to the flask with a syringe in a short period of time, and the temperature was increased to 80 °C continuously. The solution was refluxed overnight and cooled to room temperature, after which H<sub>2</sub>O (20 mL) was added and extracted with DCM (20 mL × 3), The organic layer was separated and subsequently dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The sodium sulfate was filtered off, and the solvent was removed by evaporation under vacuum. The residue was purified by column chromatography (SiO<sub>2</sub>, PE) to give TAE-1 (366 mg, 66%) as colorless transparent liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.19–7.10 (m, 5H), 6.35 (s, 1H), 6.19 (s, 1H), 2.38 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 2.05 (s, 3H), 1.76 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm): δ = 143.84, 139.54, 138.65, 137.74, 135.47, 134.63, 132.10, 129.06, 128.81, 127.98, 127.91, 127.30, 126.46, 21.97, 15.57, 15.49, 14.04. HRMS (ESI<sup>+</sup>): *m/z* calcd for C<sub>21</sub>H<sub>22</sub>S<sub>2</sub> [M + H]<sup>+</sup>: 339.1241; found: 339.1227.

**Synthesis of 3,3'-(2-((9*r*,10*r*)-9,10-dihydro-9,10-[1,2]benzenoanthracen-2-yl)prop-1-ene-1,1-diyl)bis(2,5-dimethylthiophene) (TAE-2)**

Compound **10** (274 mg, 0.61 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10.00 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (37 mg, 0.031 mmol) were added into a dry 50 mL two-necked flask orderly. 5 mL of water and 15 mL of distilled THF were added into the flask subsequently, the argon protection device was installed, and replaced the gas of the flask 3 times with argon. The reaction system gradually warmed up in the oil bath, when the temperature rose to 60 °C, borate **3** was added to the flask with a syringe in a short period of time, and the temperature was increased to 80 °C continuously. The solution was refluxed overnight and cooled to room temperature, after which H<sub>2</sub>O (20 mL) was added and

extracted with DCM (20 mL  $\times$  3), The organic layer was separated and subsequently dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The sodium sulfate was filtered off, and the solvent was removed by evaporation under vacuum. The residue was purified by column chromatography ( $\text{SiO}_2$ , PE: DCM = 60: 1, V/V) to give **TAE-2** (234 mg, 75%) as colorless transparent liquid. Mp 177.3–181.4 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.36–7.31 (m, 4H), 7.19–7.18 (d,  $J$  = 7.6 Hz, 1H), 7.09 (s, 1H), 6.98–6.96 (m, 4H), 6.81–6.79 (dd,  $J_1$  = 1.6 Hz,  $J_2$  = 7.6 Hz, 1H), 6.32 (s, 1H), 6.00 (s, 1H), 5.34 (s, 1H), 5.21 (s, 1H), 2.36 (s, 3H), 2.23 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 145.38, 145.23, 144.58, 143.36, 140.32, 139.29, 138.39, 136.96, 135.11, 134.01, 132.01, 131.83, 128.73, 127.81, 127.14, 125.05, 125.00, 124.91, 124.16, 123.43, 123.41, 122.65, 54.15, 53.73, 21.42, 15.29, 14.94, 13.83, 13.58; HRMS ( $\text{ESI}^+$ ):  $m/z$  calcd for  $\text{C}_{35}\text{H}_{30}\text{S}_2$   $[\text{M} + \text{Na}]^+$ : 537.1687; found: 537.1679.

### **Synthesis of 3,3'-(2-(4-(1,2,2-triphenylvinyl)phenyl)prop-1-ene-1,1-diyl)bis(2,5-dimethylthioph-ene) (TAE-3)**

Compound **15** (266 mg, 0.50 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (1.38 g, 10.00 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (60 mg, 0.05 mmol) were added into a dry 50 mL two-necked flask orderly. 5 mL of water and 15 mL of distilled THF were added into the flask subsequently, the argon protection device was installed, and replaced the gas of the flask 3 times with argon. The reaction system gradually warmed up in the oil bath, when the temperature rose to 60 °C, borate **3** was added to the flask with a syringe in a short period of time, and the temperature was increased to 80 °C continuously. The solution was refluxed overnight and cooled to room temperature, after which  $\text{H}_2\text{O}$  (20 mL) were added and extracted with DCM (20 mL  $\times$  3). The organic layer was separated and subsequently dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The sodium sulfate was filtered off, and the solvent was removed by evaporation under vacuum. The residue was purified by column chromatography ( $\text{SiO}_2$ , PE) to give **TAE-3** (168 mg, 57%) as colorless transparent liquid. Mp 93.2–94.6 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.14–7.07 (m, 9H), 7.05–6.98 (m, 6H), 6.89–6.82 (m, 4H), 6.31 (s, 1H), 6.15 (s, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 1.99 (s, 3H), 1.71 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 144.11, 144.06, 141.95, 141.90, 141.11, 140.94, 139.63, 138.65, 137.50, 135.42, 134.58, 132.10, 132.05, 131.61, 131.59, 130.87, 129.07, 128.12, 128.01, 127.88, 127.84, 127.28, 126.72, 126.61, 21.59, 15.50, 14.31, 13.98; HRMS ( $\text{ESI}^+$ ):  $m/z$  calcd for  $\text{C}_{41}\text{H}_{36}\text{S}_2$   $[\text{M} + \text{Na}]^+$ : 615.2156; found: 615.2153.

## **Conclusions**

In summary, a new synthesis strategy of photochromic triarylethenes with bifunctional groups was developed and a series of new triarylethenes without cis-trans were constructed. The novel design ensures a simple structure with two independent functionalities. The target compounds were conveniently obtained by straightforward synthesis and easy to purify. Results showed that they exhibited obvious photochromism in the rare yellow absorption bands in both solution and aggregation. Furthermore, **TAE-3**

performs distinctive photo-controllable fluorescence and AIE properties. These compounds are potential applications in solid photochromic and fluorescent materials.

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