Supporting Information for

Self-assembled poly[2]catenanes based on non-covalent and dynamic covalent bonds

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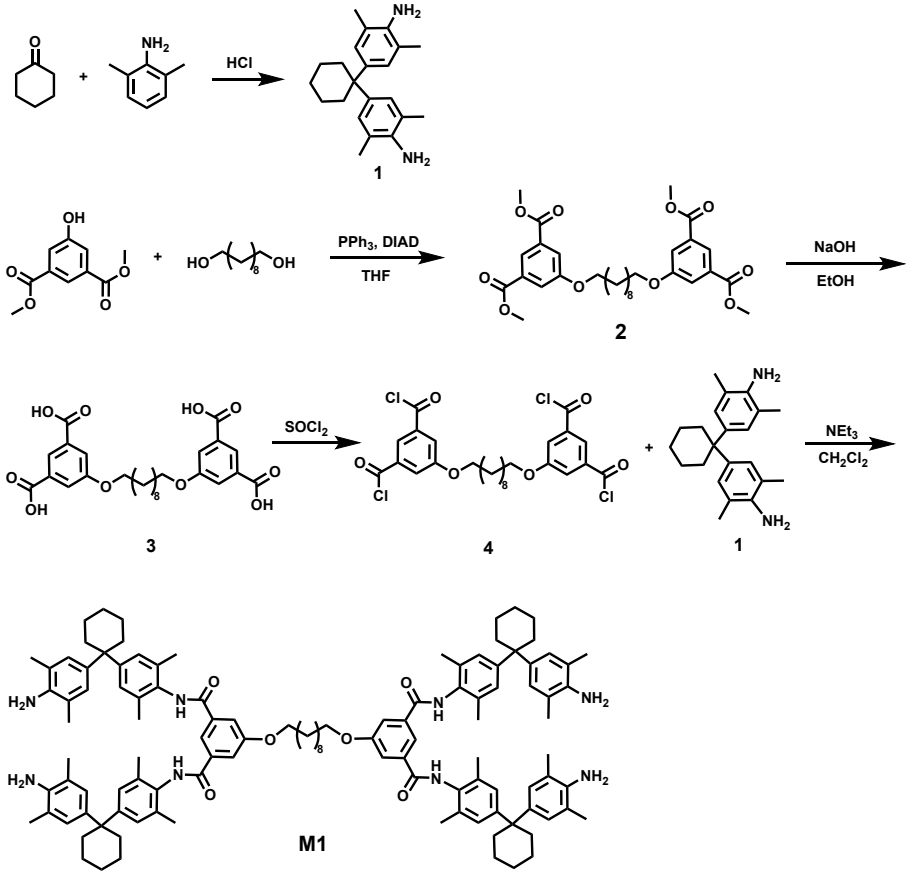
Table of Contents

1. Materials and methods

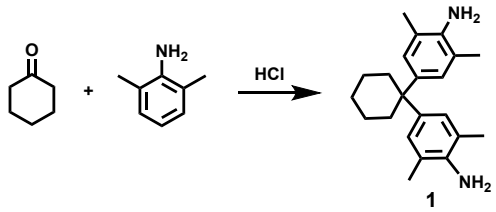
All reagents and solvents were purchased from commercial suppliers and used as received. Compounds **1** was synthesized according to literature procedures.[1] ^{1}H NMR and ^{13}C NMR spectral studies were performed using a Bruker Advance 400 MHz spectrometer. High-resolution electrospray ionization mass spectra (ESI-MS) were recorded using a Bruker microOTOF II. Gel permeation chromatography (GPC) measurements were performed using PL-GPC50 and Agilent 1100 HPLC system. Fourier transform infrared (FT-IR) spectra were recorded on an FT interferometer (Equinox 55, Bruker, Germany). The thermal stability of the polymers was evaluated using a thermogravimetric analyzer (TGA, 4000 PerkinElmer) under N_2 at a heating rate of 10 °C min^{-1} from 0 to 800 °C. Differentia scanning calorimetry (DSC, Q2000, TA) was performed at a rate of 10 °C min^{-1} under N_2. MALDI-TOF was measured by Ultraflextreme spectrometers using 1, 8, 9-trihydroxyanthracene as matrix.

2. Synthesis and characterization of monomer M1



Scheme S1. Synthetic routes to monomer **M1**.

2.1 Synthesis and characterization of compound **1**.



2, 6-dimethylaniline (30.0 mL, 252 mmol), Cyclohexanone (18.0 mL, 174 mmol) and hydrochloric acid (30 mL) were added to a 250 mL round-bottom flask, and the reaction was stopped when solid precipitated by heating reflux at 120 °C in N_2 atmosphere for about 36 h. Add water to the reaction system to adjust the pH to basic, extract with DCM, dry and concentrate the organic phase with Na_2SO_4 to get oil. The oily substance was added dropwise into a large volume of *n*-pentane, resulting in the precipitation of a significant amount of white precipitate. The precipitate was filtered, and the filter cake was dried to obtain compound **1** (12 g, 21%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 6.68 (s, 4H), 4.25 (s, 4H), 2.06 (t, J = 4.0 Hz, 4H), 2.01 (s, 12H), 1.44-1.36 (m, 4H). ^{13}CNMR (100 MHz, DMSO-d_6, 298 K) δ 141.57, 137.07, 126.52, 120.53, 43.83, 37.18, 26.55, 23.18, 18.72. HRMS (ESI$^+$) Calcd for $C_{22}H_{30}N_2$ $[M+H]^+$: 323.2482, found: 323.2499.

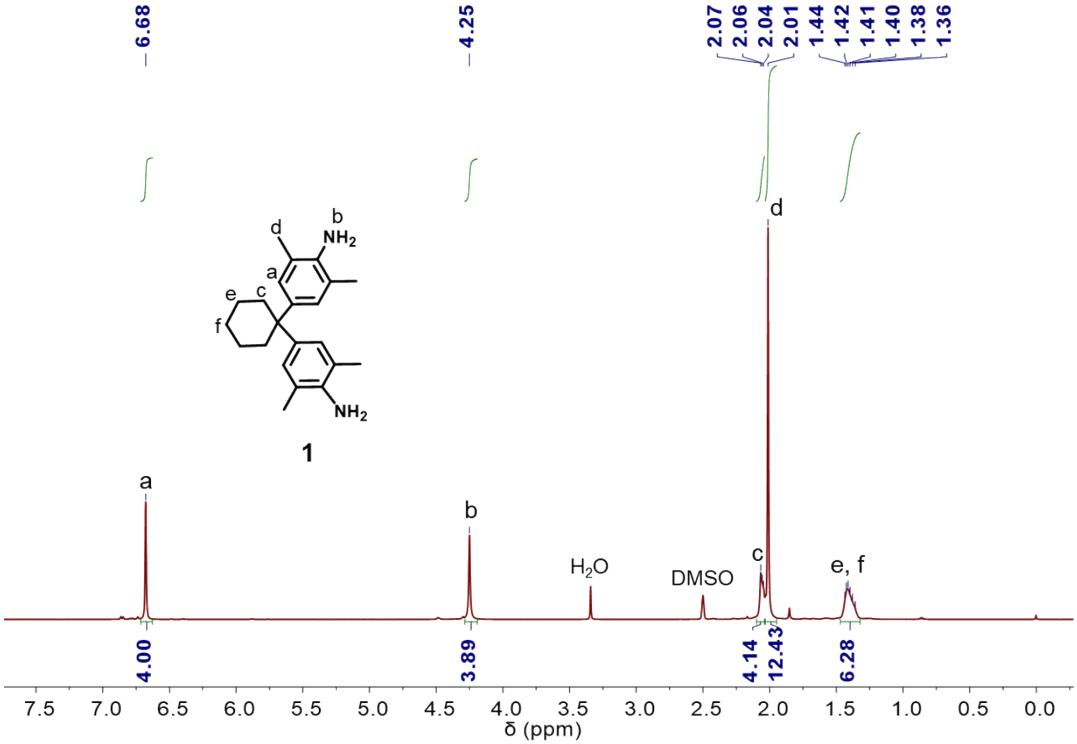


Figure S1. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz, 298 K) of **1**.

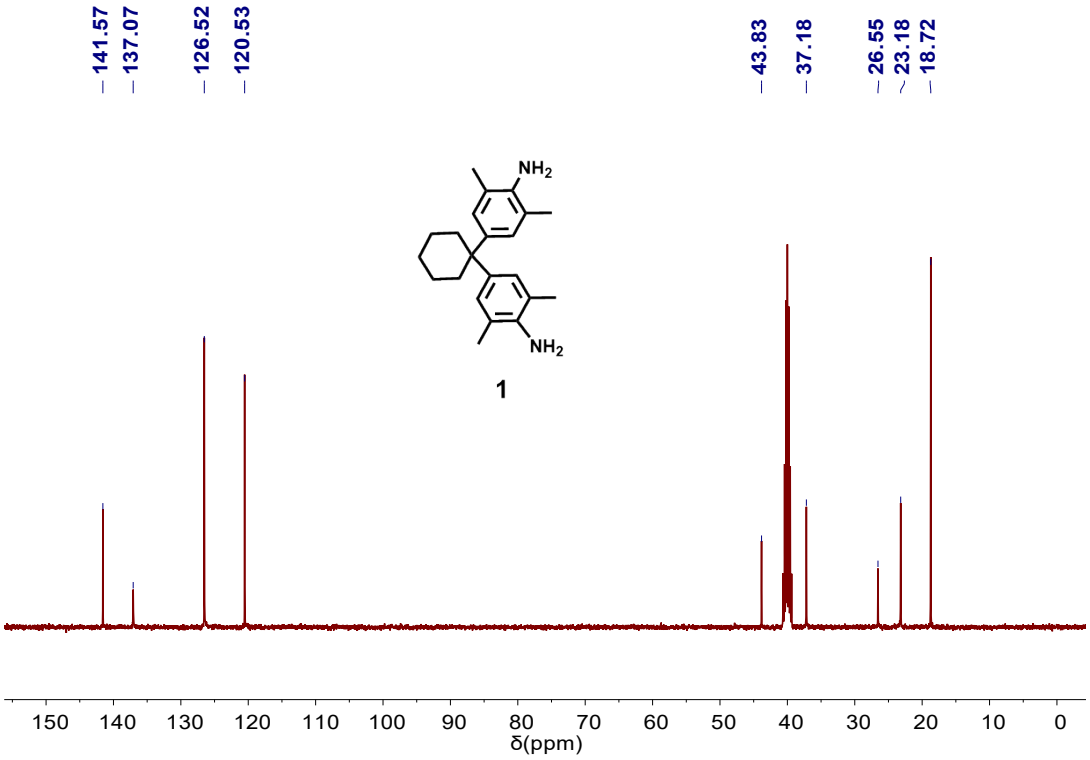


Figure S2. ^{13}C NMR spectrum (DMSO-d_6, 100 MHz, 298 K) of **1**.

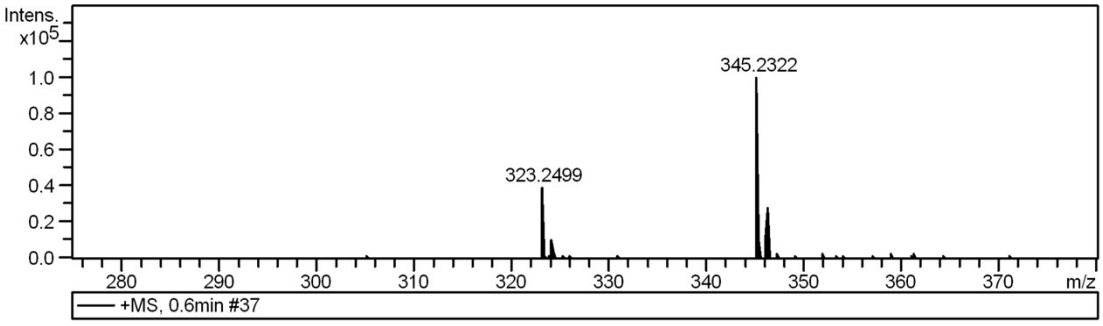
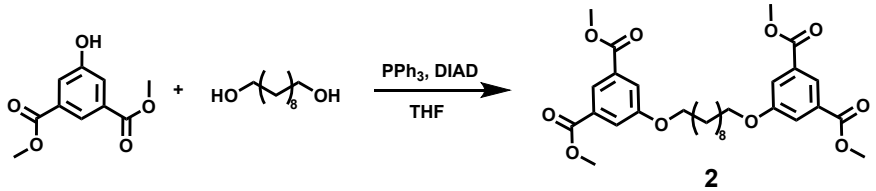


Figure S3. HR-ESI$^+$-MS spectrum of **1**.

2.2 Synthesis and characterization of compound **2**.



1, 10-decanediol (5 g, 30 mmol) and Dimethyl 5-hydroxyisophthalate (17 g, 90 mmol) were added to a 500 mL double-necked round-bottomed flask. Then THF (250 mL) was added, and then Triphenylphosphine (19 g, 72 mmol) and diisopropyl azodicarboxylate (14.5 g, 72 mmol) were added to the system, and the reaction was carried out at 50 °C under N_2 for 16 h. After the reaction, the solvent was removed, DCM was added to dissolve it, a large amount of ethanol was added, white precipitation

could be observed, and compound **2** (14 g, 84%) could be obtained by filtration and drying. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.25 (s, 2H), 7.73 (s, 4H), 4.03 (t, J = 8.0 Hz, 4H), 3.93 (s, 12H), 1.84-1.77 (m, 4H), 1.50-1.43 (m, 4H), 1.38-1.34 (m, 8H). ^{13}CNMR (100 MHz, $CDCl_3$, 298 K) δ 166.23, 159.25, 131.70, 122.75, 119.84, 68.61, 52.38, 29.46, 29.31, 29.09, 25.96. HRMS (ESI^+) Calcd for $C_{30}H_{38}O_{10}$ $[M+Na]^+$: 581.2357, found: 581.2358.

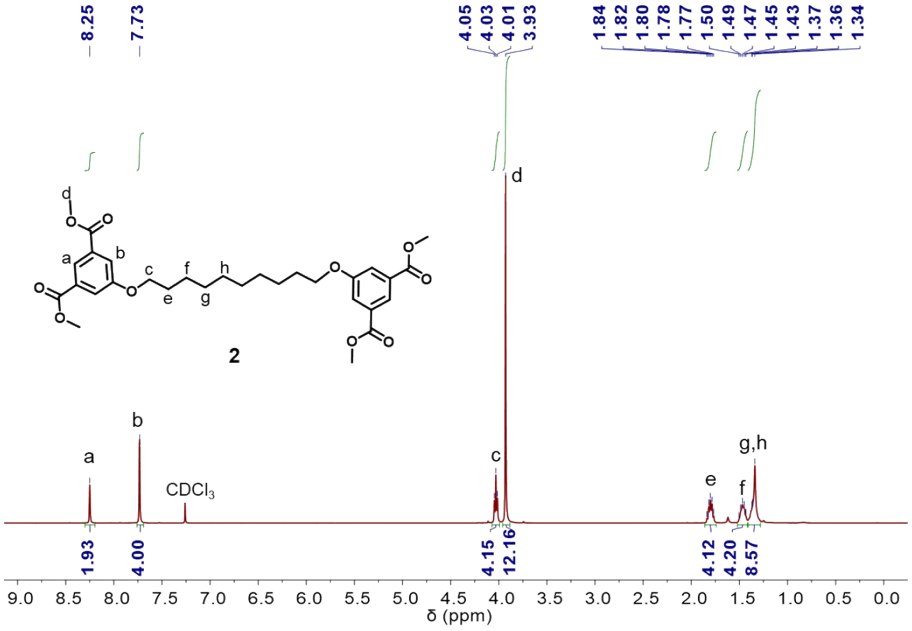


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **2**.

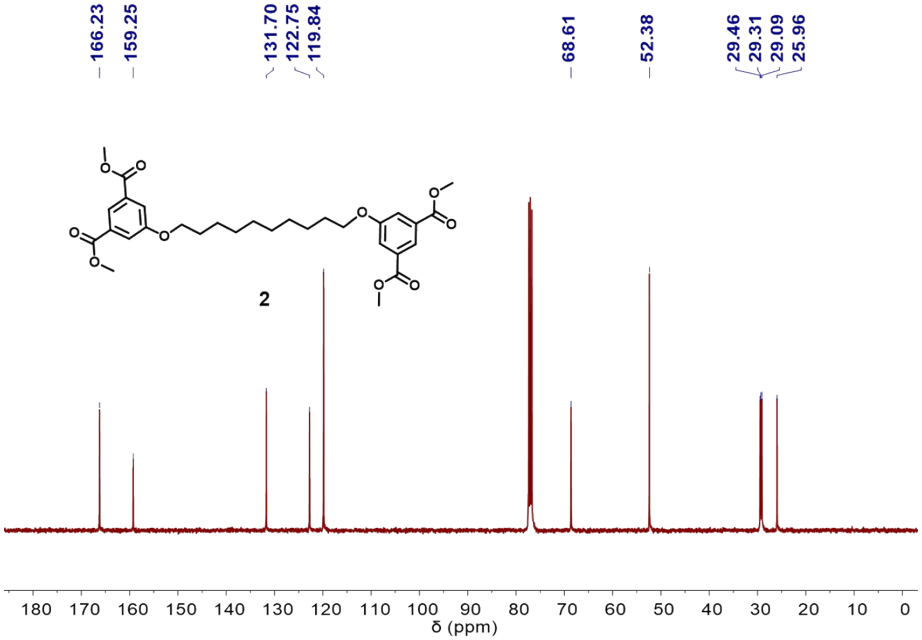


Figure S5. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **2**.

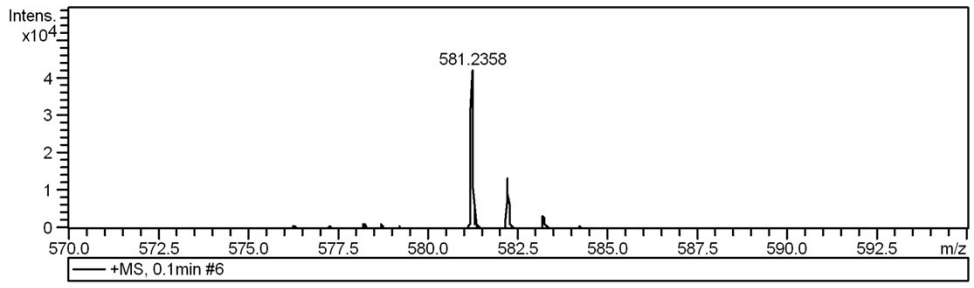
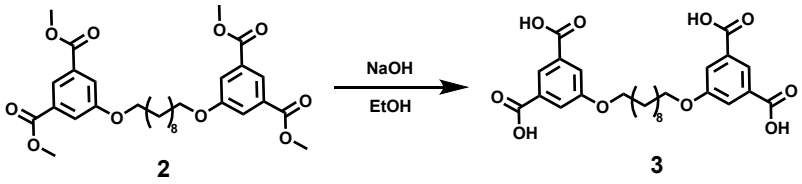


Figure S6. HR-ESI$^+$-MS spectrum of **2**.

2.3 Synthesis and characterization of compound **3**.



Compound **2** (400 mg, 0.7 mmol) was dissolved in ethanol and of 4 M NaOH solution (1.4 mL) was added to the system for reaction at 60 °C for 3 h. After the reaction, the ethanol was removed by rotary evaporation, water was added to the system and the pH was adjusted by HCl to be less than 7. Precipitation was observed, and white solid compound **3** (300 mg, 85%) was obtained by pumping and filtration. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 13.28 (s, 4H), 8.05 (s, 2H), 7.62 (s, 4H), 4.05 (t, J = 8.0 Hz, 4H), 1.75-1.68 (m, 4H), 1.44-1.37 (m, 4H), 1.34-1.29 (m, 8H). ^{13}CNMR (100 MHz, DMSO-d_6, 298 K) δ 166.89, 159.26, 133.05, 122.57, 119.47, 68.54, 29.40, 29.20, 28.96, 25.86. HRMS (ESI$^+$) Calcd for $C_{26}H_{30}O_{10}$ $[M+Na]^+$: 525.1731, found: 525.1730.

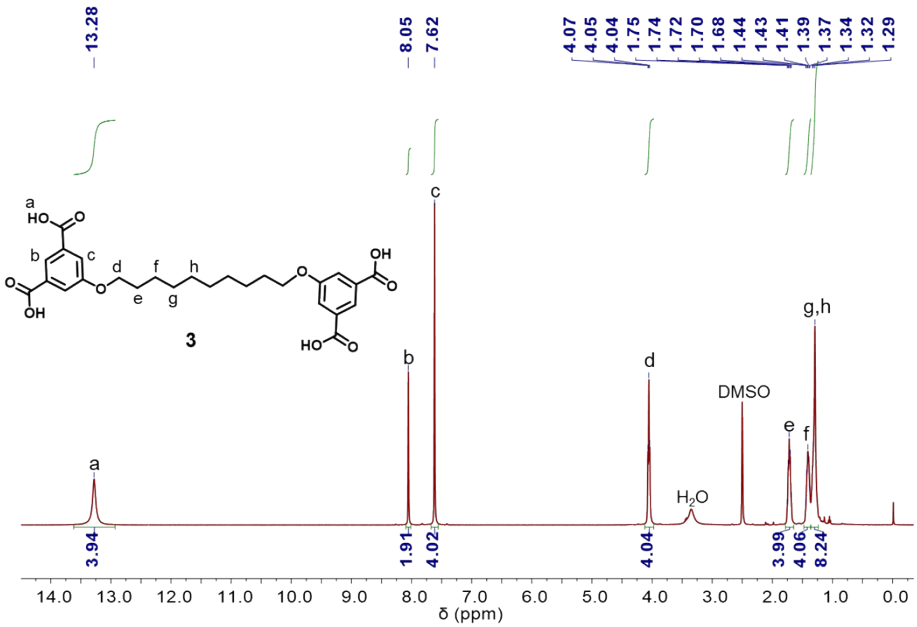


Figure S7. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz, 298 K) of **3**.

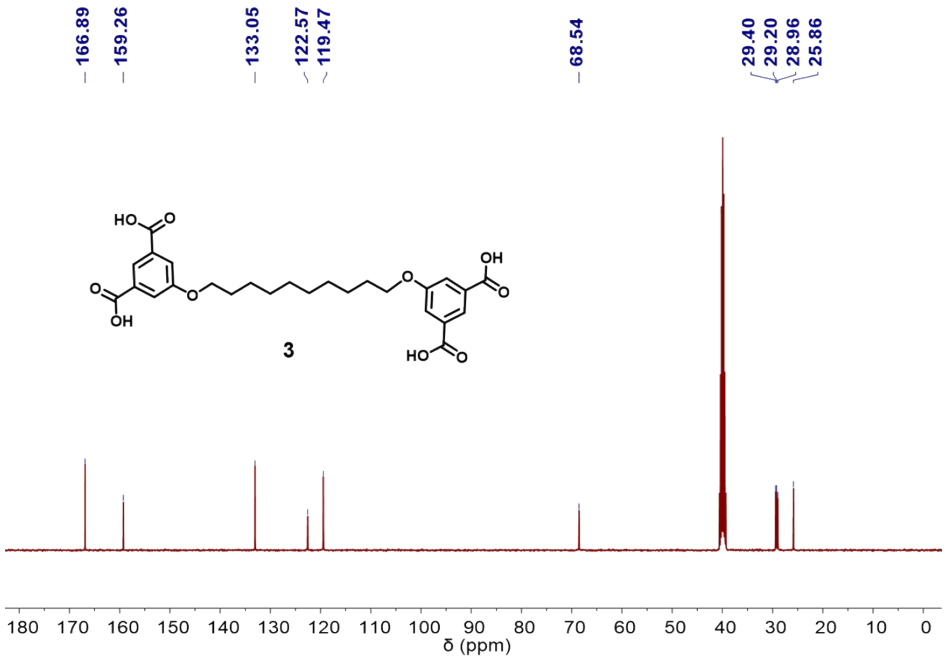


Figure S8. ^{13}C NMR spectrum (DMSO-d_6, 100 MHz, 298 K) of **3**.

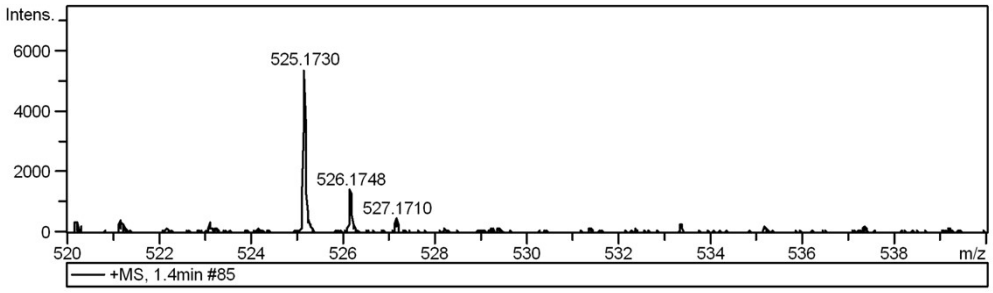
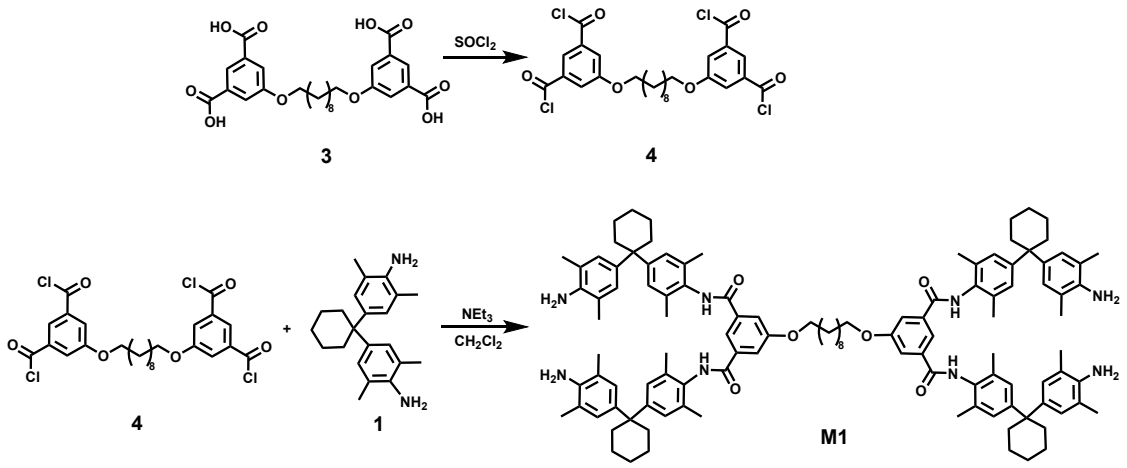


Figure S9. HR-ESI$^+$-MS spectrum of **3**.

2.4 Synthesis and characterization of compound **4** and monomer **M1**.



Compound **3** (2 g, 4 mmol) was dissolved in toluene (40 mL), $SOCl_2$ (2 mL) was added, and two drops of DMF were added as catalyst, and the reaction was heated at 80 °C for 2 h. After the reaction,

the reaction liquid was removed to obtain white solid compound **4** (1.2 g, 52%), which could be used directly for the next step without purification.

Compound **1** (2 g, 6 mmol) was dissolved in DCM (10 mL), Et_3N (280 μL) was added, and DCM solution of compound **4** (290 mg, 0.5 mmol) was added to the reaction solution under nitrogen protection for 2 h, and the reaction was carried out overnight. After the reaction was completed, the solvent was removed. Neutral alumina column chromatography (CH_2Cl_2:MeOH = 200:1) was then performed, followed by silica gel column chromatography (CH_2Cl_2:MeOH = 100:1). The resulting solid was dissolved in DCM, and PE was added. A large amount of white solid precipitated, which was obtained by filtration to obtain monomer **M1** (232 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.04 (s, 2H), 7.70 (s, 4H), 7.55 (s, 4H), 6.98 (s, 8H), 6.86 (s, 8H), 4.01 (t, J = 8.0 Hz, 4H), 3.22 (s, 8H), 2.26-2.17 (m, 16H), 2.12 (d, 48H), 1.84-1.77 (m, 4H), 1.59-1.36 (m, 36H). ^{13}CNMR (100 MHz, $CDCl_3$, 298 K) δ 165.14, 159.76, 148.73, 140.03, 137.73, 136.40, 134.73, 130.67, 127.10, 127.00, 121.56, 117.61, 116.50, 68.64, 44.96, 37.23, 29.35, 29.22, 29.12, 26.49, 25.90, 23.01, 18.79, 18.07. HRMS (ESI$^+$) Calcd for $C_{114}H_{142}N_8O_6$ $[M+H]^+$: 1720.1125, found: 1720.1134.

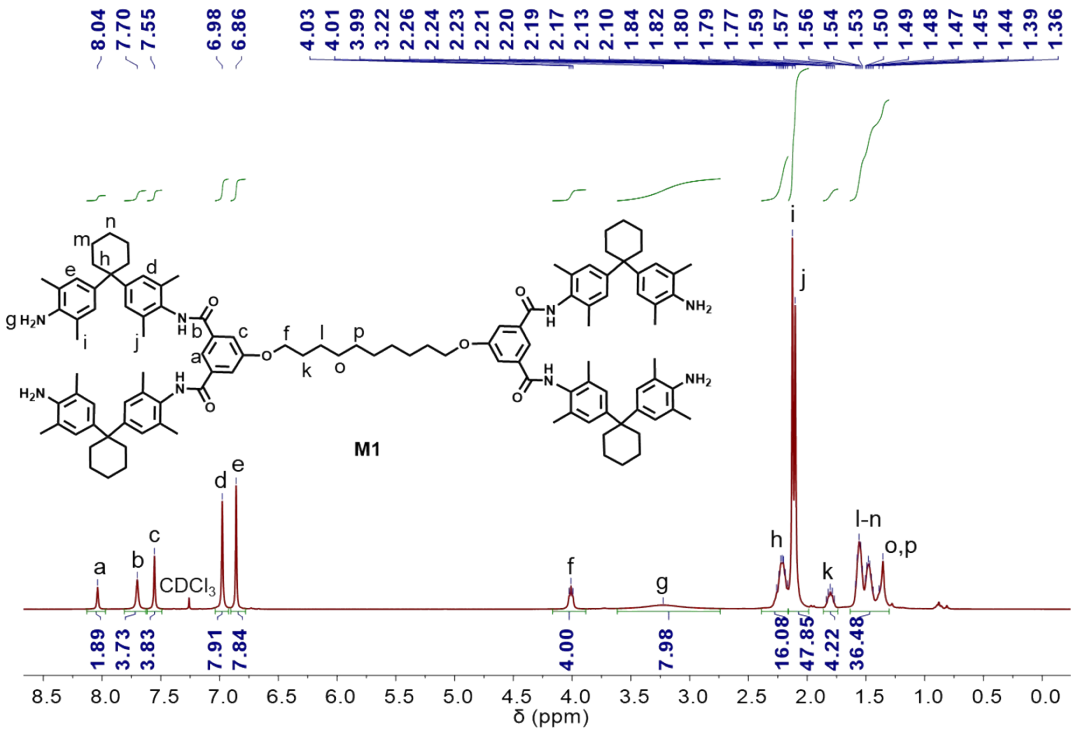


Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **M1**.

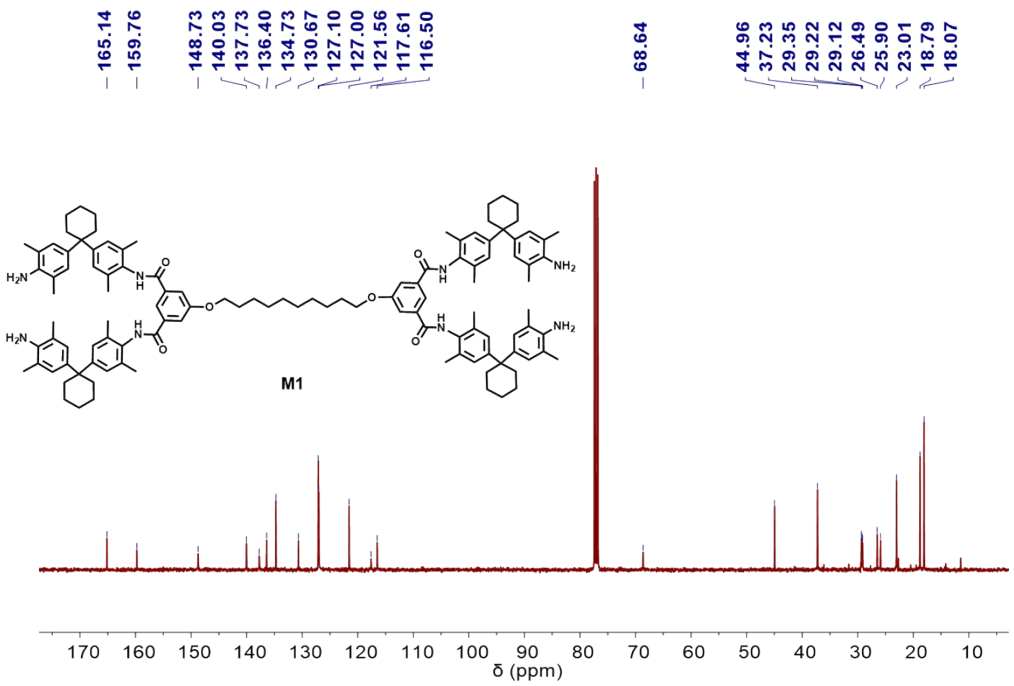


Figure S11. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **M1**.

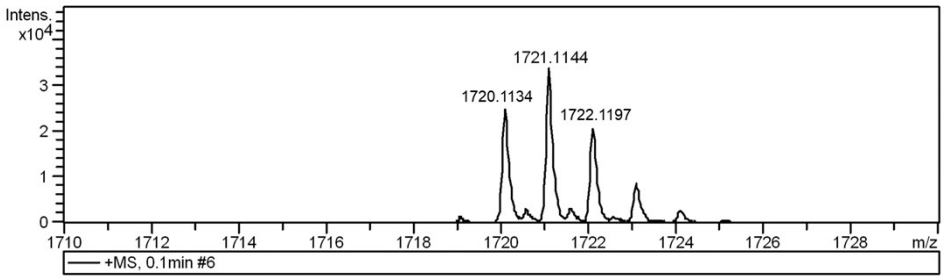


Figure S12. HR-ESI$^+$-MS spectrum of **M1**.

2.5 ^1H NMR spectra of monomer **M2**.

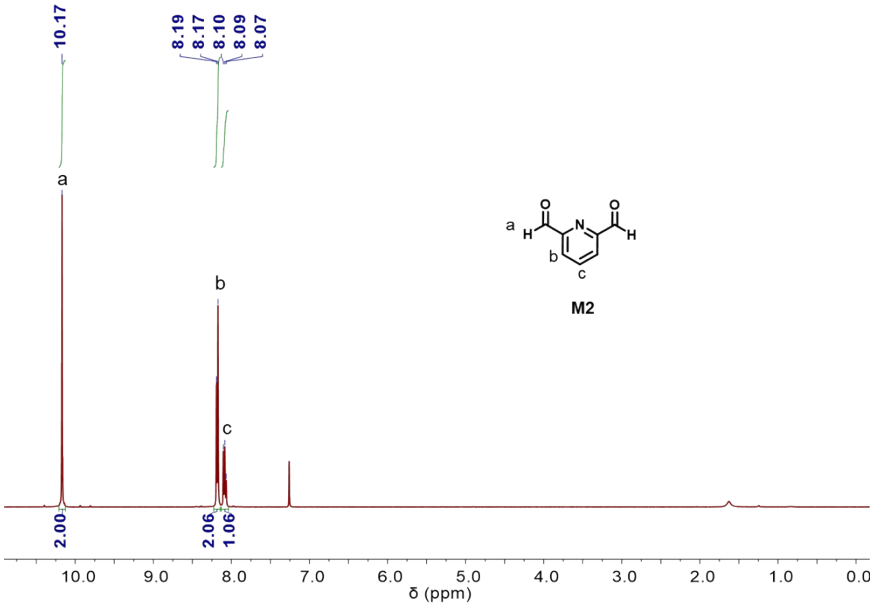


Figure S13. ^1H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **M2**.

3. Full ^{1}H NMR spectra of monomer M1 at different concentrations

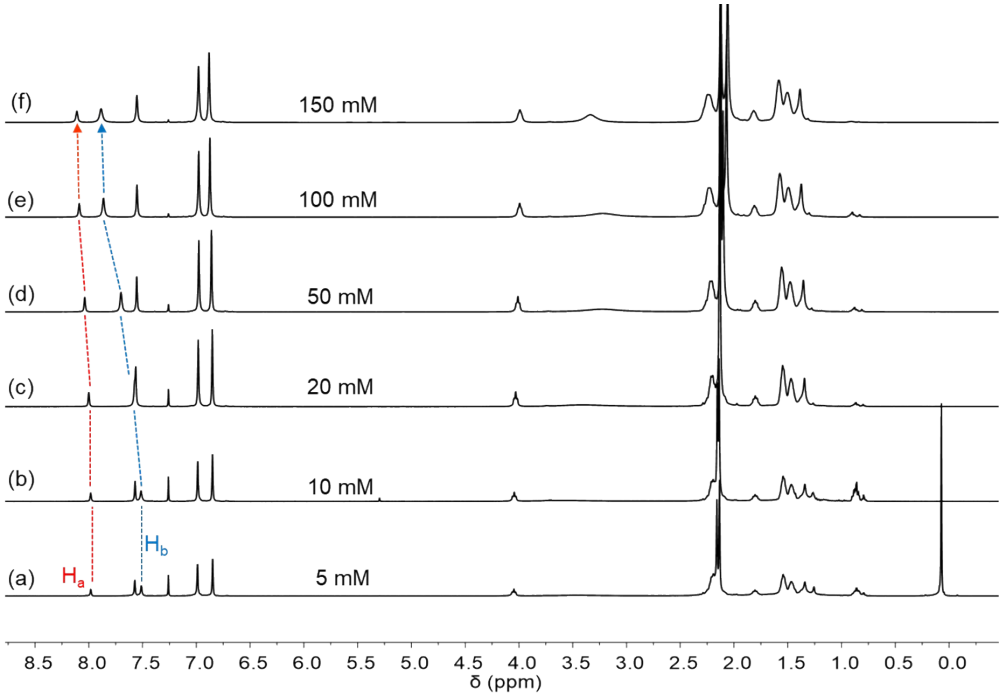


Figure S14. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of **M1** at different concentrations: (a) 5 mM, (b) 10 mM, (c) 20 mM, (d) 50 mM, (e) 100 mM, (f) 150 mM.

4. Full NOESY NMR spectra of M1 at 50 mM

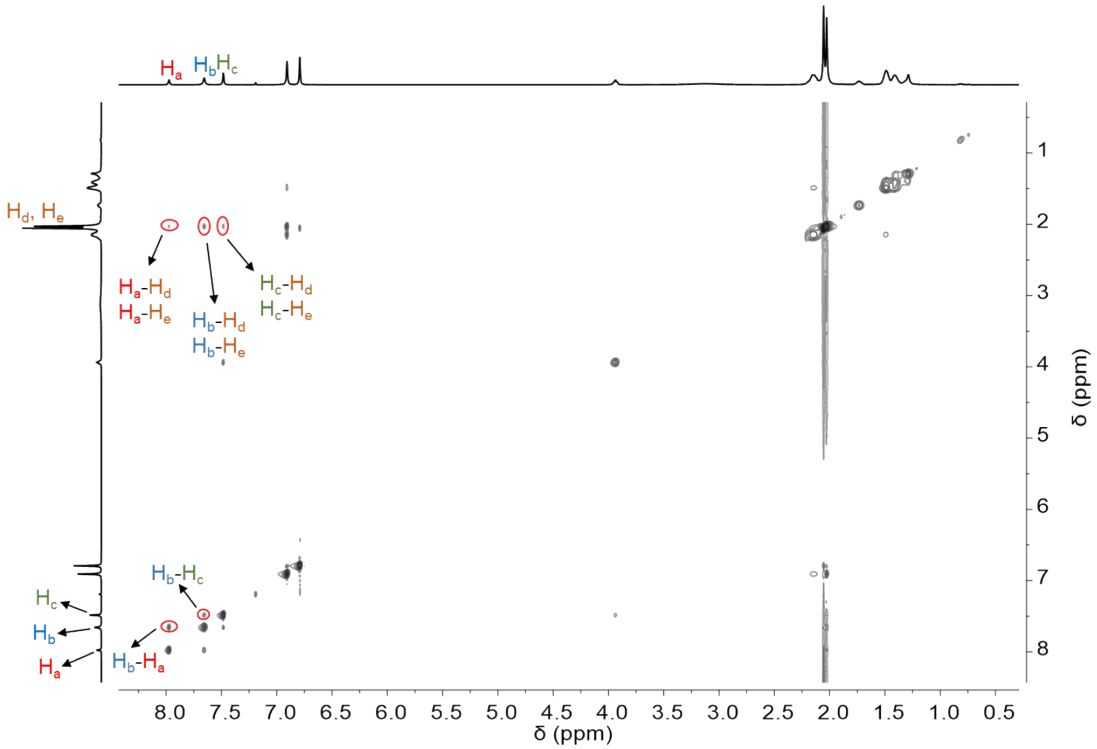


Figure S15. NOESY NMR spectra (400 MHz, $CDCl_3$, 298 K) of **M1** at 50 mM.

5. DOSY NMR spectra of M1 at different concentrations

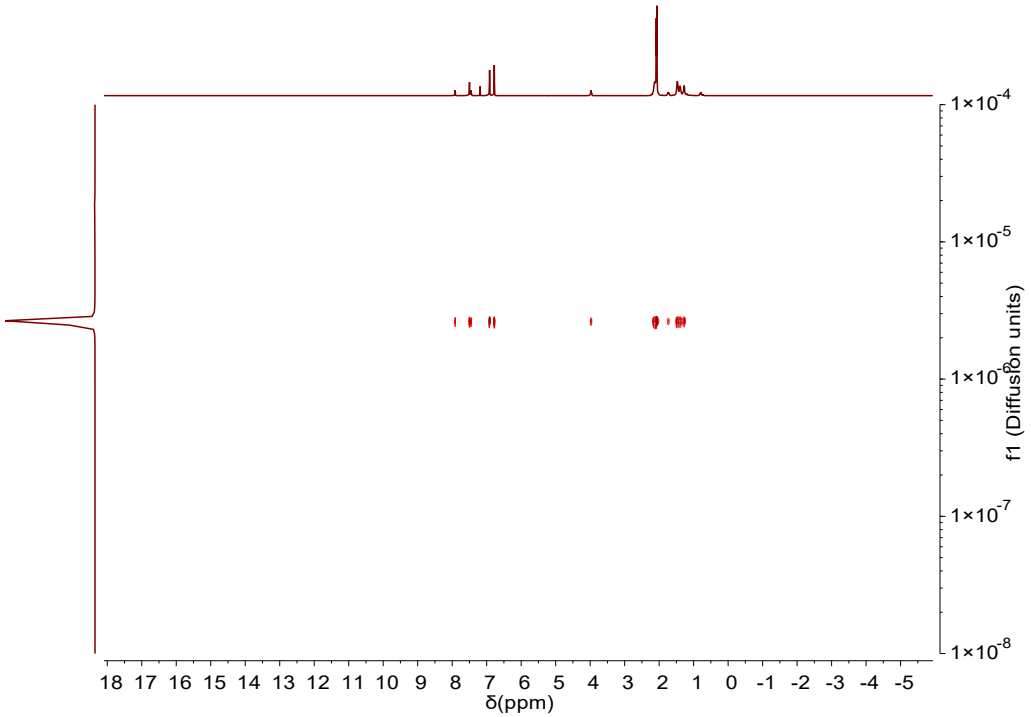


Figure S16. DOSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **M1** at 10 mM, D = 2.612 x 10^{-10} m^2 s^{-1}.

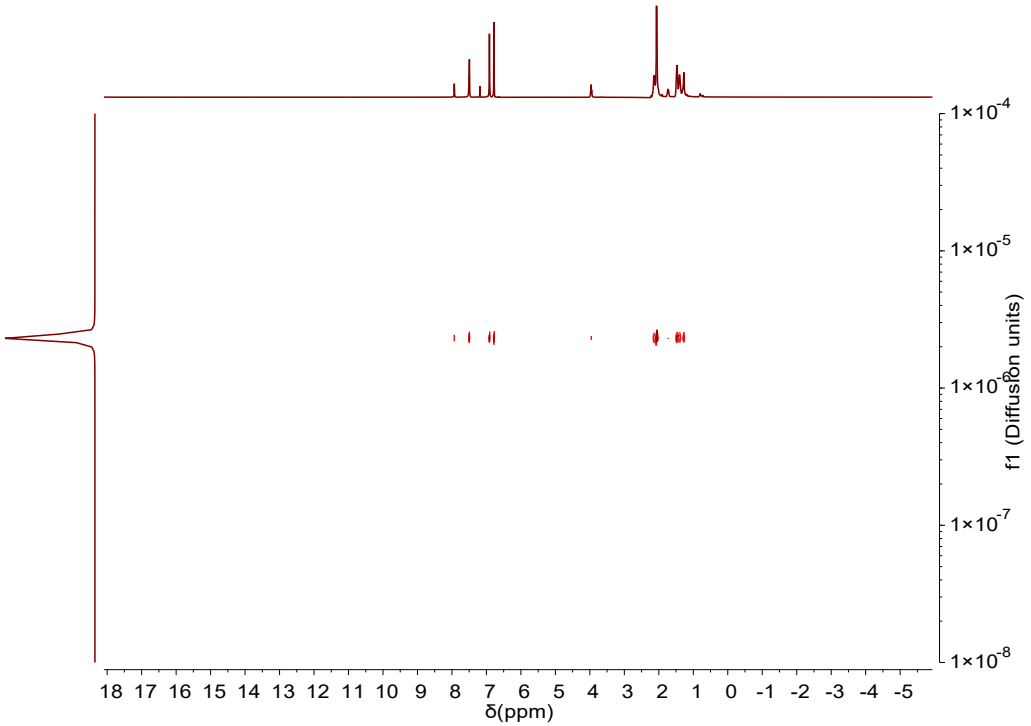


Figure S17. DOSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **M1** at 20 mM, D = 2.313 x 10^{-10} m^2 s^{-1}.

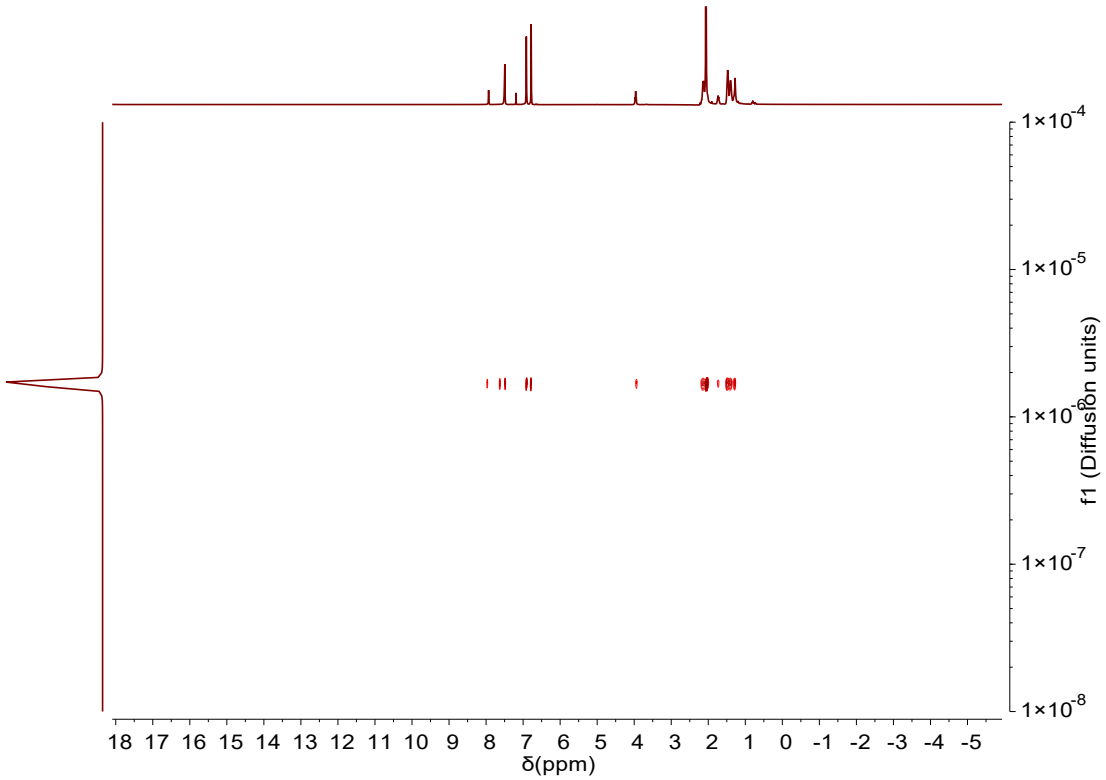


Figure S18. DOSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **M1** at 50 mM, D = 1.673 x 10^{-10} m^2 s^{-1}.

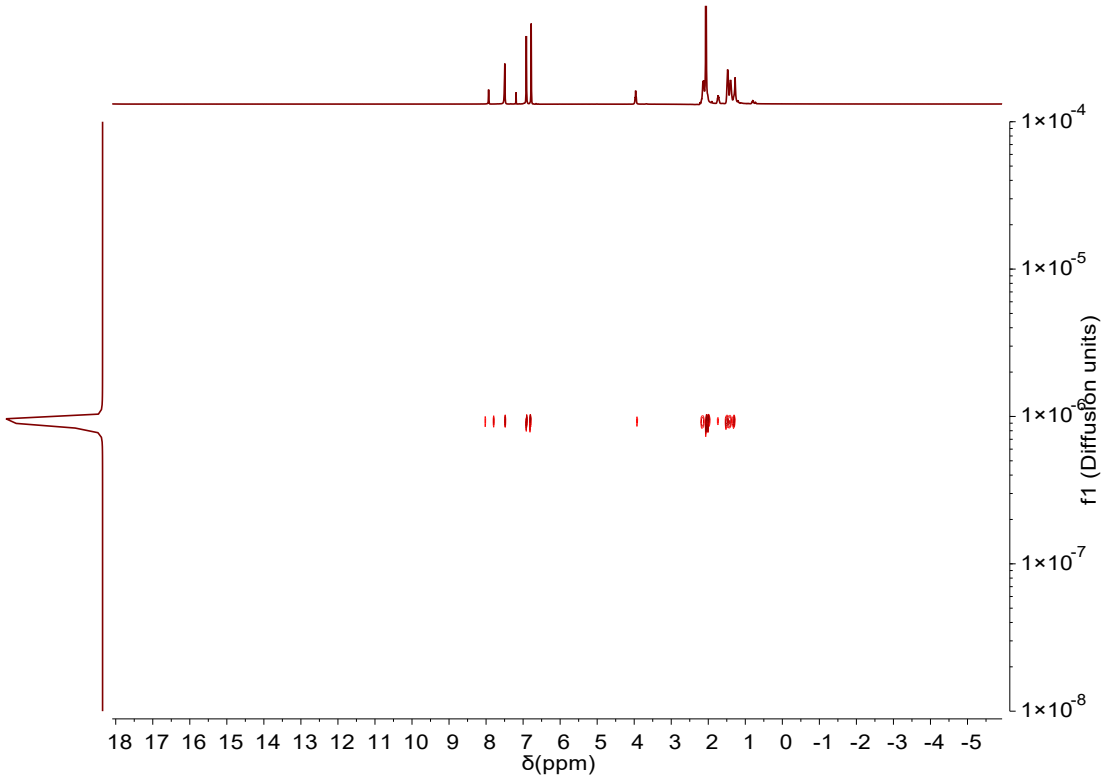


Figure S19. DOSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **M1** at 100 mM, D = 0.901 x 10^{-10} m^2 s^{-1}.

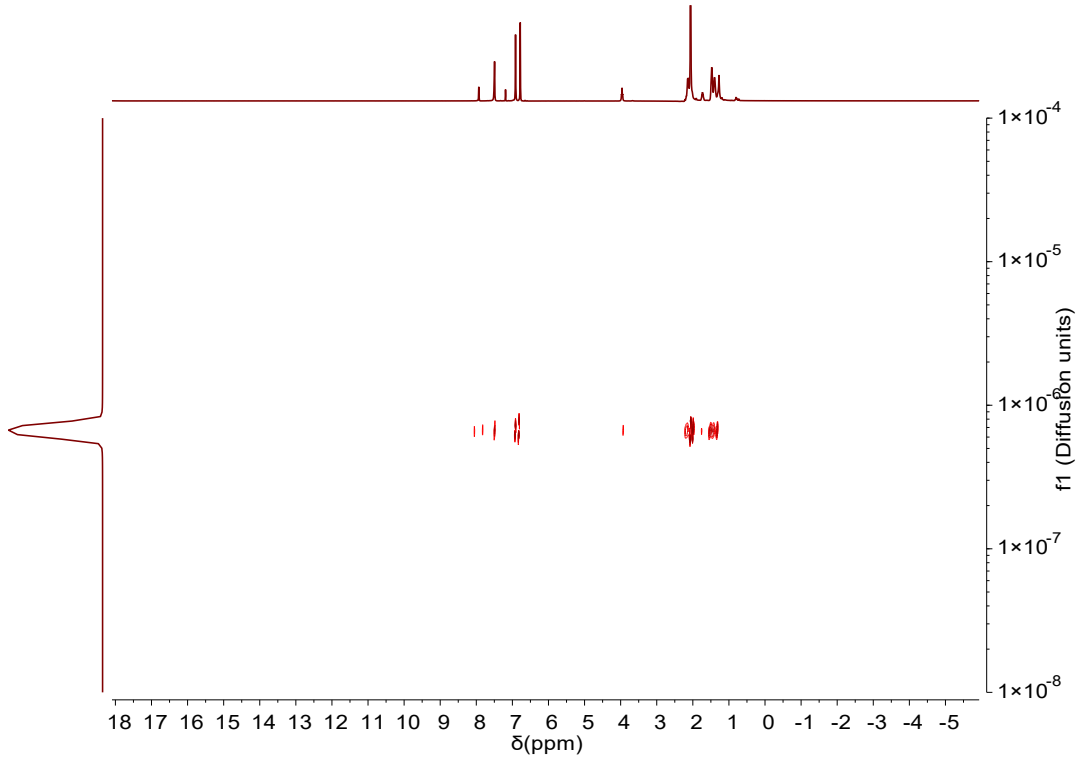


Figure S20. DOSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **M1** at 150 mM, D = 0.663 x 10^{-10} m^2 s^{-1}.

Assuming that the polymer is hydrodynamically spherical, the average degree of polymerization (DP_{DOSY}) corresponding to the formation of supramolecular polymers with different concentrations of **M1** can be calculated using the specific equation $DP_{DOSY} \approx (D(\mathbf{M1})/D(\mathbf{M1}_{c\ =\ x\ mM}))^{3}$.[2] D(**M1**) is the diffusion coefficient of **M1** at 10.0 mM, and $D(\mathbf{M1}_{c\ =\ x\ mM})$ is the diffusion coefficient of **M1** at different concentrations. The DP_{DOSY} of 10.0 mM, 20.0 mM, 50.0 mM, 100.0 mM, 150.0 mM **M1** forming SPs were 1, 1.4, 3.8, 24.4, 61.1 in order. Then according to the literature reported by Hunter, the reaction yield of catenanes by this method was known as 34%,[1] thereby the DP values of poly[2]catenanes corresponded to 0.3, 0.5, 1.3, 8.3 and 20.8. Thus, taking into account the molecular weight of the poly[2]catenanes repeating unit (1918), it could be acquired that the molecular weight of poly[2]catenanes was calculated as 0.6, 1.0, 2.5, 15.9 and 39.9 kDa (Table S1).

Table S1: Degree of polymerization for SPs, the obtained degree of polymerization as well as molecular weight for poly[2]catenanes according to the transformation efficiency.

Entry	**M1** [mM]	DP_{SPs}	$DP_{poly[2]catenanes}$	$M_{n\ poly[2]catenanes}$ [kDa]
1	10	1	0.3	0.6
2	20	1.4	0.5	1.0
3	50	3.8	1.3	2.5
4	100	24.4	8.3	15.9
5	150	61.1	20.8	39.9

6. Viscosity testing of SPs

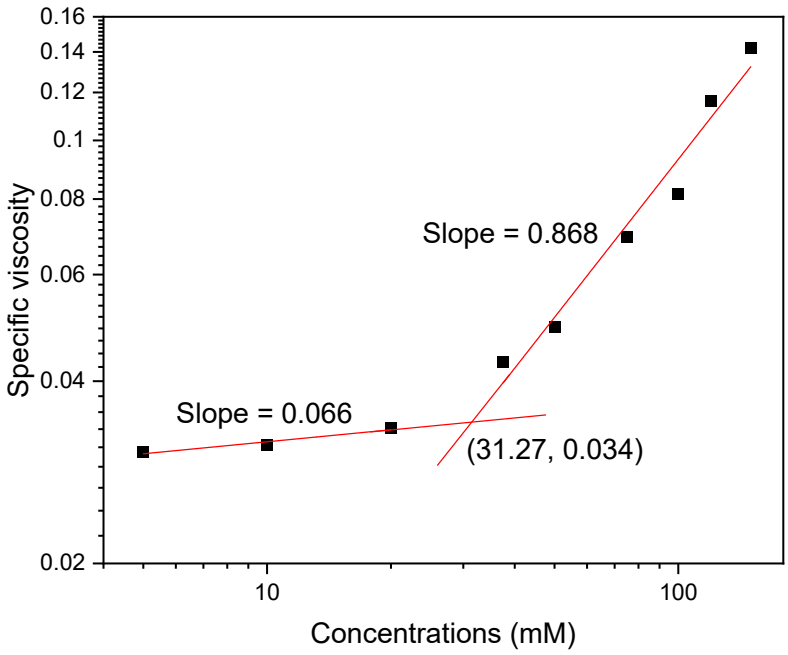


Figure S21. Specific viscosity of SPs (298 K) in a $CHCl_3$ solution versus the concentration of **M1**.

The self-assembly process of **M1** was studied using the viscosimetry. As shown in the figure S21, the self-assembly of monomer **M1** at different concentrations exhibits significant viscosity changes, and the change in the slope of the logarithmic curve of specific viscosity with concentration describes this transition. In the low concentration range, the slope of the curve is 0.066, indicating a linear relationship between specific viscosity and concentration, with oligomers mainly present in dilute solutions. When

the concentration exceeded the critical polymerization concentration (31.27 mM), a sharp increase in viscosity was observed, with a slope of 0.868, indicating the formation of SPs with increasing concentration.

7. Time-dependent ^{1}H NMR spectra of adding 2 equiv. of M2 to different concentrations of M1

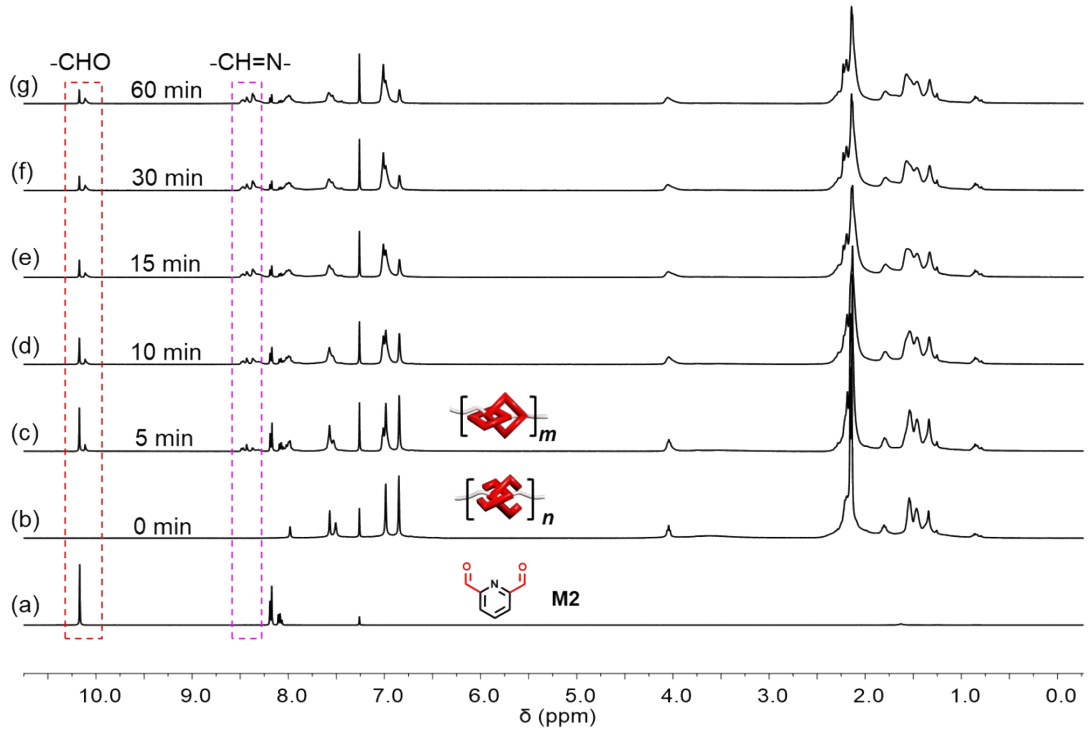


Figure S22. Time-dependent ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of adding 2 equiv. of **M2** to 10 mM **M1**.

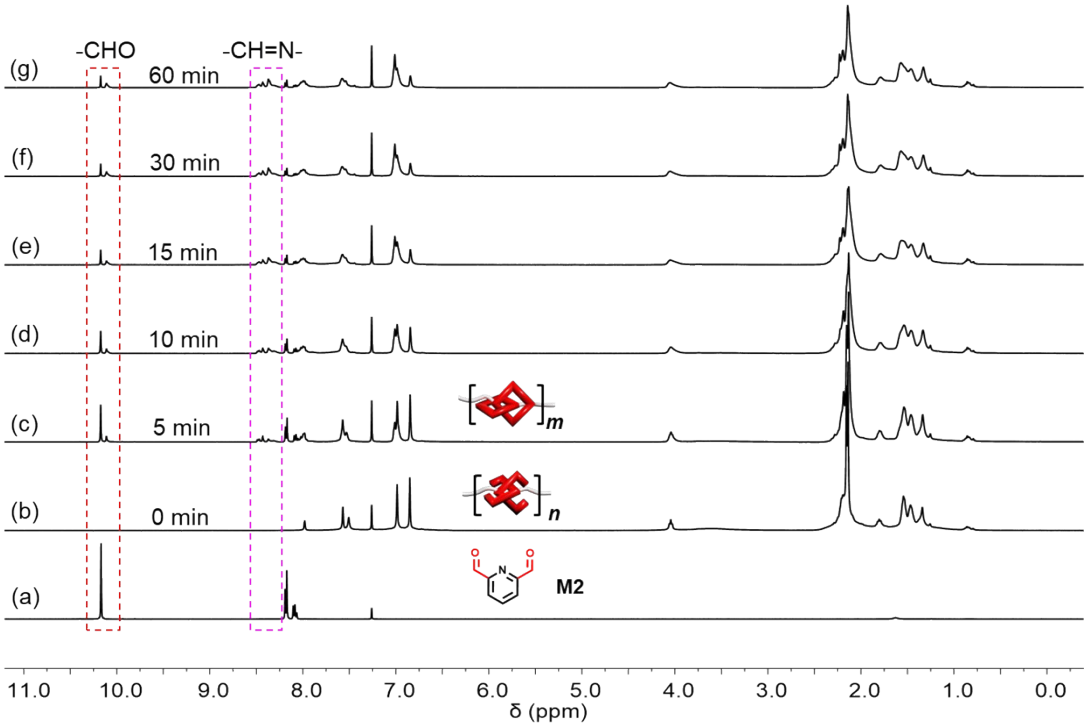


Figure S23. Time-dependent ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of adding 2 equiv. of **M2** to 20 mM **M1**.

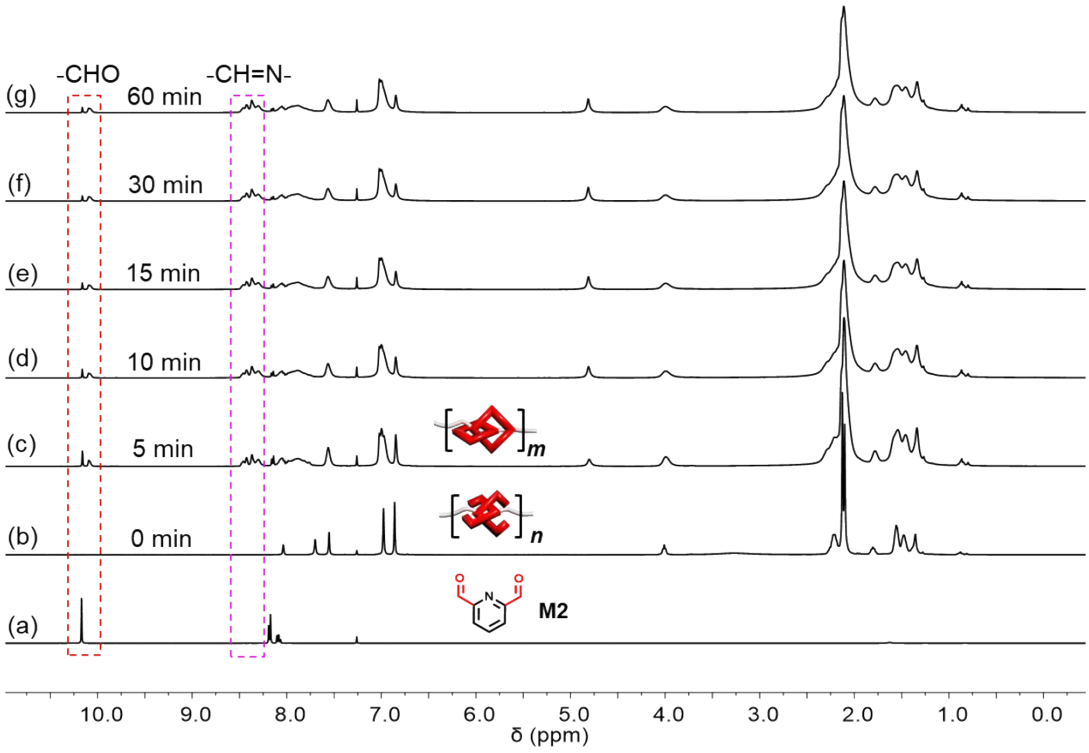


Figure S24. Time-dependent ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of adding 2 equiv. of **M2** to 50 mM **M1**.

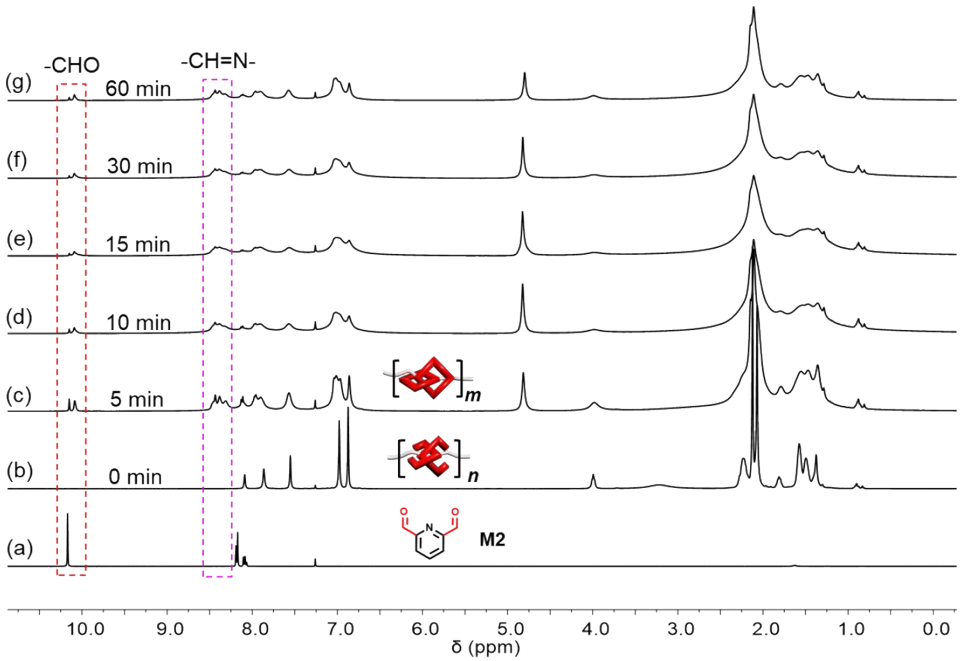


Figure S25. Time-dependent ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of adding 2 equiv. of **M2** to 100 mM **M1**.

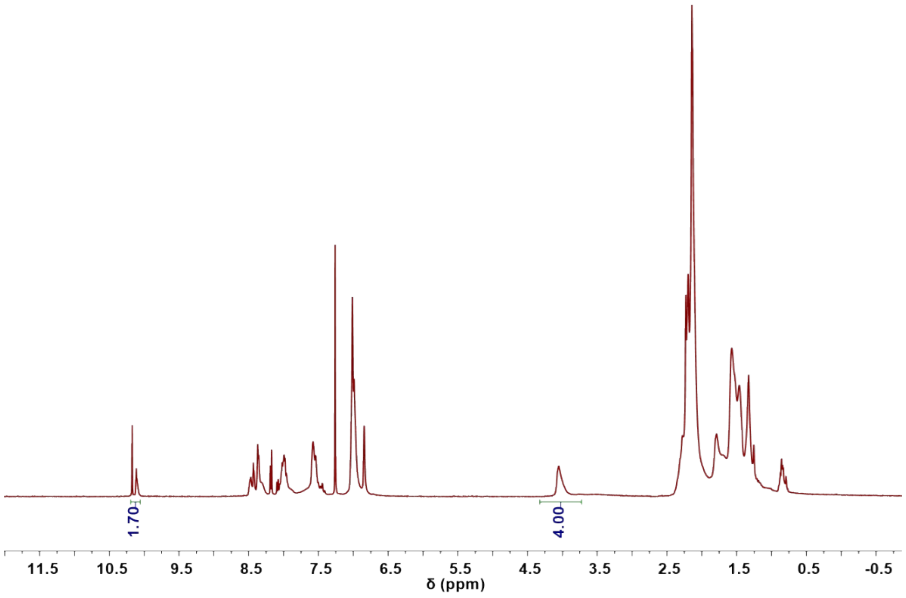


Figure S26. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of 10 mM **M1** and 20 mM **M2** reacting for 60 min.

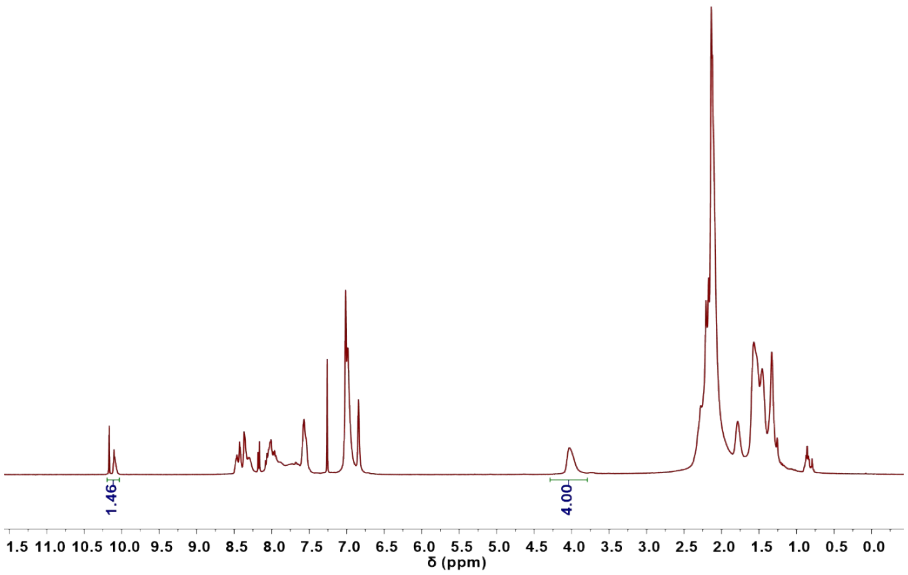


Figure S27. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of 20 mM **M1** and 40 mM **M2** reacting for 60 min.

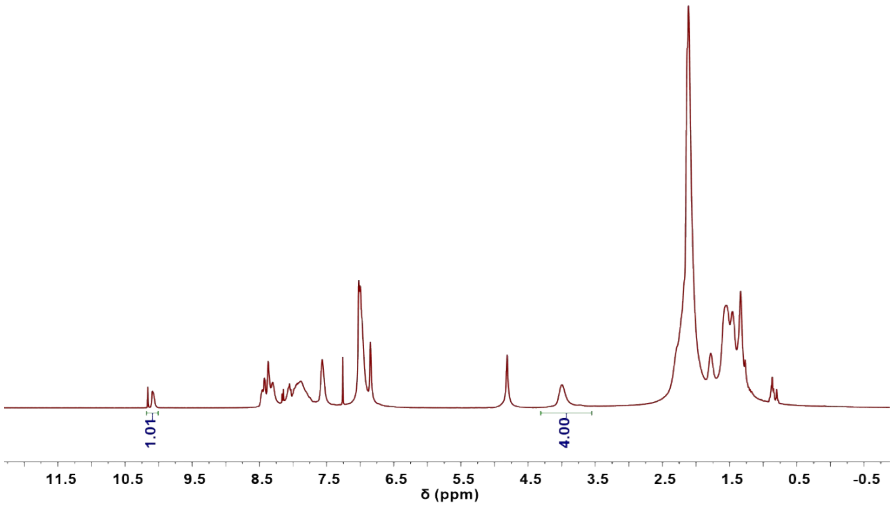


Figure S28. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of 50 mM **M1** and 100 mM **M2** reacting for 60 min.

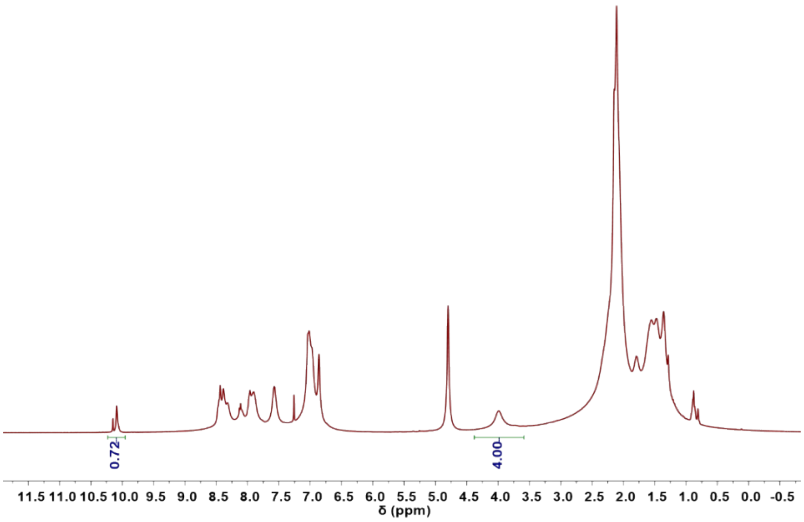


Figure S29. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of 100 mM **M1** and 200 mM **M2** reacting for 60 min.

Selecting the methylene (H_h) connected to oxygen on the alkyl chain as the standard, the ratio of methylene and aldehyde groups in the reaction system is 1:1. From this, the percentage of unreacted aldehydes in the mixture obtained from the reaction of 10 mM, 20 mM, 50 mM, and 100 mM **M1** and 2 equiv. **M2** can be calculated to be 42.5%, 36.5%, 25%, and 18% respectively.

8. Time-dependent ^{13}C NMR spectra of adding 2 equiv. of M2 to 50.0 mM M1

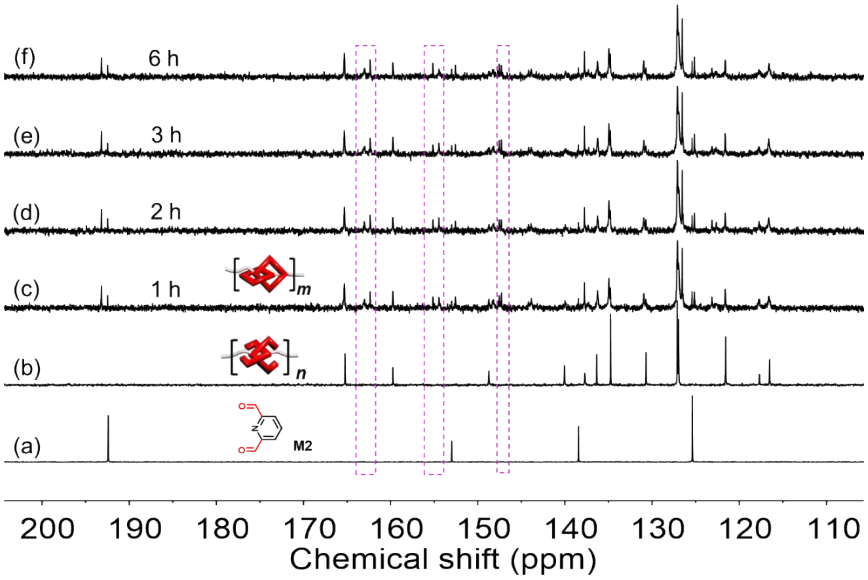


Figure S30. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of (a) **M2**, (b) **M1** (50.0 mM), (c-f) **M1** (50.0 mM) adding with **M2** (100.0 mM) for 1 h, 2 h, 3 h, 6 h.

The results demonstrated the generation of imine carbon peaks at 163.0 ppm, 162.4 ppm, 155.1 ppm, 154.5 ppm, 147.55 ppm, 147.20 ppm, consistent with the previously reported literatures.[3,4]

9. Full NOESY NMR spectra of adding 2 equiv. of M2 to 50 mM M1

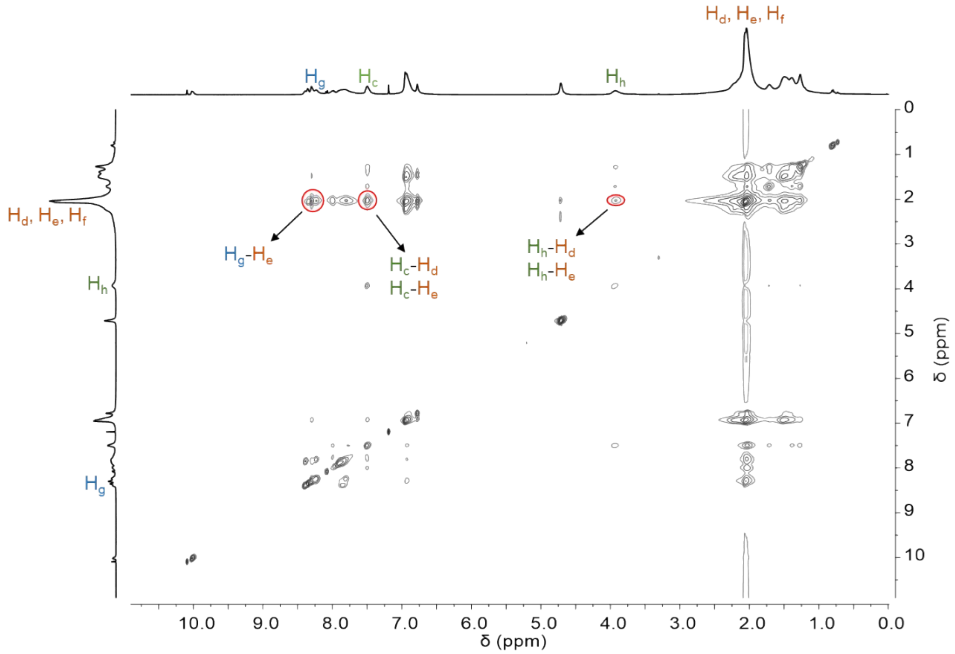


Figure S31. NOESY NMR spectra (400 MHz, $CDCl_3$, 298 K) of adding 2 equiv. of **M2** to a 50 mM solution of monomer **M1**.

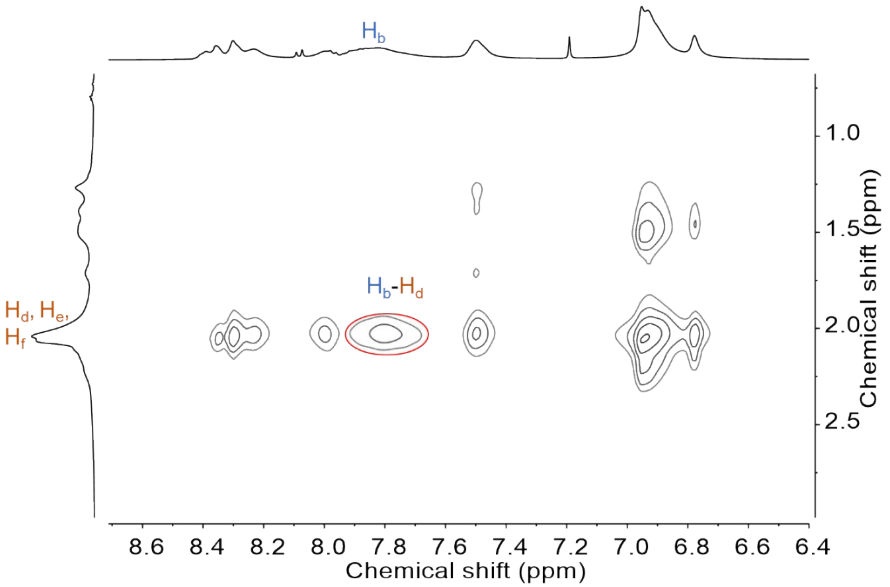


Figure S32. Partial NOESY NMR spectra (400 MHz, $CDCl_3$, 298 K) of 50.0 mM **M1** after adding 2 equiv. of **M2** self-assembly for 1 h.

10. FT-IR spectrum of adding 2 equiv. of M2 to monomer M1 at different concentrations

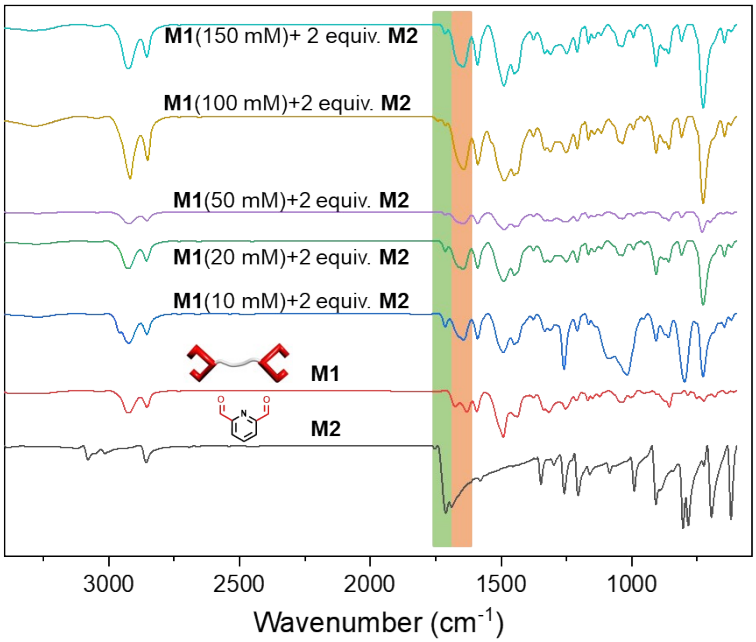


Figure S33. FT-IR spectrum of adding 2 equiv. of **M2** to monomer **M1** at 10 mM, 20 mM, 50 mM, 100 mM, 150 mM.

11. GPC curves after adding 2 equiv. of M2 to different concentrations of M1

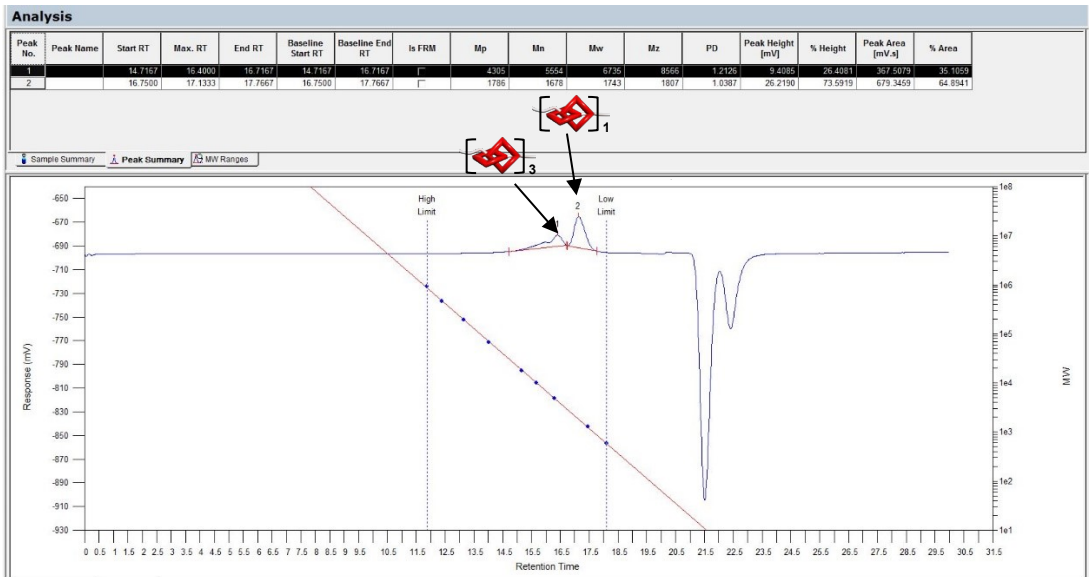


Figure S34. GPC curves of adding 2 equiv. of **M2** to monomer **M1** at 10 mM, using THF as the eluent and polystyrene as the standard.

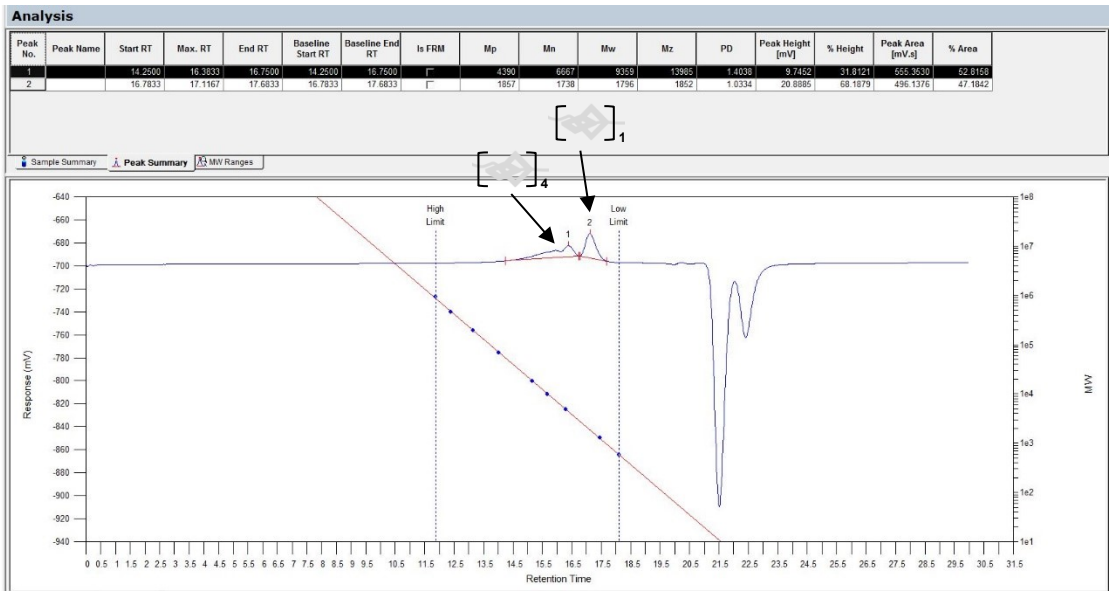


Figure S35. GPC curves of adding 2 equiv. of **M2** to monomer **M1** at 20 mM, using THF as the eluent and polystyrene as the standard.

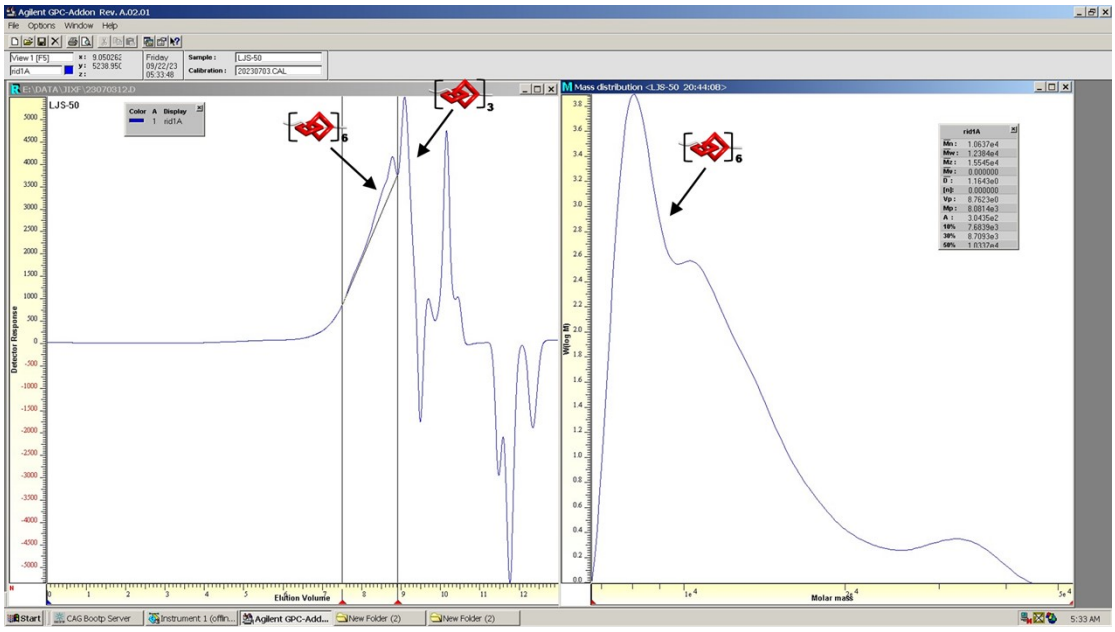


Figure S36. GPC curves of adding 2 equiv. of **M2** to monomer **M1** at 50 mM, using DMF as the eluent and polystyrene as the standard.

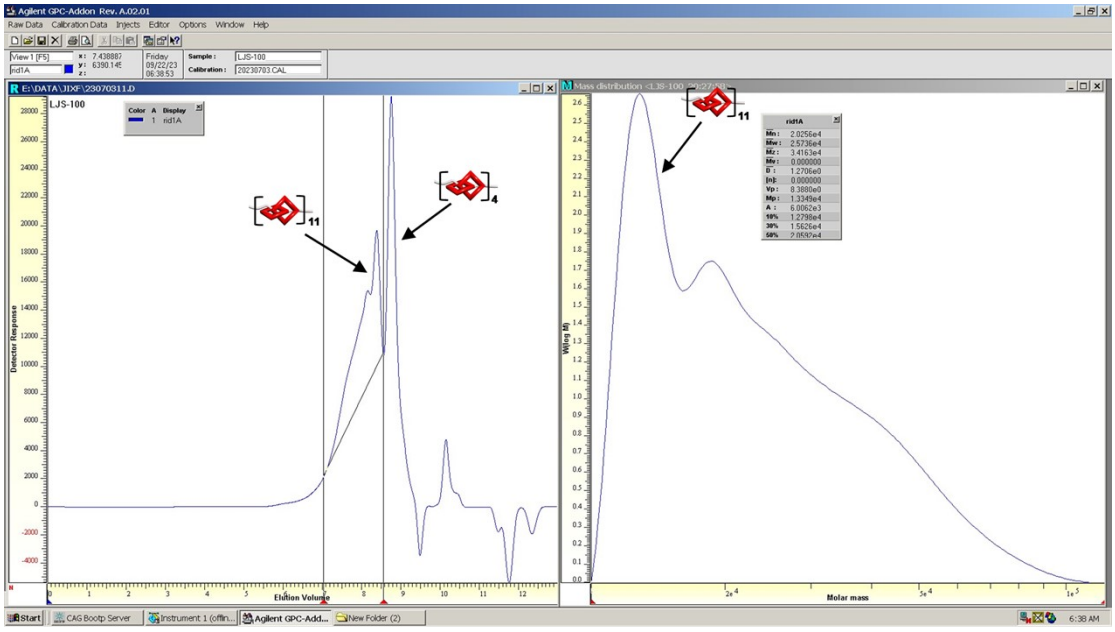


Figure S37. GPC curves of adding 2 equiv. of **M2** to monomer **M1** at 100 mM, using DMF as the eluent and polystyrene as the standard.

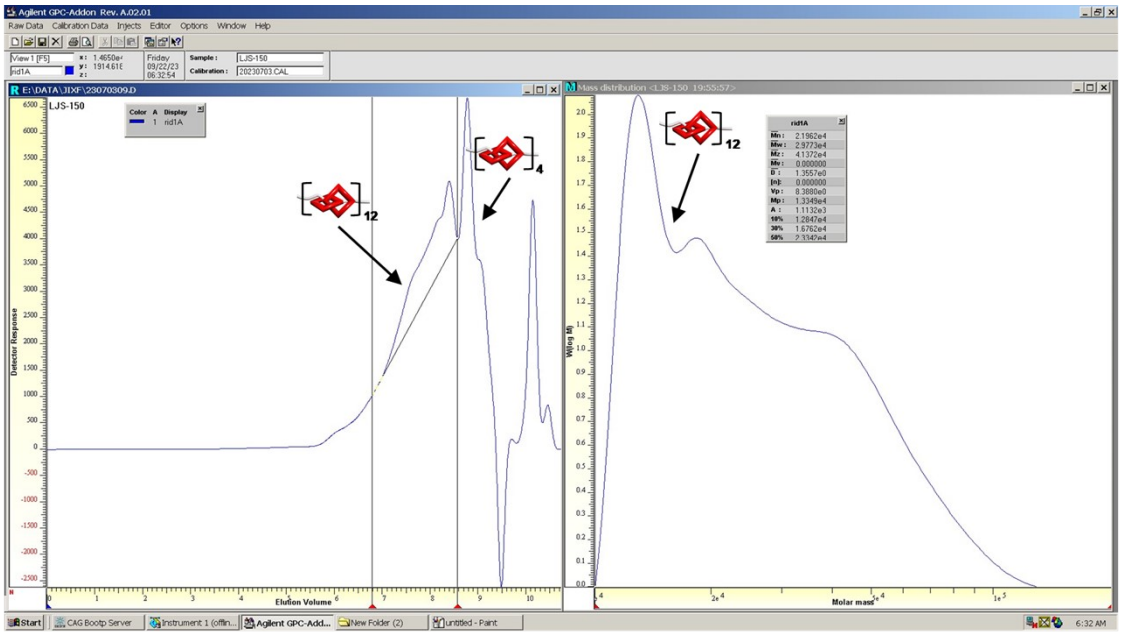


Figure S38. GPC curves of adding 2 equiv. of **M2** to monomer **M1** at 150 mM, using DMF as the eluent and polystyrene as the standard.

As shown in Table S2, when the concentrations of **M1** were 10, 20, 50, 100, and 150 mM, the molecular weight of obtained poly[2]catenanes were 5.6, 6.7, 10.6, 20.3 and 22.0 kDa, respectively (Figure S34-S38). Since the molecular weight for the repeating unit (**M1** and **M2**) of poly[2]catenanes was 1918, the degree of polymerization of which were 3, 4, 6, 11 and 12 correspondingly. Then according to the literature reported by Hunter, the reaction yield of catenanes by this method was known as 34%,[1] thereby the DP values of SPs corresponded to 9, 12, 18, 32 and 35. Thus, taking into account the molecular weight for **M1** of 1719, it could be acquired that the molecular weight of SPs was calculated as 15.5, 20.6, 30.9, 55.0 and 60.2 kDa in relation to different concentrations of **M1** (Table S2).

Table S2: Molecular weight and degree of polymerization for poly[2]catenanes by GPC, the obtained degree of polymerization as well as molecular weight for SPs according to the transformation efficiency.

Entry	**M1** [mM]	$M_{n\ \text{poly[2]catenanes}}$ [kDa]	$DP_{\text{poly[2]catenanes}}$	DP_{SPs}	$M_{n\ SPs}$ [kDa]
1	10	5.6	3	9	15.5
2	20	6.7	4	12	20.6
3	50	10.6	6	18	30.9
4	100	20.3	11	32	55.0
5	150	22.0	12	35	60.2

12. MALDI-TOF testing of poly[2]catenanes

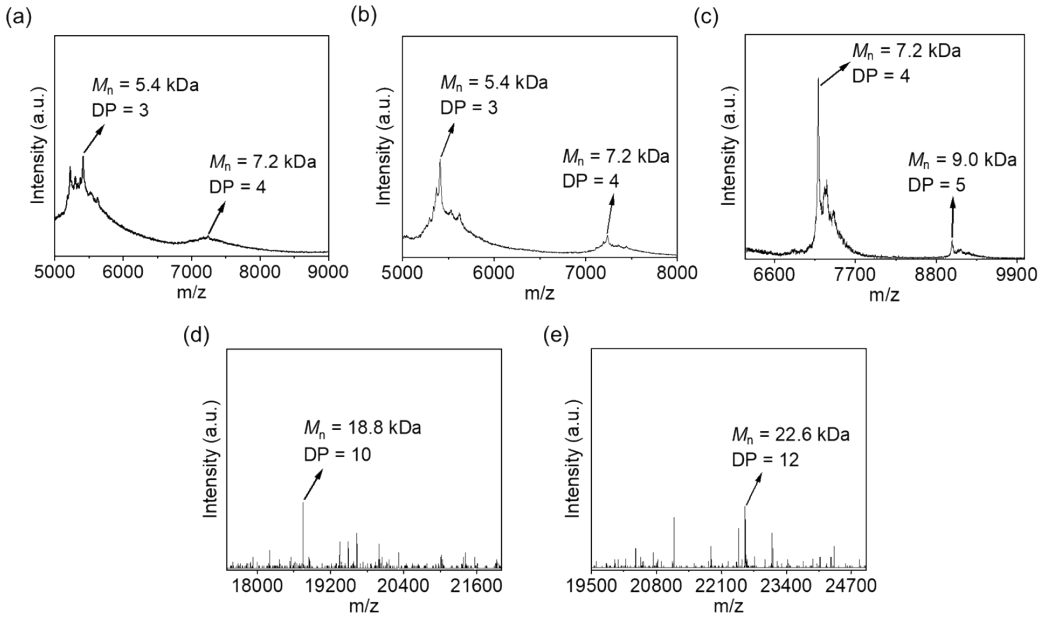


Figure S39. MALDI-TOF of adding 2 equiv. of **M2** to monomer **M1** at (a) 10.0 mM, (b) 20.0 mM, (c) 50.0 mM, (d) 100.0 mM, (e) 150.0 mM (matrix: 1, 8, 9-trihvdroxyanthracene; solvent: $CDCl_3$).

According to the MALDI-TOF results, the molecular weight of poly[2]catenanes corresponding to the concentration of **M1** (10.0 mM, 20.0 mM, 50.0 mM, 100.0 mM, 150.0 mM) was acquired as 5.4 kDa, 7.2 kDa, 9.0 kDa, 18.8 kDa, and 22.6 kDa, thus the degree of polymerization was calculated as 3, 4, 5, 10, 12. The degree of polymerization obtaining from GPC test were 3, 4, 6, 11 and 12. The polymerization degree obtained by the two testing methods was very close.

Supporting references

1. C. A. Hunter, *J. Am. Chem. Soc.*, 1992, **114**, 5303-5311.
2. J. F. Xu, Z. Huang, L. Chen, B. Qin, Q. Song, Z. Wang and X. Zhang, *ACS Macro Lett.*, 2015, **4**, 1410-1414.
3. C. Krishnaraj, A. M. Kaczmarek, H. S. Jena, K. Leus, N. Chaoui, J. Schmidt, R. Van Deun and P. Van Der Voort, *ACS Appl. Mater. Interface*, 2019, **11**, 27343-27352.
4. Q. Chen, Y. Lei, G. Wu, Q. Li, Y. Pan and H. Li, *Chem. Sci.*, 2022, **13**, 798-803.