

## **A pillar[6]arene-based [2]pseudorotaxane in solution and in the solid state and its photo-responsive self-assembly behavior in solution**

Danyu Xia, Peifa Wei, Bingbing Shi and Feihe Huang\*

*State Key Laboratory of Chemical Engineering, Center for Chemistry of High-Performance & Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China; Fax and Tel: +86-571-8795-3189; Email address: fhuang@zju.edu.cn.*

### **Electronic Supplementary Information (6 pages)**

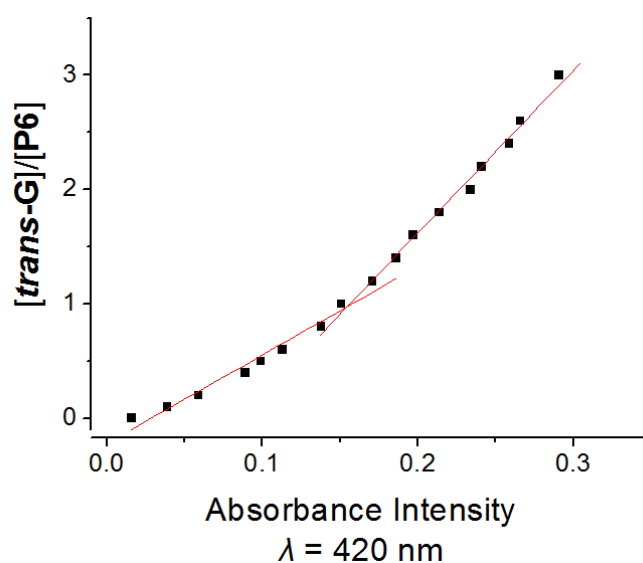
1. <i>Materials and Methods</i>	S2
2. <i>Stoichiometry and association constant determination for the complexation between <b>P6</b> and <i>trans-G</i></i>	S2
3. <i>ESIMS of <b>P6</b> and <i>trans-G</i> in acetonitrile</i>	S4
4. <i><sup>1</sup>H NMR experiments on the photo-responsive ability of <b>G</b></i>	S4
5. <i>UV-vis absorption spectroscopy of photo-responsive <i>trans-G</i></i>	S5
6. <i>X-ray crystal data of the pillar[6]arene-based [2]pseudorotaxane</i>	S5
<i>References</i>	S6

## 1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **P6**<sup>S1</sup> and *trans-G*<sup>S2</sup> were prepared according to published procedures. NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. UV-vis spectra were taken on a Perkin-Elmer Lambda 35 UV-vis spectrophotometer. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). The crystal data was collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra. The crystal structure was solved by SHELXS-97<sup>S3</sup> and refined by SHELXL-97.<sup>S4</sup>

## 2. Stoichiometry and association constant determination for the complexation between **P6** and *trans-G*

### 2.1. Stoichiometry determination for the complexation between **P6** and *trans-G*



**Fig. S1** Mole ratio plot for the complexation between **P6** and *trans-G*, indicating a 1:1 binding stoichiometry.

### 2.2. Association constant determination for the complexation between **P6** and *trans-G*

The association constant of complex **P6**–*trans-G* was determined by probing the charge-transfer band of the complex by UV-vis spectroscopy and employing a titration method. Progressive addition of a solution with high guest *trans-G* concentration ( $1.00 \times 10^{-1}$  M) and low host **P6** concentration ( $1.00 \times 10^{-3}$  M) to a solution with the same concentration of host **P6** resulted in an increase of the intensity of the charge-transfer band of the complex.

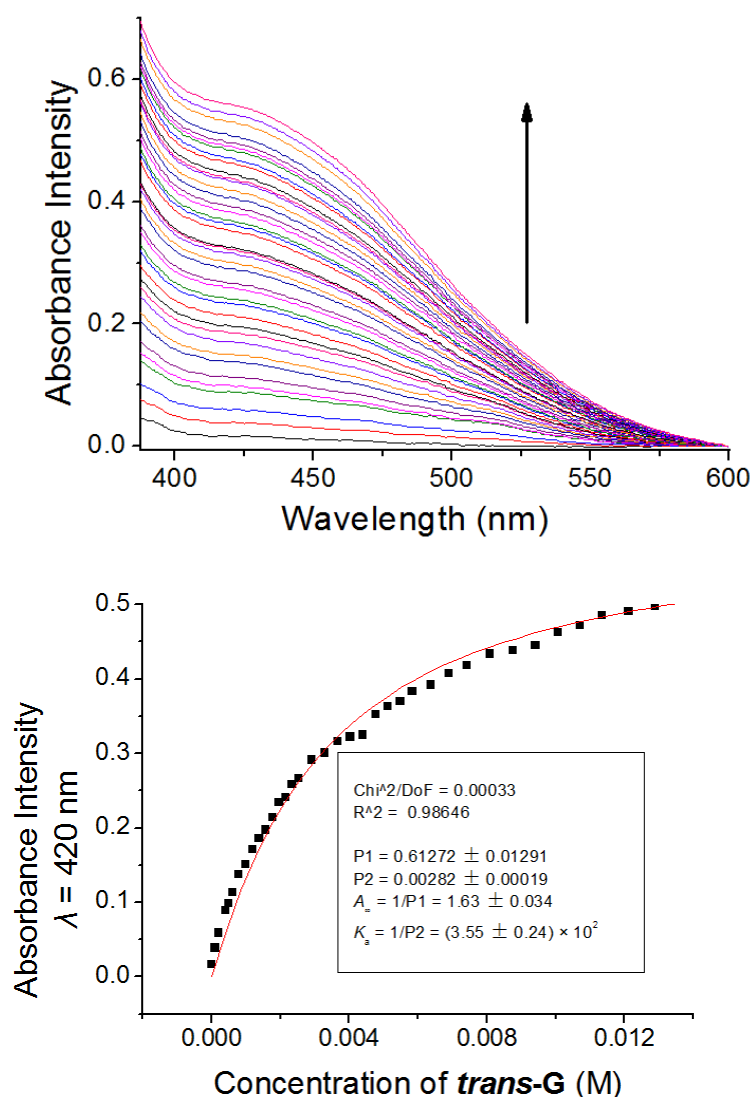
Treatment of the collected absorbance data with a non-linear curve-fitting program afforded the corresponding association constant ( $K_a$ ).

The non-linear curve-fitting was based on the equation:<sup>S5</sup>

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

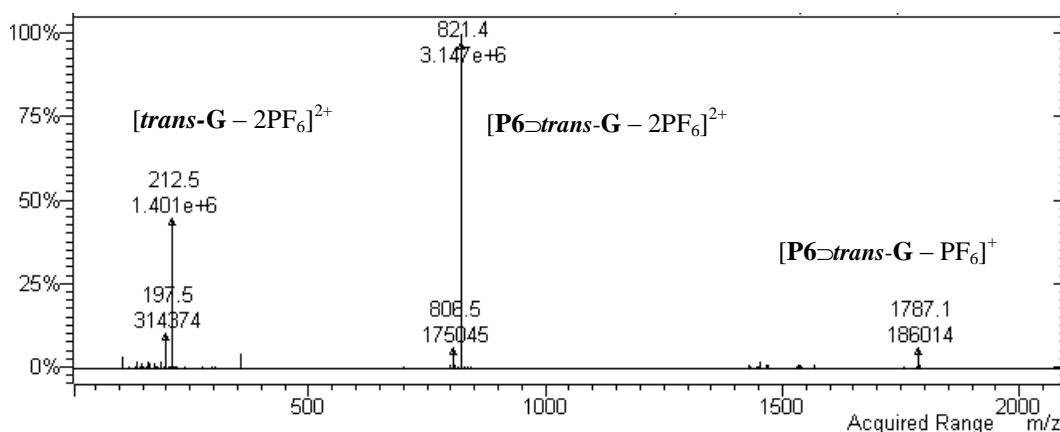
(Eq. S1)

Where  $A$  is the absorption intensity of the charge-transfer band at  $[G]_0$ ,  $A_\infty$  is the absorption intensity of the charge-transfer band when the host is completely complexed,  $[H]_0$  is the fixed initial concentration of the host **P6**, and  $[G]_0$  is the varying concentration of the guest *trans*-**G**.



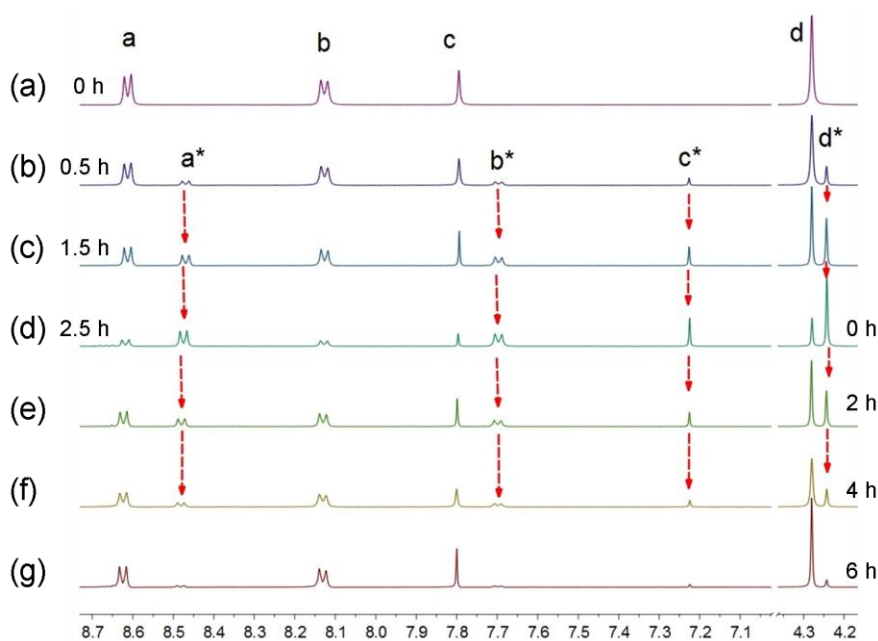
**Fig. S2** The absorption spectral changes of **P6** ( $1.00 \times 10^{-3}$  M) upon addition of *trans*-**G** (top) and the absorbance intensity changes at  $\lambda = 420$  nm upon addition of *trans*-**G** (from 0 to  $1.65 \times 10^{-2}$  M) (bottom). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

### 3. ESIMS of **P6** and **G** in acetonitrile



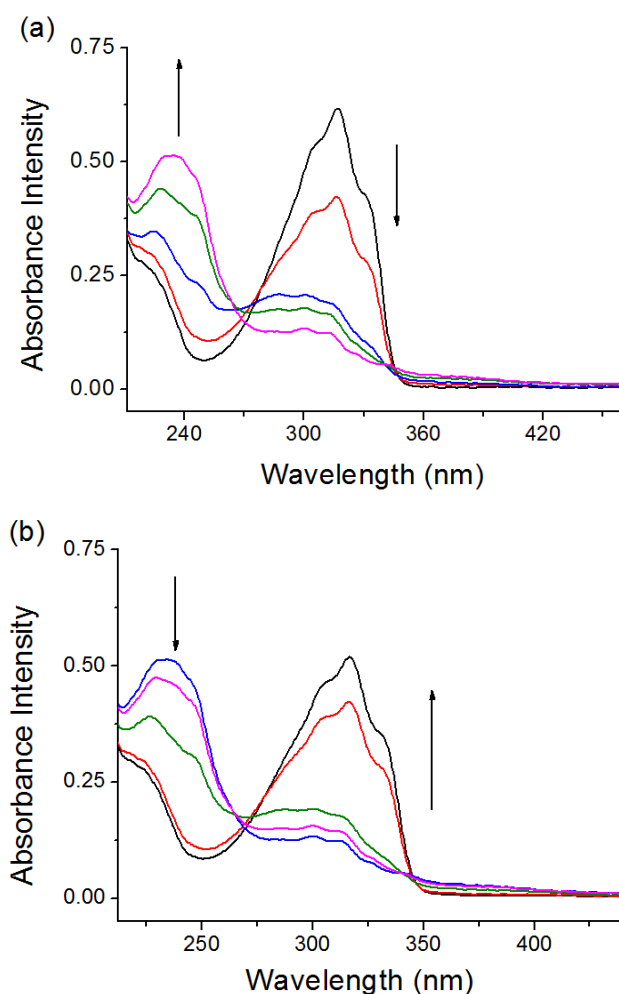
**Fig. S3.** The positive electrospray ionization mass spectrum of an equimolar mixture of **P6** and *trans-G* in acetonitrile. Mass fragments at  $m/z$  821.4 for  $[\mathbf{P6} \supset \textit{trans-G} - 2\text{PF}_6]^{2+}$  and  $m/z$  1787.1 for  $[\mathbf{P6} \supset \textit{trans-G} - \text{PF}_6]^+$  confirmed the 1:1 complexation stoichiometry between **P6** and *trans-G*.

### 4. $^1\text{H}$ NMR experiments of photo-responsive ability of **G**



**Fig. S4** Partial  $^1\text{H}$  NMR spectra: *trans-G* ( $5.00 \times 10^{-3}$  M) in  $\text{CD}_3\text{CN}$  under UV irradiation at 365 nm with different times from 0 to 2.5 h (a–d) and under further UV irradiation at 265 nm with different times from 0 to 6 h (d–g).

## 5. UV-vis absorption spectroscopy experiments of photo-responsive ability of *trans-G*



**Fig. S5** UV-vis absorption spectra of *trans-G* ( $1.00 \times 10^{-5}$  M) in acetonitrile: (a) under UV irradiation at 365 nm with different times, 0 h, 0.5 h, 1.5 h, 2 h and 2.5h; (b) under further UV irradiation at 265 nm with different times, 0 h, 1 h, 3 h, 5.5 h and 6 h.

## 6. X-ray crystal data of the pillar[6]arene-based [2]pseudorotaxane

Crystal data of the [2]pseudorotaxane **P6**⊃*trans-G*: block, red,  $C_{92}H_{126}N_2O_{24}F_{12}P_6$ ,  $FW$  2003.72, monoclinic, space group  $C1c1$ ,  $a = 31.6051(11)$ ,  $b = 13.3823(5)$ ,  $c = 24.6753(7)$  Å,  $\alpha = 90.00^\circ$ ,  $\beta = 90.155(3)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 10436.47(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.275$  g cm<sup>-3</sup>,  $T = 172(2)$  K,  $\mu = 0.133$  mm<sup>-1</sup>, 15071 measured reflections, 12597 independent reflections, 1203 parameters, 2 restraints,  $F(000) = 4234.0$ ,  $R_1 = 0.0683$ ,  $wR_2 = 0.1495$  (all data),  $R_1 = 0.0580$ ,  $wR_2 = 0.1610$  [ $I > 2\sigma(I)$ ], max. residual density 0.464 e•Å<sup>-3</sup>, and goodness-of-fit ( $F^2$ ) = 1.027. CCDC-1409431.

*References:*

- S1. X. Chi, M. Xue, Y. Ma, X. Zhou and F. Huang, *Chem. Commun.*, 2013, **49**, 8175–8177.
- S2. P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, S. Menzer, L. Pérez-García, L. Prodi, J. F. Stoddart, M. Venturi, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1995, **117**, 11171–11197.
- S3. G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1990.
- S4. G. M. Sheldrick, *SHELXS-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
- S5. K. A. Connors, *Binding Constants*; Wiley: New York, 1987; P. S. Corbin, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; 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.