Electronic Supplementary Material (ESI) for Polymer Chemistry.

Construction of a pillar[5]arene-based linear supramolecular polymer and a photo-responsive supramolecular network

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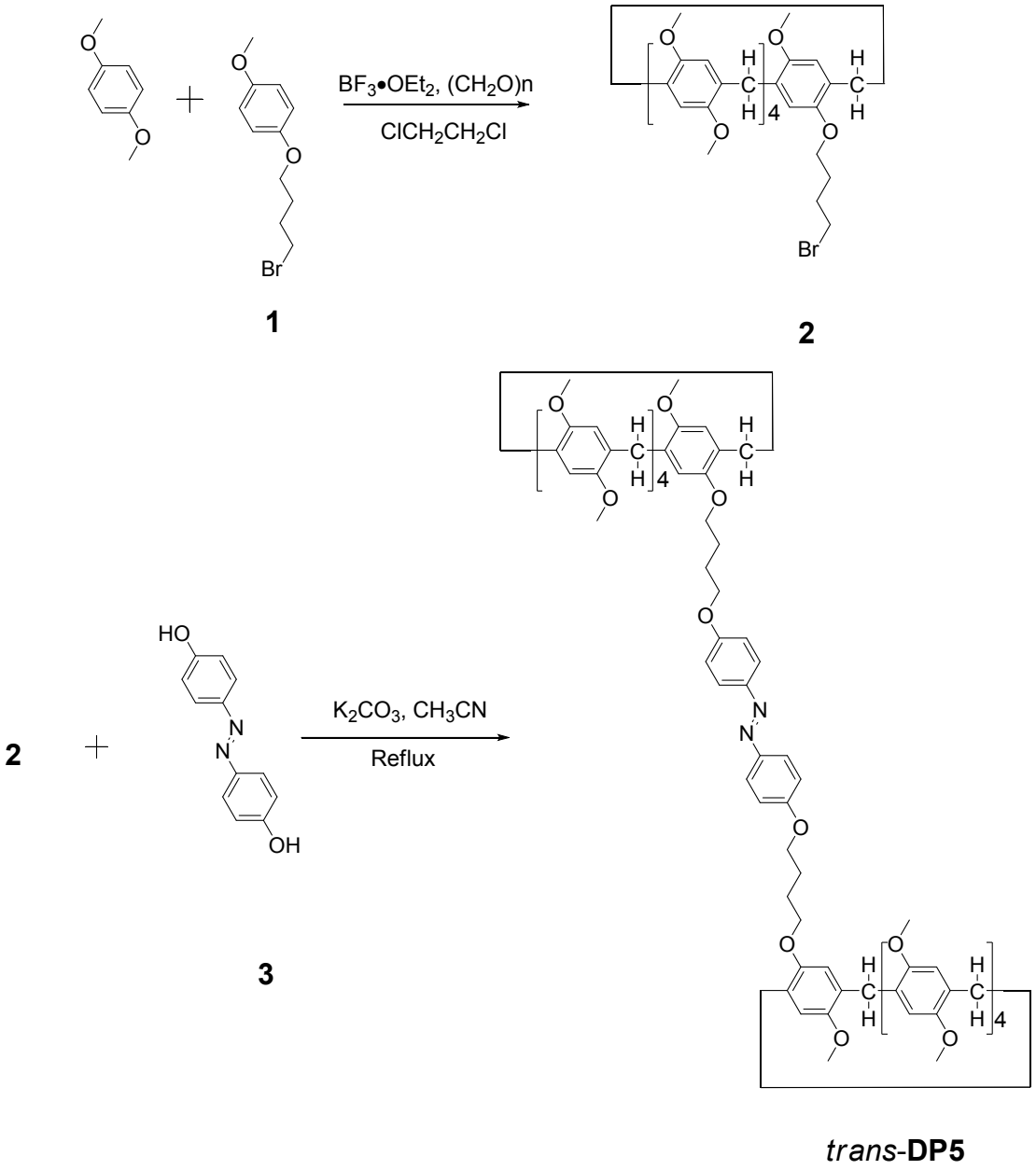
Electronic Supplementary Information (18 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **1**,[S1] **3**,[S2] **G**,[S3] **G1**[S4] and **CP1,**[S5] was 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 the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra 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. UV-Vis spectra were taken on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

*2. Synthesis of monomer trans-**DP5***

Scheme S1. Synthesis of monomer *trans-**DP5***



Compound **2**: A solution of **1** (2.59 g, 10.0 mmol), 1,4-dimethoxybenzene (11.1 g, 80.0 mmol) and paraformaldehyde (5.45 g, 180 mmol) in $ClCH_2CH_2Cl$ (250 mL) was stirred at room temperature, 11.3 mL $BF_3 \cdot OEt_2$ (12.8 g, 90 mmol) was added into the solution and kept stirring for about 20 minutes. Then the solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2. The resultant solution was washed with H_2O. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated to afford the crude product, which was isolated

by flash column chromatography to give **2** (3.50 g, 40%) as a white solid, mp 73.6−74.1 °C. The proton NMR spectrum of **2** is shown in Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.76 (m, 9H), 6.71 (s, 1H), 3.82 (t, J = 8 Hz, 2H), 3.78 (d, J = 4 Hz, 10H), 3.66–3.64 (m, 27H), 3.24 (s, 4H), 1.84 (s, 2H), 1.78 (s, 2H). The ^{13}C NMR spectrum of **2** is shown in Fig. S2. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.86, 150.80, 150.71, 150.67, 149.91, 128.57, 128.28, 128.21, 128.13, 114.83, 114.40, 114.10, 114.01, 113.84, 113.77, 67.44, 55.96, 55.80, 55.76, 55.71, 33.24, 29.79, 29.73, 29.60, 29.36, 28.91, 28.36. LRESIMS is shown in Fig. S3: *m*/*z* 890.3 $[M + NH_4]^+$, HRESIMS: *m*/*z* calcd for $[M + NH_4]^+$ $C_{48}H_{59}BrNO_{10}^+$, 888.3331; found 888.3322, error −1.0 ppm.

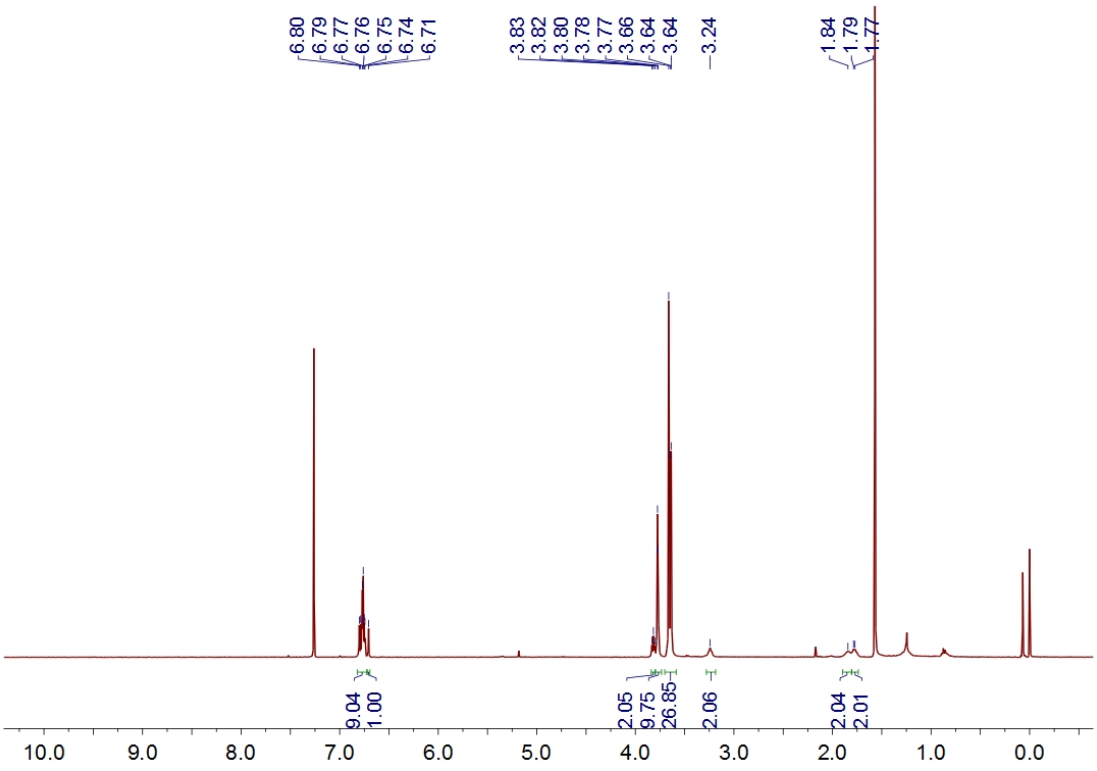


Fig. S1. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **2**.

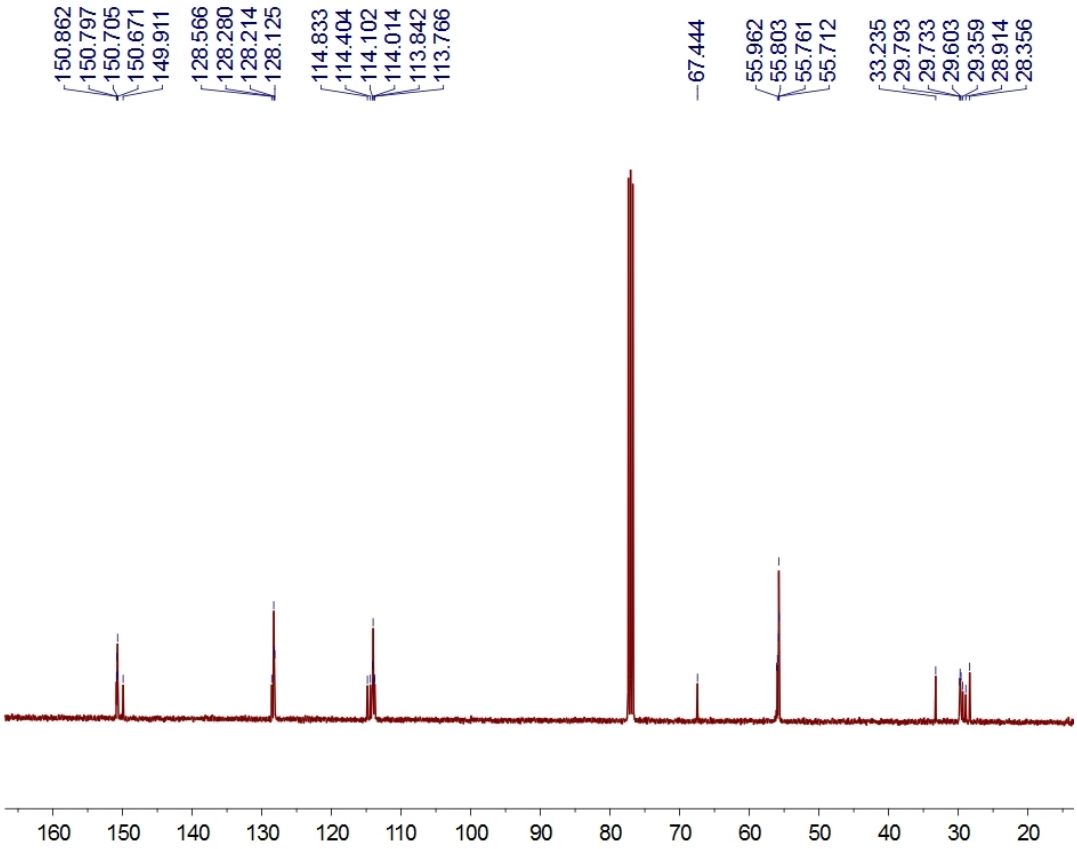


Fig. S2. ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 298 K) of **2**.

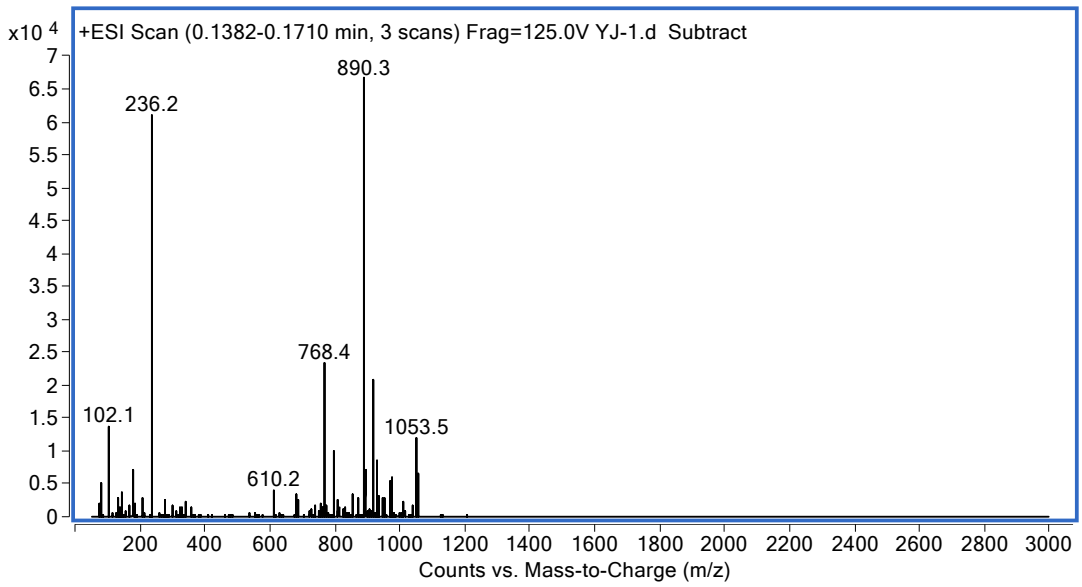


Fig. S3. Electrospray ionization mass spectrum of **2**. Assignment of the main peak: *m*/*z* 890.3 $[\mathbf{M} + NH_4]^+$ (100%).

Compound *trans*-***DP5***: A mixture of **2** (3.00 g, 3.44 mmol), **3** (0.25 g, 1.15 mmol) and K_2CO_3 (1.90 g, 13.76 mmol) in CH_3CN was stirred under N_2 at reflux for 2 days. Then the reaction mixture was cooled to room temperature and filtered. The filter cake was washed with chloroform (2 × 30 mL). The filtrate was concentrated under vacuum, and then the residue was purified by column chromatography on silica gel to afford *trans*-**DP5** as a yellow solid (1.60 g, 76%), mp: 117.8–118.5 °C. The proton NMR spectrum of *trans*-**DP5** is shown in Fig. S4. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.86 (d, J = 8 Hz, 8H), 6.97 (d, J = 8 Hz, 8H), 6.77 (t, J = 8 Hz, 20H), 4.05 (s, 4H), 3.91 (s, 4H), 3.80–3.62 (m, 75H), 1.96 (s, 8H). The ^{13}C NMR spectrum of *trans*-**DP5** is shown in Fig. S5. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.07, 150.57, 149.78, 147.03, 128.30, 128.24, 128.17, 124.39, 114.66, 114.50, 114.43, 113.79, 113.69, 67.84, 67.48, 56.13, 55.74, 55.64, 55.59, 39.37, 29.48, 26.45, 26.27. LRESIMS is shown in Fig. S6: m/z 1794.1 $[M + H]^+$. HRESIMS: m/z calcd for $[M + 2\ Na]^{2+}$ $C_{108}H_{118}N_2O_{22}Na_2^{2+}$, 920.3986, found 920.4013, error 3 ppm.

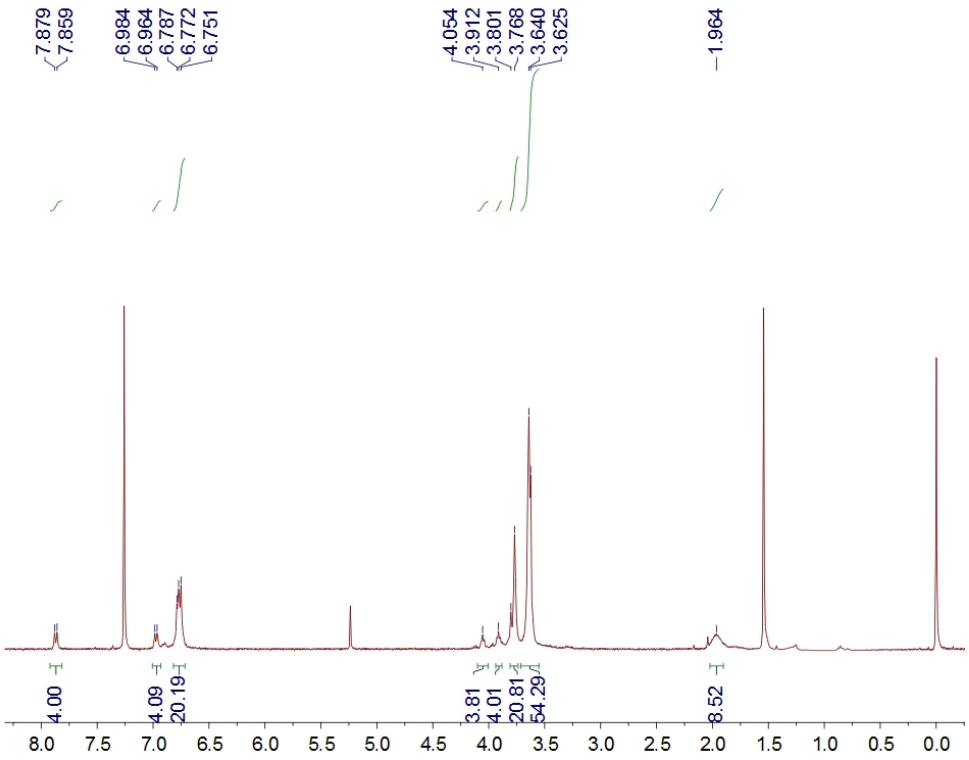


Fig. S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of *trans*-**DP5**.

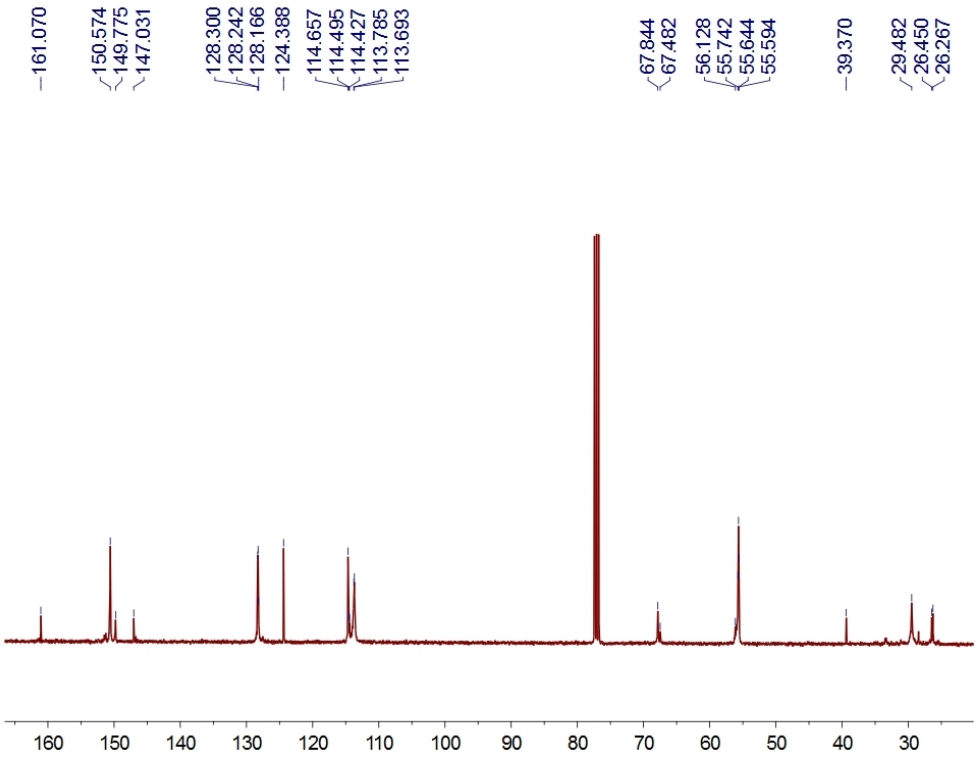


Fig. S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of *trans*-**DP5**.

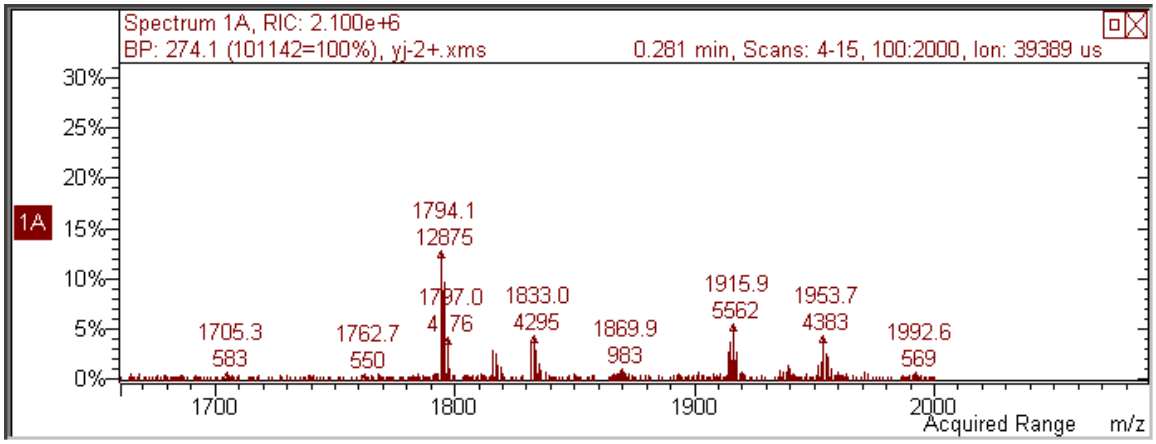
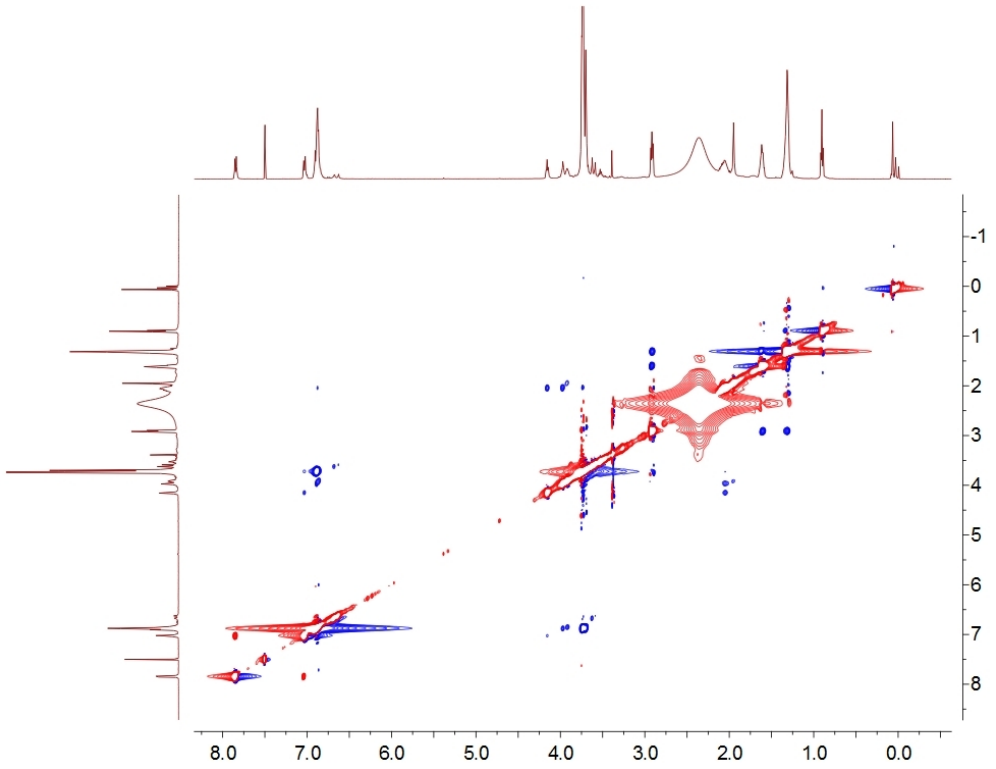


Fig. S6. Electrospray ionization mass spectrum of *trans*-**DP5**. Assignment of the main peak: *m*/*z* 1794.1 [**M** + H]$^+$ (100%).

*3. Partial NOESY NMR spectrum of monomer trans-**DP5** and **G***



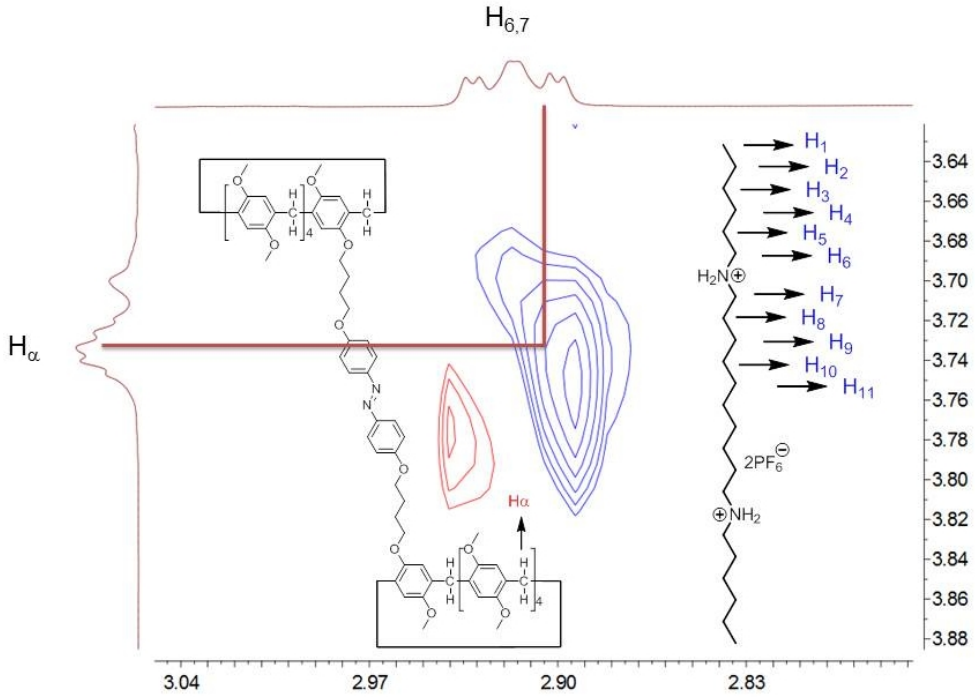


Fig. S7. NOESY NMR (500 MHz, $CDCl_3/CH_3CN$, 298 K) spectrum of a solution of **G** and *trans*-**DP5** at a concentration of 10.0 mM (top). Partial NOESY NMR spectrum (bottom).

From this NOESY NMR spectrum, strong correlations were observed between protons H_α of *trans*-**DP5** and protons $H_{6,7}$ of **G**, confirming the occurrence of complexation in $CDCl_3/CH_3CN$.

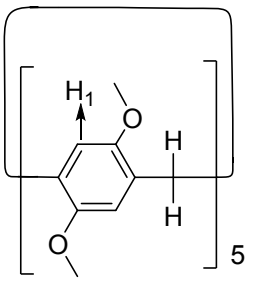
*4. Investigation of the interactions between **DMP5** and **G1***

To determine the stoichiometry and association constant for the complexation between **DMP5** and **G1**, NMR titrations were done with solutions which had a constant concentration of **DMP5** (1.00×10^{-6} M) and varying concentrations of **G1**. By a non-linear curve-fitting method, the association constant (K_a) of **DMP5⊃G1** was estimated to be 81.6 ± 2.7. By mole ratio plot, 1:1 stoichiometry was obtained for the complexation between **DMP5** and **G1**.

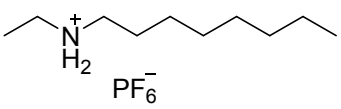
The non-linear curve-fittings were based on the equation:

$$\Delta\delta = (\Delta\delta_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a) - (0.5\ ([G]_0^2+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \quad (\text{Eq. S1})$$

Where $\Delta\delta$ is the chemical shift change of H_1 on **DMP5** at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_1 when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of **G1**.



DMP5



G1

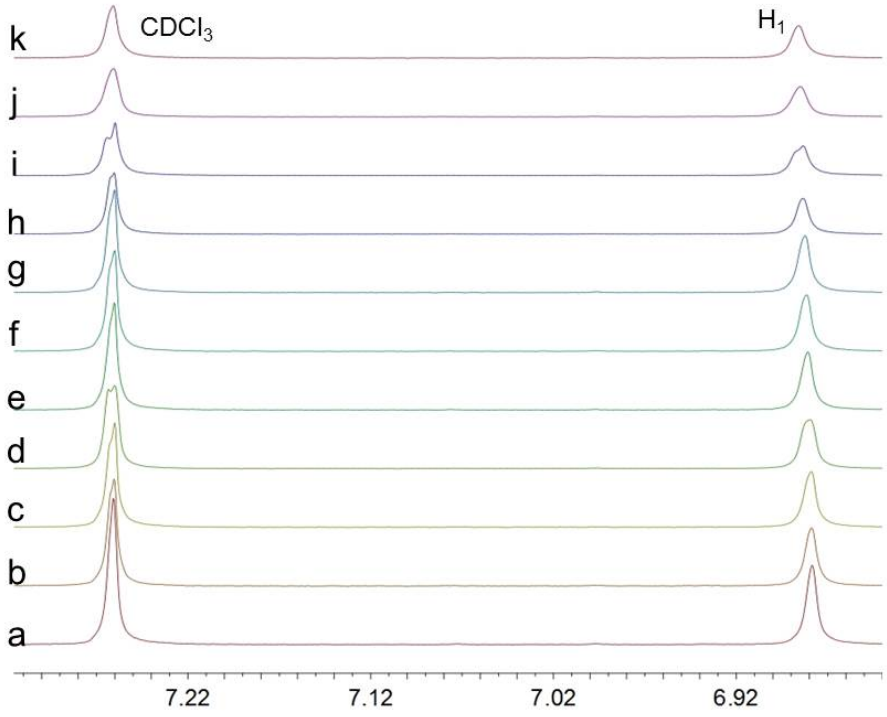


Fig. S8. Partial ^{1}H NMR (400 MHz, $CDCl_3/CH_3CN$, 298 K) spectrum of **DMP5** at a concentration of 1.00 mM upon addition of **G1** (10 mM): (a) 0.00 μL; (b) 10.0 μL; (c) 10.0 μL; (d) 10.0 μL; (e) 10.0 μL; (f) 25.0 μL; (g) 25.0 μL; (h) 50.0 μL; (i) 50.0 μL; (j) 50.0 μL; (k) 100 μL.

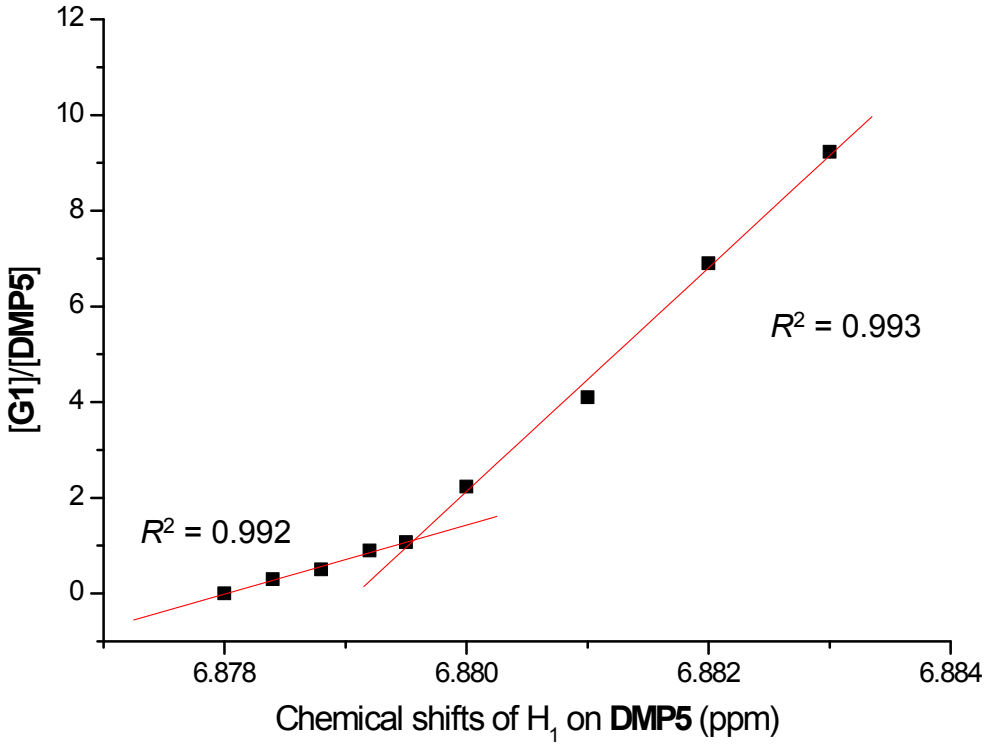


Fig. S9. Mole ratio plot for **DMP5** and **G1**, indicating a 1:1 stoichiometry.

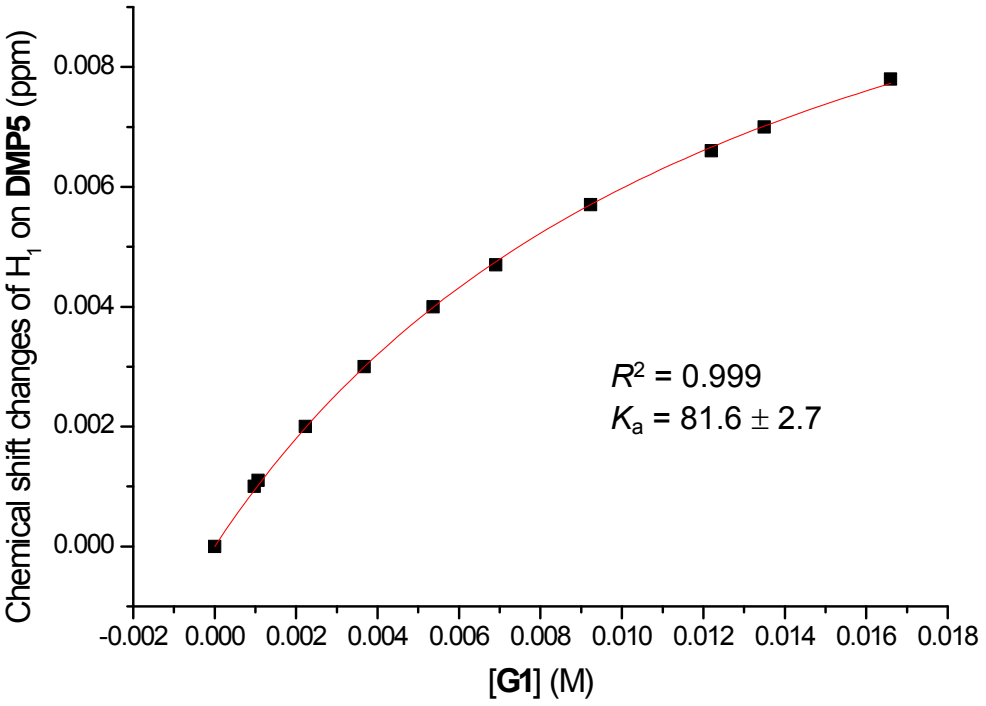


Fig. S10. The chemical shift changes of H1 on **DMP5** upon addition of **G1**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

5. Photoisomerization behavior of ***trans-DP5***

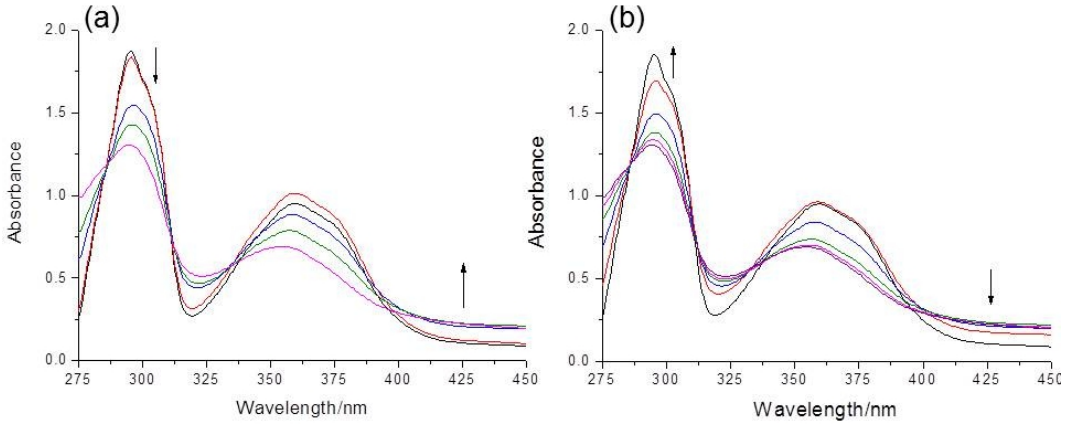


Fig. S11. UV-Vis absorption spectra of a *trans*-**DP5** solution (1:1 $CHCl_3/CH_3CN$) under UV irradiation at 365 nm of 0 s, 1 min, 3min, 5min, and 10 min (a) and later after visible irradiation at 435 nm of 0 s, 1 min, 3min, 5min, and 10 min (b). The concentration of *trans*-**DP5** was 1.00×10^{-5} M.

Upon irradiation with UV light at 365 nm (8 W), the absorption band at around 300 nm decreased remarkably, and concomitantly the band at around 425 nm increased slightly. The absorption bands of the azobenzene unit at 300 and 425 nm are ascribed to π–π* and n–π* transitions, respectively. The changes of the absorption bands induced by UV irradiation indicated the photoisomerization from the *trans* state to the *cis* state. On the contrary, upon irradiation with visible light at 435 nm (8 W), the absorption peak at 425 nm attributable to *cis* decreased, while the absorption band at 300 nm corresponding to *trans* increased, indicating a change from the *cis* form to the *trans* form.

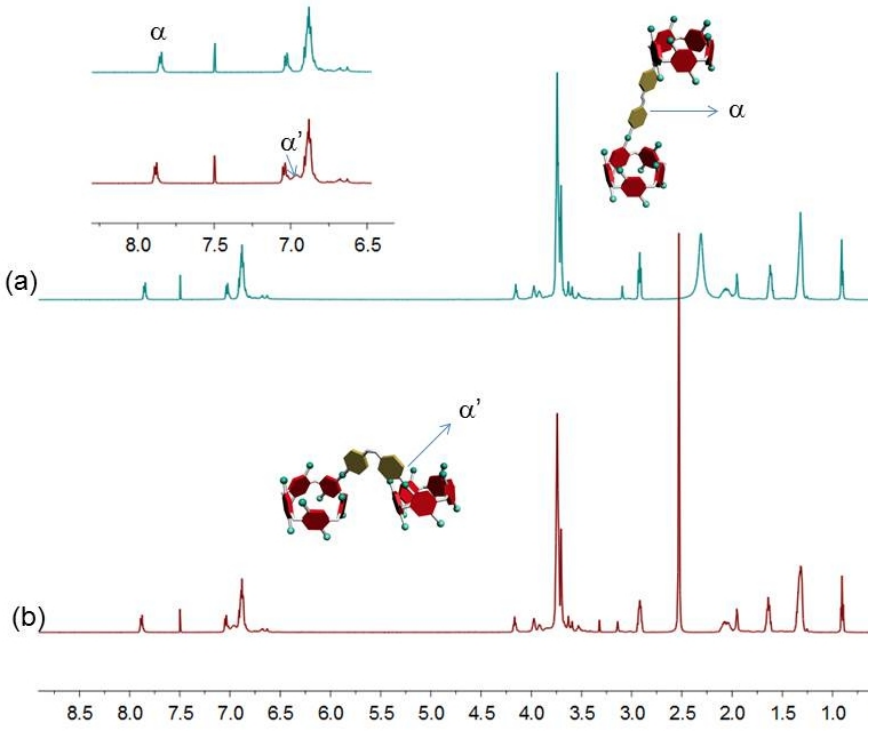


Fig. S12. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3/CH_3CN$, 298 K) of 20.0 mM *trans*-**DP5** and **G** (a), 20.0 mM *trans*-**DP5** and **G** after irradiation at 365 nm for 10 min (b).

From above spectra, when a solution of 20.0 mM *trans*-**DP5** and **G** was irradiated by UV light for 10 min, the molar ratio of the *trans* to the *cis* form changed to about 50:50.

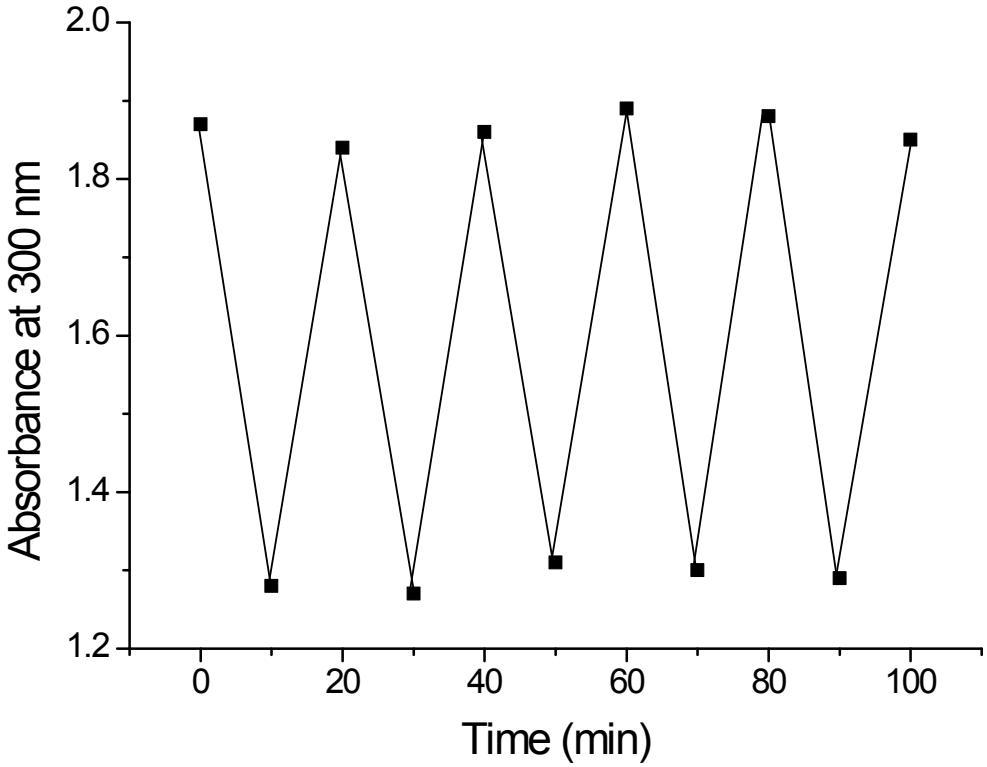


Fig. S13. Changes of the absorbance at 300 nm of *trans*-**DP5** upon alternating irradiation with UV and visible light for 10 min.

*6. The stoichiometry for the complexation between **DMP5** and **G***

To determine the stoichiometry for the complexation between **DMP5** and **G**, NMR titrations were done with solutions which had a constant concentration of **G** (1.00×10^{-3} M) and varying concentrations of **DMP5**. By mole ratio plot, 2:1 stoichiometry was obtained for the complexation between **DMP5** and **G**.

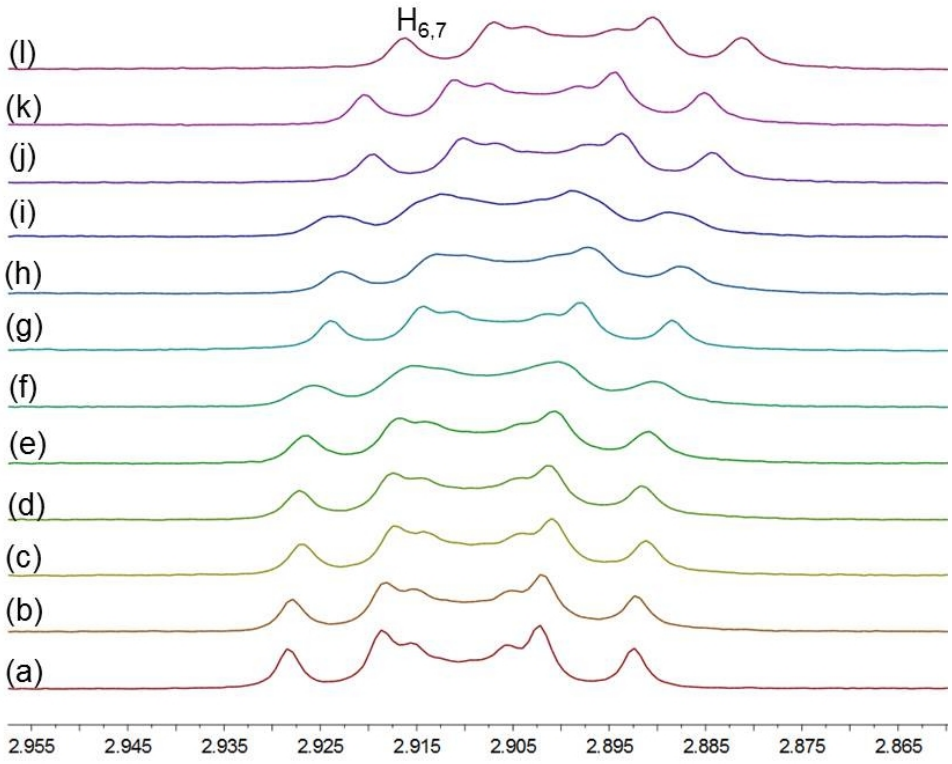


Fig. S14. Partial ^{1}H NMR (600 MHz, $CDCl_3/CH_3CN$, 298 K) spectrum of **G** at a concentration of 1.00 mM upon addition of **DMP5** (10 mM): (a) 0.00 μL; (b) 10.0 μL; (c) 10.0 μL; (d) 10.0 μL; (e) 10.0 μL; (f) 25.0 μL; (g) 25.0 μL; (h) 25.0 μL; (i) 25.0 μL; (j) 50.0 μL; (k) 50.0 μL; (L) 100 μL.

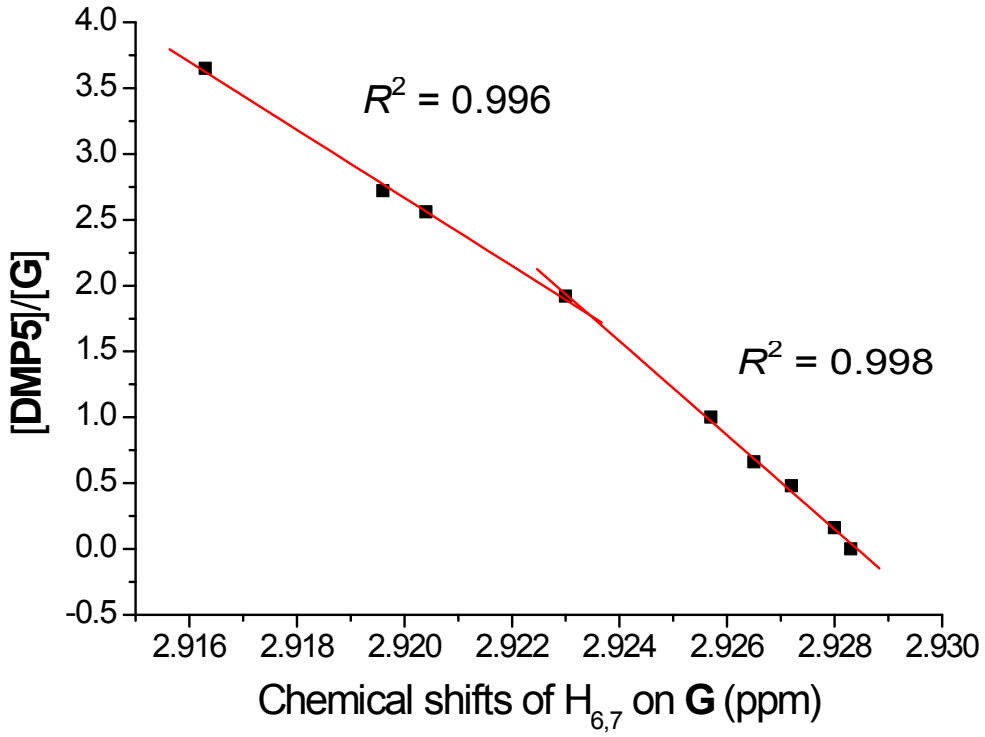


Fig. S15. Mole ratio plot for **DMP5** and **G**, indicating a 2:1 stoichiometry.

7. *Determination of diffusion coefficient D*

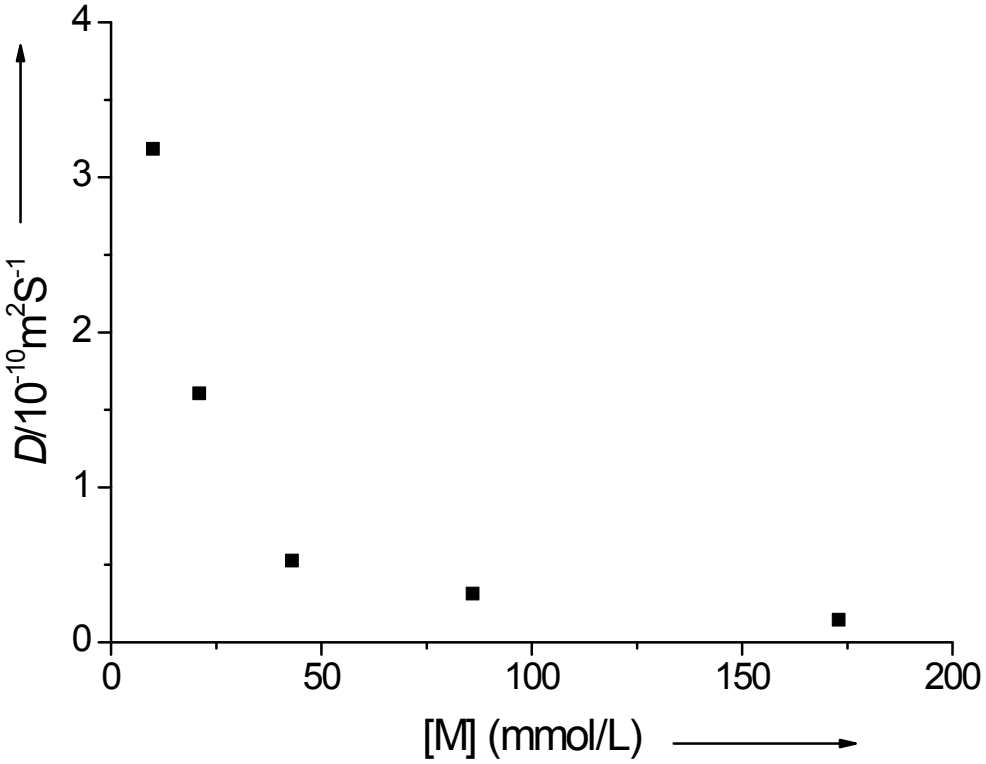


Fig. S16. Concentration dependence of diffusion coefficient *D* (500 MHz, $CDCl_3/CH_3CN$, 298 K).

As the monomer concentration increased from 10.0 mM to 175 mM in solution, the measured weighted average diffusion coefficient decreased considerably from 3.17×10^{-10} $m^2 \cdot s^{-1}$ to 1.57×10^{-11} $m^2 \cdot s^{-1}$, indicating the concentration dependence of supramolecular polymerization and the formation of a high molecular weight polymer structure.

8. References:

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S3. J. A. Goodson, L. G. Goodwin, J. H. Gorvin, M. D. Goss, K. S. Kirby, J. A. Lock, R. A. Neal, T. M. Sharp and W. Solomon, *Brit. J. Pharmacol.*, 1948, **3**, 49.

S4. C. Han, G. Yu, B. Zheng and F. Huang, *Org. Lett.* 2012, **14**, 1712-1715.

S5. L. Chen, Y.-K. Tian, Y. Ding, Y.-J. Tian and and F. Wang, *Macromolecules*, 2012, **45**, 8412.