

Electronic Supplementary Information

for

Synthesis of disulfide-bridged bispillar[5]arene and its application in supramolecular polymers

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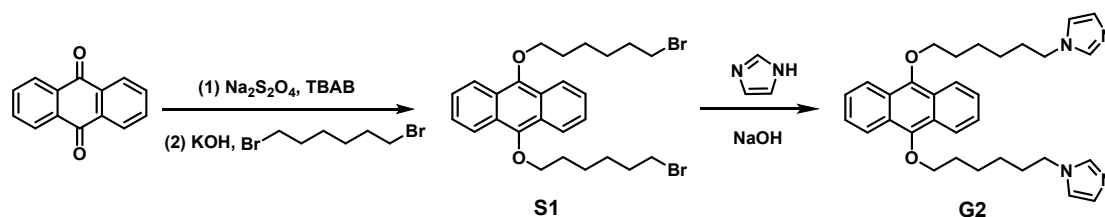
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1. Synthesis and characterization

Preparation of G1

The synthesis of **G1** was according to the previous report.^{S1} ¹H NMR (CDCl₃, 400 MHz): δ 7.45 (s, 2H), 7.05 (s, 2H), 6.90 (s, 2H), 3.94-3.90 (t, 4H), 1.78-1.74 (m, 4H), 1.29-1.24 (m, 16H). ¹³C NMR (CDCl₃, 100 MHz): δ 137.05, 129.30, 118.76, 47.01, 31.04, 29.39, 29.35, 29.02, 26.50.

Preparation of G2

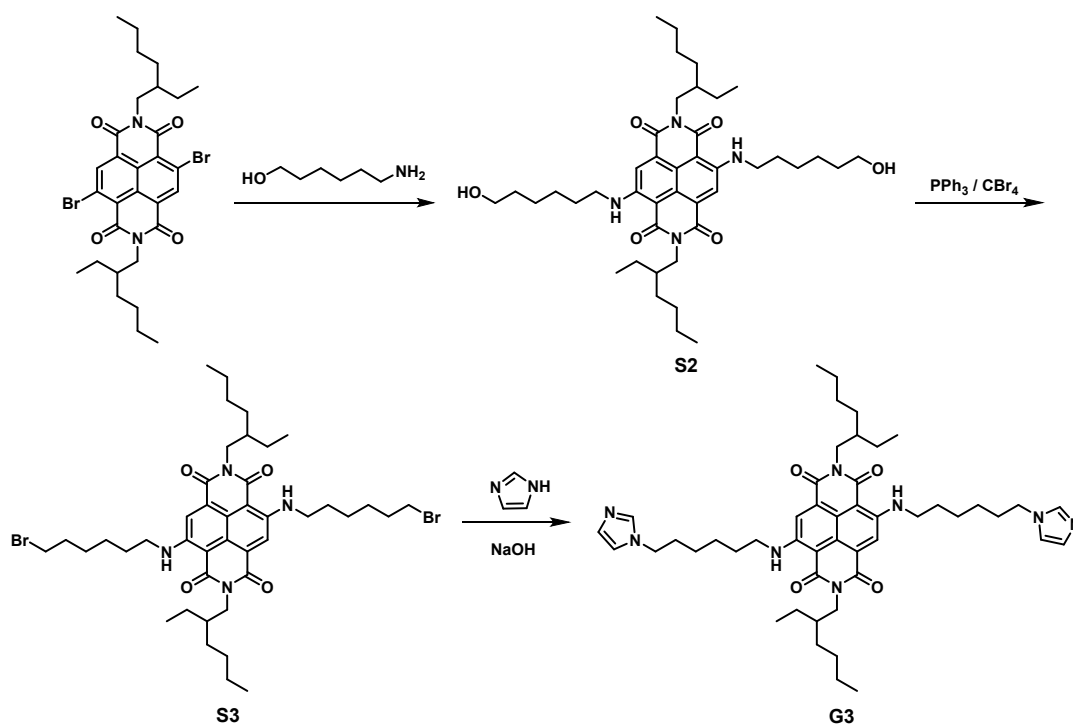


Scheme S1 Synthesis of blue-emitting bisimidazole **G2**.

(**S1**) To a solution of 9, 10-anthraquinone (1.50 g, 7.2 mmol) and tetrabutylammonium bromide (0.161 g, 0.50 mmol) in 30 mL CH₂Cl₂, was added 10 mL of sodium dithionite (15.1 g, 86 mmol) aqueous solution. After 15 minutes, aqueous KOH (16.8 g, 300 mmol) was added. After another 15 minutes, hexamethylene dibromide (46.9 mL, 192.10 mmol) was added and the reaction mixture was stirred overnight at room temperature. The mixture was then extracted with CH₂Cl₂ by three times, dried over anhydrous Na₂SO₄. After the removal of solvent by rotary evaporation, the residue was purified with column chromatography (petroleum ether/CH₂Cl₂ =1:1, v/v). **S1** (1.58 g, 2.9 mmol) was obtained as pale yellow solid. Yield: 41%. ¹H NMR (CDCl₃, 400 MHz): δ 8.26-8.24 (q, 4H), 7.47-7.45 (q, 4H), 4.16-4.12 (t, 4H), 3.46-3.42 (t, 4H), 2.07-2.00 (m, 4H), 1.98-1.91 (m, 4H), 1.72-1.65 (m, 4H), 1.62-1.53 (m, 4H).

(**G2**) A mixture of NaOH (0.151 g, 3.8 mmol) and imidazole (0.286 g, 4.2 mmol) in 5mL DMF was heated at 60°C for 2 h, followed by the addition of **S1** (0.211 g, 0.42 mmol). The resulting mixture was maintained at 60°C for another 2h. 100 mL brine was added into the cooled flask. After extraction with diethyl ether by three times, the combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation to afford product **G2** as pale yellow solid (0.206 g, 0.40 mmol). Yield: 96%. ¹H NMR (400 MHz, CDCl₃): δ 8.226-8.251 (q, 4H), 7.49-7.46 (m, 5H), 7.07(s, 2H), 6.93(s, 2H), 4.16-4.13 (t, 4H), 4.00-3.96 (t, 4H), 2.04-2.00 (m, 4H), 1.91-1.87 (m, 4H), 1.73-1.69 (m, 4H), 1.48-1.45 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 147.39, 137.08, 129.45, 125.25, 125.11, 122.62, 118.76, 75.74, 46.93, 31.04, 30.46, 26.55, 25.82. HR-ESI-MS: m/z Calcd for [M+H]⁺ C₃₂H₃₈N₄O₂: 511.3058; found: 511.3068, error: 2.0 ppm.

Preparation of G3



Scheme S2 Synthesis of red-emitting bisimidazole **G3**.

(**S2**) 6-Amino-1-hexanol (1.00 g, 8.5 mmol) and dibromonaphthalene bisimide (0.100 g, 0.15 mmol) were refluxed at 140°C for 1h. After cooling to room temperature, 200mL CH₂Cl₂ was added, the resulting solution was washed with dilute AcOH (glacial acetic acid/H₂O, 6mL/100 mL) and brine in turns and dried over anhydrous Na₂SO₄. Removal of the solvent and purification by column chromatography (CH₂Cl₂/CH₃OH =20:1, v/v) afforded **S2** as blue dye (0.776g, 0.11mmol). Yield: 73%. ¹H NMR (CDCl₃, 400 MHz): δ 9.37-9.34 (t, 2H), 8.12 (s, 2H), 4.16-4.06 (m, 4H), 3.70-3.68 (t, 4H), 3.53-3.48 (t, 4H), 1.96-1.90 (m, 2H), 1.86-1.71(m, 4H), 1.67-1.60(m, 4H), 1.54-1.49 (m, 8H), 1.40-1.26 (m, 16H), 0.95-0.87 (m, 12H).

(**S3**) To a stirred solution of **S2** (0.721 g, 0.10 mmol) in 10 mL dry CH₂Cl₂, 5 drops of acetone, CBr₄ (0.133 g, 0.40 mmol) and PPh₃ (0.105 g, 0.40 mmol) were added in sequence. The resulting mixture was stirred for 10 min and then purified with column chromatography (petroleum ether/CH₂Cl₂ =1:2, v/v) to afford the product **S3** (0.711 g 0.084 mmol). Yield: 84%. ¹H NMR (CDCl₃, 400 MHz): δ 9.35-9.32 (t, 2H), 8.08 (s, 2H), 4.15-4.05 (m, 4H), 3.52-3.47 (q, 4H), 3.45-3.42 (t, 4H), 1.95-1.89 (m, 6H), 1.86-1.79(m, 4H), 1.55-1.54 (t, 8H), 1.38-1.29 (m, 16H), 0.93-0.87 (m, 12H).

(**G3**) The procedure from **S3** to **G3** was similar with the preparation of **G2**. The pure product was blue solid (0.066g, 0.81mmol). Yield: 95%. ¹H NMR (CDCl₃, 400 MHz): δ 9.35-9.32 (t, 2H), 8.08 (s, 2H), 7.48 (s, 2H), 7.06 (s, 2H), 6.92 (s, 2H), 4.15-4.05 (m, 4H), 3.98-3.95 (t, 4H), 3.50-3.45 (q, 4H), 1.95-1.89 (m, 2H), 1.88-1.76(m, 8H), 1.55-1.51 (t, 4H), 1.44-1.29 (m, 20H), 0.94-0.86 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.58, 163.47, 149.14, 129.45, 125.77, 121.21, 118.79, 118.34, 101.88, 46.93, 44.10, 42.94, 37.91, 31.02, 30.77, 29.71, 29.20, 28.68, 26.60, 26.30, 24.08, 23.11, 14.11, 10.72. HR-ESI-MS: m/z Calcd for [M+H]⁺ C₄₈H₆₉N₈O₄: 821.5441; found: 821.5436, error: -0.6 ppm.

2. Copies of the NMR spectra

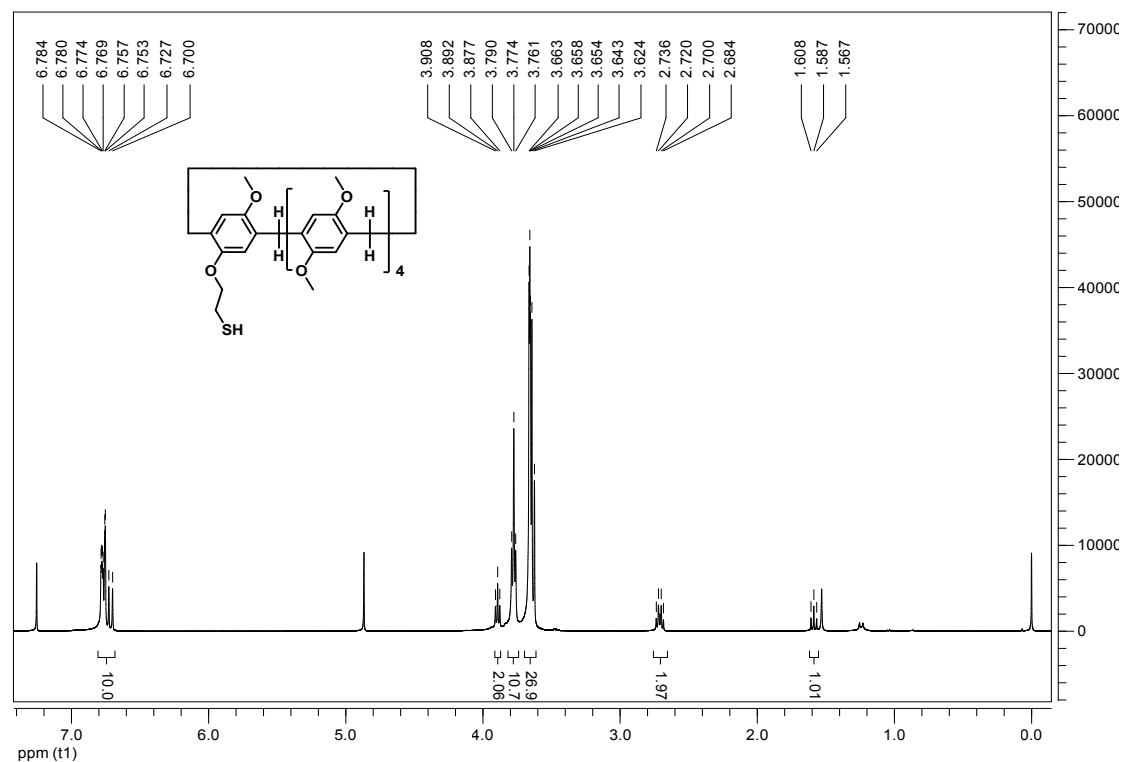


Fig. S1 (a) ¹H NMR spectrum (CDCl₃, 400 MHz) of H1.

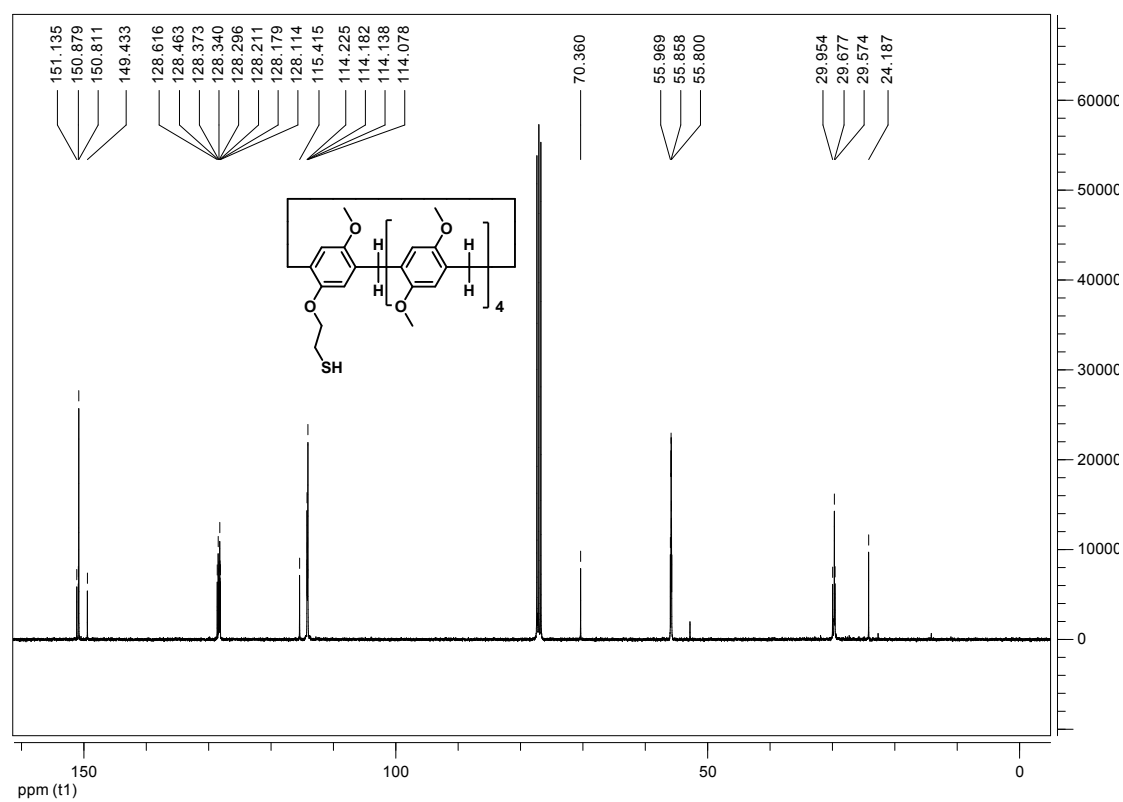


Fig. S1 (b) ¹³C NMR spectrum (CDCl₃, 100 MHz) of H1.

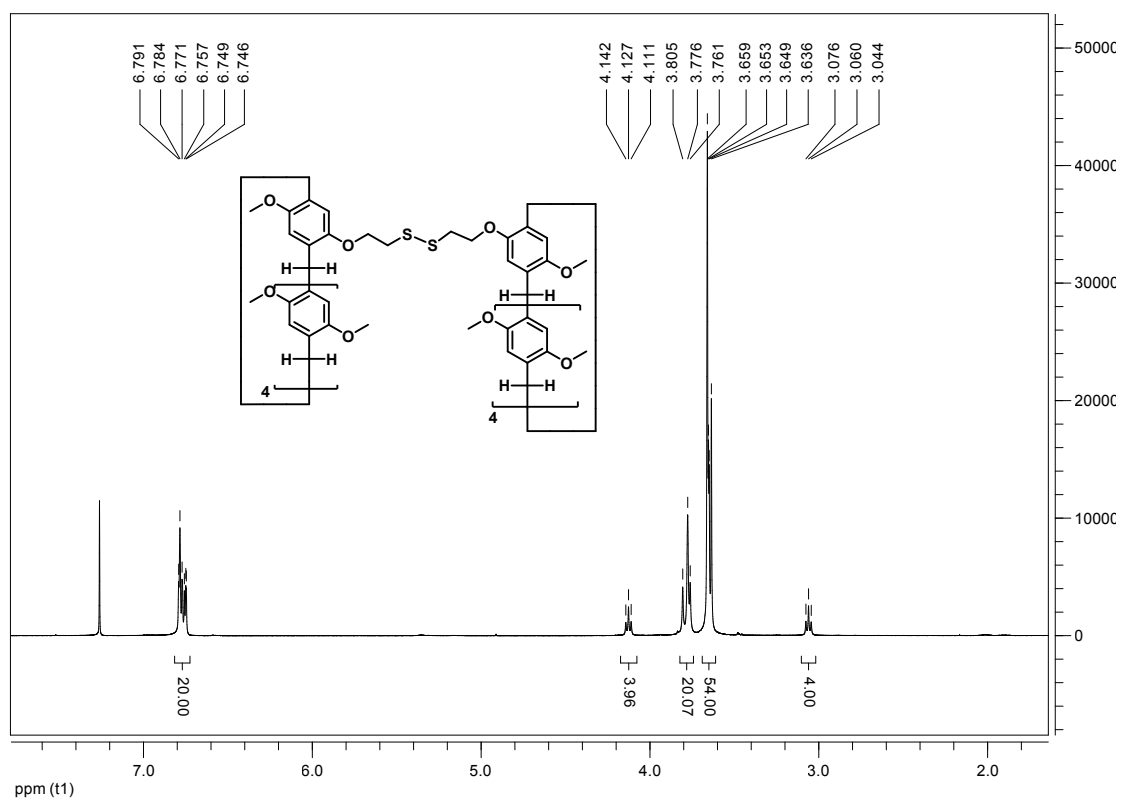


Fig. S2 (a) ¹H NMR spectrum (CDCl₃, 400 MHz) of **H2**.

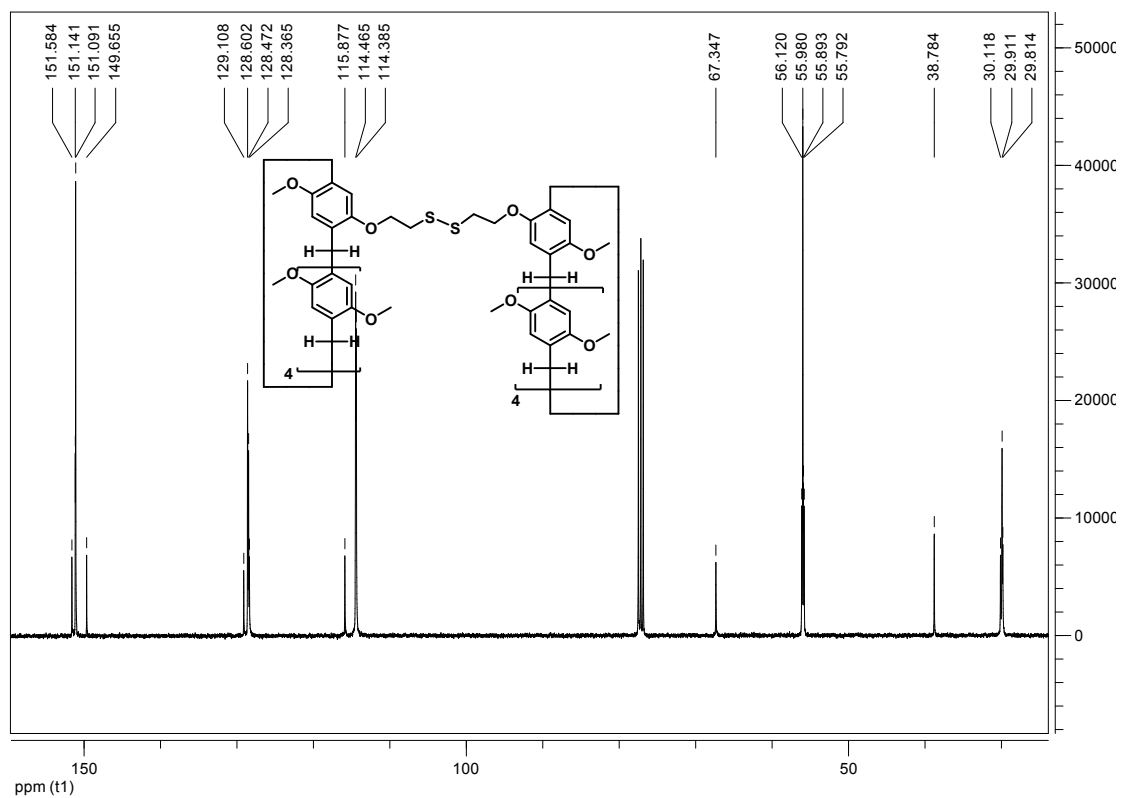


Fig. S2 (b) ¹³C NMR spectrum (CDCl₃, 100 MHz) of **H2**.

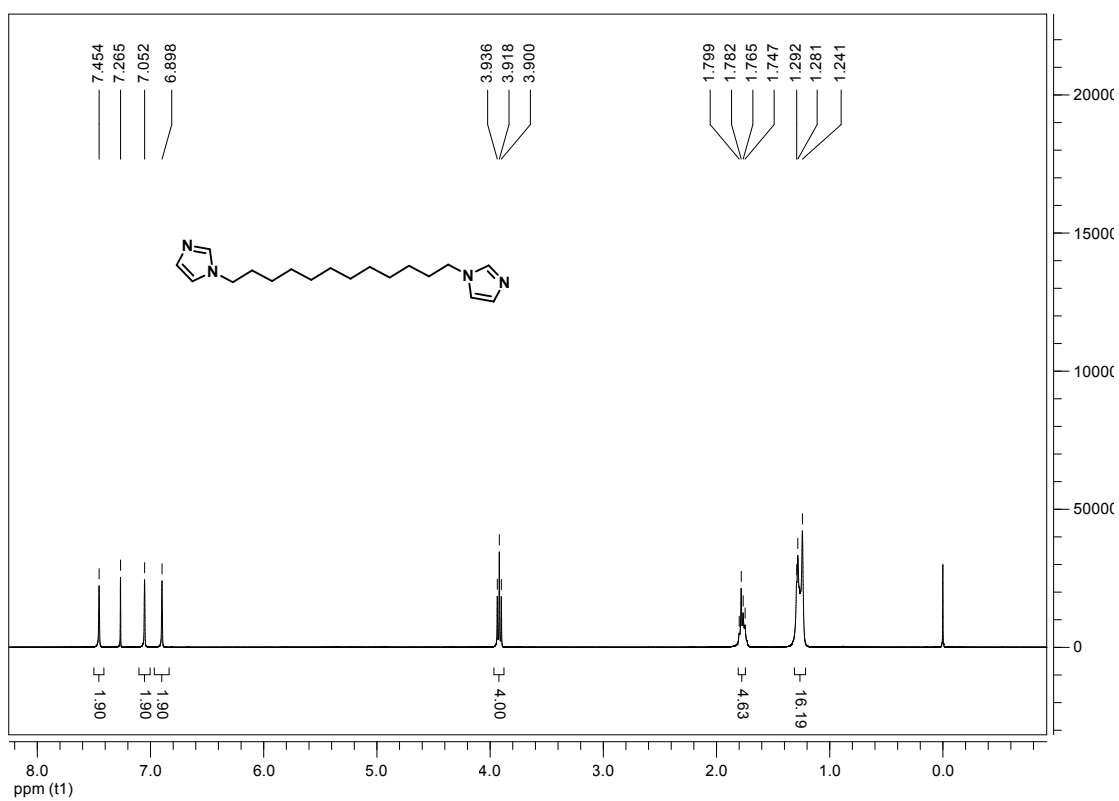


Fig. S3 (a) ^1H NMR spectrum (CDCl_3 , 400 MHz) of **G1**.

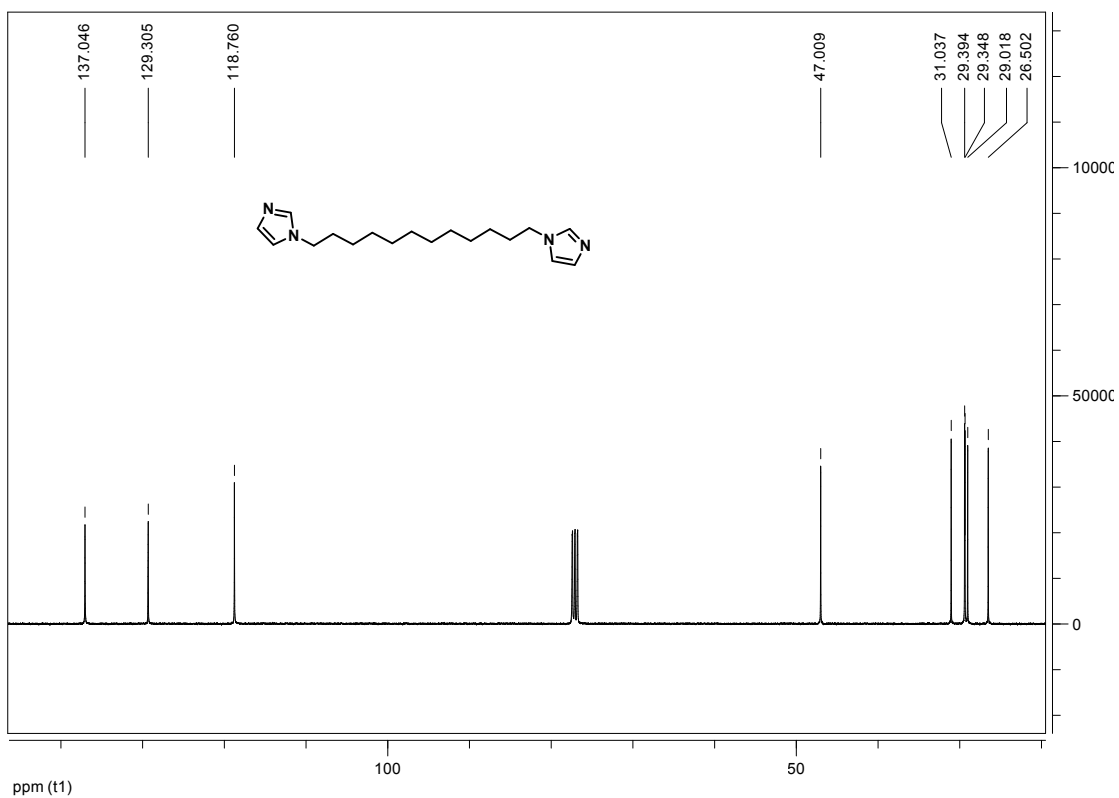


Fig. S3 (b) ^{13}C NMR spectrum (CDCl_3 , 100 MHz) of **G1**.

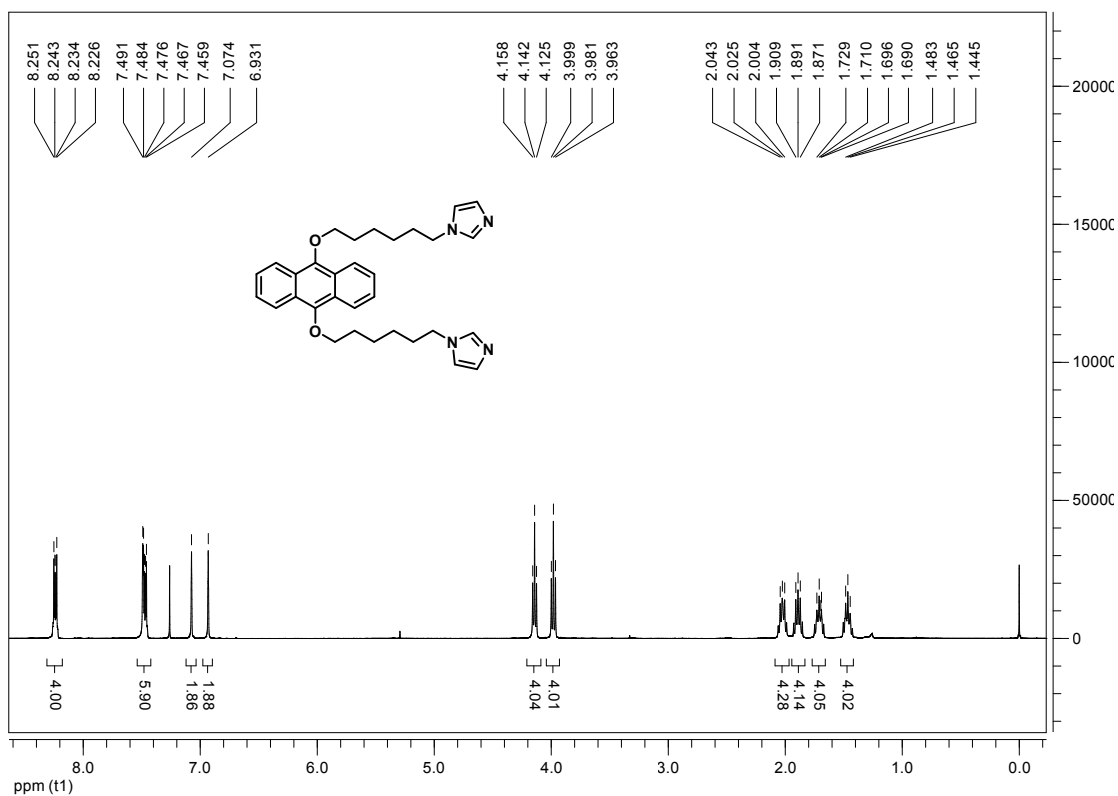


Fig. S4 (a) ^1H NMR spectrum (CDCl_3 , 400 MHz) of **G2**.

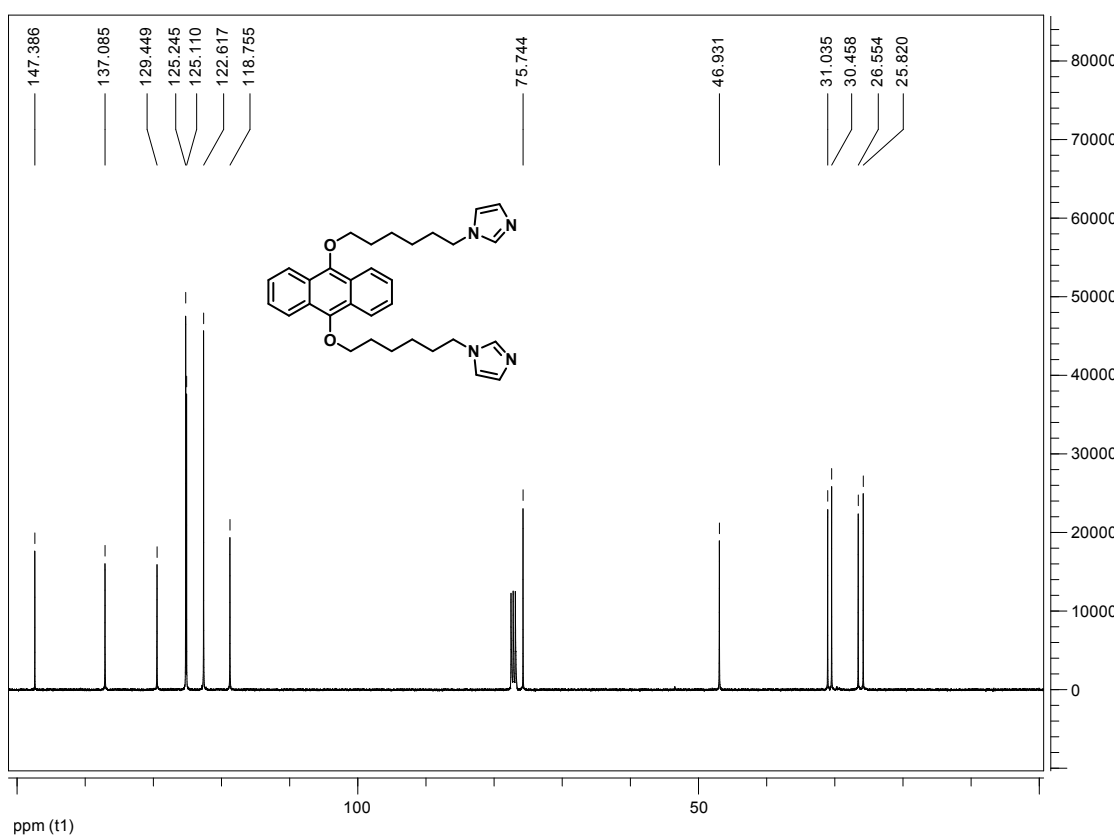


Fig. S4 (b) ^{13}C NMR spectrum (CDCl_3 , 100 MHz) of **G2**.

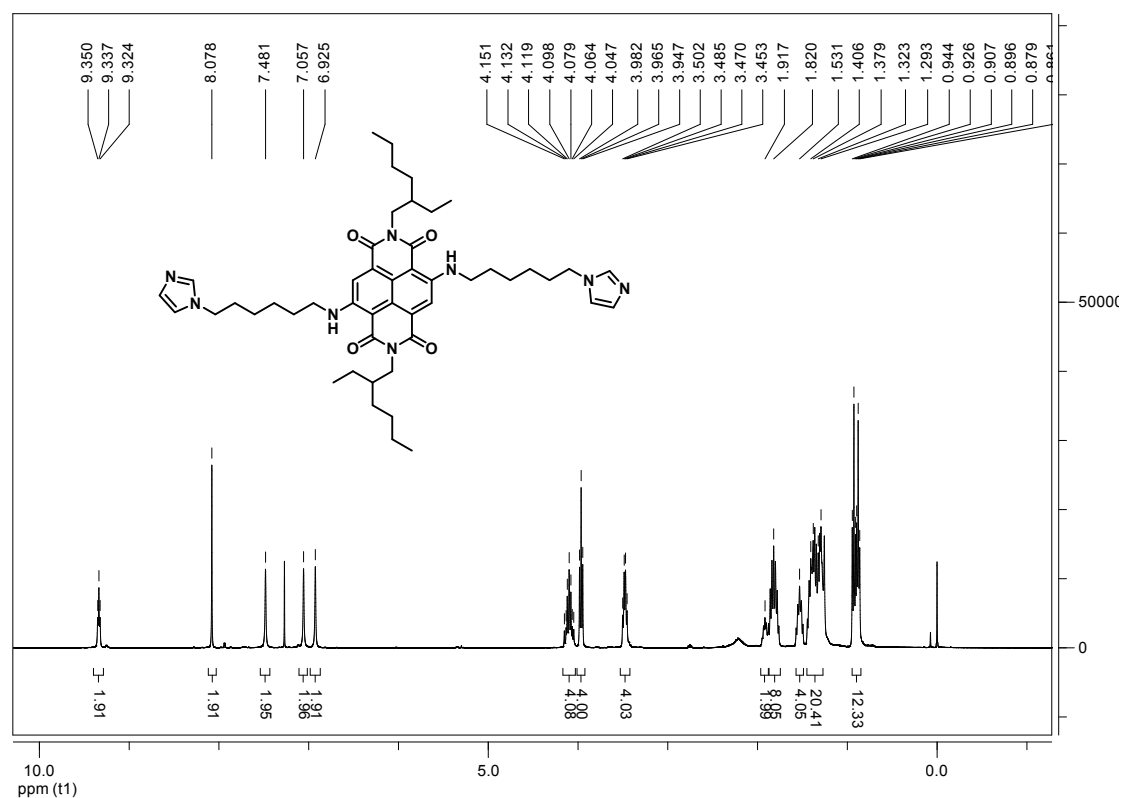


Fig. S5 (a) ¹H NMR spectrum (CDCl₃, 400 MHz) of G3.

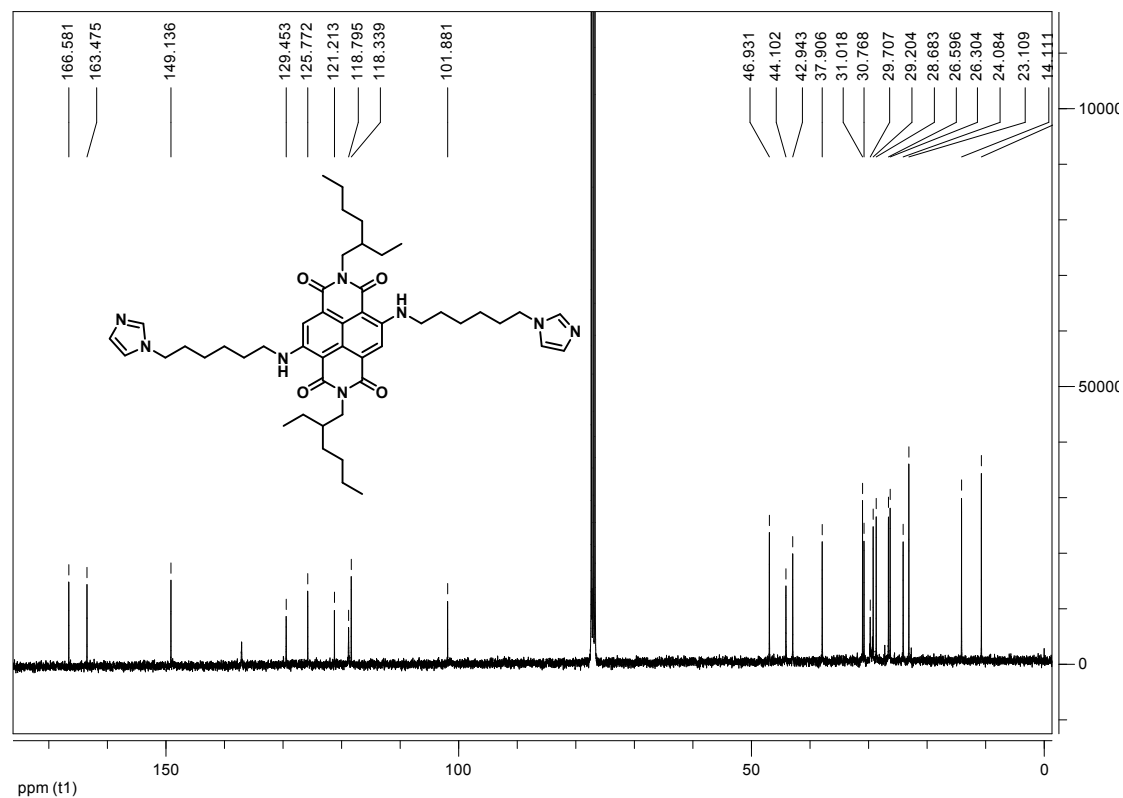


Fig. S5 (b) ¹³C NMR spectrum (CDCl₃, 100 MHz) of G3.

3. Characterization of the host-guest interaction between H2 and G1

The peaks at 6.43 ppm and 5.90 ppm were assigned to the imidazole proton in the complexed

G1, five broad peaks at 3.19 ppm, 1.65 ppm, 0.27 ppm, -0.61 ppm and -1.82 ppm were assigned to the alkyl chain protons in the complexed **G1**.

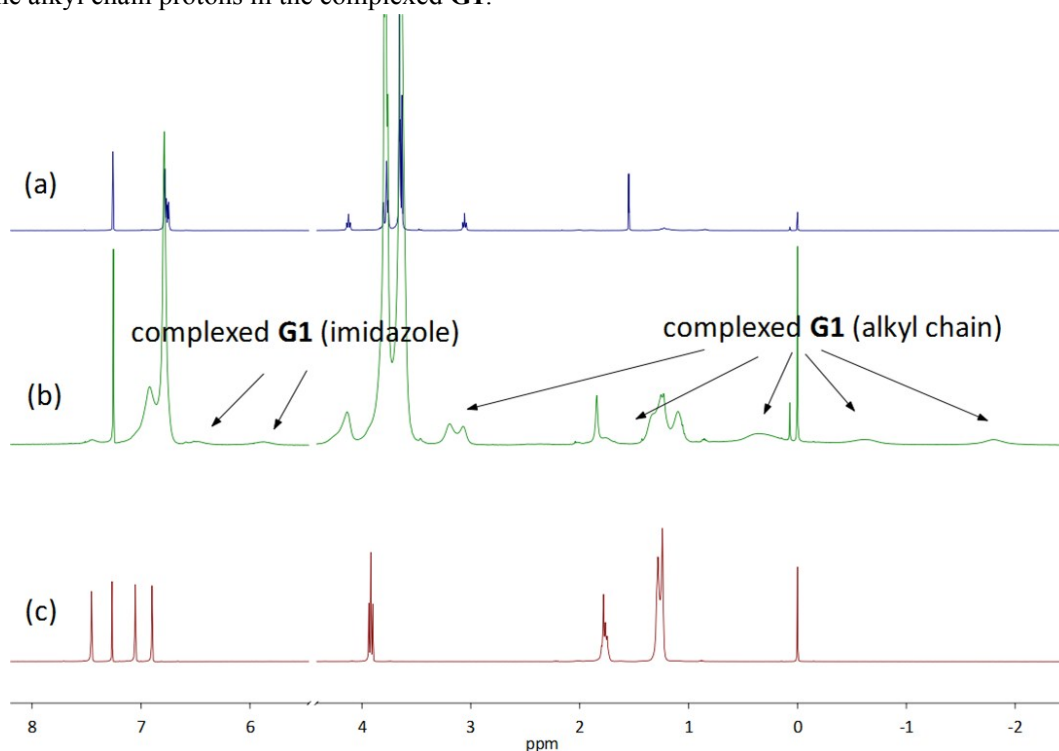


Fig. S6 ¹H NMR spectra (CDCl₃, 400 MHz) of **H2** (a, 5 mM), **G1**(c, 5 mM), and their equimolar mixture (b, 5 mM).

4. Determination of diffusion coefficient and viscosity measurements of **H2** and **G1**

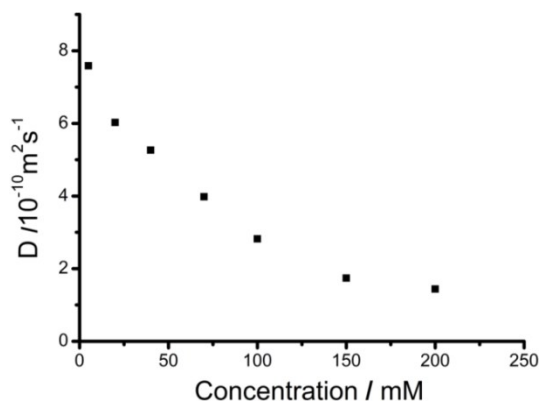


Fig. S7 (a) Concentration dependence of diffusion coefficient D (CDCl₃, 298 K, 600 MHz) of equimolar **H2** and **G1**.

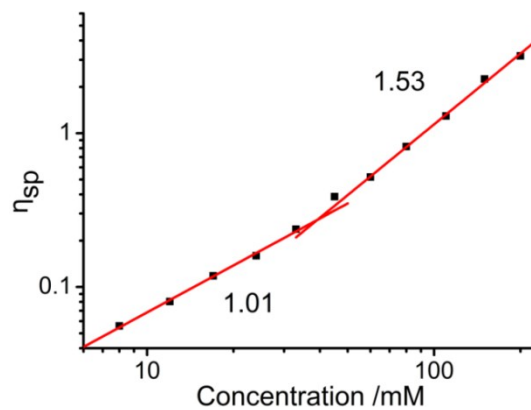


Fig. S7 (b) Specific viscosity of equimolar **H2** and **G1** in CHCl_3 at 298 K versus monomer concentration, values by the lines indicate the slopes.

5. Cyclic changes of supramolecular polymers constructed by **H2** and **G1**

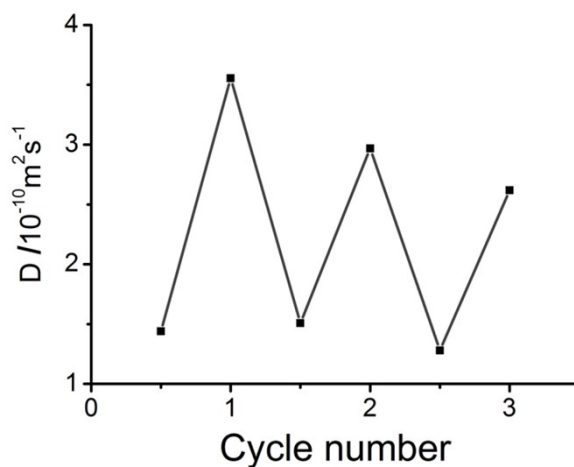


Fig. S8 Cyclic changes in the measured weight average diffusion coefficients (600 MHz, CDCl_3 , 298 K) of 200 mM **H2** and **G1**

6. Absorption and emission spectra of **G2** and **G3**

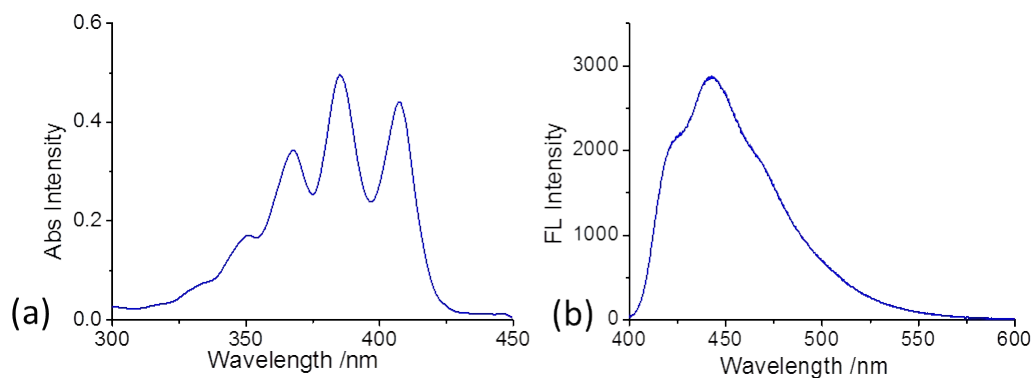


Fig. S9 The absorption spectrum (a) and the emission ($\lambda_{\text{ex}} = 380 \text{ nm}$) spectrum (b) of **G2** in CHCl_3 .

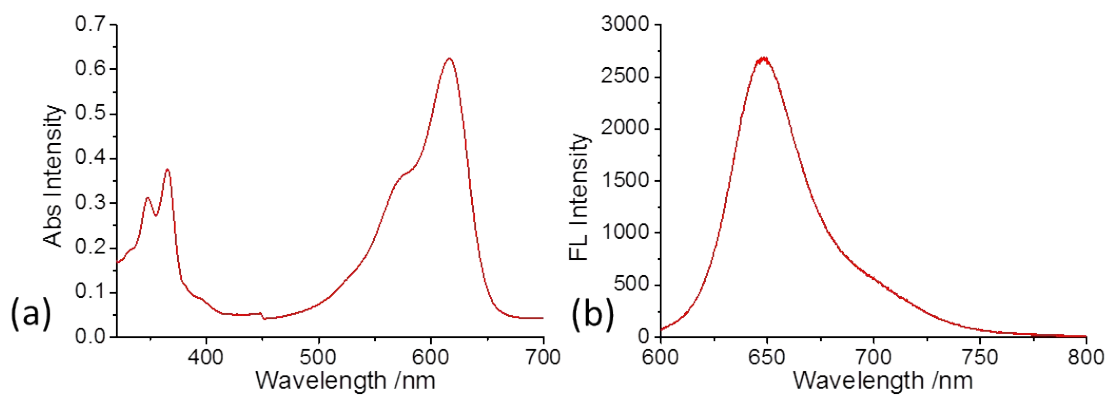


Fig. S10 The absorption spectrum (a) and the emission ($\lambda_{\text{ex}} = 580 \text{ nm}$) spectrum (b) of **G3** in CHCl_3 .

7. Characterization of the host-guest interactions between H2 and G2, G3

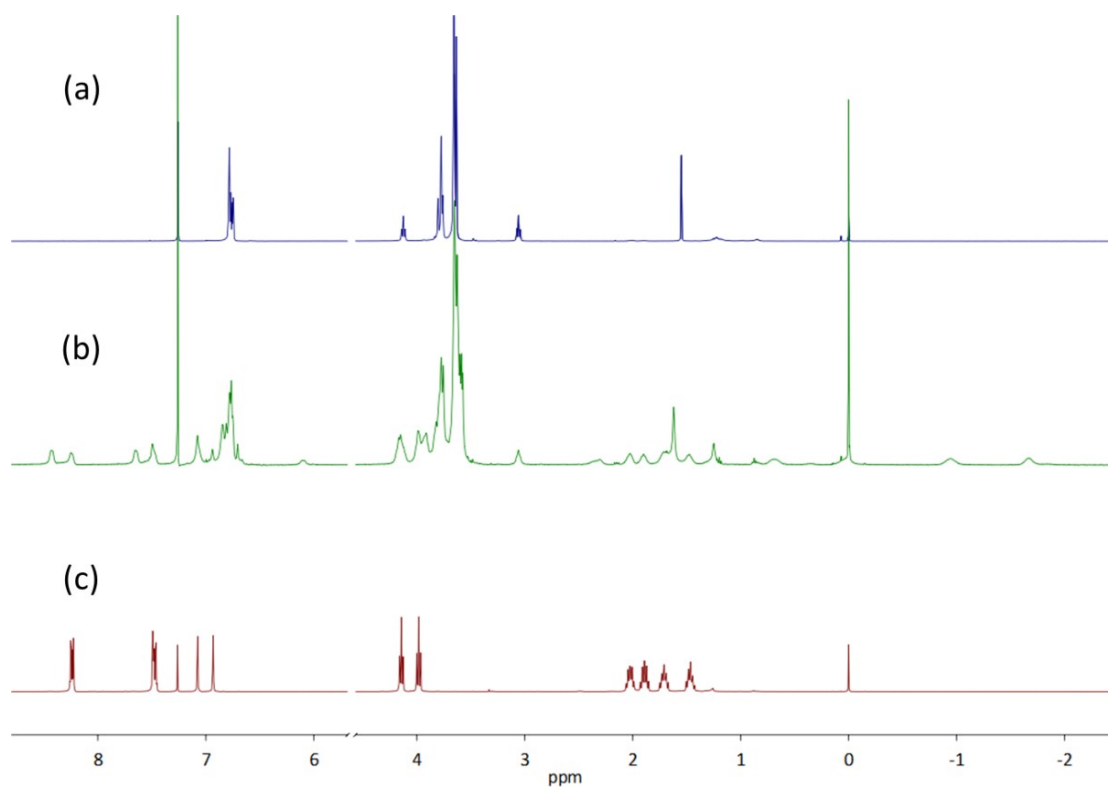


Fig. S11 ¹H NMR spectra (CDCl₃, 400 MHz) of **H2** (a, 5 mM), **G2**(c, 5 mM), and their equimolar mixture (b, 5 mM).

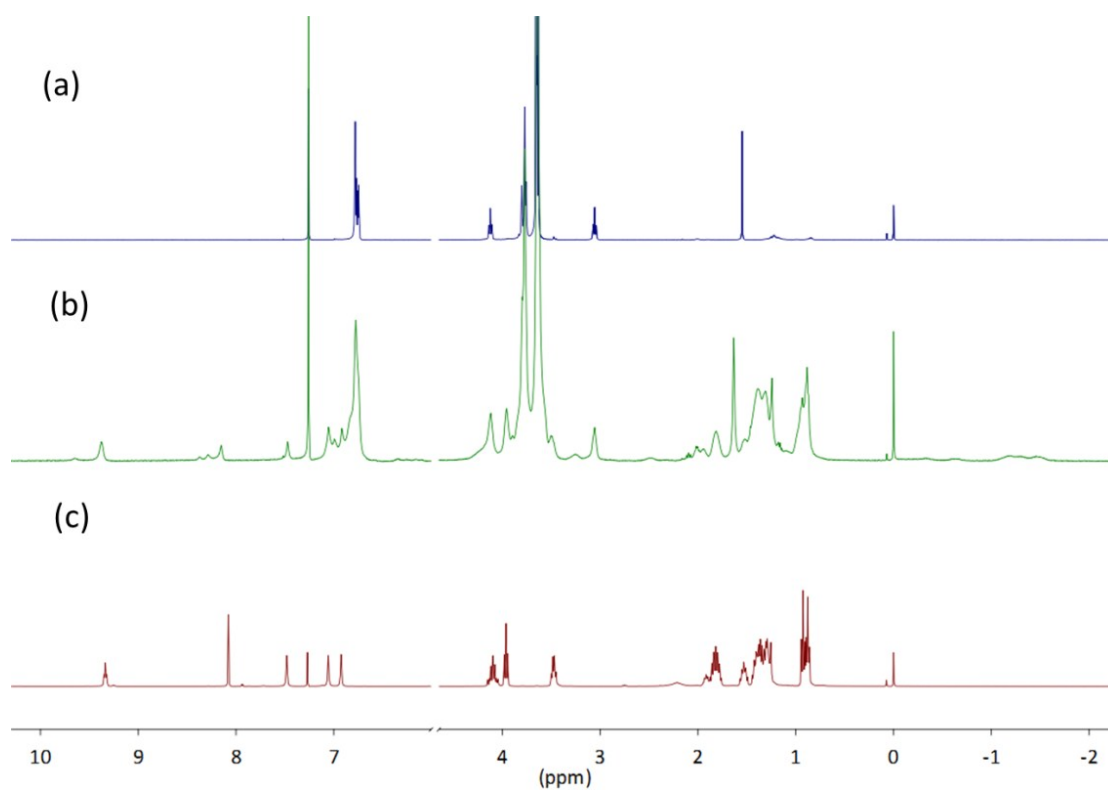


Fig. S12 ¹H NMR spectra (CDCl₃, 400 MHz) of **H2** (a, 5 mM), **G3**(c, 5 mM), and their equimolar mixture (b, 5 mM).

8. Characterization of the supramolecular polymers of H2 and G2

The formation of supramolecular polymers constructed by **H2** and **G2** was confirmed by the concentration-dependent ^1H NMR spectra (400 MHz, CDCl_3 , 298 K), DOSY and viscosity measurements of their quimolar mixture. As concentration increased, the proton signals of broadened, the diffusion coefficients decreased remarkably, and a sharp increase in specific viscosity was observed with the change of slope.

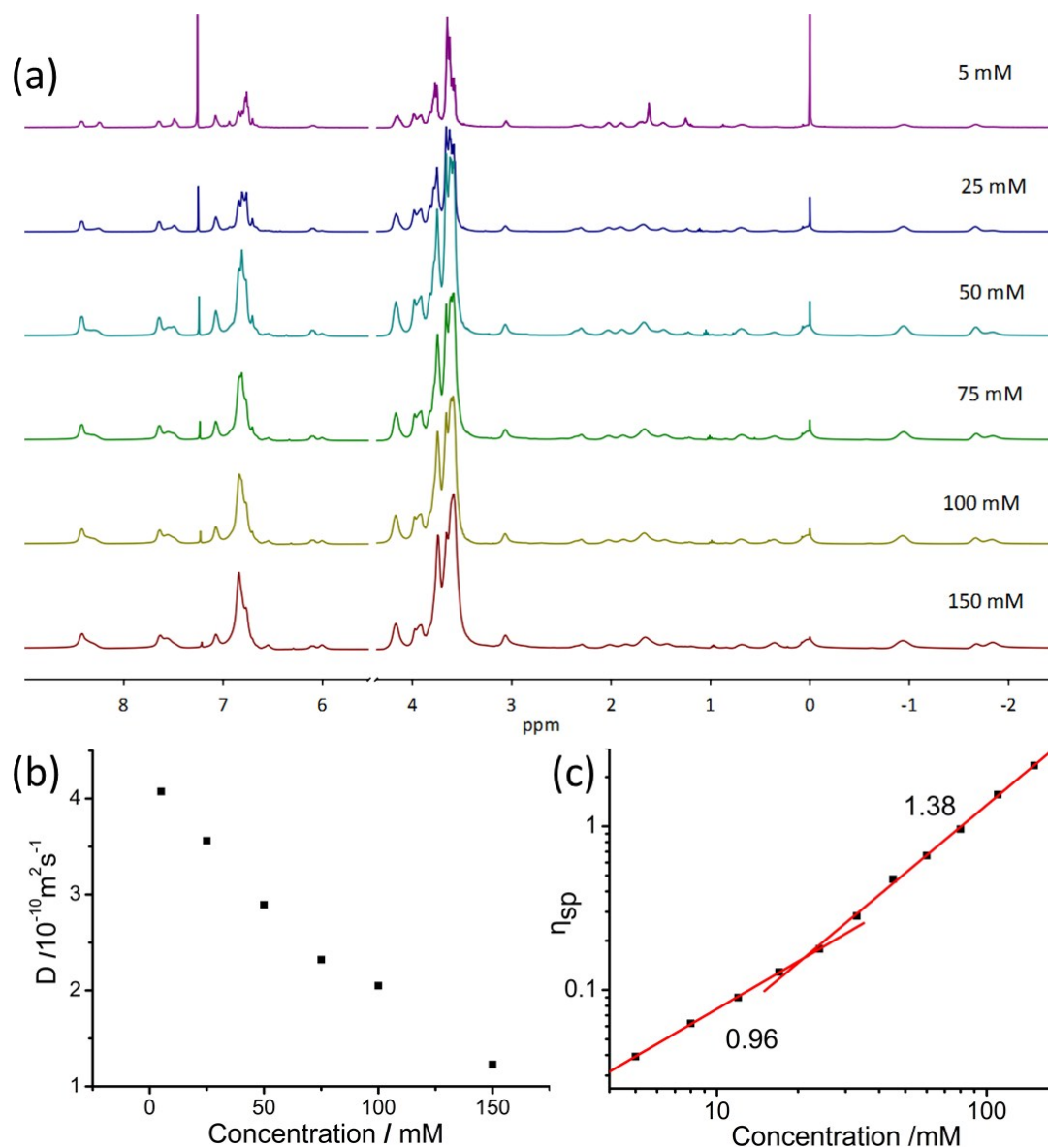


Fig. S13 Spectroscopic and physical characterization of equimolar mixture of **H2** and **G2** at various concentrations (a) Partial ^1H NMR spectra (400 MHz, CDCl_3), (b) Concentration dependence of diffusion coefficient D (600 MHz, CDCl_3 , 298 K), (c) Specific viscosity (298 K), values by the lines indicate the slopes.

9. SEM and DLS images of supramolecular nanospheres

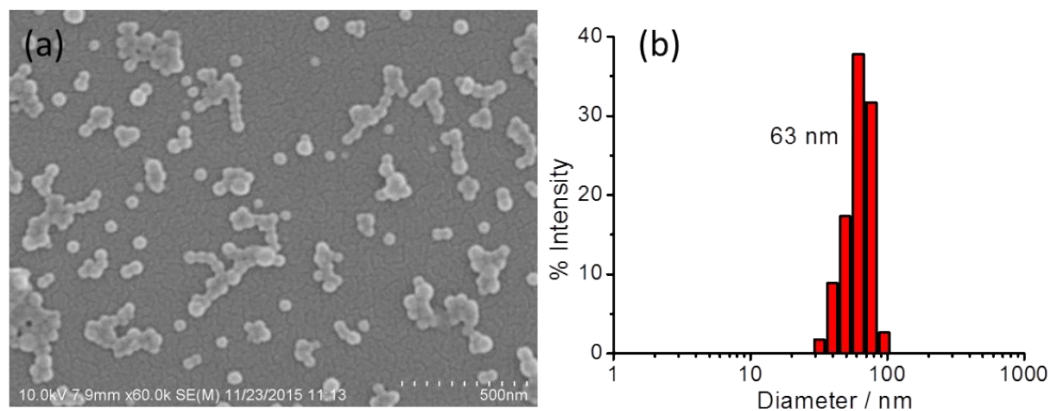


Fig. S14 SEM (a) and DLS (b) images of nanospheres prepared from supramolecular polymers of **H2** and **G2**.

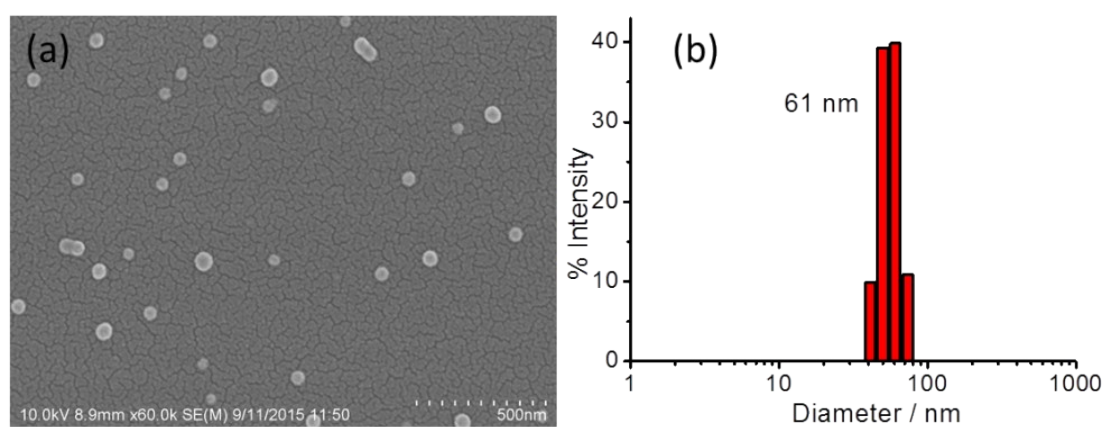


Fig. S15 SEM (a) and DLS (b) images of nanospheres prepared from supramolecular copolymers of **H2**, **G1** and **G3**.

10. References

- S1. J.-F. Xu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung and Q.-Z. Yang, *Org Lett*, 2013, **15**, 6148.