Electronic Supplementary Material (ESI) for Polymer Chemistry.

Dual-responsive cross-linked supramolecular polymer network gel : hierarchical supramolecular self-assembly driven by pillararene-based molecular recognition and metal-ligand interaction

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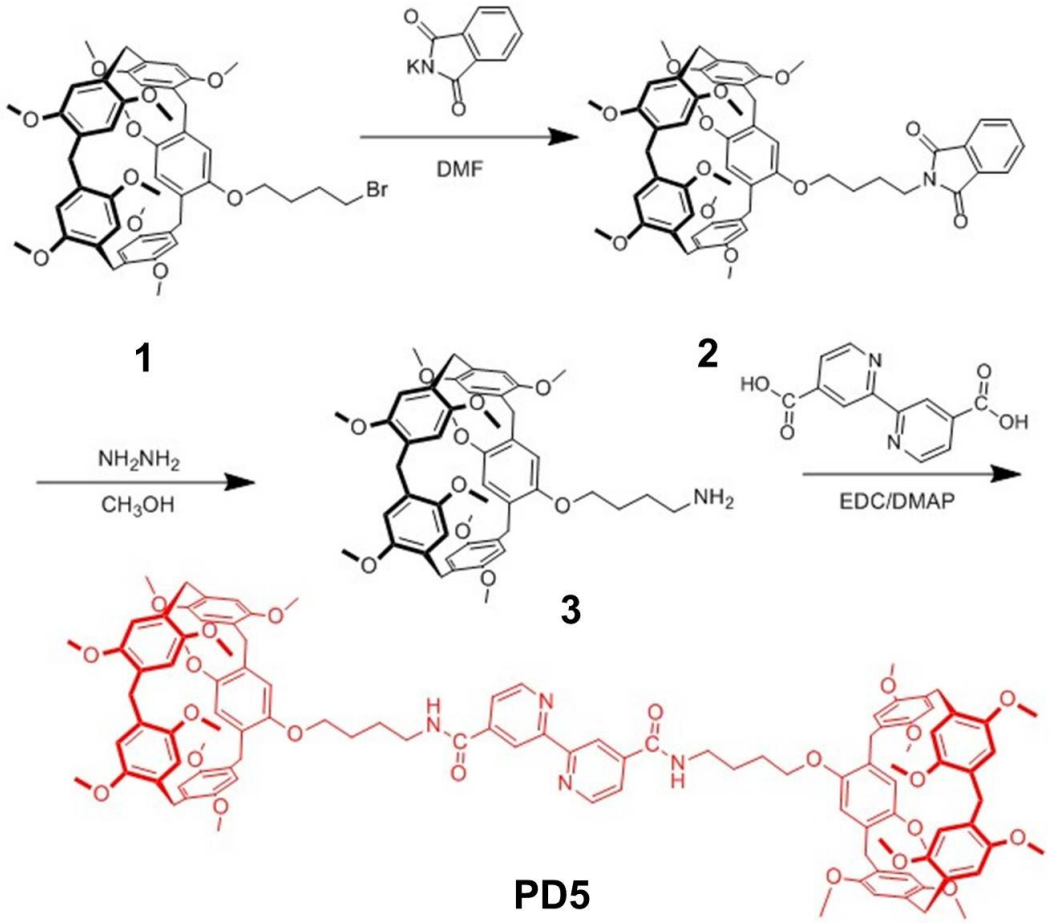
Electronic Supplementary Information (15 pages)

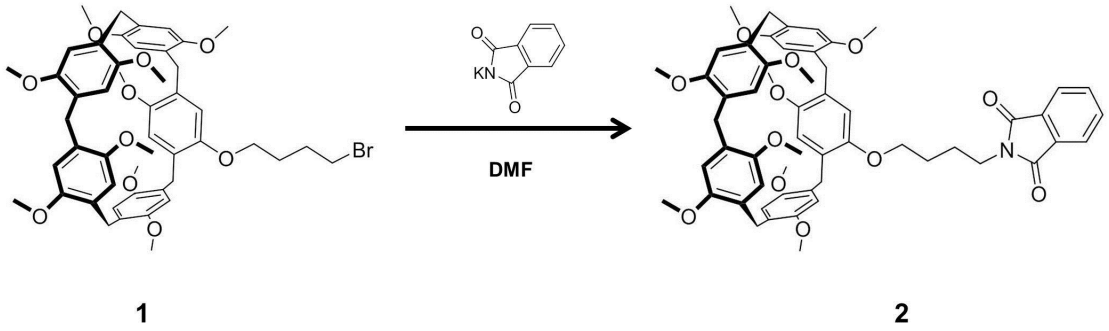
1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **1**[S1] and **G**[S2] were prepared according to the published procedures. NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and theresidual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LRESIMS) were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 298 K in water. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Dynamic light scattering was carried out on a Malvern Nanosizer S instrument at room temperature.

2. Synthesis of 2,2'-bipyridine-bridged pillar[5]arene dimers



Scheme S1. The synthetic route of **PD5**



Compound **2**: A mixture of **1** (2.00 g, 2.20 mmol) and potassium phthalimide (1.00 g, 5.00 mmol) was stirred in N, N-dimethylformamide at 90 ºC for 24 h. The solution

was evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, *v*/*v*) to afford **2** as a yellow solid (2.00 g, 93%), mp: 122.5–123.1 ºC. The ^{1}H NMR spectrum of compound **2** is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.86–7.84 (q, 2H), 7.73–7.71 (q, 2H), 6.82–6.74 (m, 10H), 3.90–3.87 (t, 2H, J = 6.4Hz), 3.80–3.74 (m, 12H), 3.69–3.67 (m, 24H), 3.63 (s, 3H), 1.98–1.91 (m, 2H), 1.89–1.82 (m, 2H). The ^{13}C NMR spectrum of **2** is shown in Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 168.96, 151.21, 151.17, 151.12, 151.10, 150.25, 134.52, 132.65, 128.89, 128.80, 123.78, 117.08, 115.38, 114.39, 114.31, 114.24, 68.39, 56.39, 56.35, 56.33, 56.27, 56.26, 56.24, 56.18, 38.36, 30.14, 30.05, 29.91, 27.81, 26.15. HRESIMS is shown in Figure S3: *m*/*z* calcd for $[M + Na]^+$ $C_{56}H_{59}NO_{12}Na^+$, 960.3929; found 960.3895, error –4 ppm.

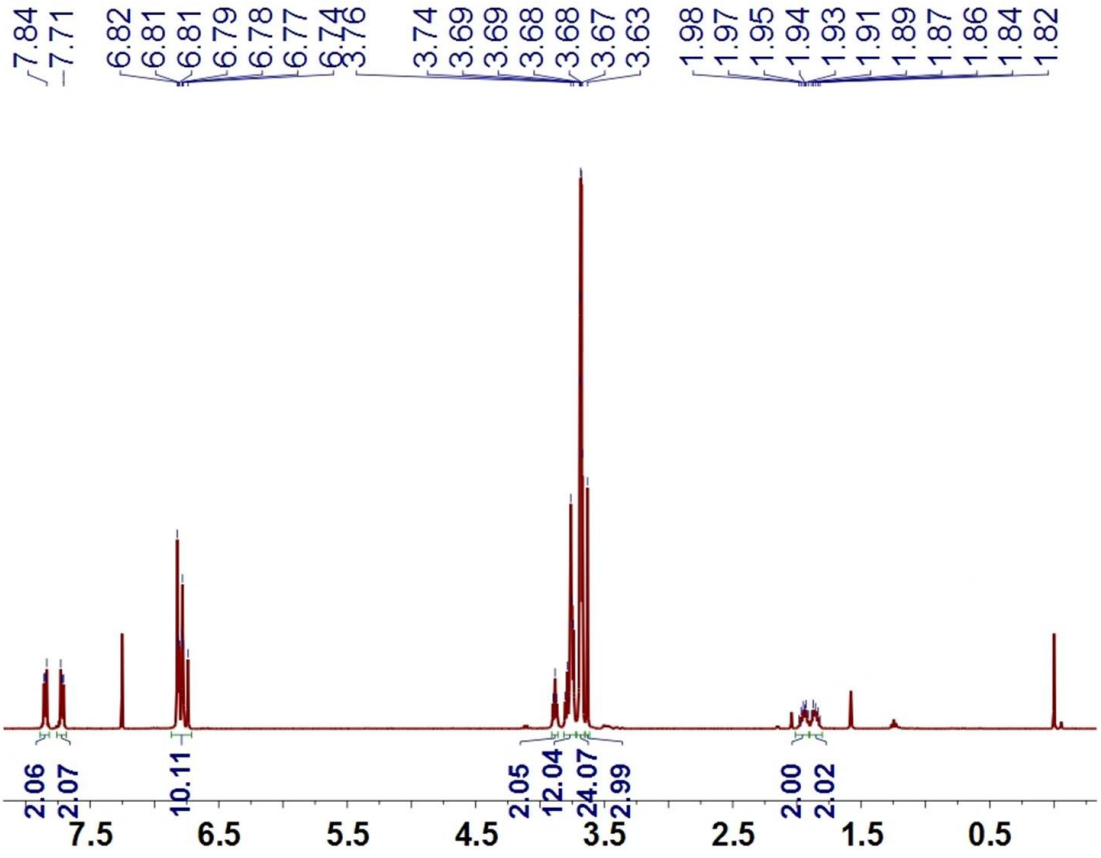


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2**.

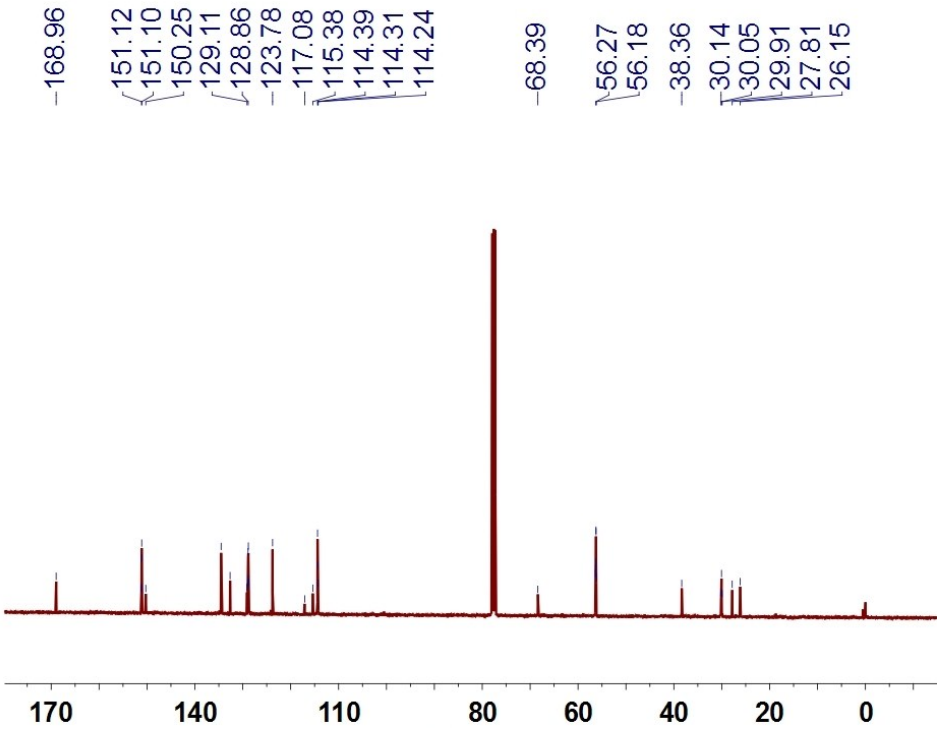


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2**.

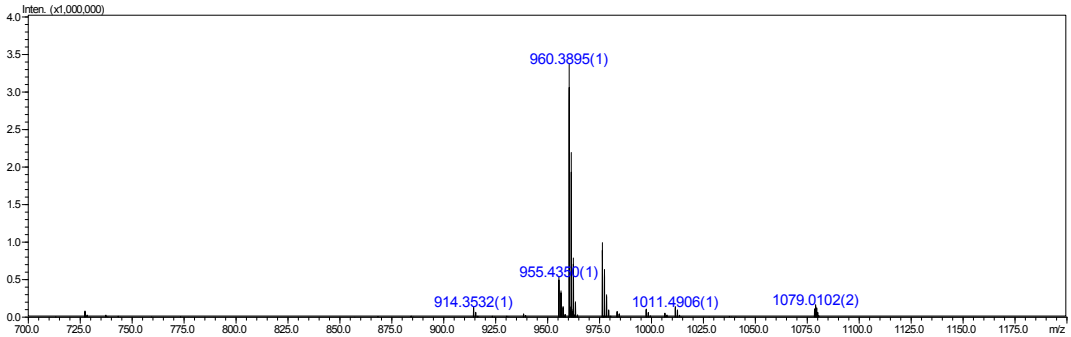
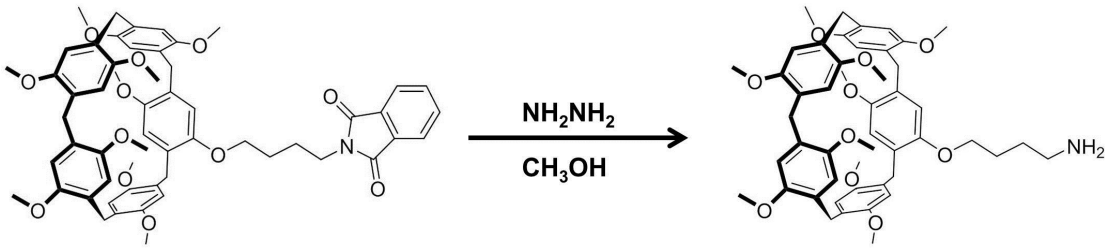


Figure S3. HRESI mass spectrum of **2**.



2 **3**

Compound **3**: A mixture of **2** (1.00 g, 1.06 mmol) and NH_2NH_2 (10 mL) was heated at reflux in methanol (20 mL) for 12 h. Then the mixture was filtered and the residue was washed with methanol (10 mL × 2) to give **3** as a white solid (0.51 g, 60%), mp: 144.4–145.1 ºC. The ^{1}H NMR spectrum of compound **3** is shown in Figure S4. ^{1}H

NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.82–6.75 (m, 10H), 3.81–3.76 (m, 12H), 3.70–3.64 (m, 27H), 2.13 (s, 2H), 1.58 (s, 2H), 1.21(s, 2H). The ^{13}C NMR spectrum of **3** is shown in Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.88, 150.80, 150.76, 150.72, 150.69, 150.67, 150.65, 150.61, 149.87, 128.61, 128.46, 128.39, 128.34, 128.29, 128.22, 128.15, 128.08, 114.87, 114.50, 114.13, 114.04, 113.95, 113.88, 113.56, 68.65, 56.09, 55.94, 55.88, 55.86, 55.78, 55.71, 55.62, 40.95, 30.06, 29.78, 29.72, 29.59, 29.36, 26.78. LRESIMS is shown in Figure S6: *m/z* 808.6 $[M + H]^+$; *m/z* calcd for $[M + H]^+$ $C_{48}H_{58}NO_{10}^+$, 808.4055; found 808.4026, error –4 ppm.

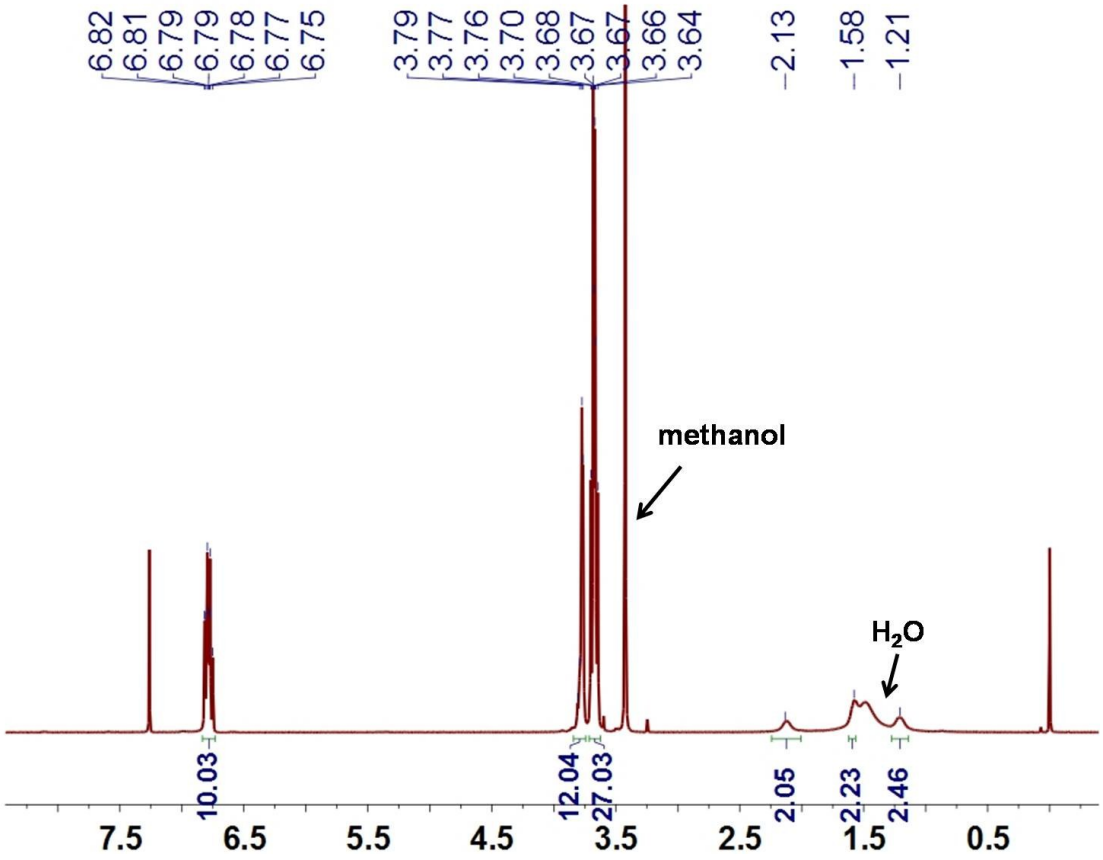


Figure S4. ^1H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3**.

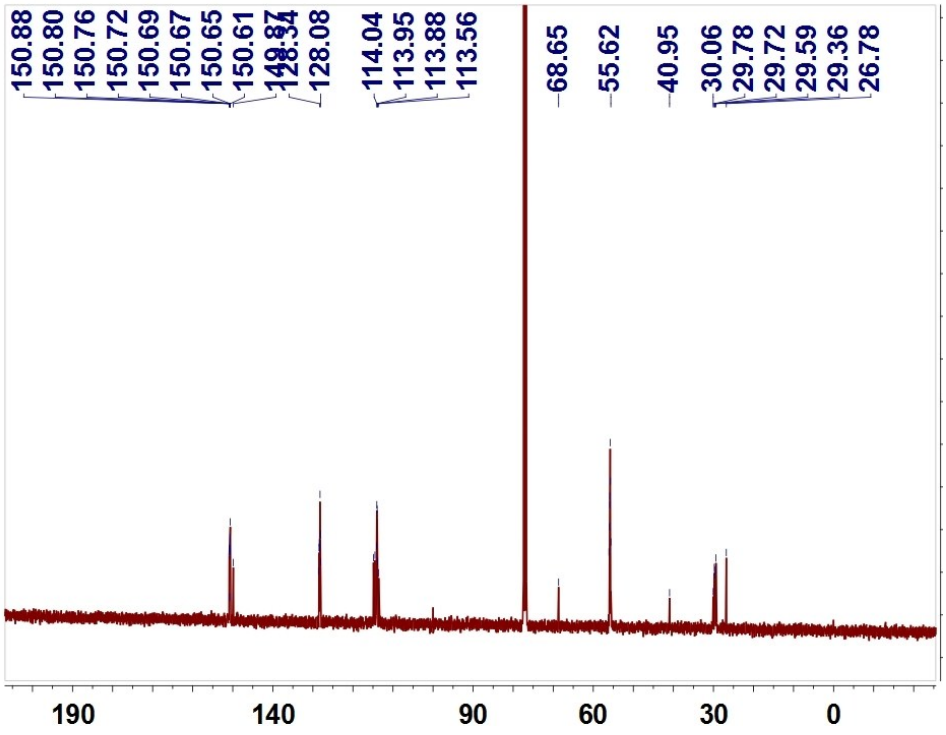


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3**.

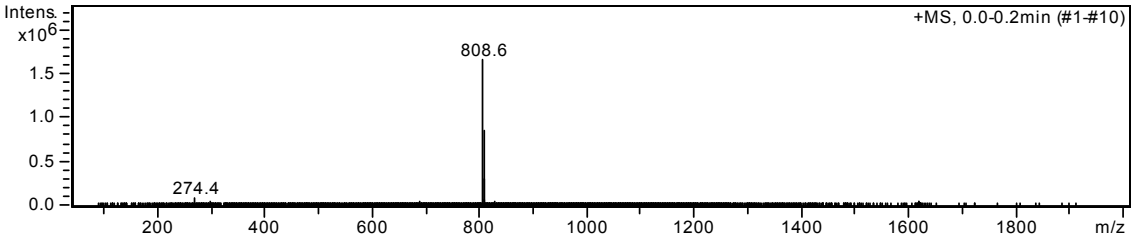
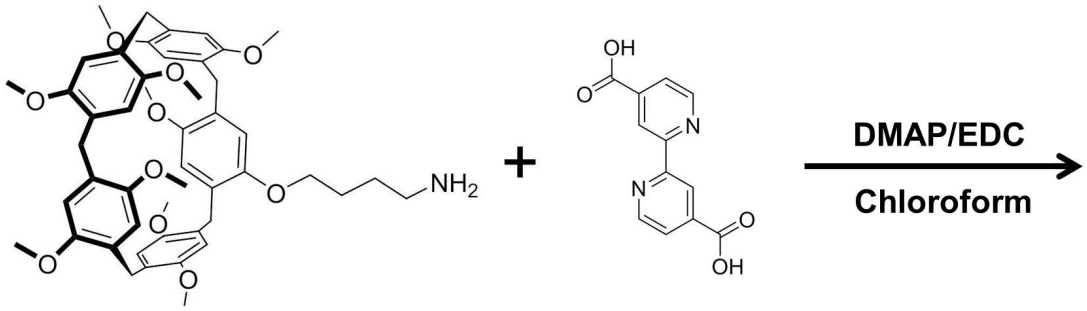
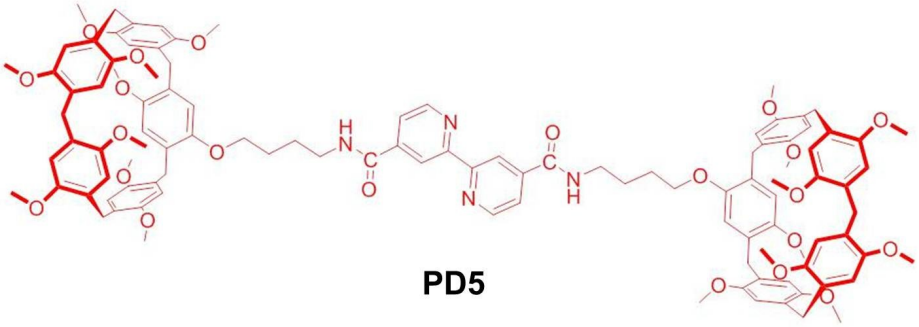


Figure S6. LRESI mass spectrum of **3**.



3



PD5

Compound **PD5**: DMAP (catalytic amount) and EDC (0.96 g, 5.00 mmol) were added to a solution of **3** (2.00 g, 2.48 mmol) and 2, 2'-bipyridine-4, 4'-dicarboxylic acid (0.30 g, 1.23 mmol) in chloroform (50 ml), and then the mixture was stirred for 48 h at room temperature. The organic layer was washed with water, saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel eluted with $CHCl_3$/MeOH of 100:1 to 10:1 ratio (*v*/*v*) to afford **PD5** as a pink solid (680 mg, 30%), mp: 187.5–188.5 ºC. The ^{1}H NMR spectrum of compound **PD5** is shown in Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.78–8.76 (d, 2H, J = 4.8 Hz), 8.70 (s, 2H), 7.78–7.77 (d, 2H, J = 4.8 Hz), 6.85 (s, 2H), 6.80–6.72 (m, 20H), 3.86 (s, 4H), 3.76–3.74 (m, 20H), 3.66 (m, 36H), 3.62 (m, 12H), 3.59 (s, 6H), 3.54–3.53 (d, 4H), 1.81 (s, 8H). The ^{13}C NMR spectrum of **PD5** is shown in Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 165.47, 156.02, 151.04, 150.76, 150.69, 150.15, 149.73, 142.96, 128.68, 128.43, 128.31, 128.25, 128.22, 128.15, 128.10, 122.24, 117.54, 114.79, 114.67, 114.15, 114.08, 113.96, 113.94, 113.88, 67.62, 56.43, 55.91, 55.84, 55.80, 55.79, 55.71, 55.69, 53.29, 50.88, 40.01, 29.90, 29.57, 29.49, 27.09, 26.52. LRESIMS is shown in Figure S9: *m/z* 1846.7 $[M + Na]^+$ (50%), *m/z* 935.5 $[M + 2Na]^{2+}/2$ (100%); *m/z* calcd for $[M + Na]^+$ $C_{108}H_{118}N_4O_{22}^+$,

1846.8163; found 1846.8192, error 2 ppm.

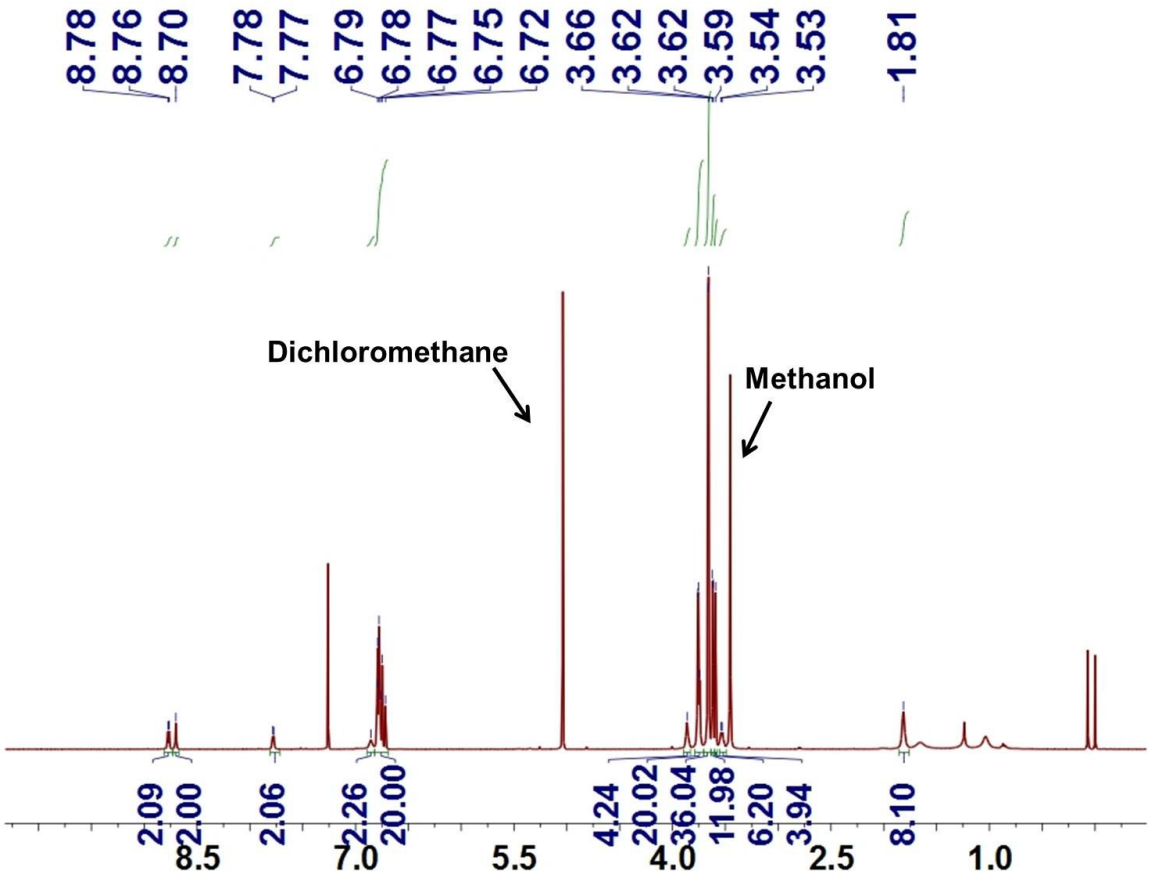


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **PD5**.

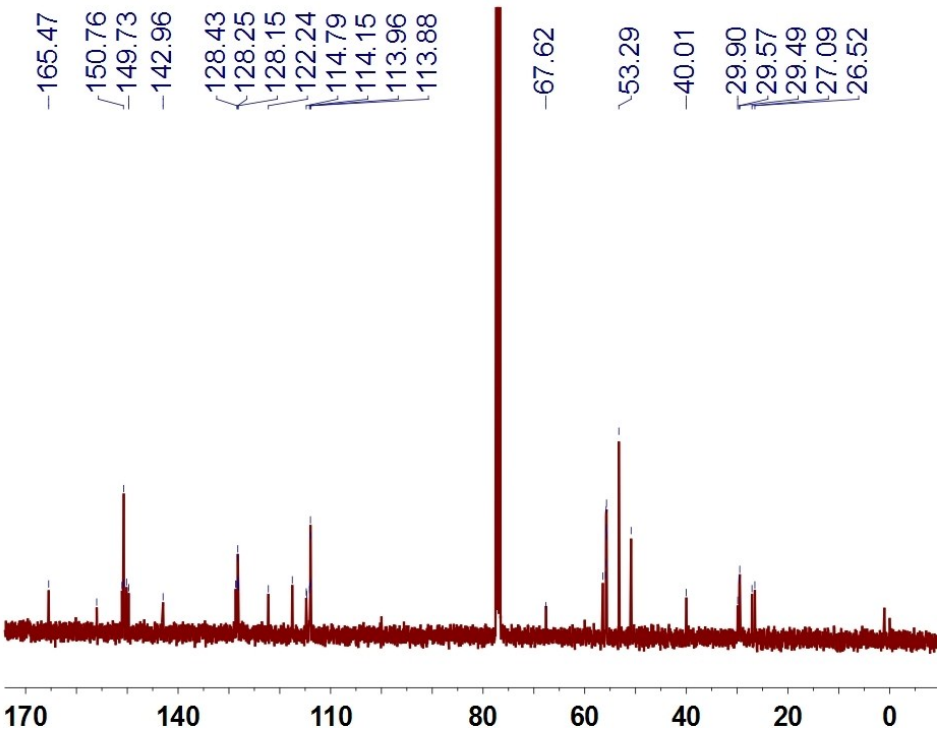


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **PD5**.

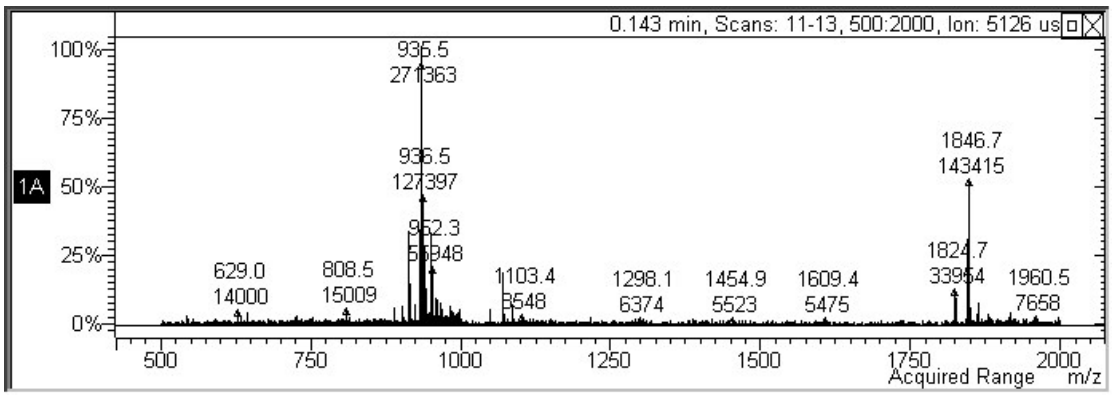


Figure S9. LRESI mass spectrum of **PD5**.

*3. Partial DOSY NMR spectra of a mixture of **PD5** and **G** in different concentrations.*

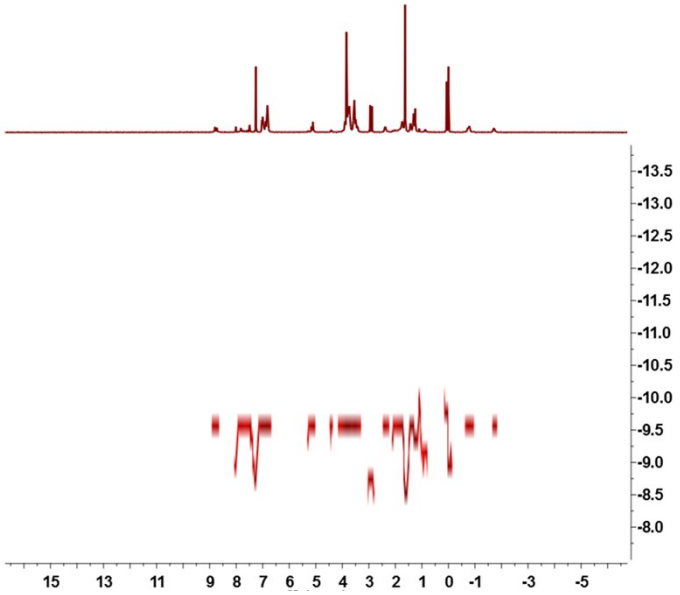


Figure S10. DOSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***PD5*** *and* ***G*** at 5.00 mM.

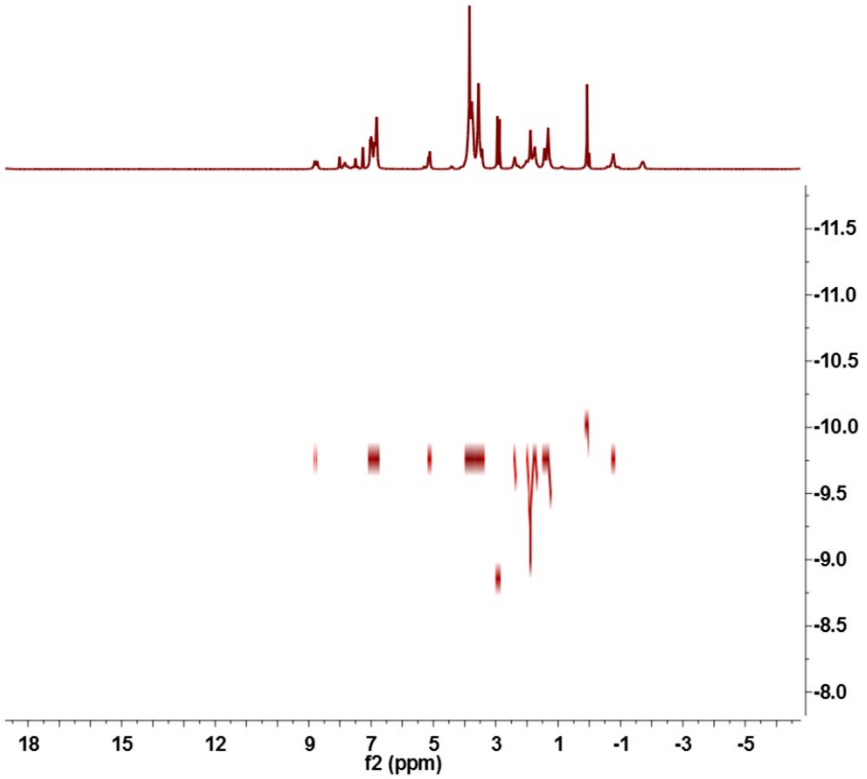


Figure S11. DOSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***PD5*** *and* ***G*** at 20.0 mM.

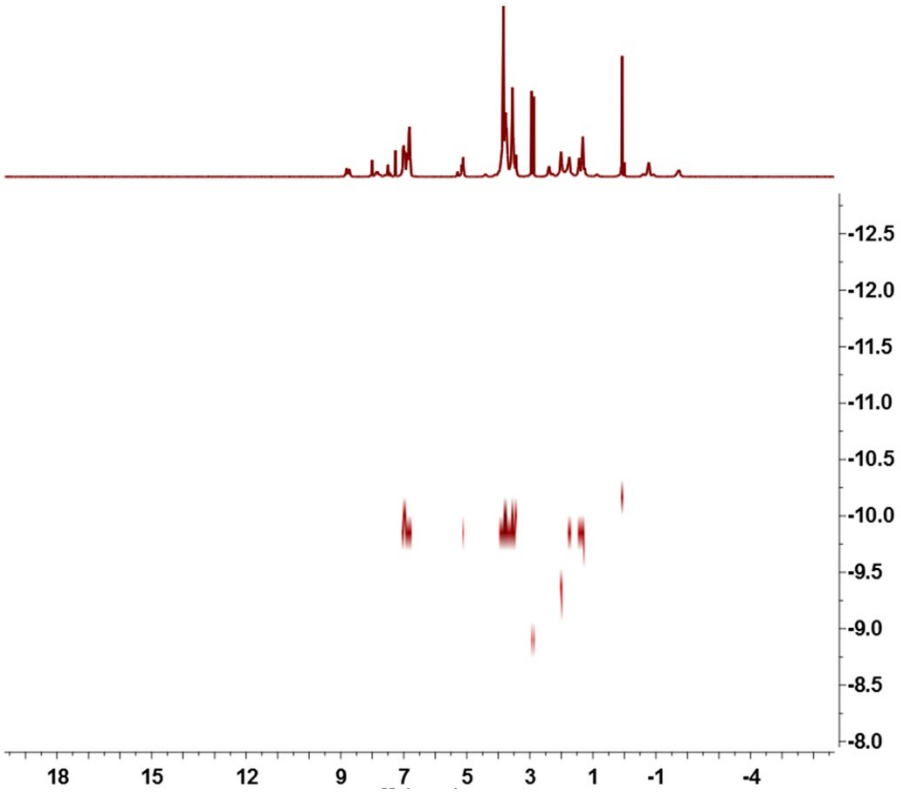


Figure S12. DOSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***PD5*** *and* ***G*** at 30.0 mM.

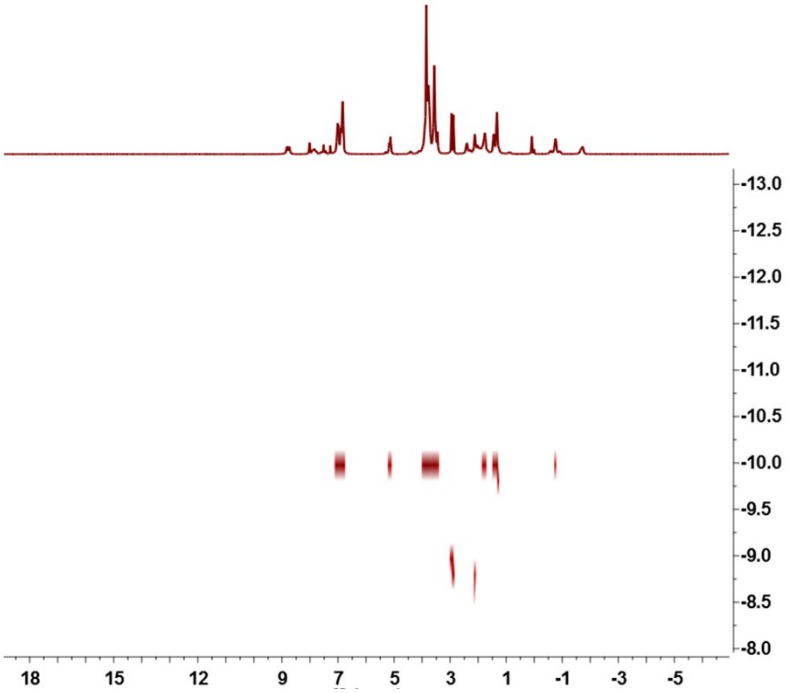


Figure S13. DOSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***PD5*** *and* ***G*** at 45.0 mM.

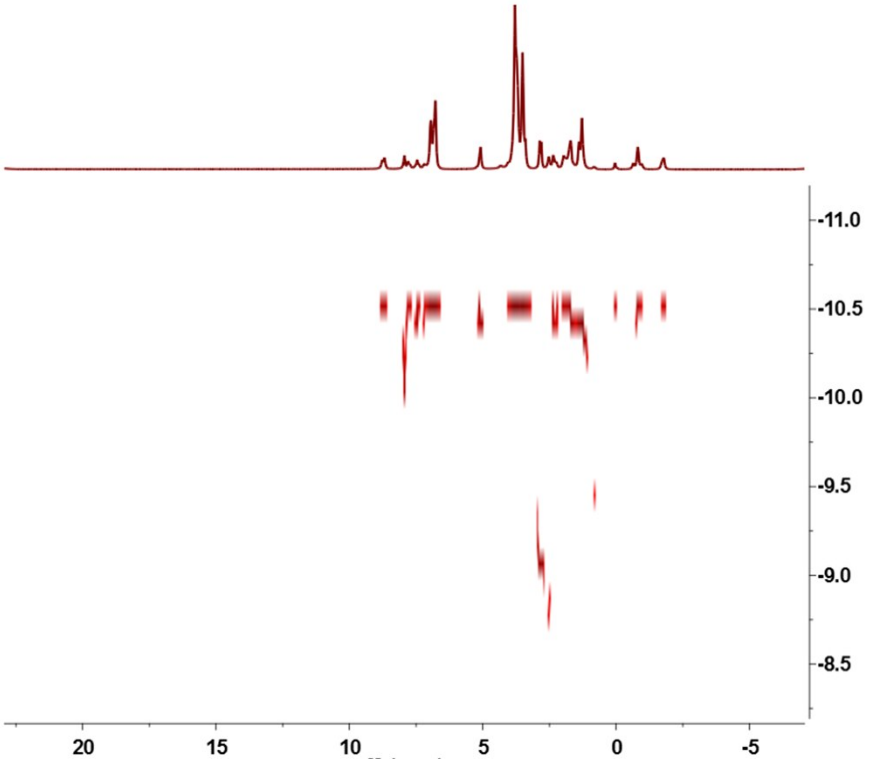


Figure S14. DOSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***PD5*** *and* ***G*** at 80.0 mM.

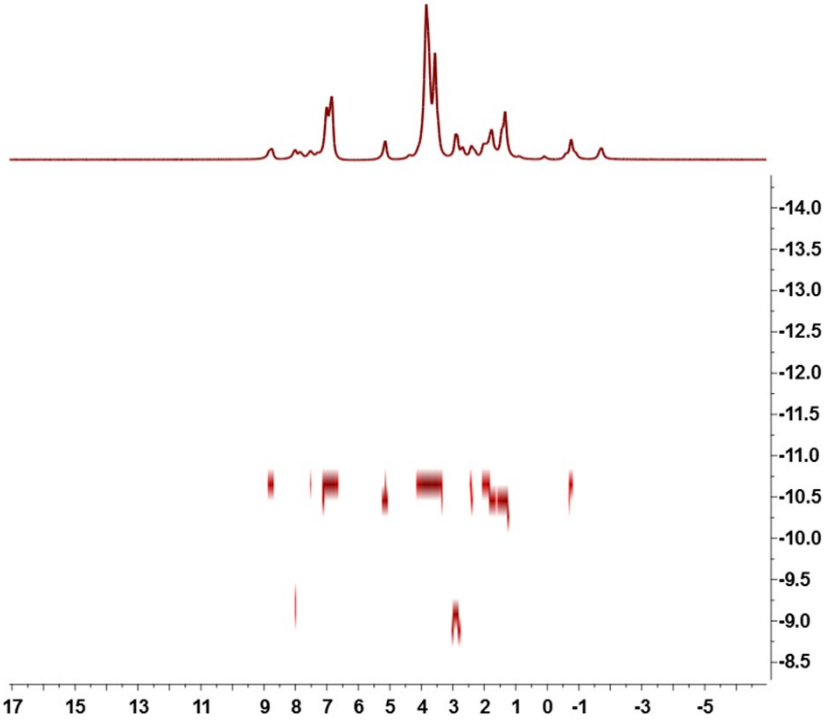


Figure S15 DOSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***PD5*** *and* ***G*** at 100 mM.

4. Size distributions of ***PD5*** *and* ***PD5*** *+* ***G.***

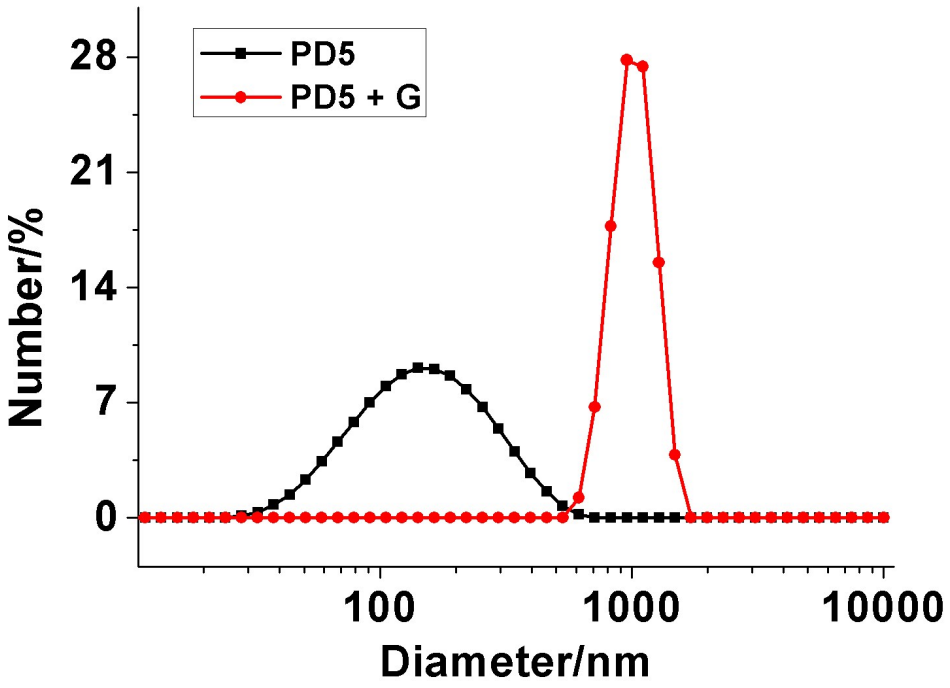


Figure S16 Size distributions of **PD5** and **PD5** + **G** (c = 55.0 mM).

*5. Partial ^{1}H NMR spectra of **PD5** and **PD5** + **G** in the presence and absence of **Zn^{2+}** in $CDCl_3$*

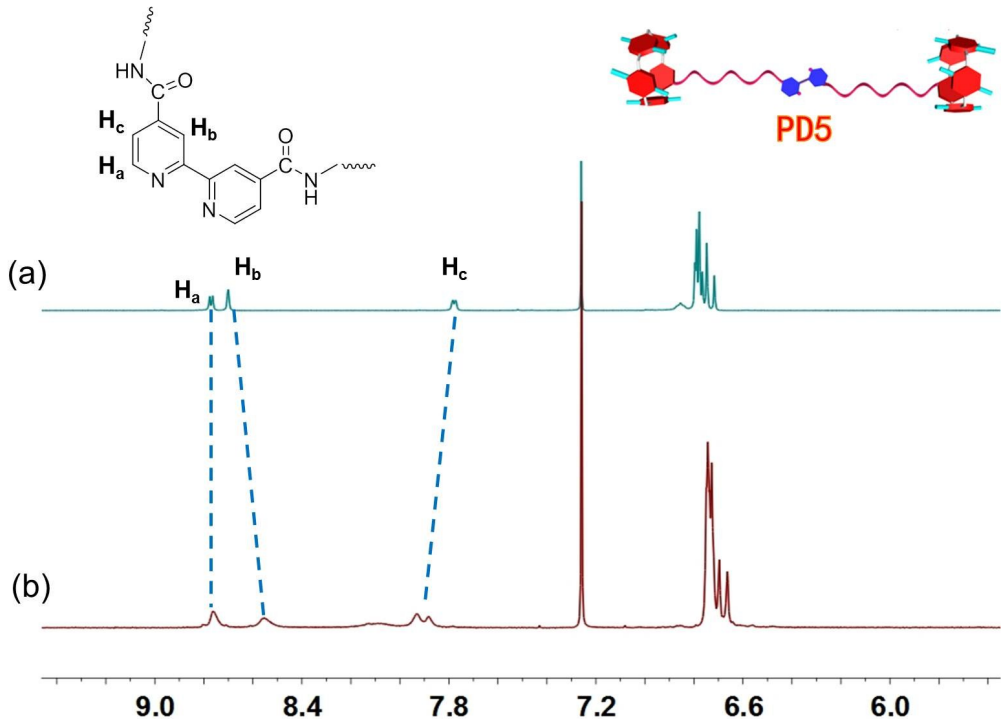


Figure S17 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of 5.00 mM **PD5** in the absence (a) and presence (b) of 0.33 equiv. of $Zn(NTf_2)_2$.

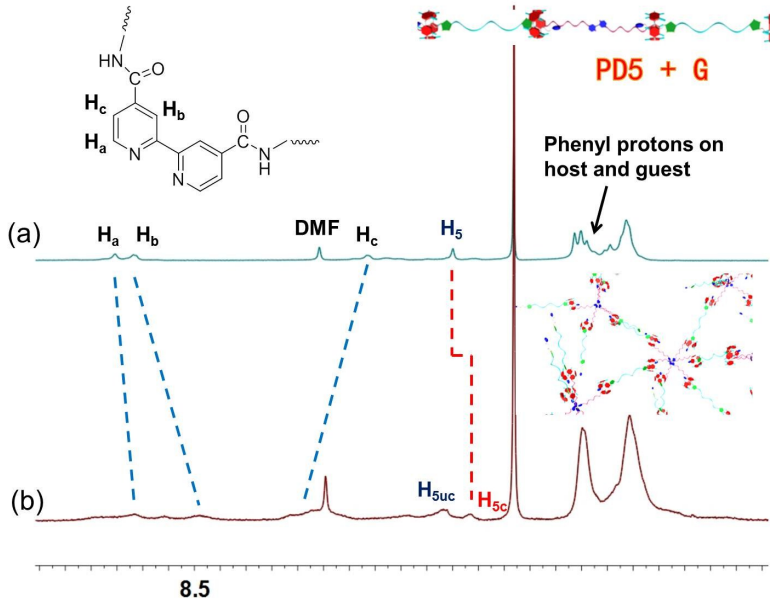


Figure S18 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of 20.0 mM **PD5** and **G** in the absence (a) and presence (b) of 0.33 equiv. of $Zn(NTf_2)_2$.

6. Reduced viscosity

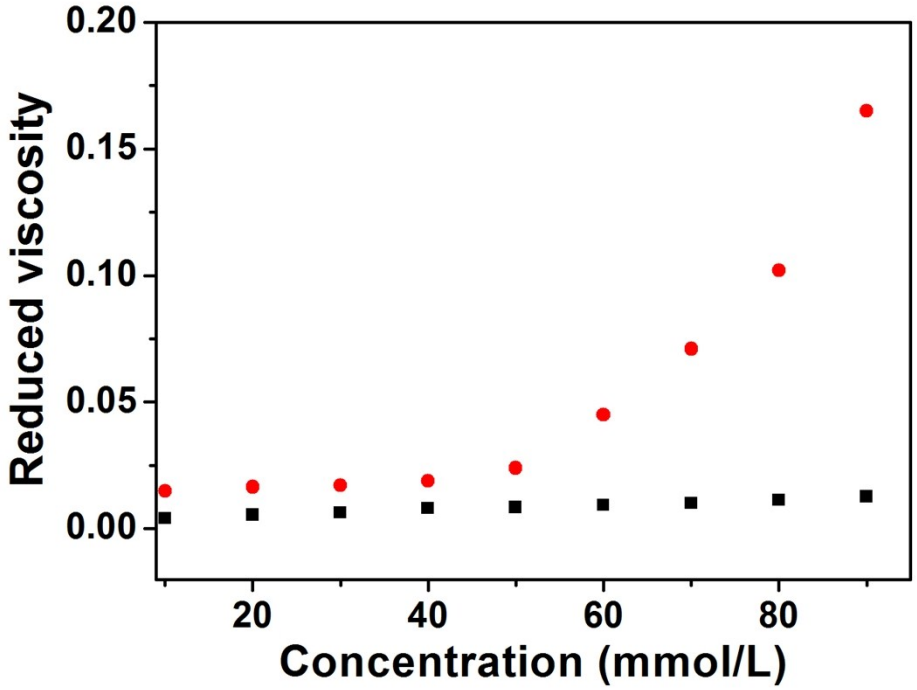


Figure S19 Reduced viscosity (chloroform 298 K) of a 1:1 molar mixture of **PD5** and **G** (■) and 1:3:3 molar mixture of $\mathbf{Zn^{2+}}$, **PD5** and **G** (●).

7. *The rheological properties of the gel*

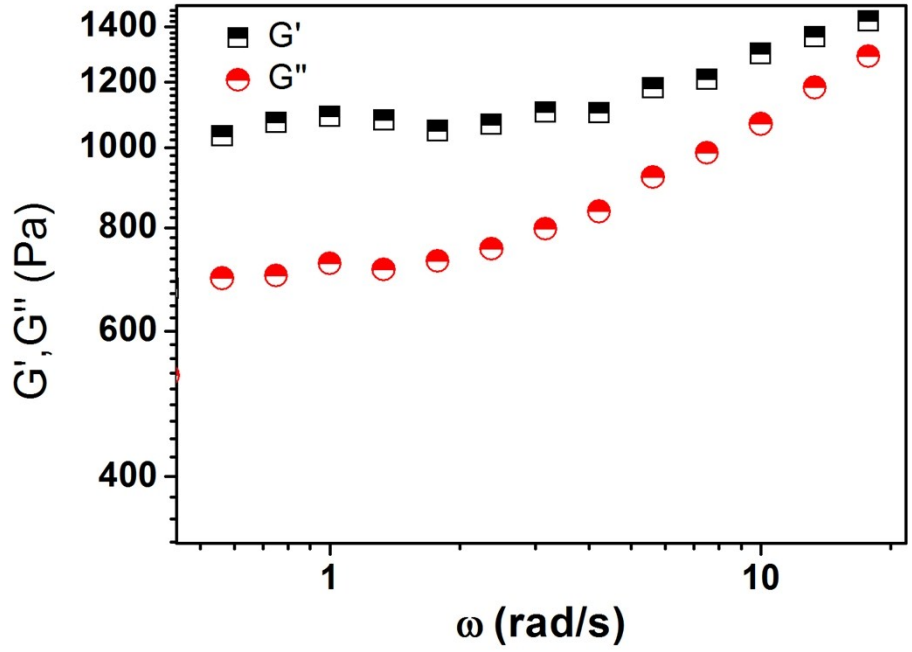


Figure S20 Frequency dependency of the storage modulus *G'* and loss modulus *G''* of the gel.

8. References:

S1. J. Yang, Z. Li, Y. Zhou and G. Yu, *Polym. Chem.*, 2014, **5**, 6645−6650.

S2. B. Shi, K. Jie, Y. Zhou, D. Xia and Y. Yao, *Chem. Commun*., 2015, **51**, 4503−4506.