Electronic Supplementary Information (ESI)

# Benzothiazolium-functionalized tetraphenylethene: an AIE luminogen with tunable solid-state emission

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### **Experimental section**

#### **Materials and Instrumentations**

Tetrahydrofuran (THF), toluene and ethanol were distilled from sodium benzophenone ketyl, calcium hydride and magnesium, respectively, under nitrogen immediately prior to use. Other chemicals were purchased from Aldrich and used as received without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AV 400 spectrometer in deuterated chloroform, dimethylsulfoxide (DMSO) or methanol using tetramethylsilane (TMS;  $\delta = 0$ ) as internal reference. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operated in MALDI-TOF mode. UV spectra were measured on a Milton Roy

Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The PL quantum yields ( $\Phi_F$ ) of 1 in THF and THF/water mixtures were determined using 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran ( $\Phi_F = 82\%$  in dimethylforamide) as standard. The morphologies of the nanoaggregates of 1 were investigated using JOEL 2010 TEM and JOEL 6700F SEM at an accelerating voltage of 200 and 5 kV, respectively. Thermogravimetric analysis (TGA) was carried on a TGA Q5000 under air at a heating rate of 10 °C/min. Thermal transitions of the luminogen were investigated by differential scanning calorimetry (DSC) using a TA DSC Q1000 under air at a heating rate of 10 °C/min. Powder X-ray diffraction (XRD) patterns were recorded on a X'pert PRO, PANalytical diffractometer. Cu-Ka radiation was used at 40 kV and 40 mA. Single crystal X-ray diffraction intensity data were collected at 100 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Cu-Ka radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). The ground-state geometries were optimized using the density functional (DFT) with B3LYP hybrid functional at the basis set level of 6-31G\*. All the calculations were performed using Gaussian 03 package.

### **Preparation of Nanoaggregates**

Stock THF solution of **1** with a concentration of  $2 \times 10^{-3}$  M was prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish  $2 \times 10^{-5}$  M solutions with different water contents (0–99 vol %). The PL measurements of the resulting solutions were then performed immediately.

## Synthesis

Compound 2 and 3 were prepared according to the synthetic route shown in Scheme S1. Details can be found in the previous publications.<sup>1-2</sup> Their characterization data are given below.

**3-Ethyl-2-methyl-1,3-benzothiazol-3-ium iodide (2)**. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD),  $\delta$  (TMS, ppm): 8.33 (d, J = 7.8 Hz, 2H), 8.30 (d, J = 8.4 Hz, 2H), 7.92 (dd, J<sub>1</sub> = 7.8 Hz, J<sub>2</sub> = 8.4 Hz, 2H), 7.81 (dd, J<sub>1</sub> = 7.8 Hz, J<sub>2</sub> = 8.4 Hz, 2H), 4.85 (q, J = 7.5 Hz, 4H), 3.27 (s, 3H), 1.60 (t, 6H, J = 7.5 Hz, 6H). HRMS (MALDI-TOF): *m*/*z* 178.0660 [(M–I)<sup>+</sup>, calcd 178.0690]

**4-(1,2,2-Triphenylvinyl)benzaldehyde (3).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 9.90 (s, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.11 (m, 9 H), 7.02 (m, 6H). HRMS (MALDI-TOF): m/z 361.1588 [(M+1)<sup>+</sup>, calcd 360.1514]

## 3-{2-[4-(1,2,2-triphenylvinly)phenyl]vinyl}-2-methyl-1,3-benzothiazol-3-ium

hexafluorophosphate (1). A solution of **3** (200 mg, 0.55 mmol) and iodide salt of **2** (169 mg, 0.55 mmol) in dry EtOH (15 mL) was refluxed under nitrogen for 48 h. After cool to ambient temperature, the solvent was evaporated under reduced pressure. The solid was dissolved in acetone (5 mL) and a saturated aqueous solution of KPF<sub>6</sub> (5 mL) was then added. After stirring for 30 min, the solution was evaporated to dryness. The residue was purified by a silica gel column chromatography using dichloromethane and acetone mixture (5:1 v/v) as eluent to give a yellow product in 62% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 8.41 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 15.6 Hz, 1H), 7.94 (d, J = 16 Hz 1H), 7.75–7.88 (m 4H), 7.02–7.15 (m 11H), 6.96–7.00 (m 6H), 4.91 (q, 2H), 1.42 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm): 171.4, 148.4, 147.5, 142.6, 142.4, 142.0, 140.8, 139.6, 131.3, 130.6, 130.5, 130.4, 129.5, 129.3, 128.2, 127.8, 127.7, 126.9, 126.7, 124.3, 116.5, 112.9, 44.4, 14.0. HRMS (MALDI-TOF): *m/z* 520.2281 [(M–PF<sub>6</sub>)<sup>+</sup>, calcd 520.2099]. Anal. Calcd for C<sub>37</sub>H<sub>30</sub>F<sub>6</sub>NPS: C, 66.76; H, 4.54; N, 2.10. Found: C, 67.26; H, 4.45; N, 2.18.

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Scheme S1. Synthetic route to intermediate 2 and 3.



Figure S1. ORTEP drawings of (A) 1, (B) 1.2/3 THF and (C) 1.EtOAc. Inset: fluorescent images of the crystals taken under UV irradiation on a fluorescence microscope.



Figure S2. Absorption spectrum of 1 in THF solution and PL spectra of crystals of 1,  $1 \cdot 2/3$  THF and  $1 \cdot EtOAc$ .

	1	<b>1</b> ·2/3 THF	1.EtOAc
Empirical formula	$C_{37}H_{30}F_6NPS$	C <sub>43</sub> H <sub>42</sub> F <sub>6</sub> NO <sub>1.50</sub> PS	$C_{41}H_{38}F_6NO_2PS$
Formula weight	665.65	773.81	753.75
Crystal dimensions, mm	0.38 $ imes$ $0.35$ $ imes$	$0.38$ $\times$ $0.29$ $\times$	0.40 $ imes$ $0.15$ $ imes$
	0.15	0.06	0.04
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a, Å	9.6816(4)	9.7467(4)	9.6552(4)
b, Å	17.8079(10)	17.3887(8)	17.4019(11)
c, Å	20.1801(10)	23.8490(10)	23.8103(11)
α, deg	73.460(5)	72.962(4)	72.469(5)
β, deg	76.508(4)	85.952(3)	84.653(4)
γ, deg	84.393(4)	83.053(4)	82.064(4)
$V, Å^3$	3241.4(3)	3833.6(3)	3772.6(3)
Ζ	4	4	4
$D_{\text{calcd.}}, \text{gcm}^3$	1.364	1.341	1.327
$F_{000}$	1376	1616	1568
Temp, (K)	173.1(5)	173.00(14)	172.9(3)
Radiation ( $\lambda$ ), Å	1.5418	1.5418	1.5418

**Table S1.** Summary of crystal data and intensity collection parameters for 1, 1.2/3 THF and  $1.EtOAc_{-}$ 

$\mu$ (Cu K $\alpha$ ) mm <sup>-1</sup>	1.895	1.707	1.731
$2\theta_{\rm max}$ , deg (completeness)	66.50 (98.5%)	66.50 (97.5%)	66.50 (97.7%)
No. of collected reflns.	20032	22938	22017
No. of unique reflns.	11388 (0.0505)	13263 (0.0469)	13132 (0.0462)
$(R_{\rm int})$			
Data/restraints/parameters	11388/132/855	13263/78/984	13132/165/1025
$R_1$ , w $R_2$ [obs I> $2\sigma$ (I)]	0.0751, 0.2030	0.0680, 0.1762	0.0597, 0.1583
$R_1$ , w $R_2$ (all data)	0.0895, 0.2193	0.0859, 0.1897	0.0824, 0.1760
Residual peak/hole e. Å <sup>-3</sup>	0.895/-0.652	0.549/-0.456	0.696/-0.387
Transmission ratio	1.00/0.92	1.00/0.74	1.00/0.84
Goodness-of-fit on $F^2$	1.035	1.041	1.028
CCDC number	883789	883790	883791



**Figure S3.** C–H··· $\pi$  (red line),  $\pi$ ··· $\pi$  (pink), C–H···F (green line) and S···F (purple) interactions in **1**. Anions are omitted for clarity.



**Figure S4.** C–H··· $\pi$  (red line),  $\pi$ ··· $\pi$  (pink), C–H···F (green line) and S···F (purple) interactions in 1·2/3 THF. Anions are omitted for clarity.



**Figure S5.** C–H···· $\pi$  (red line),  $\pi$ ··· $\pi$  (pink), C–H···F (green line), C–H···O (yellow line) and S···F (purple) interactions in **1**·EtOAc. Anions are omitted for clarity.



**Figure S6.** Molecular orbital amplitude plots of HOMO and LUMO energy levels of crystals of (A) **1**, (B)  $1 \cdot 2/3$ THF and (C)  $1 \cdot EtOAc$  calculated using B3LYP/6-31G(d) basis set.



**Figure S7.** (A and C) TEM and (B and D) SEM images of (A and B) amorphous and (C and D) crystalline aggregates of **1** formed in 90% aqueous mixture (A and D) before and (C and D) after the solution was standing at room temperature for 30 min. Inset in (A and C): ED patterns of the amorphous and crystalline aggregates.



**Figure S8.** (A) Change in the PL spectrum of **1** by grinding–heating process at  $150 \,^{\circ}$ C for 10 min. (B) Repeated switching of the solid-state fluorescence of **1** by repeated grinding and heating cycles.



Figure S9. (A) XRD diffractograms and (B) DSC thermograms of 1 at different aggregated phases recorded at a heating rate of  $10 \,^{\circ}C/min$ 

## References

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