Electronic Supplementary Information

AIE-active supramolecular cross-linked polymer gel based on multiple orthogonal non-covalent interactions with stimulus-responsive properties

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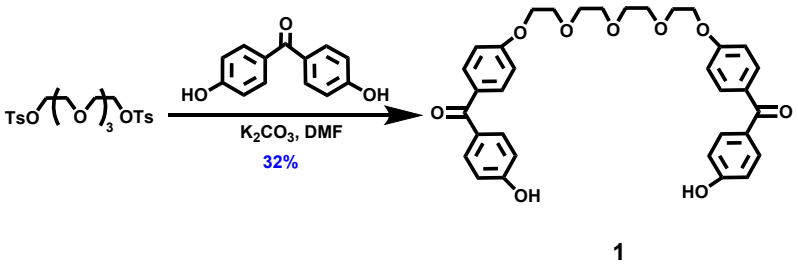
1. General information

The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literatures. All reactions were performed under nitrogen atmosphere unless otherwise stated. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel plates. Column chromatography was performed with silica gel (200-300 mesh) produced by Shanghai Titan Scientific Co., Ltd. All yields were given as isolated yields. NMR spectra (^{1}H NMR, ^{13}C NMR, and 2D NMR) were recorded on a Bruker Avance 400 MHz spectrometer at room temperature, with tetramethylsilane (TMS) as internal standard and solvent signals as internal references. Chemical shifts (δ) are reported in parts per million (ppm). Multiplicities were abbreviated as follows: d = doublet, t = triplet, q = quartet, m = multiplet, and coupling constant (*J*) in Hertz (Hz). High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Orbitrap Exploris 120 equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. UV-visible spectra were recorded with a Shimadzu UV 1780 UV-Vis Spectrophotometer. Scanning electron microscope (SEM) investigations were carried out using a FEI Quanta FEG 250 instrument. Fluorescence spectra were recorded on a Gangdong SCI F-380 fluorescence spectrophotometer. The quantum yields were carried out on a FLS1000 instrument with the integrating sphere. Compounds **4**[1] and **6**[2] were synthesized according to the reported procedures.

2. Synthetic procedures and characterization data

Synthesis of host molecule BCE



Scheme S1 Synthesis route of compound **1**.

Synthesis of compound **1**

Under a nitrogen atmosphere, K_2CO_3 (0.45 g, 3 mmol), 4,4'-dihydroxybenzophenone (0.92 g, 4 mmol), and DMF (60 mL) were added to a reaction flask. A solution of tetraethylene glycol di(*p*-methylphenyl sulfonate) (1 g, 2 mmol) in DMF (100 mL) was then added dropwise over 1 h. Subsequently, the reaction solution was refluxed at 95°C overnight. After the reaction is completed, the solvent was removed under reduced pressure, and the crude product was extracted with H_2O and EA. The organic phase was collected

and purified by silica gel column chromatography (DCM/CH_3OH = 100:1, *v*/*v*) to afford compound **1** as a yellow oil (0.38 g, 0.65 mmol, yield: 32%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 10.31 (s, 2H), 7.66 (d, *J* = 8.2 Hz, 4H), 7.61 (d, *J* = 8.1 Hz, 4H), 7.06 (d, *J* = 8.2 Hz, 4H), 6.88 (d, *J* = 7.9 Hz, 4H), 4.18 (m, 4H), 3.78 (m, 4H), 3.58 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ 193.53, 162.78, 162.05, 161.94,, 132.61, 132.15, 130.77, 128.95, 115.56, 115.48, 114.60, 70.41, 70.30, 69.24, 67.94. HR-ESI-MS *m/z*: [**1** + H]$^+$ calcd for $[C_{34}H_{35}O_9]^+$, 587.2276; found: 587.2278.

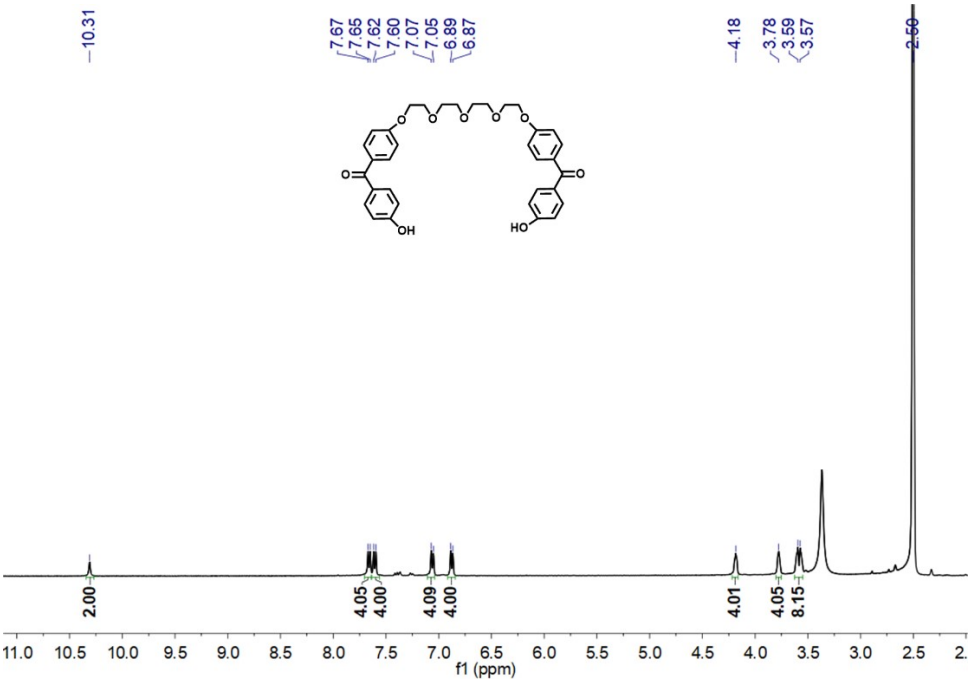


Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **1**.

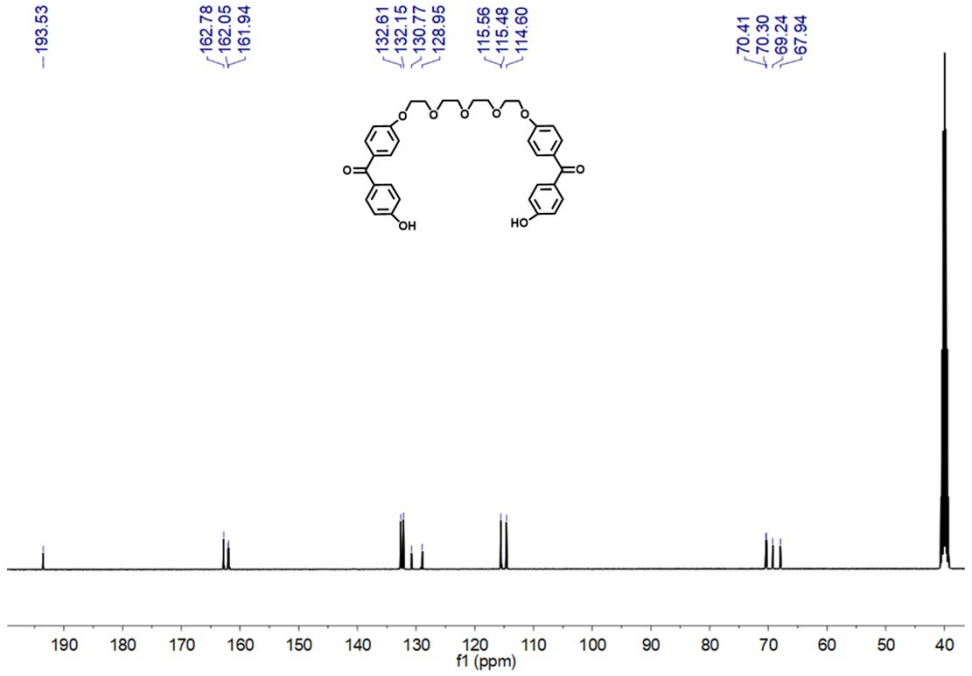


Fig. S2 ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) spectrum of compound **1**.

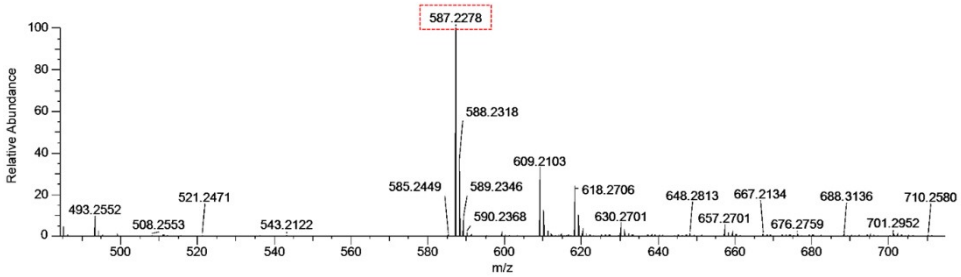
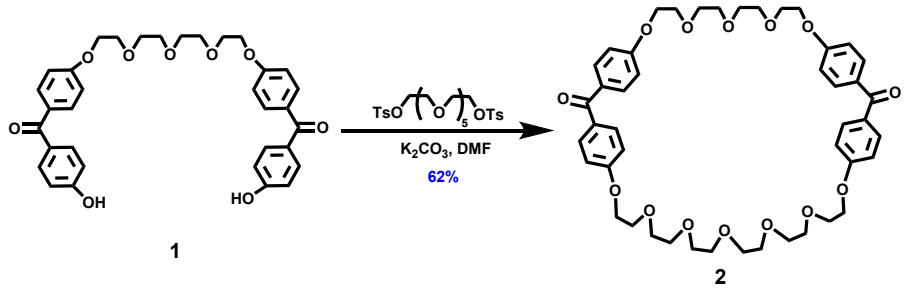


Fig. S3 HR-ESI-MS spectrum of compound **1**.

Synthesis of compound **2**



Scheme S2 Synthesis route of compound **2**.

Under a nitrogen atmosphere, K_2CO_3 (1.95 g, 14.14 mmol), compound **1** (0.48 g, 0.89 mmol), and DMF (150 mL) were added to a reaction flask. A solution of hexylene glycol di(*p*-methylphenyl sulfonate) (0.37 g, 0.89 mmol) in DMF (100 mL) was then added dropwise over 1 h. Subsequently, the reaction solution was refluxed at 95℃ overnight. After the reaction is completed, the solvent was removed under reduced pressure, and the crude product was extracted with H_2O and EA. The organic phase was collected and purified by silica gel column chromatography (PE/EA = 1:1, *v/v*) to afford compound **2** as a white powder (0.46 g, 0.56 mmol, yield: 62%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.70 (d, J = 8.7 Hz, 8H), 6.91 (d, J = 8.6 Hz, 8H), 4.19 – 4.09 (m, 8H), 3.86 (dd, J = 9.0, 4.5 Hz, 8H), 3.73 – 3.59 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 194.29, 162.10, 132.16, 130.86, 114.11, 70.97, 70.86, 70.75, 69.61, 69.58, 67.75, 67.71. HR-ESI-MS *m/z*: [**2** + H]$^+$ calcd for $[C_{46}H_{57}O_{14}]^+$, 833.3743; found: 833.3750.

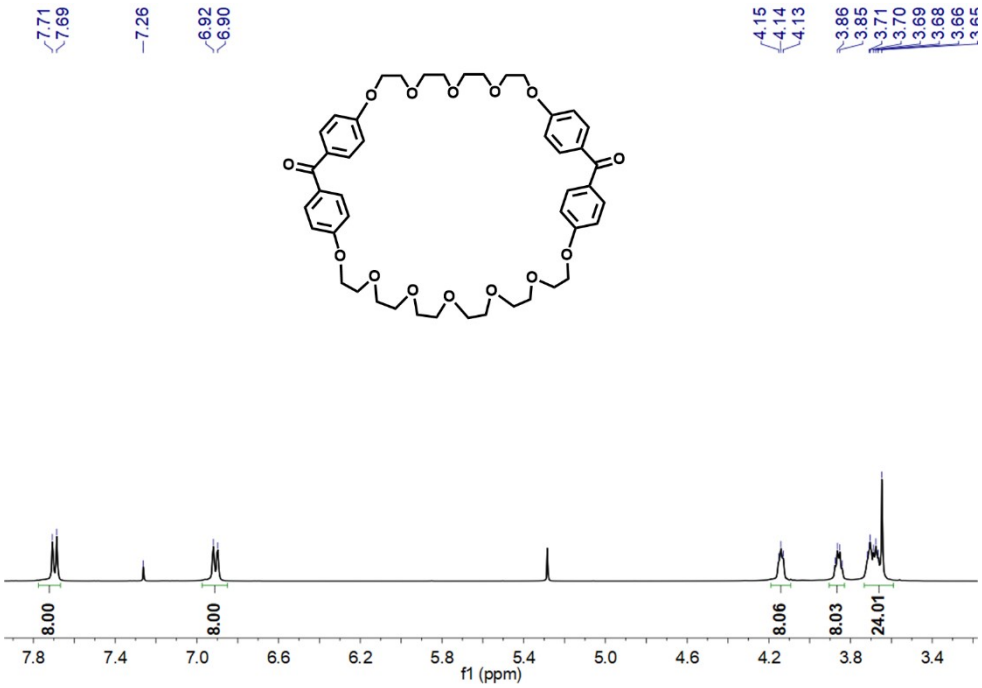


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **2**.

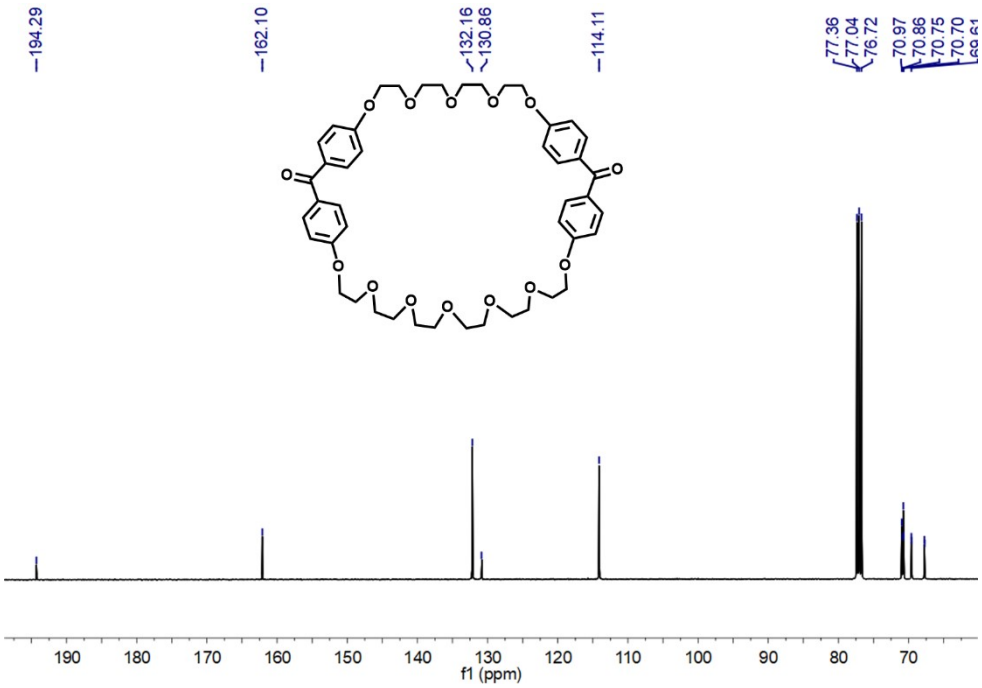


Fig. S5 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **2**.

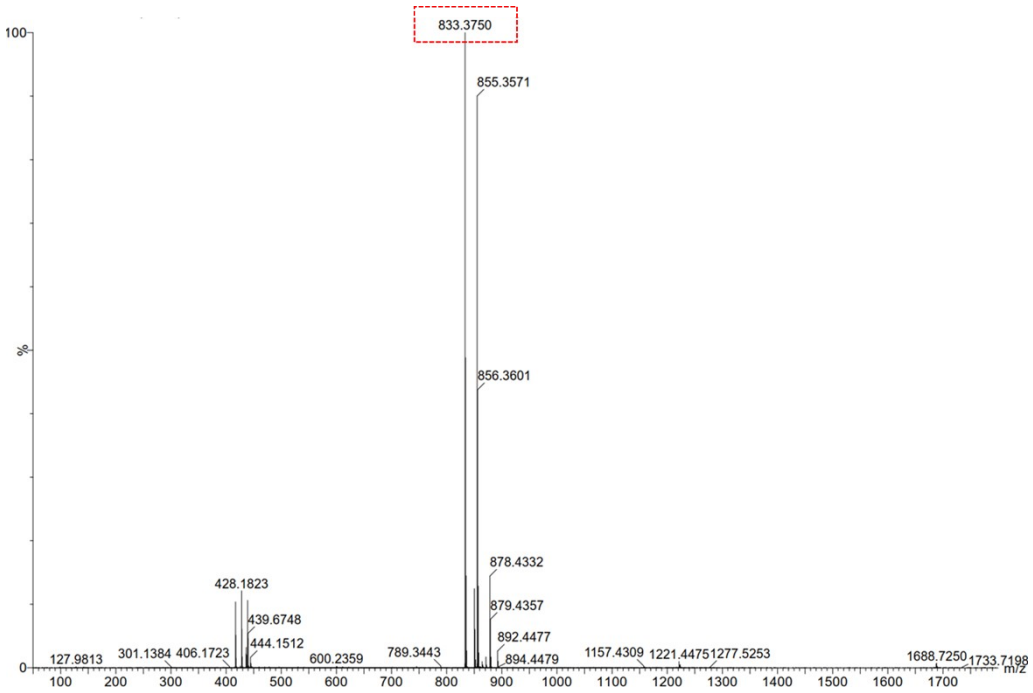
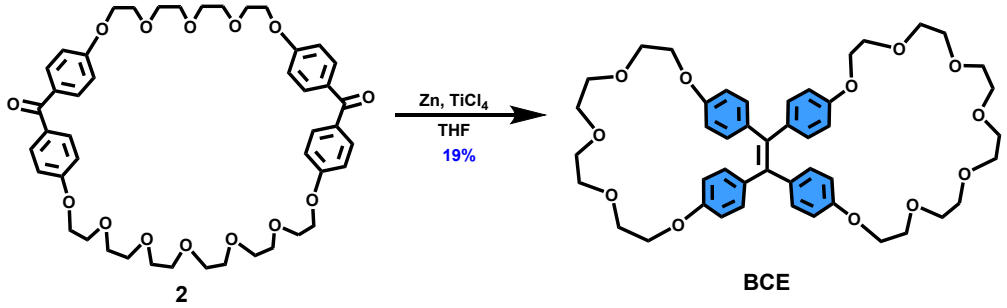


Fig. S6 HR-ESI-MS spectrum of compound **2**.

Synthesis of compound **BCE**



Scheme S3 Synthesis route of compound **BCE**.

Under a nitrogen atmosphere, zinc powder (0.31 g, 4.8 mmol), compound **2** (0.1 g, 0.12 mmol), and THF (7 mL) were added to a reaction flask. The mixture was cooled to −10°C, and $TiCl_4$ (0.26 mL, 2.4 mmol) was slowly added dropwise. After stirring for 1 h, the reaction mixture was warmed to room temperature and then heated refluxed overnight. Upon completion, the reaction was quenched with 1 M HCl (20 mL). The mixture was filtered, and the organic layer was collected and concentrated. The crude product was purified by silica gel column chromatography (PE/EA = 1:1, *v*/*v*) to afford compound **BCE** as a white powder (0.06 g, 0.02 mmol, yield: 19%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.95 (d, J = 7.7 Hz, 4H), 6.88 (d, J = 7.8 Hz, 4H), 6.67 (d, J = 8.0 Hz, 8H), 4.15 (m, 4H), 4.09 (m, 4H), 3.82 (m, 4H), 3.76 (m, 4H), 3.70 (m, 4H), 3.67 (m, 12H), 3.62 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 157.18, 139.05, 137.23, 136.37, 132.46, 114.37, 113.84, 71.20, 71.00, 70.86, 70.70, 70.65, 69.67, 67.96, 67.39. HR-ESI-MS *m/z*: [**BCE** + Na]$^+$ calcd for $[C_{46}H_{56}O_{12}Na]^+$, 823.3664; found: 823.3684.

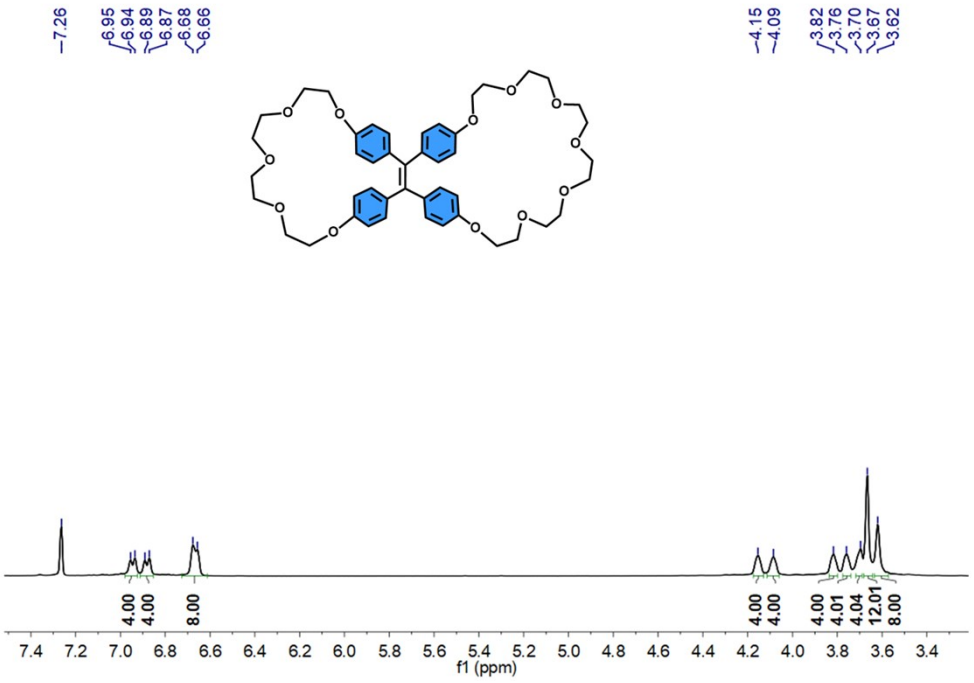


Fig. S7 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **BCE**.

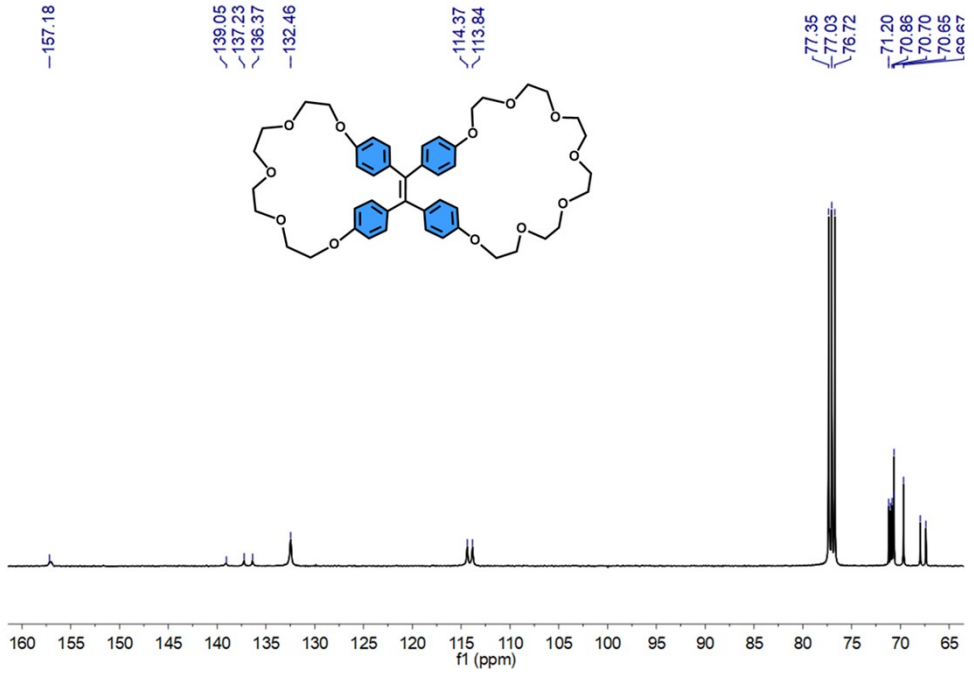


Fig. S8 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **BCE**.

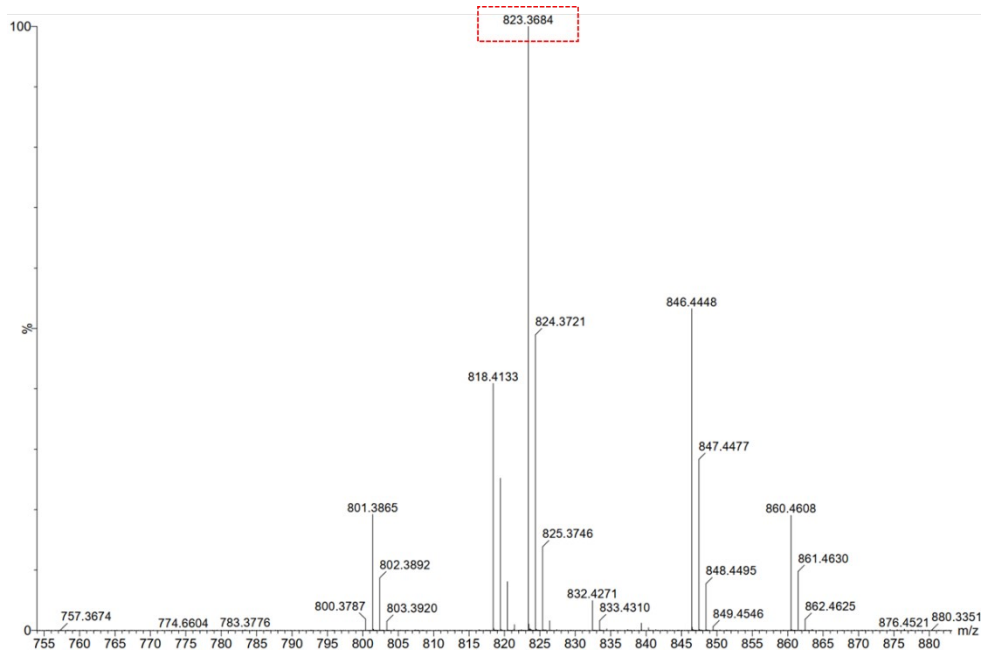
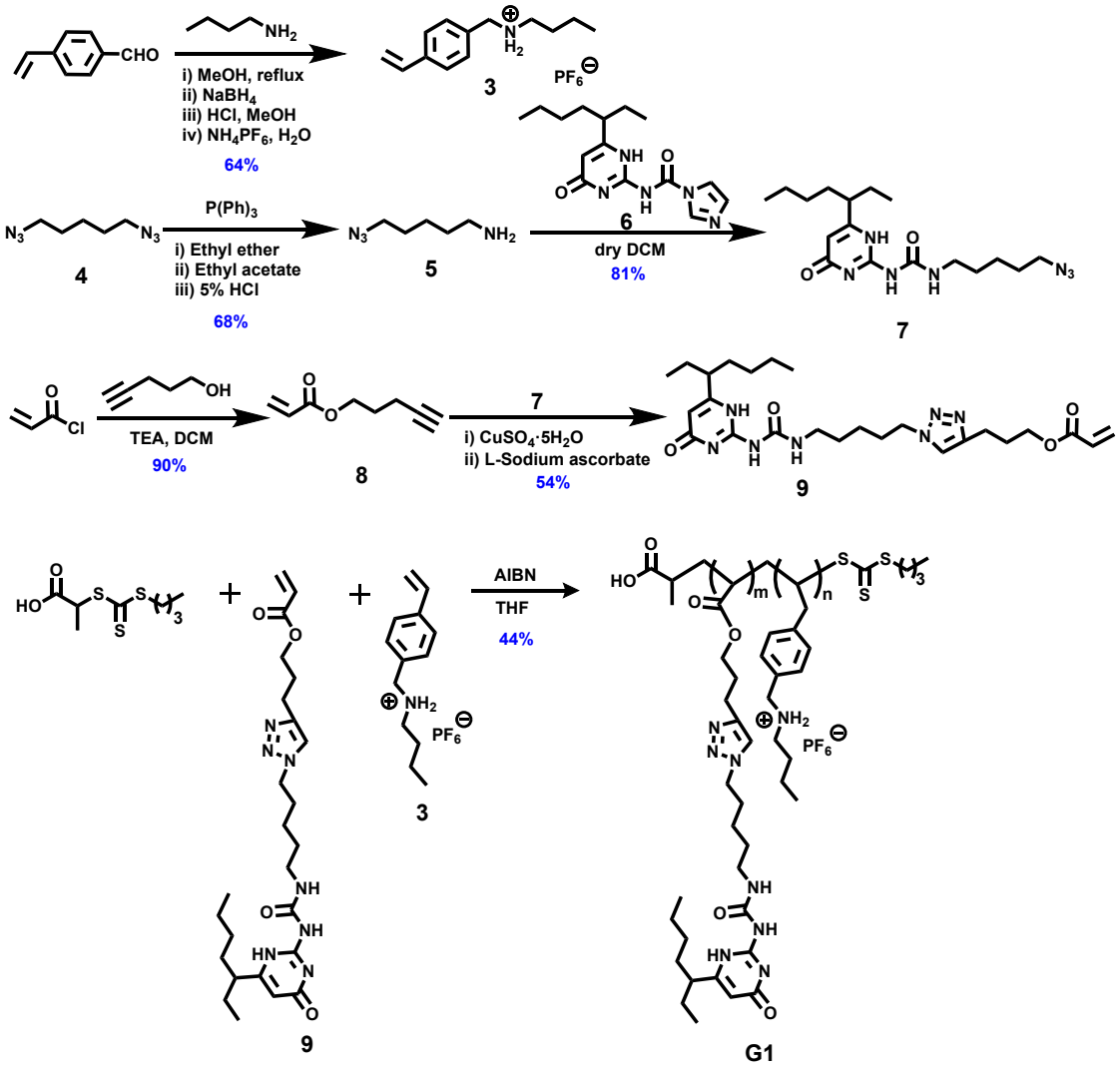


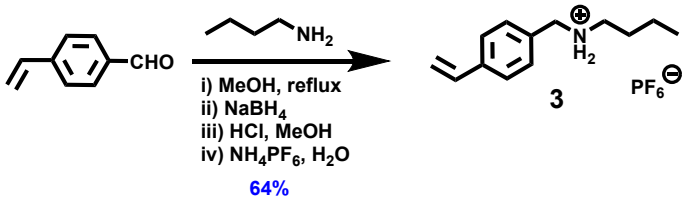
Fig. S9 HR-ESI-MS spectrum of compound **BCE**.

Synthesis of polymer G1



Scheme S4 Synthesis route of polymer **G1**.

Synthesis of compound **3**[3]



Scheme S5 Synthesis route of compound **3**.

Under a nitrogen atmosphere, 4-vinylbenzaldehyde (0.25 g, 1.89 mmol), *n*-butylamine (0.21 mL, 2.08 mmol), and CH_3OH (6 mL) were heated at reflux overnight. After cooling the reaction mixture to room temperature, $NaBH_4$ (0.29 g, 7.56 mmol) was added in batches over 1 h under ice-bath conditions. The solution was stirred under ambient conditions for another 24 h, after which 3 M HCl was added to neutralize the excess $NaBH_4$. The mixture was filtered, and CH_3OH was removed by rotary evaporator. H_2O was added, and the solution was added to saturated NH_4PF_6 solution to produce a precipitate. The precipitate was collected by filtration and recrystallized three times from deionized H_2O to afford compound **3** as a white powder (0.43 g, 1.22 mmol, yield: 64%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 8.65 (s, 2H), 7.56 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.91 (d, J = 17.7 Hz, 1H), 5.33 (d, J = 10.9 Hz, 1H), 4.14 (s, 2H), 2.90 (s, 2H), 1.58 (dt, J = 15.4, 7.7 Hz, 2H), 1.39 – 1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

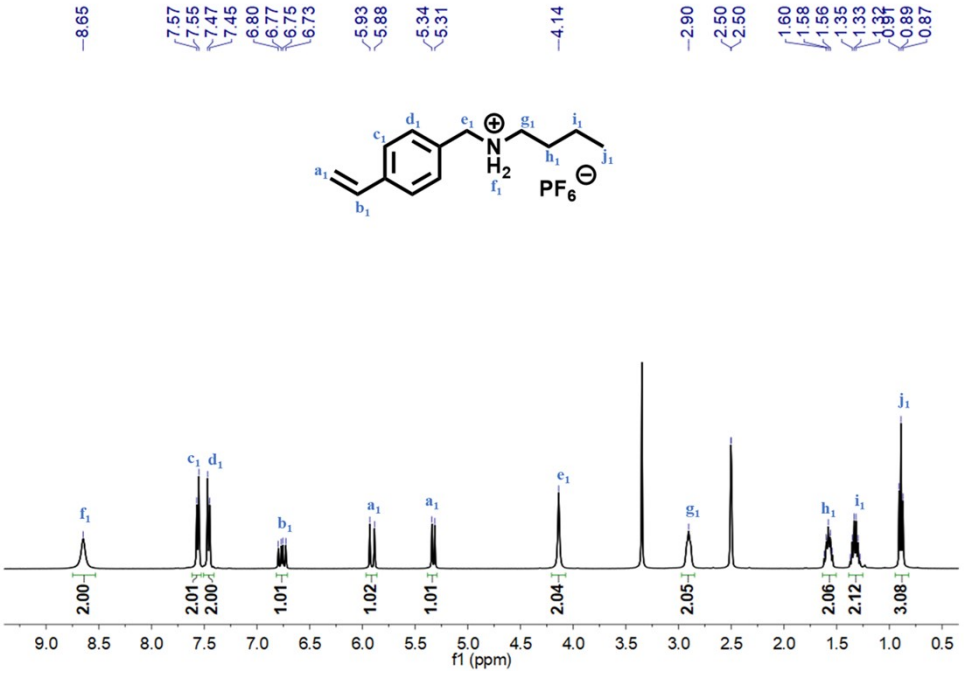
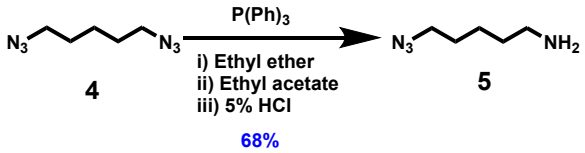


Fig. S10 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **3**.

Synthesis of compound **5**[1]



Scheme S6 Synthesis route of compound **5**.

Under a nitrogen atmosphere, compound **4** (0.15 g, 1 mmol), ethyl ether (1 mL), EA (1 mL), and 5% HCl (3 mL) were added to a reaction flask. Triphenylphosphine (0.25 g, 0.95 mmol) was added portionwise at 0°C. After completion of addition, the reaction mixture was stirred at room temperature for 24 h. The organic layer was discarded, and the aqueous layer was washed with DCM (3 × 6 mL). The resulting aqueous phase was alkaline with sodium hydroxide (pH > 12) and then extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford compound **5** as a yellow oil (0.09 g, 0.69 mmol, yield: 68%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.25 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 1.85 (d, *J* = 24.1 Hz, 2H), 1.58 (dd, *J* = 14.4, 7.1 Hz, 2H), 1.50 – 1.35 (m, 4H).

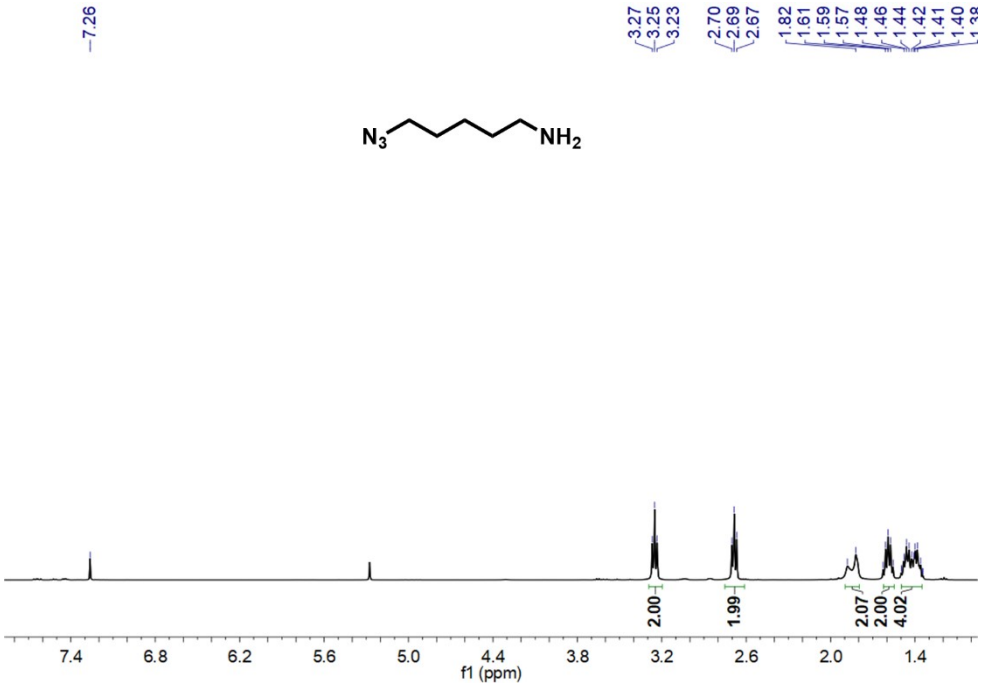
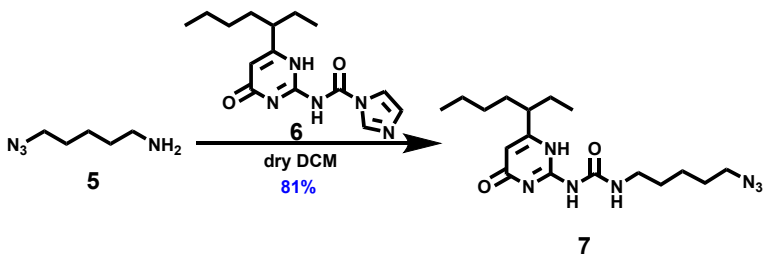


Fig. S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **5**.

Synthesis of compound **7**[4]



Scheme S7 Synthesis route of compound **7**.

Under a nitrogen atmosphere, compound **6** (0.24 g, 0.79 mmol), compound **5** (0.09 g, 0.71 mmol), and DCM (5 mL) were added to a reaction flask. The mixture was stirred at room temperature for 4 h. Upon completion of the reaction, the reaction was quenched with H_2O and stirred for 10 minutes. The reaction mixture was washed three times with saturated $NaHCO_3$ solution. The resulting organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to afford compound **7** as a yellow oil (0.21 g, 0.58 mmol, yield: 81%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 13.16 (s, 1H), 11.87 (s, 1H), 10.19 (s, 1H), 5.75 (s, 1H), 3.20 (dd, J = 13.6, 6.8 Hz, 4H), 2.28 – 2.19 (m, 1H), 1.62 – 1.47 (m, 8H), 1.41 – 1.34 (m, 2H), 1.25 – 1.15 (m, 4H), 0.85 – 0.78 (m, 6H). HR-ESI-MS *m/z*: [**7** + H]$^+$ calcd for $[C_{17}H_{30}O_2N_7]^+$, 364.2455; found: 364.2462.

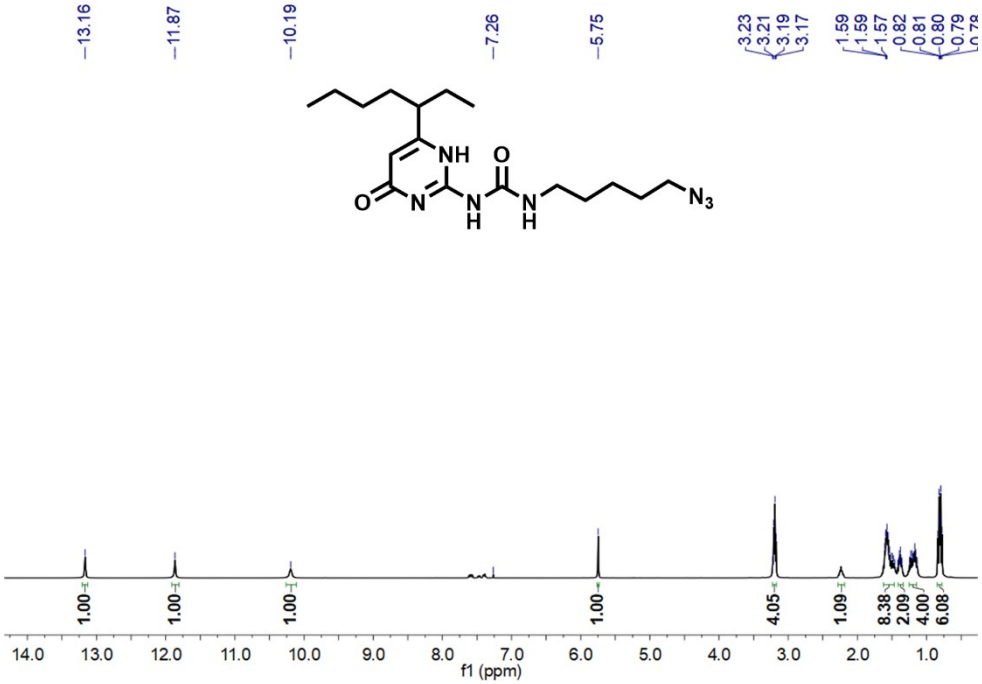


Fig. S12 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **7**.

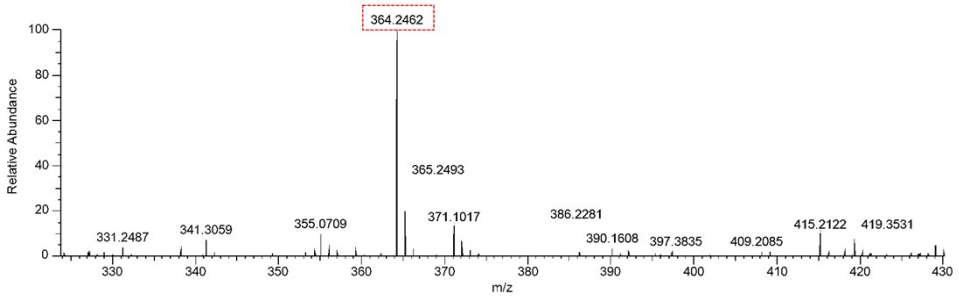
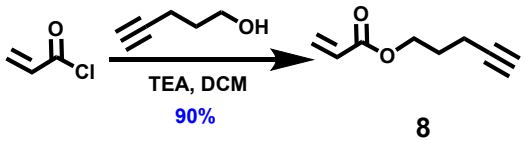


Fig. S13 HR-ESI-MS spectrum of compound **7**.

Synthesis of compound **8**[5]



8

Scheme S8 Synthesis route of compound **8**.

Under a nitrogen atmosphere, 4-pentyn-1-alcohol (1 g, 11.9 mmol), triethylamine (3.13 mL, 23.86 mmol), and DCM (8 mL) were added to a reaction flask. After cooling to 0°C, a solution of acryloyl chloride (0.25 mL, 15.53 mmol) in DCM (10 mL) was added dropwise. The reaction mixture was stirred at 0°C for 1 h and then at room temperature for 4 h. After quenching with H_2O (20 mL), the crude product was washed with H_2O and saturated brine several times. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to afford compound **8** as a colorless oil (1.48 g, 10.75 mmol, yield: 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.39 (dd, J = 17.3, 1.4 Hz, 1H), 6.10 (dd, J = 17.3, 10.4 Hz, 1H), 5.81 (dd, J = 10.4, 1.4 Hz, 1H), 4.24 (t, J = 6.3 Hz, 2H), 2.32 – 2.27 (m, 2H), 1.96 (t, J = 2.7 Hz, 1H), 1.92 – 1.85 (m, 2H).

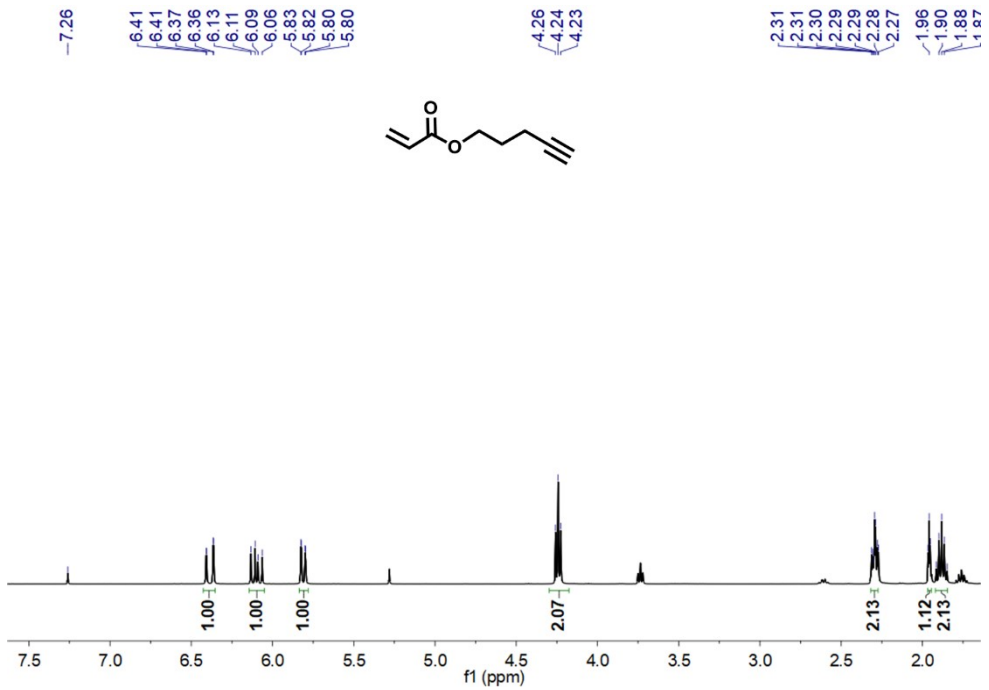
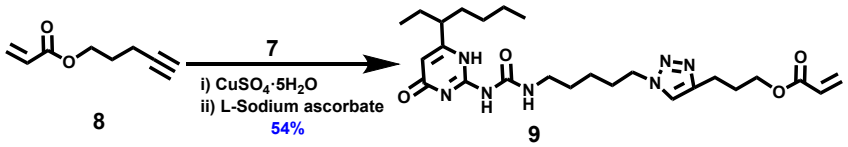


Fig. S14 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **8**.

Synthesis of compound **9**



Scheme S9 Synthesis route of compound **9**.

Under a nitrogen atmosphere, compound **7** (0.46 g, 1.26 mmol), compound **8** (0.60 g, 1.64 mmol), $CuSO_4·5H_2O$ (0.11 g, 0.46 mmol), L-sodium ascorbate (0.28 g, 1.38 mmol), and a mixed solution of DMF/H_2O (20 mL, 5:1, *v/v*) were added to the reaction flask and stirred overnight at 70°C. Upon completion, the solvent was removed under reduced pressure. The residue was dissolved in organic solvent and washed successively with saturated aqueous Na_2CO_3 solution and then dried over anhydrous

Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (DCM/CH_3OH = 100:1, *v/v*) to afford compound **9** as a white powder (0.35 g, 0.69 mmol, yield: 54%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 11.49 (s, 1H), 9.64 (s, 1H), 7.88 (s, 1H), 7.37 (s, 1H), 6.32 (d, *J* = 17.2, 1H), 6.18 (dd, *J* = 17.3, 10.2 Hz, 1H), 5.94 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.74 (s, 1H), 4.29 (t, *J* = 7.0 Hz, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 3.13 (dd, *J* = 12.6, 6.4 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.23 (dd, *J* = 10.3, 4.8 Hz, 1H), 1.94 (dt, *J* = 13.9, 6.8 Hz, 2H), 1.81 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.48 (dd, *J* = 16.3, 9.2 Hz, 4H), 1.24 (m, 6H), 1.13 (dd, *J* = 9.3, 5.8 Hz, 2H), 0.84 – 0.74 (m, 6H). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 13.22 (s, 1H), 11.92 (s, 1H), 10.27 (s, 1H), 7.32 (s, 1H), 6.41 (d, *J* = 17.5 Hz, 1H), 6.13 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.83 (d, *J* = 13.4 Hz, 2H), 4.33 (t, *J* = 7.3 Hz, 2H), 4.22 (t, *J* = 6.4 Hz, 2H), 3.26 (dd, *J* = 12.7, 6.5 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.32 (d, *J* = 5.3 Hz, 1H), 2.08 (dt, *J* = 13.9, 6.8 Hz, 2H), 1.93 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.67 (d, *J* = 7.8 Hz, 4H), 1.56 (m, 2H), 1.46 – 1.38 (m, 2H), 1.31 – 1.21 (m, 4H), 0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 173.22, 166.31, 156.75, 155.64, 146.92, 130.89, 128.46, 120.75, 63.71, 50.14, 45.37, 39.64, 32.93, 30.05, 29.35, 26.65, 22.52, 22.22, 11.77. HR-ESI-MS *m/z*: [**9** + H]$^+$ calcd for $[C_{25}H_{40}N_7O_4]^+$, 502.3136; found: 502.3112.

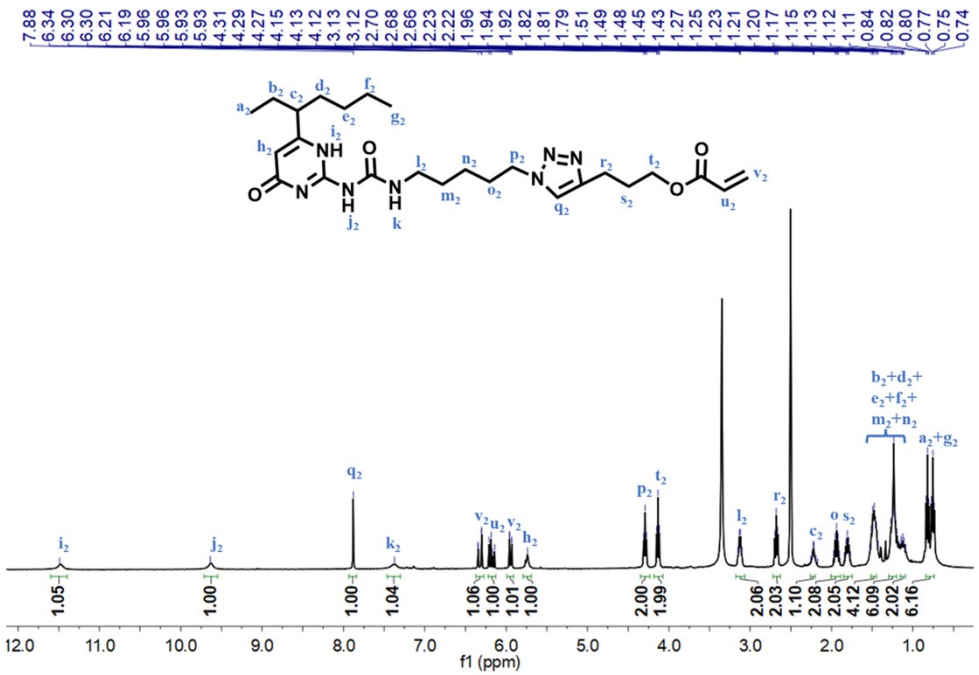


Fig. S15 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **9**.

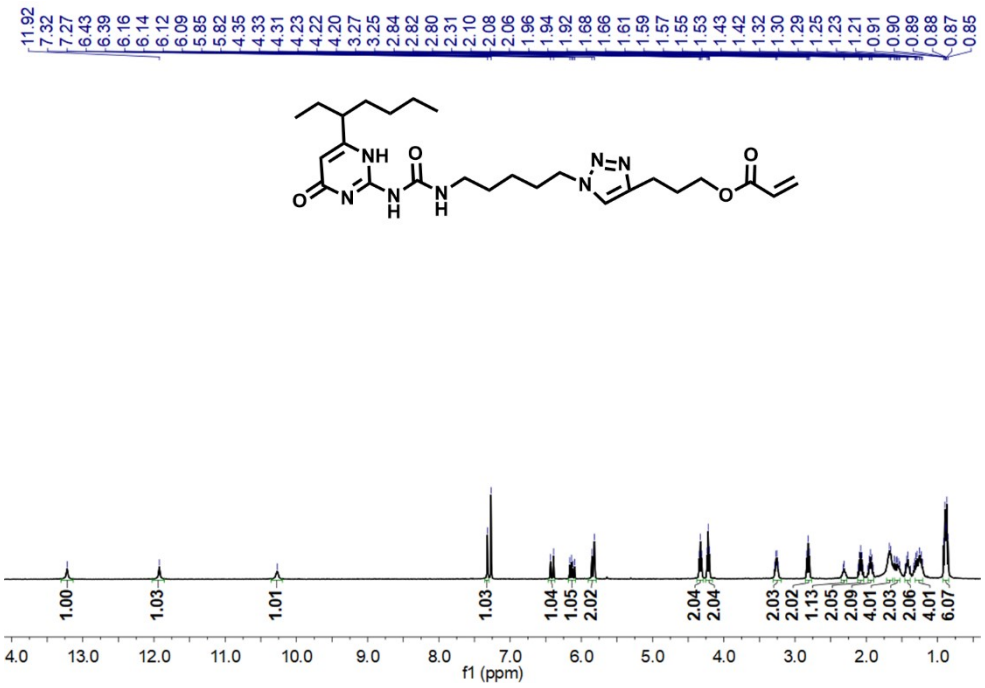


Fig. S16 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **9**.

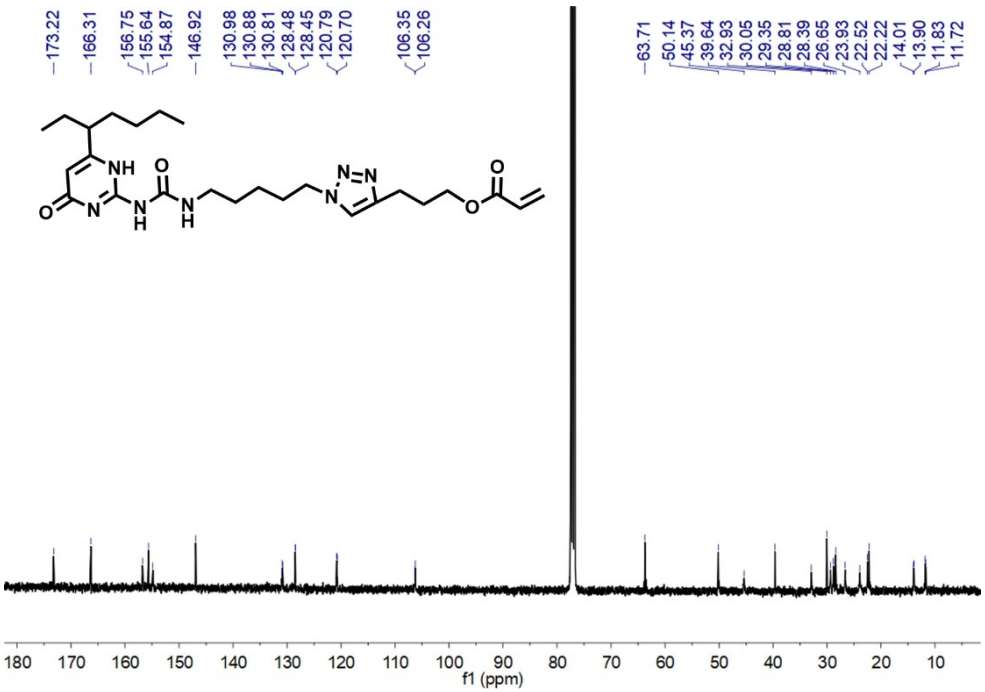


Fig. S17 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **9**.

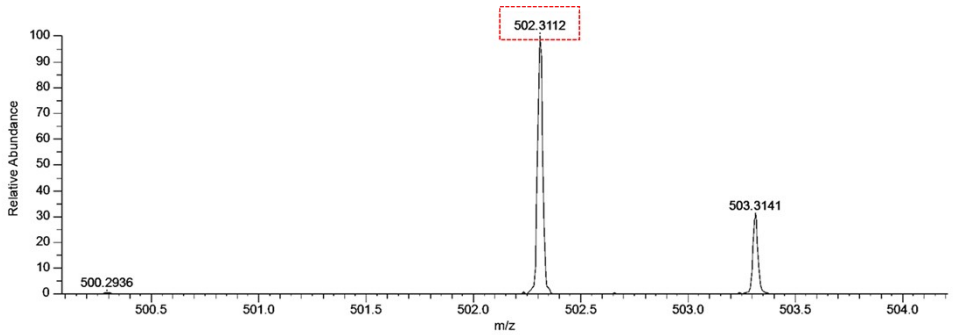


Fig. S18 HR-ESI-MS spectrum of compound **9**.

Synthesis of polymer **G1**

After RAFT polymerization, the ^{1}H NMR spectra of the monomers and polymer **G1** were compared. The disappearance of the signals corresponding to the terminal double bonds of the monomers provided preliminary evidence of successful polymerization. Subsequently, ^{1}H NMR integration was performed on polymer **G1** to quantify its composition. Based on the integration of the peaks corresponding to the UPy units and dialkylammonium salt groups, the *m*/*n* ratio was calculated to be 1:1. Therefore, the incorporation ratios of both components in polymer **G1** are 50 mol%.

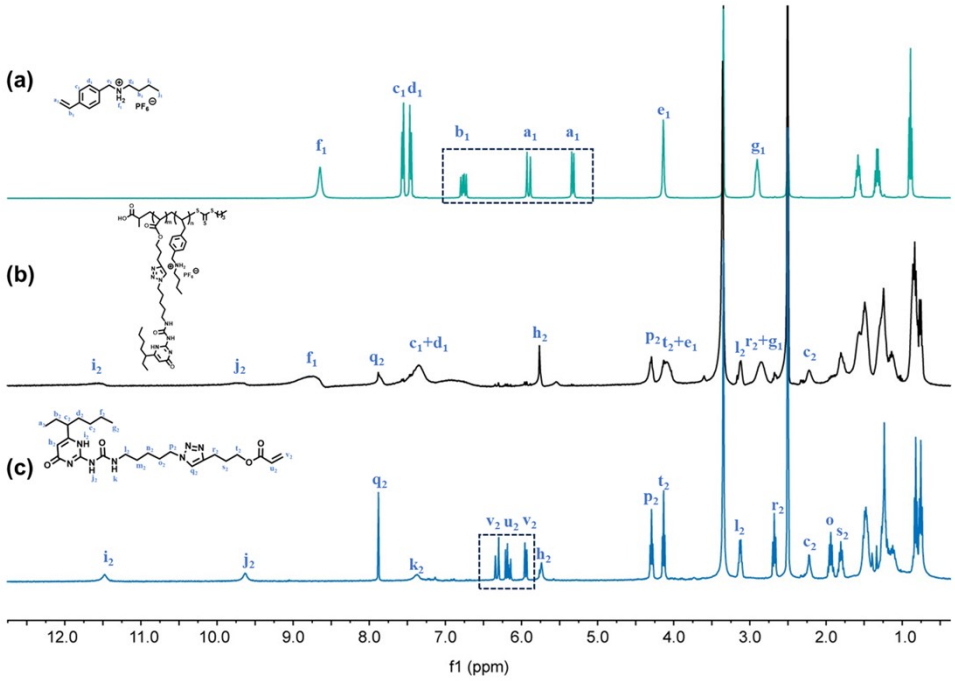


Fig. S19 ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectra: (a) monomer **3**, (b) polymer **G1**, and (c) monomer **9**.

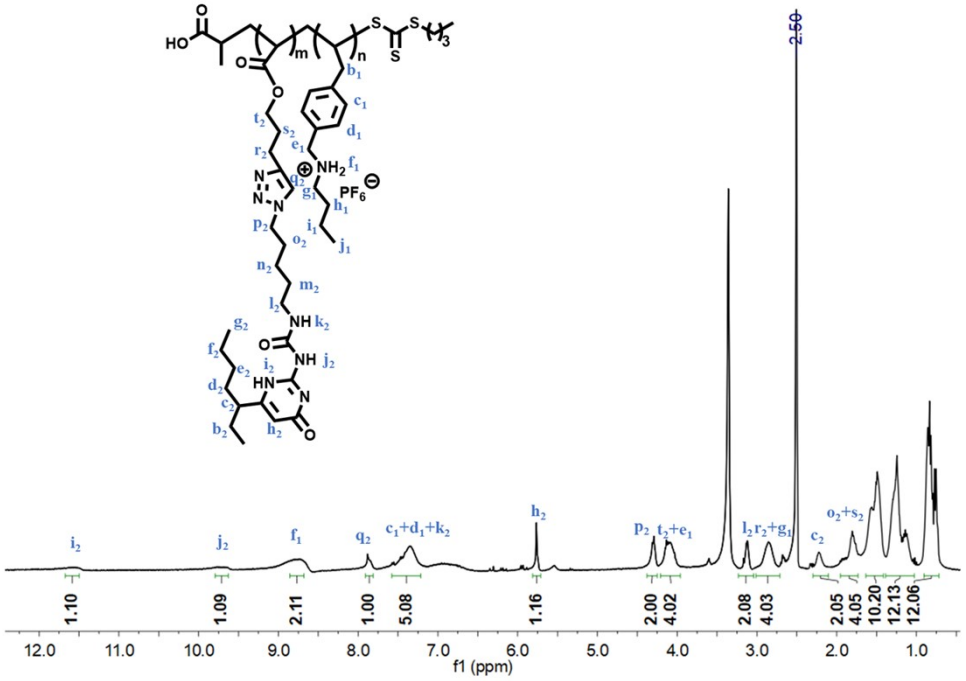
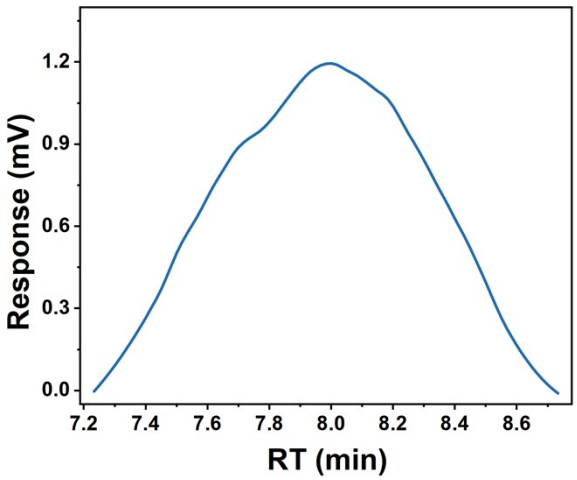


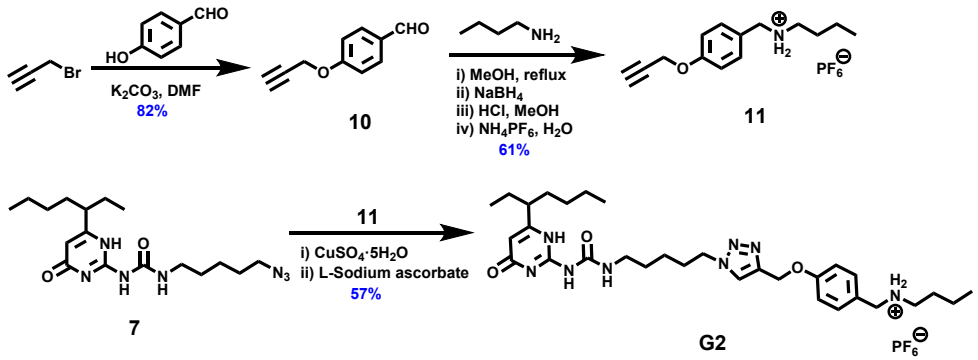
Fig. S20 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of polymer **G1**.



M_n	M_w	M_p	M_z	M_{z+1}	PDI
53254	84706	67760	134326	189911	1.59

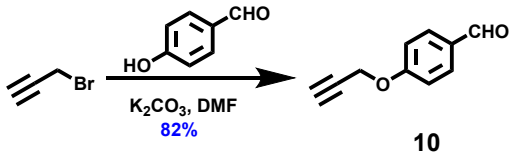
Fig. S21 GPC analysis of polymer **G1** using conventional calculations and DMF as the solvent.

Synthesis of compound G2



Scheme S10 Synthesis route of compound **G2**.

Synthesis of compound **10**[6]



Scheme S11 Synthesis route of compound **10**.

Under a nitrogen atmosphere, *p*-hydroxybenzaldehyde (0.5 g, 4.0 mmol), K_2CO_3 (1.6 g, 12.0 mmol), 3-bromo-1-propyne (0.57 g, 4.8 mmol), and DMF (20 mL) were added to a reaction flask. The reaction mixture was refluxed for 24 h. After the reaction is completed, the solvent was removed under reduced pressure, and the crude product was extracted with H_2O and DCM. The organic phase was collected and purified by silica gel column chromatography (PE/EA = 10:1, *v/v*) to afford compound **10** as a white powder (0.53 g, 3.3 mmol, yield: 82%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.89 (s, 1H), 7.85 (d, *J* =

8.6 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 4.77 (d, J = 2.1 Hz, 2H), 2.57 (s, 1H).

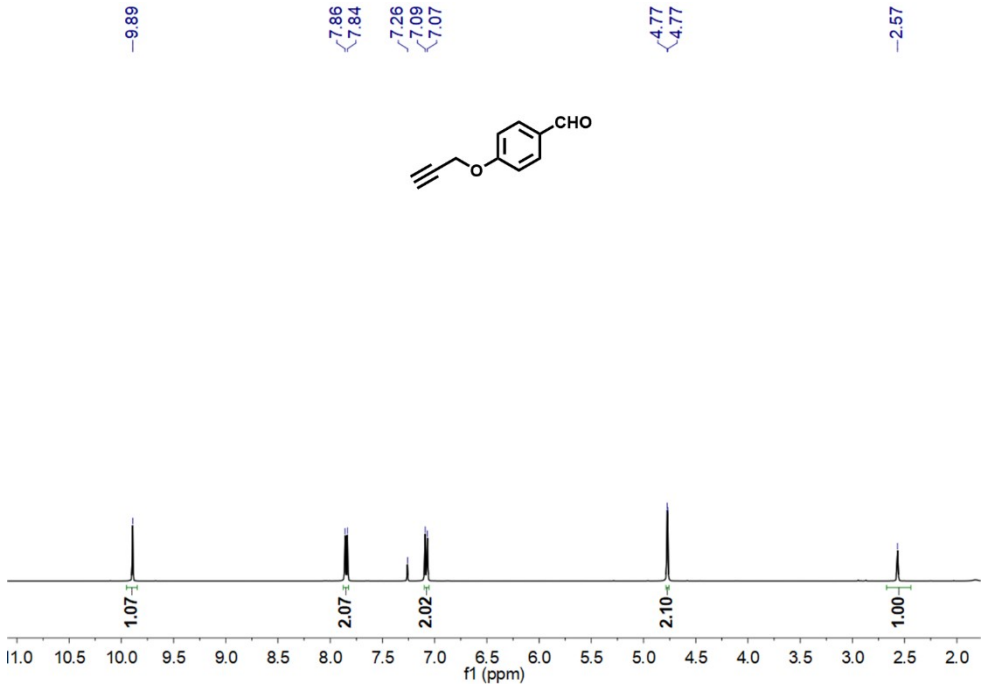
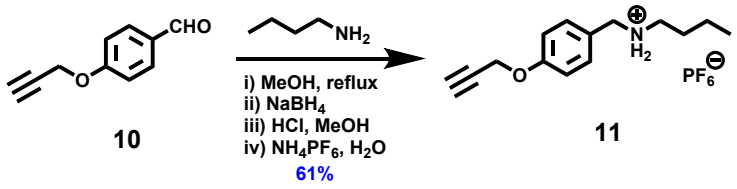


Fig. S22 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **10**.

Synthesis of compound **11**[7]



Scheme S12 Synthesis route of compound **11**.

Under a nitrogen atmosphere, compound **10** (0.2 g, 1.24 mmol) and *n*-butylamine (0.17 mL, 1.38 mmol) were sequentially heated to reflux overnight in CH_3OH (6 mL). After cooling the reaction mixture to room temperature, $NaBH_4$ (0.1 g, 2.6 mmol) was added to the stirred solution in batches over a period of 1 h under ice-bath conditions. The solution was stirred under ambient conditions for another 24 h, after which 3 M HCl was added to neutralize the excess $NaBH_4$. The mixture was filtered and CH_3OH was removed by rotary evaporator. H_2O was added and the solution was added to saturated NH_4PF_6 solution to produce a precipitate, which was collected by filtration and recrystallized three times in deionized H_2O to afford compound **11** as a white powder (0.25 g, 0.68 mmol, yield: 61%). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 7.43 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 4.80 (d, J = 2.2 Hz, 2H), 4.12 (s, 2H), 3.06 – 2.99 (m, 2H), 2.87 (s, 1H), 1.68 – 1.60 (m, 2H), 1.40 (dt, J = 14.8, 7.3 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H).

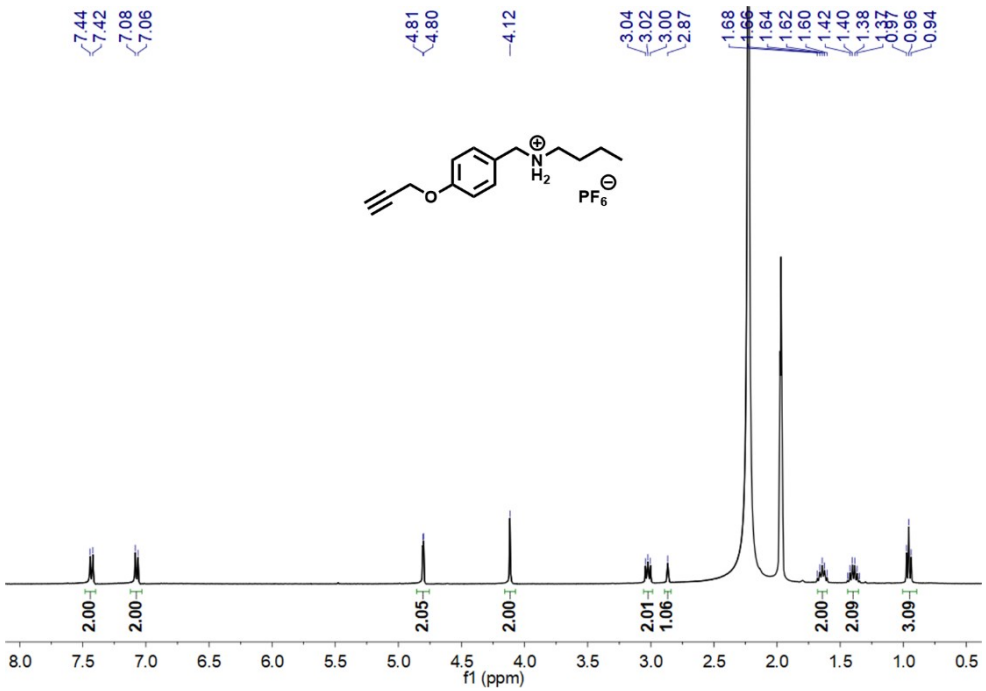
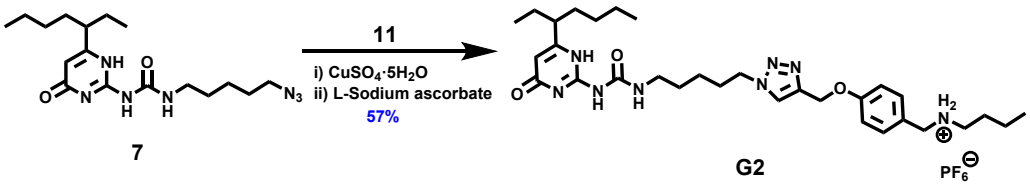


Fig. S23 ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of compound **11**.

Synthesis of compound **G2**



Scheme S13 Synthesis route of compound **G2**.

Under a nitrogen atmosphere, compound **7** (0.2 g, 0.63 mmol), compound **11** (0.3 g, 0.82 mmol), $CuSO_4 \cdot 5H_2O$ (0.06 g, 0.23 mmol), L-sodium ascorbate (0.14 g, 0.69 mmol), and a mixed solution of DMF/H_2O (8.4 mL, 5:1, *v/v*) were added to the reaction flask and stirred overnight at 70°C. When the reaction was completed. The solvent was removed by vacuum concentration, the organic phase was successively washed with a saturated sodium carbonate solution in water, and then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (DCM/CH_3OH = 100:1, *v/v*) to afford compound **G2** as a yellow oil (0.26 g, 0.36 mmol, yield: 57%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 11.50 (s, 1H), 9.66 (s, 1H), 8.56 (s, 2H), 8.25 (s, 1H), 7.41 (d, J = 8.7 Hz, 3H), 7.11 (d, J = 8.7 Hz, 2H), 5.75 (s, 1H), 5.15 (s, 2H), 4.37 (t, J = 7.0 Hz, 2H), 4.08 (s, 2H), 3.13 (dd, J = 12.5, 6.4 Hz, 2H), 2.88 (s, 2H), 2.27 – 2.19 (m, 1H), 1.87 – 1.80 (m, 2H), 1.60 – 1.45 (m, 8H), 1.33 – 1.21 (m, 6H), 1.12 (d, J = 8.6 Hz, 2H), 0.89 – 0.74 (m, 9H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ 159.01, 131.94, 124.91, 124.57, 115.32, 61.63, 55.38, 50.02, 49.73, 46.58, 33.50, 29.80, 29.56, 29.06, 27.88, 27.04, 23.60, 22.65, 19.74, 14.35,13.95, 12.28. HR-ESI-MS *m/z*: [**G2** — PF_6^-]$^+$ calcd for $[C_{31}H_{49}N_8O_3]^+$, 581.3922; found: 581.3934.

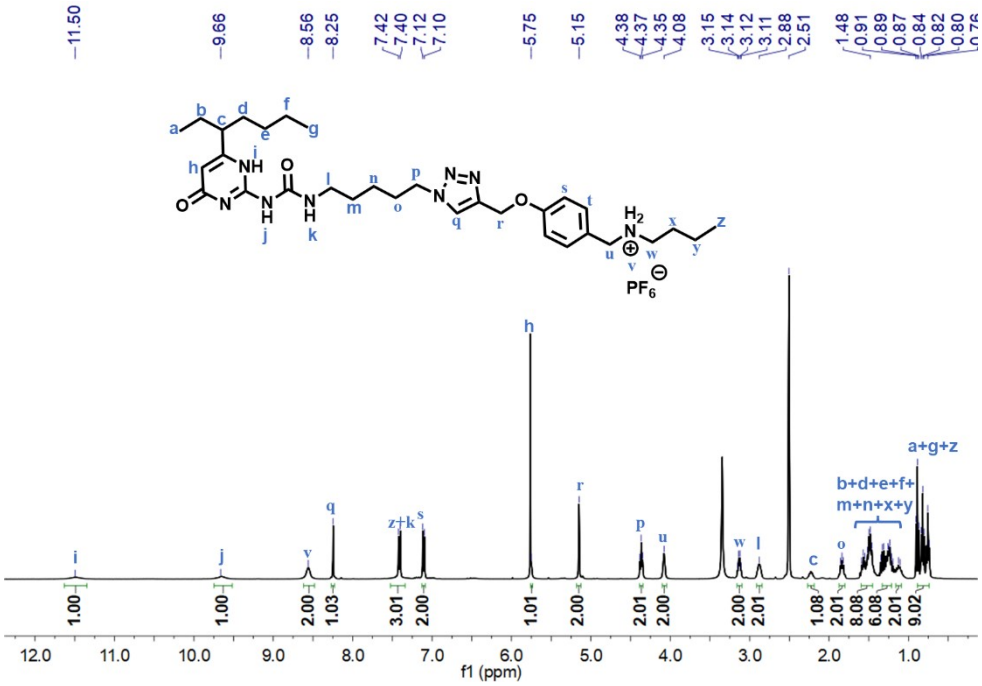


Fig. S24 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **G2**.

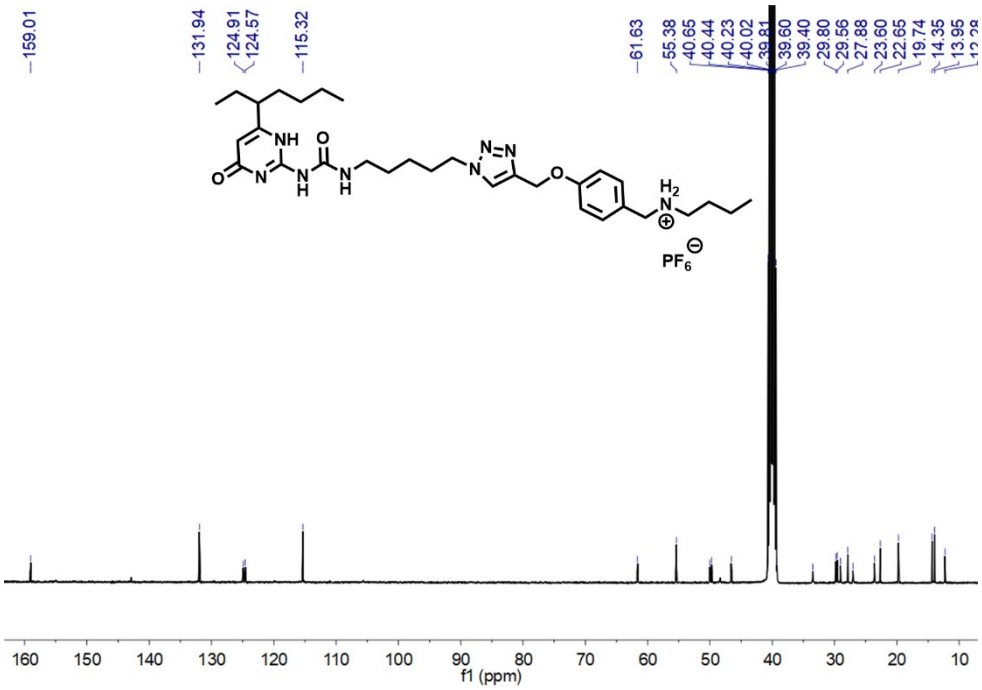


Fig. S25 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298 K) of compound **G2**.

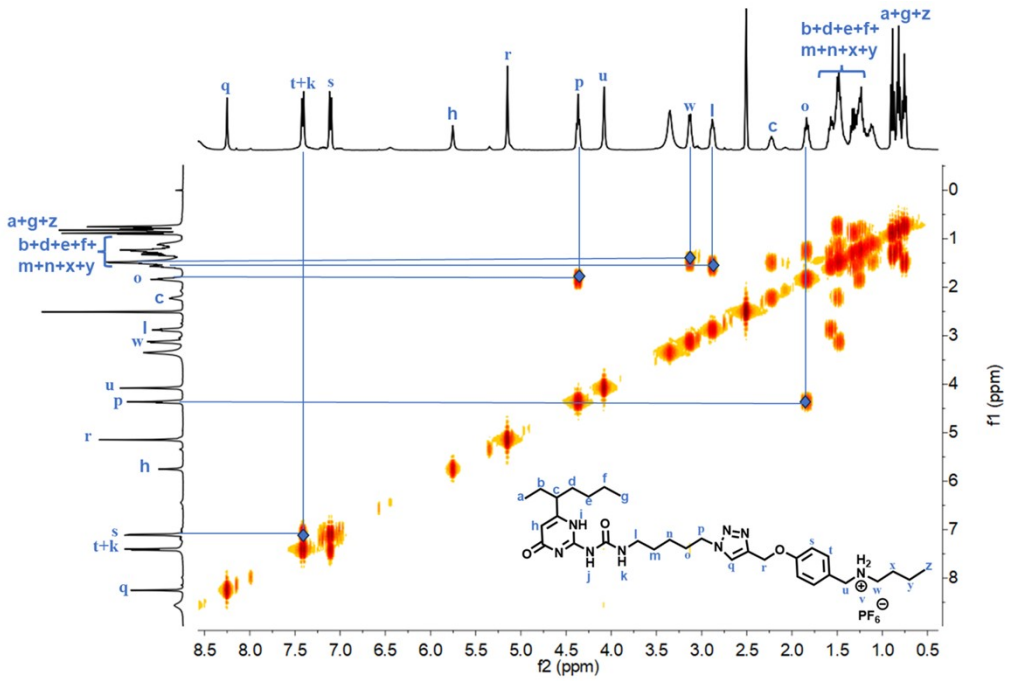


Fig. S26 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **G2**.

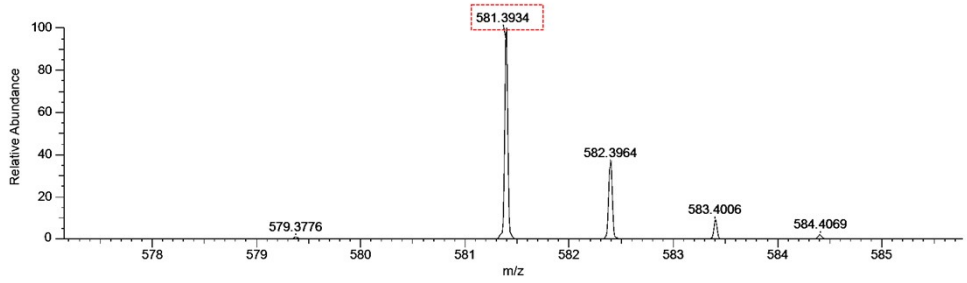
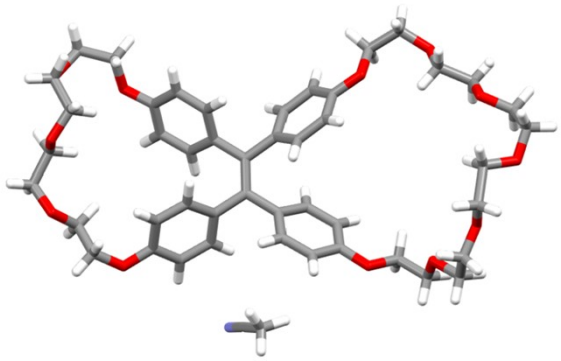


Fig. S27 HR-ESI-MS spectrum of compound **G2**.

3. Crystallographic data for BCE



Structure name	**BCE**
CCDC number	2374870
Temperature	170.00 K
Formula sum	C48H59NO12
Mr	841.96
Crystal system	triclinic
Space-Group	$P\bar{1}$
Cell parameters	a = 12.4293(7) Å
	b = 12.6498(5) Å
	c = 15.7096(7) Å
	α = 106.8050(10)°
	β = 106.9150(10)°
	γ = 99.8640(10)°
Cell volume	2172.45(18) Å^3
Z	2
D_{calcd}	1.287 g cm^{-3}
μ	0.479 mm^{-1}
F(000)	900.0
R_{all}	0.0745

Fig. S28 Crystal structure and data of **BCE.** (Oxygen atoms, red; Carbon atoms, gray; Hydrogen atoms, white; Nitrogen atom, blue)

4. AIE properties study

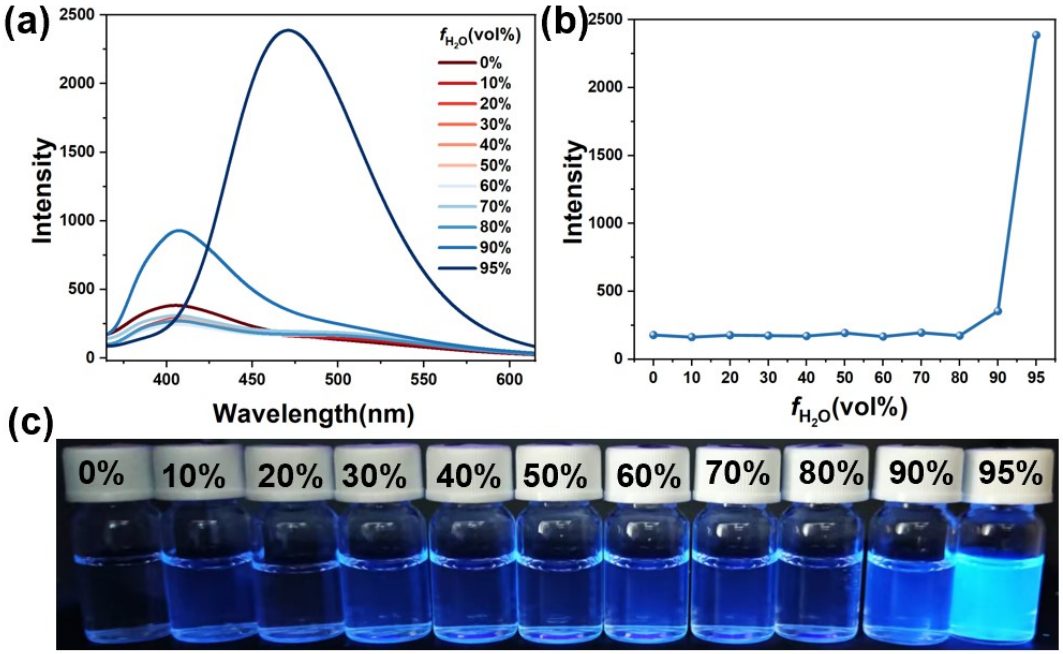


Fig. S29 (a) Fluorescence spectra of **BCE** in the THF-H_2O mixture with different H_2O contents (0-95%). (b) Plot of maximum emission intensity of **BCE** (λ_{em} = 470 nm). (c) Emission photos of **BCE** in the THF-H_2O mixture with different H_2O contents (0-95%) under 365 nm UV-light. [**BCE**] = 2 × 10^{-5} M.

5. Fluorescence quantum yields

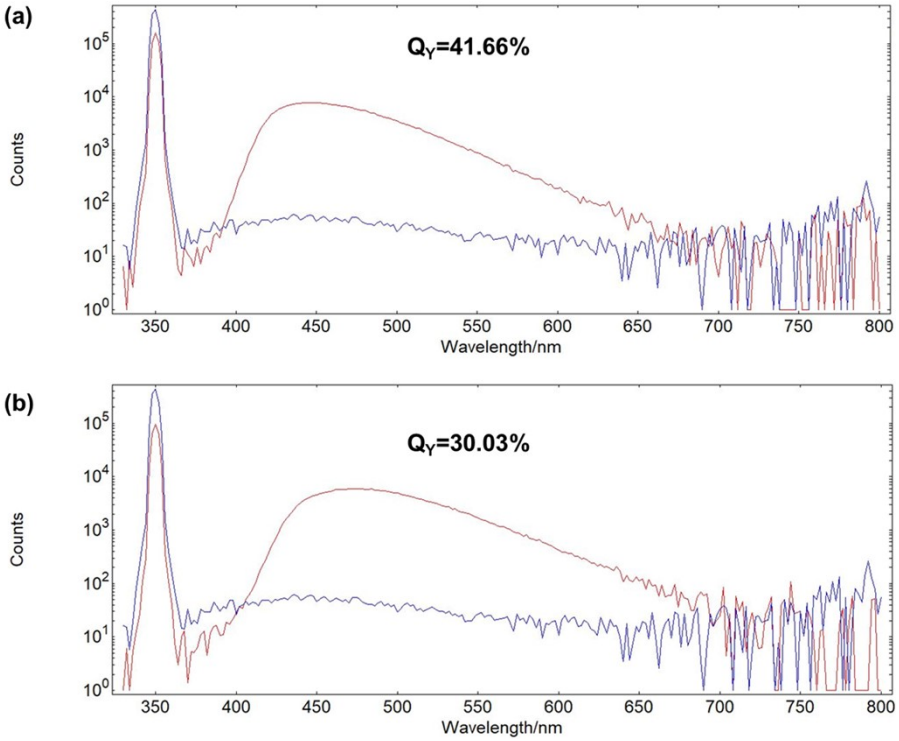


Fig. S30 Absolute fluorescence quantum yields ($\Phi_{f(Abs)}$) of (a) solid compound **BCE** and (b) the gel **BCE⊃G1** upon excitation at 350 nm.

6. Host-guest interaction study

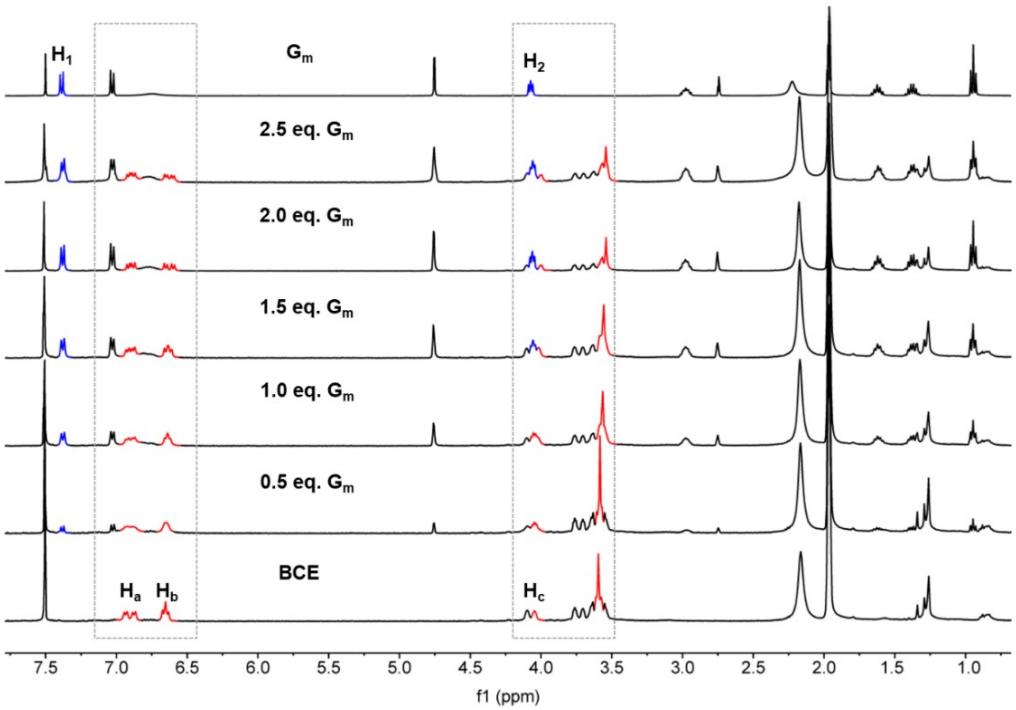


Fig. S31 ^{1}H NMR titration spectra (400 MHz, 298 K) of **BCE** (3.0 mM) titrated by $\mathbf{G_m}$ (0-2.5 equiv.) in $CDCl_3/CD_3CN$ (2:1, *v/v*).

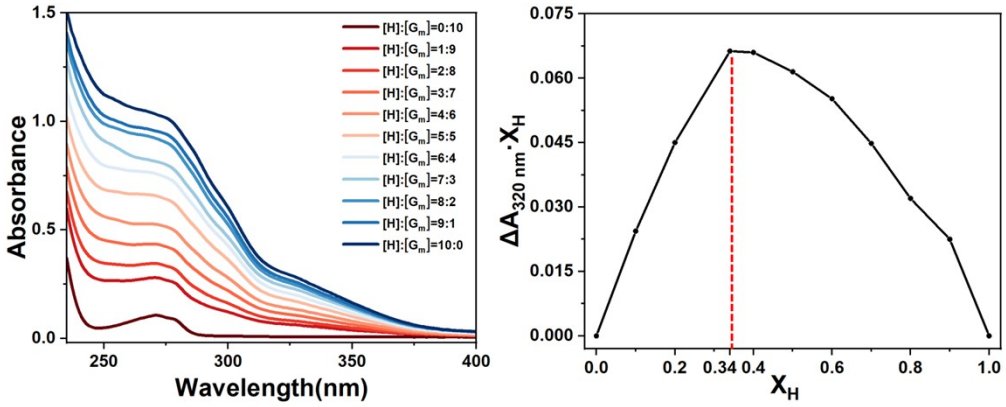


Fig. S32 UV-vis absorption spectra of **BCE** (H)⊃$\mathbf{G_m}$ complex and Job's plot of the 2:1 binding ratio between **BCE** and $\mathbf{G_m}$ ([**BCE**] + [$\mathbf{G_m}$] = 4.0 × 10^{-5} M, solvent: $CDCl_3/CD_3CN$ (2:1, *v/v*)).

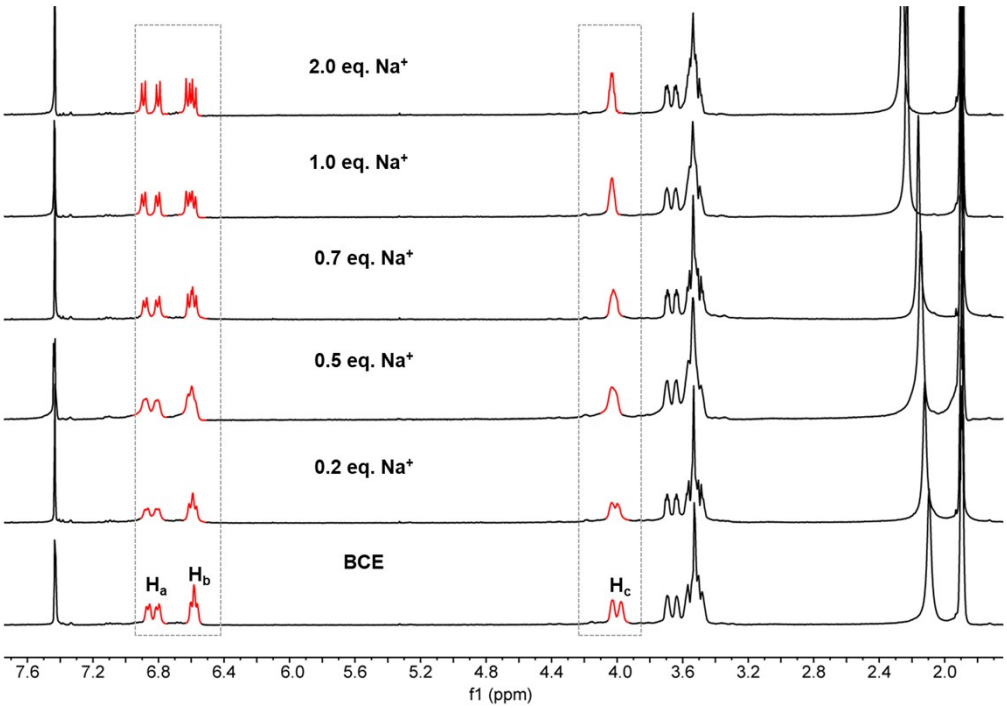


Fig. S33 ^{1}H NMR titration spectra (400 MHz, 298 K) of **BCE** (3.0 mM) titrated by Na^+ (0-2.0 equiv.) in $CDCl_3/CD_3CN$ (2:1, *v/v*), where $NaPF_6$ serves as the source of Na^+.

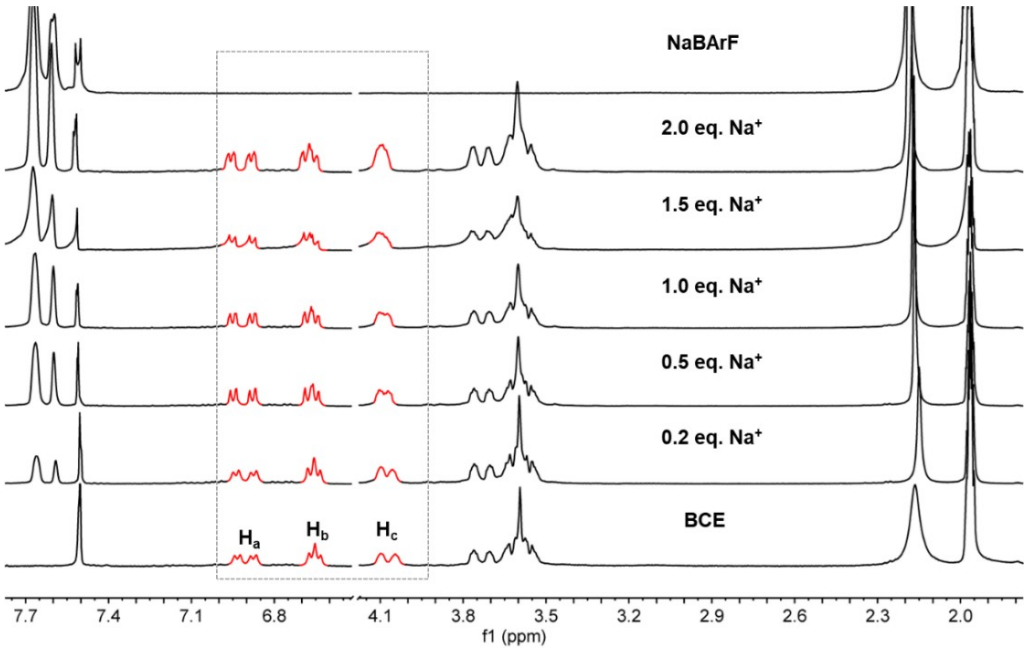


Fig. S34 ^{1}H NMR titration spectra (400 MHz, 298 K) of **BCE** (3.0 mM) titrated by Na^+ (0-2.0 equiv.) in $CDCl_3/CD_3CN$ (2:1, *v/v*), where NaBArF serves as the source of Na^+.

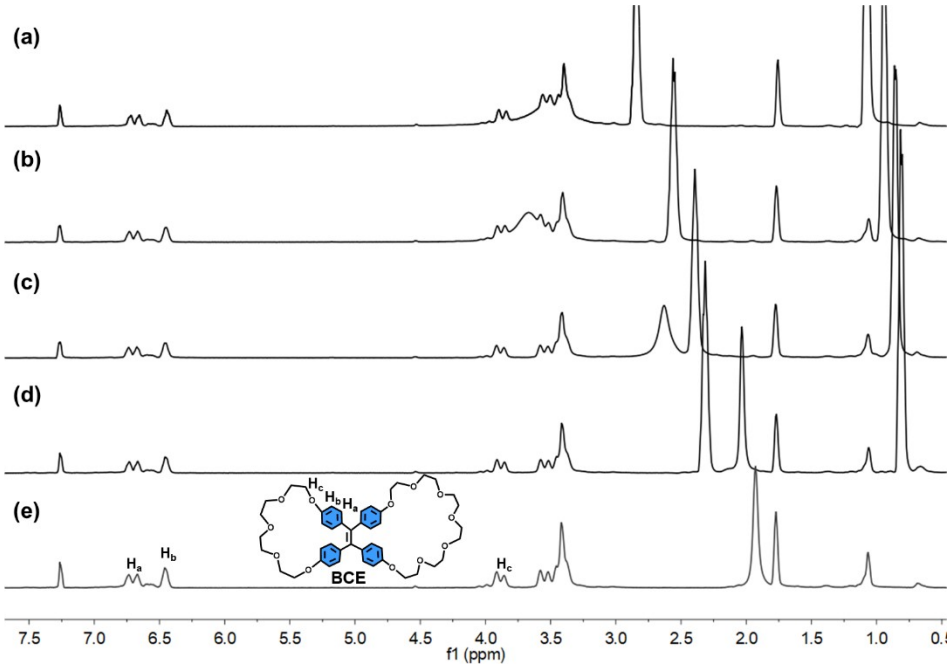


Fig. S35 ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ (2:1, *v/v*), 298 K): (a) **BCE**+Et_3N+Na^+ (2.0 eq.), (b) **BCE**+Et_3N+Na^+ (1.0 eq.), (c) **BCE**+Et_3N+Na^+ (0.5 eq.), (d) **BCE**+Et_3N, and (e) **BCE**.

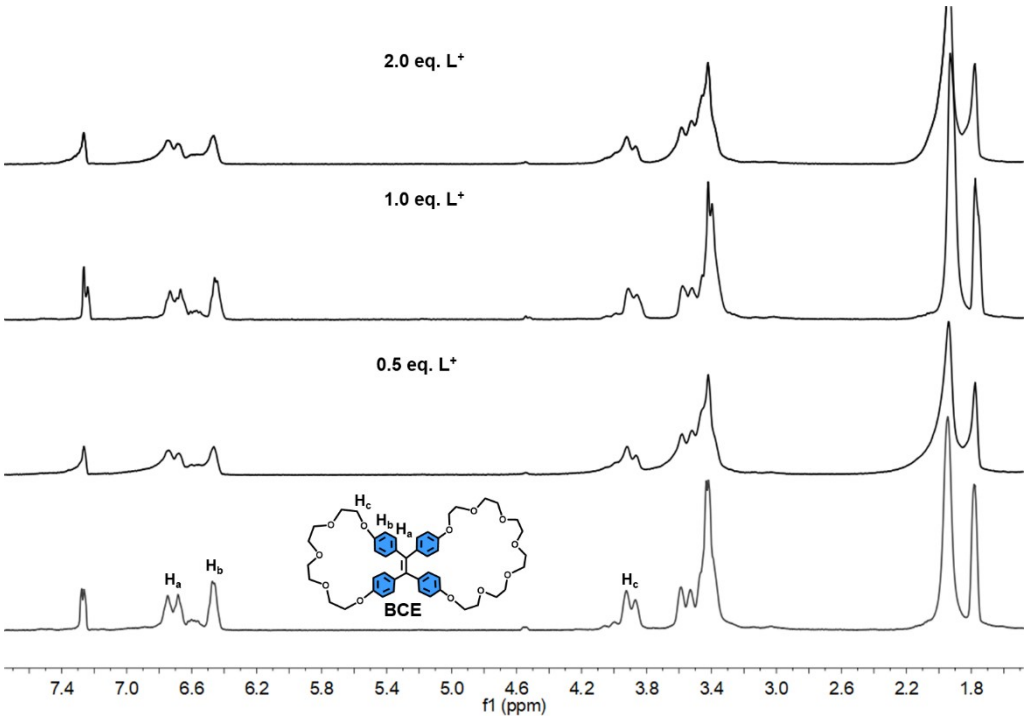


Fig. S36 ^{1}H NMR titration spectra (400 MHz, 298 K) of **BCE** (3.0 mM) titrated by Li^+ (0-2.0 equiv.) in $CDCl_3/CD_3CN$ (2:1, *v/v*), where $LiPF_6$ serves as the source of Li^+.

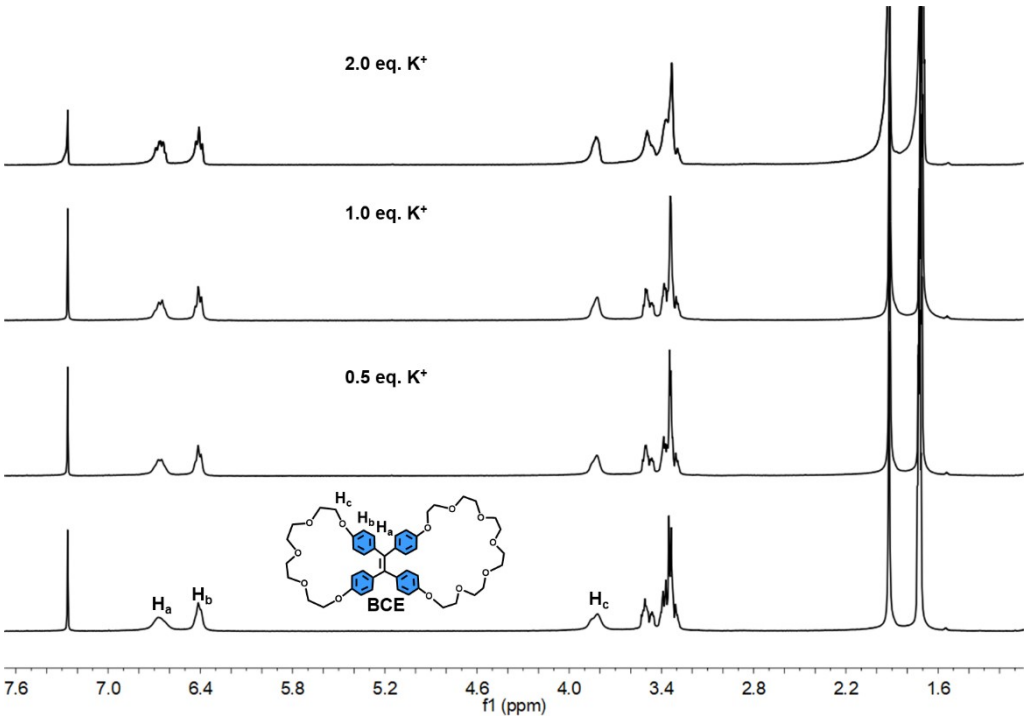


Fig. S37 ^{1}H NMR titration spectra (400 MHz, 298 K) of **BCE** (3.0 mM) titrated by K^+ (0-2.0 equiv.) in $CDCl_3/CD_3CN$ (2:1, *v/v*), where KPF_6 serves as the source of K^+.

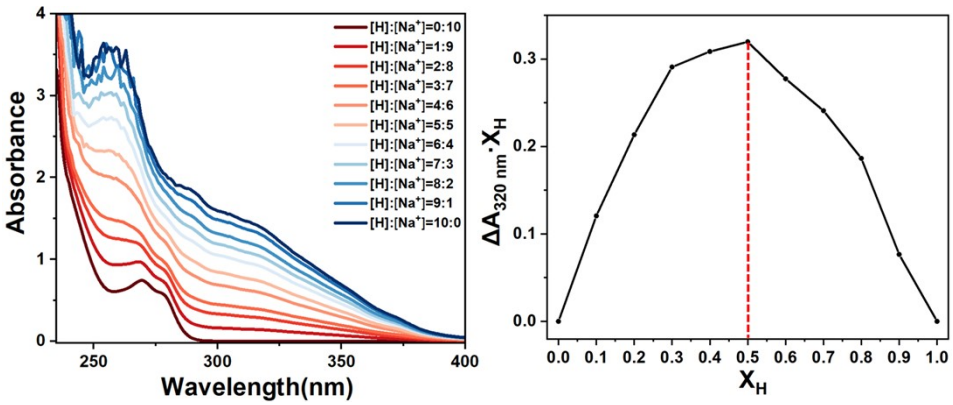


Fig. S38 UV-vis absorption spectra of **BCE** (H) ⊃Na^+ complex and Job's plot of the 1:1 binding ratio between **BCE** and Na^+ ([**BCE**] + [Na^+] = 4.0 × 10^{-4} M, solvent: $CDCl_3/CD_3CN$ (2:1, *v/v*)), where NaBArF serves as the source of Na^+.

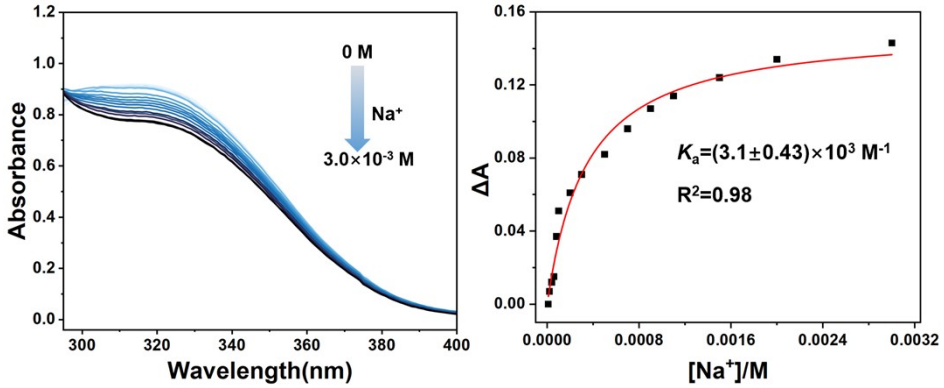


Fig. S39 UV-vis absorption spectra of **BCE** (1.0 × 10^{-4} M) with gradually addition of Na^+ (0-3.0 × 10^{-3} M) in $CDCl_3/CD_3CN$ (2:1, *v/v*) and the association constant (K_a) value of the complex between **BCE** and Na^+, where NaBArF serves as the source of Na^+.

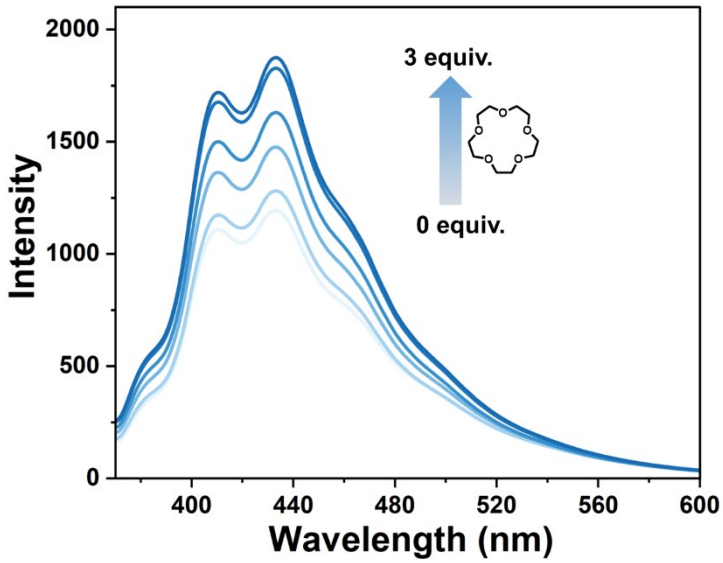


Fig. S40 Fluorescence titrations of the polymer network **BCE⊃G1**+Na^+ with increasing the concentrations of 15-crown-5 (0 to 3.0 equiv.) in $CDCl_3/CD_3CN$ (2:1, *v/v*). (λ_{ex} = 350 nm, [**BCE**] = 1 × 10^{-4} M, NaBArF offer Na^+).

6. Stability of the gel BCE⊃G1 in solution

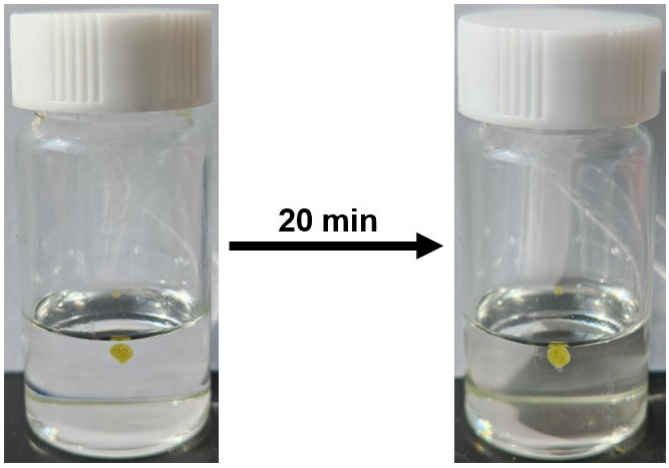


Fig. S41 The changes of the gel **BCE⊃G1** after being immersed in $CDCl_3$ for 20 min at room temperature.

It was observed that both the volume and mass of the gel **BCE⊃G1** remained relatively constant before and after the soaking process.

7. References

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