Architecture transition of supramolecular polymer through hierarchical self-assembly: from supramolecular polymer to fluorescence material

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Supporting information

1. 2D ^{1}H-^{1}H COSY NMR spectra

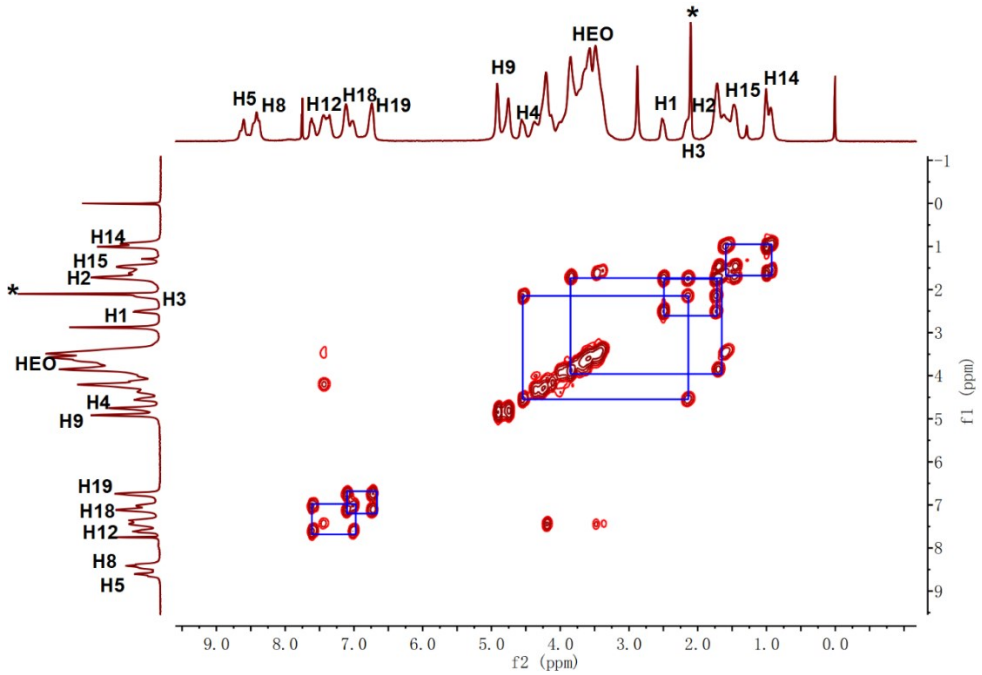


Fig. S1 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K, 20mM) of AB2+C2. The strong correlations between the protons H_1 and H_2 and between H_3 and H_4 on AB2 were observed, the correlation between H_{14} and H_{15} and between H_{18} and H_{19} on C2 were also observed at the same time. By means of the ^{1}H–^{1}H COSY experiment, the complexed ^{1}HNMR spectrum of AB2+C2 was accurately identified.

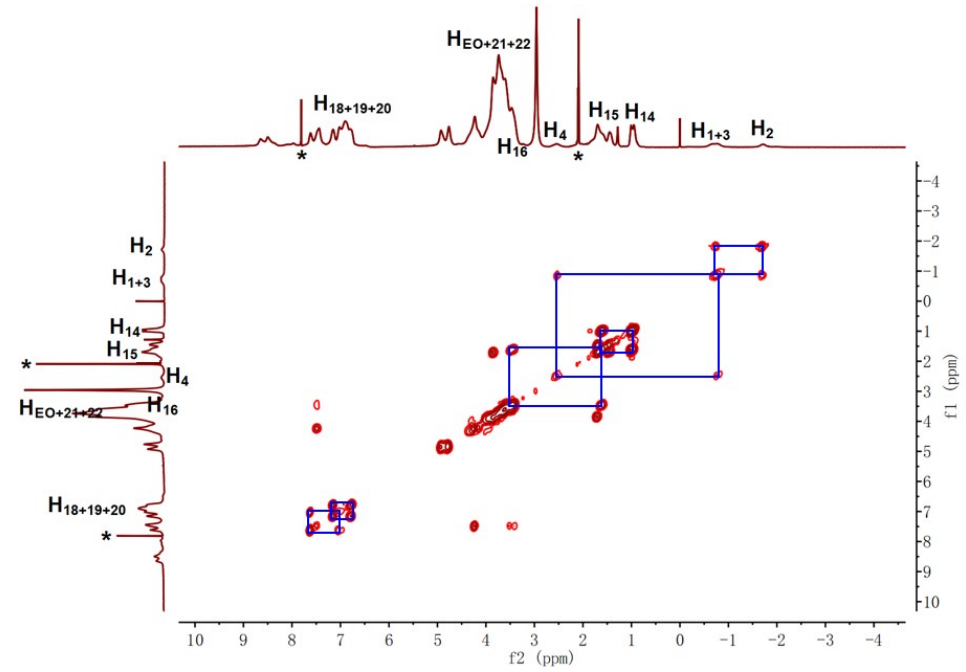


Fig. S2 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K, 15mM) of AB2+C2+TP4.

2. Concentration-dependent ^{1}H NMR spectra

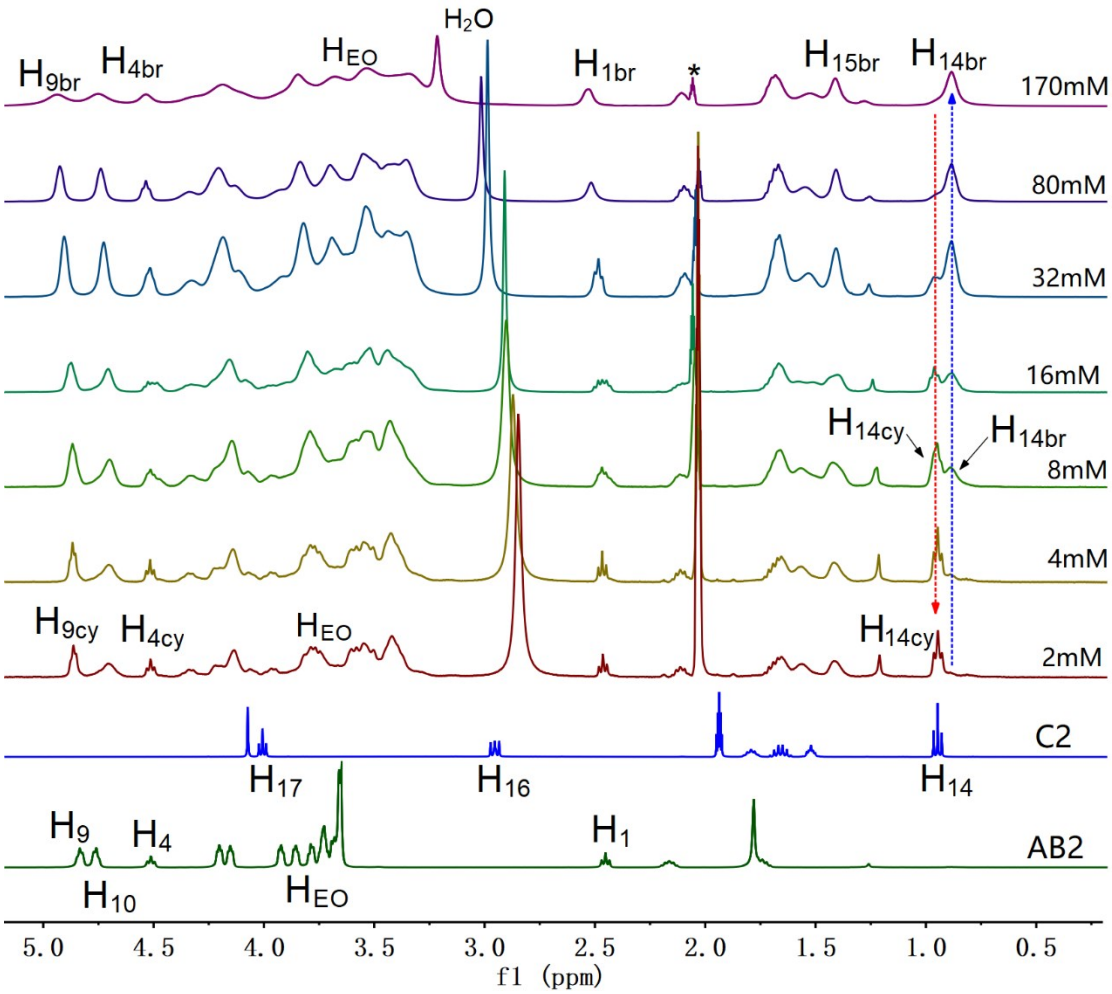


Fig. S3 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K) of (a) individual AB2, (b) individual C2; AB2+C2 (molar ratio: AB2:C2=1:1) at different concentrations (c) 2 mM, (d) 4 mM, (e) 8 mM, (f) 16 mM, (g) 32 mM, (h) 80 mM, (i) 170mM. Peaks of cyclic oligomers and the hyperbranched polymers were marked as cy, and br, respectively.

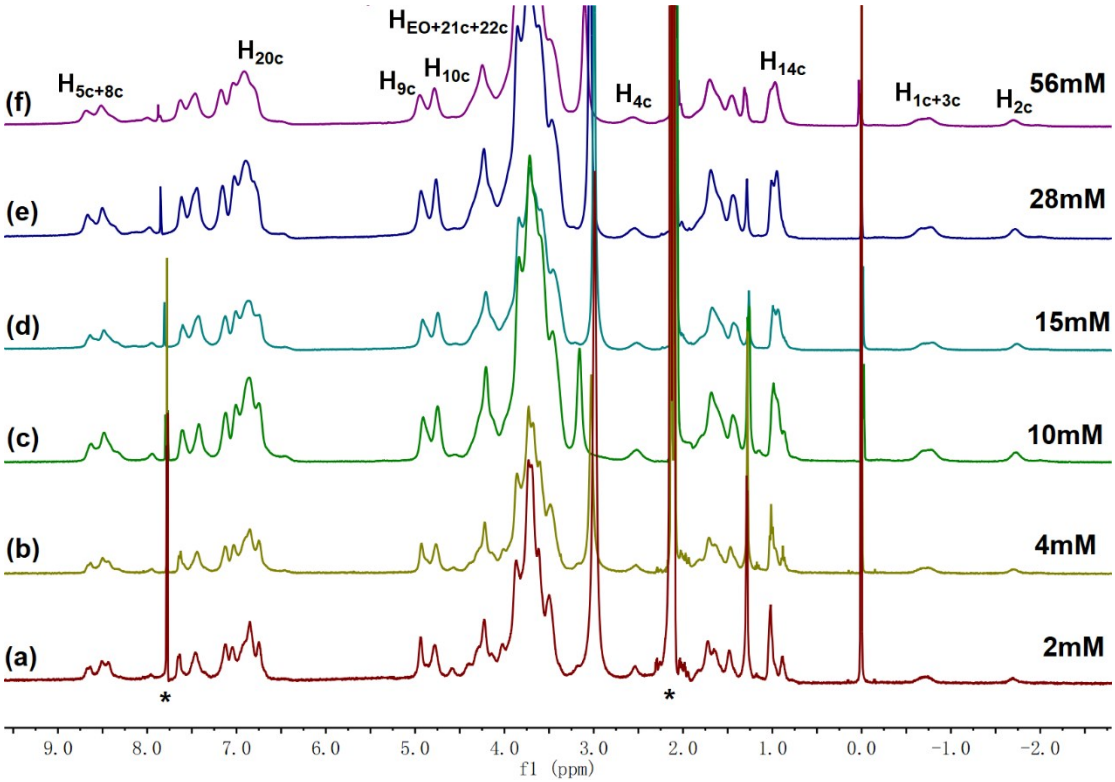


Fig. S4 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K) of AB2+C2+TP4 (molar ratio: AB2:C2:TP4=4:4:1) at different concentrations (a) 2 mM, (b) 4 mM, (c) 10 mM, (d) 15 mM, (e) 28 mM, (h) 56 mM. Complexed protons were marked as c.

3. 2D NOESY NMR spectra

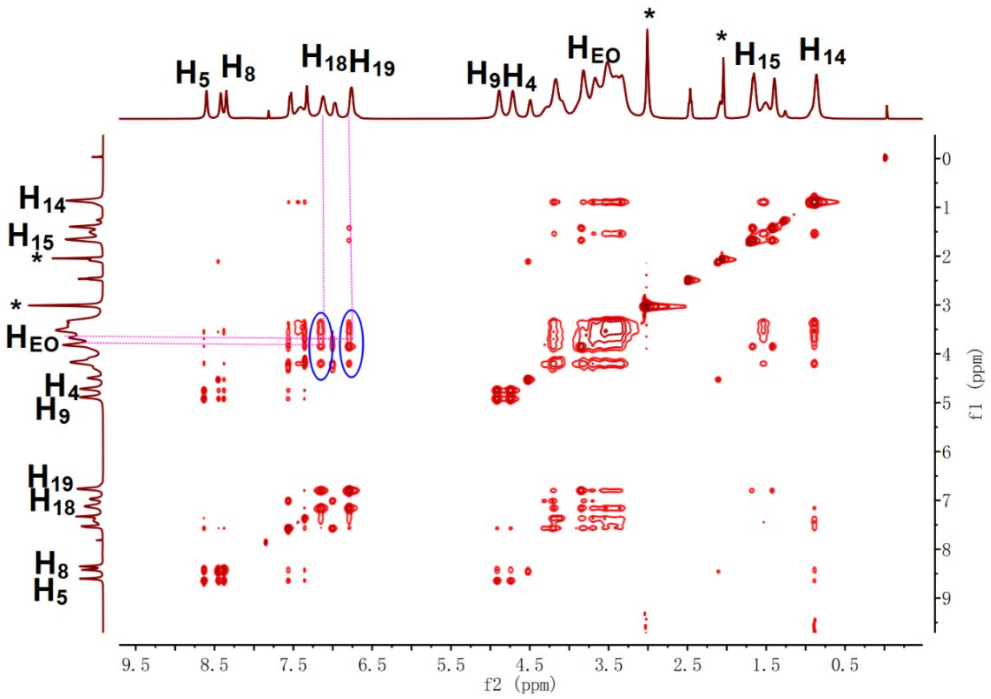


Fig. S5 NOESY NMR (400 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K, 70mM) spectrum of AB2+C2. The strong correlations between $H_{18\text{-}19}$ from C2 and H_{EO} from AB2 indicated that the dialkylammonium group of C2 was complexed tightly with the B21C group of AB2 in the solution.[S1]

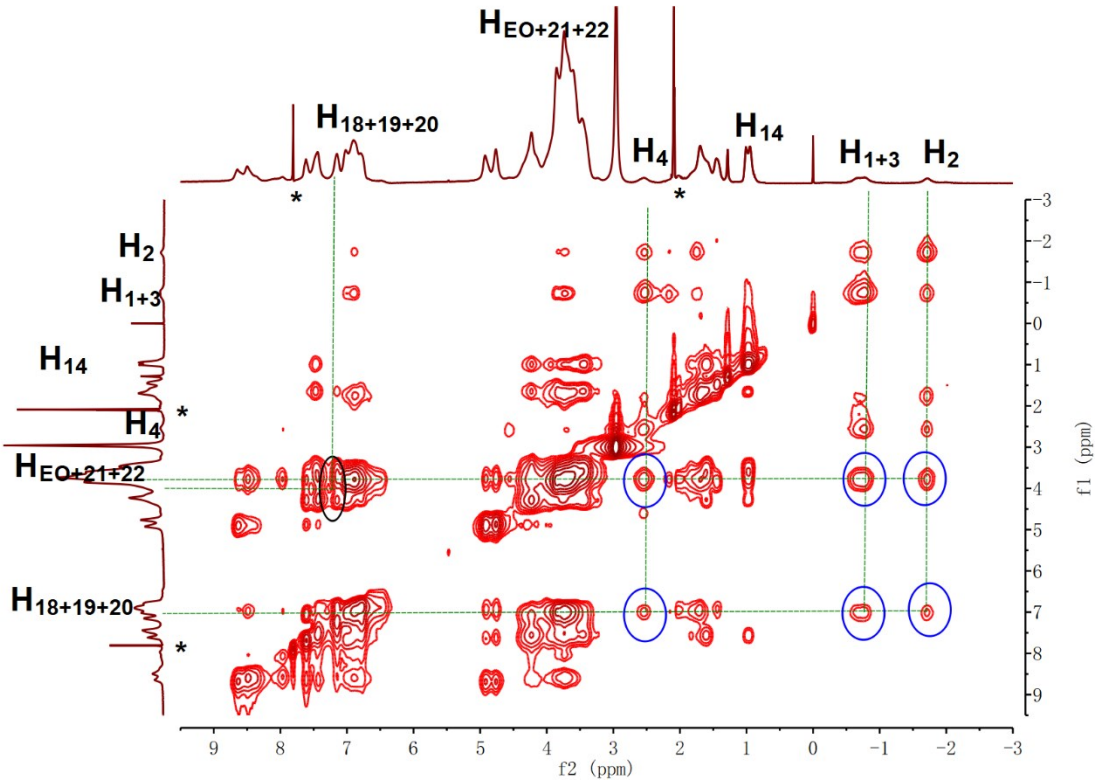


Fig. S6 NOESY NMR (400 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K, 25mM) spectrum of AB2+C2+TP4. The strong correlation between H_{18} from C2 and H_{EO} from AB2 indicated that the dialkylammonium group of C2 was complexed tightly with the B21C group of AB2 in the solution. In addition, the $H_{1\text{-}4}$ from AB2 and H_{20}-H_{22} were clearly observed, suggesting that the TAPN threaded into the cavity of P5.[S2]

4. 2D DOSY NMR spectra

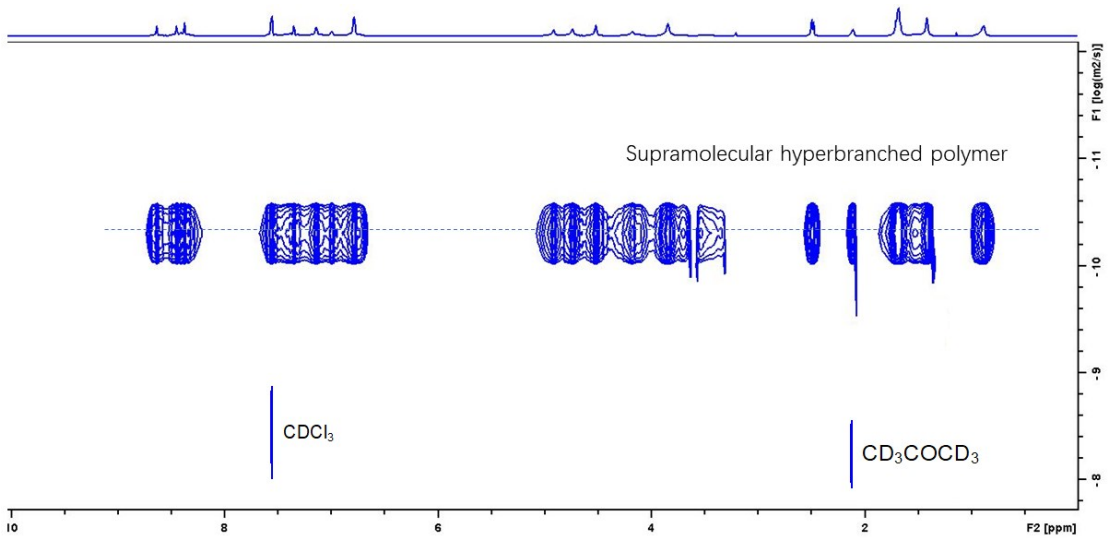


Fig. S7 Representative DOSY spectrum (500 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K) of AB2+C2, the AB2 concentration is 140 mM.

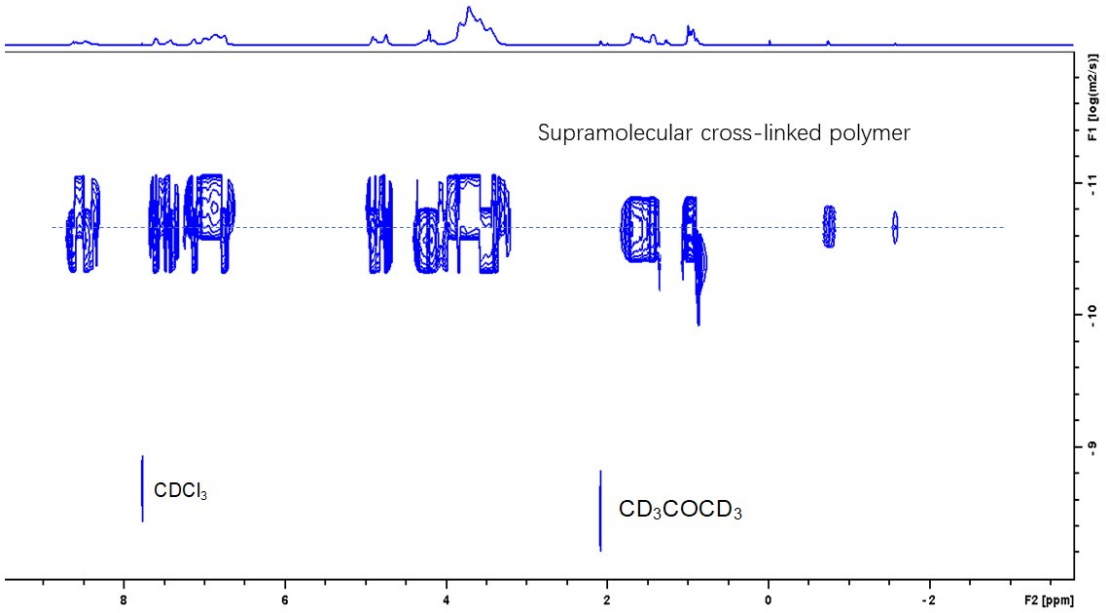


Fig. S8 Representative DOSY spectrum (500 MHz, $CDCl_3$-CD_3COCD_3 = 2/1, v/v, 298 K) of AB2+C2+TP4, the AB2 concentration is 56 mM.

5. TEM photograph

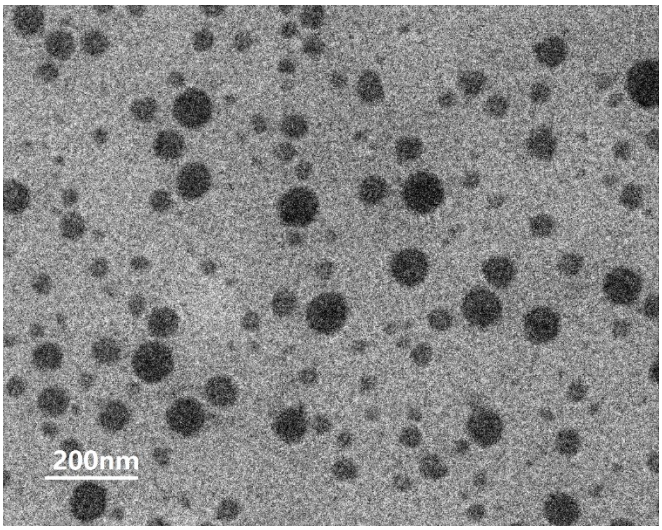


Fig. S9 Representative TEM image of the supramolecular hyperbranched polymer (SHP1).

6. Disassembly and reassembly of supramolecular polymers by adding -removing K^+

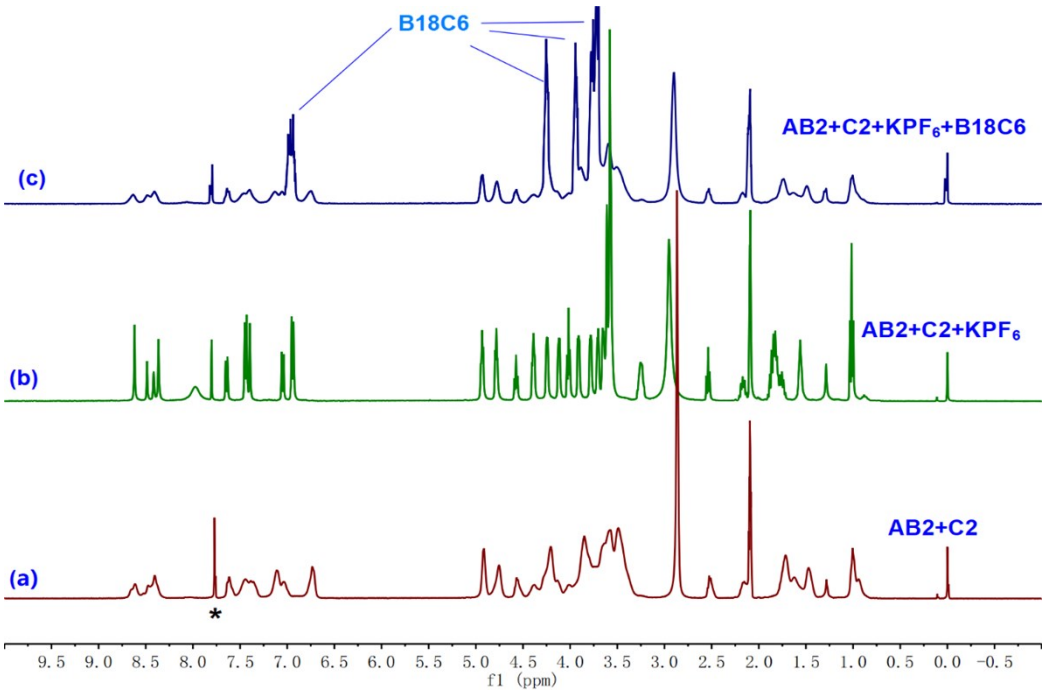


Fig. S10 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3COCD_3= 2/1, v/v, 298 K, 20 mM) of (a) AB2+C2, (b) after the addition of 2 equiv. KPF_6, and (c) after the addition of 2.2 equiv. B18C6.

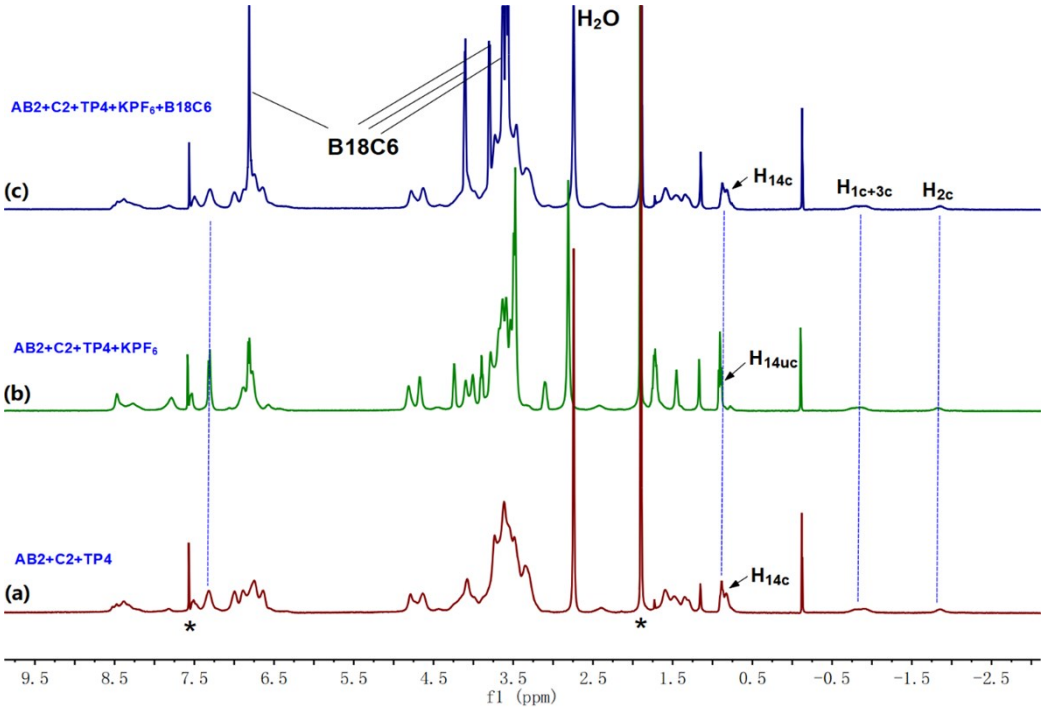


Fig. S11 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3COCD_3= 2/1, v/v, 298 K, 20 mM) of (a) AB2+C2+TP4, (b) after the addition of 2 equiv. KPF_6, and (c) after the addition of 2.2 equiv. B18C6.

7. Disassembly of SCP1 by adding adiponitrile

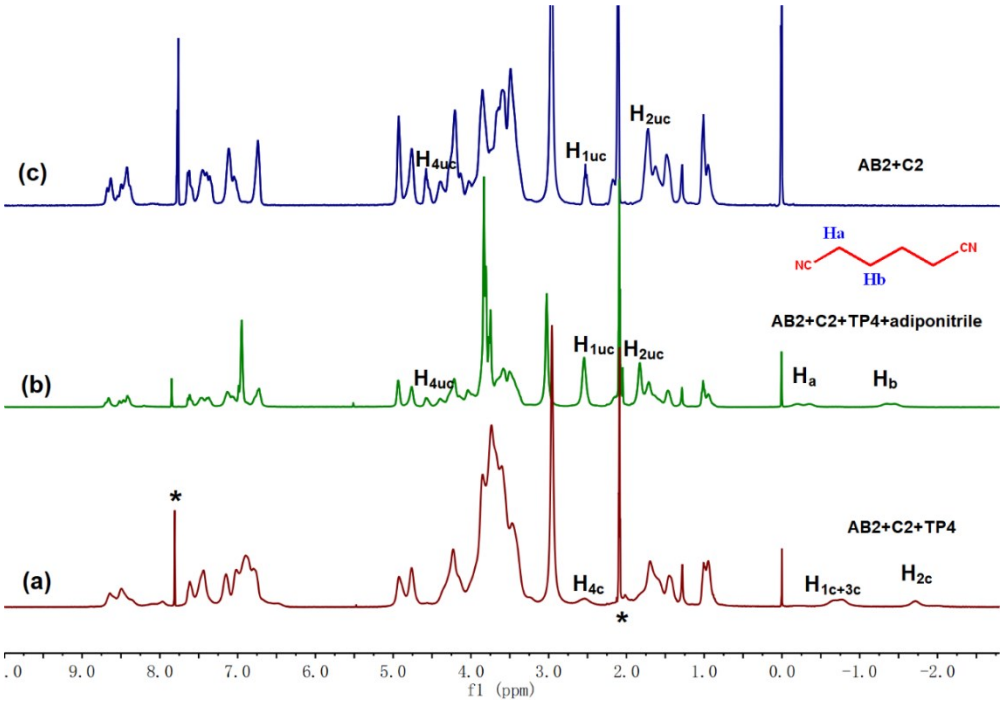


Fig. S12 ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$-CD_3COCD_3, 20 mM) of (a) AB2+C2+TP4, (b) after the addition of 1.1 equiv. adiponitrile to the solution of AB2+C2+TP4, (c) AB2+C2.

8. Fluorescence titrations

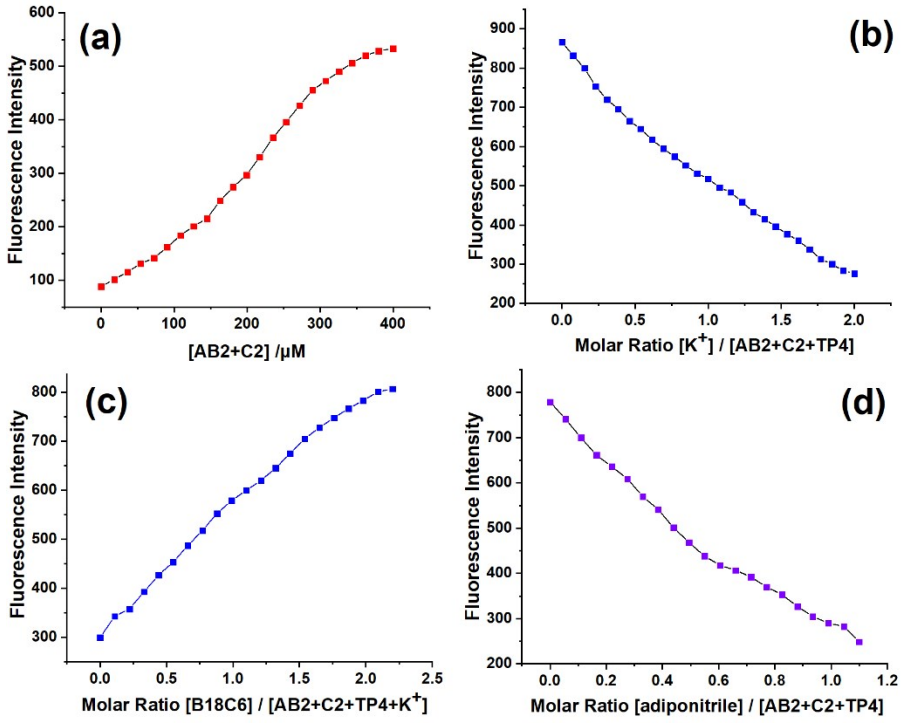
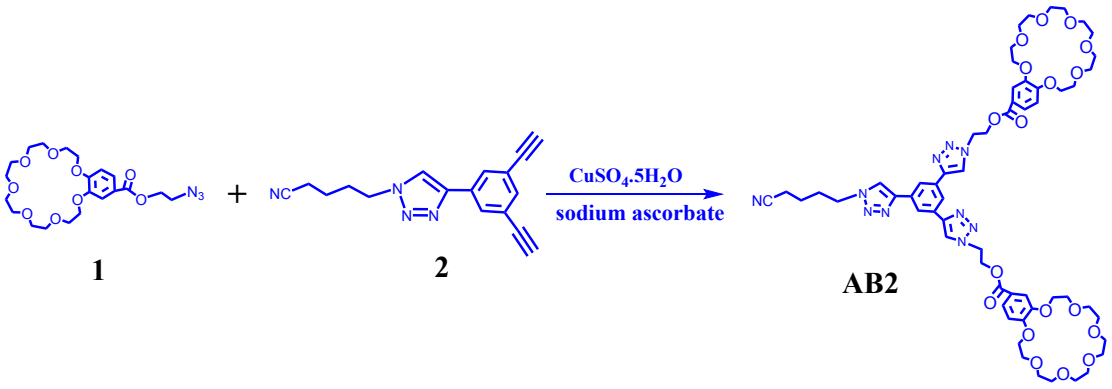


Fig. S13 (a) fluorescence intensity changes versus the concentrations of AB2+C2. (b) fluorescence intensity changes

versus molar ratios of [K^+]/[AB2+C2+TP4]. (c) fluorescence intensity changes versus molar ratios of [B18C6]/[AB2+C2+TP4+K^+]. (d) fluorescence intensity changes versus molar ratios of [adiponitrile]/[AB2+C2+TP4].

9. Synthesis of Monomers

The synthesis of monomer AB2



Scheme S1 Synthetic route of monomer AB2.

Compounds 1 (3.00g, 6.45mmol) and 2 (0.71g, 2.91mmol) were added into a solution of tetrahydrofuran and water (5:1, 150 mL) in the presence of $CuSO_4$•$5H_2O$ (144mg, 0.57 mmol) with sodium ascorbate (273.6 mg, 1.43 mmol), the mixture was stirred at 70 ℃ for 14h. After the reaction mixture was cooled to ambient temperature, the solvent was evaporated under reduced pressure. The resultant residue was dissolved in CH_2Cl_2 (100 mL) and washed twice with water (100 mL). The organic phase was combined and dried over anhydrous Na_2SO_4, the solvent was evaporated to afford the crude product and the crude product was subjected to column chromatography (CH_2Cl_2/CH_3OH= 50:1), to give AB2 (2.18g, 40 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): ppm = 8.32 (s, 2H), 8.28 (s, 1H), 8.09 (s, 2H), 7.99 (s, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.49 (s, 1H), 6.92 (d, J = 8.4 Hz, 1H), 4.85-4.87(m, 4H), 4.77-4.79(m, 4H), 4.52 (t, J = 6.8 Hz, 2H), 4.19-4.23 (m, 4H), 4.13-4.18 (m, 4H), 3.90-3.94 (m, 4H), 3.82-3.87 (m, 4H), 3.78-3.81 (m, 4H), 3.71-3.76 (m, 8H), 3.64-3.69 (m, 20H), 2.46 (t, J = 6.8 Hz, 2H), 2.15-2.19 (m, 2H), 1.72-1.77 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.9, 153.7, 148.6, 147.4, 131.9, 124.9, 122.7, 122.1, 121.4, 120.7, 119.2, 114.8, 112.7, 71.5, 71.4, 71.3, 71.2, 71.1, 70.7, 69.8, 69.7, 69.6, 69.4, 62.9, 49.8, 49.6, 29.3, 22.6, 16.9. HR-ESI-MS ($C_{59}H_{76}N_{10}O_{18}$): *m/z* calcd for $[M+Na]^+$ = 1235.5231, found =1235.5216, error 1.2 ppm.

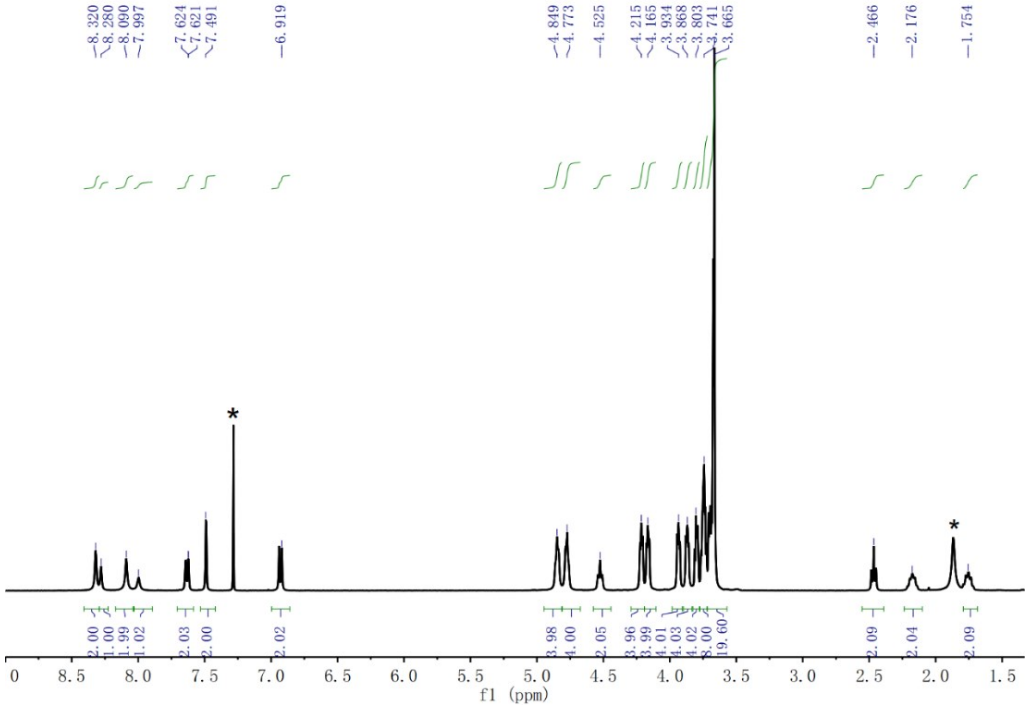


Fig. S14 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of compound AB2.

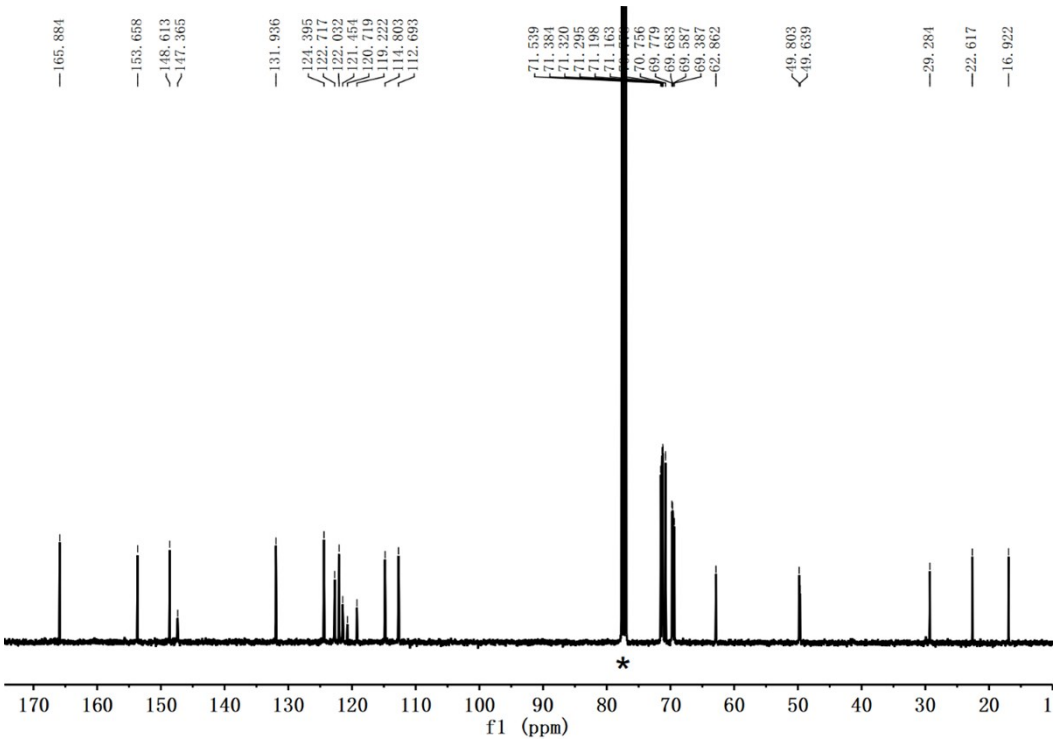


Fig. S15 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of compound AB2.

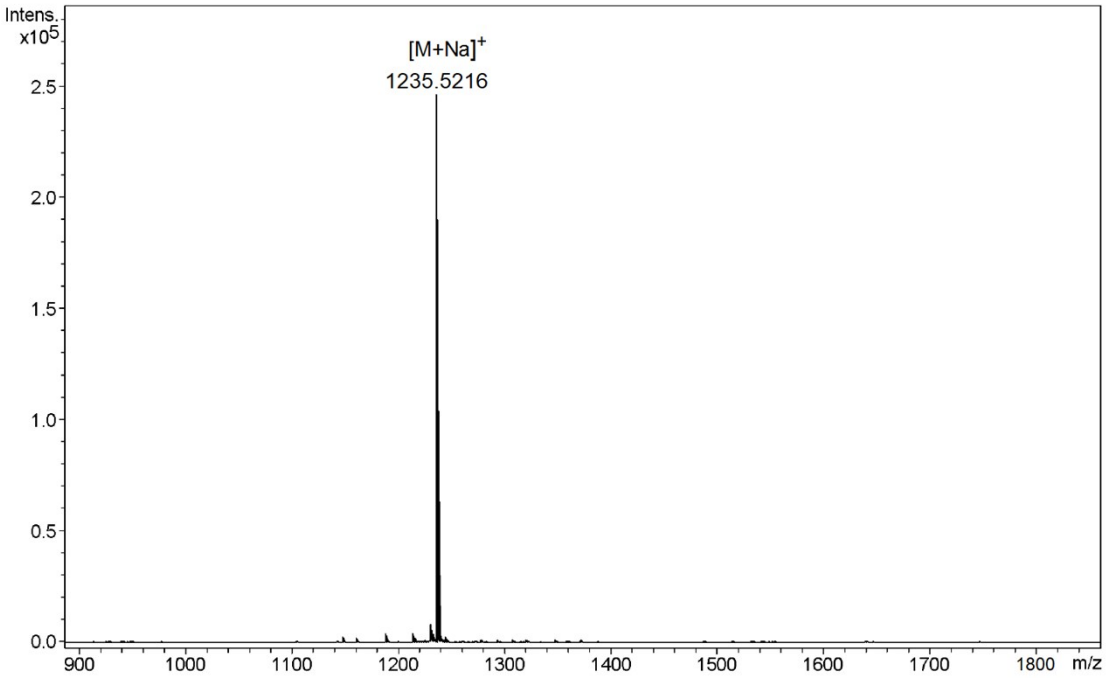
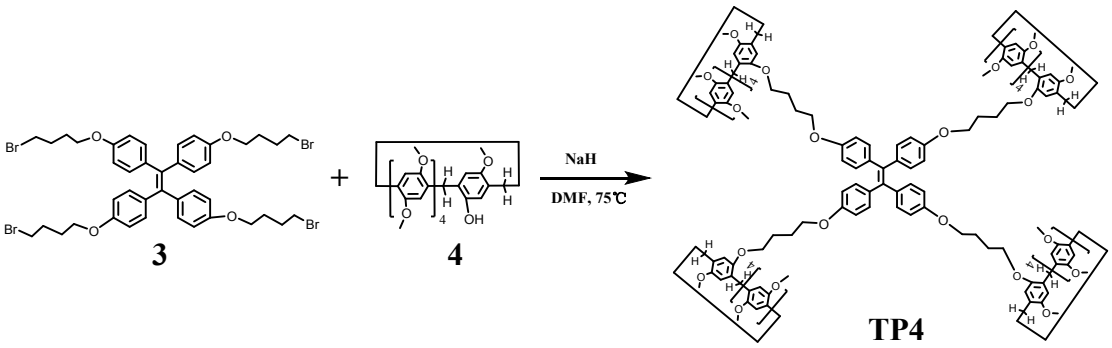


Fig. S16 Electrospray ionization mass spectrum of compound AB2.

The synthesis of monomer TP4



Scheme S2 Synthetic route of monomer TP4.

Compound TP4 was synthesized by reference to the literature procedure.[S3] A mixture of compound 3 (1.0 g, 1.1 mmol), 4 (3.1g, 4.2mmol), NaH (0.21 g, 9.0 mmol), and DMF (50ml) were added to a 150 mL flask under N_2. After the mixture was stirred at 75 ℃ for 14 h, the reaction mixture was cooled and poured into saturated brine (100 mL) and the resulting solution was extracted with dichloromethane (50 mL×3). The organic phase was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was purified by flash column chromatography (dichloromethane /ethyl acetate, 100:1, v/v) to give TP4 (1.68g. 46%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$,

298 K): ppm =6.98 (d, *J* = 8.8 Hz, 8H), 6.72-6.81 (m, 40H), 6.66 (d, *J* = 8.8 Hz, 8H), 3.93-3.98 (m, 8H), 3.83-3.91 (m, 8H), 3.73-3.82 (m, 40H), 3.60-3.70 (m, 108H), 1.92-1.97 (m, 16H).

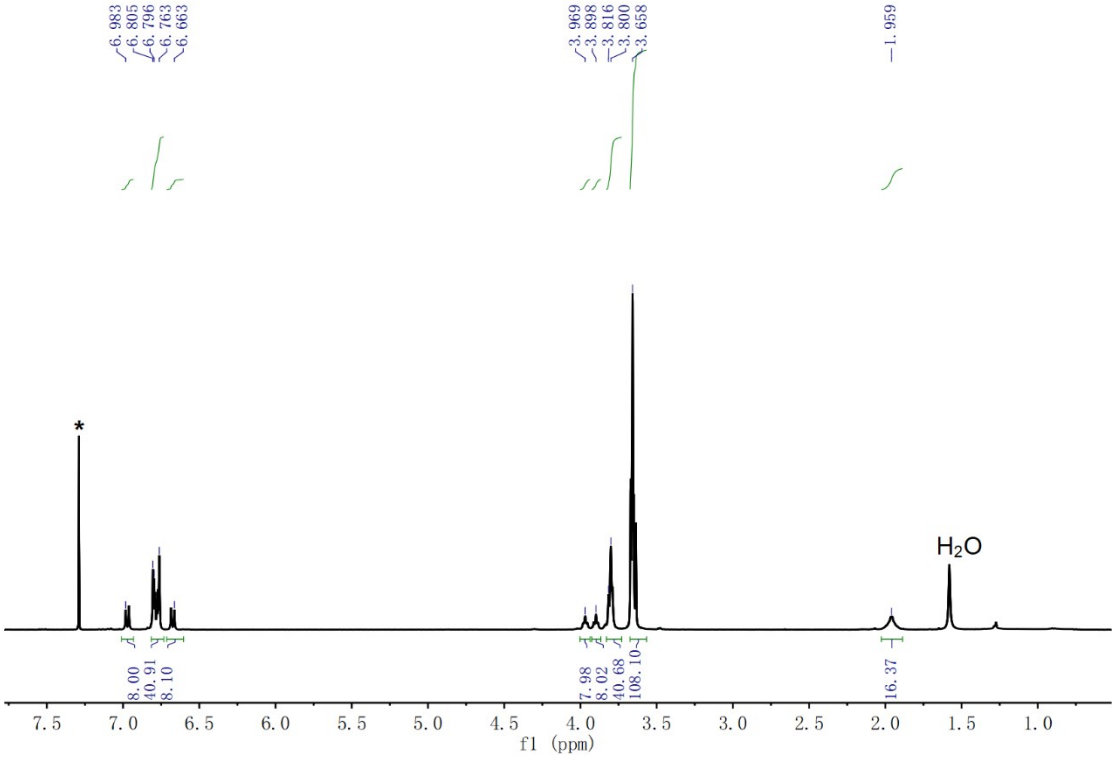
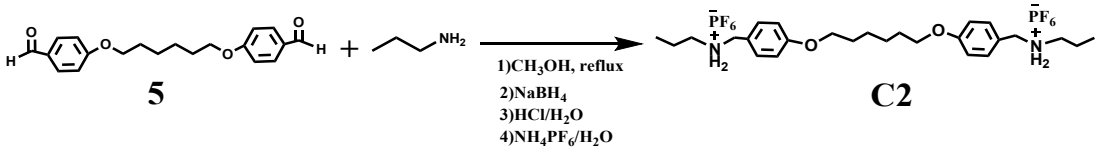


Fig. S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of compound TP4.

The synthesis of monomer C2



Scheme S3 Synthetic route of monomer C2.

The synthetic method of C2 has been reported elsewhere.[S4] Bisaldehyde 5 (1.21g, 3.7mmol) and propylamine (0.44g, 7.4mmol) were dissolved in ethanol (40 mL) and was stirred at 75 ℃ under N_2 atmosphere overnight. After the reaction mixture was cooled to ambient temperature, $NaBH_4$(0.28 g, 7.5mmol) was added to the solution in small portion and the mixture was stirred at room temperature for another 8 h. Water (50 mL) and 2 M HCl were added to quench the remaining $NaBH_4$ and acidify the amine. The solvent was removed under reduced pressure to give a white solid which was suspended in acetone (40 mL). Saturated aqueous NH_4PF_6 solution was added until the suspension become clear. The resulting solution was evaporated under reduced pressure. The residue was washed with copious amount of water and filtrated to afford the product (1.30 g, 50%).^{1}H NMR (400 MHz, CD_3CN, 298 K): ppm =7.73 (br, 4H), 7.35 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4H), 4.07 (s, 4H), 4.01 (t, *J* = 6.4 Hz, 4H), 2.93 (t, *J* = 7.8 Hz, 4H), 1.75-1.82 (m, 4H), 1.62-1.69(m, 4H), 1.50-1.57 (m, 4H), 0.95(t, *J* = 7.4 Hz, 6H).

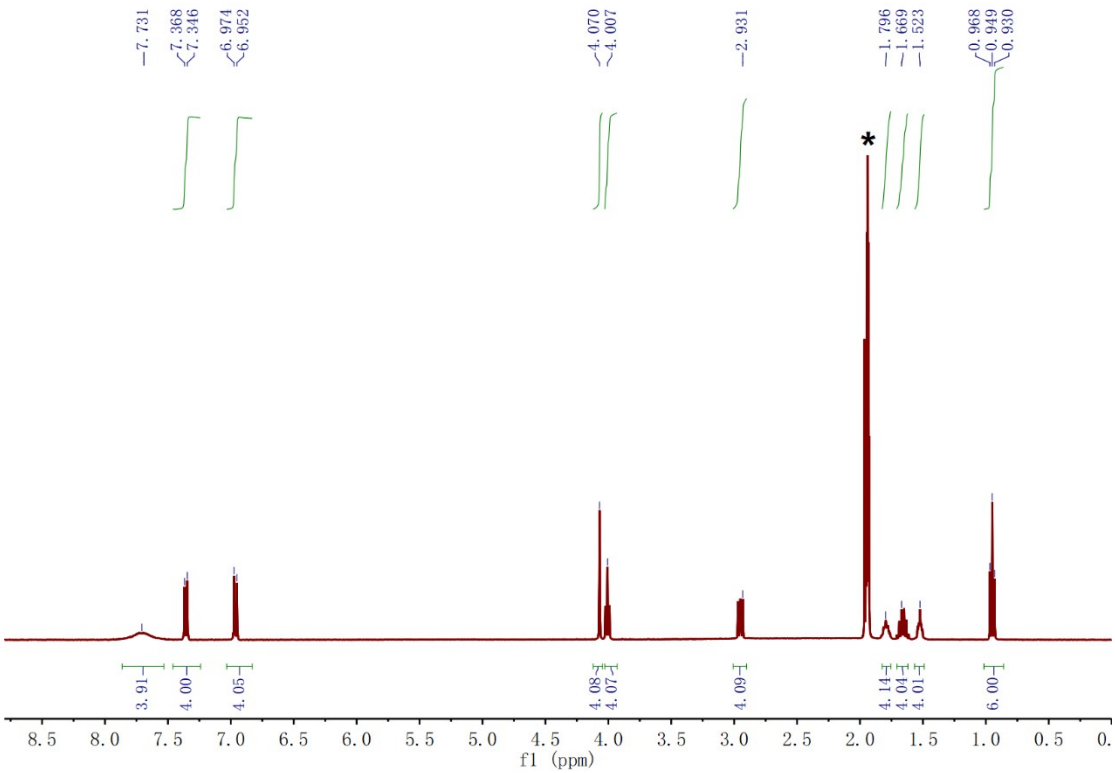


Fig. S18 ^{1}H NMR spectrum (400 MHz, CD_3CN, room temperature) of C2.

References

S1. C. J. Zhang, S. J. Li, J. Q. Zhang, K. L. Zhu, N. Li, F. H. Huang, *Org. Lett.* 2007, **9**, 5553-5556.

S2. C. J. Li, K. Han, J. Li, Y. Y. Zhang, W. Chen, Y. H. Yu, X. S. Jia. *Chem. - Eur. J.*, 2013, **19**, 11892–11897.

S3. H. Li, Z. Z. Duan, Y. Yang, F. F. Xu, M. F. Chen, T. X. Liang, Y. Bai and R. Q. Li. *Macromolecules*, 2020, 53, 4255−4263.

S4. Y. Yang, H. Li, J. M. Chen, F. F. Xu, Z. Z. Duan, T. X. Liang, Y. Liu and W. Tian. *Polym. Chem.*, 2019, **10**, 6535–6539.