Formation of fluorescent supramolecular polymeric assemblies *via* orthogonal pillar[5]arene-based molecular recognition and metal ion coordination

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Electronic Supplementary Information (16 pages)

Materials and m	ethods	• • • • • • • •					S2	
Synthesis and characterizations of compounds						<i>S3</i>		
Partial ¹ H NMR	spectra of $l_2 \cdot Z$	n•2 at	t different co	ncentrations			S13	
Concentration	dependence	of	diffusion	coefficient	D	of	1 ₂ •Zn•2	
	<i>S14</i>							
Absorbance spectra of $1_2 \bullet 2$ and $1_2 \bullet 2n \bullet 2$							<i>S</i> 15	
Fluorescence spectra of $1_2 \cdot 2$ and $1_2 \cdot 2n \cdot 2$								
References							S16	

General methods

All reagents were commercially available and used as supplied without further purication. ¹H or ¹³C NMR spectra were recorded with a Bruker Avance DMX 500 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 semi-micro dilution viscometer at 25.0 °C in chloroform/acetonitrile (v/v = 1/1). Scanning electron microscopy investigation was carried out on a JEOL 6390LV instrument. The fluorescence spectra were recorded on a Perkin Elmer LS55 fluorescence spectrophotometer. UV–Vis spectra were taken on a Perkin-Elmer Lambda 35 UV–Vis spectrophotometer. Compounds **2** and **1a** were prepared according to reported procedures.^{1, 2}

SEM sample preparation

SEM samples were prepared by dissolving $1_2 \cdot Zn \cdot 2$ in chloroform/acetonitrile (v/v = 1/1) at high concentration via the vacuum freeze-drying methodology for the supramolecular polymer.

Synthesis of guest molecule 2



The proton NMR spectrum of **2a** is shown in Fig. S1. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 6.92 (d, J = 8 Hz, 4H), 6.84 (d, J = 8 Hz, 4H), 4.63 (s, 4H), 3.90 (t, J = 12 Hz, 4H), 2.50 (t, J = 8 Hz, 2H), 1.77–1.73 (m, 4H), 1.45–1.42 (m, 4H), 1.32 (m, 8H). The ¹³C NMR spectrum of **2a** is shown in Fig. S2. The ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm): 154.05, 151.56, 116.10, 115.32, 78.96, 75.30, 68.54, 56.62, 29.51, 29.40, 29.37, 26.06.



Fig. S1 ¹H NMR spectrum (400 MHz, CDCl₃, 298K) of 2a.



Fig. S2 ¹³C NMR spectrum (100 MHz, CDCl₃, 298K) of 2a.



¹H NMR spectrum of 5-azidopentanenitrile is shown in Fig. S3. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 1.75 (t, *J* = 4 Hz, 4H), 2.41 (t, *J* = 12 Hz, 2H), 3.37 (t, *J* = 12 Hz, 2H).



Fig. S3 ¹H NMR spectrum (400 MHz, CDCl₃, 298K) of 5-azidopentanenitrile.



The proton NMR spectrum of **2** is shown in Fig. S4. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 7.60 (s, 2H), 6.92 (d, J = 8 Hz, 4H), 8.84 (d, J = 8 Hz, 4H), 5.16 (s, 4H), 4.43 (t, J = 12 Hz, 4H), 3.90 (t, J = 8 Hz, 4H), 2.41 (t, J = 8 Hz, 4H), 2.11–2.08 (m, 4H), 1.77–1.63 (m, 9H), 1.45–1.32 (m, 14H). The ¹³C NMR spectrum of **2** is shown in Fig. S5. The ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm): 153.79, 152.16, 144.89, 122.53, 118.91, 115.81, 115.41, 68.57, 62.73, 49.24, 29.48, 29.36, 29.06, 26.04, 22.32, 16.71.



Fig. S4 ¹H NMR spectrum (400 MHz, CDCl₃, 298K) of 2.



Fig. S5 ¹³C NMR spectrum (100 MHz, CDCl₃, 298K) of 2.

Synthesis of pillar[5]arene 1



The proton NMR spectrum of **1a** is shown in Fig. S6. ¹H NMR (400 MHz, CD₃CN, 298K) δ (ppm): 6.94–6.90 (m, 10H), 3.90 (t, J = 12 Hz, 2H), 3.77–3.71 (m, 37H), 3.41 (t, J = 12 Hz, 2H), 1.85–1.81 (m, 2H), 1.77–1.73 (m, 2H), 1.57–1.53 (m, 2H), 1.35–1.30 (m, 10H). The ¹³C NMR spectrum of **1a** is shown in Fig. S7. The ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm): 150.55, 150.40, 150.31, 150,19, 150.10, 149.54, 128.39, 128.23, 128.07, 128.01, 127.98, 127.91, 127.84, 114.54, 113.83, 113.14, 113.03, 68.16, 55.66, 55.41, 55.34, 55.27, 55.21, 33.63, 31.53, 29.28, 29.15, 27.59.



Fig. S6 ¹H NMR spectrum (400 MHz, CD₃CN, 298K) of pillar[5]arene 1a.



Fig. S7 ¹³C NMR spectrum (100 MHz, CDCl₃, 298K) of pillar[5]arene 1a.



In a 250 mL round–bottom flask, compound 1a (2.4 g, 2.5 mmol), K₂CO₃ (1.38 g, 10 mmol), KI (0.08 g, 0.5 mmol), compound 1b (1.6 g, 5.0 mmol) and acetonitrile (150 mL) were added. The reaction mixture was stirred at reflux for 48 hours. After the solid was filtered off, the solvent was removed. The solid was dissolved in CHCl₃ (200 mL) and washed twice with H₂O (200 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was isolated by flash column chromatography using acetone/ethyl acetate (5:1) ($R_{\rm f} = 0.25$). The fractions containing the product were combined and concentrated under vacuum to give 1 (2.85 g, 95.0 %) as a white solid. The proton NMR spectrum of 1 is shown in Fig. S8. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 8.75–8.67 (m, 6H), 7.90–7.87 (m, 4H), 7.38-7.34 (m, 2H), 7.02 (d, J = 8 Hz, 2H), 6.86-6.78 (m, 10H), 3.93 (t, J = 10012 Hz, 2H), 3.78–3.76 (m, 10H), 3.70–3.65 (m, 26H), 1.79 (m, 2H), 1.60 (m, 2H) 1.23 (m, 16H). The ¹³C NMR spectrum of 1 is shown in Fig. S9. The ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm):160.27, 156.43, 155.85, 150.79, 150.73, 150.67, 150.62, 150.46, 149.91, 149.82, 149.13, 149.13, 136.90, 130.33, 128.49, 128.37, 128.32, 128.22, 128.15, 128.09, 123.80, 121.41, 118.75, 114.22, 114.14, 113.97, 113.77, 113.69, 68.29, 67.89, 56.00, 55.77, 55.74, 55.67, 55.64, 55.53, 31.56, 29.70, 29.45, 28.88, 28.83, 28.58, 25.44, 25.14, 22.62, 14.15. ESI-MS m/z: (M + H)⁺ Calcd for C₇₅H₈₁N₃O₁₁H⁺ 1200.6; Found 1201.2, error : 0.5 ppm. MS (MALDI-TOF) m/z: (M + H)⁺ Calcd for C₇₅H₈₁N₃O₁₁H⁺ 1200.59; Found 1200.76, error : 0.1 ppm.



Fig. S8 ¹H NMR spectrum (400 MHz, CDCl₃, 298K) of pillar[5]arene 1.



Fig. S9 ¹³C NMR spectrum (100 MHz, CDCl₃, 298K) of pillar[5]arene 1.



Fig. S10 ESI-MS spectrum of pillar[5]arene 1.



Fig. S11 MOLDI-TOF MS spectrum of pillar[5]arene 1.



Fig. S12 Partial ¹H NMR spectra (500 MHz, 298 K) of **1**₂•**Zn**•**2** in CD₃CN/CDCl₃ (*v*/*v* = 1/1) at various concentrations: (A) 100 mM; (B) 80 mM; (C) 61.5 mM; (D) 44 mM; (E) 30 mM; (F) 22 mM; (G) 11 mM; (H) 5.5 mM; (I) 2.8 mM; (J) 0.5 mM.



Fig. S13 Partial ¹H NMR spectra (500 MHz, 298 K) of **1**₂•**Zn**•**2** in CD₃CN/CDCl₃ (*v*/*v* = 1/1) at various concentrations: (A) 100 mM; (B) 80 mM; (C) 61.5 mM; (D) 44 mM; (E) 30 mM; (F) 22 mM; (G) 11 mM; (H) 5.5 mM; (I) 2.8 mM; (J) 0.5 mM.



Fig. S14 Concentration dependence of diffusion coefficient *D* (from ¹H NMR spectroscopy; 500 MHz, 293 K) of $1_2 \cdot Zn \cdot 2$ in CD₃CN/CDCl₃ ($\nu/\nu = 1/1$).



Fig. S15 Absorbance spectra of $1_2 \cdot 2$ and $1_2 \cdot Zn \cdot 2$ in CH₃CN/CHCl₃ (v/v = 1/1) at the concentration of 1.0 mM. Inset: photograph shows the colour of $1_2 \cdot Zn \cdot 2$ in CH₃CN/CHCl₃ (v/v = 1/1).



Fig. S16 Fluorescence spectra of $1_2 \cdot 2$ and $1_2 \cdot 2n \cdot 2$ upon an excitation at 293 nm in CH₃CN/CHCl₃ (v/v = 1/1) at the concentration of 1.0 mM. Inset: visual fluorescence emission of $1_2 \cdot 2n \cdot 2$ in CH₃CN/CHCl₃ (v/v = 1/1) on excitation at 365 nm using UV lamp at RT.

References

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