# A novel supramolecular polymer gel constructed by crosslinking pillar[5]arene-based supramolecular polymers through metal–ligand interactions

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#### 1. Materials and methods

Compounds 2,<sup>S1</sup> 8,<sup>S1</sup> and 1,4-dimethoxypillar[5]arene<sup>S2</sup> were synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. Transmission electron microscopy (TEM) investigations were carried out on a JEM-1200EX instrument. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).



A mixture of 138 mg (1 mmol) of 2,4-dihydroxybenzaldehyde and 600 mg (2.00 mmol) of 1,10dibromodecane was refluxed in the presence of 140 mg (1.4 mmol) of KHCO<sub>3</sub> in 50 mL of dry acetone for 60 h. At the end of this period, the solvent from the reaction mixture was removed in a rotavapor, 5 mL of water was added to it, and then the solvent was extracted with  $3 \times 10$  mL portions of CHCl<sub>3</sub>. The combined chloroform extracts were evaporated to dryness and then purified by column chromatography over silica gel (60–120 mesh) using 2–3% EtOAc in light petroleum (60–80 °C boiling fraction). Upon chromatographic purification, **5** was obtained as a white crystalline solid in *ca*. 60% yield. The <sup>1</sup>H NMR spectrum of **5** is shown in Figure S1. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 11.42 (1 H, s), 9.64 (1 H, s), 7.35 (1 H, d, *J* = 8.7), 6.46 (1 H, dd, *J* = 8.7, 2.3), 6.34 (1 H, d, *J* = 2.1), 3.93 (2 H, t, *J* = 6.5), 3.34 (2 H, t, *J* = 6.8), 1.84–1.66 (4 H, m), 1.42–1.20 (14 H, m). The <sup>13</sup>C NMR spectrum of **5** is shown in Figure S2. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 194.33, 166.46, 164.54, 115.01, 108.80, 101.04, 77.34, 77.03, 76.71, 68.57, 34.07, 32.80, 29.39, 29.34, 29.24, 28.73, 28.15, 25.90. LRESIMS is shown in Figure S3: *m/z* 356.9 [M + H]<sup>+</sup>.

Scheme S1. Synthetic route to 1.



Figure S2. <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, 298 K) of 5.



Figure S3. LRESI mass spectrum of 5.

Compound **5** (1.46 g, 4.10 mmol) and trimethylamine (33 % in ethanol, 30.0 mL, 105 mmol) were added to ethanol (55.0 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation and deionized water (35.0 mL) was added. After filtration, water was removed by evaporation to obtain **6** as a colorless solid (1.13 g, 93 %). The <sup>1</sup>H NMR spectrum of **6** is shown in Fig. S4. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K)  $\delta$  (ppm): 10.99 (1 H, s), 10.01 (1 H, s), 7.61 (1 H, d, *J* = 8.7), 6.55 (1 H, dd, *J* = 8.7, 1.7), 6.49 (1 H, s), 4.02 (2 H, t, *J* = 6.4), 3.32–3.25 (2 H, m), 3.06 (9 H, s), 1.77–1.60 (4 H, m), 1.35 (13 H, d, *J* = 41.2). The <sup>13</sup>C NMR spectrum of **6** is shown in Figure S5. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, 298 K)  $\delta$  (ppm): 190.96, 132.15, 116.08, 107.66, 101.16, 67.96, 65.19, 40.10, 39.89, 39.68, 39.47, 39.26, 39.06, 38.85, 28.82, 28.69, 28.63, 28.44, 28.37, 25.70, 25.35, 21.99. LRESIMS is shown in Figure S6: *m/z* 336.2 [M – Br]<sup>+</sup>.



*Figure S4.* <sup>1</sup>H NMR spectrum (500 MHz, DMSO-*d*<sub>6</sub>, 298 K) of **6**.



*Figure S5.* <sup>13</sup>C NMR spectrum (125 MHz, DMSO-*d*<sub>6</sub>, 298 K) of **6**.



Figure S6. LRESI mass spectrum of 6.

Anhydrous potassium carbonate (0.56 g, 4.05 mmol) was added to a solution of **2** (1 g, 1.07 mmol) and 4nitrophenol (0.150 g, 1.07 mmol) in dry acetonitrile (50 mL) under vigorous stirring. The mixture was stirred at 80 °C for 24 hours under nitrogen atmosphere. After removal of the inorganic salt, the solvent was evaporated and the residue was directly used for the next step because compound **3** was hard to be purified by chromatography on silica gel. Compound **3** was dissolved in 20 mL THF and then 4 mL hydrazine hydrate and about 1 g Raney Nickel was added. The mixture was stirred at 60 °C for 3 hours. The solvent was evaporated and the residue was purified by chromatography on silica gel (dichloromethane/ethyl acetate, v/v 50:1) to give **4** as a white solid (630 mg, 60%). The <sup>1</sup>H NMR spectrum of **4** is shown in Fig. S7. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 6.78–6.63 (12 H, m), 6.57 (2 H, d, J = 8.7), 3.81 (1 H, t, J = 6.1), 3.72–3.52 (20 H, m), 3.33 (1 H, s), 1.76–1.67 (1 H, m), 1.42 (1 H, s), 1.31–1.04 (4 H, m), 0.94 (1 H, s), 0.78 (2 H, dd, J = 14.4, 11.4). The <sup>13</sup>C NMR spectrum of **4** is shown in Figure S8. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 149.62, 148.83, 127.13, 127.09, , 127.02, 115.38, 114.37, 113.59, 112.87, 76.33, 76.01, 75.70, 67.58, 54.62, 28.73, 28.28, 0.01. LRESIMS is shown in Figure S9: m/z 984.2 [M – Br]<sup>+</sup>.



Figure S7. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of 4.



Figure S8. <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, 298 K) of 4.



Compound **4** (983 mg, 1 mmol) and compound **6** (415 mg, 1 mmol) were dissolved in 100 mL of methanol and the mixture was stirred at 65 °C for 24 hours. After the solvent was evaporated, the residue was purified by chromatography on silica gel (dichloromethane/methanol, v/v 20:1) to give **1** as a yellow solid (1.24 g, 90%). The <sup>1</sup>H NMR spectrum of **1** is shown in Fig. S10. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 13.97 (1 H, s), 8.43 (1 H, s), 6.72 (18 H, s), 6.43 (2 H, s), 3.83 (54 H, d, J = 105.7), 2.70 (8 H, s), 1.78 (9 H, s), 1.45 (6 H, s), 1.23 (17 H, dd, J = 35.7, 19.5), 0.84–0.57 (3 H, m), 0.34 (1 H, s), -0.27 (1 H, d, J = 45.0), -1.96 (3 H, s). The <sup>13</sup>C NMR spectrum of **1** is shown in Figure S11. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 162.87, 162.02, 158.18, 157.02, 149.63, 132.21, 127.90, 120.92, 114.06, 112.17, 106.17, 100.47, 76.34, 76.08, 75.76, 67.27, 66.98, 65.81, 51.41, 27.81, 25.08, 0.01. LRESIMS is shown in Figure S12: m/z 1302.1 [M – Br]<sup>+</sup>.



Figure S11. <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, 298 K) of 1.



Figure S12. LRESI mass spectrum of 1.



Compound **8** (342 mg, 1 mmol) and trimethylamine (33 % in ethanol, 15.0 mL, 53 mmol) were added to ethanol (30.0 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation and deionized water (35.0 mL) was added. After filtration, water was removed by evaporation to obtain **G** as a colorless solid (373 mg, 93 %). The <sup>1</sup>H NMR spectrum of **G** is shown in Fig. S13. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 6.76 (4 H, d, J = 1.5), 3.83 (1 H, dd, J = 6.5, 5.2), 3.69 (1 H, d, J = 1.6), 3.55–3.48 (0 H, m), 3.40 (2 H, d, J = 1.3), 1.72–1.62 (1 H, m), 1.31 (3 H, dd, J = 37.8, 14.2). The <sup>13</sup>C NMR spectrum of **7** is shown in Figure S14. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 152.63, 152.24, 114.41, 113.60, 67.57, 65.98, 54.74, 52.34, 29.93, 28.31, 28.24, 28.15, 25.12, 24.97, 22.16. LRESIMS is shown in Figure S15: *m/z* 322.4 [M – Br]<sup>+</sup>.



Figure S14. <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, 298 K) of G.



Figure S15. LRESI mass spectrum of G.

## 3. Complexation study on DMP5 and model guest G

To determine the stoichiometry and association constant between **DMP5** and **G**, <sup>1</sup>H NMR titration was done with solutions which had a constant concentration of **G** (1.00 mM) and different concentrations of **DMP5**. By a non-linear curve-fitting method, the association constant between the **DMP5** and **G** was calculated. By a mole ratio plot, a 1:1 stoichiometry was obtained for this system

The non-linear curve-fitting was based on the equation:

 $\Delta \delta = (\Delta \delta_{\infty}/[H]_0) (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5([G]_0^2 + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$ (Eq. S1) wherein  $\Delta \delta$  is the chemical shift change of  $H_{G2}$  on **G** at  $[G]_0, \Delta \delta_{\infty}$  is the chemical shift change of  $H_{G2}$  when the guest is completely complexed,  $[G]_0$  is the fixed initial concentration of the guest, and  $[H]_0$  is the varying concentration of **DMP5**.



*Figure S16.* Partial <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>, 298 K) of **G** at a concentration of 1.00 mM with different concentrations of **DMP5**: (a) 0.00 mM; (b) 1.18 mM; (c) 2.23 mM; (d) 3.18 mM; (e) 4.03 mM; (f) 4.80 mM; (g) 6.94 mM; (h) 8.85 mM; (i) 9.87 mM; (j) 10.9 mM; (k) 11.8 mM; (l) 12.5 mM; (m) 13.7 mM.



Figure S17. Mole ratio plot for the complexation between DMP5 and G, indicating a 1:1 stoichiometry.



*Figure S18.* The chemical shift changes of  $H_{G2}$  on G upon addition of **DMP5**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

4. Concentration dependence of diffusion coefficient D and partial DOSY NMR spectra of **1** at different concentrations



Figure S19. Concentration dependence of diffusion coefficient D (500 MHz, CDCl<sub>3</sub>, 298 K).



Figure S20. DOSY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of 1 at 15.0 mM.



Figure S21. DOSY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of 1 at 60.0 mM.



Figure S22. DOSY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of 1 at 100 mM.



Figure S23. DOSY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of 1 at 142 mM.



Figure S24. DOSY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of 1 at 250 mM.

5. Log-log plot of specific viscosity of monomer 1 versus the monomer concentration at 298 K.



Figure S25. Log-log plot of specific viscosity of monomer 1 versus the monomer concentration at 298 K.

6. Partial NOESY NMR spectrum of 1 at a concentration of 60.0 mM



*Figure S26.* NOESY NMR spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of **1** at 60.0 mM. Strong correlations were observed between the aromatic protons  $H_{a-c}$  of the pillar[5]arene unit and the methyl proton  $H_d$  on the trimethylammonium group, as well as the methylene protons  $H_f$  and  $H_e$ , suggesting that the trimethylammonium group deeply threaded into the cavity of the pillararene host

7. Size distributions of 1 and  $1 + Cu^{2+}$  in CHCl<sub>3</sub>



*Figure S27.* Size distributions of 1 and  $1 + Cu^{2+}$  in CHCl<sub>3</sub>. c = 80.0 mM. The average hydrodynamic diameter ( $D_h$ ) of the linear supramolecular polymers formed by monomer 1 at a concentration of 80.0 mM was determined to be 142 nm and after 0.500 equiv. of Cu<sup>2+</sup> ions was added, the corresponding  $D_h$  value increased obviously to 825 nm, which are consistent with the above-discussed <sup>1</sup>H NMR experiments. This observation proved an increase in the average aggregation size owing to the conversion from low-molecular-weight aggregates to 3D supramolecular network.



## 8. Photos to show the detection of $Cu^{2+}$ by the change of fluorescence

*Figure S28.* (a) Photograph of a film of linear supramolecular polymer formed by dilute CHCl<sub>3</sub> solution of 1 at 60.00 mM, illuminated at 365 nm. (b) Photograph of the film after adding one drop of  $Cu(OAc)_2 \cdot H_2O$  in CH<sub>3</sub>CN, illuminated at 365 nm.

9. Time stability, photostability, reversibility and repeatability experiments



*Figure S29.* (a) time stability experiment, **1** showed excellent time stability after 24 hours; (b) photostability experiment, the fluorescence intensity of **1** has barely changed after irradiated by 365nm about 24 hours; (c) reversibility experiment, the fluorescence spectra of **1**, **1** + Cu<sup>2+</sup> and **1** + Cu<sup>2+</sup> + CN<sup>-</sup>, **1** + Cu<sup>2+</sup> shows very weak fluorescence, however, the fluorescence of **1** + Cu<sup>2+</sup> + CN<sup>-</sup> was dramatically enhanced, it showed good reversibility; (d) repeatability experiment, fluorescence intensity changed after addition of Cu<sup>2+</sup> and CN<sup>-</sup>, demonstrating that this process was reversible.

#### 10. Calculated values of polymerization degree n at different concentrations of 1

Using the Carothers equation and assuming that the same average association constant holds for each successive step (isodesmic) and that cyclic species can either be ignored or taken into account, the average degree of polymerization, n, is easily derived as being related to the equilibrium constant  $K_a$  and the initial monomer concentration as follows:<sup>S3</sup>

If we now define p = extent of complexation,

$$K_{\rm a} = p[{\rm H}]_0 / (1 - p)^2 [{\rm H}]_0^2$$

Solving this quadratic equation leads to

$$1 - p = \{(1 + 4K_{a}[H]_{0})^{1/2} - 1\}/2K_{a}[H]_{0}$$

$$n = 1/(1 - p) = 2K_{a}[H]_{0}/\{(1 + 4K_{a}[H]_{0})^{1/2} - 1\}$$
(1)
if  $4K_{a}[H]_{0} \gg 1$ ,  $n = 2K_{a}[H]_{0}/\{(4K_{a}[H]_{0})^{1/2} - 1\}$  and
if  $(4K_{a}[H]_{0})^{1/2} \gg 1$ ,  $n = (K_{a}[H]_{0})^{1/2}$ (2)

In this system p is the extent of complexation and  $[H]_0 = [1]_0$ . Therefore, degrees of polymerization calculated in this way represent maximum values that in practice will be reduced by formation of cyclics and possibly by reduction in the association constant as the suprapolymer grows ("attenuation"). As the concentration increases, the calculated size of aggregates increases to large values.

[monomer 1] <sub>0</sub> (mM)	р	max n
0.500	0.300	1.43
15.0	0.794	4.86
60.0	0.891	9.17
100	0.914	11.7
142	0.927	13.8
250	0.945	18.2

*Table S1.* Calculated values of *p* and *n* at different concentrations of monomer 1.

#### 11. References:

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