

# Photo-responsive linear and cross-linked supramolecular polymers based on host–guest interactions

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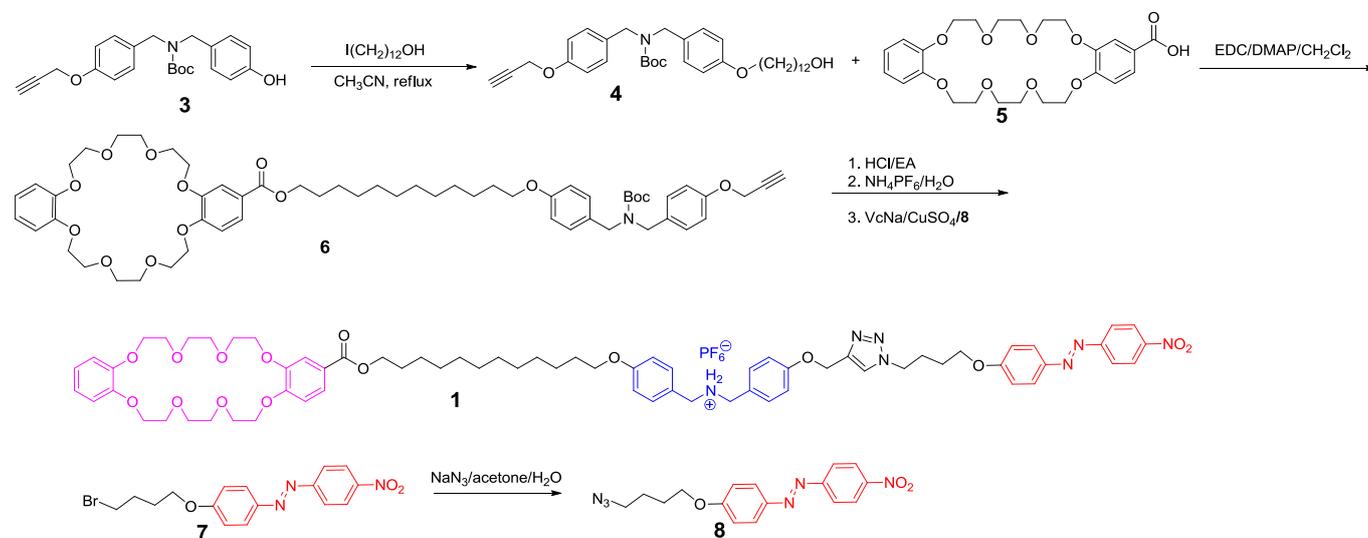
## Electronic Supplementary Information (13 pages)

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### *1. Materials and methods*

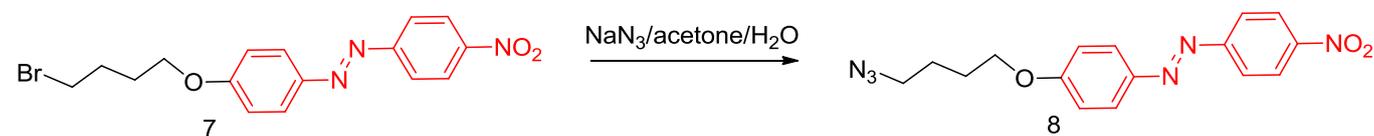
All reagents were commercially available and used as supplied without further purification. Compounds **3**<sup>S1</sup>, **5**<sup>S2</sup>, and **7**<sup>S3</sup> were prepared according to the published procedures. <sup>1</sup>H NMR spectra were collected on a temperature-controlled Bruker 400 MHz spectrometer or Bruker AVIII 500 MHz spectrometer. <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer (0.45 mm inner diameter) at 25 °C in CH<sub>2</sub>Cl<sub>2</sub>.

## 2. Synthesis of monomer **1**



Scheme S1. Synthesis of monomer **1**.

### 2.1. Synthesis of compound **4**



Compound **7** (3.78 g, 10.0 mmol) and  $NaN_3$  (3.25 g, 50.0 mmol) in acetone/water (4:1, 100 mL) were refluxed for 24 hours. After removal of the solvent, water was added to the mixture. The mixture was extracted with  $CH_2Cl_2$  three times. The organic phases were combined, washed with water and brine, and dried over  $Na_2SO_4$  overnight. After filtration, the solvent was evaporated to yield compound **8** as a red solid (3.24 g, 95.3%), mp 84.4–87.3 °C. The  $^1H$  NMR spectrum of compound **8** is shown in Figure S1.  $^1H$  NMR (400 MHz,  $CDCl_3$ , room temperature)  $\delta$  (ppm): 8.38 (d,  $J = 8.8$  Hz, 2H), 7.98 (d,  $J = 8.8$  Hz, 4H), 7.02 (d,  $J = 8.8$  Hz, 2H), 4.11 (d,  $J = 6.0$  Hz, 2H), 3.40 (d,  $J = 6.0$  Hz, 2H), 1.94 (m, 2H), 1.83 (m, 2H). The  $^{13}C$  NMR spectrum of **8** is shown in Figure S2.  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , room temperature)  $\delta$  (ppm): 25.94, 26.66, 51.38, 67.91, 115.13, 123/35, 124.95, 125.87, 147.17, 148.48, 156.25, 162.80. LRESIMS is shown in Figure S3:  $m/z$  341.1  $[M + H]^+$  (100%). HRESIMS:  $m/z$  calcd for  $[M]^+ C_{16}H_{16}N_6O_3^+$ , 340.1284, found 340.1285, error 0.3 ppm.

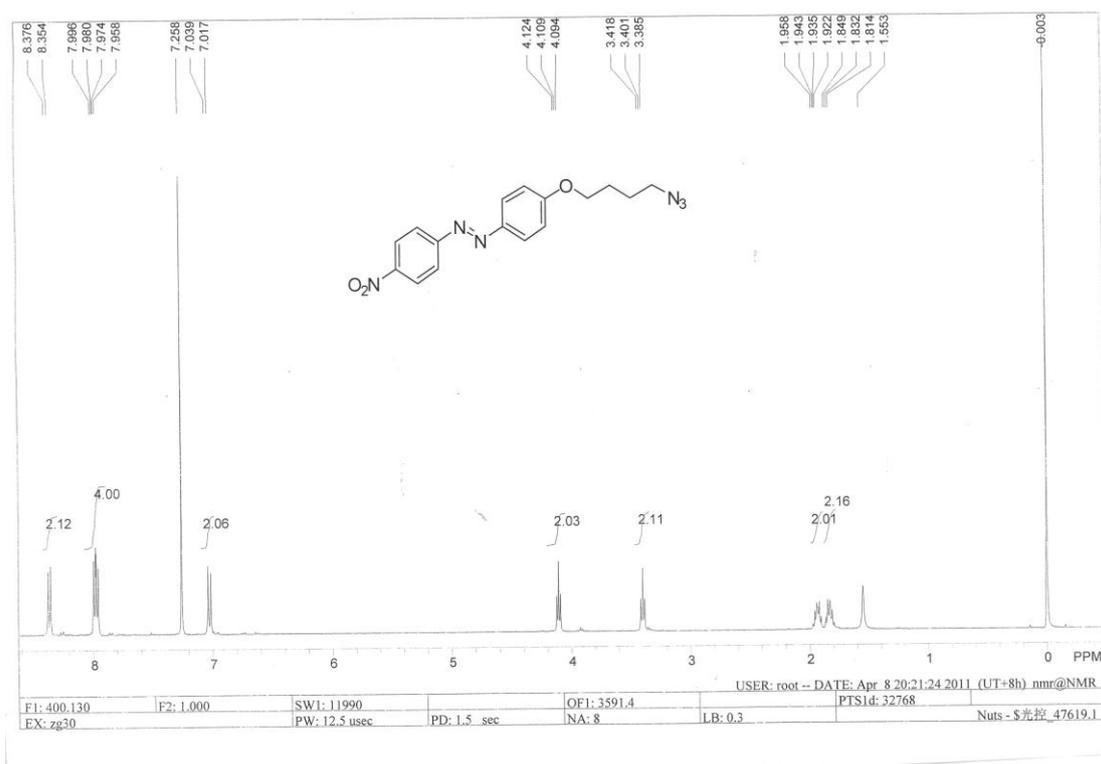


Figure S1. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, room temperature) of **8**.

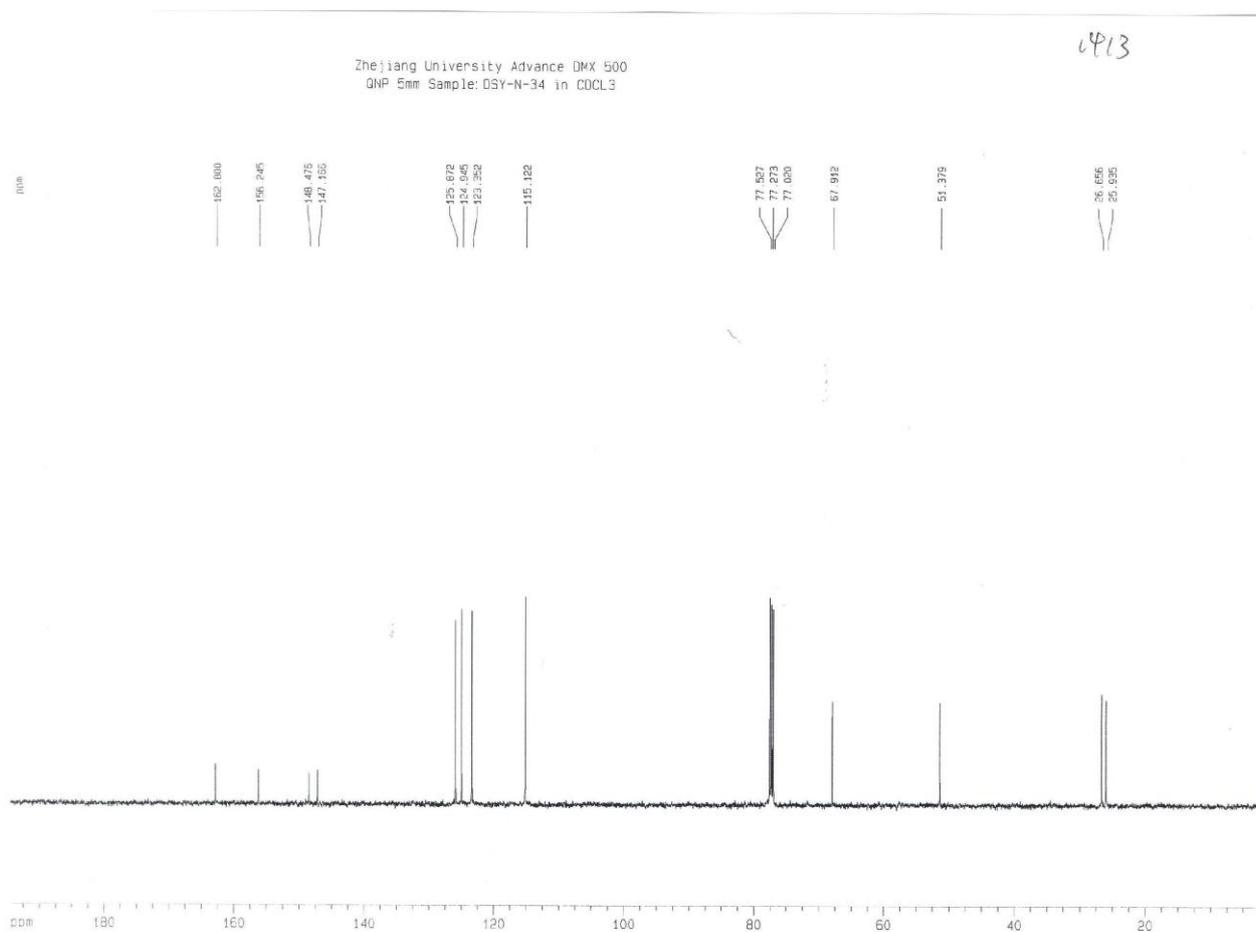


Figure S2. <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, room temperature) of **8**.

### Display Report

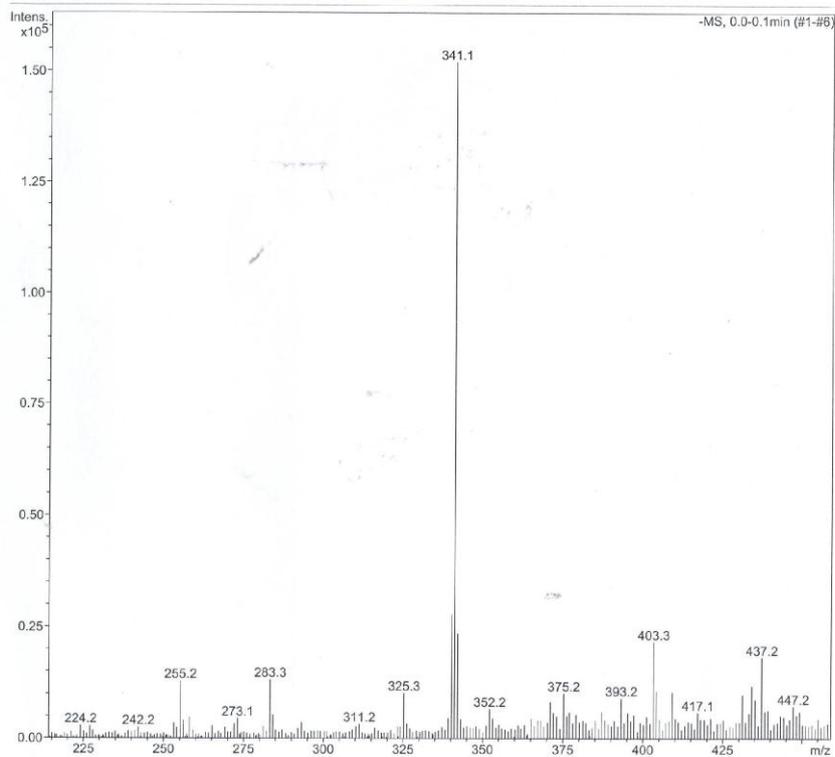
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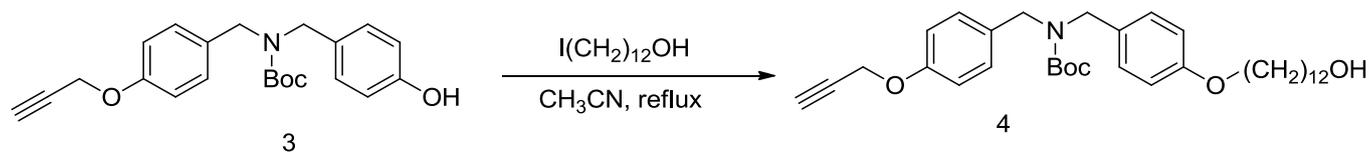
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Accumulation Time	12381 $\mu$ s	Averages	8 Spectra	Auto MS/MS	off



**Figure S3.** Electrospray ionization mass spectrum of **8**.

## 2.2. Synthesis of compound 4



Compound **3** (3.67 g, 10.0 mmol), 12-iodododecan-1-ol (3.12 g, 10.0 mmol) and  $\text{K}_2\text{CO}_3$  (2.76 g, 20.0 mmol) in  $\text{CH}_3\text{CN}$  (125 mL) were refluxed for 24 hours. The reaction mixture was filtered and the solvent was removed under vacuum to give a yellow oil. After removal of  $\text{CH}_3\text{CN}$ , water was added to the mixture. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  three times. The organic phases were combined, washed with water and brine, and dried over  $\text{Na}_2\text{SO}_4$  overnight. After filtration and solvent evaporation, the crude product was purified by flash column chromatography (PE/EA, 1:1, v/v) to yield compound **4** as a colorless oil (4.42 g, 80.2%). The  $^1\text{H}$  NMR spectrum of compound **4** is shown in Figure S4.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , room temperature)  $\delta$  (ppm): 7.10 (s, 4H), 6.95 (d,  $J = 4.0$  Hz, 2H), 6.86 (d,  $J = 4.0$  Hz, 2H), 4.40 (d,  $J = 4.0$  Hz, 2H), 4.34 (s, 2H), 4.25 (s, 2H), 3.94 (t,  $J = 8.0$  Hz, 2H), 3.63 (t,  $J = 8.0$  Hz, 2H), 3.37 (s, 1H), 2.02 (m, 2H), 1.42–1.59 (m, 13H), 1.29–1.37 (m, 14H). The  $^{13}\text{C}$  NMR spectrum of **4** is shown in Figure S5.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , room temperature)  $\delta$  (ppm): 25.97, 26.26, 28.70, 29.49, 29.60, 29.65, 29.77, 29.80, 31.15, 33.01, 48.31, 48.51, 55.27, 56.06, 63.22, 68.23, 75.75, 78.80, 80.16, 114.68, 115.09, 128.98, 129.54, 129.99, 131.35, 156.15, 156.98, 158.61. LRESIMS is shown in Figure S3:  $m/z$  574.3  $[\text{M} + \text{Na}]^+$  (20%),  $m/z$  610.2  $[\text{M} + \text{C}_3\text{H}_7\text{O}]^+$  (100%). HRESIMS:  $m/z$  calcd for  $[\text{M}]^+ \text{C}_{34}\text{H}_{49}\text{NO}_5^+$ , 551.3611, found 551.3602, error  $-1.6$  ppm.

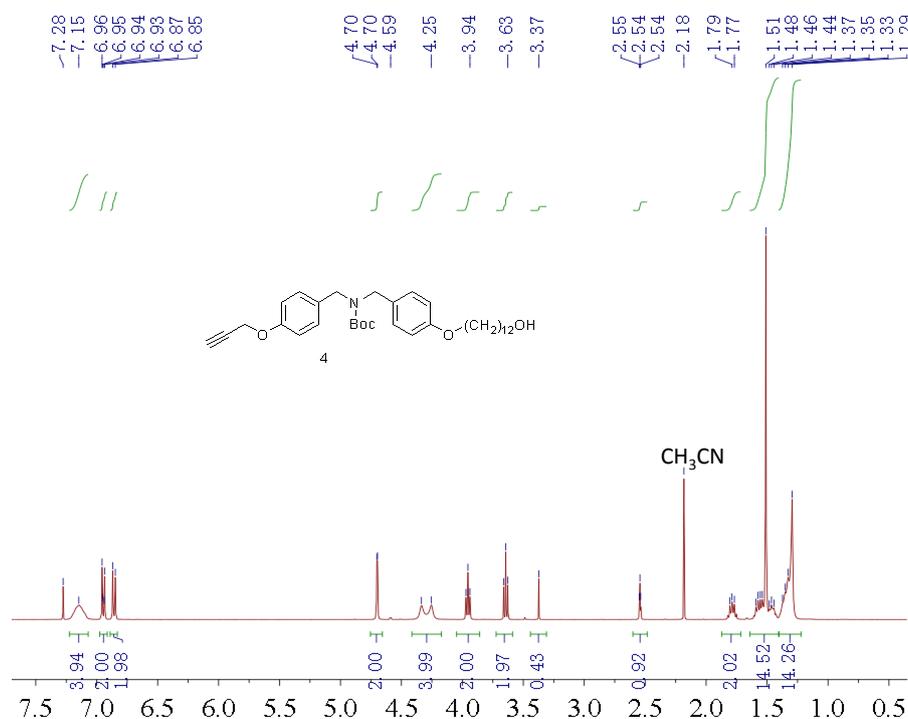


Figure S4.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of **4**.



### Display Report

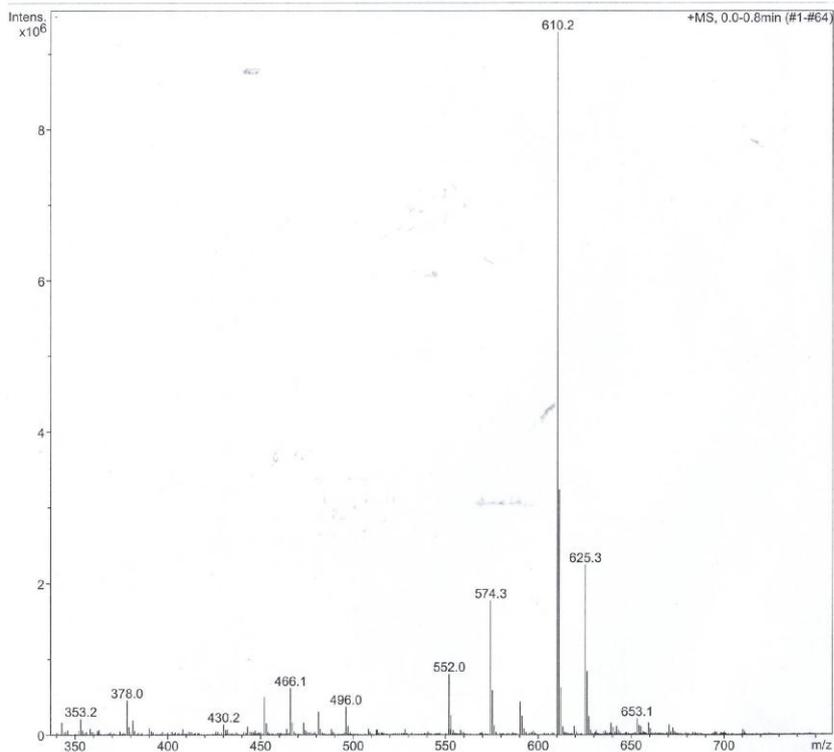
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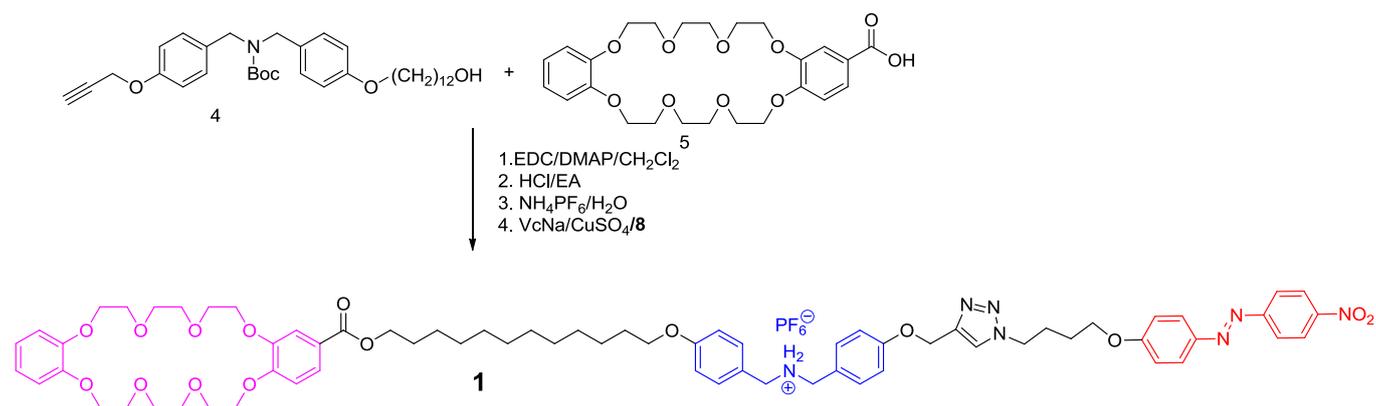
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**Figure S6.** Electrospray ionization mass spectrum of **4**.

### 2.3. Synthesis of monomer **1**



A mixture of **4** (5.51 g, 10.0 mmol), 4-dimethylaminopyridine (DMAP, catalytic amount), 1-(3'-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 6.00 g, 30.0 mmol) and **5** (4.92 g, 10.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (65 mL) was stirred for 48 hours at room temperature. The reaction mixture was filtered and the solvent was removed under vacuum to give a yellow oil. This yellow oil was dissolved in 10% HCl/ethyl acetate (35 mL) and stirred overnight. The white solid was filtered, washed with ethyl acetate (EA) thoroughly, and dissolved in warm deionized water/acetonitrile (250 mL, 5:1, v:v). A saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added to afford a white precipitate, which was filtered off and washed with deionized water. This white solid and compound **8** (3.40 g, 10.0 mmol) were dissolved in DMF/H<sub>2</sub>O (4:1, 50 mL) in the presence of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.10 g, 0.40 mmol) with sodium ascorbate (0.20 g, 1.0 mmol) and the mixture was stirred for 48 hours at 50 °C. The reaction mixture was poured into a mixture of cold water and diethyl ether to yield monomer **1** as a red solid (3.82 g, 27.1%), mp 92.7–94.3 °C. The <sup>1</sup>H NMR spectrum of compound **1** is shown in Figure S7. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO, room temperature) δ (ppm): 8.41 (d, *J* = 9.2 Hz, 2H), 8.28 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.38 (m, 5H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 9.2 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.92 (m, 4H), 6.84 (m, 2H), 5.16 (s, 2H), 4.48 (t, *J* = 6.8 Hz, 2H), 4.21 (t, *J* = 6.8 Hz, 2H), 4.16–4.22 (m, 16H), 3.95 (m, 8H), 3.65 (s, 8H), 2.01 (m, 2H), 1.66–1.74 (m, 6H), 1.25–1.37 (m, 16H). The <sup>13</sup>C NMR spectrum of **1** is shown in Figure S8. <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO, room temperature) δ (ppm): 25.92, 26.03, 26.94, 28.65, 29.09, 29.23, 29.39, 31.16, 49.56, 61.63, 64.85, 67.99, 69.16, 69.35, 69.40, 69.50, 69.63, 70.90, 70.99, 112.97, 114.22, 114.47, 114.53, 114.97, 115.28, 115.78, 121.60, 122.67, 123.62, 123.82, 125.07, 125.54, 125.93, 131.88, 146.70, 148.31, 148.47, 148.92, 153.08, 155.84, 158.93, 159.58, 162.92, 165.90. LRESIMS is shown in Figure S6: *m/z* *m/z* 1266.7 [M – PF<sub>6</sub>]<sup>+</sup> (100%). HRESIMS: *m/z* calcd for [M – PF<sub>6</sub>]<sup>+</sup> C<sub>70</sub>H<sub>88</sub>N<sub>7</sub>O<sub>15</sub><sup>+</sup>, 1266.6338, found 1266.6293, error –3.6 ppm.

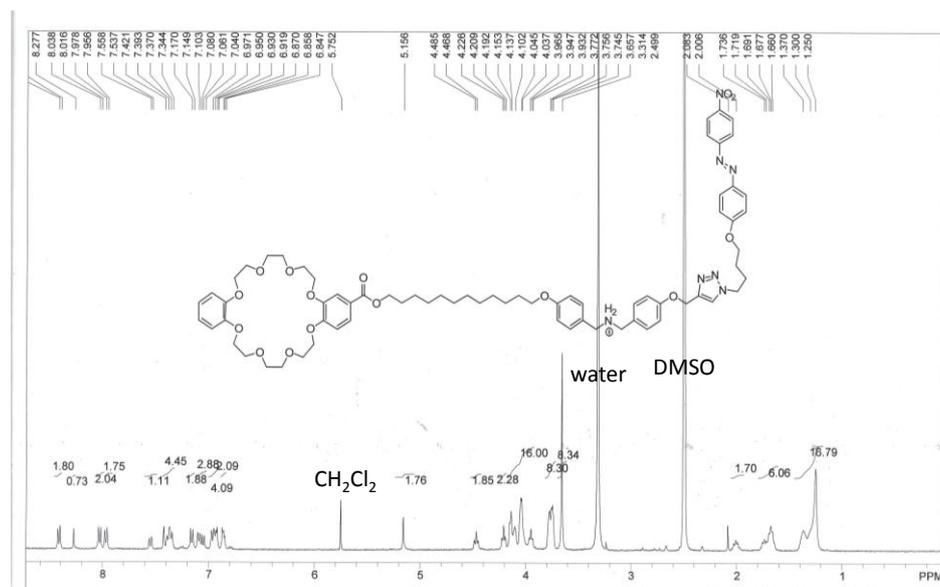


Figure S7. <sup>1</sup>H NMR spectrum (400 MHz, [D<sub>6</sub>]DMSO, room temperature) of **1**.

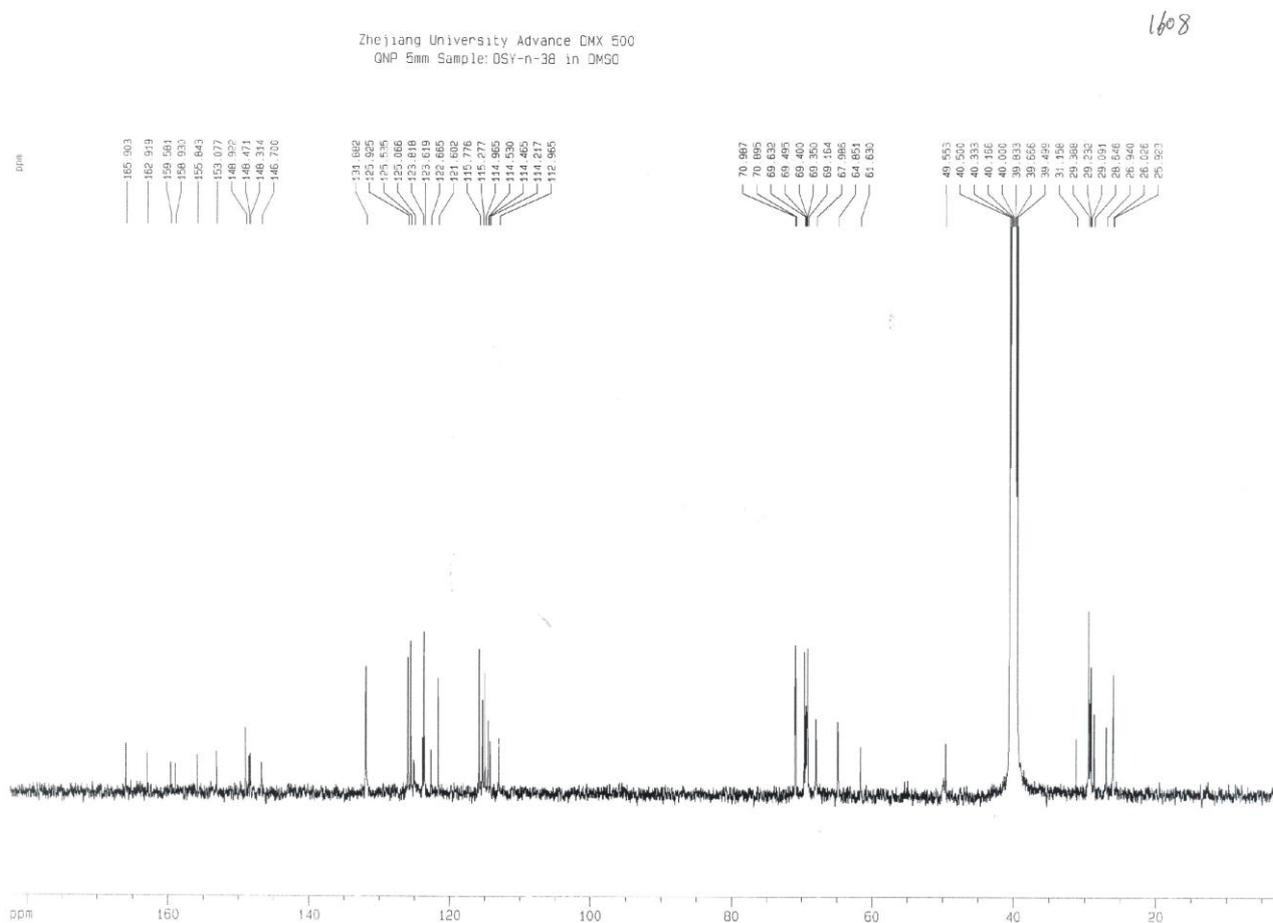
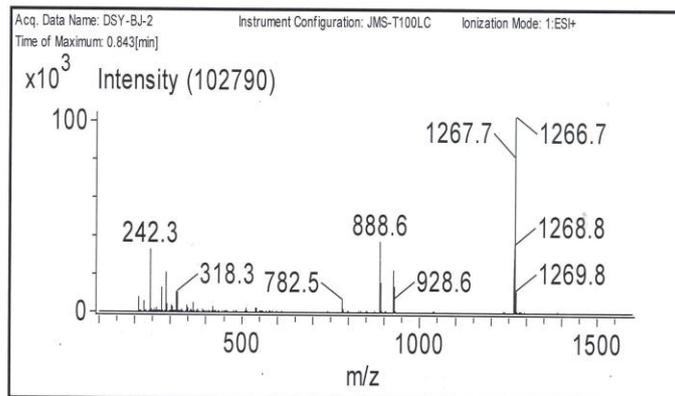


Figure S8. <sup>13</sup>C NMR spectrum (125 MHz, [D<sub>6</sub>]DMSO, room temperature) of **1**.



Sample name: DSY-BJ-2  
Polarity: positive  
m/z Tolerance (ppm):10.0

Mass	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	$^{12}\text{C}$	$^1\text{H}$	$^{14}\text{N}$	$^{16}\text{O}$	Unsaturation Number
1266.62927	1266.63384	-4.56	-3.60	70	88	7	15	30.5

Figure S9. Electrospray ionization mass spectrum of **1**.

### 3. Specific viscosities of cross-linked supramolecular polymers before/after UV irradiation

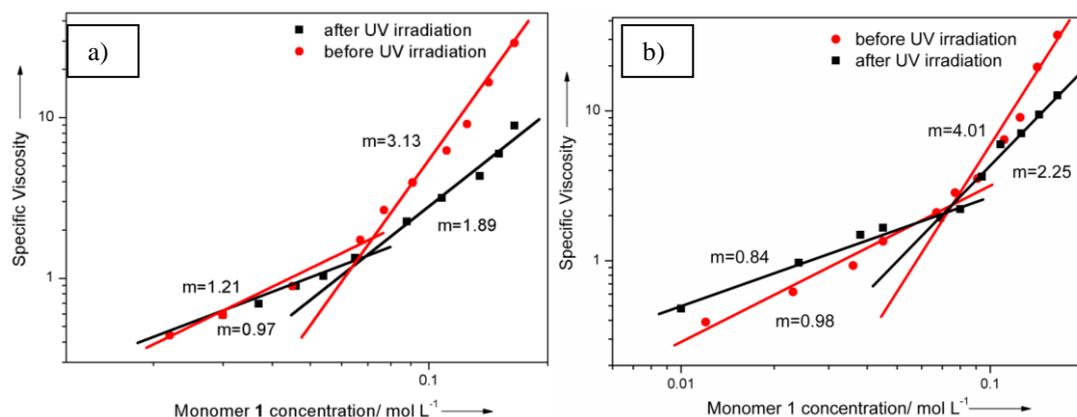


Figure S10. Specific viscosities of a dichloromethane solution of linear polymers (a) and cross-linked polymers (containing 10 mol% PdCl<sub>2</sub>(PhCN)<sub>2</sub>) versus the monomer **1** concentration at 25 °C: linear polymers before UV irradiation (black line in a) and linear supramolecular polymers after UV irradiation for 10 min (red line in a); cross-linked supramolecular polymers before UV irradiation (black line in b) and cross-linked supramolecular polymers after UV irradiation for 10 min (red line in b). Cross-linked supramolecular polymers and linear supramolecular polymers did not show obvious differences in the CGC before UV irradiation and after UV irradiation, respectively. At low concentration, UV irradiation showed slight influence on both linear and cross-linked polymers.

### 4. A possible gelation mechanism of cross-linked supramolecular polymers

At first, due to the host–guest interactions between DB24C8 and DBA, linear supramolecular polymers were formed in solution. When 10 mol% PdCl<sub>2</sub>(PhCN)<sub>2</sub> was added to the linear polymers, linear polymers were cross-linked *via* metal-coordination interactions. At high monomer concentration, these cross-linked polymers would form a three-dimensional network (other weak interactions, such as van der Waals force and electrostatic interactions would also exist), and by incorporating solvent molecules, a supramolecular gel was finally formed.

*References:*

- S1 L. Ao,; J.-H. Tu,; X. Huang and B.-Y. Ding, *Acta. Cryst.* 2011, **E67**, o2642
- S2 X.-B. Shao,; X.-K. Jiang,; X.-Z. Wang,; Z.-T. Li and S.-Z. Zhu, *Tetrahedron* 2003, **59**, 4881–4889.
- S3 G. Pangadhar,; C. Robert,; Y. Zhang,; C. C. Bazuin and A. M. Ritcey, *Langmuir* 2003, **19**, 8859–8866.