An AIEE fluorescent supramolecular cross-linked polymer network 

based on pillar[5]arene host−guest recognition: construction and 
application in explosive detection

Li Shao, Jifu Sun, Bin Hua* and Feihe Huang*

State Key Laboratory of Chemical Engineering, Center for Chemistry of High-Performance & Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China;

Email: huabin@zju.edu.cn; fhuang@zju.edu.cn

Electronic Supplementary Information (19 pages)

1. Materials and methods S2
2. Synthesis of P5-TPE and G S3
3. UV-vis spectra of TPE-2 and P5-TPE in CHCl₃ S14
4. Fluorescence spectra of TPE-2 and P5-TPE in CHCl₃ S15
5. Partial DOSY NMR spectra of P5-TPE in the absence and presence of G S15
6. Specific viscosity of P5-TPE and 1:6 molar mixtures of P5-TPE and G at 298 K S16
7. Cartoon representation of the formation of a supramolecular cross-linked network 
and its disassembly induced by different signals S17
8. Fluorescence changes of the supramolecular polymer network induced by external stimuli S18
9. Fluorescence change of a film made from the supramolecular polymer network 
before and after exposing to nitrobenzene vapour S18
10. References S19
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 1H NMR spectrum of compound 2 is shown in Figure S1. 1H NMR (400 MHz, CDCl₃, 298 K) δ (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 13C NMR spectrum of 2 is shown in Figure S2. 13C NMR (100 MHz, CDCl₃, 298 K) δ (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]+ C₅₆H₉₉NO₁₂Na+, 960.3929; found 960.3895, error −4 ppm.
Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of 2.

Figure S2. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, 298 K) of 2.
Compound 3: A mixture of 2 (1.00 g, 1.06 mmol) and NH₂NH₂ (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 ¹H NMR spectrum of compound 3 is shown in Figure S4. ¹H NMR (400 MHz, CDCl₃, 298 K) δ (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 ¹³C NMR spectrum of 3 is shown in Figure S5. ¹³C NMR (100 MHz, CDCl₃, 298 K) δ (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, 114.85, 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]⁺. HRESIMS: m/z caled for [M + H]⁺ C₄₈H₅₈NO₁₀⁺, 808.4055; found 808.4026, error –4 ppm.
Figure S4. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of 3.

Figure S5. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, 298 K) 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 NaHCO₃ solution and brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel eluted with CH₂Cl₂/MeOH of 200:1 to 20:1 ratio (v/v) to afford **PD5** as a pink solid (1.52 g, 60%), mp: 174.5–175.3 °C. The ¹H NMR spectrum of compound **PD5** is shown in Figure S7. ¹H NMR (400 MHz, CDCl₃, 298 K) δ (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 $^{13}$C NMR spectrum of PD5 is shown in Figure S8. $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) δ (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]$^+$. HRESIMS: m/z calcd for [M + Na]$^+$ C$_{106}$H$_{118}$I$_2$N$_2$O$_{24}$Na$^+$, 2079.6062; found 2079.6136, error 4 ppm.

Figure S7. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of PD5.
Figure S8. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, 298 K) of PD5.

Figure S9. LRESI mass spectrum of PD5.
The compound TPE-2 was synthesized according to previous literature.\textsuperscript{S3}

\begin{equation}
\begin{array}{c}
\text{Scheme S2. The synthetic route to TPE-2.}
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{Figure S10. } ^1\text{H NMR spectrum (400 MHz, CDCl}_3, 298 \text{ K) of (a) TPE-1 and (b) TPE-2.}
\end{array}
\end{equation}
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 MgSO₄. 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). $^1$H NMR (CDCl₃, 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).
Figure S11 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of P5-TPE.

Figure S12 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of (a) PD5, (b) P5-TPE and (c) 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.

![Figure S13 GPC result of P5-TPE.](image)

3. **UV-vis absorption spectra of TPE-2 and P5-TPE in CHCl₃**

![Figure S14 UV-vis absorption spectra of TPE-2 and P5-TPE in CHCl₃.](image)
4. **Fluorescence spectra of TPE-2 and P5-TPE in CHCl₃**

![Fluorescence spectra graph]

*Figure S15* Fluorescence spectra of TPE-2 and P5-TPE in CHCl₃.

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

![DOSY NMR spectrum graph]

*Figure S16* DOSY NMR spectrum (500 MHz, CDCl₃, 298 K) of P5-TPE at 5.00 mM.
Figure S17 DOSY NMR spectrum (500 MHz, CDCl₃, 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 CHCl₃ 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

![Fluorescence spectra](image)

**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

![Fluorescence spectra and cartoon](image)

**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

