## An AIEE fluorescent supramolecular cross-linked polymer network based on pillar[5]arene host-guest recognition: construction and application in explosive detection

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## 1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds  $1^{S1}$  and  $G^{S2}$  were prepared according to the published procedures. NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LRESIMS) were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). UV-vis absorption spectra were taken on a Shimadzu UV-2550 UV-vis spectrophotometer. Dynamic light scattering (DLS) measurements were performed on a goniometer ALV/CGS-3 using a UNIPHASE He-Ne laser operating at 632.8 nm. 2. Synthesis of **P5-TPE** and **G** 



Scheme S1. The synthetic route to P5-TPE.



Compound **2**: A mixture of **1** (2.00 g, 2.20 mmol) and potassium phthalimide (1.00 g, 5.00 mmol) was stirred in 20 mL of *N*,*N*-dimethylformamide at 90 °C for 24 h. The solution was evaporated under vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) to afford **2** as a yellow solid (2.00 g, 93%), mp: 122.5–123.1 °C. The <sup>1</sup>H NMR spectrum of compound **2** is shown in Figure S1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 7.86–7.84 (q, 2H, *J* = 4 Hz), 7.73–7.71 (q, 2H, *J* = 4 Hz), 6.82–6.74 (m, 10H), 3.90–3.87 (t, 2H, *J* = 6 Hz), 3.80–3.74 (m, 12H), 3.69–3.67 (m, 24H), 3.63 (s, 3H), 1.98–1.91 (m, 2H), 1.89–1.82 (m, 2H). The <sup>13</sup>C NMR spectrum of **2** is shown in Figure S2. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 168.96, 151.21, 151.17, 151.12, 151.10, 150.25, 134.52, 132.65, 128.89, 128.80, 123.78, 117.08, 115.38, 114.39, 114.31, 114.24, 68.39, 56.39, 56.35, 56.33, 56.27, 56.26, 56.24, 56.18, 38.36, 30.14, 30.05, 29.91, 27.81, 26.15. HRESIMS is shown in Figure S3: *m/z* calcd for [M + Na]<sup>+</sup> C<sub>56</sub>H<sub>59</sub>NO<sub>12</sub>Na<sup>+</sup>, 960.3929; found 960.3895, error –4 ppm.



*Figure S2.* <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 298 K) of **2**.



Compound **3**: A mixture of **2** (1.00 g, 1.06 mmol) and NH<sub>2</sub>NH<sub>2</sub> (10 mL) was heated at reflux in methanol (20 mL) for 12 h. Then the mixture was filtered and the residue was washed with methanol (10 mL × 2) to give **3** as a white solid (0.51 g, 60%), mp: 144.4–145.1 °C. The <sup>1</sup>H NMR spectrum of compound **3** is shown in Figure S4. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 6.82–6.75 (m, 10H), 3.81–3.76 (m, 12H), 3.70–3.64 (m, 27H), 2.13 (s, 2H), 1.58 (s, 2H), 1.21(s, 2H). The <sup>13</sup>C NMR spectrum of **3** is shown in Figure S5. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 150.88, 150.80, 150.76, 150.72, 150.69, 150.67, 150.65, 150.61, 149.87, 128.61, 128.46, 128.39, 128.34, 128.29, 128.22, 128.15, 128.08, 114.87, 114.50, 114.13, 114.04, 113.95, 113.88, 113.56, 68.65, 56.09, 55.94, 55.88, 55.86, 55.78, 55.71, 55.62, 40.95, 30.06, 29.78, 29.72, 29.59, 29.36, 26.78. LRESIMS is shown in Figure S6: *m/z* 808.6 [M + H]<sup>+</sup>. HRESIMS: *m/z* calcd for [M + H]<sup>+</sup> C<sub>48</sub>H<sub>58</sub>NO<sub>10</sub><sup>+</sup>, 808.4055; found 808.4026, error –4 ppm.



Figure S5.  $^{13}$ C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 298 K) of **3**.



Figure S6. LRESI mass spectrum of 3.





Compound **PD5**: DMAP (catalytic amount) and EDC (0.96 g, 5.0 mmol) were added to a solution of compounds **3** (2.00 g, 2.48 mmol) and **4** (0.59 g, 1.2 mmol) in chloroform (50 ml), and then the mixture was stirred for 48 h at room temperature. The organic layer was washed with water, a saturated aqueous NaHCO<sub>3</sub> solution and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel eluted with CH<sub>2</sub>Cl<sub>2</sub>/MeOH of 200:1 to 20:1 ratio ( $\nu/\nu$ ) to afford **PD5** as a pink solid (1.52 g, 60%), mp: 174.5–175.3 °C. The <sup>1</sup>H NMR spectrum of compound **PD5** is shown in Figure S7. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 7.13 (s, 2H), 6.89–6.85 (t, 2H, J = 4 Hz), 6.77–6.69 (m, 20H), 4.44 (s, 4H), 3.89–3.88 (t, 4H, J = 4 Hz), 3.78–3.74 (m, 20H), 3.65–3.64 (m, 42H), 3.61–3.60

(m, 12H), 3.50–3.47 (q, 4H, J = 4 Hz), 1.86 (s, 8H). The <sup>13</sup>C NMR spectrum of **PD5** is shown in Figure S8. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 169.50, 154.41, 153.56, 153.48, 153.45, 153.41, 153.37, 153.35, 153.33, 152.38, 131.09, 130.94, 130.88, 130.84, 130.81, 130.75, 130.67, 125.42, 117.77, 116.86, 116.79, 116.71, 116.60, 116.57, 88.72, 71.41, 70.56, 58.52, 58.47, 58.42, 58.36, 58.28, 41.64, 32.56, 32.49, 32.45, 32.44, 32.36, 32.25, 32.02, 29.91, 29.20. LRESIMS is shown in Figure S9: m/z 2079.7 [M + Na]<sup>+</sup>. HRESIMS: m/z calcd for [M + Na]<sup>+</sup> C<sub>106</sub>H<sub>118</sub>I<sub>2</sub>N<sub>2</sub>O<sub>24</sub>Na<sup>+</sup>, 2079.6062; found 2079.6136, error 4 ppm.









Figure S9. LRESI mass spectrum of PD5.



The compound **TPE-2** was synthesized according to previous literature.<sup>S3</sup>

*Scheme S2.* The synthetic route to **TPE-2**.



Figure S10. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 298 K) of (a) TPE-1 and (b) TPE-2.



**P5-TPE:** To an argon degassed mixture of **PD5** (0.1 mmol, 205 mg) and **TPE-2** (0.1 mmol, 38 mg) in dry THF (10 mL) and dry triethylamine (5 mL) were added bis(triphenylphosphine)palladium(II) chloride (5 mol%) and copper(I) iodide (10 mol%) and the reaction mixture was stirred at reflux until TLC indicated complete conversion. After cooling to room temperature, the precipitated ammonium salt was filtered off. The solution was washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvents, the residue was further purified by five repeated cycles of dissolution in THF and precipitation into a large volume of diethyl ether to afford a yellow solid **P5-TPE** (92 mg, 48%,  $M_{n,GPC}$  =7.4 kDa,  $M_{w,GPC}$  = 11.4 kDa,  $M_{p,GPC}$  = 9.8 kDa, PDI = 1.59, degree of polymerization = 6). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.49 (m, 2H), 7.22 (m, 4H), 7.09 (m, 6H), 6.99 (m, 10H), 6.73 (m, 20H), 4.50 (s, 4H), 3.76 (m, 26H), 3.61 (m, 56H), 3.35 (s, 4H), 1.69 (s, 8H).



**TPE-2**.

Compared with Figure S12c, Figure S12b did not show the resonance peak of protons of alkynyl group, indicating the successful polymerization and the formation of **P5-TPE**.



3. UV-vis absorption spectra of TPE-2 and P5-TPE in CHCl<sub>3</sub>



Figure S14 UV-vis absorption spectra of TPE-2 and P5-TPE in CHCl<sub>3</sub>.

4. Fluorescence spectra of **TPE-2** and **P5-TPE** in CHCl<sub>3</sub>



Figure S15 Fluorescence spectra of TPE-2 and P5-TPE in CHCl<sub>3</sub>.

5. Partial DOSY NMR spectra of **P5-TPE** in the absence and presence of **G**.



Figure S16 DOSY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of P5-TPE at 5.00 mM.



*Figure S17* DOSY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of 5.00 mM **P5-TPE** and 30.0 mM **G**.

6. Specific viscosity of **P5-TPE** and the 1:6 molar mixtures of **P5-TPE** and **G** at 298 *K* 



*Figure S18* Specific viscosity of **P5-TPE** and 1:6 molar mixtures of **P5-TPE** and **G** in CHCl<sub>3</sub> at 293 K versus the concentration of **P5-TPE**.

7. Cartoon representation of the formation of a supramolecular cross-linked polymer network and its disassembly induced by different signals



*Scheme S3* Cartoon representation of the formation of a supramolecular cross-linked polymer network and its disassembly induced by different signals.

8. Fluorescence changes of supramolecular polymer network induced by external stimuli



*Figure S19* Fluorescence emission spectra of the mixtures of P5-TPE (0.50 mM) and G (3.00 mM) after treatment with heating at 50 °C or adding competitive guest adiponitrile (12.0 mM).

9. Fluorescence change of a film made from the supramolecular polymer network before and after exposing to nitrobenzene vapour



*Figure S20* (a) Fluorescence emission spectra of a thin film made from the supramolecular polymer network before and after exposing to nitrobenzene vapour. (b) Cartoon

representation of exposure of the film to nitrobenzene vapour. (c) Photograph of the film before exposing to the nitrobenzene vapour, illuminated at 365 nm. (d) Photograph of the film after exposing to the nitrobenzene vapour, illuminated at 365 nm.

## 10. References

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