# Photochromism

# **Reversible Multistimuli-Response Fluorescent Switch Based on Tetraphenylethene–Spiropyran Molecules**

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Abstract: Two tetraphenylethene (TPE)-functionalized spiropyran (SP) molecules with very similar structure were designed and synthesized. The two molecules exhibit aggregation-induced emission (AIE) properties, as well as multistimuli-responsive color-changing properties, such as photochromism and acidchromism. The investigation of their dif-

# Introduction

Spiropyrans and their derivatives are well known as molecular switches, which show distinctive absorption characteristics during structural isomerization between the ring-closed form (CF) and ring-open form (OF) upon external stimulus.<sup>[1]</sup> Up to now, various stimuli, such as UV/Vis light,<sup>[1,2]</sup> acid/base,<sup>[3]</sup> heat,<sup>[4]</sup> electricity,<sup>[5]</sup> and mechanoforce<sup>[6]</sup> all have been reported to accelerate this CF-OF transformation. Due to their excellent stimuli-response properties, spiropyrans have been widely studied for use in data storage,<sup>[7]</sup> chemical sensors,<sup>[8]</sup> smart materials,<sup>[9]</sup> and biological imaging<sup>[10]</sup> etc. However, the weak emission of spiropyran in the aggregation state limited some of the above applications. Thus the development of highly emissive organic luminescent materials with multistimuli-response color-changing properties is of important significance to gain multifunctional sensor materials to further widen the field of applications. Twisted  $\pi$ -conjugated molecules, such as TPE and its derivatives, have become a research hotspot in recent years due to their aggregation-induced emission (AIE) properties,<sup>[11]</sup> which have conquered the drawbacks from the notorious quenching effect caused by aggregation of the traditional dyes with a planer conformation and realized their wide applications in organic light emitting devices (OLED)<sup>[12]</sup> and bio-labels.<sup>[13]</sup> Therefore, the combination of spiropyran with TPE is envisioned to realize a new type of multiresponsive luminescent material. Zhang et al. reported multicolored tunable

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http://dx.doi.org/10.1002/chem.201405426.

Chem. Eur. J. 2014, 20, 1-8

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ferent photochromic and acidchromic characteristics and dual-response fluorescent switch during isomerization indicated that the different link position between TPE and SP will significantly affect the extended  $\pi$ -conjugated system, resulting in completely different photochromic and acidchromic properties.

emission organogels by blending tetraphenylethene gel with spiropyran gel.<sup>[14]</sup> Based on the photoisomerization of spiropyran, the emission of the organogels can be switched by alternating UV/Vis illumination. Thus, it is envisaged that the combination of SP with TPE by a covalent bond may directly improve their performances and expand their application fields.

Herein, we designed and synthesized two new molecules (TPE-SP1 and TPE-SP2) by covalently linking TPE with spiropyran by using carbon-carbon double bonds (Scheme 1). The two molecules exhibit AIE properties and obvious photochromic and acidchromic properties. The investigation of the photochromism of the two compounds indicated that although they have very similar molecular structure, their photochromic characteristics are different. In addition, the modulation of the two emission colors, switch of TPE-SP1 and the emission onoff switch of TPE-SP2, can be realized in the solid state upon acid/base treatment. To the best of our knowledge, the solid fluorescence switch of spiropyran systems triggered by acid/ base has rarely reported. The related origin of the different luminescent changes under external stimuli was then investigated by combining experimental analyses with theoretical calculations. The results indicated that TPE-MC1 with much larger  $\pi$ conjugation length between the TPE moiety and merocyanine (MC) moiety will give a red emission, whereas TPE-MC2 will have completely guenched emission due to poor conjugation and the intramolecular energy and electron-transfer quenching.

## **Results and Discussion**

#### **Design and synthesis**

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TPE-SP1 and TPE-SP2 were synthesized by a series of chemical reactions according to Scheme 1. The detailed synthetic procedure and characterizations are described in the Experimental Section and Supporting Information.





Scheme 1. Synthetic route to TPE-SP1 and TPE-SP2.

#### Aggregation-induced emission properties

The AIE properties of TPE-SP1 and TPE-SP2 were investigated in their THF/water solution, and both the two compounds show obvious AIE properties as shown in Figure 1. When the water fraction ( $f_w$ ) is lower than 70%, the PL curve is almost flat lines parallel to the abscissa, which indicated that there is no emission in pure THF solution. However, both cyan emissions with peaks at 482 nm for TPE-SP1 and 483 nm for TPE-SP2 turn on when large amounts (>70%) of water, a poor solvent, was added into their THF solution. The mechanism for



this AIE phenomenon has already been thoroughly researched and the increased fluorescent intensity attributed to the formation of molecular aggregates, in which the intramolecular free rotation has been blocked.<sup>[15]</sup>

# Photochromic properties in the solution state

Similar to the reported spiropyran molecular switches, the CF– OF isomerization of both two molecules can be triggered by UV light. Herein, the isomerizations of TPE-SP1 and TPE-SP2 in dichloromethane and phenylcarbinol solution were investigated respectively. As can be seen

from the UV/Vis absorption of TPE-SP1 and TPE-SP2 in Figure 2, the two compounds can undergo reversible photoisomerization between their unconjugated CF isomer and conjugated OF isomer under the irradiation of a 254 nm hand-held ultraviolet lamp. The absorption peak at 366 nm for CF of TPE-SP1 gradually decreased and a new absorption peak at 528 nm assigned to the OF appeared and increased with exposure duration (Figure 2a). For contrast, TPE-SP2 has a gradually decreased CF absorption peak at about 350 nm and a new generated and increased OF absorption peak at about 476 nm



under continuous UV irradiation (Figure 2b). The OF absorption peak of TPE-SP1 (528 nm) has an obvious redshift compared with that of TPE-SP2 (476 nm), which confirmed that the OF of TPE-SP1 has a better  $\pi$ -conjugation than that of TPE-SP2. Interestingly, TPE-SP1 more easily transforms from CF to OF, because TPE-SP1 can achieve the maximum ring-open ratio after 7 min UV irradiation, whereas TPE-SP2 needs nearly 30 min. Thus, the different link position between TPE and SP will lead to the different photochromic behaviors and capacity. The reason may be that the better  $\pi$ -conjugation between TPE and MC in TPE-MC1 improves the stability of the MC moiety by dispersing the positive charge of the nitrogen cation of indoline and makes photochromism easier.[16] In contrast to the absorption change

**Figure 1.** a,c) Fluorescent images of TPE-SP1 and TPE-SP2, respectively, in different water fraction ( $f_w$ ) mixtures under 365 nm UV illumination. b,d) Fluorescence spectra of TPE-SP1 and TPE-SP2 ( $10^{-5} \text{ m}$ ), respectively, in THF/ H<sub>2</sub>O mixtures with different  $f_w$  values. Insets: plot of *I*/*I*<sub>0</sub> versus water fraction, in which *I* and *I*<sub>0</sub> represent the fluorescence intensities in a THF/water mixture with a specific  $f_w$  and in pure THF.

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**Figure 2.** Time-dependent UV/Vis absorption spectra of a) TPE-SP1 and b) TPE-SP2  $(10^{-5} \text{ M})$  in dichloromethane recorded under 254 nm hand-held ultraviolet lamp irradiation.

creased emission of CF at 490 nm and gradually increased new emission of the OF at 615 nm with time in the dark (Figure 3c and d). This reverse process with an obvious fluorescent switch can be realized many times under alternating visible-light on-off irradiation. However, TPE-SP2 is not sensitive to light when dissolved in phenylcarbinol, and it cannot transform to CF when exposed to visible light. Besides, even under the continuous irradiation of 254 nm UV light for 10 min, TPE-SP2 cannot increase the ratio of the OF (Figure S2, Supporting Information).

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in response to UV light, the PL spectra during the whole process in dichloromethane were less obvious because of the weak emission of the TPE unit in good solvent as it can dissipate the energy of excited molecules by free rotation.<sup>[17]</sup>

To investigate the PL change during this process, phenylcarbinol was selected as another solvent due to its high viscosity that can be used to restrict the intramolecular rotations of the TPE unit to a certain degree and then result in the enhanced emission in their solution. It appears that the two compounds can partially convert into OF once dissolved in phenylcarbinol

because the OF is highly stabilized in alcohols by the strong H-bonding interaction with solvent molecules.<sup>[4]</sup> Additionally, TPE-SP1 in phenylcarbinol was supersensitive to light because the OF TPE-SP1 can easily isomerize to the CF upon visiblelight (>500 nm) irradiation and then CF reverts to OF when left immediately in the dark (Figure 3a). The corresponding absorption spectra of TPE-SP1 in phenylcarbinol shows significant absorbance changes at two distinct wavelengths with time in darkness (Figure 3b). Fluorescence excitation spectra of TPE-SP1 in phenylcarbinol are shown in Figure S1 (Supporting Information), and the best excitation wavelength for CF and OF is about 380 and 540 nm, which were then selected as the exciting light. The PL spectra show the CF-OF isomerization accompanied with the gradually dePhotophysical properties in solution and aggregation state

Due to the introduction of a high-emissive TPE moiety, the powders of the two compounds have high quantum yields ( $\Phi_{\text{TPE-SP1}} = 58\%$ ,  $\Phi_{\text{TPE-SP2}} = 83\%$ ). As shown in Figure 4, the red-shifted emissions of TPE-SP1 (473, 484 nm) compared to TPE-SP2 (460, 475 nm) in their THF solutions and powders indicated that TPE-SP1 has a better extended  $\pi$ -conjugation, which was further confirmed by the corresponding absorption spectra in dichloromethane solution (Figure 2) and diffused reflec-



**Figure 3.** a) Visible and fluorescent pictures taken under visible light and 365 nm UV light. Time-dependent UV (b) and corresponding PL spectra (c,d) of TPE-SP1  $(10^{-5} \text{ M})$  in phenylcarbinol with time in the dark.

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**Figure 4.** PL spectra of TPE-SP1 and TPE-SP2 in solution and the solid state.  $\Box$ : TPE-SP1 in THF;  $\bigcirc$ : TPE-SP1 in powder;  $\triangle$ : TPE-SP2 in THF;  $\bigtriangledown$ : TPE-SP2 in powder.

tance absorption spectra of their powders (Figure S3, Supporting Information).

#### Acidchromic properties in the aggregation state

As the isomerization of spiropyrans can also be triggered by

acid, the acid-stimuli responsive solid emissions of the two molecules were investigated. Letters "JLU" and "SSM", abbreviations of Jilin University and supermolecular structure and materials, were written on the TLC plate with TPE-SP1 and TPE-SP2 as fluorescent dyes, respectively (Figure 5a and c). Interestingly, the two dye molecules written on the TLC plate have totally different emission change. The PL spectra of TPE-SP1 show that the emission intensity at 482 nm decreased at first and then a new emission at about 630 nm appears and increased gradually, while the emission intensity at 480 nm for TPE-SP2 decreased all the time. With the solvent evaporation, acidic silica gel in the TLC plate can trigger the two molecules to open the spiro ring and isomerize to the OF, and then an emission change from cyan to red occurs on the TLC plate for TPE-SP1 during this transformation, whereas TPE-SP2 merely shows cyan emission quenching as time goes by. The exposure of the powders of TPE-SP1 and TPE-SP2 to vapors of concentrated hydrochloric acid can also result in the protonation of the phenolate fragment of the OF. Indeed, the new absorption spectra (in Figure S3, Supporting Information) of corresponding protonated OF (POF) shows the band at 620 and 580 nm, respectively. Fascinatingly, the emissions for both POF of TPE-SP1 and TPE-SP2 also show totally different changing trends in Figure 5b and d, which is similar to the fluorescence change on the TLC plate. In fact, the POF emission of TPE-SP1 has a red emission at about 630 nm with 3.4% quantum yield, whereas TPE-SP2 merely has totally quenched emission (quantum yield < 0.01%). The reversible fluorescent switch can be realized by fuming the POF of the two dyes with triethylamine (TEA) and then the emission color can switch back to bright cyan.

#### Mechanism research

The different fluorescence change trend for the two molecules under the same stimuli was then investigated by the experimental research and theoretical calculation. The mechanism for fluorescence quenching is proposed to be the photoinduced activation of the intramolecular energy and electrontransfer process within a fluorophore–photochrome dyad that



**Figure 5.** a,c) Time-dependent fluorescent pictures and corresponding PL spectra of TPE-SP1 and TPE-SP2, respectively, on the TLC plate. b,d) Fluorescent pictures and corresponding PL spectra of initial, HCl fumed and then TEA fumed powders of TPE-SP1 and TPE-SP2, respectively. Insets of b,d): reversible switching of the emission of TPE-SP1 and TPE-SP2 by the HCl/TEA fuming cycle.

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**Figure 6.** a) UV/Vis absorption spectra of SP, MC, and MCH, and emission spectra of TPE. b) Energy diagrams and the pictorial representations of HOMO and LUMO orbitals of TPE, MC, MCH, and SP in their ground state calculated by using B3LYP/6-31G<sup>\*\*</sup> by Gaussian 09.  $\Box$ : SP;  $\odot$ : MC;  $\triangle$ : MCH;  $\nabla$ : TPE.

can encourage the transformation of the photochrome from d one state to another.<sup>[18]</sup> The energy-transfer process is support-

THF, toluene, and ethanol were distilled in the presence of sodium benzophenoneketyl, calcium hydride, and magnesium, respectively, then stored under nitrogen

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ed by a wide range of spectral overlaps between the absorption spectra of MC/MCH and the emission band of TPE (Figure 6a). Besides, the calculated much lower LUMO energy level of MC/ MCH than that of TPE indicates that the intramolecular electrontransfer pathway from TPE to MC/MCH may also occur in this system (Figure 6b).

Although the energy and electron transfer may also exist for TPE-SP1 according to the significantly decreased fluorescence quantum yield during the ringopening process, the better conjugation of the OF/POF structure seems to be critical to keep the red emission. As shown in Figure 7, due to lack of effective conjugation length as in TPE-



Figure 7. Possible origin for two different modes of fluorescent switches.

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MC1, TPE-MC2 will only have a completely quenched emission due to the combination effect of the energy and electron-transfer processes.

# Conclusions

The reversible and different dual-response fluorescent switches triggered by UV/Vis and acid/base have been realized during the CF-OF transformation of both TPE-SP1 and TPE-SP2. The comparisons of two OF/POF molecules indicate the different link position between TPE and SP will result in the different  $\pi$ conjugated system that will finally lead to totally different photochromic and acidchromic properties. This reversible and different multistimuli-response fluorescence switch for the two molecules may have potential applications in the fluorescent sensors in the future.

**Experimental Section** 



immediately prior to use. DMF and Dimethylacetamide (DMAc) were distilled under vacuum from phosphorus pentoxide. 2,3,3-Trimethylindolenine and 5-bromosalicylaldehyde were purchased from Energy Chemical. Benzophenone and 4-bromobenzophenone were purchased from Alfa Aesar. Diphenylmethane, *n*-butyllithium (*n*BuLi), *p*-toluenesulfonic acid (PTSA), iodomethane, and all the other chemicals were purchased from Aladdin and used as received without further purification. 4-Bromo-2-hydroxybenaldehyde, *N*-methyl-2,3,3-trimethylindolenine iodide, tetraphenylethene, and 1,3,3-trimethylindolenizopyrylospiran (SP) were synthesized according to previous literature reports.<sup>[11h,19-21]</sup>

#### Instruments

<sup>1</sup>H NMR spectra were recorded on a 500 MHz Bruker Avance, by using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as an internal standard ( $\delta$  = 0.00 ppm). <sup>13</sup>C NMR spectra were recorded on a 125 MHz Bruker Avance, using CDCl<sub>3</sub> as a solvent and CDCl<sub>3</sub> as an internal standard ( $\delta$  = 77.00 ppm). LC-HRMS was obtained by Agilent 1290-microTOF Q II. Element analyses were performed on a FlashEA1112 spectrometer. GCMS were recorded on a Thermo Fisher ITQ1100. UV/Vis spectra were measured on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were recorded by Shimadzu RF-5301 PC spectrometer and Maya2000Pro optical fiber spectrophotometer. Solid PL efficiencies were measured by using an integrating sphere (C-701, Labsphere), with 365 and 470 nm Ocean Optics LLS-LED as the excitation source, and the light was introduced into the integrating sphere through optical fiber. The fluorescence microscopy images were obtained on an Olympus BX51 fluorescence microscope. The ground state geometries were fully optimized by the DFT method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G\*\* basis set by using the Gaussian 03 software package.

#### Synthesis and characterizations

Tetraphenylethene–spiropyran (TPE-SP1 and TPE-SP2) was prepared according to the synthetic routes shown in Scheme 1. Compound **1a** and **1b** were synthesized according to the literature method.<sup>[21]</sup> Compounds **2** and **3** were synthesized according to the literature method.<sup>[22–24]</sup>

#### 1,3,3-Trimethylindolino-7'-bromobenzopyrylospiran (1 a)

<sup>1</sup>H NMR (500 MHz,  $CDCI_3$ , TMS):  $\delta = 7.18$  (t, J = 7.6 Hz, 1 H), 7.07 (d, J = 7.2 Hz, 1 H), 6.95 (dd, J = 8.0, 1.8 Hz, 1 H), 6.92–6.89 (m, 2 H), 6.85 (t, J = 7.4 Hz, 1 H), 6.81 (d, J = 10.3 Hz, 1 H), 6.53 (d, J = 7.7 Hz, 1 H), 5.71 (d, J = 10.3 Hz, 1 H), 2.72 (s, 3 H), 1.30 (s, 3 H), 1.16 ppm (s, 3 H); MS (EI): m/z: calcd for  $C_{19}H_{18}BrNO$ : 355.06; found: 354.95.

#### 1,3,3-Trimethylindolino-6'-bromobenzopyrylospiran (1b)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.22–7.12 (m, 3 H), 7.07 (d, *J* = 7.2 Hz, 1 H), 6.85 (t, *J* = 7.4 Hz, 1 H), 6.78 (d, *J* = 10.2 Hz, 1 H), 6.60 (d, *J* = 9.3 Hz, 1 H), 6.53 (d, *J* = 7.7 Hz, 1 H), 5.72 (d, *J* = 10.3 Hz, 1 H), 2.71 (s, 3 H), 1.29 (s, 3 H), 1.16 ppm (s, 3 H); MS (EI): *m/z*: calcd for C<sub>19</sub>H<sub>18</sub>BrNO: 355.06; found: 354.96.

#### 1-(4-Bromophenyl)-1,2,2-triphenylethene (2)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$ =7.22 (d, J=8.5 Hz, 2H), 7.15–7.08 (m, 9H), 7.05–6.99 (m, 6H), 6.90 ppm (d, J=8.5 Hz, 2H); MS (EI): *m*/*z*: calcd for C<sub>26</sub>H<sub>19</sub>Br: 410.07; found: 410.35.

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#### 1-(4-Formyl)-l,2,2-triphenylethylene (3)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 9.90 (s, 1 H), 7.61 (d, *J*=8.2 Hz, 2 H), 7.19 (d, *J*=8.2 Hz, 2 H), 7.13–7.10 (m, 9 H), 7.05–6.99 ppm (m, 6 H). LC-HRMS (ESI): *m/z*: calcd: 361.1587; found: 361.1582 [*M*+H]<sup>+</sup>.

#### Synthesis of 1-(4-vinylphenyl)-l,2,2-triphenylethylene (4)

4-(1,2,2-Triphenylvinyl)benzaldehyde (3) (3.6 g, 10 mmol) and methyltriphenylphosphonium bromide (4.3 g, 12 mmol) were dissolved in THF (15 mL) and THF (25 mL) solution containing potassium tertbutoxide (1.68 g, 15 mmol) was slowly added dropwise at 0°C under a N<sub>2</sub> atmosphere. The reaction went on for 10 h. Then the reaction mixture was guenched with the addition of a saturated aqueous solution of sodium chloride (10 mL). The organic layer was extracted with dichloromethane (3×50 mL), and the combined organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in a rotary evaporator and the crude product was purified using column chromatography (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 4:1 v/v) to yield compound 4 (3.4 g, 67%) as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 7.14$  (d, J = 7.9 Hz, 2H), 7.12–7.07 (m, 9H), 7.06– 7.00 (m, 6H), 6.98 (d, J=7.8 Hz, 2H), 6.61 (dd, J=17.6, 11.0 Hz, 1H), 5.66 (d, J=17.6 Hz, 1 H), 5.18 ppm (d, J=10.9 Hz, 1 H); MS (EI): m/z: calcd for C<sub>28</sub>H<sub>22</sub>: 358.17; found: 358.76.

#### Synthesis of TPE-SP1

1-(4-Vinylphenyl)-l,2,2-triphenylethylene (4) (1 mmol, 0.36 g), 1,3,3trimethylindolino-7'-bromobenzopyrylospiran (1 a) (1 mmol, 0.35 g),  $K_3PO_4$  (3 mmol, 0.65 g), and Pd(OAc)<sub>2</sub> as the catalyst (200 mg) were dissolved in dry DMAc (5 mL). The reaction mixture was heated to 110°C in an oil bath and stirred for 24 h under a N<sub>2</sub> atmosphere. After being cooled to room temperature, the reaction mixture was poured into water and filtered to get the precipitated solid. The product was then purified by flash column chromatography (petroleum ether/ethyl acetate, 50:1 v/v) to give TPE-SP1 as a yellow solid (0.25 g, 39%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 7.22-6.81$ (m, 28 H), 6.54 (d, J=7.7 Hz, 1 H), 5.68 (d, J=10.2 Hz, 1 H), 2.74 (s, 3 H), 1.33 (s, 3 H), 1.18 ppm (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 154.67, 148.21, 143.71, 143.68, 143.62, 143.24, 141.07, 140.56,$ 139.04, 136.78, 135.17, 131.66, 131.37, 131.32, 131.30, 129.13, 128.66, 127.88, 127.74, 127.65, 127.59, 126.79, 126.49, 126.45, 126.39, 125.82, 121.47, 119.23, 119.12, 118.99, 118.40, 112.05, 106.80, 104.30, 51.73, 28.94, 25.84, 20.16 ppm; LC-HRMS (ESI): m/z: calcd: 634.3104; found: 634.3084 [*M*+H]<sup>+</sup>; elemental analysis calcd (%) for C47H39NO: C 89.06, H 6.20, N 2.21, O 2.52; found: C 89.02, H 6.20, N 2.18, O 2.60.

#### Synthesis of TPE-SP2

1-(4-Vinylphenyl)-l,2,2-triphenylethylene (4) (1 mmol, 0.36 g), 1,3,3trimethylindolino-6'-bromobenzopyrylospiran (1 b) (1 mmol, 0.35 g),  $K_3PO_4$  (3 mmol, 0.65 g), and  $Pd(OAc)_2$  as the catalyst (200 mg) were dissolved in dry DMAc (5 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h under N<sub>2</sub> atmosphere. After being cooled to room temperature, the reaction mixture was poured into water and filtered to give the precipitated solid. The product was then purified by flash column chromatography (petroleum ether/ethyl acetate, 50:1 v/v) to give TPE-SP2 as a pale-yellow solid (0.22 g, 34%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.24–6.77 (m, 27 H), 6.69 (d, J = 8.4 Hz, 1 H), 6.53 (d, J = 7.7 Hz, 1 H), 5.71 (d, J=10.2 Hz, 1 H), 2.73 (s, 3 H), 1.31 (s, 3 H), 1.17 ppm (s, 3 H);  ${}^{13}$ C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 154.27$ , 148.15, 143.77, 143.70, 142.73, 140.94, 140.63, 136.71, 135.62, 131.67, 131.40,

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131.34, 129.64, 129.33, 127.91, 127.80, 127.74, 127.65, 127.60, 126.45, 126.38, 126.18, 125.49, 124.62, 121.49, 119.84, 119.13, 118.82, 115.28, 106.80, 104.46, 51.74, 28.91, 25.87, 20.12 ppm; LC-HRMS (ESI): m/z: calcd: 634.3104; found: 634.3117 [M+H<sup>+</sup>]; elemental analysis calcd (%) for C<sub>47</sub>H<sub>39</sub>NO: C 89.06, H 6.20, N 2.21, O 2.52; found: C 89.08, H 6.16, N 2.20, O 2.56.

#### Sample preparation for AIE measurements

AlE performance of TPE-SP1 or TPE-SP2: Stock THF solution of TPE-SP1 or TPE-SP2 with a concentration of  $1 \times 10^{-4}$  M was prepared. The stock solution (1 mL) was added to 10 mL volumetric flasks. After an appropriate amount of THF was added, water was added dropwise under vigorous stirring to prepare  $1 \times 10^{-5}$  M solutions with different water fractions (0–90 vol%). The PL spectra measurements of the resulting solutions were then performed immediately.

### Acknowledgements

This work was supported by the 973 Program (No. 2013CB834702), the Natural Science Foundation of China (No. 21204027, 21221063), program for Chang Jiang Scholars and Innovative Research Team in University (No. IRT101713018), and Graduate Innovation Fund of Jilin University (No. 2014013).

**Keywords:** acidchromism · aggregation induced emission · fluorescent switch · isomerization · photochromism

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Received: September 26, 2014 Published online on ■■ ■, 0000

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# **FULL PAPER**





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## 

Reversible Multistimuli-Response Fluorescent Switch Based on Tetraphenylethene–Spiropyran Molecules



**Unlocking emission**: Two tetraphenylethene (TPE)-functionalized spiropyran (SP) molecules were designed and synthesized that exhibit not only aggregation-induced emission properties but also multistimuli-responsive properties,

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such as photochromism and acidchromism. The reversible and different dual-response fluorescent switches triggered by UV/Vis and acid/base have been realized during the ring-closed (CF) to ringopen (OF) transformation (see scheme).