Supporting Information for

A dual-responsive hyperbranched supramolecular polymer constructed by cooperative host−guest recognition and hydrogen-bond interactions

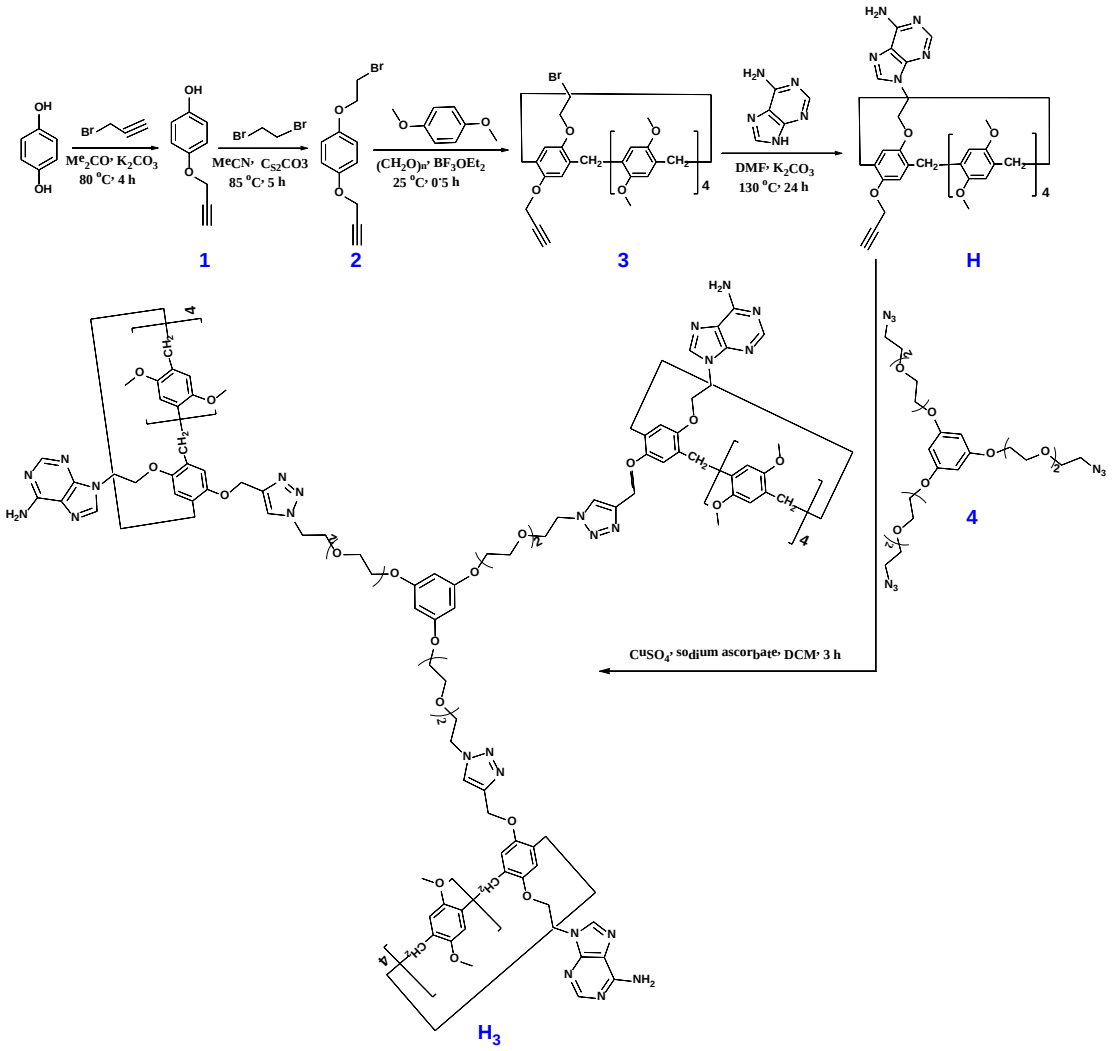
Yu-Qin Jiang, Kai Wu, Qian Zhang*, Ke-Qing Li, Yan-Yan Li, Peng-Yang Xin, Wei-Wei Zhang and Hai-Ming Guo*

Contents

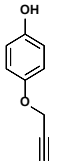
1. General information

^{1}H NMR (Nuclear Magnetic Resonance) spectroscopy were recorded on BRUKER 400 MHz or BRUKER 600 MHz. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quaternary, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (101/151MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. DOSY spectra were recorded on commercial instruments (BRUKER 600). Mass spectra were recorded by means of MALDI-TOF or ESI or EI techniques. Viscosity measurements were carried out with Brookfield viscometers at 293K in chloroform. Samples for SEM measurement were prepared by drop-casting onto silicon substrates, and the images were acquired by a JSM-6390LV. Melting points (m. p.) were determined using commercial apparatus and were not corrected. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

2. General procedure for the synthesis and characterization of compound H_3.



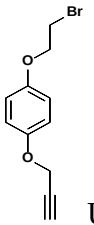
Scheme S1 the synthesis of compound **H_3**



Under a nitrogen atmosphere, hydroquinone (1.10g, 10.0 mmol) and potassium carbonate (2.07g, 15.0 mmol) were added into 50 mL acetone. The mixture was stirred for 30 minutes. Then bromopropyne (1.18g, 15.0 mmol) was added dropwise and the reaction mixture was stirred at reflux for another 4 h. After cooled to room temperature, the reaction mixture was filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (eluent: petroleum

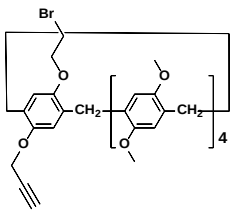
ether/ ethyl acetate 20:1) to give compound **1** as a pale yellow oil (0.86g, 58% yield. Lit: yellow oil [S1]).

^{1}H NMR ($CDCl_3$, 400 MHz, 298K) δ (ppm): 6.88 (d, *J* = 9.2 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.63 (d, *J* = 2.4 Hz, 2H), 4.43 (s, 1H), 2.51 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz, 298K) δ 151.7, 150.3, 116.4, 116.1, 78.9, 75.4, 56.7. MS (EI): m/z for $C_9H_8O_2^+$: 148.



Under a nitrogen atmosphere, compound **1** (0.86 g, 6.0 mmol) and cesium carbonate (0.94 g, 3.0 mmol) was added to 40 mL acetonitrile. The mixture was stirred for 30 minutes. Then 1, 2-dibromoethane (3.35g, 17.0 mmol) was added dropwise and the mixture was stirred at reflux for another 5 h. After cooled to room temperature, the reaction mixture was filtered and the solvent was removed. The remaining solid was added to CH_2Cl_2 (50 ml） and washed with H_2O (25 mL). The aqueous layer was washed with CH_2Cl_2 (2 × 20 mL). Then organic phase was combined and dried over anhydrous Na_2SO_4. After the solvent was removed under vacuum, the residue was purified by column chromatography (eluent: petroleum ether/ ethyl acetate 25:1) to give compound **2** as a white solid (0.56g, 38% yield).

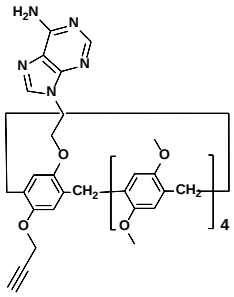
m. p. 41.5–42.7 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz, 298K) δ 6.93 (d, *J* = 9.2 Hz, 2H), 6.87 (d, *J* = 9.2 Hz, 2H), 4.65 (d, *J* = 2.4 Hz, 2H), 4.24 (t, *J* = 6.2Hz, 2H), 3.61 (t, *J* = 6.2 Hz, 2H), 2.51 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ 152.9, 152.3, 116.2, 115.9, 78.8, 77.4, 68.7, 56.5, 29.3. MS (EI): m/z for $C_{11}H_{12}BrO_2^+$ 254.



Under a nitrogen atmosphere, compound 1 (0.25g, 1.0 mmol), 1, 4-dimethoxybenzene (2.21g, 16.0 mmol) and paraformaldehyde (1.44g, 48.0 mmol) was added to 60 mL 1,2-dichloroethane. The mixture was stirred for 30 minutes at

25℃. Then boron trifluoride etherate (2.41g, 17.0 mmol) was added dropwise and the mixture was stirred at 25 ℃. When the starting material was consumed completely (detected by Thin layer chromatography, TLC), the mixture was poured into 100 mL CH_3OH. The reaction mixture was filtered and the filtrate was removed under vacuum. The residue was purified by column chromatography (eluent: CH_2Cl_2) to give compound **3** as an off-white solid (0.11g, 13% yield).

m. p. 108.9–110.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 6.80 (s, 2H), 6.79 (s, 1H), 6.78 (s, 1H), 6.77 (s, 2H), 6.75–6.73 (m, 4H), 5.11 (s, 1H), 4.43 (d, *J* = 2.0Hz, 2H), 4.12 (t, *J* = 6.2 Hz, 2H), 3.82 (s, 2H), 3.78 (d, *J* = 3.2 Hz, 6H), 3.76 (s, 2H), 3.69 (s, 6H), 3.68 (t, *J* = 0.8 Hz, 9H), 3.66 (s, 3H), 3.65 (s, 3H), 3.62 (s, 3H), 3.52 (t, *J* = 6.0Hz, 2H), 1.83 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 298K) δ 150.8, 150.7, 150.6, 149.5, 149.4, 129.2, 129.0, 128.6, 128.4, 148.4, 128.2, 128.1, 127.6, 115.9, 115.5, 114.4, 114.2, 114.1, 113.9, 113.8, 78.7, 74.8, 68.9, 56.1, 55.9, 55.8, 55.7, 53.0, 30.3, 30.0, 29.7, 29.5, 29.2. HRMS (MALDI-TOF-MS) m/z calcd for $[M]^+$ $C_{48}H_{52}BrO_{10}^+$, 866.2744, found 866.2644.



To the solution of adenine (0.81g, 6.0 mmol) and potassium carbonate (0.83g, 6.0 mmol) in 15mL DMF, compound **3** (0.87g, 1.0 mmol) was added. The reaction mixture was stirred at 130℃ and detected by TLC. After compound **3** was consumed completely, the reaction mixture was filtered and the solvent was removed under vacuum. The remaining solid was added to CH_2Cl_2 (50 ml) and washed with H_2O (25 mL) The aqueous layer was washed with CH_2Cl_2 (2 × 20 mL). Then organic phase was combined and dried over anhydrous Na_2SO_4. After the solvent was removed, the residue was purified by column chromatography (eluent: CH_2Cl_2 / MeOH = 50:1) to give **H** as a pale yellow solid (0.46g, 50% yield).

m. p. 147.6–149.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.38 (s, 1H), 8.05 (s, 1H), 6.80 (s, 2H), 6.76 (s, 1H), 6.73 (s, 1H), 6.72 (s, 1H), 6.71 (s, 1H), 6.69 (s, 1H), 6.68 (s,

2H), 6.48 (s, 1H), 5.72 (s, 2H), 4.55 (t, *J* = 4.8 Hz, 2H), 4.34 (d, *J* = 2.4 Hz, 2H), 4.21 (t, *J* = 4.8 Hz, 2H), 3.77 (s, 6H), 3.73(s, 2H), 3.71 (s, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.66 (s, 6H), 3.62 (s, 3H), 3.59 (s, 3H), 3.54 (s, 6H), 1.54 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 151.9, 149.8, 149.7, 149.6, 149.5, 148.9, 148.3, 148.1, 140.3, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0, 127.9, 126.3, 118.4, 114.3, 113.4, 113.3, 113.0, 112.9, 112.7, 77.2, 73.7, 65.8, 54.9, 54.8, 54.7, 51.9, 42.5, 29.7, 28.9, 28.5, 28.4, 27.6. HRMS (ESI): m/z Calcd for $C_{53}H_{56}N_5O_{10}$ $[M+H]^+$: 922.2027, found 922.2184.

Compound 4 was synthesized according to the reported method.[S2]

Yellow oil (Lit: yellow oil [S2]); ^{1}H NMR (600 MHz, $CDCl_3$, 298K) δ 6.11 (s, 3H), 4.07 (t, *J* = 4.8 Hz, 6H), 3.83 (t, *J* = 4.8 Hz, 6H), 3.73–3.71 (m, 6H), 3.69–3.67 (m, 12H), 3.38 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, 298K) δ 160.5, 94.4, 70.9, 70.7, 70.1, 69.8, 67.4, 50.7. HRMS(ESI): m/z Calcd for $C_{24}H_{39}N_9O_9$ Na$[M+Na]^+$: 620.2768, found 620.2731.

Synthesis of **H_3:** The mixture solution of **H** (303.9 mg, 0.3 mmol), compound **3** (59.7 mg, 0.1mmol), copper sulfate (6.0 mg, 0.03 mmol), sodium ascorbate (11.9 mg, 0.06 mmol) in 4 ml tert-butanol/water (1:1, V/V) was stirred at 50 ℃. The reaction was monitored by TLC. After the reaction was completed, 10 ml water was added and the mixture is extracted with CH_2Cl_2. Then the organic phases were combined and dried over anhydrous Na_2SO_4. After the solvent was removed, the residue was purified by column chromatography（eluent: CH_2Cl_2/MeOH = 20:1) to give **H_3** as a pure pale yellow powdery solid (252.1 mg, 75% yield).

m. p. 124.0–127.2℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 3H), 8.05 (s, 3H), 7.16 (s, 3H), 6.89 (s, 9H), 6.85 (s, 3H), 6.82 (s, 6H), 6.79 (s, 3H), 6.70 (s, 3H), 6.69 (s, 3H), 6.54 (s, 1H), 5.94 (s, 3H), 5.27 (s, 6H), 4.57 (t, *J* = 4.4 Hz, 6H), 4.26 (t, *J* = 4.4 Hz, 6H), 3.99 (t, *J* = 4.4 Hz, 6H), 3.79 (s, 6H), 3.76 (s, 6H), 3.74 (s, 12H), 3.73 (s, 12H), 3.72 (s, 18H), 3.69 (s, 12H), 3.64 (s, 12H), 3.45 (s, 18H), 3.39 (s, 9H), 2.90 (t, *J* = 4.2 Hz, 6H), 2.62 (t, *J* = 4.4 Hz, 6H), 2.12 (s, 6H), 1.93 (t, *J* = 6.4 Hz, 6H), 1.72 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 153.1, 150.9, 150.8, 150.7, 150.6, 150.5, 150.4, 150.0, 149.3, 148.9, 144.3, 141.1, 129.4, 128.8, 128.7, 128.5, 128.3,

128.2, 127.8, 124.2, 119.3, 115.9, 115.1, 114.5, 114.2, 114.1, 114.0, 113.9, 113.4, 71.6, 67.9, 67.8, 67.6, 67.2, 61.9, 61.5, 56.1, 56.0, 55.9, 55.8, 55.7, 55.6, 49.8, 43.7, 29.7, 29.6, 29.4, 29.2, 28.7. MALDI-TOF-MS: m/z calcd for $C_{183}H_{204}N_{24}O_{39}Na^+$ [M+Na]$^+$: 3386.4676, found 3386.4661.

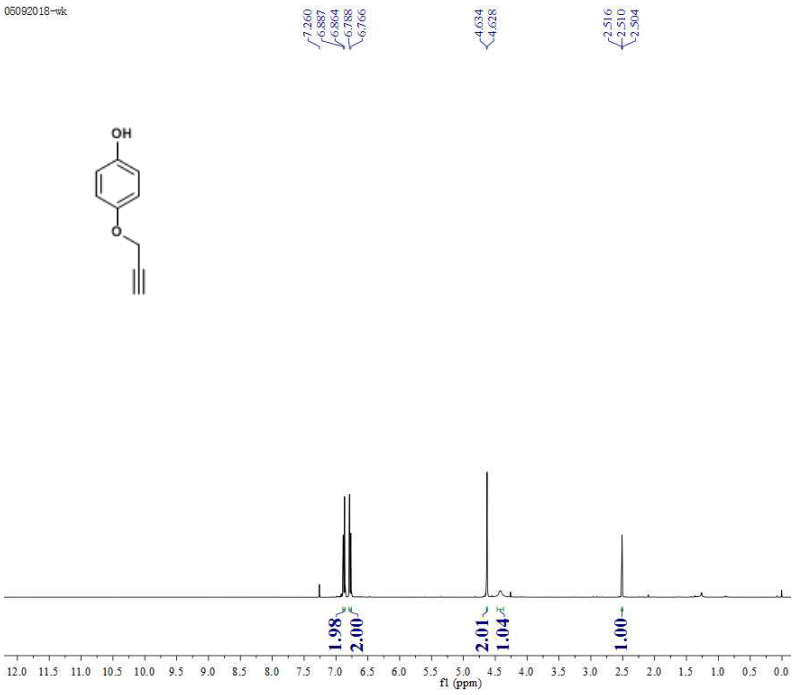


Fig. S1 ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

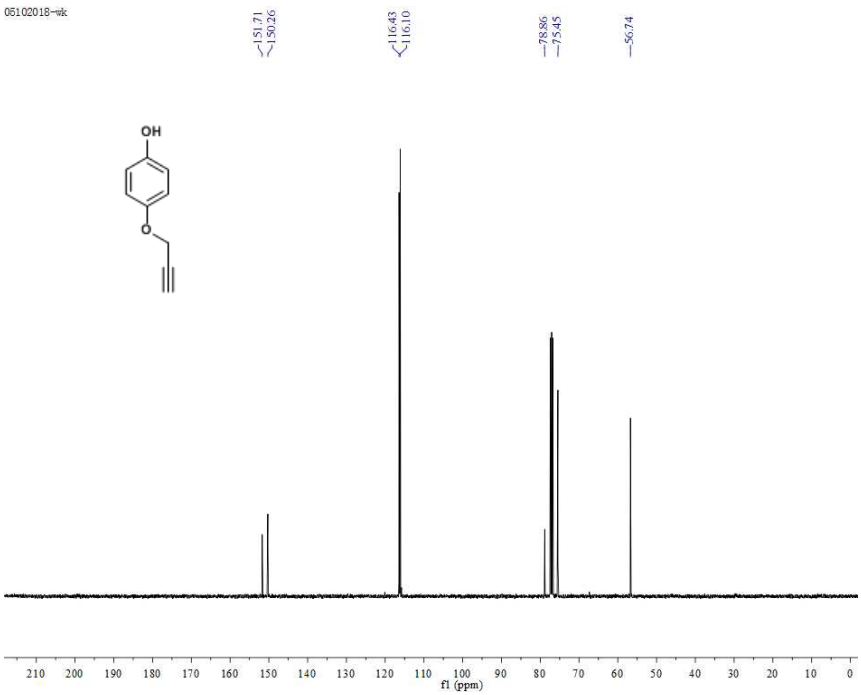


Fig. S2 ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

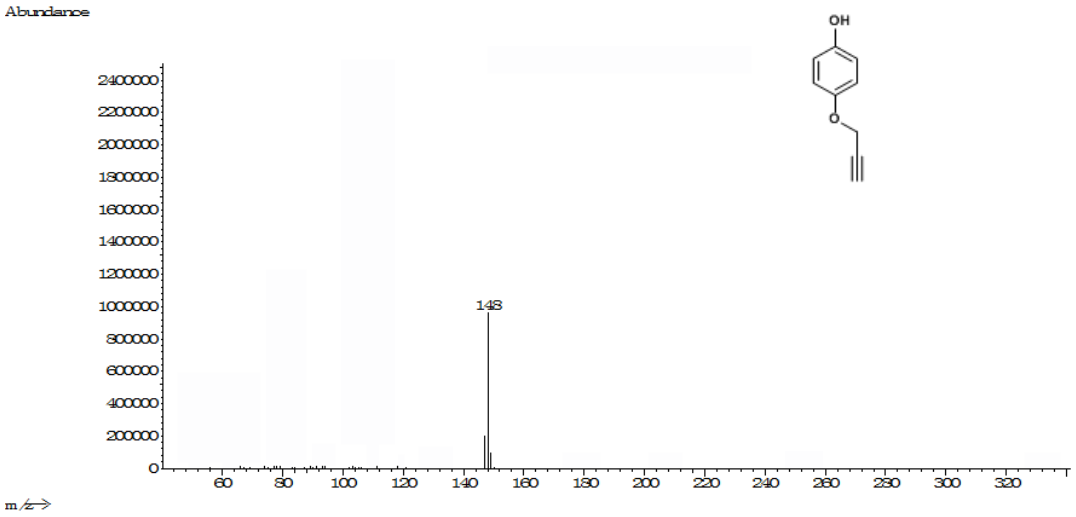


Fig. S3 EI-MS of compound **1.**

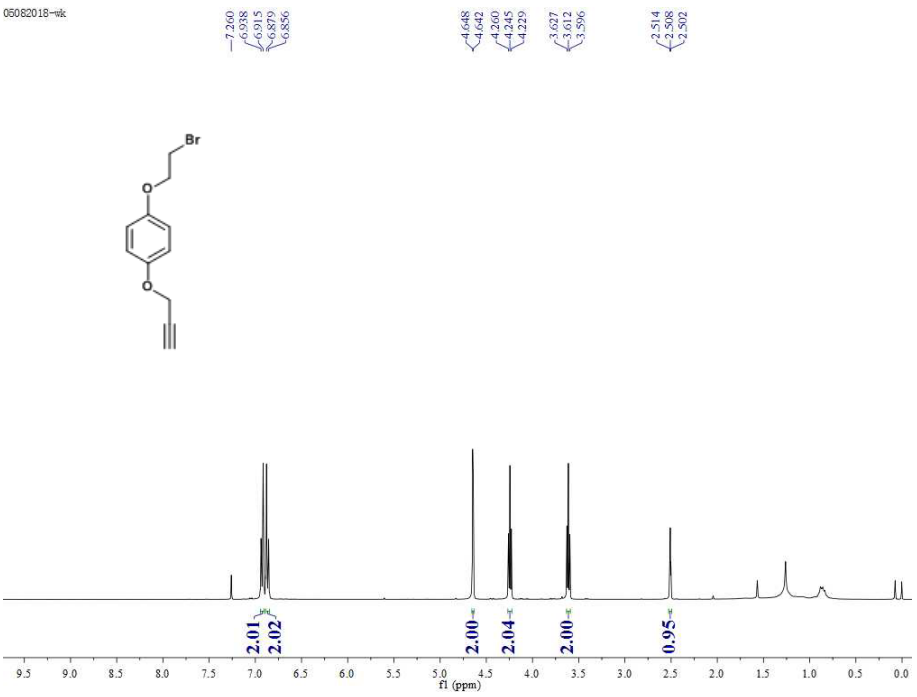


Fig. S4 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

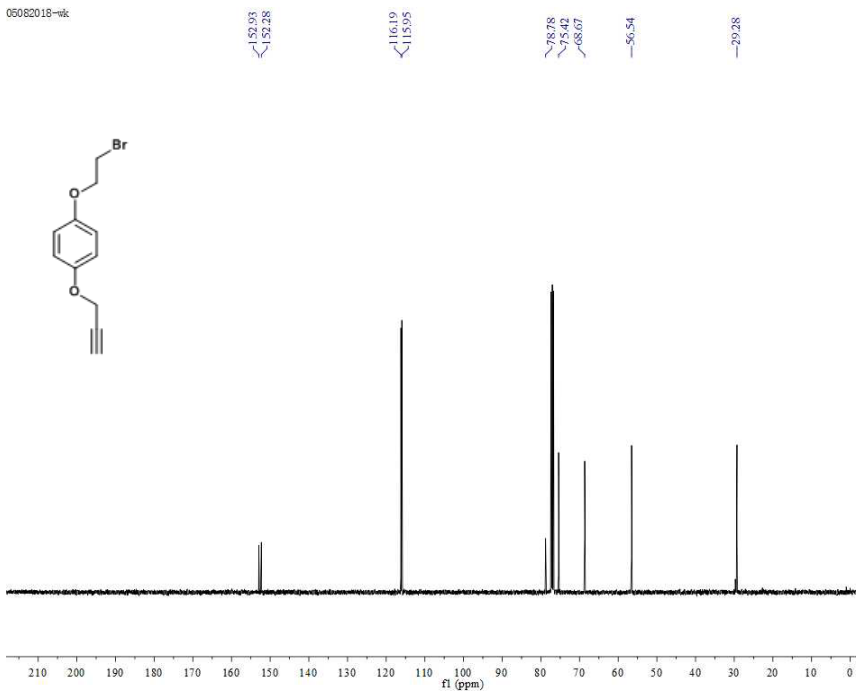


Fig. S5 ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

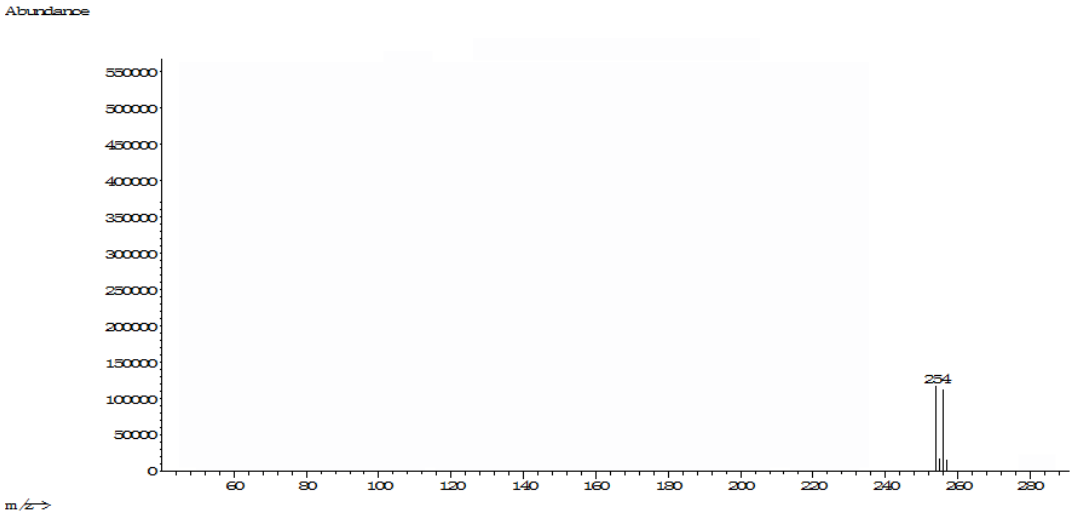


Fig. S6 EI-MS of Compound **2.**

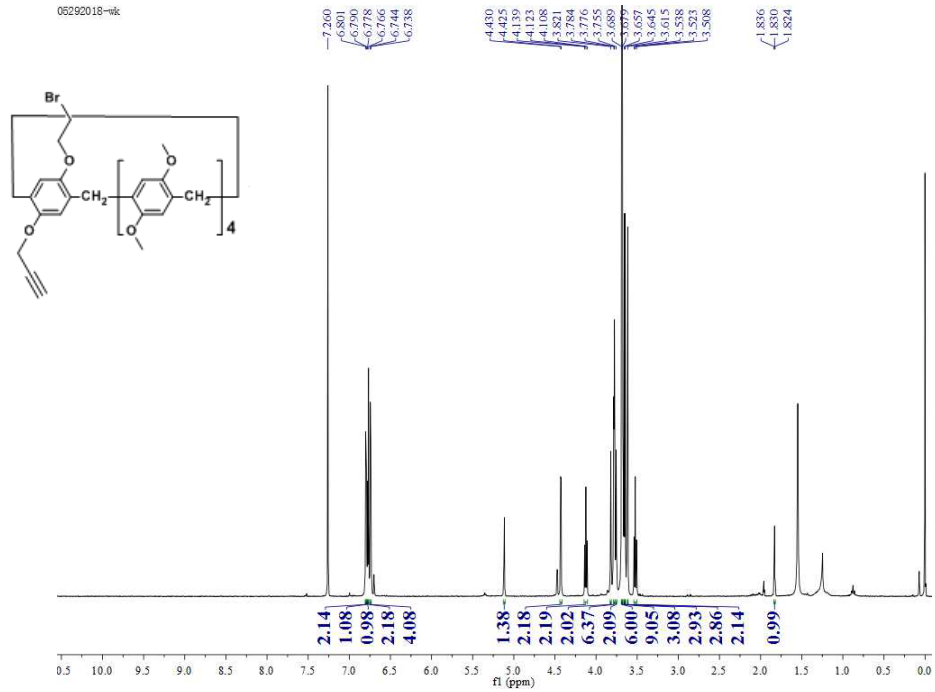


Fig. S7 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

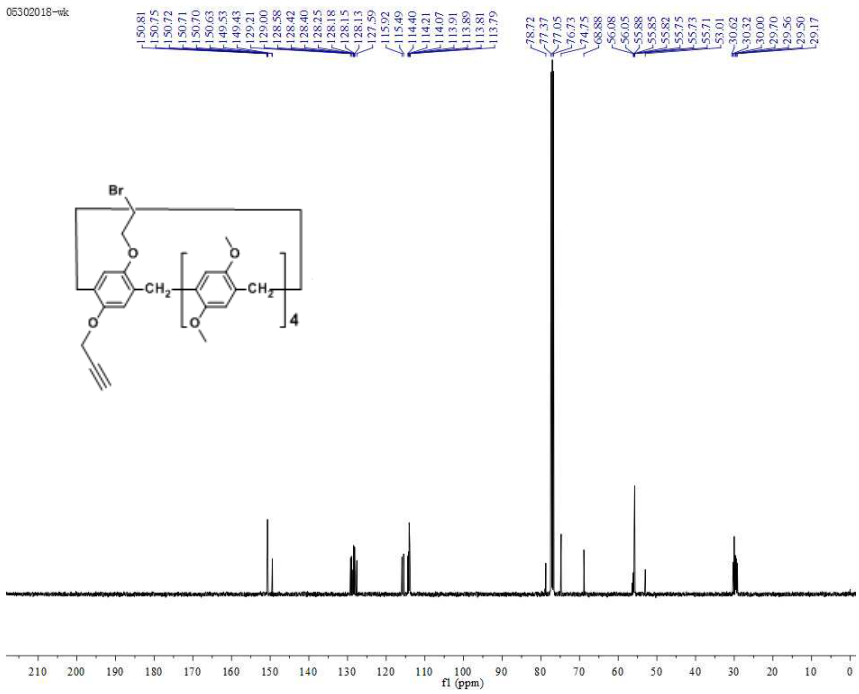


Fig. S8 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

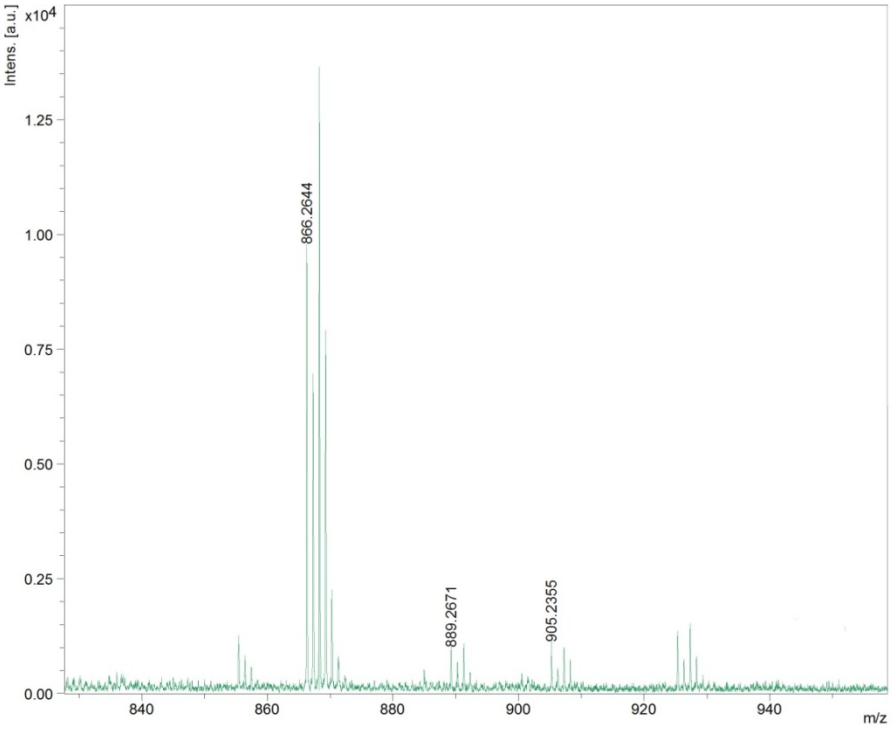


Fig. S9 MALDI-TOF-MS spectrum of compound **3**.

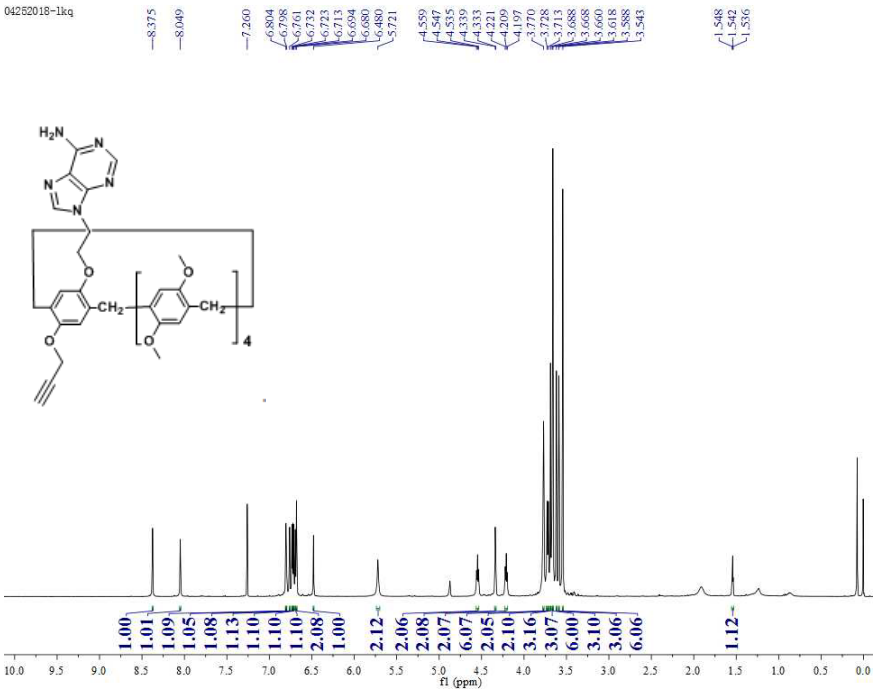


Fig. S10 ^{1}H NMR spectrum of **H** in $CDCl_3$.

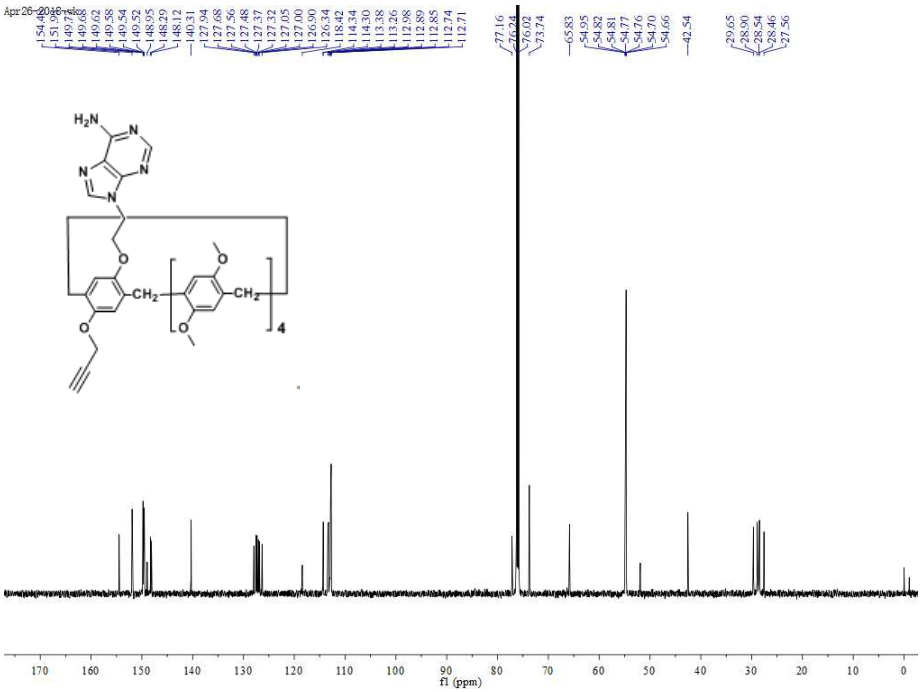


Fig. S11 ^{13}C NMR spectrum of **H** in $CDCl_3$.

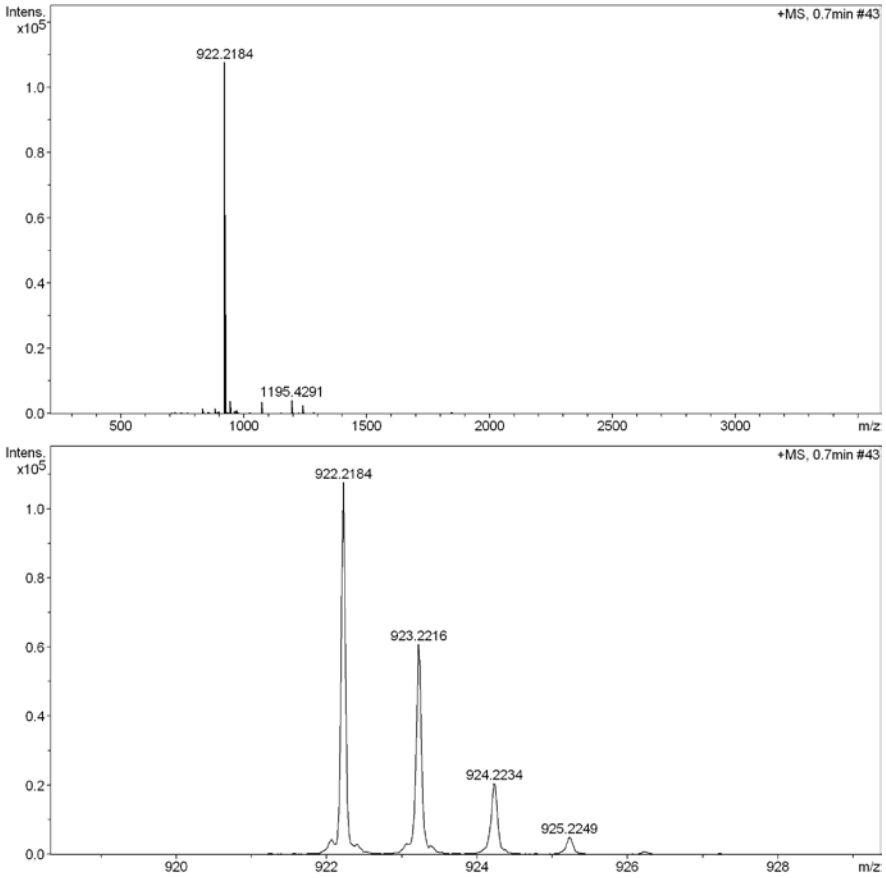


Fig. S12 HR-MS of **H**.

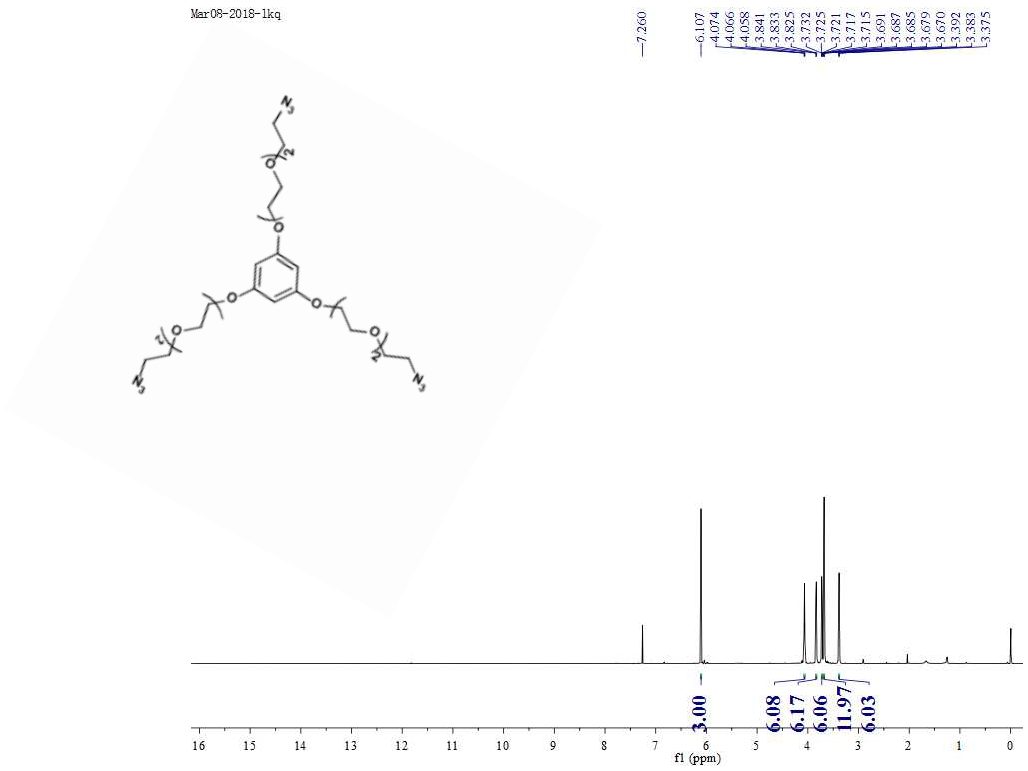


Fig. S13 ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

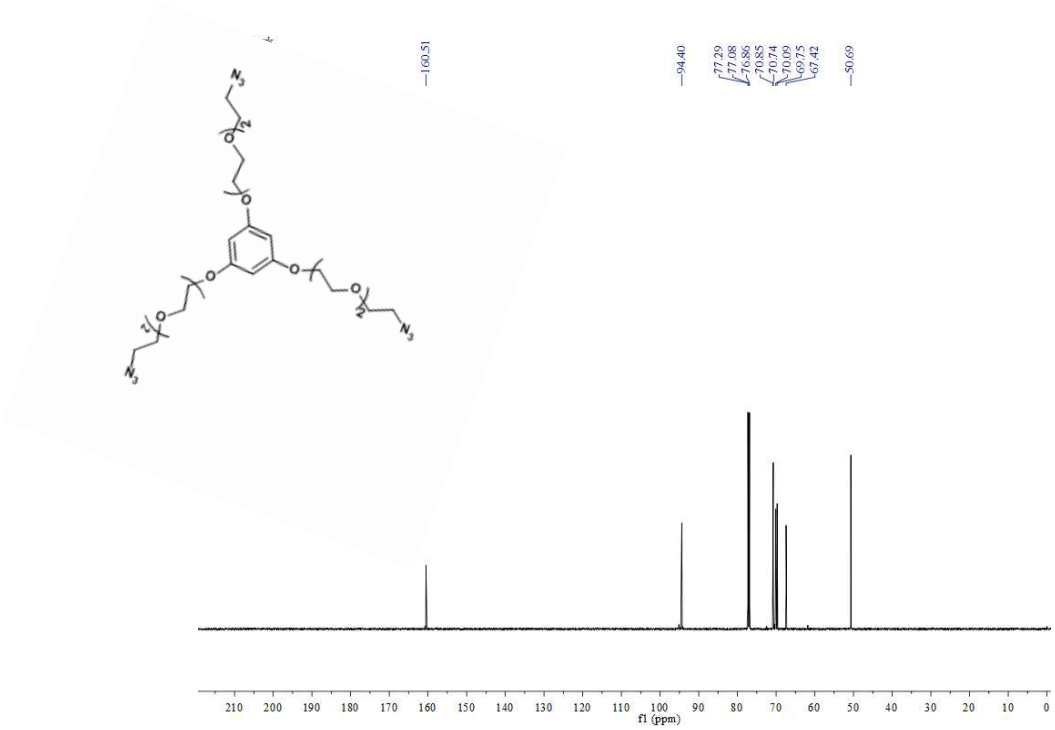


Fig. S14 ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

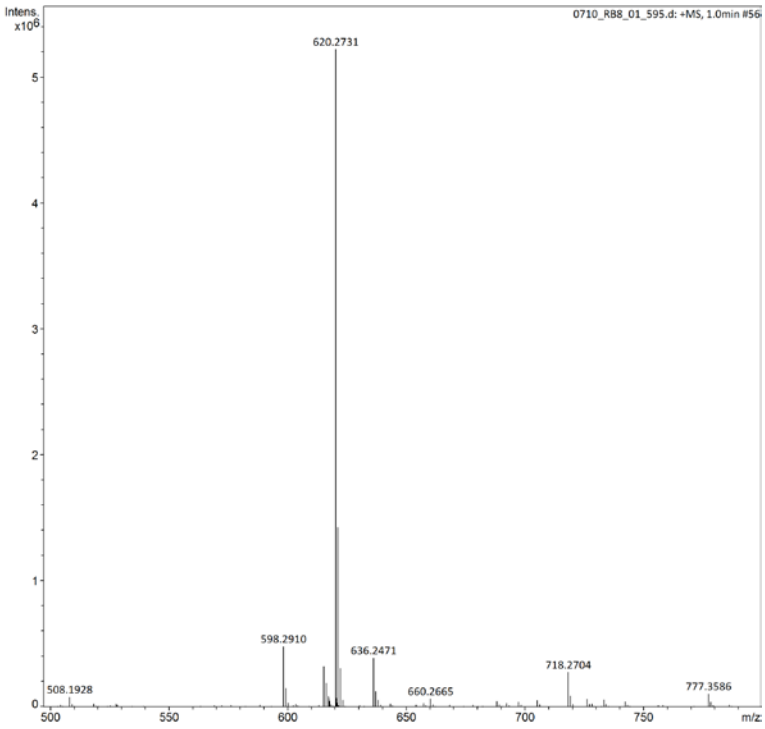


Fig. S15 HR-MS of compound **4**.

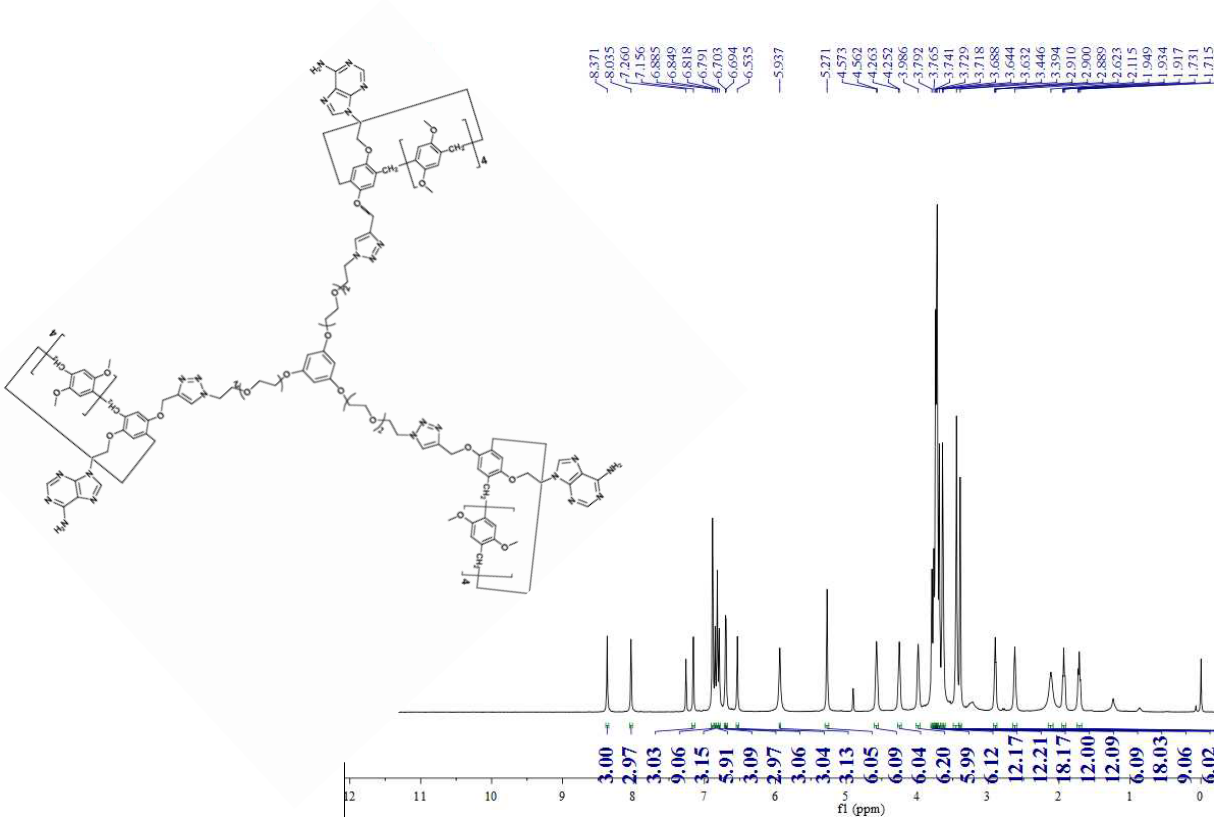


Fig. S16 ^{1}H NMR spectrum for **H3** in $CDCl_3$.

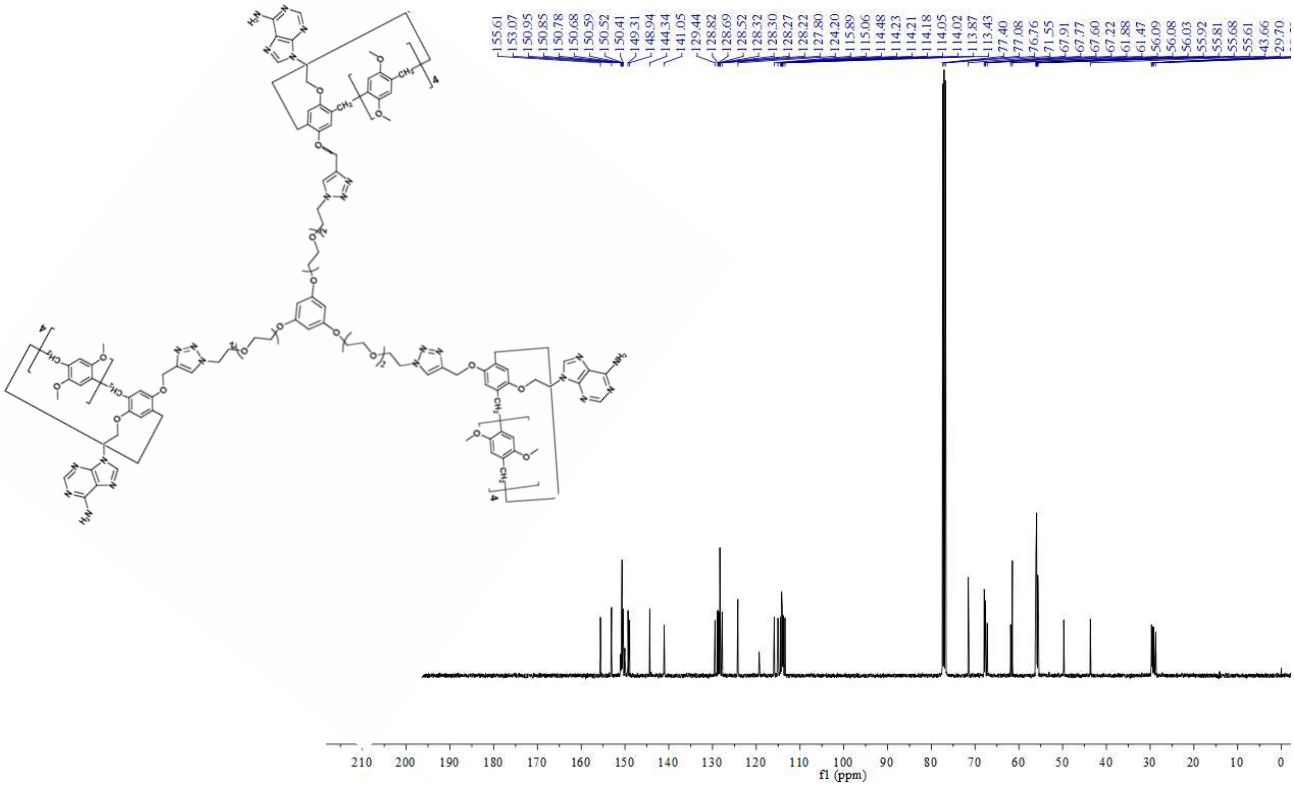


Fig. S17 ^{13}C NMR spectrum for **H3** in $CDCl_3$.

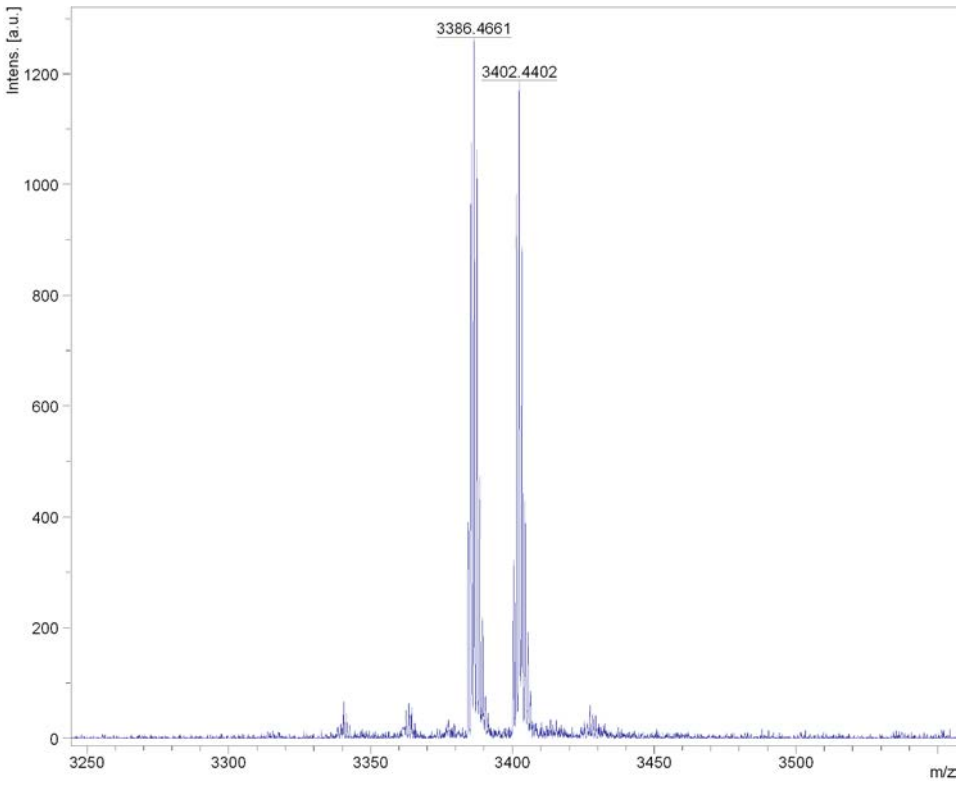


Fig. S18 MALDI-TOF-MS spectrum of **H3**.

3 Determination of the binding stoichiometry, association constant and the maximum possible polymerization degrees (n_{max} values) of HSP-H_3G at different concentrations

Determination of the binding stoichiometry.

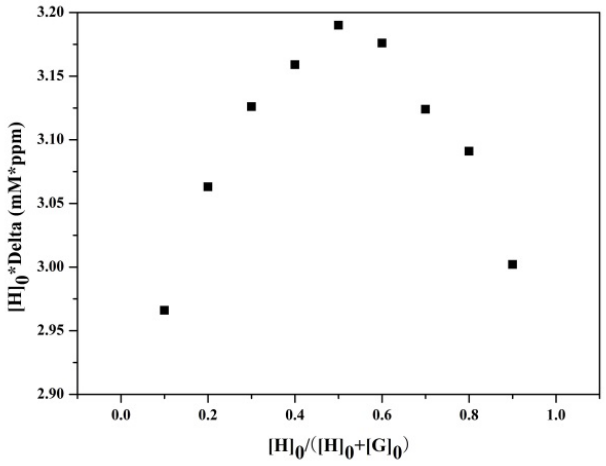


Fig. S19 Job plots showing the 1:1 stoichiometry of the complex between **H** and **G** in $CDCl_3$. The sum of initial concentration of **H** and **G** was 10.0 mM. Delta was chemical shift change of $\mathbf{H_{5'}}$ of **G**.

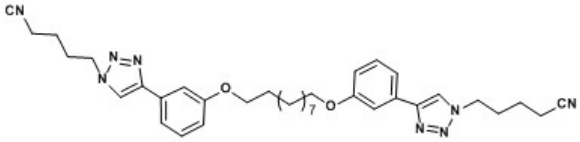
Determination of association constant.

For **G**⊂ **H** host–guest complex, chemical exchange was slow on the NMR time scale and peaks were observed for both complexed and uncomplexed species in the NMR spectra. So association constant (K_a) for this complex could be determined by integration from a 1:1 mixture using the ^{1}H NMR single point method.[S3] Three solutions of equimolar mixtures of **G** and **H** (1.0, 1.5 and 2.0 mM) were measured and the K_a value for **G**⊂**H** complex was determined to be $(7.2 \pm 0.2) \times 10^4$ M^{-1} in $CDCl_3$.

$$K_a = \frac{[\mathbf{H \cdot G}]_c}{[\mathbf{H}]_{uc}\ [\mathbf{G}]_{uc}}$$

Calculated n_{max} values of HSP-H_3G at different concentrations

For the present system in slow exchange on the NMR timescale, the maximum possible polymerization degrees (n_{max}) of **HSP-H_3G** could be estimated using a well-defined method reported by Gibson *et al.* [S4, S5] From the slow-exchange NMR spectra of host–guest mixture in very dilute solutions, the extents of complexation are within the Weber rule limits of 20-80%, and the association constant for spramolecular polymer (K_{sp}) can be calculated. Due to the hydrogen-bond interactions between two [2]pseudorotaxane are very strong, compound **5**[S4b] was used to replace guest **G** to determine the association constant K_{sp} and the K_{sp} was calculated as (6.0 ± 0.2) × 10^4.[S4a]



5

Fig. S20 The chemical structure of compound **5.**

Using the Carothers equation[S5a], the maximum possible degree of polymerization (n_{max}) could be easily provide according to the following formula:

$$n_{max} = (2K_{sp}[\text{Host}]_0)^{1/2},$$

where $[\text{Host}]_0 = 2\,[H_3]$ [S4]

Table S1. Calculated values of n_{max} for **5**⊂**H_3** at different initial concentrations of H_3 (3:2 molar ratio of **5** and H_3 in $CDCl_3$). We think the n_{max} for **G**⊂**H_3** was similar with that of **5**⊂**H_3**.

[H_3] (mM)	n_{max}
20.0	69 ± 3
17.0	64 ± 3
13.3	56 ± 2
10.0	49 ± 1
7.8	43 ± 1

4 DOSY experiments

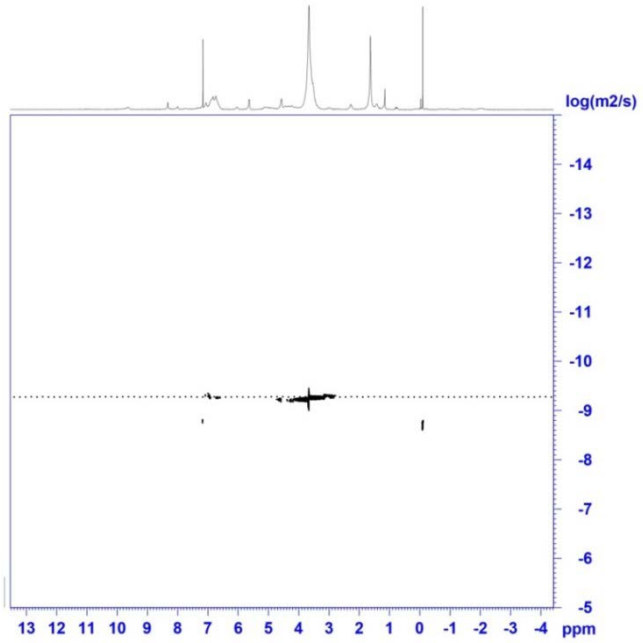


Fig. S21 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixed solution of **H₃ (**1.7 mM) and **G** (5.1 mM). One set of signals could be observed from the DOSY spectrum (D= 2.2×10^{-9} m^2 S^{-1}).

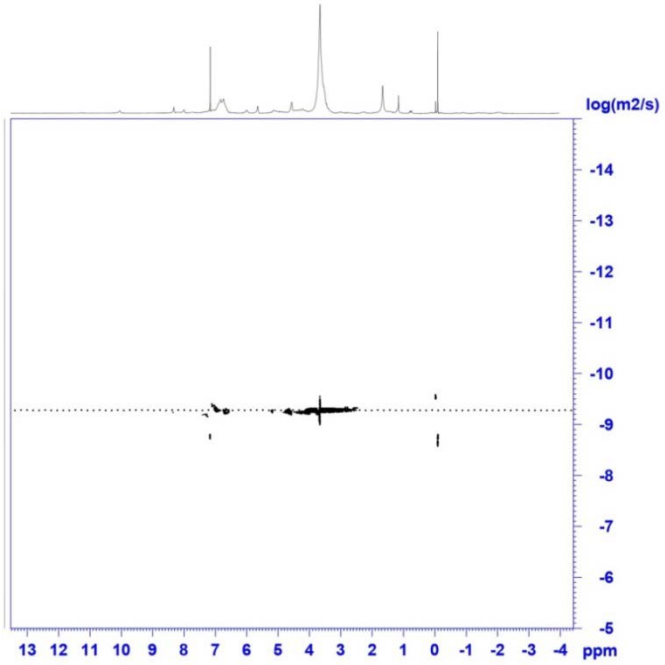


Fig. S22 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixed solution of **H₃ (**3.3 mM) and **G** (9.9 mM). One set of signals could be observed from the DOSY spectrum (D= 2.1×10^{-9} m^2 S^{-1}).

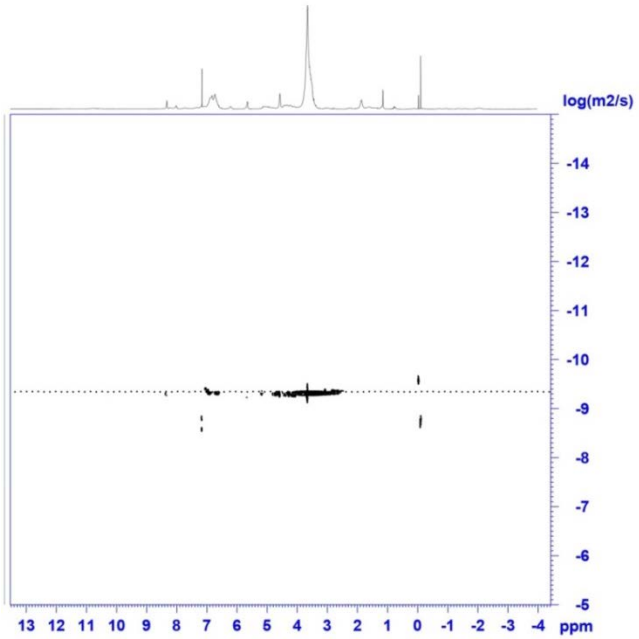


Fig. S23 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of the mixed solution of **H_3 (**6.7 mM) and **G** (20.1 mM). One set of signals could be observed from the DOSY spectrum (D= 1.5×10^{-9} m^2 S^{-1}).

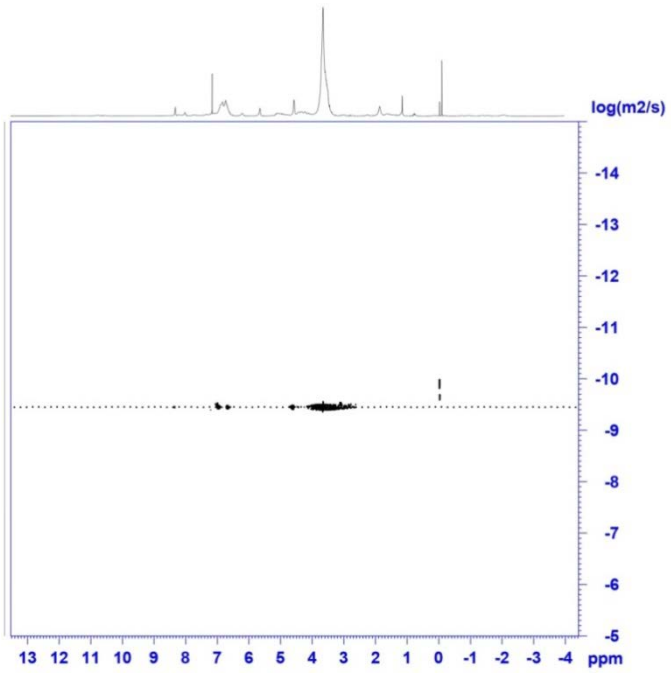


Fig. S24 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixed solution of **H_3 (**10.0 mM) and **G** (30.0 mM). One set of signals could be observed from the DOSY spectrum (D= 1.3×10^{-9} m^2 S^{-1}).

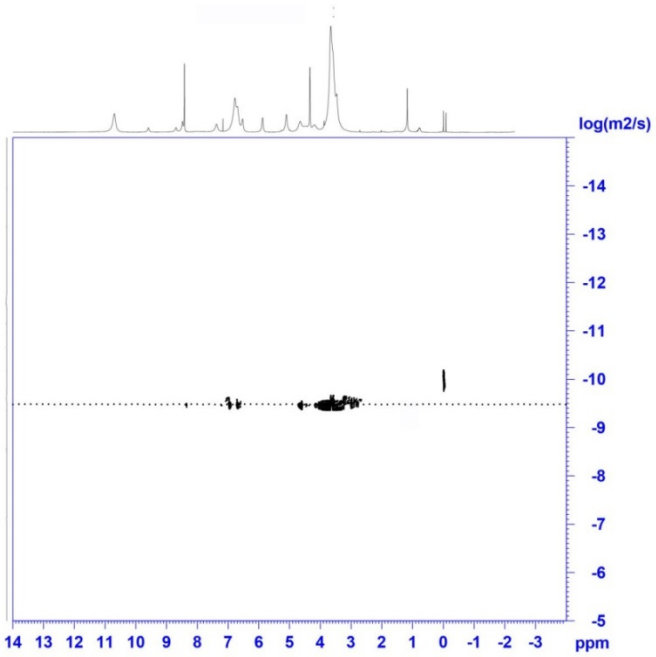


Fig. S25 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixed solution of **H_3 (**13.3 mM) and **G** (39.9 mM). One set of signals could be observed from the DOSY spectrum (D= 1.2×10^{-9} m^2 S^{-1}).

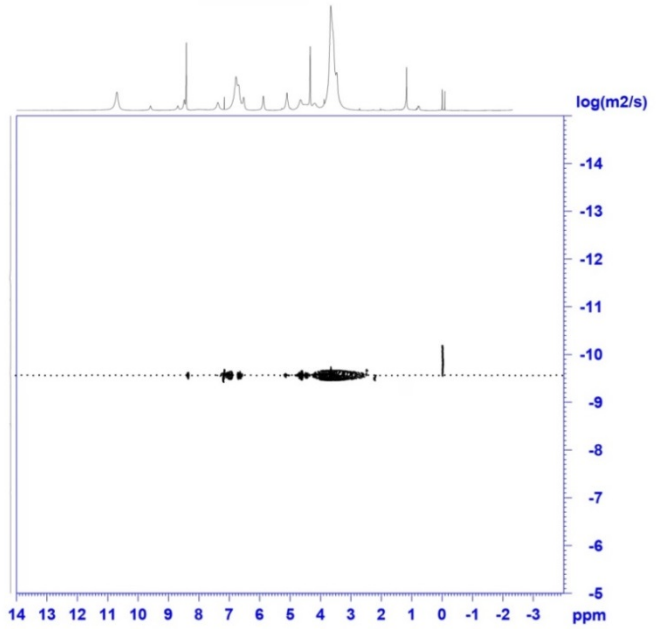


Fig. S26 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixture of **H_3 (**17 .0 mM) and **G** (51.0 mM). One set of signals could be observed from the DOSY spectrum (D= 1.0×10^{-9} m^2 S^{-1}).

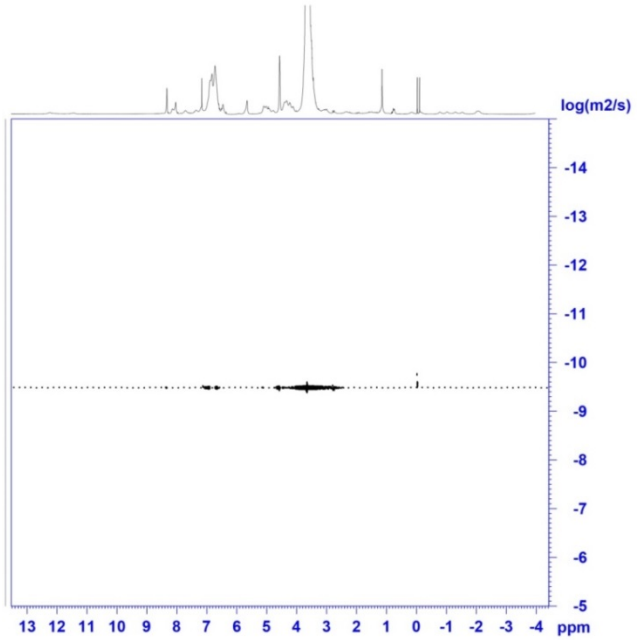


Fig. S27 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixed solution of **H_3** **(**20.0 mM) and **G** (60.0 mM). One set of signals could be observed from the DOSY spectrum (D= 6.1×10^{-10} m^2 S^{-1}).

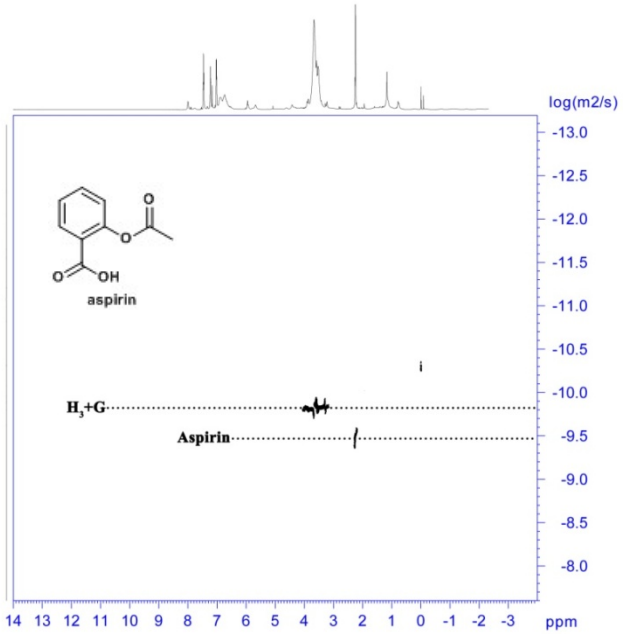


Fig. S28 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixed solution of **H_3** **(**20.0 mM), **G** (60.0 mM) and **aspirin** (60.0mM). Signals corresponding to **H_3+G** could be observed from the DOSY spectrum (D= 1.2×10^{-9} m^2 S^{-1}).

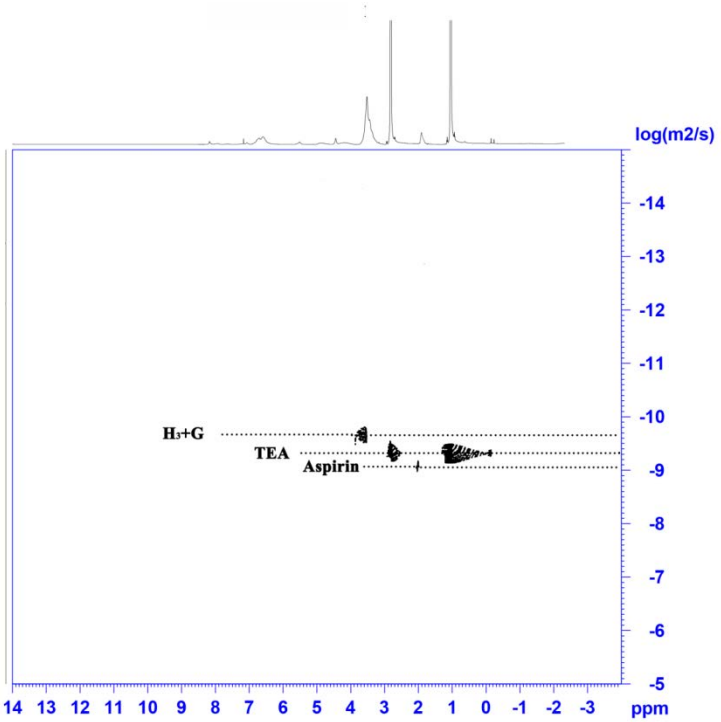


Fig. S29 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the mixed solution of **H_3** (20.0 mM), **G** (60.0 mM), **aspirin** (60.0 mM) and **Et_3N** (63.0 mM). Signals corresponding to **H_3+G** could be observed from the DOSY spectrum (D= 6.0×10^{-10} m^2 S^{-1}).

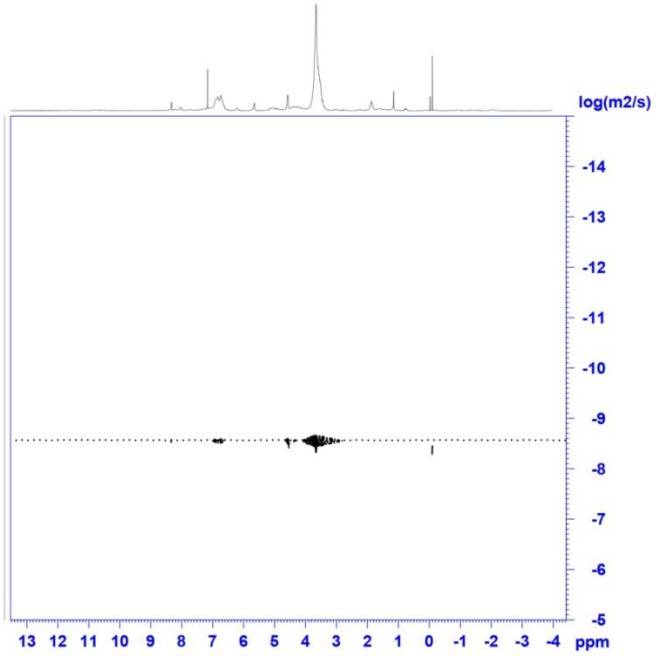


Fig. S30 DOSY NMR spectrum (600 MHz, $CDCl_3$, 323K) of the mixture of **H_3** (20.0 mM) and **G** (60.0 mM). One set of signals could be observed from the DOSY spectrum (D= 1.0×10^{-8} m^2 S^{-1}).

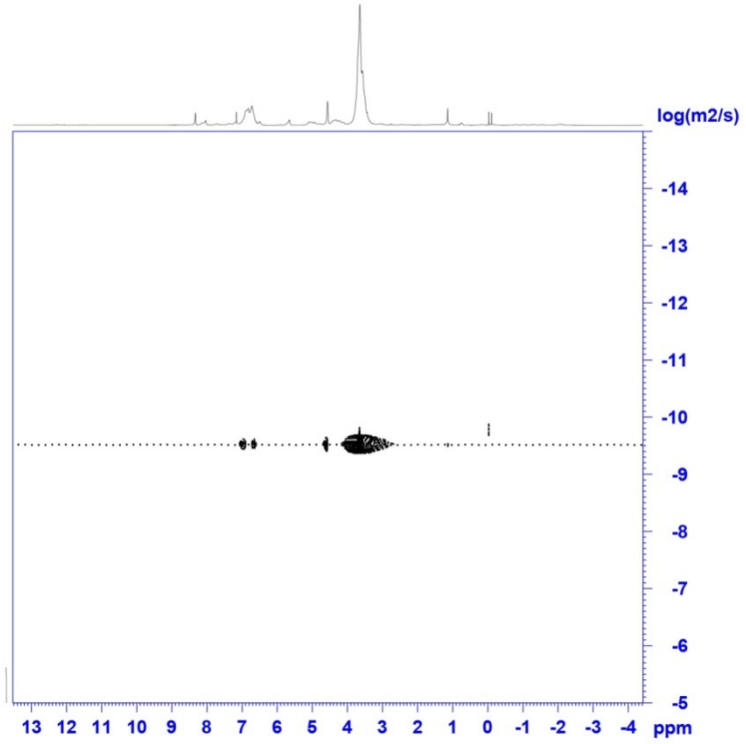


Fig. S31 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298K) of the solution cooled from 323K. One set of signals could be observed from the DOSY spectrum (D= 5.8 × 10^{-10} m^2 S^{-1}).

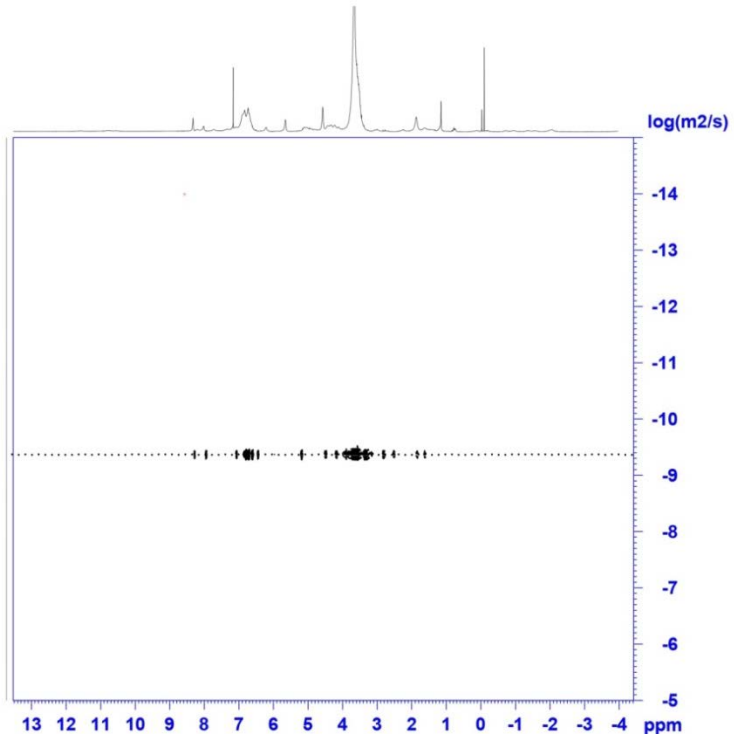


Fig. S32 DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **H_3** at 20.0 mM. One set of signals could be observed from the DOSY spectrum (D= 1.2× 10^{-9} m^2 S^{-1}).

5. Viscosity experiments

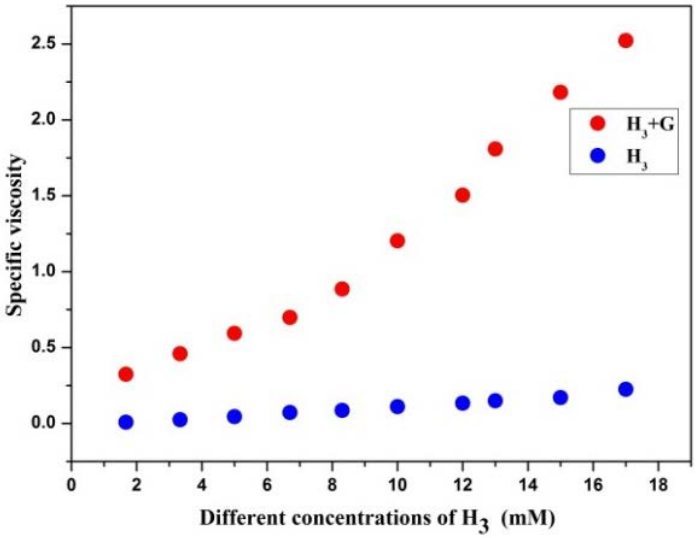


Fig. S33 Specific viscosity of **HSP-H$_3$G** (●) and **H$_3$** (●) in $CHCl_3$ at 298 K versus **H$_3$** concentration.

6. The morphology of the supramolecular polymer HSP-H$_3$G

Different concentrations of **HSP-H$_3$G** solution were used to preparing SEM samples and varisized nanoparticles were found in SEM images. Typical images were shown in Fig. S34 and large spherical nanoparticles were observed. The aggregation of the supramolecular polymers was random and thus the nanoparticles in SEM image were not uniform. Such spherical morphology was similar to the reports by Martin[S6] and Li [S7].

(a) **(b)**

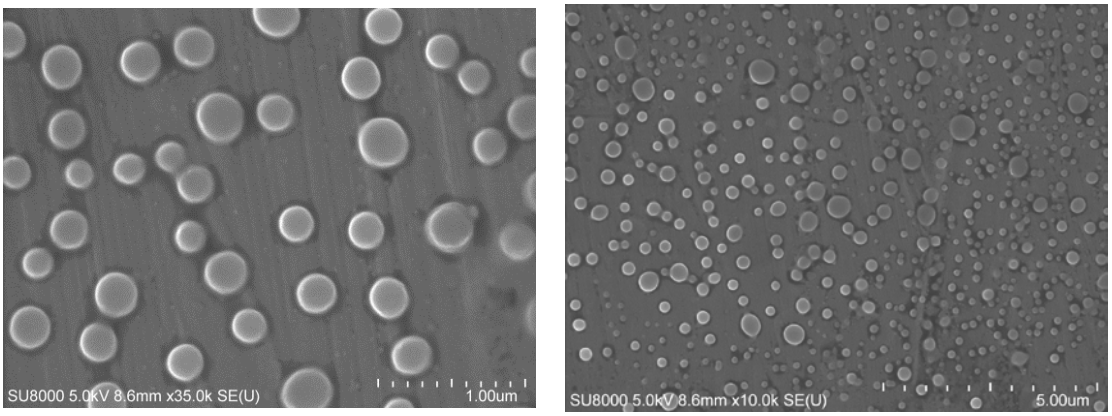


Fig. S34 SEM images of supramolecular polymer HSP-H$_3$G. (a) Sample were prepared from 20 mM solution; (b) Sample were prepared from 15

mM solution.

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