

Cross-Linked Supramolecular Polymer Networks Constructed by Pillar[5]arene-Based Host–Guest Recognition and Coordination/Oxidation of Catechol

Yuezhou Liu, Liqing Shangguan, Baodong Zhao, Bin Chen, Bingbing Shi* and
Yinglei Wang*

Xi'an Modern Chemistry Research Institute, Xi'an 710065, China. E-mail:
wangyl204@163.com

*Key Laboratory of Eco-Functional Polymer Materials of the Ministry of Education, College
of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070,
China. E-mail: bingblingshi@nwnu.edu.cn*

State Key Laboratory of Fluorine & Nitrogen Chemicals, Xi'an 710065, China

*Department of Orthopaedic Surgery, Sir Run Run Shaw Hospital, Medical College of
Zhejiang University, Hangzhou, Zhejiang 310016, China*

*Key Laboratory of Musculoskeletal System Degeneration and Regeneration Translational
Research of Zhejiang Province, Hangzhou, Zhejiang 310016, China*

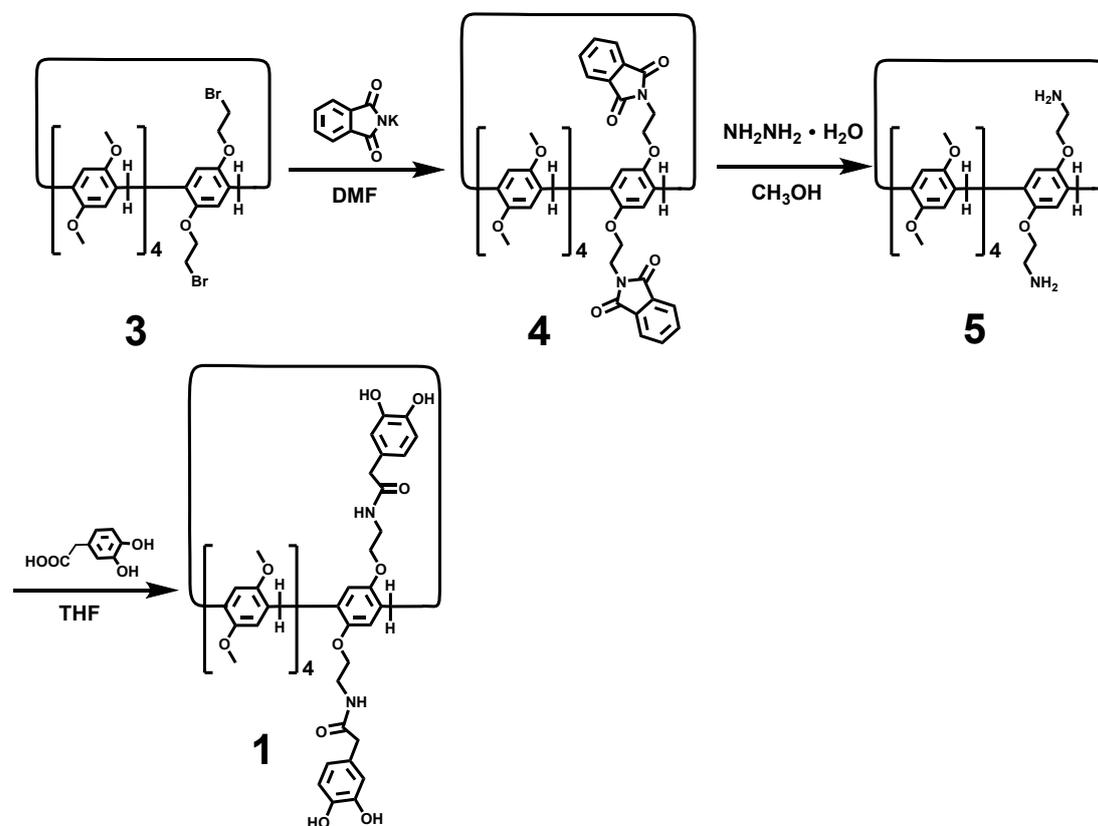
Electronic Supplementary Information (15 pages)

1. <i>Materials and instrumentations</i>	S2
2. <i>Synthesis and characterizations of compounds</i>	S3
3. <i>pH-dependent catechol-Fe³⁺ coordination</i>	S10
4. <i>2D NOESY NMR spectrum of a mixture of 1 and 2</i>	S11
5. <i>MALDI-TOF mass spectrum of a mixture of compound 1 and BPO</i>	S11
6. <i>Concentration-variant 2D DOSY NMR spectra of 1·Fe³⁺·2</i>	S12
7. <i>Digital photos of supramolecular glues</i>	S14
8. <i>The temperature-variant NMR spectra of a mixture of 1 and 2</i>	S15
9. <i>References</i>	S15

1. Materials and instrumentations

All reagents were commercially available and used as supplied without further purification. ^1H NMR spectra, ^{13}C NMR spectra, NOESY and DOSY were recorded with an Agilent 600 MHz DirectDrive2 with use of the deuterated solvent as the lock and the residual solvent as the internal reference. UV-vis spectra were taken on a PerkinElmer Lambda 35 UV-vis spectrophotometer. 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 mass spectrometric experiments were performed with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Matrix-assisted laser desorption/ionization time of flight mass spectrometric experiments were performed on a Bruker Ultraflex MALDI-TOF mass spectrometer with a 355 nm Nd: YAG laser (Smartbeam II) and 25 kV ion source voltage. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. SEM samples were prepared at the concentration of 1.00 mM via the vacuum freeze-drying methodology. The compounds **2** and **3** were prepared according to previous work.^{S1,S2}

2. Synthesis and characterizations of compounds



Scheme S1 The synthetic route to compound **1**.

The compound **3** was prepared according to previous work.^{S1} The ^1H NMR spectrum of **3** is shown in Fig. S1. ^1H NMR spectrum of **3** (600 MHz, 298 K) in CDCl_3 δ (ppm): 6.79–6.82 (m, 10 H), 4.09–4.12 (t, $J = 9$ Hz, 4 H), 3.78–3.79 (br, 10 H), 3.71 (s, 18 H), 3.68 (s, 6 H), 3.50–3.52 (t, $J = 6$ Hz, 4 H).

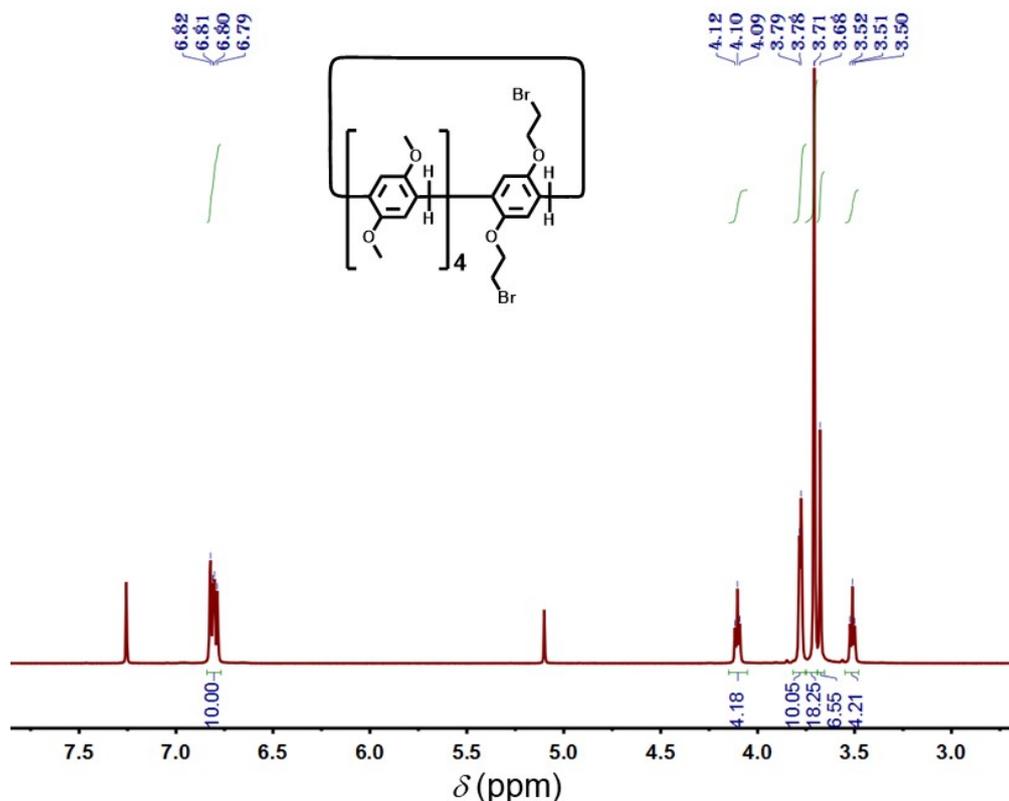


Fig. S1 ^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) of **3**.

Synthesis of compound **4**: A mixture of compound **3** (3.00 g, 3.20 mmol) and potassium phthalimide (3.72 g, 20.0 mmol) was stirred in *N,N*-dimethylformamide at 90 °C for 24 h. The solution was evaporated under vacuum. The crude product was dissolved in CH_2Cl_2 (400 mL) and washed three times with H_2O (100 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford a yellow solid, which was further purified by column chromatography using petroleum ether/ethyl acetate ($v : v = 3 : 1$). The fractions containing the product were concentrated to give **4** as a yellow solid. The ^1H NMR spectrum of **4** is shown in Fig. S2. ^1H NMR spectrum of **4** (600 MHz, 298 K) in CDCl_3 δ (ppm): 7.82–7.83 (m, 4 H), 7.67–7.69 (m, 4 H), 6.69 (s, 2 H), 6.79–6.80 (d, $J = 6$ Hz, 4 H), 6.75 (s, 2 H), 6.72 (s, 2 H), 4.21–4.25 (m, 2 H), 4.03–4.10 (m, 4 H), 3.97–4.01 (m, 2 H), 3.57–3.78 (m, 34 H). The ^{13}C NMR spectrum of **4** is shown in Fig. S3. ^{13}C NMR spectrum of **4** (150 MHz, 298 K) in CDCl_3 δ (ppm): 170.8, 153.4, 153.3, 153.2, 136.6, 134.7, 131.0, 130.8, 125.9, 117.1, 116.7, 116.6, 116.4, 68.0, 58.5, 40.5, 32.1. LRESIMS is shown in Fig. S4: m/z 1086.23 $[\text{M} + \text{NH}_4]^+$.

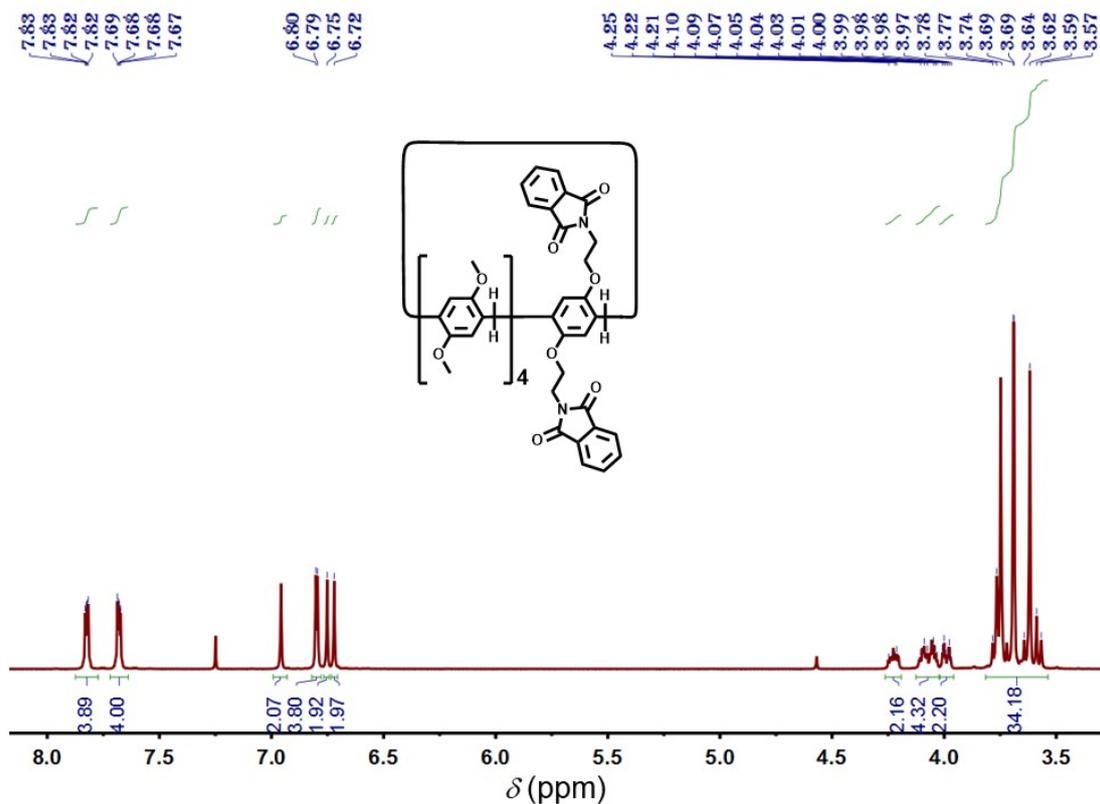


Fig. S2 ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of 4.

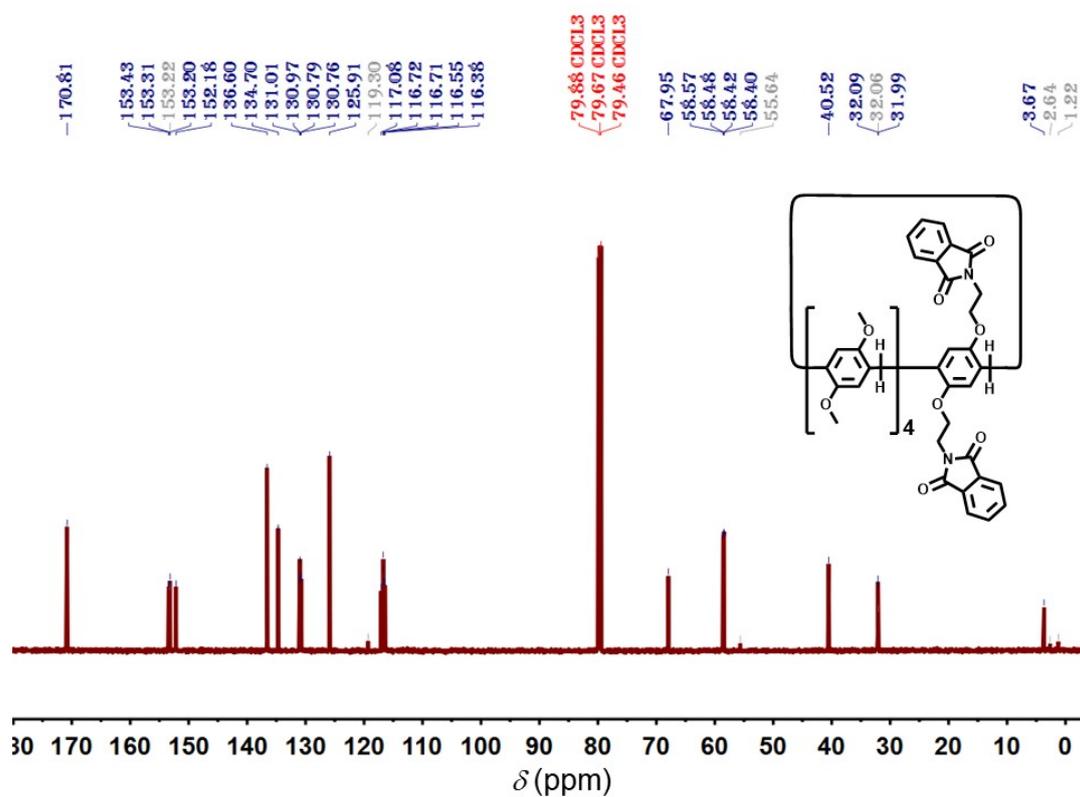


Fig. S3 ¹³C NMR spectrum (150 MHz, CDCl₃, 298 K) of 4.

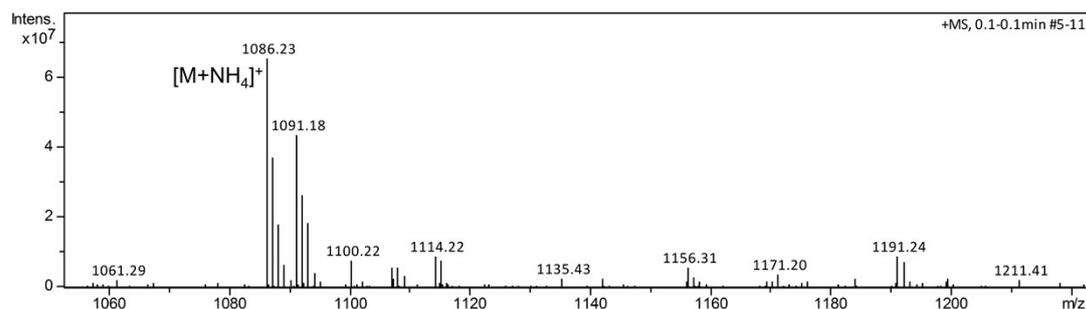


Fig. S4 LRESIMS spectrum of **4** in CHCl_3 .

Synthesis of compound **5**: A mixture of **4** (2.00 g, 2.48 mmol) and hydrazine hydrate (25 ml) was heated at reflux in methanol (40 mL) for 10 h. Then the mixture was filtered and washed with methanol to give **5** as a white solid. The ^1H NMR spectrum of **5** is shown in Fig. S5. ^1H NMR spectrum of **5** (600 MHz, 298 K) in CDCl_3 δ (ppm): 6.78 (s, 2 H), 6.73 (d, $J = 6$ Hz, 4 H), 6.67 (s, 2 H), 6.65 (s, 2 H), 3.77–3.78 (br, 14 H), 3.67 (s, 6 H), 3.64 (s, 6 H), 3.60 (s, 12 H), 2.85–2.87 (m, $J = 6$ Hz, 4 H), 1.39 (s, 4 H). The ^{13}C NMR spectrum of **5** is shown in Fig. S6. ^{13}C NMR spectrum of **5** (150 MHz, 298 K) in CDCl_3 δ (ppm): 153.5, 152.5, 131.2, 116.9, 73.6, 58.6, 44.3, 32.5. LRESIMS is shown in Fig. S7: m/z 809.48 $[\text{M} + \text{H}]^+$. m/z calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{47}\text{H}_{57}\text{N}_2\text{O}_{10}^+$, 809.4013; found 809.4011, error -0.25 ppm.

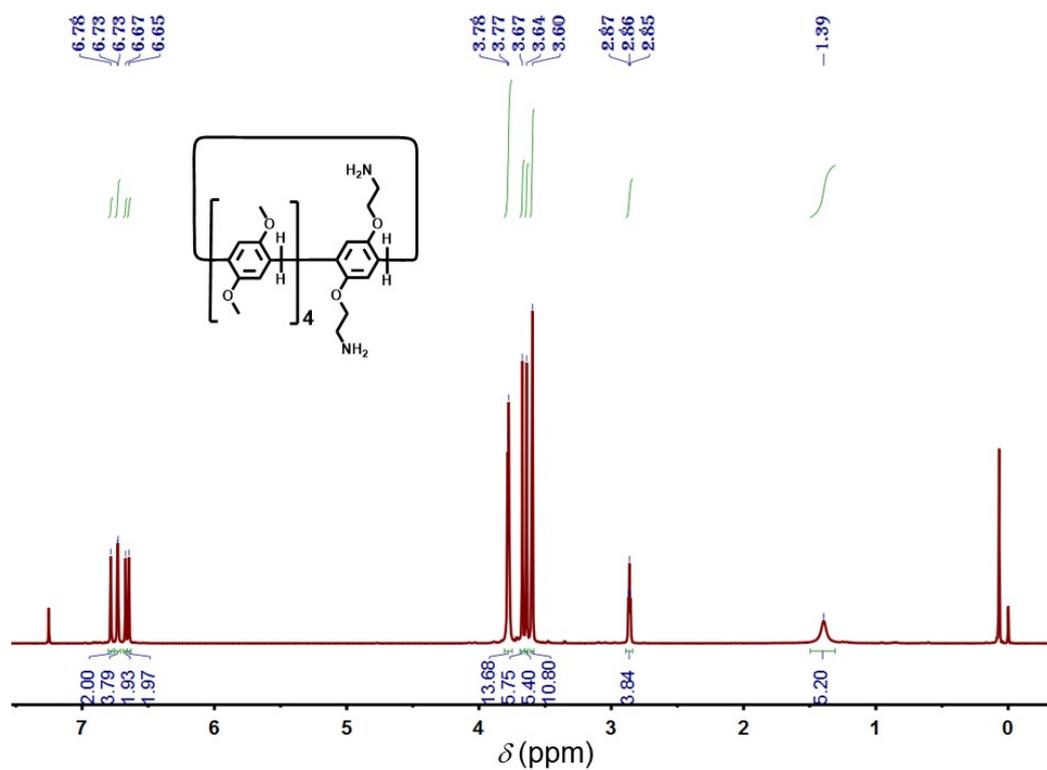


Fig. S5 $^1\text{H NMR}$ spectrum (600 MHz, CDCl_3 , 298 K) of 5.

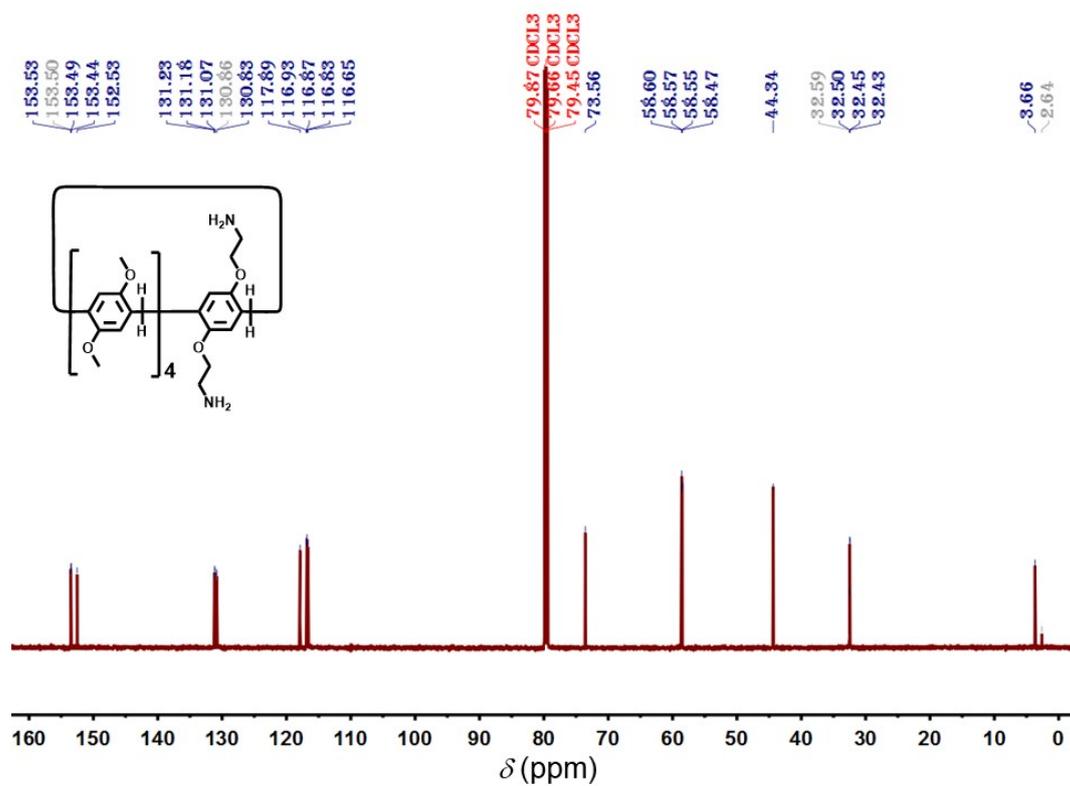


Fig. S6 $^{13}\text{C NMR}$ spectrum (150 MHz, CDCl_3 , 298 K) of 5.

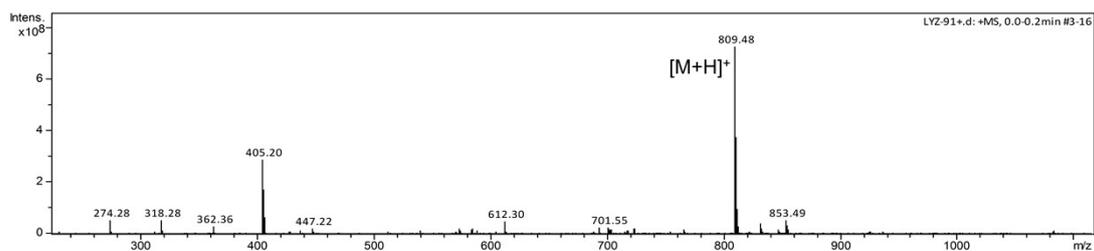


Fig. S7 LRESIMS spectrum of **5** in CHCl_3

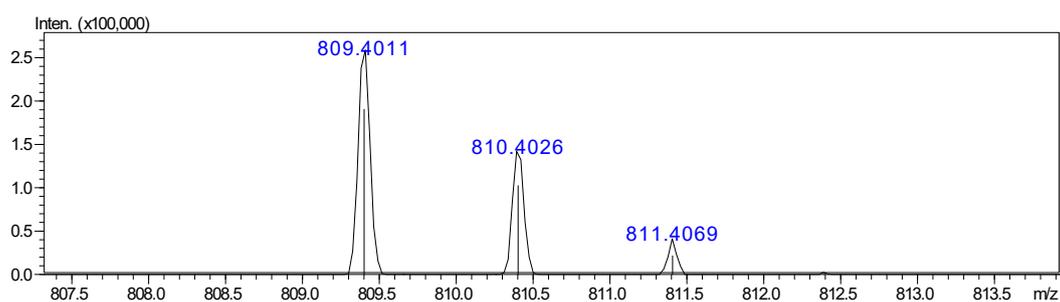


Fig. S8 HRESIMS spectrum of **5** in CHCl_3

Synthesis of compound **1**: A mixture of compound **5** (2.00 g, 2.47 mmol), DOPAC (1.18 g, 7.00 mmol), EDC (1.34 g, 7.00 mmol) and DMAP (catalytic amount) was stirred at room temperature in dry THF (200 ml) for 24 hours. After the solid was filtered off, the solvent was concentrated by rotary evaporation. The crude product was dissolved in CH_2Cl_2 (100 mL) and washed three times with H_2O (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford a brown solid, which was further purified by column chromatography using dichloromethane/methanol ($v : v = 25 : 1$). The fractions containing the product were concentrated to give **1** as a white solid. The ^1H NMR spectrum of **1** is shown in Fig. S9. ^1H NMR spectrum of **1** (600 MHz, 298 K) in CDCl_3 δ (ppm): 6.40–6.70 (m, 18 H), 3.31–3.70 (m, 46 H). The ^{13}C NMR spectrum of **1** is shown in Fig. S10. ^{13}C NMR spectrum of **1** (150 MHz, 298 K) in CDCl_3 δ (ppm): 172.4, 150.0, 149.7, 148.7, 143.7, 142.8, 127.8, 127.5, 127.0, 125.2, 120.2, 115.3, 114.2, 55.0, 52.4, 41.7, 38.5, 28.6. LRESIMS is shown in Fig. S11: m/z 1107.45 $[\text{M} - \text{H}]^-$. m/z calcd for $[\text{M} - \text{H}]^-$ $\text{C}_{63}\text{H}_{67}\text{N}_2\text{O}_{16}^-$, 1107.4496; 1107.4483, error -1 ppm.

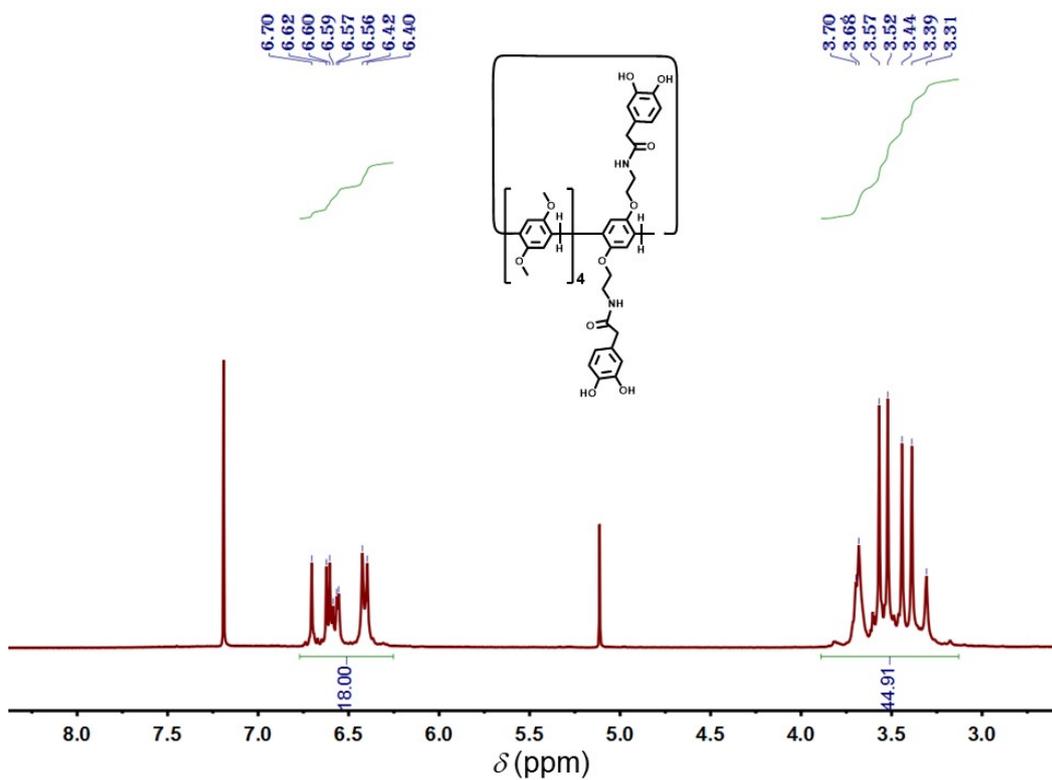


Fig. S9 ^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) of 1.

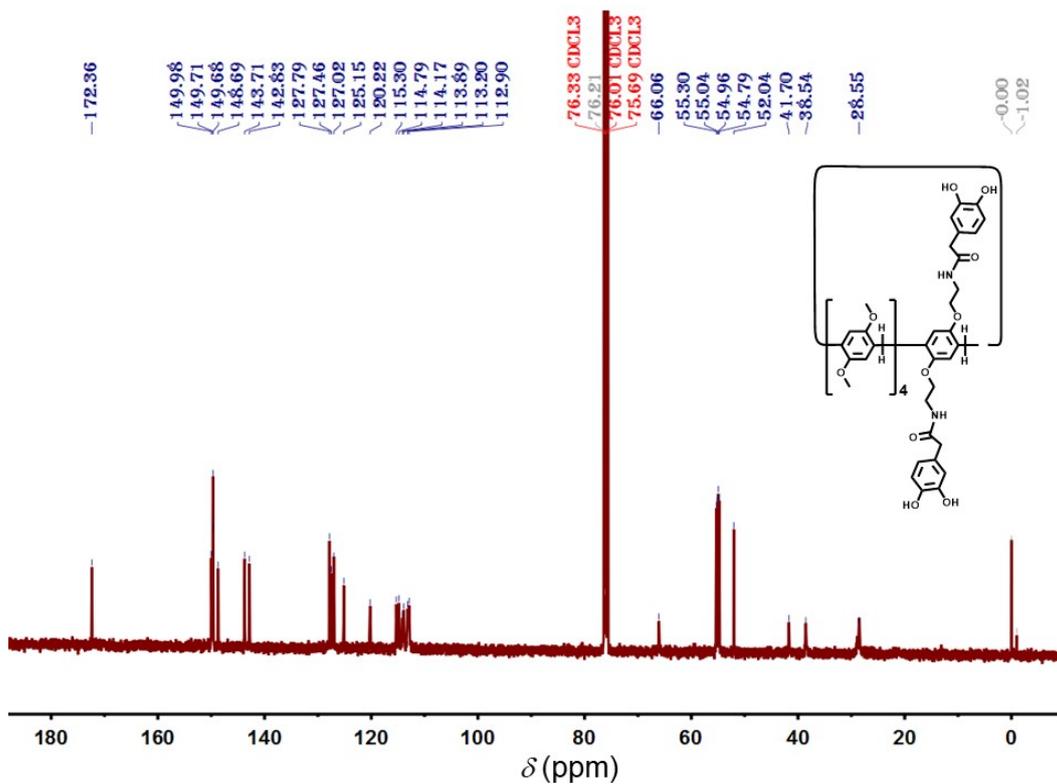


Fig. S10 ^{13}C NMR spectrum (150 MHz, CDCl_3 , 298 K) of 1.

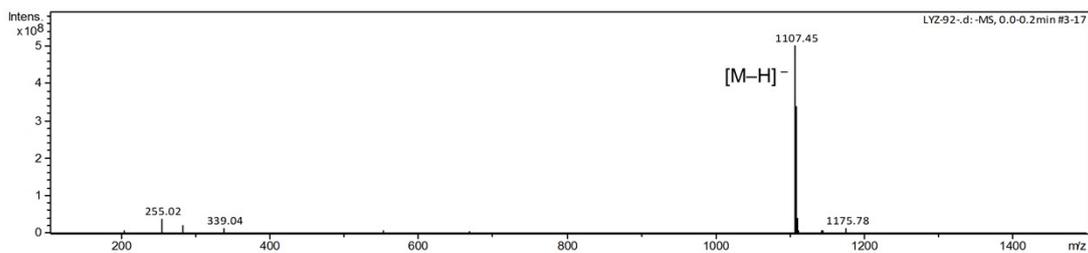


Fig. S11 LRESIMS spectrum of **1** in CHCl_3

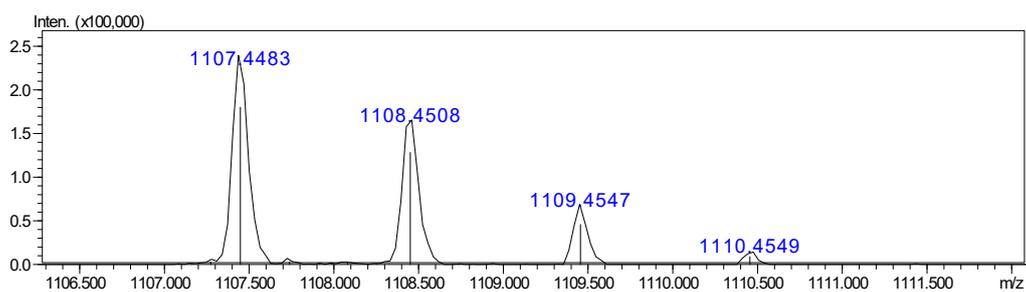
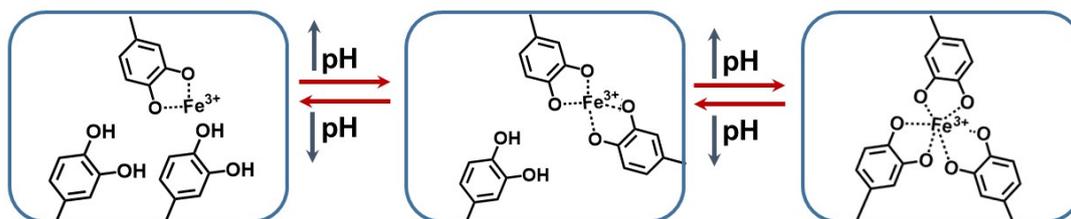


Fig. S12 HRESIMS spectrum of **1** in CHCl_3 .

3. pH-dependent catechol- Fe^{3+} coordination



Scheme S2 pH-dependent catechol- Fe^{3+} coordination.

4. 2D NOESY NMR spectrum of a mixture of 1 and 2

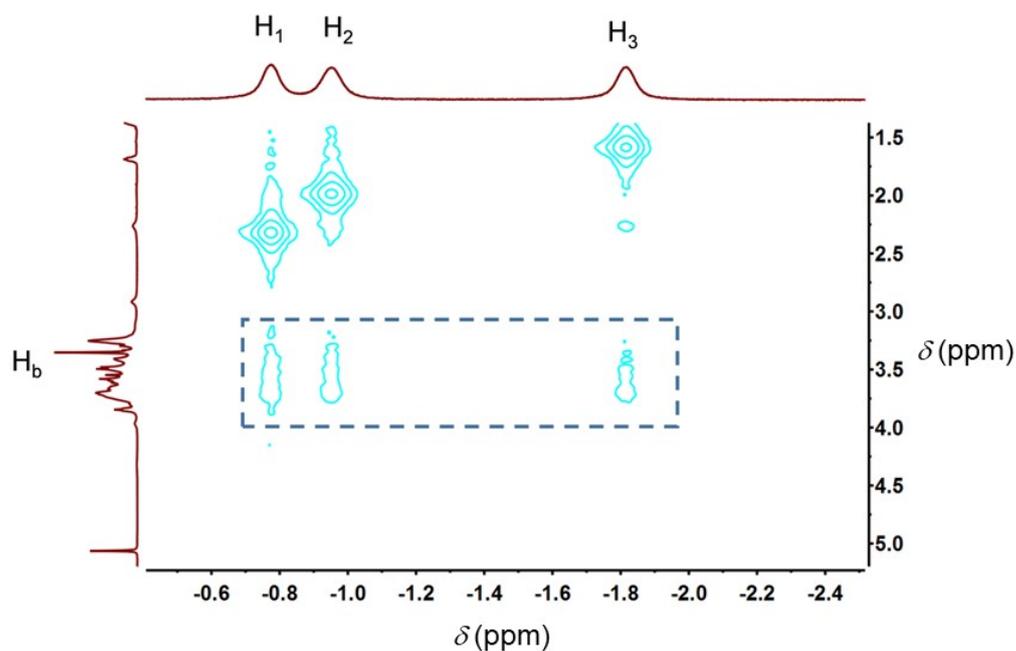


Fig. S13 2D NOESY NMR spectrum (600 MHz, 298 K) in $\text{CDCl}_3/\text{CD}_3\text{OD}$ ($\nu : \nu = 10 : 1$) of 10.0 mM **1** and 5.00 mM **2**.

5. MALDI-TOF mass spectrum of a mixture of compound 1 and BPO

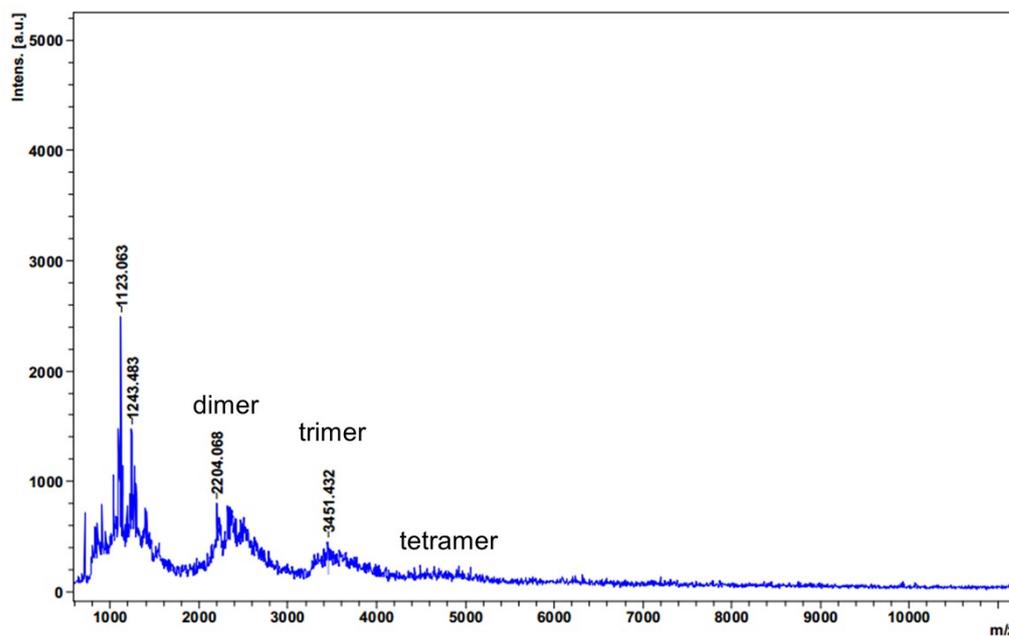


Fig. S14 MALDI-TOF mass spectrum of **1** (1.00 mM) and BPO (2.00 mM) after mixing for 3 hours.

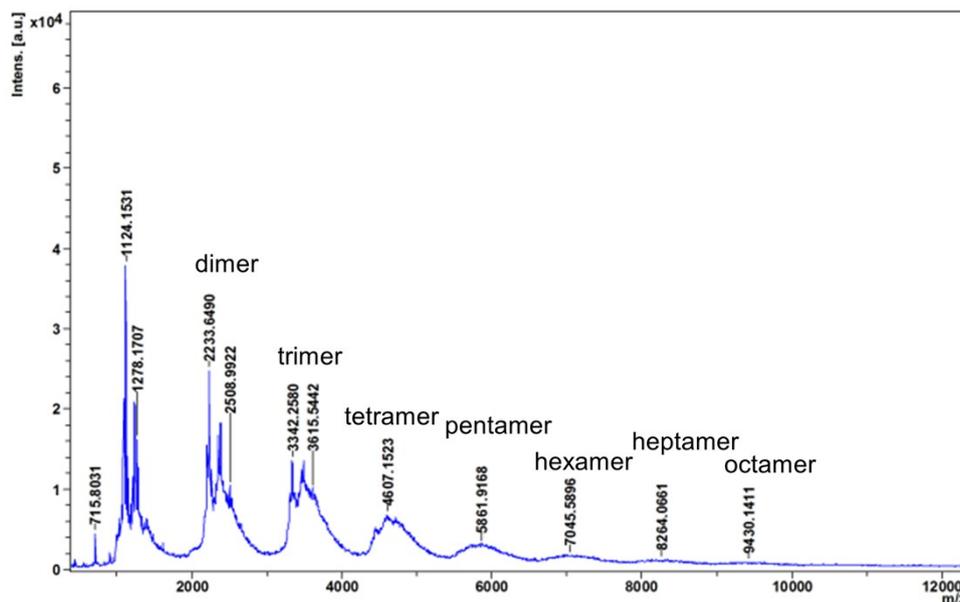


Fig. S15 MALDI-TOF mass spectrum of **1** (1.00 mM) and BPO (2.00 mM) after mixing for 12 hours.

6. Concentration-variant 2D DOSY NMR spectra of $1 \cdot Fe^{3+} \cdot 2$

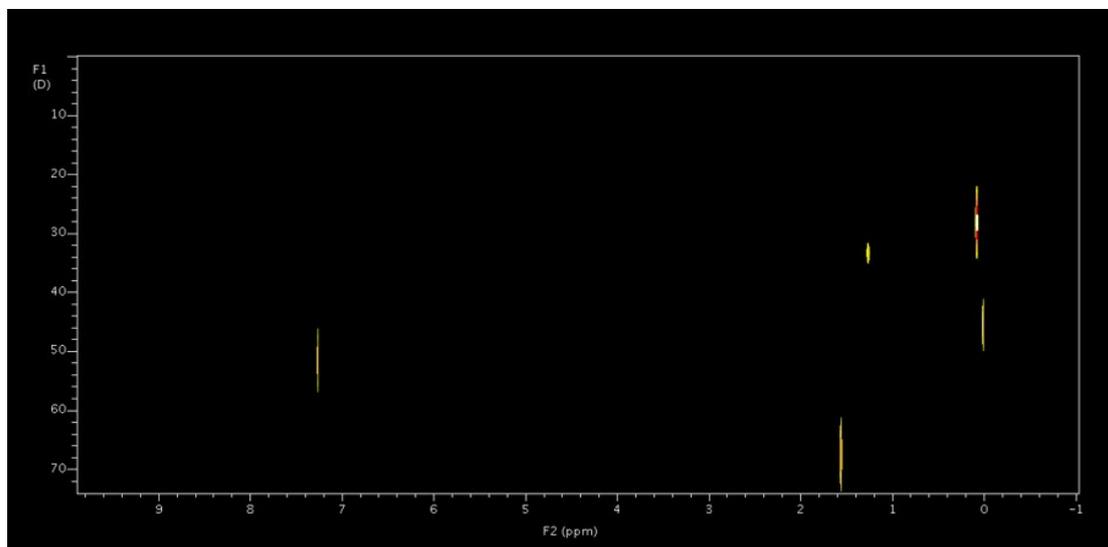


Fig. S16 2D DOSY NMR spectrum (600 MHz, 298 K) of $CHCl_3$ in $CDCl_3$ (99.9%).

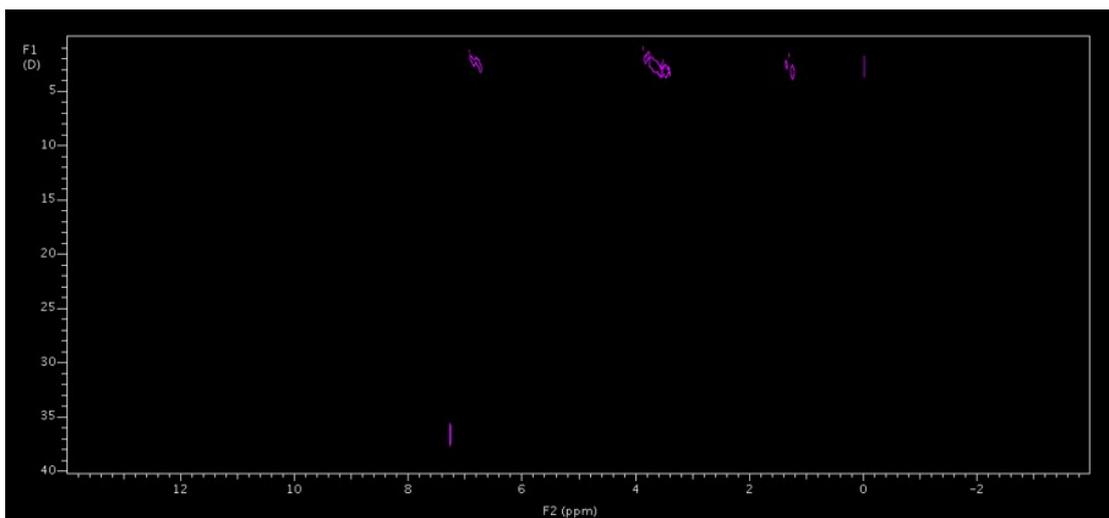


Fig. S17 2D DOSY NMR spectrum (600 MHz, 298 K) of polymer **a** at 50.0 mM of **1** in CDCl₃/CD₃OD ($\nu : \nu = 10 : 1$).

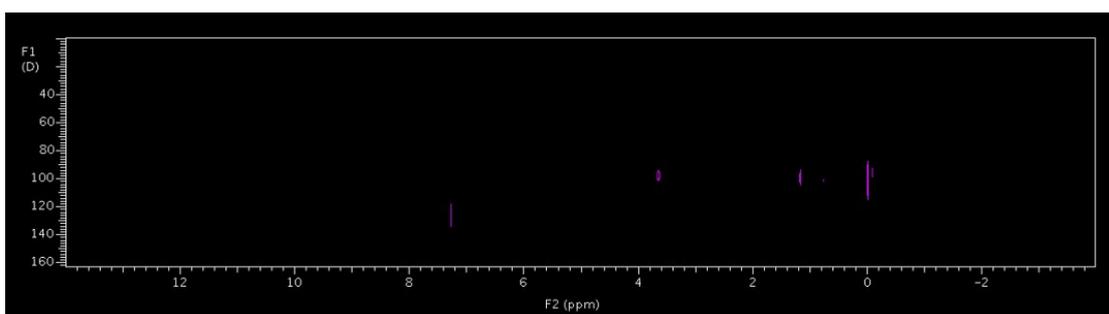


Fig. S18 2D DOSY NMR spectrum (600 MHz, 298 K) of polymer **a** at 5.00 mM of **1** in CDCl₃/CD₃OD ($\nu : \nu = 10 : 1$).

We first measured the diffusion constant D of CHCl₃ in CDCl₃ (99.9%) resulting in a value of 52.5×10^{-10} m²/s at 298 K. And then 2D DOSY NMR experiments on polymer **a** at 50.0 mM and 5.00 mM of **1** in CDCl₃/CD₃OD ($\nu : \nu = 10 : 1$) were carried out, respectively. The values for the diffusion constant D of residual CHCl₃ in solution deviated from the diffusion constant D measured in CDCl₃ (99.9%). Therefore, we corrected the measured values according to the measured value of the diffusion constant D of CHCl₃ in CDCl₃ (99.9%).^{S3}

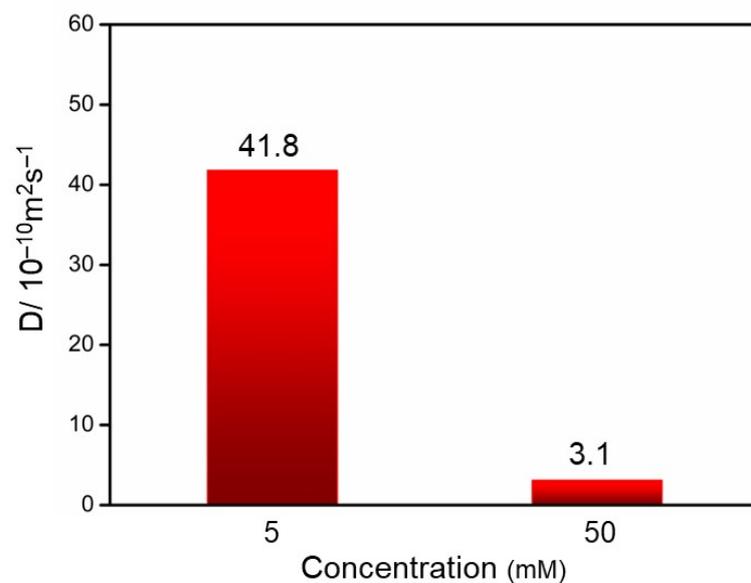


Fig. S19 Concentration dependence of diffusion coefficient D (600 MHz, 298 K) in $\text{CDCl}_3/\text{CD}_3\text{OD}$ ($v : v = 10 : 1$) of polymer **a** at different concentrations of **1**: 50.0 mM, 5.00 mM.

7. Digital photos of supramolecular glues

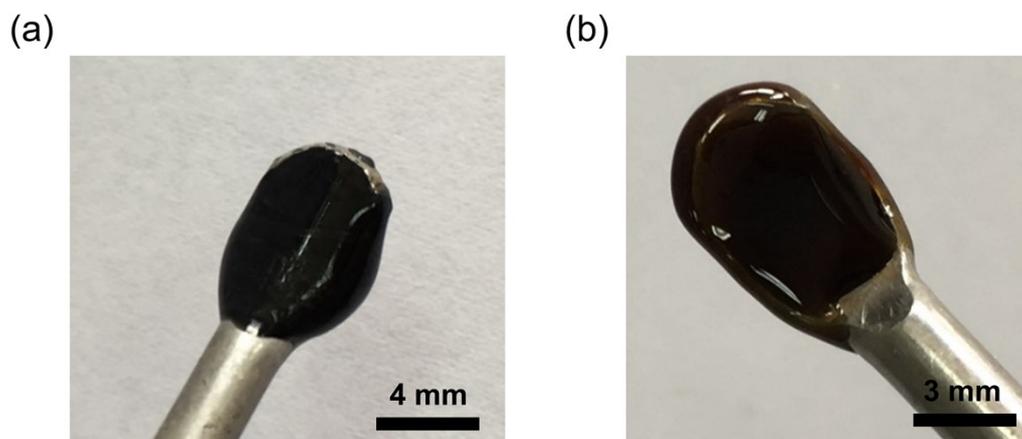


Fig. S20 Digital photos of the supramolecular glues: (a) glue **a**; (b) glue **b**.

8. The temperature-variant NMR spectra of a mixture of 1 and 2

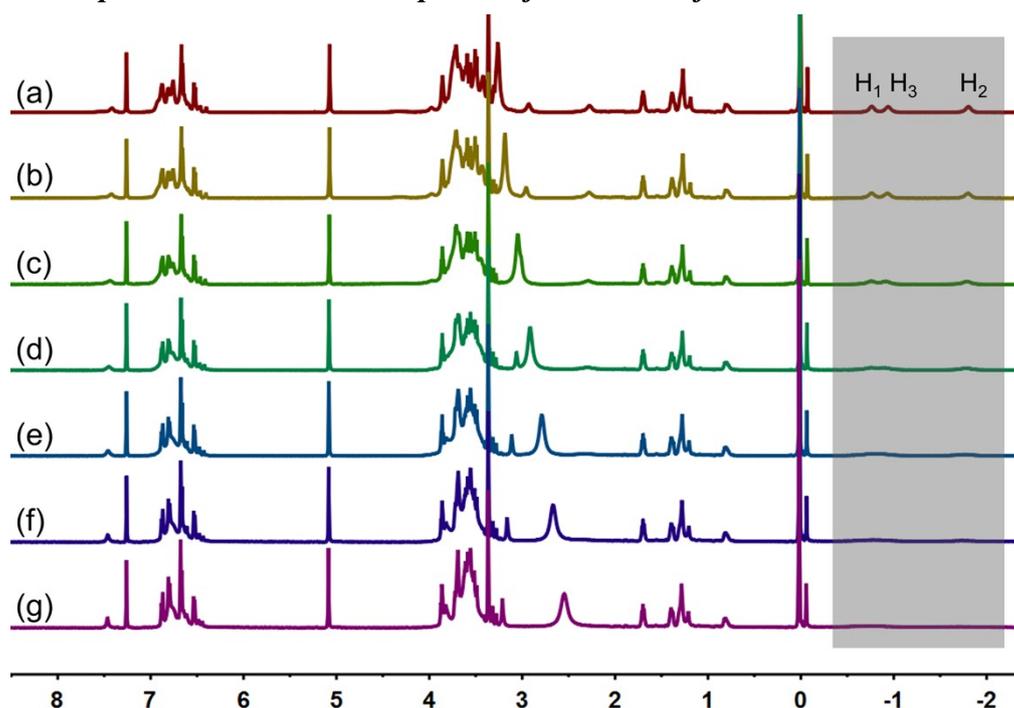


Fig. S21 ^1H NMR spectra (600 MHz) of a 1 : 2 molar ratio mixture of **2** and **1** at 5.00 mM **1** in $\text{CDCl}_3/\text{CD}_3\text{OD}$ ($v : v = 10 : 1$) at various temperatures: (a) 298 K; (b) 303 K; (c) 308 K; (d) 313 K; (e) 318 K; (f) 323 K; (g) 328 K.

9. References

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