# A pH-responsive fluorescent [5]Pseudorotaxane formed by self-assembly of cationic water-soluble pillar[5]arenes and a tetraphenylethene derivative

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## **Electronic Supplementary Information**

#### 1. Complexation studies on model compounds 1 and 3

To determine the stoichiometry and association constant between 1 and 3, <sup>1</sup>H NMR titrations were done with solutions which had a constant concentration of 3 (1.00 mM) and varying concentrations of 1. By a non-linear curve-fitting method, the association constant between the 3 and 1 was calculated. By a mole ratio plot, a 1:1 stoichiometry was obtained for both system.

The non-linear curve-fitting was based on the equation:<sup>S1</sup>

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

Wherein  $\Delta \delta$  is the chemical shift change of H<sub>9</sub> on **3** at [H]<sub>0</sub>,  $\Delta \delta_{\infty}$  is the chemical shift change of H<sub>9</sub> when the host is completely complexed, [G]<sub>0</sub> is the fixed initial concentration of the guest, and [H]<sub>0</sub> is the varying concentration of **1**.



*Figure S1.* Partial <sup>1</sup>H NMR spectra (400 MHz, D<sub>2</sub>O, 298 K) of **3** at a concentration of 1.00 mM with different concentrations of **1**: (a) 0.00 mM, (b) 1.13 mM, (c) 2.14 mM, (d) 3.05 mM, (e) 3.87 mM, (f) 4.61 mM, (g) 6.67 mM, (h) 8.24 mM, (i) 9.47 mM, (j) 10.5 mM, (k) 11.3 mM, (l) 12.0 mM, (m) 13.1 mM, (n) 14.0 mM, (o) 14.6 mM.



*Figure S2.* The chemical shift changes of  $H_9$  on **3** upon addition of **1**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.



Figure S3. Mole ratio plot for the complexation between 1 and 3, indicating a 1:1 stoichiometry.

2. Partial <sup>1</sup>H NMR spectra of the pH-controlled complexation between 1 and 2



*Fig. S4.* Partial <sup>1</sup>H NMR spectra (400 MHz,  $D_2O$ , 298 K): a) **2**; b) a solution of 12.0 mM **1** and 3.00 mM 2; c) a solution of 20.0 mM aqueous HCl solution, 12.0 mM **1** and 3.00 mM **2**; d) a solution of 20.0 mM of aqueous HCl solution, 20.0 mM NaOH, 12.0 mM **1** and 3.00 mM **2**; and e) **1**.

However, the chemical shift changes of the protons on the 2 after complexation could not be fully recovered. Three possible reasons are: 1) the solution was diluted; 2) the ionic strength of the solution increased; 3) different counterions were introduced, influencing ion pairing.



3. Electrospray ionization mass spectrum of a water solution of 1 and 2



Fig. S5. Electrospray ionization mass spectrum of a water solution of 12.0 mM 1 and 3.00 mM 2.

#### 4. Fluorescence properties between 1 and 3



*Fig. S6.* Fluorescence spectral changes of **3** (2.00  $\mu$ M) upon addition of **1** (0.00–16.0 equiv.) in water ( $\lambda_{ex} = 330$  nm,  $\lambda_{em} = 490$  nm; slits, 5 nm/5 nm).

### References:

S1. (a) K. A. Connors, *Binding Constants*; Wiley: New York, 1987; (b) Corbin, P. S. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; (c) P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.* 1996, **118**, 4931–4951.