Electronic Supplementary Information

A π -Electron Rich Cage via the Friedel-Crafts Reaction

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1. Materials and general methods

All reagents and solvents were purchased from commercial sources and used without further purification. Manipulations/modifications were performed under a normal atmosphere unless otherwise indicated. The cage precursor 1,3,5-tri(furan-2-yl) benzene (**2**) was prepared according to reported procedure^[S1] and 1,4-diisopropenylbenzene (**3**) was commercially available. The guest molecules (**4**, **5**, **6**) were purchased as their chloride salt forms, and used after counterion exchange with ammonium hexafluorophosphate. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K using Bruker AVANCE III 400/500 and Agilent DD2 600 spectrometers, with working frequencies of 400/500/600 MHz for ¹H NMR, and 100/125/150 MHz for ¹³C NMR, respectively. Chemical shifts are reported in ppm relative to the residual internal non-deuterated solvent signals (CDCl₃: δ = 7.26 ppm for ¹H and δ = 77.16 for ¹³C; CD₃CN: δ = 1.94 ppm for ¹H and δ = 118.26 for ¹³C). High-resolution mass spectra (HRMS) were recorded on a Fourier transform ion cyclotron resonance mass spectrometer.

2. Synthetic Procedures



Figure S1. Synthesis of cage 1.

Synthesis of cage 1

1,3,5-tri(furan-2-yl) benzene (**2**) (200 mg, 0.72 mmol) and 1,4-diisopropenylbenzene (**3**) (178 mg, 1.125 mmol) were dissolved in 1,2-dichloroethane (DCE) (50 mL). Ca(NTf₂)₂ (108.07 mg, 0.18 mmol) and NBu₄PF₆ (69.74 mg, 0.18 mmol) was added to the solution. The reaction mixture was stirred under reflux at 85 °C in an oil bath. The reaction progress was monitored by TLC. After the reaction reached its equilibrium after 16 h, the reaction mixture was poured into water (50 mL), which was extracted with 40 mL DCM three times. The organic layer was collected and then washed with brine (50 mL). After dried with Na₂SO₄, the solvent was removed under vacuum. The crude product was further purified by column chromatography on silica gel (DCM/petroleum ether = 1:3) to yield cage **1** as an off-white powder (148 mg, 40%). ¹H NMR (600 MHz, CDCl₃): δ 7.49 (s, 6H), 6.85 (s, 12H), 6.53 (d, *J* = 3.2 Hz, 6H), 6.25 (d, *J* = 3.3 Hz, 6H), 1.67 (s, 36H). ¹³C NMR (CDCl₃, 150 MHz): δ 162.0 (C), 152.7 (C), 146.4 (C), 132.2 (C), 125.6 (CH), 118.7 (CH), 107.3 (CH), 106.3 (CH), 40.5 (CH3), 28.5 (C). HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₇₂H₆₇O₆ 1027.4938; Found 1027.4940; [M+Na]⁺ Calcd for C₇₂H₆₆O₆Na 1049.4757; Found 1049.4777.

3. Characterization



Figure S2. ¹H NMR spectrum of 1 (CDCl₃, 600 MHz, 298 K).



Figure S3. ¹³C NMR spectrum of 1 (CDCl₃, 150 MHz, 298 K).



Figure S4.¹H-¹H COSY NMR spectrum of **1** (CDCl₃, 500 MHz, 298 K). Key correlation peaks are labeled in the spectrum.



Figure S5. ¹H-¹H NOESY NMR spectrum of **1** (CDCl₃, 500 MHz, 298 K). Key correlation peaks are labeled in the spectrum. Mixing time: 0.5 s.



Figure S6. ¹H-¹³C HSQC NMR spectrum of 1 (CDCl₃, 500 MHz, 298 K).



Figure S7. ¹H-¹³C HMBC NMR spectrum of 1 (CDCl₃, 500 MHz, 298 K).



Figure S8. ESI-HRMS of **1**, full range (top), and expanded (bottom). Molecular ions bearing one positive charge by taking proton, and sodium cations are observed. M is referred to as the cage **1**.



Figure S9. Experimental (bottom) and simulated (top) isotopic patterns of the peaks in ESI-HRMS, corresponding to a) $[M+H]^+$ and b) $[M+Na]^+$ for cage 1; c) $[M+4]^{2+}$ and d) $[M+4+PF_6^-]^+$ for complex $[4^{2+}\cdot 2PF_6^- \subset 1]$. M is referred to as the cage 1.

4. ¹H NMR titration



Scheme S1. ¹H NMR titration of the host and guest.

Fast Host-guest exchange on the NMR time scale was observed, as inferred from the results that before and after adding guests, only one set of peaks corresponding to the host and guests were observed. Binding affinities of the host-guest complexes were calculated by using ¹H NMR spectroscopic titration experiments. Solvent is a mixture of CDCl₃ and CD₃CN (1:1, ν/ν). In all samples during titration, the concentration of the cage **1** was kept constant. The association constants (K_a) could be deprived from a plot of the resonance changes of a proton on the host cage **1** versus the concentration of the guest added into the solution of the cage **1**. K_a was calculated by using the plot to fit in the following equation^[s2]:

$$A = ((1+1/K_a/[H]_0+[G]/[H]_0) - A_{\infty}((1+1/K_a/[H]_0+[G]/[H]_0)^2 - 4[G]/[H]_0)^{0.5})/2$$

Where *A* is the resonance changes of the aromatic proton on **1** (host) in the presence of the guest whose concentration is [G], A_{∞} is the chemical shift change of H_e when the cavity of the host is completely occupied by the guest, and [H]₀ is the concentration of the host which was kept constant.



Figure S10. Partial ¹H NMR spectra (CDCl₃:CD₃CN = 1:1, v/v, 298K, 600 MHz) of **1** (1 mM) upon adding methyl viologen with different concentrations, whose counterion is PF₆⁻ (**4**^{2+.}2PF₆⁻).



Figure S11. Plots of the shifts of the resonance corresponding to protons H_a , H_b and H_c versus $[4^{2+}\cdot 2PF_6^{-}]/[1]$, respectively, based on ¹H NMR spectroscopic results in Figure **S10**. K_a of **1** to recognize 4^{2+} was calculated to be $(3.8\pm1.2)\times10^4$ M⁻¹, by averaging the three numbers.



Figure S12. Partial ¹H NMR spectra (CDCl₃:CD₃CN = 1:1, v/v, 298K, 600 MHz) of **1** (1 mM) upon adding *N*-methyl-quinolinium with different concentrations, whose counterion is PF_6^- (**5**⁺·PF₆⁻).



Figure S13. Plots of the shifts of the resonance corresponding to protons H_a , H_b and H_c versus $[5^+ \cdot PF_6^-]/[1]$, respectively, based on ¹H NMR spectroscopic results in Figure **S12**. K_a of **1** to recognize **5**⁺ was calculated to be $(8.9\pm2.0)\times10^3$ M⁻¹, by averaging the three numbers.





Figure S14. a) Partial ¹H NMR spectra (CDCl₃:CD₃CN = 1:1, ν/ν , 298K, 500 MHz) of **1** (1 mM) upon adding *N*-methyl-pyridinium with different concentrations, whose counterion is PF₆⁻⁻ (**6**⁺·PF₆⁻⁻).



Figure S15. Plot of the upfield shifts of the resonance corresponding to protons H_a , H_b and H_c *versus* [6⁺·PF₆⁻]/[1], respectively, based on ¹H NMR spectroscopic results in Figure S14. K_a of 1 to recognize 6⁺ was calculated to be (5.4±1.9)x10³ M⁻¹, by averaging the three numbers.

5. X-ray crystallography

Solid-state structure of cage 1

Methods

Single crystals of the cage 1, suitable for X-ray crystallography, were obtained by slow vapor diffusion of diethyl ether into a solution of 1 in $CHCl_3$ after 10 days. Data were collected at 193 K on a Bruker D8 Venture Diffractometer equipped with a GaK α I μ S source and MX optic.

Crystal parameters

 $[C_{72}H_{66}O_6]$, colorless block, hexagonal, space group P 63/m, a = 13.706(3) Å, b = 13.706(3) Å, c = 21.677(6) Å, a = 90°, $\beta = 90$ °, $\gamma = 120$ °, V = 3526.56 Å³, Z = 3, T = 193 K, μ (GaK α) = 1.394 mm⁻¹. A total of 2260 reflections were collected, of which 1459 were unique. Final R₁(I > 2σ (I)) = 0.1284 and $wR_2 = 0.2888$ (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2121981.



Figure S16. Different views of the solid-state structure of cage **1**. Color code: Carbon, grey; oxygen red; Disordered solvent molecules, and hydrogen atoms are omitted for clarity.



Figure S17. Thermal ellipsoid plot for cage 1, the ellipsoid contour level is 50 %.

Solid-state structure of complex $4^{2+} \cdot 2PF_6 \subset 1$

Methods

Single crystals of the complex $4^{2+}\cdot 2PF_6^{-} \subset 1$, suitable for X-ray crystallography, were obtained by slow vapor diffusion of diethyl ether into a solution of $4^{2+}\cdot 2PF_6^{-}$ in a mixture of CHCl₃:CH₃CN = 1:1(ν/ν) after 7 days. Data were collected at 213 K on a Bruker D8 Venture Diffractometer equipped with a GaK α IµS source and MX optic.

Crystal parameters

 $[C_{90}H_{88}F_{12}N_3O_6P_2]$, red block, monoclinic, space group P 1 21/c 1, a = 15.5630(6) Å, b = 25.9415(11) Å, c = 20.2308(8) Å, $\alpha = 90^\circ$, $\beta = 108.499(2)^\circ$, $\gamma = 90^\circ$, V = 7745.7(5) Å³, Z = 4, T = 213 K, $\mu(GaK\alpha) = 0.794$ mm⁻¹. A total of 14744 reflections were collected, of which 8346 were unique. Final $R_1(I > 2\sigma(I)) = 0.0946$ and $wR_2 = 0.2958$ (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2121986.



Figure S18. Different views of the solid-state structure of $4^{2+}\cdot 2PF_6 \subset 1$. Color code: Carbon, grey; oxygen, red; nitrogen, blue. Disordered solvent molecules, and partial hydrogen atoms are omitted for clarity.



Figure S19. Thermal ellipsoid plot for $4^{2+} \cdot 2PF_6 \subset 1$, the ellipsoid contour level is 50 %.

Solid-state structure of complex $6^+ \cdot PF_6 \subset 1$

Methods

Single crystals of the complex $6^+ \cdot PF_6^- \subset 1$, suitable for X-ray crystallography, were obtained by slow vapor diffusion of diethyl ether into a solution of $5^+ \cdot PF_6^-$ in a mixture of CHCl₃:CH₃CN = 1:1(v/v) after 7 days. Data were collected at 210 K on a Bruker D8 Venture Diffractometer equipped with a GaK α IµS source and MX optic.

Crystal parameters

 $[C_{82}H_{76}F_6NO_6P]$, yellow prism, hexagonal, space group P 63/m, a = 15.4504(4) Å, b = 20.5736(5) Å, c = 27.7314(7) Å, $a = 90^\circ$, $\beta = 90.362(2)$, $\gamma = 90^\circ$, V = 8814.8(4) Å³, Z = 4, T = 210 K, μ (GaK α) = 1.044 mm⁻¹. A total of 16765 reflections were collected, of which 8926 were unique. Final R₁ (I > 2 σ (I)) = 0.1008 and $wR_2 = 0.2787$ (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2121983.

Solid-state structure



Figure S20. Different views of the solid-state structure of $6^+ \cdot PF_6 \subset 1$. Color code: Carbon, grey; oxygen, red; nitrogen, blue. Disordered solvent molecules, and partial hydrogen atoms are omitted for clarity.



Figure S21. Thermal ellipsoid plot for $6^+ \cdot PF_6^- \subset 1$, the ellipsoid contour level is 50 %.

6. References

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