Electronic Supplementary Information

A pentapyrene-based bis(crown ether) host: synthesis and its complexation with cyclobis(paraquat-\(p\)-phenylene)

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S1
1. Synthetic procedure for host 1

**General methods.** Melting points, taken on an electrothermal melting point apparatus, are uncorrected. $^1$H NMR, $^{13}$C NMR and $^1$H-$^1$H COSY spectra were recorded on a DMX300 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. UV spectrum was recorded on a UV-2041PC Shimadzu photometer. Materials obtained commercially were used without further purification. Cyclobis(paraquat-$p$-phenylene) tetra(hexafluorophosphate) 2 was prepared according to literature procedure.$^{S1}$ The association constant for the complex 1·2 was determined according to the literature method.$^{S2}$

![Chemical structure](image)

Compound 3. A mixture of 2,3-dimethoxyanthracene (1.213 g, 5.1 mmol), benzoquinone (0.27 g, 2.5 mmol) and $p$-chloranil (1.24 g, 5.0 mmol) in HOAc (120 mL) was refluxed for 48 hr. The reaction mixture was concentrated under reduced pressure, and then resolved by CH$_2$Cl$_2$, washed by water for several times, after which the organic layer was dried over anhydrous sodium sulfate. The solvent was concentrated under reduced pressure, and the crude product was purified by column chromatography over silica gel (eluent: CH$_2$Cl$_2$ and then 50:1 CH$_2$Cl$_2$/ethyl acetate) to give 3 (0.62 g) in 41% yield and 3' (0.64 g) in 43% yield, respectively. Mp: >300 °C. IR: $\nu$ 1643 cm$^{-1}$. $^1$H
NMR (300 MHz, CDCl₃): δ 3.79 (s, 12H), 5.67 (s, 4H), 6.91-6.98 (m, 8H), 7.31-7.36 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 47.2, 56.3, 109.4, 123.9, 125.3, 136.5, 144.2, 146.5, 151.6, 180.1. MALDI-TOF MS: m/z 580.3 [M]+, 603.2 [M+Na]+. Anal. Calcd for C₃₈H₂₈O₆·3/₄CH₂Cl₂: C, 72.23; H, 4.61. Found: C, 72.26; H, 4.76.

Compound 4. NaHCO₃ (0.59 g, 7 mmol) and Na₂S₂O₄ (5.7 g, 33 mmol) were added to a solution of 3 (0.58 g, 1 mmol) in DMF (20 mL). The mixture was heated under Ar at 100 °C overnight. The cooled solution was poured into 300 mL of water, and the white precipitate was collected and dried under vacuum to afford 4 in 98% yield as white solid. ¹H NMR (300 MHz, CDCl₃): δ 3.67 (s, 12H), 5.58 (s, 4H), 6.86-6.89 (m, 8H), 7.24-7.26 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 47.3, 56.3, 109.1, 123.2, 124.9, 131.6, 138.4, 139.7, 145.9, 146.0. MALDI-TOF MS: m/z 582.2 [M]+, 605.2 [M+Na]+, 621.1 [M+K]+.

Compound 5. A mixture of pentiptycene hydroquinone 4 (509 mg, 0.87 mmol), 2-methoxyethyl 4-methylbenzenesulfonate (431 mg, 1.87 mmol), and K₂CO₃ (972 mg,
7.04 mmol) in 50 mL of dry DMF was refluxed under Ar for 2 days. The mixture was filtered and the filtration was concentrated under reduced pressure, then 50mL CH₂Cl₂ was added and the solution was washed by diluted HCl, dried over anhydrous sodium sulfate, after which the solvent was concentrated under reduced pressure. Column chromatography using 20:1 CH₂Cl₂/ethyl acetate as eluent afforded 5 (580 mg, 83%) as a white solid. Mp: 138-139 °C. ¹H NMR (300 MHz, CDCl₃): δ 3.67 (s, 6H), 3.77 (s, 12H), 3.88-3.90 (t, 4H), 4.00-4.28 (t, 4H), 5.67 (s, 4H), 6.89-6.96 (m, 8H), 7.28-7.33 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 47.9, 56.4, 59.3, 71.9, 74.8, 109.1, 123.2, 125.0, 136.9, 138.2, 145.7, 146.0, 146.2. MALDI-TOF MS: m/z 698.2 [M]⁺, 721.3 [M+Na]⁺, 737.2 [M+K]⁺. Anal. Calcd for C₄₄H₄₂O₈·0.5H₂O: C, 74.66, H, 6.12. Found: C, 74.84; H, 6.36.

Compound 6. A mixture of 5 (300 mg, 0.43 mmol) and CAN (1.43 g, 2.61 mmol) in acetonitrile (30 mL) and water (6 mL) was stirred at room temperature for 30 min. The reaction mixture was extracted with CH₂Cl₂. The organic layer was dried over anhydrous sodium sulfate and then concentrated under reduced pressure, the crude product was further purified by column chromatography over silica gel (eluent: 10:1 CH₂Cl₂/ethyl acetate) to give 6 (220 mg) in 80% yield as an orange solid. Mp: >300 °C. IR: ν 1644 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 3.63 (s, 6H), 3.86-3.87 (t, 4H), 4.07
(brs, 4H), 5.63 (s, 4H), 6.38 (s, 4H), 7.20-7.23 (m, 4H), 7.37-7.40 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 46.2, 59.3, 71.6, 75.9, 122.0, 124.7, 128.2, 132.9, 138.6, 146.4, 152.4, 179.8. MALDI-TOF MS: $m/z$ 642.3 [M+4H]$^+$. Anal. Calcd for C$_{40}$H$_{30}$O$_8$·1.2H$_2$O: C, 72.76; H, 4.95. Found: C, 72.50; H, 4.81.

 Compound 1. Reduction of the o-quinone 6 (0.40 g, 0.61 mmol) with catalytic hydrogenation gave 7 (0.397 g, 0.62 mmol) as a white solid in 98% yield, which was used in the next reaction without further purification. A suspension of cesium carbonate (1.66 g, 5.1 mmol) in anhydrous DMF (70 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100 °C. To the mixture was added dropwise a solution of 7 (0.397 g, 0.62 mmol) and bistosylate 8$^\text{S2a}$ (0.847 g, 1.24 mmol) in anhydrous DMF (70 mL) over 12h. The reaction mixture was stirred at 100 °C for another 3d. After cooling down to ambient temperature, the mixture was filtered and washed with CH$_2$Cl$_2$ (60 mL). The filtrate was concentrated under reduced pressure to give a gray solid, which was dissolved in CH$_2$Cl$_2$ (250 mL) and washed with diluted HCl. The organic layer was dried over anhydrous sodium sulfate. Removal of the
solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 100:1 CH$_2$Cl$_2$/CH$_3$OH and then 60:1 CH$_2$Cl$_2$/CH$_3$OH) 0.295 g (36 %) of 1 as an off-white solid was obtained. Mp: 78-79 °C. $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ 3.55-3.57 (m, 22H), 3.64-3.69 (m, 16H), 3.82-3.83 (m, 4H), 3.96-4.01 (m, 20H), 5.70 (s, 4H), 6.84 (s, 8H), 6.91-6.93 (m, 4H), 7.00 (s, 4H), 7.28-7.32 (m, 4H). $^{13}$C NMR (75 MHz, CD$_3$CN): $\delta$ 47.0, 58.2, 68.4, 69.0, 69.2, 69.3, 70.2, 70.3, 71.2, 74.8, 111.4, 113.7, 120.9, 123.0, 124.7, 137.0, 138.2, 145.3, 145.6, 145.7, 148.5. MALDI-TOF MS: $m/z$ 1341.6 [M+Na]$^+$. Anal. Calcd for C$_{76}$H$_{86}$O$_{20}$: C, 69.18; H, 6.57. Found: C, 69.13; H, 6.72.
2. $^1$H NMR and $^{13}$C NMR spectra of compounds 1, 3–6

**Figure S1.** $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 3.

**Figure S2.** $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 3.
Figure S3. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 4.

Figure S4. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 4.
Figure S5. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 5.

Figure S6. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 5.
**Figure S7.** $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 6.

**Figure S8.** $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 6.
**Figure S9.** $^1$H NMR spectrum (300 MHz, CD$_3$CN) of 1.

**Figure S10.** $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 1.
3. $^1$H-$^1$H COSY spectrum of complex 1·2

Figure S11. $^1$H-$^1$H COSY spectrum (300 MHz, CD$_3$CN) of a solution of 1 and 1 equiv of 2. [1]$_0$ = 1 mM.
4. $^1$H NMR spectra of complex 1·2 at low temperatures

Figure S12. Partial $^1$H NMR spectra (600 MHz, CD$_3$CN) of a solution of 1 and 1 equiv of 2 at (a) 293 K, (b) 273 K, (c) 253 K, and (d) 233 K. [1]$_0$ = 1 mM.

5. CV curves for a solution of the host in the absence and presence of the guest

Figure S13. CV curves for a solution of 1 ($2.5 \times 10^{-4}$ M) in CH$_3$CN-(NBu$_4$)PF$_6$ (0.1 M) in the absence (black line) and the presence (red line) of guest 2$^{4+}$ ($1.0 \times 10^{-3}$ M). Working electrode: Pt. Reference electrode: Ag/AgNO$_3$. Scan rate: 0.2Vs$^{-1}$. 

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6. Determination of the association constant

![Graph showing mole ratio plot for the complexation of 1 and 2 in CD$_3$CN at 298 K.]

**Figure S14.** Mole ratio plot for the complexation of 1 and 2 in CD$_3$CN at 298 K.

![Graph showing determination of $\Delta_0$ of H$_7$ for the complexation of 1 and 2 in CD$_3$CN at 298 K.]

**Figure S15.** Determination of $\Delta_0$ of H$_7$ for the complexation of 1 and 2 in CD$_3$CN at 298 K.
Figure S16. Scatchard plot for the complexation of 1 and 2 in CD$_3$CN at 298K.

7. ESI-MS spectrum of complex 1·2

Figure S17. ESI-MS spectrum of the complex 1·2.
8. Color change and UV spectra of 1, 2 and complex 1·2

Figure S18. Color change from colorless of 1 (1×10^{-3} moldm^{-3}) to orange on complexation with 2 (colorless, 1×10^{-3} moldm^{-3}).

Figure S19. Absorption spectra of 2 (1×10^{-3} moldm^{-3}) in the absence and presence of 1 (1×10^{-3} moldm^{-3}) in CH_{3}CN at 298K.

9. Single crystal analysis of complex 1·2

Application of 108 least-squares restraints is for confining the thermal vibration parameters of fluoride atom of the disorder PF_{6} ion, which can make them be isotropic.
Figure S20. Crystal packing of the complex viewed along the $a$-axis (a), and $b$-axis (b). Solvent molecules, PF$_6^-$ counterions and hydrogen atoms were omitted for clarity.

9. References
