### **Supporting Information**

# A Novel Triptycene-based Cylindrical Macrotricyclic Host: Synthesis and Complexation with Paraquat Derivatives

Qian-Shou Zong<sup>a,b</sup> and Chuan-Feng Chen<sup>a,\*</sup>

<sup>a</sup>Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080,

China

<sup>b</sup>Graduate School, Chinese Academy of Sciences, Beijing 100049, China

Email: cchen@iccas.ac.cn

#### Contents

I. Synthetic procedures	S2 S3		
II. <sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of compounds 6, 7, 8 and 1 III. <sup>1</sup> H- <sup>1</sup> H COSY and <sup>1</sup> H NMR titration experiments IV. Determination of the association constants V. ESI MS spectra of the complexes 1·2, 1·3 and 1·4	S4 - S7 S8 - S10 S11 - S15 S16 - S17		
		VI. Crystal structures of the host 1 and the complexes 1.2 and 1.4	S18 S19

### I. Synthetic procedures



Compound **6.** To a stirred solution of compound **5** (3.26 g, 10 mmol) in CH<sub>2</sub>ClCH<sub>2</sub>Cl (120 mL) and propylene oxide (8 mL) was added 2-carboxy-benzenediazonium chloride (3.69 g, 20 mmol). The reaction mixture was stirred at reflux for 4h, then filtered and concentrated. The crude product was recrystallized from ethanol to afford compound **6** (3.42 g, 85 %) as a white solid. Mp: 250-251 °C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$ 2.38 (s, 6H), 3.84 (s, 12H), 6.94 (s, 4H), 6.97-7.03 (m, 2H), 7.29-7.34 (m, 2H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ 13.8, 48.0, 56.4, 106.0, 119.9, 124.6, 141.6, 145.8, 149.0. EI-MS: *m/z* 402 (M<sup>+</sup>). Elemental analysis calcd. for C<sub>26</sub>H<sub>26</sub>O<sub>4</sub>: C 77.59, H 6.51; found: C 77.71, H 6.58.



Compound **7.** To the solution of **6** (3.0 g, 7.5 mmol) dissolved in dried  $CH_2Cl_2$  (60 mL) at 0 °C was quickly injected BBr<sub>3</sub> (3 mL). After being stirred for 4h, the reaction mixture was quenched with cold water, filtered, washed with water, and then dried to yield **7** (2.44 g, 94 %). Mp: 210 °C (dec.). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$ 2.21 (s, 6H), 6.85 (s, 4H), 6.93-6.96 (m, 2H), 7.25-7.28 (m, 2H). <sup>13</sup>C NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$ 14.2, 48.0, 109.8, 120.4, 124.9, 141.7, 141.8, 150.7. EI MS: *m/z* 346 (M<sup>+</sup>). HRMS (EI) calcd. for C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>: 346.1205 (M<sup>+</sup>), found: 346.1207.



Compound **8.** To a stirred solution of **7** (1.1 g, 3.2 mmol) and 8-tosyloxy-3,6-dioxaoctanol (4.3 g, 14 mmol) in dried CH<sub>3</sub>CN (70 mL) was added K<sub>2</sub>CO<sub>3</sub> (3.6 g, 26 mmol). The reaction mixture was stirred at reflux for 28h, cooled to ambient temperature and then filtered. The filtrate was concentrated to give a residue, which was dissolved in dried CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and fresh Ag<sub>2</sub>O (5.7 g, 25 mmol), TsCl (3.4 g, 18 mmol) and KI (0.53 g, 3.3 mmol) were added. The reaction mixture was stirred at room temperature for 8h, then filtered through a small pad of silica gel, and washed with EtOAc. Evaporation of the solvent, followed by column chromatography (SiO<sub>2</sub>: EtOAc/petroleum 3:1) yielded **8** (3.15 g, 66 %) as a pale yellow solid. Mp: 75-76 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.30 (s, 6H), 2.38 (s, 12H), 3.53-3.56 (m, 8H), 3.60-3.65 (m, 16H), 3.72-3.75 (m, 8H), 4.06-4.13 (m, 16H), 6.95 (s, 4H), 6.97-7.00 (m, 2H), 7.27-7.29 (m, 2H), 7.29 (d, *J*=9.0 Hz, 8H), 7.77 (d, *J*=9.0 Hz, 8H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  13.8, 21.6, 47.9, 68.7, 69.3, 69.7, 67.0, 70.3, 70.7, 110.0, 120.0, 124.6, 127.9, 129.8, 133.0, 142.5, 144.8, 145.8, 148.8. MALDI-TOF MS: *m*/z 1490.6 (M<sup>+</sup>). Elemental analysis calcd. for C<sub>74</sub>H<sub>90</sub>O<sub>24</sub>S<sub>4</sub>: C 59.58, H 6.08; found: C 59.26, H 6.16.



Compound 1: A solution of **8** (730 mg, 0.49 mmol) and **7** (170 mg, 0.49 mmol) in DMF (70 mL) was added via a funnel into a suspension containing cesium carbonate (1.28 g, 4.0 mmol) in DMF (80 mL) at 110 °C. After being stirred at 110 °C for 4 days, the reaction mixture was cooled down to ambient temperature. Removment of DMF under reduced pressure gave a residue, which was dissolved in chloroform and then filtered. The filtrate was washed with water twice, dried over anhydrous magnesium sulfate and concentrated to afford a crude product, which was purified by flash column chromatography with chloroform and methanol (100:1, v/v) as eluant to afford **1** (114 mg, 20 %) as a white solid. M.p.>300°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.24 (s, 12H), 3.68-3.73 (m, 8H), 3.78-3.85 (m, 24H), 3.96-4.00 (m, 8H), 4.05-4.10 (m, 8H), 6.83 (s, 8H), 6.96-7.0 (m, 4H), 7.25-7.27 (m, 4H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  13.7, 47.8, 69.9, 71.0, 109.0, 119.9, 124.5, 142.2, 145.6, 148.8. MALDI-TOF MS: *m/e* 1148.1. Elemental analysis calcd. for C<sub>68</sub>H<sub>76</sub>O<sub>16</sub>: C 71.06, H 6.67; found: C 71.03, H 7.09.



Figure S2. <sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>) of 6.



Figure S3. <sup>1</sup>H NMR spectrum (300 MHz, acetone- $d_6$ ) of 7.



**Figure S4.** <sup>13</sup>C NMR spectrum (75 MHz, acetone- $d_6$ ) of **7.** 





Figure S6. <sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>) of 8.





Figure S8. <sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>) of 1.

# III. <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H NMR titration experiments



**Figure S9.** <sup>1</sup>H-<sup>1</sup>H COSY Spectrum (600 MHz,  $CD_3CN:CDCl_3=1:1$ ) of a solution of **1** and 1.5 equiv of **2**. [**1**]<sub>0</sub> = 4 mM.



**Figure S10.** Partial <sup>1</sup>H NMR spectra (300 MHz,  $CD_3CN:CDCl_3=1:1$ , 295K) of a) free host **1**, b) **1** and 0.5 equiv of **2**, c) **1** and 1.0 equiv of **2**, d) **1** and 1.5 equiv of **2**, e) free guest **2**. [**1**]<sub>0</sub> = 4 mM.



**Figure S11.** Partial <sup>1</sup>H NMR spectra (300MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub>=1:1, 295K) of a) free host **1**, b) host **1** and 1.0 equiv of **3**, c) free guest **3**.  $[\mathbf{1}]_0 = 0.8 \text{ mM}$ .



**Figure S12.** Partial <sup>1</sup>H NMR spectra (300MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub>=1:1, 295K) of a) free host **1**, b) host **1** and 1.0 equiv of **4**, c) free guest **4**,  $[\mathbf{1}]_0 = 0.8$  mM.



**Figure S13.** Partial <sup>1</sup>H NMR spectra (300MHz, 295K) of a) free host **1**, b) host **1** and 1.0 equiv of **2**, c) free guest **2** in DMSO- $d_6$ . [**1**]<sub>0</sub> = 6 mM.

### IV. Determination of the association constants



Figure S14. Mole ratio plot for the complexation between 1 and 3 in CDCl<sub>3</sub>/CD<sub>3</sub>CN=1:1 at 295K.



**Figure S15.** Determination of  $\Delta_0$  of H<sub>1</sub> for the complexation between **1** and **3** in CDCl<sub>3</sub>/CD<sub>3</sub>CN=1:1 at 295K.



Figure S16. Scatchard plot for the complexation of host 1 and guest 3 in  $CDCl_3/CD_3CN=1:1$  at 295K.



Figure S17. Mole ratio plot for the complexation between 1 and 4 in CDCl<sub>3</sub>/CD<sub>3</sub>CN=1:1 at 295K.



**Figure S18.** Determination of  $\Delta_0$  of H<sub>1</sub> for the complexation between **1** and **4** in CDCl<sub>3</sub>/CD<sub>3</sub>CN=1:1 at 295K.



**Figure S19.** Scatchard plot for the complexation of host **1** and guest **4** in CDCl<sub>3</sub>/CD<sub>3</sub>CN=1:1 at 295K.



Figure S20. Mole ratio plot for the complexation between 2 and BMP34C10-diol in  $CDCl_3/CD_3CN=1:1$  at 295K.



Figure S21. Determination of  $\Delta_0$  of H<sub>f</sub> for the complexation between 2 and BMP34C10-diol in CDCl<sub>3</sub>/CD<sub>3</sub>CN =1:1 at 295K.



Figure S22. Scatchard plot for the complexation of host BMP32C10-diol and guest 2 in  $CDCl_3/CD_3CN = 1:1$  at 295K.



Figure S23. Calibration curve correlating the observed chemical shift with the concentration of complex present in solution.

### V. ESI MS spectra of the complexes 1.2, 1.3 and 1.4



ESI-MS Spectrum, 2qs-16

Figure S24. ESI MS of a solution of 1 and 2 in acetonitrile-chloroform (1:1).

ESI-MS Spectrum, zqs-050413



Figure S25. ESI MS of a solution of 1 and 3 in acetonitrile-chloroform (1:1).

#### ESI-MS Spectrum, 29s050419



#:1 Ret.Time:Single 3.033(Scan#:183) Mass Peaks:208 Base Peak:765.55(9871711) Polarity:Pos Segment1 - Event1 Intensity

Figure S26. ESI MS of a solution of 1 and 4 in acetonitrile-chloroform (1:1).

### VI. Crystal structures of the host 1 and the complexes 1.2 and 1.4



**Figure S27.** (a) Top view and (b) side view of the crystal structure of the host **1.** Solvent molecules and hydrogen atoms are omitted for clarity.



**Figure S28.** (a) Top view and (b) side view of the crystal structure of the complex **1-2**. Solvent molecules and hydrogen atoms not involved in the interactions are omitted for clarity.



**Figure S29.** (a) Top view and (b) side view of the crystal structure of the complex **1-4.** Solvent molecules and hydrogen atoms not involved in the interactions are omitted for clarity.