# **Electronic Supplementary Information**

# A pillar[5]arene-fused cryptand: from orthogonal selfassembly to supramolecular polymer

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#### 1. Materials and methods

All reactions were performed in atmosphere unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Compounds  $2,^{S1} 3,^{S2} 4,^{S3} 5,^{S4} 6,^{S2} 7,^{S5}$  and  $8^{S6}$  were prepared according to literature procedure. NMR spectra were recorded on a Bruker DPX 300 MHz or 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts ( $\delta$ ) were expressed in ppm and *J* values were given in Hz. DOSY experiments were performed on a Bruker DPX 400 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan MatTSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

#### 2. Synthesis of cryptand 1



Scheme S1 Synthesis of cryptand 1.

A solution of **7** (0.09 g, 0.14 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added very slowly to a solution of **8** (0.11 g, 0.14 mmol) and Et<sub>3</sub>N (1.00 mL) in dry CH<sub>2</sub>Cl<sub>2</sub> (170 mL) under nitrogen gas protection. After complete addition, the mixture was stirred at room temperature for 2 days. After the solvent was removed under vacuum, the residue was purified by column chromatography (silica, CHCl<sub>3</sub>) to afford **1** as a white solid (0.12 g, 60%). M.p. 113–115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 6.85–6.52 (m, 16H), 4.04–3.27 (m, 74H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 167.6, 160.1, 151.3, 151.0, 150.9, 150.7, 136.7, 129.3, 128.9, 128.4, 128.3, 115.2, 114.2, 114.1, 114.0, 106.0, 105.1, 71.0, 69.7, 68.2, 68.0, 56.7, 56.1, 56.0, 55.9, 41.0, 29.9, 29.7. LR-ESI-MS: *m/z* calcd. for [M + H]<sup>+</sup> = 1397.62, found 1397.50 (100%); [M + NH<sub>4</sub>]<sup>+</sup> = 1414.65, found 1414.50 (25%); [M + Na]<sup>+</sup> = 1419.60, found 1419.50 (42%). HR-ESI-MS: *m/z* calcd. for [M + Na]<sup>+</sup> C<sub>77</sub>H<sub>92</sub>N<sub>2</sub>NaO<sub>22</sub><sup>+</sup>, 1419.6039, found 1419.6035, error –0.3 ppm.

#### -7.26 6.85 6.84 6.84 6.73 6.73 6.53









Fig. S2  $^{13}$ C NMR spectrum (75 MHz, CDCl<sub>3</sub>, 298 K) of 1.





x10 <sup>5</sup>	x10 <sup>5</sup> +ESI Scan (0.230-0.297 min, 5 Scans) Frag=175.0V wq(14.10.30)1sample1691.d Subtract	
1.6-	1.6-1419/6035	
1.4-	14	
1.2-	12	
1-	1	
0.8-	08-	6093
0.6-	06-	
0.4-	0.4-	
0.2-	02-	1422 0122
0-	0	

Fig. S4 HR-ESI-MS spectrum of 1.

3. UV-vis spectrum of  $1 \supset 2$  in chloroform/acetonitrile (1/1, v/v)



Fig. S5 UV-vis absorption spectra of 1, 2, and  $1 \supset 2$  (1:1, molar ratio), respectively in chloroform/acetonitrile (1/1, v/v) (the concentration for 1 and 2 is  $8 \times 10^{-4}$  mM, respectively).

4. Job plots for the complexes of  $1 \supset 2$  and  $1 \supset 3$ 



**Fig. S6** Job Plots showing the 1:1 stoichiometry of the complexation between 1 and 2 (a) and 1 and 3 (b) in  $CDCl_3/CD_3CN(1/1, v/v)$ . ([**H**] + [**G**] = 4 mM).

#### 5. LR-ESI-MS spectra of the complexes of $1 \supset 2$ and $1 \supset 3$



**Fig. S7** LR-ESI-MS of an equimolar mixture of **1** and **2**. Assignment of main peaks: m/z 1812.30 (100%) for  $[1 \supset 2 - PF_6]^+$ . This result confirmed the 1:1 complexation stoichiometry between **1** and **2**.



**Fig. S8** LR-ESI-MS of an equimolar mixture of **1** and **3**. Assignment of main peaks: m/z 1738.45 (100%) for  $[1 \supset 2+H]^+$ . This result confirmed the 1:1 complexation stoichiometry between **1** and **3**.

# 6. Determination of the association constants of $1 \supset 2$ and $1 \supset 3$ by <sup>1</sup>H NMR

To determine the association constant between the host **1** and the guest (**2** or **3**), <sup>1</sup>H NMR titration experiments were performed with a constant concentration of the guest (1.00 mM) and varying concentrations of the host. Using a non-linear curvefitting method, the association constant was obtained for each host-guest combination from the following equation:<sup>S7</sup>

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

Where  $\Delta \delta$  is the chemical shift change of H<sub>a</sub> on G at [H]<sub>0</sub>,  $\Delta \delta_{\infty}$  is the chemical shift change of H<sub>a</sub> when the guest is completely complexed, [G]<sub>0</sub> is the fixed initial concentration of the guest, and [H]<sub>0</sub> is the initial concentration of the host.



Scheme S2 Chemical structures of pillar[5]arene-fused cryptand 1, guests 2, 3.



**Fig. S9** Partial <sup>1</sup>H NMR spectral changes (300 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1/1, v/v, 298 K) of **2** at a concentration of 1.00 mM upon addition of **1**: (a) 0.00, (b) 0.60, (c) 0.80, (d) 1.00, (e) 1.50, (f) 2.00, (g) 3.00, (h) 4.00, (i) 6.00, (j) 10.0, (k) 13.0, (l) 16.0 mM.



Fig. S10 The chemical shift changes of  $H_{2b}$  on 2 upon addition of 1. The red solid line was obtained from the non-linear curve-fitting using Eq.S1. The association constant ( $K_a$ ) of  $1 \supset 2$  was estimated to be about  $107 \pm 2.5$  M<sup>-1</sup>.



**Fig. S11** Partial <sup>1</sup>H NMR spectral changes (300 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1/1, v/v, 298 K) of **3** at a concentration of 1.00 mM upon addition of **1**: (a) 0.00, (b) 0.60, (c) 0.80, (d) 1.00, (e) 1.50, (f) 2.00, (g) 3.00, (h) 4.00, (i) 6.00, (j) 10.0, (k) 13.0, (l) 16.0 mM.



**Fig. S12** The chemical shift changes of  $H_{3e}$  on **3** upon addition of **1**. The red solid line was obtained from the non-linear curve-fitting using Eq.S1. The association constant ( $K_a$ ) of **1** $\supset$ **3** was estimated to be about 48 ± 3.2 M<sup>-1</sup>.

## 7. Orthogonality test of the two host-guest interactions



Fig. S13 Partial <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1/1, v/v, 298 K): (a) 1; (b) 4.00 mM 1 and 4.00 mM 2; (c) 2.





**Fig. S14** Partial <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1/1, v/v, 298 K): (a) **1**; (b) 4.00 mM **1** and 4.00 mM **3**; (c) **3**.



**Fig. S15** Partial <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1/1, v/v, 298 K): (a) 4.00 mM **1** and 4.00 mM **2**; (b) mixtures of 4.00 mM **1**, 4.00 mM **2** and 4.00 mM **3**; (c) 4.00 mM **1** and 4.00 mM **3**.

# 8. X-ray crystal data of $1 \supset 4$

CCDC number	1026404
Empirical formula	$C_{89}H_{106}F_{12}N_4O_{22}P_2$
Formula weight	1873.72
Temperature	293(2)
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
а	18.690(3) Å
b	26.430(4) Å
С	43.505(7) Å
α	90.00°
β	97.138(3)°
γ	90.00°
Volume	21324(6) Å <sup>3</sup>
Z	8
Density (calculated)	1.167
Absorption coefficient	0.125
F(000)	7856
Crystal size	$0.27\times0.24\times0.20\ mm^3$
Theta range for data collection	2.20 to 18.88°
Index ranges	-22<=h<=22, -21<=k<=31, -50<=l<=51
Reflections collected	57432
Independent reflections	16789 [R(int) = 0.0588]
Completeness to theta = $25.00^{\circ}$	100 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on $F^2$
Goodness-of-fit on F2	0.917
Final R indices [I > 2sigma(I)]	R1 = 0.0796, wR2 = 0.2183
<i>R</i> indices (all data)	R1 = 0.1660, wR2 = 0.2479
Largest diff. peak and hole	0.966 and -0.301 e·Å <sup>-3</sup>
	1

Table 1 Crystal data and structure refinement for  $1 \supset 4$ 

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