

## Electronic Supplementary Information (ESI)

Thiophene-containing tetraphenylethene derivatives with different aggregation-induced emission (AIE) and mechanofluorochromic characteristics

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### Table of Contents

<b>1. Experimental Section.....</b>	<b>S2</b>
<b>2. References.....</b>	<b>S7</b>
<b>3. Figs. S1-S6.....</b>	<b>S8</b>
<b>4. Tables S1-S4.....</b>	<b>S11</b>
<b>5. Copies of NMR spectra and Mass spectra.....</b>	<b>S13</b>

## 1. Experimental Section

### Materials and measurements

General: All operations were carried out under an argon circumstance using standard Schlenk techniques. The starting materials thiophen-2-ylboronic acid and (5-formylthiophen-2-yl)boronic acid purchased from Alfa Aesar were used as received. The other starting materials were purchased from J&K Chemical Ltd. (Shanghai, China). All reagents were obtained as analytical-grade from commercial suppliers and used without further purification. Compounds **1-1** [1] and **1-2** [2] were prepared by procedures described in the literature. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). <sup>1</sup>H NMR spectra are reported as followed: chemical shift in ppm ( $\delta$ ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constant (Hz). <sup>13</sup>C NMR chemical shifts reported in ppm ( $\delta$ ) relative to the central line of triplet for CDCl<sub>3</sub> at 77 ppm. Mass spectra were obtained using Thermo scientific DSQ II. Elemental analyses (C, H) were carried out with a PE CHN 2400 analyzer. The absorption spectra were measured on an Agilent 8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F-4600 fluorescence spectrophotometer. XRD studies were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered and graphite-

monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ , 40 kV, 30 mA). The X-ray crystal-structure determinations of compounds **1** and **2** were obtained on a Bruker APEX DUO CCD system. The DMF-water mixtures with various water fractions were prepared by tardily adding ultra-pure water into the DMF solution of samples. The aggregate behaviors of compounds **1-4** were investigated by NanoBrook 90Plus (Brookhaven Instruments). Absolute luminescence quantum yields were measured by HAMAMATSU ABSOLUTE PL QUANTUM YIELD SPECTROMETER C11347. Column chromatographic separations were carried out on silica gel (200-300 mesh). TLC was performed by using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm.

### **Crystallographic Details**

Single crystals of compounds **1** and **2** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a trichloromethane solution containing small amounts of **1** or **2**. A crystal of **1** with approximate dimensions of  $0.26 \times 0.24 \times 0.19 \text{ mm}^3$  for **1** was mounted on a glass fiber for diffraction experiment. A crystal of **2** with approximate dimensions of  $0.25 \times 0.20 \times 0.11 \text{ mm}^3$  for **2** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo K $\alpha$  radiation ( $0.71073 \text{ \AA}$ ) at room temperature. The structures were

solved by a combination of direct methods (SHELXS-97) [3] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97) [4]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Detailed crystal information are showed in Table S1 and Table S2. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 1935026 (compound **1**) and 1935027 (compound **2**)

#### **General procedure for the synthesis of compound 1**

A mixture of compound **1-1** (1.0 mmol, 0.5 g), **1-3** (2.2 mmol, 0.28 g), K<sub>2</sub>CO<sub>3</sub> (10 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.2 mmol) were stirred in THF (50 ml) and H<sub>2</sub>O (5 ml) for two days under an argon atmosphere at 80 °C. After completion of present reaction, the mixture was extracted with dichloromethane (3 × 50 mL), and the combined organic layers were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The residues were purified by column chromatography using petroleum ether: dichloromethane (volume ratio = 5:1) as eluent, affording the expected white solid product in a yield of 67.1%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) = 7.30 (d, *J* = 8 Hz, 4H), 7.20-7.17 (m, 4H), 7.06 (d, *J* = 4 Hz, 6H), 7.01-6.96 (m, 10H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ (ppm) = 144.2, 143.6, 142.8, 141.4, 139.8, 132.4, 131.9, 131.3, 128.0, 127.8, 126.6,

125.1, 124.6, 122.9. EI-MS:  $m/z = 496.3[M]^+$ . Anal. Calcd. For  $C_{34}H_{24}S_2$ : C, 82.22; H, 4.87. Found: C, 82.29; H, 4.83.

### **General procedure for the synthesis of compound 2**

A mixture of compound **1-1** (1.0 mmol, 0.5 g), **1-4** (2.2 mmol, 0.34 g),  $K_2CO_3$  (10 mmol),  $Pd(PPh_3)_4$  (0.2 mmol) were stirred in THF (50 ml) and  $H_2O$  (5 ml) for two days under an argon atmosphere at  $80^\circ C$ . After completion of present reaction, the mixture was extracted with dichloromethane ( $3 \times 50$  mL), and the combined organic layers were washed with brine, dried ( $Na_2SO_4$ ), and concentrated in vacuo. The residues were purified by column chromatography using petroleum ether: dichloromethane (volume ratio = 1:2) as eluent, affording the expected yellow solid product in a yield of 65.8%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 9.80 (s, 2H), 7.64 (d,  $J = 4$  Hz, 2H), 7.38 (s, 2H), 7.36 (s, 2H), 7.28 (d,  $J = 4$  Hz, 2H), 7.08 (d,  $J = 4$  Hz, 6H), 7.03 (s, 2H), 7.01 (d,  $J = 8$  Hz, 6H).  $^{13}C$  NMR (100.6 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 182.6, 153.9, 144.8, 143.1, 143.0, 142.3, 138.9, 137.3, 132.2, 131.3, 131.2, 127.9, 127.0, 125.8, 123.9. EI-MS:  $m/z = 552.4[M]^+$ . Anal. Calcd. For  $C_{36}H_{24}O_2S_2$ : C, 78.23; H, 4.38. Found: C, 78.19; H, 4.45.

### **General procedure for the synthesis of compound 3**

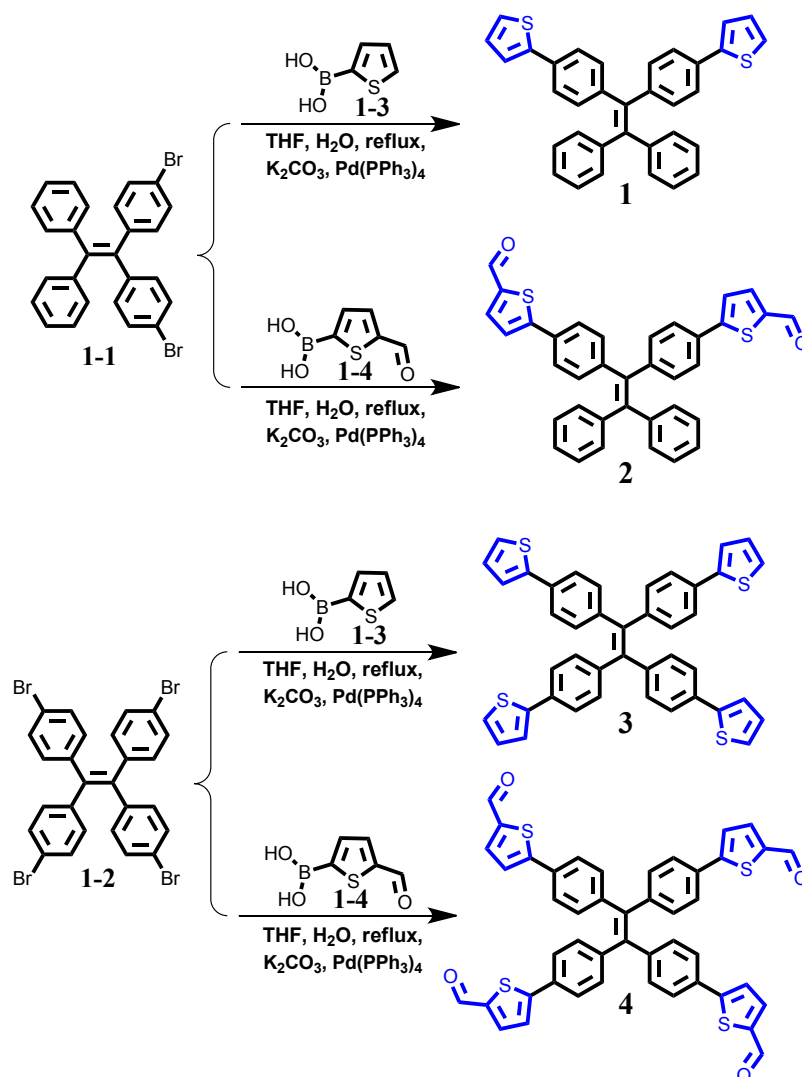
A mixture of compound **1-2** (0.77 mmol, 0.5 g), **1-3** (3.36 mmol, 0.43 g),  $K_2CO_3$  (10 mmol),  $Pd(PPh_3)_4$  (0.2 mmol) were stirred in THF (50 ml) and  $H_2O$  (5 ml) for two days under an argon atmosphere at  $80^\circ C$ .

After completion of present reaction, the mixture was extracted with dichloromethane ( $3 \times 50$  mL), and the combined organic layers were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated in vacuo. The residues were purified by column chromatography using petroleum ether: dichloromethane (volume ratio = 5:1) as eluent, affording the expected yellow solid product in a yield of 58.3%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 7.34 (d,  $J = 8$  Hz, 8H), 7.22 (d,  $J = 4$  Hz, 4H), 7.18 (d,  $J = 4$  Hz, 4H), 7.03 (d,  $J = 8$  Hz, 8H), 6.98-6.96 (m, 4H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 144.1, 142.7, 140.2, 132.6, 132.0, 128.0, 125.2, 124.7, 123.0. EI-MS:  $m/z = 660.4[\text{M}]^+$ . Anal. Calcd. For  $\text{C}_{42}\text{H}_{28}\text{S}_4$ : C, 76.32; H, 4.27. Found: C, 76.26; H, 4.31.

#### **General procedure for the synthesis of compound 4**

A mixture of compound **1-2** (0.77 mmol, 0.5 g), **1-4** (3.33 mmol, 0.52 g),  $\text{K}_2\text{CO}_3$  (10 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.2 mmol) were stirred in THF (50 ml) and  $\text{H}_2\text{O}$  (5 ml) for two days under an argon atmosphere at  $80^\circ\text{C}$ . After completion of present reaction, the mixture was extracted with dichloromethane ( $3 \times 50$  mL), and the combined organic layers were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated in vacuo. The residues were purified by column chromatography using petroleum ether: dichloromethane (volume ratio = 1:3) as eluent, affording the expected yellow solid product in a yield of 55.3%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 9.87 (s, 4H), 7.72 (d,  $J = 4$  Hz, 4H), 7.49 (d,  $J = 8$  Hz, 8H), 7.38

(d,  $J = 4$  Hz, 4H), 7.14 (d,  $J = 8$  Hz, 8H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 182.6, 153.5, 144.0, 142.5, 140.8, 137.3, 132.1, 131.8, 126.0, 124.2. Anal. Calcd. For  $\text{C}_{46}\text{H}_{28}\text{O}_4\text{S}_4$ : C, 71.48; H, 3.65. Found: C, 71.55; H, 3.60.



**Scheme S1.** Synthesis of the compounds 1-4.

## 2. References

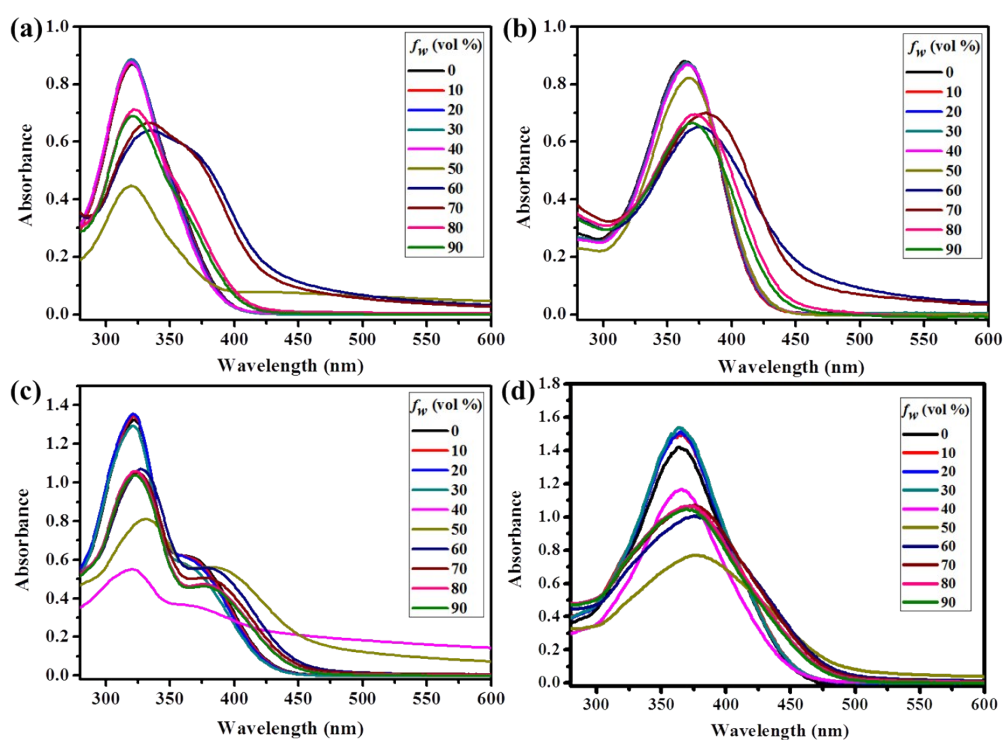
[1] X. Zhou, H. Li, Z. Chi, X. Zhang, J. Zhang, B. Xu, Y. Zhang, S. Liu and J. Xu, *New J. Chem.*, 2012, **36**, 685-693.

[2] K. Y. Kim, S. H. Jung, J.-H. Lee, S. S. Lee and J. H. Jung, *Chem. Commun.*, 2014, **50**, 15243-15246.

[3] G. M. Sheldrick, *SHELXS-97: Program for crystal structure solution*, Göttingen, Germany, 1997.

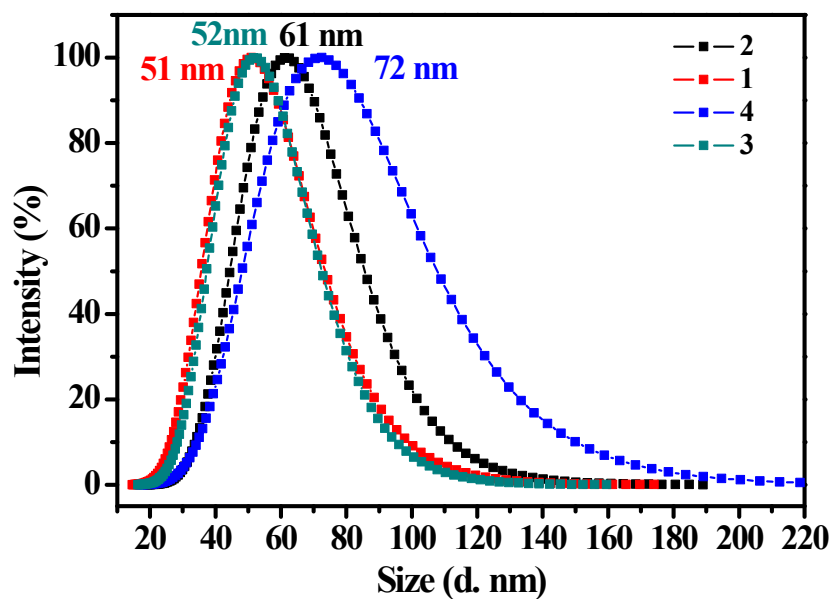
[4] G. M. Sheldrick, *SHELXL-97, Program for crystal structure refinement*. Göttingen, Germany, 1997.

### 3. Figs. S1-S6

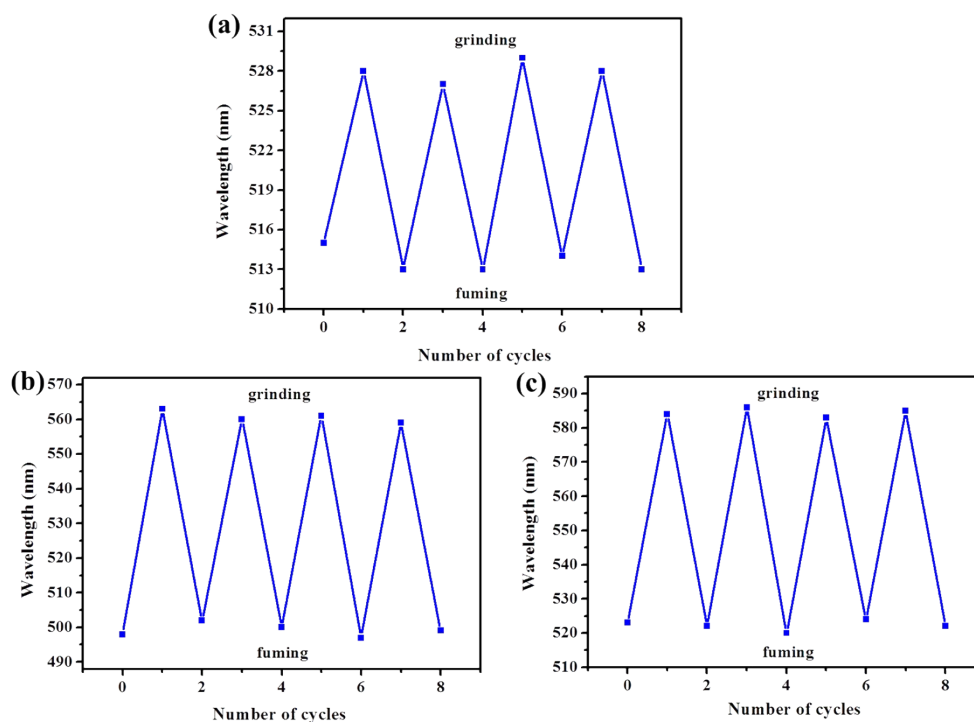


**Fig. S1** UV-Vis absorption spectra of compounds **1-4** ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) in DMF-water mixtures with various water contents (0-90%). (a) for compound **1**. (b) for compound **2**. (c) for compound **3**. (d) for compound **4**.



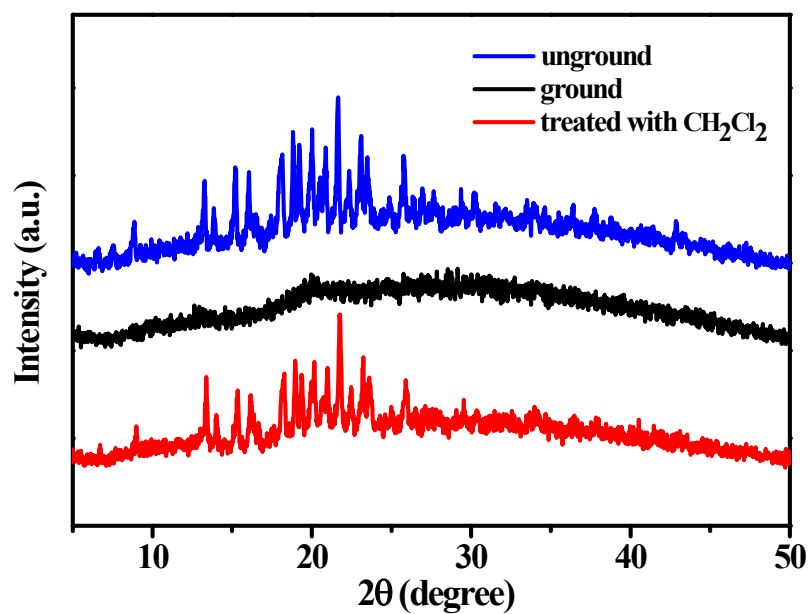


**Fig. S2** Size distribution curves of compounds 1-4 ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) in DMF-water mixtures with 90% volume fraction of water.

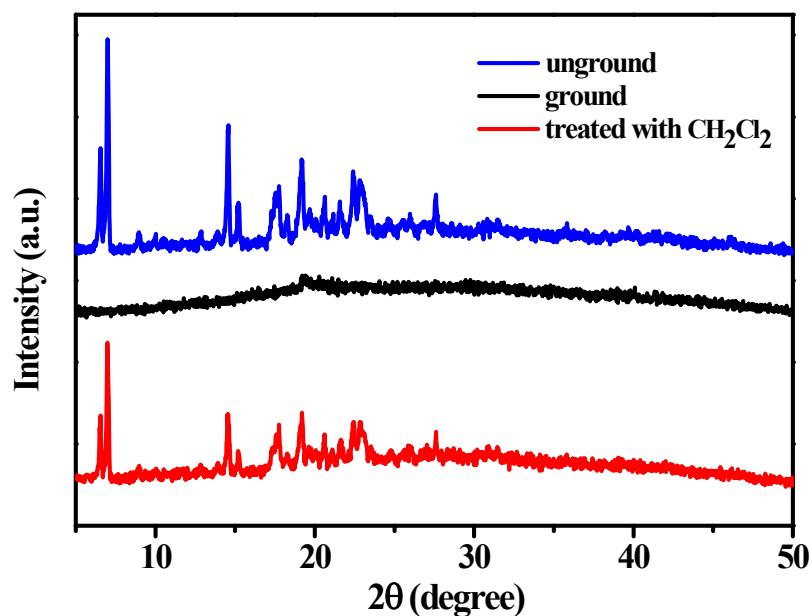


**Fig. S3** (a) Repetitive experiment of mechanochromic behavior for compound 2. (b) Repetitive experiment of mechanochromic behavior for compound 3. (c) Repetitive

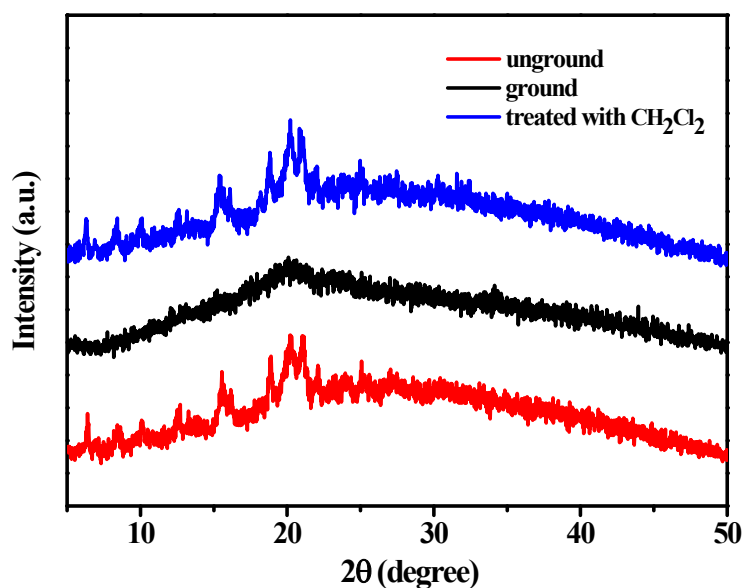
experiment of mechanochromic behavior for compound 4.



**Fig. S4** XRD patterns of compound 2: unground, ground and after treatment with dichloromethane solvent vapor.



**Fig. S5** XRD patterns of compound 3: unground, ground and after treatment with dichloromethane solvent vapor.



**Fig. S6** XRD patterns of compound **4**: unground, ground and after treatment with dichloromethane solvent vapor.

#### 4. Tables S1-S4

**Table S1** Structure determination summary for the compound **1**.

Empirical formula	$C_{34}H_{24}S_2$
Formula weight	496.65
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	P-1
$a$ (Å)	9.5899(10)
$b$ (Å)	10.0614(10)
$c$ (Å)	14.8767(15)
$\alpha$ (deg)	108.0500(10)
$\beta$ (deg)	104.7140(10)
$\gamma$ (deg)	91.5680(10)
$V$ (Å <sup>3</sup> )	1311.2(2)
$Z$	2
Absorption coefficient (mm <sup>-1</sup> )	0.224
F (000)	520
Theta range for data collection	2.897 to 25.997

(deg)	
Index ranges	-11<=h<=11, -12<=k<=12, -18<=l<=17
<b>Table S2</b> Structure determination summary for the compound <b>2</b> .	
Empirical formula	C <sub>36</sub> H <sub>24</sub> O <sub>2</sub> S <sub>2</sub>
Formula weight	552.67
Temperature (K)	296(2)
Crystal system	Orthorhombic
Space group	P 21 21 21
<i>a</i> (Å)	9.0738(19)
<i>b</i> (Å)	11.139(2)
<i>c</i> (Å)	28.078(6)
$\alpha$ (deg)	90
$\beta$ (deg)	90
$\gamma$ (deg)	90
<i>V</i> (Å <sup>3</sup> )	2837.9(10)
<i>Z</i>	4
Absorption coefficient (mm <sup>-1</sup> )	0.220
F (000)	1152
Theta range for data collection (deg)	2.673 to 27.558
Index ranges	-11<=h<=10, -14<=k<=-14, -28<=l<=-28

**Table S3** The maximum emission wavelengths of **1-4** in different solid states.

Compound	Different solid states	Em <sub>max</sub> (nm)
<b>1</b>	As-synthesized powder sample	444
	Ground powder sample	507
	Powder sample after fuming	445
<b>2</b>	As-synthesized powder sample	515
	Ground powder sample	528
	Powder sample after fuming	513
<b>3</b>	As-synthesized powder sample	498
	Ground powder sample	563
	Powder sample after fuming	502
<b>4</b>	As-synthesized powder sample	523
	Ground powder sample	584
	Powder sample after fuming	522

**Table S4** The maximum absorption wavelengths and the maximum emission wavelengths of **1-4** in DMF-H<sub>2</sub>O mixtures with various volume fractions of water (0-90%), and the fluorescence quantum yields of **1-4** in DMF-H<sub>2</sub>O mixtures with various

volume fractions of water (0% and 90%).

Compound	Water Content (%)	0	10	20	30	40	50	60	70	80	90
<b>1</b>	$\lambda_{\text{abs}}$ (nm)	321	320	320	320	320	320	336	333	322	321
	$\text{Em}_{\text{max}}$ (nm)	413	414	413	419	496	501	502	503	502	504
	Quantum Yields (%)	0.04	-	-	-	-	-	-	-	-	30.81
<b>2</b>	$\lambda_{\text{abs}}$ (nm)	364	363	365	365	366	366	374	379	372	369
	$\text{Em}_{\text{max}}$ (nm)	530	530	552	563	569	590	518	518	520	520
	Quantum Yields (%)	0.04	-	-	-	-	-	-	-	-	30.67
<b>3</b>	$\lambda_{\text{abs}}$ (nm)	322	323	322	321	321	331	328	326	323	323
	$\text{Em}_{\text{max}}$ (nm)	532	531	531	525	488	538	541	541	541	541
	Quantum Yields (%)	0.05	-	-	-	-	-	-	-	-	45.57
<b>4</b>	$\lambda_{\text{abs}}$ (nm)	364	363	365	364	365	379	375	376	372	369
	$\text{Em}_{\text{max}}$ (nm)	549	549	559	563	566	559	560	560	559	562
	Quantum Yields (%)	0.46	-	-	-	-	-	-	-	-	26.53

## 5. Copies of NMR spectra and Mass spectra

