Fabrication of a cross-linked supramolecular polymer on the basis of cucurbit[8]uril-based host–guest recognition with tunable AIE behaviors

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds a and d were prepared according to the published procedures. NMR spectra were recorded with 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 were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 298 K in water. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. Scanning electron microscopy (SEM) investigations were carried out on a Multimode 8 instrument. MALDI-TOF-MS spectra were performed on a AXIMA Performance-MALDI TOF/TOF (Matrix: 2,5-dihydroxy-benzoic acid). Viscosity measurements were carried out with Cannon-Ubbelohde semi-micro dilution viscometers at 25 °C in water. Monomers 1 and 2 were measured with a 0.30 mm inner diameter viscometer due to their relative low viscosity. The viscosity of the ternary supramolecular polymer was measured with a 0.50 mm inner diameter viscometer due to its relative high viscosity. The inner diameter of the viscometer did not affect the obtained results. Compound 1 (1.00 mM) and compound 2 (2.00 mM) were mixed in water and the solution was stirred for 1 h. CB[8] (4.00 mM) was added gradually into the solution and the mixture was stirred at 50 °C for another 1 h, and then the solution was cooled down to give the cross-linked supramolecular polymer. Electrospun supramolecular polymer nanofibers were obtained under the following conditions, 25 kV, 2.0 mL/h syringe flow rate, and 10 cm working distance, from a concentrated solution (1.50 mM) of CB[8]/1/Trans-2.
2. Synthesis of 1 and 2

![Scheme S1. Synthesis of 2](image)

Compound PEG-OTs: Polyethylene glycol (20.0 g, 10.0 mmol) and sodium hydroxide solution (3.00 M, 100 mL) were placed in a 500 mL round-bottomed flask. A THF (100 mL) solution of p-toluenesulfonyl chloride (19.1 g, 100 mmol) was added dropwise to the mixture, which was stirred mechanically for about 3 h at 0 °C and then for 24 h at room temperature. When the reaction was complete, THF was removed in vacuo, the aqueous solution was extracted with CH$_2$Cl$_2$ (3 × 100 mL). The organic phase was combined, dried with anhydrous Na$_2$SO$_4$, and then CH$_2$Cl$_2$ was removed in vacuo to afford PEG-OTs as a oil (18.3 g, 77%). The molecular weight and composition of PEG-OTs were determined by GPC (Fig. S2) and $^1$H NMR spectroscopy (Fig. S1).

![Fig. S1 $^1$H NMR spectrum (400 MHz, chloroform-d, 298 K) of PEG-OTs.](image)
Compound 2: A mixture of PEG-OTs (11.5 g, 5.00 mmol), 3 (3.96 g, 20.0 mmol) and K$_2$CO$_3$ (13.7 g, 100 mmol) in CH$_3$CN was stirred under N$_2$ at reflux for 2 days. Then the reaction mixture was cooled to room temperature and filtered. The filter cake was washed with chloroform (2 × 30 mL). The filtrate was concentrated under vacuum, and then the residue was purified by column chromatography on silica gel to afford 2 as a yellow oil (9.25 g, 76%). The molecular weight and composition of 2 were determined by GPC (Fig. S4) and $^1$H NMR spectroscopy (Fig. S3).
Fig. S3 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of PEG-Azo.

$M_n = 2433$, PDI = 1.08

Fig. S4 GPC curves of PEG-Azo.
**Synthesis of b:** a (3.96 g, 10.0 mmol) and K$_2$CO$_3$ (13.7 g, 100 mmol) were added to a solution of 1,6-dibromohexane (24.3 g, 100 mmol) in CH$_3$CN (500 mL). The mixture was heated in a three-necked flask under nitrogen atmosphere at reflux for 2 d. The cooled reaction mixture was filtered and washed with chloroform. The filtrate was evaporated under vacuum to give the crude product, which was purified by flash column chromatography (dichloromethane/petroleum ether, 4:1 v/v) to yield b as a white solid (6.99 g, 67%). The proton NMR spectrum of b is shown in Fig. S5. $^1$H NMR (400 MHz, chloroform-d, room temperature) $\delta$ (ppm): 6.94 (d, $J$ = 8 Hz, 8H), 6.63 (d, $J$ = 8 Hz, 8H), 3.90 (t, $J$ = 8 Hz, 8H), 3.44 (t, $J$ = 8 Hz, 8H), 1.96–1.87 (m, 8H), 1.85–1.74 (m, 8H), 1.54–1.47 (m, 16H). The $^{13}$C NMR spectrum of b is shown in Fig. S6. $^{13}$C NMR (100 MHz, chloroform-d, room temperature) $\delta$ (ppm): 157.25, 138.31, 136.98, 136.83, 132.55, 113.52, 67.50, 55.09, 33.84, 32.68, 29.16, 27.96, 25.34. LRESIMS is shown in Fig. S7: m/z 1049.151 [M + H]$^+$ (100%). HRESIMS: m/z calcd for [M + H]$^+$ C$_{50}$H$_{65}$Br$_4$O$_4$, 1049.1584, found 1049.1596, error 1.1 ppm.
Fig. S5 \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\), 298 K) of b.

Fig. S6 \(^13\)C NMR spectrum (100 MHz, CDCl\(_3\), 298 K) of b.
Fig. S7 MALDI-TOF-MS of b. Assignment of the main peak: \( m/z \) 1049.151 \([M + H]^+\).

Scheme S3. Synthesis of c.

Synthesis of c: a mixture of b (2.09 g, 2.00 mmol) and NaN₃ (1.63 g, 25.0 mmol) was heated in acetone (40 mL) and water (4 mL) at 50 °C for 12 h. The solution was concentrated under reduced pressure. The precipitate was filtered off under suction and washed with water (5 × 20 mL) to give c as a white solid (1.68 g, 94%). The proton NMR spectrum of c is shown in Fig. S8. \(^1\)H NMR (400 MHz, chloroform-\(d\), room temperature) \( \delta \) (ppm): 6.94 (d, \( J = 8 \) Hz, 8H), 6.66 (d, \( J = 8 \) Hz, 8H), 3.90 (t, \( J = 8 \) Hz, 8H), 3.30 (t, \( J = 8 \) Hz, 8H), 1.82–1.73 (m, 8H), 1.70–1.61 (m, 8H), 1.51–1.40 (m, 16H). The \(^{13}\)C NMR spectrum of 3 is shown in Fig S9. \(^{13}\)C NMR (100 MHz, chloroform-\(d\), room temperature) \( \delta \) (ppm): 157.23, 138.37, 136.81, 132.53, 113.42,
67.48, 55.08, 51.39, 28.80, 26.53, 25.72. LRESIMS is shown in Fig. S10: \( m/z \) 919.8 \([M + Na]^+\) (100%). HRESIMS: \( m/z \) caled for \([M + Na]^+\) \( C_{50}H_{64}N_{12}NaO_4 \), 919.5071, found 919.5074, error 3.2 ppm.

Fig. S8 \(^1\)H NMR spectrum (400 MHz, chloroform-\(d\), room temperature) of \( c \).

Fig. S9 \(^{13}\)C NMR spectrum (100 MHz, chloroform-\(d\), room temperature) of \( c \).
**Fig. S10** Electrospray ionization mass spectrum of c. Assignment of the main peak: $m/z$ 919.8 [M + Na]$^+$ (100%).

**Scheme S4.** Synthesis of 1.

Synthesis of 1: Compound c (1.60 g, 1.80 mmol), copper sulphate pentahydrate (30.0 mg, 0.120 mmol) and sodium ascorbate (225 mg, 1.60 mmol) were added to a solution of d (4.63 g, 10.0 mmol) in the mixture of water (50 mL) and THF (50 mL). The mixture was stirred at room temperature under nitrogen atmosphere for 12 h. THF was removed under reduced pressure, the precipitate was filtered off under suction and washed with water (5 × 20 mL). The obtained precipitate was dissolved in hydrochloric acid solution and the solution was lyophilized to give 1 as a light yellow solid (4.64 g, 94%). The proton NMR spectrum of 1 is shown in Fig. S11. $^1$H NMR (500 MHz, DMSO-$d_6$, room temperature) (ppm): 9.36 (d, $J = 8$ Hz, 16H), 8.76 (d, $J = 8$ Hz, 16H), 8.01 (s, 4H), 6.82 (d, $J = 8$ Hz, 8H), 6.65 (d, $J = 8$ Hz, 8H), 5.00 (t, $J = 8$ Hz, 8H), 4.70 (t, $J = 8$ Hz, 8H), 4.32 (t, $J = 8$ Hz, 8H), 3.83 (t, $J = 8$ Hz, 8H), 3.47 (t, $J$
= 8 Hz, 8H), 1.87–1.72 (m, 8H), 1.61–1.57 (m, 20H), 1.40–1.31 (m, 8H), 1.26–1.19 (m, 8H). The $^{13}$C NMR spectrum of 1 is shown in Fig. S12. $^{13}$C NMR (100 MHz, DMSO-$d_6$, room temperature) δ (ppm): 157.86, 157.30, 148.84, 146.44, 146.05, 138.42, 136.59, 132.40, 127.00, 126.83, 114.06, 113.63, 67.56, 60.33, 57.07, 55.34, 49.98, 30.02, 29.02, 27.11, 26.04, 25.42, 16.73. LRESIMS is shown in Fig. S13: $m/z$ 1031.3 [M – 2Cl]$^{2+}$ (100%). HRESIMS: $m/z$ calcd for [M – 2Cl]$^{2+}$ C$_{114}$H$_{136}$Cl$_6$N$_{20}$O$_4$, 1031.4589, found 1031.4576, error 1.2 ppm.

**Fig. S11** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, room temperature) of 1.
Fig. S12 $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$, room temperature) of 1.

Fig. S13 Electrospray ionization mass spectrum of 1. Assignment of the main peak: $m/z$ 1031.3 [M – 2Cl]$^{2+}$ (100%).
3. Photoisomerization behavior of 2

![Fig. S14. UV-Vis absorption spectra of the aqueous solution containing 2 (0.1 mM) under UV irradiation at 365 nm of 0 s, 5 s, 10 s, 30 s, 1 min, 3min, 5min, 10 min (left) and later after visible irradiation at 435 nm of 0 s, 5 s, 10 s, 30 s, 1 min, 3min, 10 min (right).](image)

Upon irradiation with UV light at 365 nm, the absorption band at around 318 nm decreased remarkably, and concomitantly the band at around 435 nm increased slightly. The absorption bands of the azobenzene unit at 318 and 435 nm are ascribed to \( \pi-\pi^* \) and \( n-\pi^* \) transitions, respectively. The changes of the absorption bands induced by UV irradiation indicated the photoisomerization from the \textit{trans} state to the \textit{cis} state. On the contrary, upon irradiation with visible light at 435 nm, the absorption peak at 435 nm attributable to \textit{cis} decreased, while the absorption band at 318 nm corresponding to \textit{trans} increased, indicating a change from the \textit{cis} form to the \textit{trans} form.
**Fig. S15** Partial $^1$H NMR (500 MHz, D$_2$O, 293 K) spectra of: (a) Trans-2 (0.25 mM); (b) Trans-2, DMV$^{2+}$ and CB[8]; (c) Trans-2 and DMV$^{2+}$; (d) DMV$^{2+}$ (0.50 mM); (e) DMV$^{2+}$ and CB[8]; (f) CB[8] 0.50 mM.

**Fig. S16** UV spectra of 1 in acetone (a) and water (b). Fluorescent spectra of 1 in acetone (c) and water (d)
4. References:
