

First water soluble pillar[5]arene dimer: synthesis and construction of a reversible fluorescent supramolecular polymer network in water†

Yan Sun,^{a,*} Jin Wang,^c and Yong Yao^{a,b*}

^aCollege of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu, 225002, P. R. China.

^bDepartment of Chemistry, University of Utah, Salt Lake City, 84112, USA.

^cResearch and Development Center, China Tobacco Yunnan Industrial Co.,Ltd., Kunming, 650231, China.

E-mail: yaoyong@zju.edu.cn, ysun@iccas.ac.cn;

Electronic Supplementary Information (8 pages)

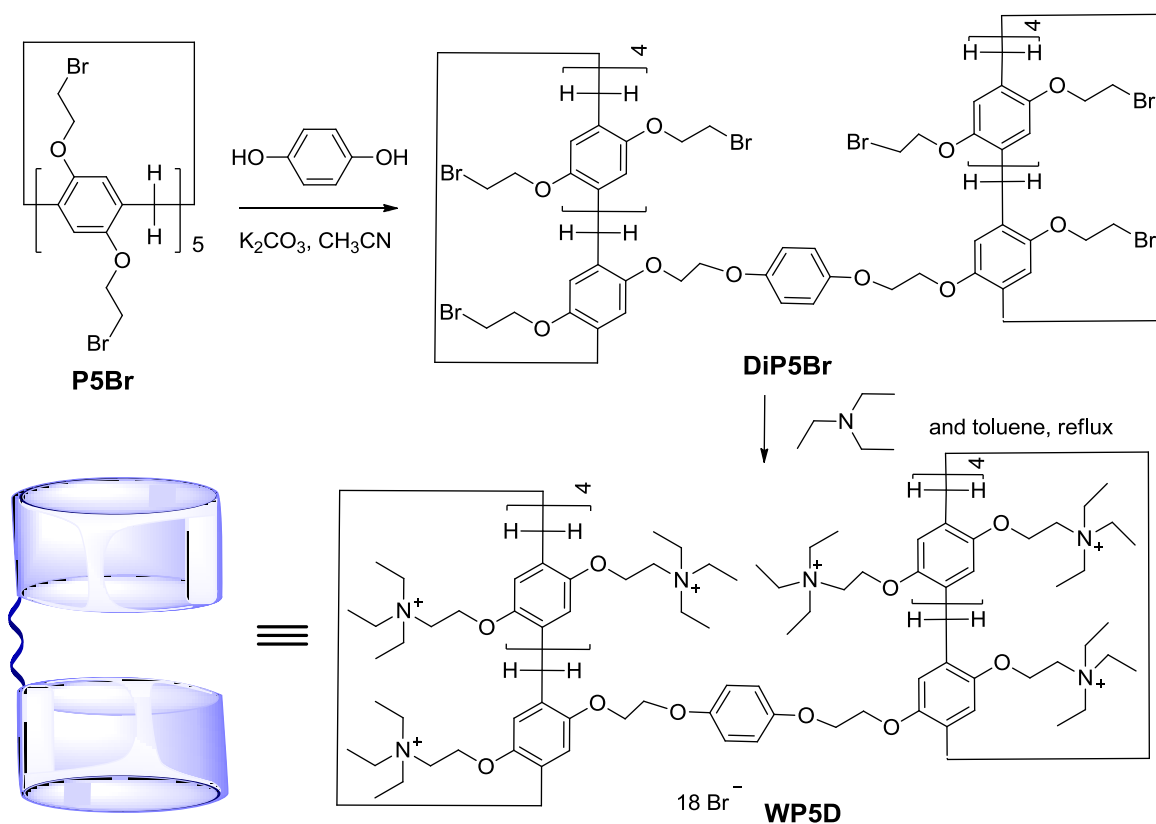
1. <i>Materials and methods</i>	S2
2. <i>Syntheses of water soluble pillar[5]arene dimer</i>	S3
3. <i>Characterization of supramolecular polymer networks</i>	S7
4. <i>References</i>	S8

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. **P5Br** was prepared according to the literature procedure.^{S1} ^1H or ^{13}C NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Viscosity measurements were carried out with a Cannon-Ubbelohde semimicro dilution viscometer at 298K in water. Scanning electron microscopy investigation was carried out on a JEOL 6390LV instrument. The fluorescence spectra were recorded on a Perkin Elmer LS55 fluorescence spectrophotometer. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with IonSpec 4.7 Tesla FTMS.

2. Syntheses of water soluble pillar[5]arene dimer

Scheme S1. Synthetic route for water soluble pillar[5]arene dimer



DiP5Br: In a 500 mL round-bottom flask, **P5Br** (8.62 g, 5.00 mmol), K₂CO₃ (1.55 g, 11.25 mmol), hydroquinone (0.11 g, 1.00 mmol) and acetonitrile (350 ml) was added and the reaction mixture was stirred under N₂ for 12 h at 80 °C. After removal of the inorganic salt by filtration, the solvent was evaporated and the residue was dissolved in CH₂Cl₂. The resultant solution was washed with H₂O. The organic phase was collected and dried over anhydrous Na₂SO₄. The solvent was evaporated to provide a crude product, which was purified by column chromatography (eluent: petroleum ether/ CH₂Cl₂, 10:1) to give **DiP5Br** (2.04 g, 60.0 %) as a white solid. Mp: 98.3–97.5 °C. The proton NMR spectrum of **DiP5Br** is shown in Fig. S1. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 7.08 (s, 4H), 6.78–6.67 (m, 16H), 6.57 (s, 2H), 6.48 (s, 2H), 4.42 (s, 4H), 3.86–3.68 (m, 50H), 3.42 (m, 4H), 3.16 (m, 4H), 3.05 (m, 4H), 2.75 (m, 8H), 2.68 (m, 8H), 2.56 (m, 8H).

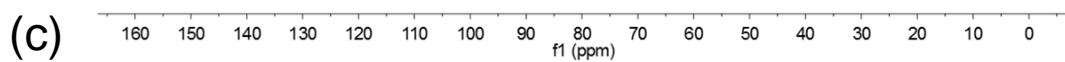
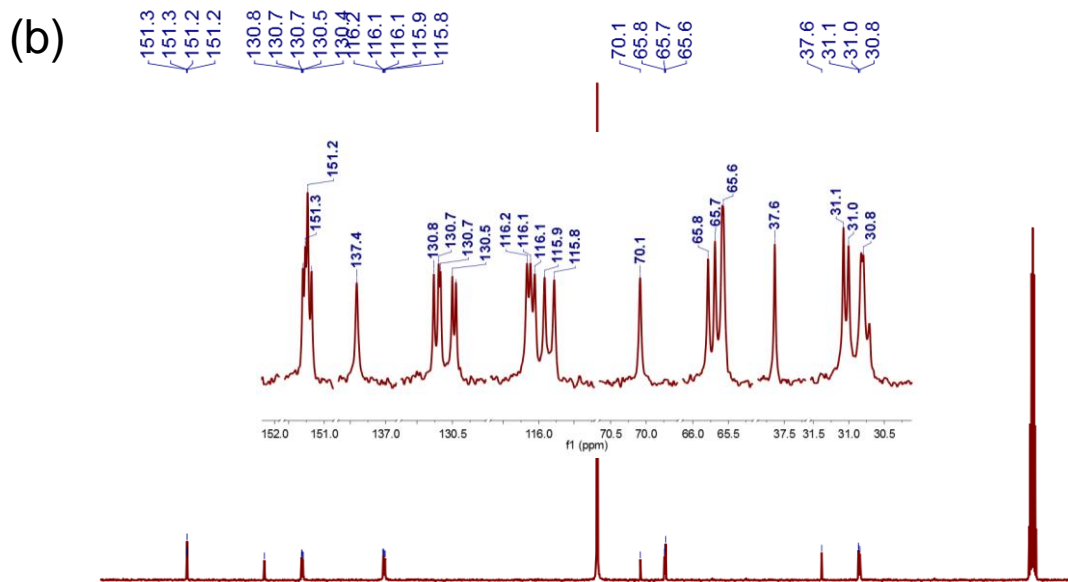
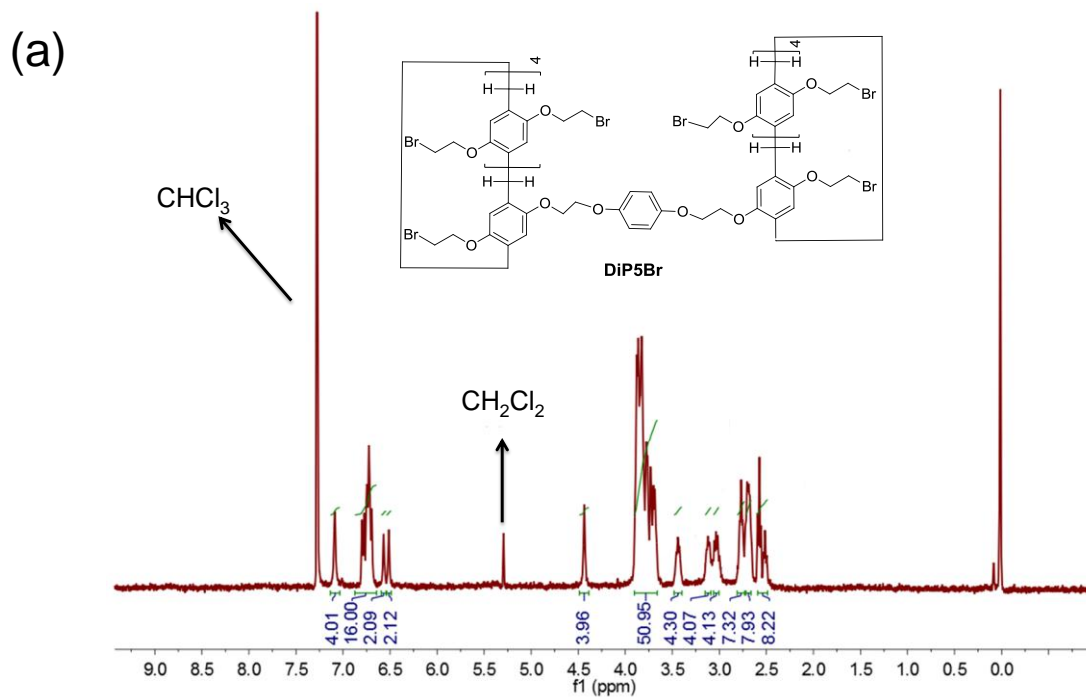


Figure S1. (a) ¹H NMR spectrum (400 Hz, CDCl₃, rt) of **DiP5Br**. (b) ¹³C NMR spectrum (100 Hz, CDCl₃, rt) of **DiP5Br**. (c) Electrospray ionization mass spectrum of **DiP5Br**.

WP5D: A mixture of **DiP5Br** (1.70 g, 0.500 mmol) and triethylamine (11.0 g, 100.0 mmol) in toluene (125 mL) was stirred in a 200 mL round-bottom flask at 120 °C for 24 hours. After cooling, the solvent was removed and the residue was recrystallized from ethanol/diethyl ether (1:2) to give a white solid (2.08 g, 81%). The ^1H NMR spectrum of **WP5D** is shown in Figure S2. ^1H NMR (400 MHz, D_2O , rt) δ (ppm): 6.92-6.69 (m, 24H), 4.12-3.54 (m, 80H), 1.70-1.14 (m, 162H). The ^{13}C NMR spectrum of **WP5D** is shown in Figure S3. ^{13}C NMR (100 MHz, D_2O , rt) δ (ppm): 149.91, 149.61, 149.44, 149.23, 148.62, 114.91, 114.61, 114.41, 113.73, 113.57, 65.31, 64.27, 64.00, 63.80, 63.54, 49.69, 14.58, 14.49. LRESIMS is shown in Figure S4: m/z 776.2 $[\text{M} - 6\text{Br}]^{6+}$, 1203.3 $[\text{M} - 4\text{Br}]^{4+}$. HRESIMS is shown in Figure S5: m/z of $[\text{M} - 3\text{Br}]^{3+}$ $\text{C}_{224}\text{H}_{394}\text{N}_{18}\text{O}_{22}\text{Br}_{15}$ 1630.94; $[\text{M} - 4\text{Br}]^{4+}$ $\text{C}_{224}\text{H}_{394}\text{N}_{18}\text{O}_{22}\text{Br}_{14}$ 1203.48.

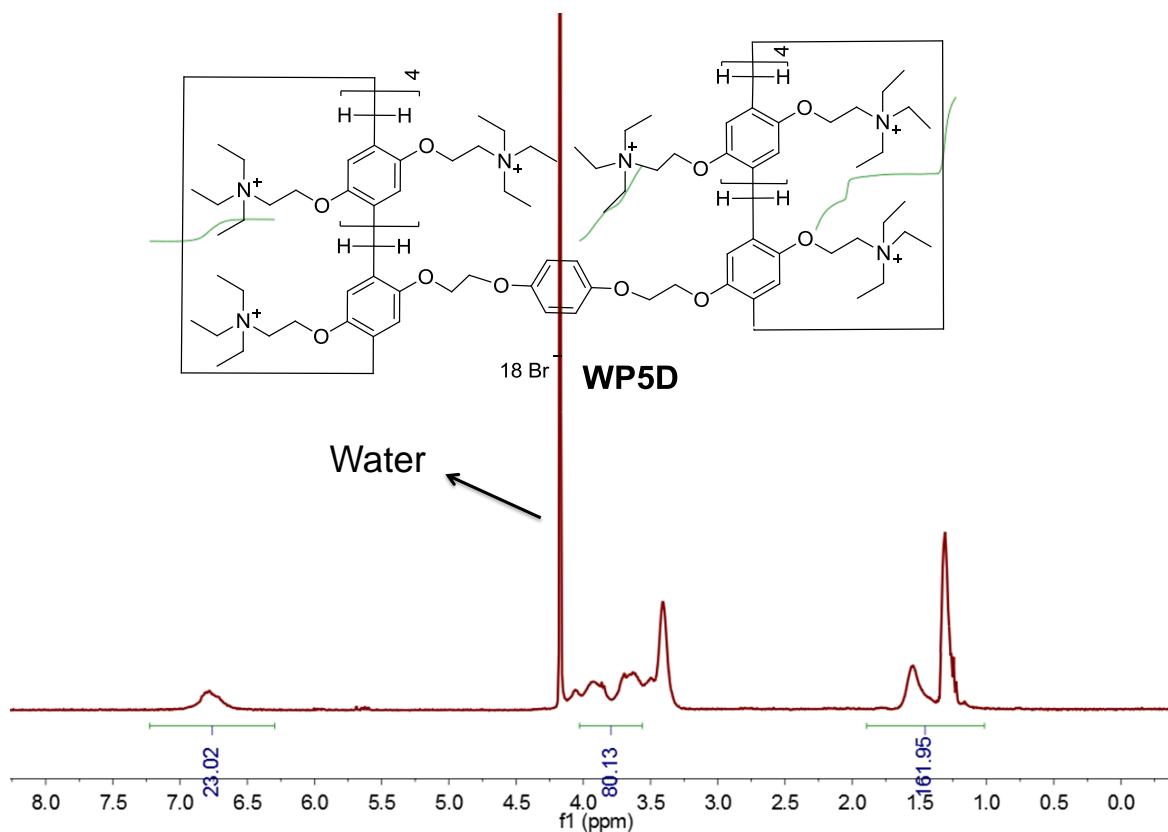


Figure S2. ^1H NMR spectrum (400 MHz, D_2O , rt) of **WP5D**.

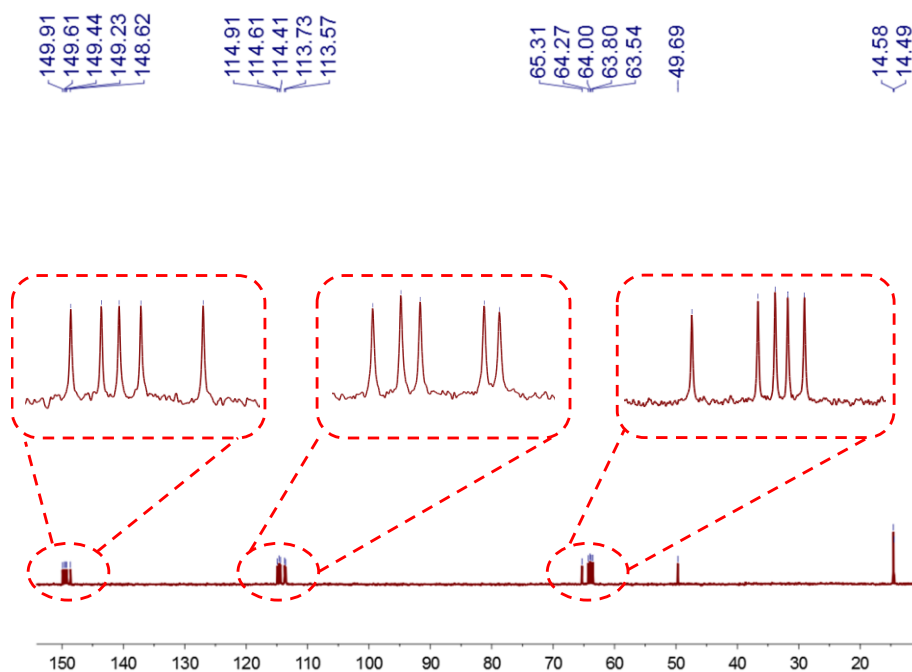


Figure S3. ^{13}C NMR spectrum (100 MHz, D_2O , rt) of WP5D.

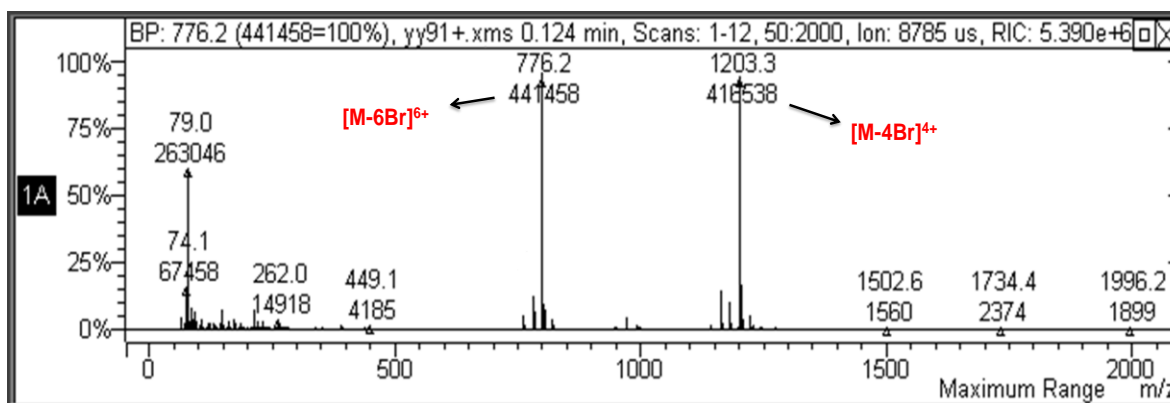


Figure S4. Electrospray ionization mass spectrum of WP5D. Assignment of main peaks: m/z 1203.3 $[\text{M}-4\text{Br}]^{4+}$ and 776.2 $[\text{M}-6\text{Br}]^{6+}$.

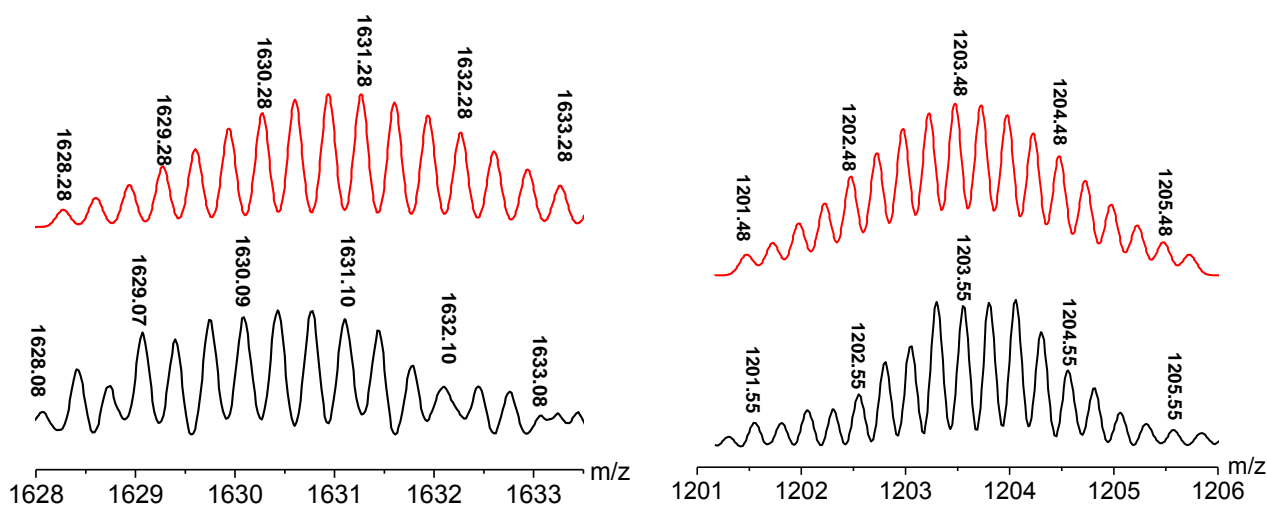


Figure S5. Experimental (black) and calculated (red) ESI-TOF-MS spectra of WP5D $[\text{M}-3\text{Br}]^{3+}$ and $[\text{M}-4\text{Br}]^{4+}$.

3. Characterization of supramolecular polymer networks

3.1 Host-guest interaction between model pillar[5]arene and guest

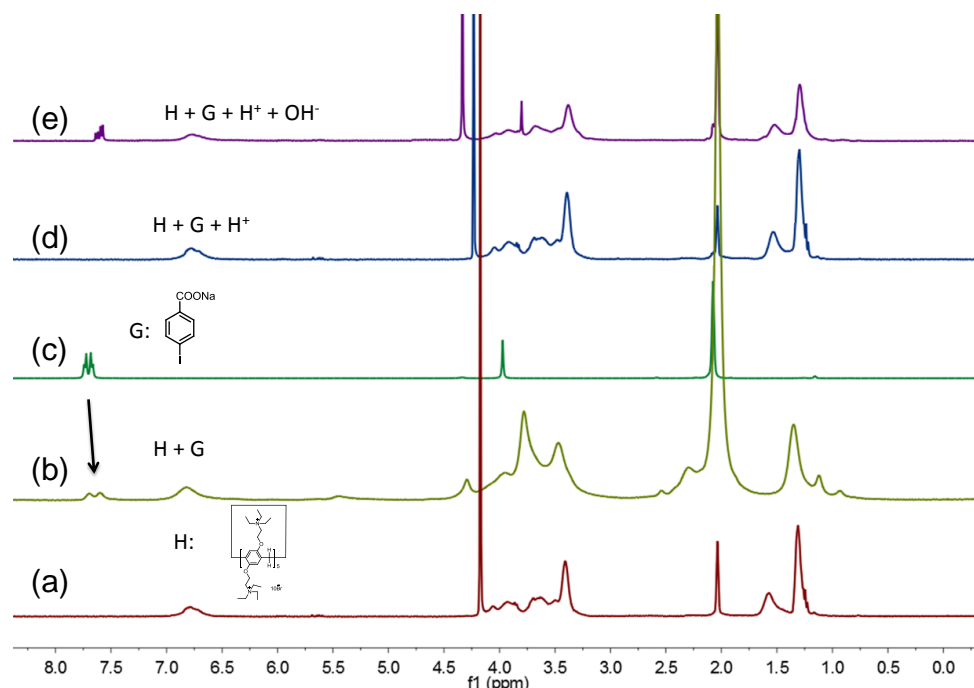


Figure S6. ^1H NMR spectrum (400 MHz, $\text{D}_2\text{O}/\text{acetone-}d_6$, rt) of (a) model pillar[5]arene, (b) model pillar[5]arene and guest, (c) model guest, (d) addition of H^+ to (c), (e) addition of OH^- to (d). $[\text{pillar}[5]\text{arene}] = [\text{guest}] = 2.0 \times 10^{-3} \text{ M}$.

3.2 Characterization of supramolecular polymer networks

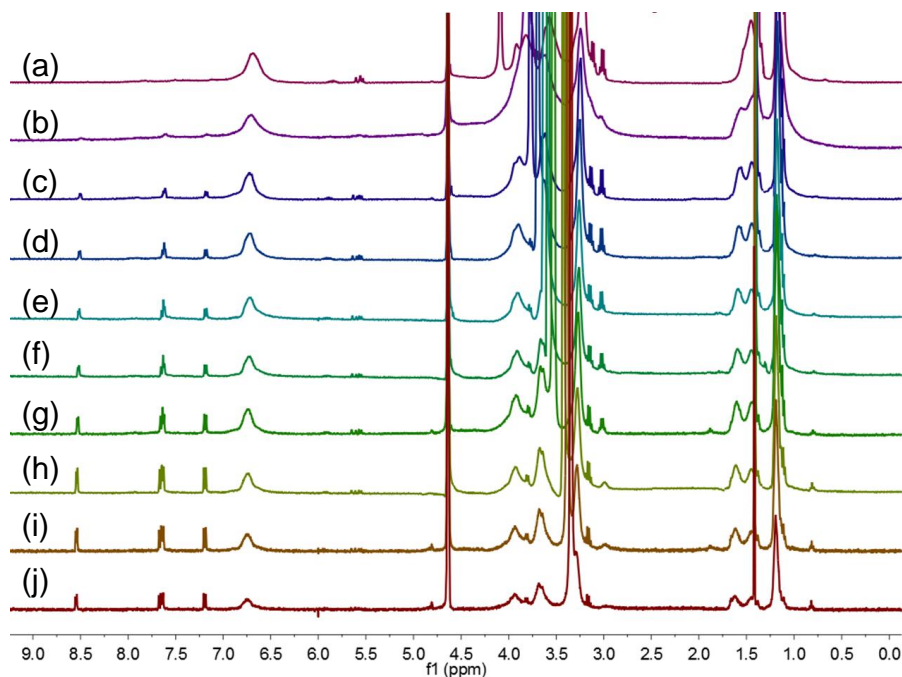


Figure S7. Partial ^1H NMR spectra (400 MHz, 298 K) of **(WP5-dimer) $_2$ carboxylate-TPE** in D_2O at various concentrations: (a) 200 mM; (b) 100 mM; (c) 50.0 mM; (d) 25.0 mM; (e) 15.0 mM; (f) 10.0 mM; (g) 7.00 mM; (h) 5.00 mM; (i) 2.00 mM; (i) 1.00 mM. Here, the concentration is the original **TPE'** concentration.

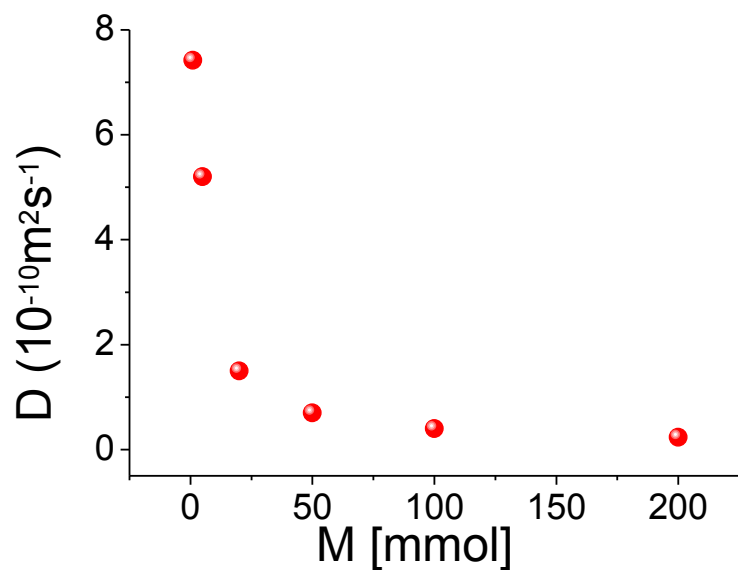


Figure S8. Concentration dependence of diffusion coefficient D (400 MHz, D_2O , 298K).

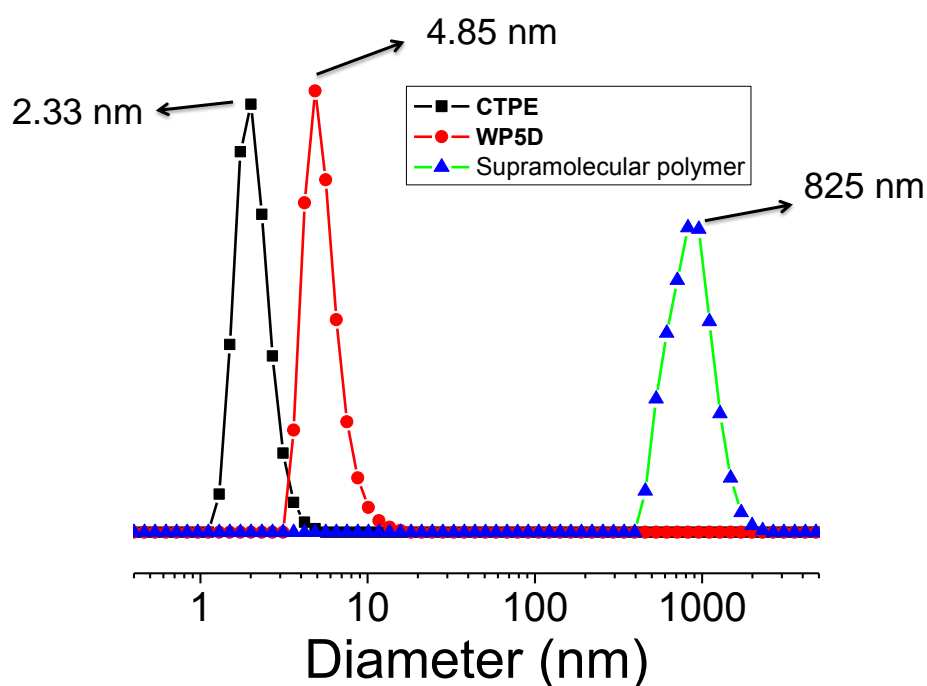


Figure S9. DLS experiments of **WP5D** (50 mM, red line), **CTPE** (25 mM, black line) and the supramolecular polymer (green line) in water.

4. References:

- S1. Y. Ma, X. Ji, F. Xiang, X. Chi, C. Han, J. He, Z. Abliz, W. Chen and F. Huang, *Chem. Commun.*, 2011, **47**, 12340–12342.