## Supporting Information

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

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## I. Synthetic procedures



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


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


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2) $\mathrm{TsCl}, \mathrm{Ag}_{2} \mathrm{O}, \mathrm{KI}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$


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


Compound 1: A solution of $\mathbf{8}(730 \mathrm{mg}, 0.49 \mathrm{mmol})$ and $7(170 \mathrm{mg}, 0.49 \mathrm{mmol})$ in DMF ( 70 mL ) was added via a funnel into a suspension containing cesium carbonate ( $1.28 \mathrm{~g}, 4.0 \mathrm{mmol}$ ) in DMF ( 80 mL ) at $110^{\circ} \mathrm{C}$. After being stirred at $110^{\circ} \mathrm{C}$ 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 ( $100: 1, \mathrm{v} / \mathrm{v}$ ) as eluant to afford $\mathbf{1}(114 \mathrm{mg}, 20 \%)$ as a white solid. M.p. $>300^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.24(\mathrm{~s}, 12 \mathrm{H}), 3.68-3.73(\mathrm{~m}, 8 \mathrm{H}), 3.78-3.85$ (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). ${ }^{13} \mathrm{C}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 13.7,47.8,69.9,71.0,109.0,119.9,124.5,142.2,145.6,148.8$. MALDI-TOF MS: $m / e$ 1148.1. Elemental analysis calcd. for $\mathrm{C}_{68} \mathrm{H}_{76} \mathrm{O}_{16}$ : $\mathrm{C} 71.06, \mathrm{H} 6.67$; found: C 71.03, H 7.09.

## II. ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR spectra of $6,7,8$ and 1



Figure S1. ${ }^{1} \mathrm{H}$ NMR spectrum ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of $\mathbf{6}$.


Figure S2. ${ }^{13} \mathrm{C}$ NMR spectrum $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of $\mathbf{6}$.


Figure S3. ${ }^{1} \mathrm{H}$ NMR spectrum ( 300 MHz , acetone $-d_{6}$ ) of $\mathbf{7}$.


Figure S4. ${ }^{13} \mathrm{C}$ NMR spectrum ( 75 MHz , acetone- $d_{6}$ ) of 7 .


Figure S5. ${ }^{1} \mathrm{H}$ NMR spectrum $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of $\mathbf{8}$.


Figure S6. ${ }^{13} \mathrm{C}$ NMR spectrum ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of $\mathbf{8}$.


Figure S7. ${ }^{1} \mathrm{H}$ NMR spectrum $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of $\mathbf{1}$.


Figure S8. ${ }^{13} \mathrm{C}$ NMR spectrum $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of $\mathbf{1}$.

## III. ${ }^{1}{ }^{H}-{ }^{1} \mathrm{H}$ COSY and ${ }^{1} \mathrm{H}$ NMR titration experiments



Figure S9. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY Spectrum ( $600 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}: \mathrm{CDCl}_{3}=1: 1$ ) of a solution of $\mathbf{1}$ and 1.5 equiv of 2. $[\mathbf{1}]_{0}=4 \mathrm{mM}$.


Figure S10. Partial ${ }^{1} \mathrm{H}$ NMR spectra ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}: \mathrm{CDCl}_{3}=1: 1,295 \mathrm{~K}$ ) of a) free host 1, b) $\mathbf{1}$ and 0.5 equiv of $\mathbf{2}$, c) $\mathbf{1}$ and 1.0 equiv of $\mathbf{2}$, d) $\mathbf{1}$ and 1.5 equiv of $\mathbf{2}$, e) free guest $\mathbf{2}$. $[\mathbf{1}]_{0}=4 \mathrm{mM}$.


Figure S11. Partial ${ }^{1} \mathrm{H}$ NMR spectra ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}: \mathrm{CDCl}_{3}=1: 1,295 \mathrm{~K}$ ) of a) free host 1, b) host $\mathbf{1}$ and 1.0 equiv of $\mathbf{3}, \mathrm{c}$ ) free guest 3. $[\mathbf{1}]_{0}=0.8 \mathrm{mM}$.


Figure S12. Partial ${ }^{1} \mathrm{H}$ NMR spectra ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}: \mathrm{CDCl}_{3}=1: 1,295 \mathrm{~K}$ ) of a) free host 1, b) host $\mathbf{1}$ and 1.0 equiv of $\mathbf{4}, \mathrm{c})$ free guest $\mathbf{4},[\mathbf{1}]_{0}=0.8 \mathrm{mM}$.


Figure S13. Partial ${ }^{1} \mathrm{H}$ NMR spectra $(300 \mathrm{MHz}, 295 \mathrm{~K})$ of a) free host $\mathbf{1}$, b) host $\mathbf{1}$ and 1.0 equiv of $\mathbf{2}$, c) free guest $\mathbf{2}$ in DMSO $-d_{6}$. $[\mathbf{1}]_{0}=6 \mathrm{mM}$.

## IV. Determination of the association constants



Figure S14. Mole ratio plot for the complexation between $\mathbf{1}$ and $\mathbf{3}$ in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295 K .


Figure S15. Determination of $\Delta_{0}$ of $\mathrm{H}_{1}$ for the complexation between $\mathbf{1}$ and $\mathbf{3}$ in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295 K .


Figure S16. Scatchard plot for the complexation of host $\mathbf{1}$ and guest $\mathbf{3}$ in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295K.


Figure S17. Mole ratio plot for the complexation between $\mathbf{1}$ and $\mathbf{4}$ in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295 K .


Figure S18. Determination of $\Delta_{0}$ of $\mathrm{H}_{1}$ for the complexation between $\mathbf{1}$ and $\mathbf{4}$ in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295 K .


Figure S19. Scatchard plot for the complexation of host $\mathbf{1}$ and guest $\mathbf{4}$ in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295K.



Figure S20. Mole ratio plot for the complexation between 2 and BMP34C10-diol in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295 K .


Figure S21. Determination of $\Delta_{0}$ of $\mathrm{H}_{\mathrm{f}}$ for the complexation between 2 and BMP34C10-diol in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295 K .


Figure S22. Scatchard plot for the complexation of host BMP32C10-diol and guest 2 in $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{CN}=1: 1$ at 295 K .


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

## V. ESI MS spectra of the complexes $\mathbf{1 \cdot 2 , 1 . 3}$ and 1.4



Figure S24. ESI MS of a solution of $\mathbf{1}$ and $\mathbf{2}$ in acetonitrile-chloroform (1:1).
ESI-MS Spectrum, zqs-050413


Figure S25. ESI MS of a solution of $\mathbf{1}$ and $\mathbf{3}$ in acetonitrile-chloroform (1:1).

ESI-MS Spectrum, 29s050419


Figure S26. ESI MS of a solution of $\mathbf{1}$ and $\mathbf{4}$ 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.

