## Supramolecualr main-chain polycatenanes formed by orthogonal metal ion coordination and pillar[5]arene-based host-guest interaction

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## **Electronic Supplementary Information (15 pages)**

1.	Materials and methods	<i>S2</i>
2.	Synthesis of compound 1 and 3	<i>S3</i>
3.	Partial <sup>1</sup> H NMR spectra of $1 \cdot Zn \cdot 2_2$ in CHCl <sub>3</sub> /CH <sub>3</sub> CN (1/1, v/v) at various concentrations	<i>S9</i>
4.	Partial NOESY NMR spectrum of $1 \cdot 2_2$ at a concentration of 25.0 mM	<i>S10</i>
5.	Concentration dependence of diffusion coefficient D and partial DOSY NMR spectra of	<i>S11</i>
	$1 \cdot Zn \cdot 2_2$ at different concentrations	
6.	Size distributions of 1, 2, and $1 \cdot Zn \cdot 2_2$ in CHCl <sub>3</sub> /CH <sub>3</sub> CN (1/1, v/v)	<i>S14</i>
7.	Rheology measurements for two supramolecular polymers	<i>S15</i>
8.	References	<i>S16</i>

## 1. Materials and methods

Compounds  $2^{S1}$   $5^{S2}$   $6^{S1}$  and 5-azidopentanenitrile<sup>S3</sup> were synthesized according to literature procedures. Compounds **3** and **4** were synthesized modifying from previous report<sup>S4</sup>. 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. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25.0 °C in chloroform/acetonitrile (v/v = 1/1). Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. Rheological test was carried out by using an AR-2000ex (TA Instruments Ltd) implemented with a 40-mm diameter parallel plate that was attached to a transducer. The gap in the setup for rheological testing of the gels was 1.0 mm and experiments were conducted at 25 °C. Scheme S1. Synthetic route to 1.



Compound **5** (4.33 g, 19.5 mmol) and hydroxybenzotriazole (5.53 g, 40.9 mmol) were dissolved in dry THF (100 mL) and the solution cooled in ice. Dicyclohexylcarbodiimide (8.45 g, 40.9 mmol) was added in four portions over 20 minutes and the mixture strried overnight. The solid was removed by filtration and the filtrate added dropwise to a stirred, ice cooled solution of 4-aminobenzylamine (5.00 g, 40.9 mmol) in dry THF (100 mL) over 60 minutes. After the addition, the mixture was stirred overnight. The solvent was removed under reduced pressure and the oil taken up in ethyl acetate (150 mL) and washed with sodium hydroxide solution. The ethyl acetate was dried over magnesium sulphate, filtered and the solvent removed under reduced pressure and the resulting thick oil crystallized from ethanol/water. Filtration afforded compound **4** as a colorless powder (6.55 g, 78.0%). The <sup>1</sup>H NMR spectrum of **4** is shown in Fig. S1. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K)  $\delta$  (ppm): 8.90 (2H, t, *J* = 7.50 Hz), 7.98 (1H, t, *J* = 1.55 Hz), 7.59 (2H, d, *J* = 1.55 Hz), 7.00 (4H, d, *J* = 10.0 Hz), 6.53 (4H, d, *J* = 15.0), 4.96 (4H, s), 4.89 (2H, d, *J* = 5.00 Hz), 4.29 (4H, d, *J* = 5.00 Hz). The <sup>13</sup>C NMR spectrum of **4** is shown in Fig. S2. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, 298 K)  $\delta$  (ppm): 165.07, 157.01, 147.53, 136.07, 128.35, 126.24, 119.19, 117.54, 116.14, 113.64, 90.65, 78.82, 78.60, 66.99, 55.84, 47.47, 42.47, 33.32, 25.29, 24.44.



*Figure S2.* <sup>13</sup>C NMR spectrum (125 MHz, DMSO-*d*<sub>6</sub>, 298 K) of **4**.

A 2 litre round bottomed flask was charged with compound 4 prepared above (1.50 g, 3.50 mmol), a large stirring bar and dry acetonitrile (40 mL). The mixture was heated and swirled till compound 4 dissolved. Dry dichloromethane (1.2 litres) and trimethylamine (1.10 mL, 0.80 g, 7.90 mmol) were added. A 150 mL pressure equilibrated dropping funnel and a drying tube were attached and charged with dry dichloromethane (100 mL) and sebacoyl chloride (0.75 mL, 0.84 g, 3.50 mmol) and the mixture added to the rapidly stirred solution over about 15 minutes. After 5 minutes, the solution becomes cloudy and striring was continued for 12 hours. The reaction mixture was filtered and the solids washed with chloroform. The filtrate was washed with aqueous hydrochloric acid and saturated sodium bicarbonate solution, dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The solvent was removed to about 10 mL and this was transferred to a small conical flask. The reaction flask was rinsed with an additional 5 mL of dichloromethane and this was also added to the conical flask. The flask was stopped and allowed to stand for 24 hours. Catenane **3** was separated by filtration as a colorless solid (0.46 g, 22.0%). The <sup>1</sup>H NMR spectrum of **3** is shown in Fig. S3. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , 298 K) δ (ppm): 9.73 (4H, s), 8.38 (4H, s), 7.72 (2H, s), 7.44 (4H, s), 7.32 (8H, s), 6.92 (8H, s), 4.50 (4H, s), 4.36 (2H, s), 4.08 (8H, s), 2.14 (8H, s), 1.30 (8H, s), 0.81 (16H, s). The <sup>13</sup>C NMR spectrum of **3** is shown in Fig. S4. <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ , 298 K)  $\delta$  (ppm): 174.53, 171.39, 171.08, 169.60, 165.66, 153.58, 138.04, 128.44, 128.17, 127.63, 118.95, 118.78, 90.50, 78.56, 52.49, 49.45, 47.49, 43.04, 36.00, 34.01, 33.74, 33.30, 31.66, 30.33, 29.03, 28.61, 28.50, 25.42, 24.50.



*Figure S4.* <sup>13</sup>C NMR spectrum (125 MHz, DMSO-*d*<sub>6</sub>, 298 K) of **3**.

Compound **3** (300 mg, 0.252 mmol) and 5-azidopentanenitrile (78 mg, 0.630 mmol) were added to a solution of sodium ascorbate (25.2 mg, 0.126 mmol) and Copper(II) sulfate pentahydrate (12.5 mg, 0.050 mmol) in DMF (15 mL) and Water (2 mL). The mixture was stirred at 80 °C for 24 hours under nitrogen atmosphere. After removal of the solvent, the residue was purified by chromatography on silica gel (dichloromethane/methanol, v/v 50:1) to give **1** as a yellow solid (230 mg, 60.8%). The <sup>1</sup>H NMR spectrum of **1** is shown in Fig. S5. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K)  $\delta$  (ppm): 9.71 (4H, s), 8.41 (4H, s), 8.25 (2H, s), 7.74 (2H, s), 7.44 (4H, s), 7.32 (8H, d, *J* = 10 Hz), 6.93 (8H, d, *J* = 10 Hz), 4.45 (4H, d, *J* = 5 Hz), 4.37 (2H, s), 4.08 (8H, t, *J* = 5 Hz), 2.26 (4H, t, *J* =7.5 Hz), 2.14 (8H, s), 1.92 (6H, m), 1.55 (8H, m), 1.30 (8H, s), 0.81 (16H, s). The <sup>13</sup>C NMR spectrum of **1** is shown in Fig. S6. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, 298 K)  $\delta$  (ppm): 171.37, 165.78, 165.63, 157.81, 142.27, 138.04, 136.37, 136.28, 133.48, 132.57, 128.44, 138.16, 124.51, 120.38, 118.92, 118.73, 116.21, 61.34, 48.52, 43.02, 36.00, 29.05, 28.75, 27.93, 25.21, 21.92, 15.63. LRESIMS is shown in Figure S7: *m/z* 1460.2 [M + Na]<sup>+</sup>. HRESIMS for **1**: *m/z* calcd for [M]<sup>+</sup>C<sub>80</sub>H<sub>92</sub>N<sub>16</sub>O<sub>10</sub> 1436.7182; found 1436.7165; error –1.2 ppm.



*Figure S6.* <sup>13</sup>C NMR spectrum (125 MHz, DMSO-*d*<sub>6</sub>, 298 K) of **1**.



Figure S7. LRESI mass spectrum of 1.

3. Partial <sup>1</sup>H NMR spectra of  $1 \cdot Zn \cdot 2_2$  in CHCl<sub>3</sub>/CH<sub>3</sub>CN (1/1, v/v) at various concentrations



*Figure S8.* Partial <sup>1</sup>H NMR spectra (500 MHz, 298 K) of  $1 \cdot Zn \cdot 2_2$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> (v/v = 1/1) at various concentrations: (a) 220 mM; (b) 100 mM; (c) 50.0 mM; (d) 25.0 mM; (e) 12.5 mM; (f) 6.25 mM; (g) 3.15 mM; (h) 1.65 mM; (i) 0.75 mM.



*Figure S9.* Partial <sup>1</sup>H NMR spectra (500 MHz, 298 K) of  $1 \cdot Zn \cdot 2_2$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> ( $\nu/\nu = 1/1$ ) at various concentrations: (a) 220 mM; (b) 100 mM; (c) 50.0 mM; (d) 25.0 mM; (e) 12.5 mM; (f) 6.25 mM; (g) 3.15 mM; (h) 1.65 mM; (i) 0.75 mM.

4. Partial NOESY NMR spectrum of  $1 \cdot 2_2$  at a concentration of 25.0 mM



*Figure S10.* NOESY NMR spectrum (500 MHz, 298 K) of  $1 \cdot 2_2$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> (v/v = 1/1) at 25.0 mM.



*Figure S11.* NOESY NMR spectrum (500 MHz, 298 K) of  $1 \cdot 2_2$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> (v/v = 1/1) at 25.0 mM.

5. Concentration dependence of diffusion coefficient D and partial DOSY NMR spectra of  $1 \cdot Zn \cdot 2_2$  at different concentrations



*Figure S12.* Concentration dependence of diffusion coefficient *D* (500 MHz, 298 K) of  $1 \cdot Zn \cdot 2_2$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> (v/v = 1/1).



*Figure S13.* DOSY NMR spectrum (500 MHz, 298 K) of **1**•Zn•2<sub>2</sub> in CD<sub>3</sub>CN/CDCl<sub>3</sub> (*v*/*v* = 1/1) at 12.5 mM.



*Figure S14.* DOSY NMR spectrum (500 MHz, 298 K) of  $1 \cdot Zn \cdot 2_2$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> (v/v = 1/1) at 25.0 mM.



*Figure S15.* DOSY NMR spectrum (500 MHz, 298 K) of  $1 \cdot Zn \cdot 2_2$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> (v/v = 1/1) at 50.0 mM.



*Figure S16.* DOSY NMR spectrum (500 MHz, 298 K) of **1**•*Z***n**•**2**<sub>2</sub> in CD<sub>3</sub>CN/CDCl<sub>3</sub> (*v*/*v* = 1/1) at 100 mM.



*Figure S17.* DOSY NMR spectrum (500 MHz, 298 K) of 1•Zn•2<sub>2</sub> in CD<sub>3</sub>CN/CDCl<sub>3</sub> (*v*/*v* = 1/1) at 220 mM.

6. Size distributions of 1, 2, and  $1 \cdot Zn \cdot 2_2$  in CHCl<sub>3</sub>/CH<sub>3</sub>CN (1/1, v/v)



*Figure S18.* Size distributions of 1, 2, and  $1 \cdot Zn \cdot 2_2$  in CHCl<sub>3</sub>/CH<sub>3</sub>CN (1/1, v/v). c = 70.0 mM.

7. Rheology measurements for two supramolecular polymers



Figure S19. Illustration of the formation of two supramolecular polymers.



*Figure S20.* Storage modulus (G') and loss modulus (G'') of two supramolecular polymers versus scanning frequency.

## 8. References:

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