# Chemical-responsive complexation between a pillar[10]arene with mono(ethylene oxide) substituents and 2,7diazapyrenium salt

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# **Electronic Supplementary Information (11 pages)**

1.	Materials and methods	<i>S2</i>
2.	Synthetic route to pillar[10]arene 1	<i>S2</i>
3.	Synthesis of pillar[10]arene 1	<i>S2</i>
4.	Stoichiomestry and association constant determination for the complexation	
	between $1$ and $G$	<i>S5</i>
5.	UV-vis spectroscopy investigation of the complexation between $1$ and $G$ in	
	acetonitrile	<i>S8</i>
6.	Electrospray ionization mass spectrometry of an equimolar mixture of $1$ and $G$	<i>S8</i>
7.	2D NOESY NMR spectrum of $1 \supset G$	<i>S9</i>
8.	A photo showing color changes after host-guest complexation	<i>S10</i>

## 1. Materials and methods:

Pillar[10]arene **2**, **3**<sup>S1</sup> were synthesized according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. <sup>1</sup>H NMR spectra were collected on a temperaturecontrolled 400 MHz spectrometer. <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. 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. High-resolution mass spectrometer. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

#### 2. Synthetic route to pillar[10]arene 1



Scheme S1 Synthetic route to pillar[10]arene 1.

#### 3. Synthesis of pillar[10]arene 1

To a solution of **3** (0.50 g, 0.28 mmol) in dried chloroform (25 mL) was added largely excessive boron tribromide. The mixture was stirred at room temperature for 12 h. Then the mixture was added into ice water. The resulting precipitated product **2** was collected by filtration, washed with water and dried completely under vacuum. *per*-Hydroxylated pillar[10]arene **2** (0.25 g, 0.21 mmol) was dissolved in CH<sub>3</sub>CN (50 mL). K<sub>2</sub>CO<sub>3</sub> (0.85 g, 6.2 mmol) was added and the reaction mixture was stirred. Then 2-methoxyethyl *p*-toluenesulfonate (1.4 g, 6.2 mmol) was added and the reaction mixture was stirred under N<sub>2</sub> at reflux for 3 days. The solvent was evaporated and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The resultant solution was washed with H<sub>2</sub>O and brine. The organic phase was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to give a crude solid. Column chromatography (silica gel; CH<sub>2</sub>Cl<sub>2</sub> : CH<sub>3</sub>OH = 40 : 1 ) afforded a light yellow solid (150 mg, 30%). M.p. 110.3–112.7 °C. The <sup>1</sup>H NMR spectrum of pillar[10]arene **1** is shown in Figure S1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, room temperature)  $\delta$  (ppm): 6.69 (s, 12H), 3.91 (t, *J* = 8.0 Hz, 24H), 3.85 (s, 12H), 3.59 (t, *J* = 8.0 Hz, 24H), 3.30 (s, 36H). The <sup>13</sup>C NMR spectrum of pillar[10]arene **1** is shown in Figure S2. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, room temperature)  $\delta$  (ppm): 150.95, 128.35, 114.94, 71.35, 68.05, 59.01, 29.85. LRESIMS: *m/z* 2402.5 [M + Na]<sup>+</sup> (100%). HRMALDIMS: *m/z* calcd. for [M + Na]<sup>+</sup> C<sub>130</sub>H<sub>180</sub>O<sub>40</sub>Na, 2404.1948, found 2404.1482.



Fig. S1 <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, room temperature) of pillar[10]arene 1.

![](_page_3_Figure_0.jpeg)

Fig. S2 <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, room temperature) of pillar[10]arene 1.

![](_page_3_Figure_2.jpeg)

Fig. S3 LRESI mass spectrum of pillar[10]arene 1. Assignment of the main peak: m/z 2402.5  $[M + Na]^+ (100\%)$ .

*4. Stoichiomestry and association constant determination for the complexation between* **1** *and G* 

To determine the stoichiometry and association constant for the complexation between **1** and **G**, fluorescence titration experiments were done with solutions which had a constant concentration of **G** ( $5.00 \times 10^{-6}$  M) and varying concentrations of **1**. By a non-linear curve-fitting method, the association constant ( $K_a$ ) of **1** $\supset$ **G** was determined. By a mole ratio plot, 1:1 stoichiometry was obtained for the complexation between **1** and **G**.

The non-linear curve-fitting was based on the equation:<sup>S2</sup>

 $\Delta F = (\Delta F_{\infty} / [G]_0) (0.5[H]_0 + 0.5([G]_0 + 1/K_a) - (0.5 ([H]_0^2 + (2[H]_0 (1/K_a - [G]_0)) + (1/K_a + [G]_0)^2)^{0.5}))$ 

Where  $\Delta F$  is the fluorescence intensity change at 405 nm at  $[G]_{0,} \Delta F_{\infty}$  is the fluorescence intensity change at 405 nm when **G** is completely complexed,  $[H]_{0}$  is the initial concentration of **1**, and  $[G]_{0}$  is the fixed initial concentration of **G**.

![](_page_4_Figure_5.jpeg)

*Fig. S4.* Fluorescence spectra of **G** at a concentration of  $5.00 \times 10^{-6}$  M in acetonitrile at room temperature upon gradual addition of 1(excitation at 247 nm).

![](_page_5_Figure_0.jpeg)

Fig. S5. Mole ratio plot for 1 and G, indicating a 1:1 complexation stoichiometry.

![](_page_6_Figure_0.jpeg)

*Fig. S6.* The fluorescence intensity changes of G upon addition of 1. The red solid line was obtained from the non-linear curve-fitting method based on the above equation.

5. UV-vis spectroscopy investigation of the complexation between 1 and G in acetonitrile

![](_page_7_Figure_1.jpeg)

*Fig. S7.* UV-vis spectra of (a)  $1.00 \times 10^{-3}$  M **1**, (b)  $1.00 \times 10^{-3}$  M **G**, and (c)  $1.00 \times 10^{-3}$  M **1** with equimolar **G** in acetonitrile at room temperature.

## 6. Electrospray ionization mass spectrometry of an equimolar mixture of 1 and G.

![](_page_7_Figure_4.jpeg)

Fig. S8 Electrospray ionization mass spectrometry of an equimolar mixture of 1 and G.

7. 2D NOESY NMR spectrum of  $1 \supset G$ 

![](_page_8_Figure_1.jpeg)

Fig. S9 2D NOESY NMR spectrum (600 MHz, CD<sub>3</sub>CN, 22 °C, mixing time = 1.0 s) of 2.0 mM 1 and G.

8. A photo showing color changes of chemical-responsive complexation between 1 and G after host-guest complexation

![](_page_9_Figure_1.jpeg)

**Fig. S10** A photo showing color changes of chemical-responsive complexation between **1** and **3**: (a) **1** alone; (b) equimolar mixture of 1.00 mM **1** and DMDAP; (c) after addition of 10.0 equiv. of DEA to (b); (d) after addition of 10.0 equiv. of TFA to (d); (e) DMDAP alone.

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