Guest recognition enhanced by lateral interactions

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Supporting Information

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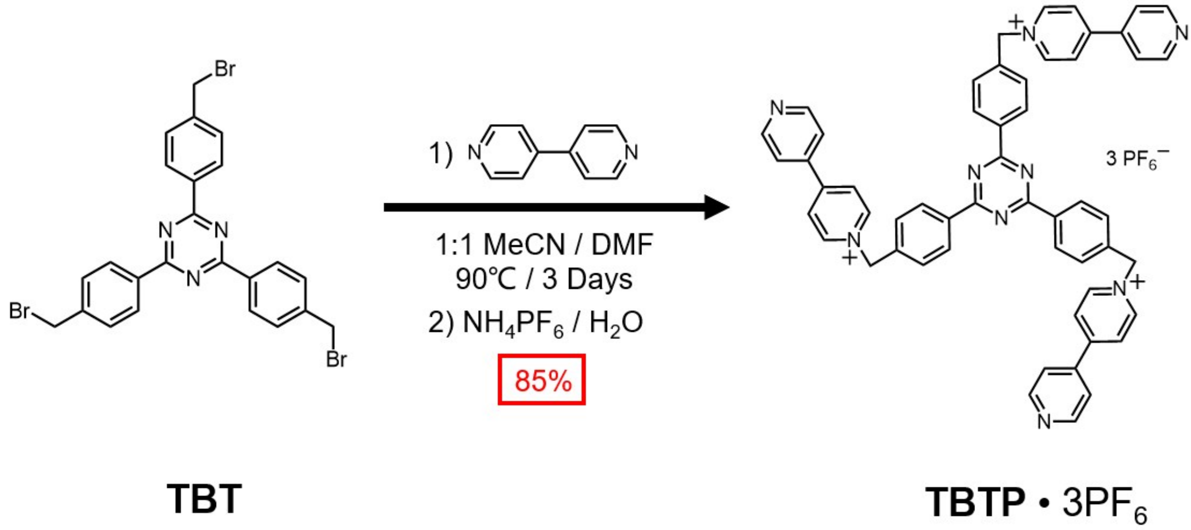
1. Materials and General Methods

Chemicals were purchased as reagent grade and employed without further purification. Commercial grades of anhydrous MeCN and *N*,*N*-dimethylformamide (DMF) were used as solvents in all reactions. 2,4,6-Tris[4-(bromomethyl)phenyl]-1,3,5-triazine (**TBT**) was prepared according to literature procedures.[1] Thin layer chromatography (TLC) was performed on silica gel 60F254 (E Merck). Column chromatography was carried out on silica gel 60F (Merck 9385, 0.040–0.063 mm). All UV-Vis-NIR spectra were recorded in MeCN solvent using a Shimadzu UV-3600 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on Bruker Avance 500 and 600 spectrometers, with working frequencies of 500 and 600 MHz for ^{1}H, and 125 and 150 MHz for ^{13}C nuclei, respectively. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ = 7.26 ppm, CD_3CN: δ =1.94 ppm, D_2O: δ = 4.79 ppm). High-resolution mass spectra were recorded on an Agilent 6210 Time-of-Flight (TOF) LC-MS, using an ESI source, coupled with Agilent 1100 HPLC stack, using direct infusion (0.6 mL min^{-1} Measurements at X-band (9.5 GHz) were performed with a Bruker Elexsys E580, equipped with a variable Q dielectric resonator (ER-4118X-MD5-W1). Cyclic voltammetry experiments were performed on a Gamry multipurpose instrument interfaced to a PC, using a glassy carbon working electrode (0.071 cm^2, Cypress system). The electrode surface was polished routinely with an alumina/water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was an AgCl coated Ag wire. The concentrations of the samples were 0.5 mM in 100 mM electrolyte solutions of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in DMF.

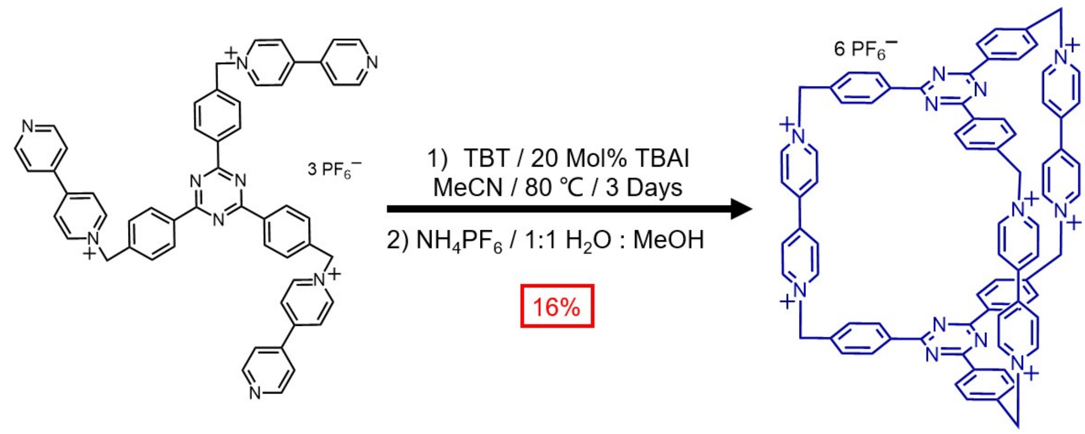
2. Synthetic Procedures

Scheme S1. Synthesis of **TBTP•**$3PF_6$



TBTP•$3PF_6$: A suspension of **TBT** (1.05 g, 1.8 mmol) in MeCN (20 mL) was added in five aliquots slowly over 6 h into a refluxing solution of 4,4′-bipyridine (6.03, 38 mmol) in a mixed anhydrous solvent containing DMF (50 mL) and MeCN (50 mL) at 90 °C. The reaction mixture was further stirred for another 72 h at 90 °C. After cooling to room temperature, the yellow precipitate was collected by filtration and washed with Me_2CO and CH_2Cl_2. The precipitate was dissolved in H_2O (250 mL) followed by the addition of NH_4PF_6 (~2 g), resulting in precipitation of pure **TBTP•**$3PF_6$ (1.90 g, 85%) as a light red solid that was collected by filtration. ^1H NMR (600 MHz, CD_3CN): δ = 8.90 (d, J = 6.9 Hz, 6H), 8.87−8.85 (m, 12H), 8.36 (d, J = 6.9 Hz, 6H), 7.81 (d, J_1 = 6.2 Hz, 6H), 7.70 (d, J_1 = 8.3 Hz, 6H), 5.88 (s, 6H). ^{13}C NMR (125 MHz, CD_3CN): δ = 172.1, 155.7, 152.0, 146.1, 142.2, 138.5, 138.1, 130.8, 130.6, 127.3, 122.9, 64.6. HRMS (ESI): *m/z* calcd for $C_{54}H_{42}F_{12}N_9P_2$ $[M - PF_6]^+$ 1106.2847, found 1106.2831; calcd for $C_{54}H_{42}F_6N_9P$ $[M - 2PF_6]^{2+}$ 480.6597, found 480.6609.

Scheme S2. Synthesis of **AzaEx²Cage**•$6PF_6$



TBTP • $3PF_6$ **AzaEx²Cage • $6PF_6$**

AzaEx²Cage•$6PF_6$: **TBT** (176.5 mg, 0.30 mmol) and **TBTP**•$3PF_6$ (375.5 mg, 0.30 mmol) were stirred in anhydrous MeCN (150 mL) at 60 °C under a N_2 atmosphere until all solids had been completely dissolved. TBAI (15.0 mg, 0.04 mmol) was added to the above solution. The reaction mixture was stirred for another 72 h under reflux. After that the reaction mixture was cooled to room temperature, yielding a yellow precipitate which was collected by filtration and washed with Me_2CO and CH_2Cl_2. Then the precipitate was dissolved in mixed solvent containing MeOH (250 mL) and H_2O (600 mL), in which NH_4PF_6 (~15 g) was added, yielding a yellow precipitate. The solid material was collected by centrifuge and then subjected to column chromatography using silica gel and 1% NH_4PF_6 in MeCN (w/v) as the eluent. The pure fractions were combined, concentrated under vacuum. Addition of H_2O into the solution led to precipitation of **AzaEx²Cage**•$6PF_6$ (98 mg, 16 %) as a white crystalline solid, which was collected by filtration and washed with H_2O (200 mL). ^1H NMR (500 MHz, CD_3CN): δ = 9.02 (d, J = 7.1 Hz, 12H), 8.73 (d, J = 8.3 Hz, 12H), 8.25 (d, J = 7.1 Hz, 12H), 7.80 (d, J = 8.3 Hz, 12H), 5.88 (s, 12H). ^{13}C NMR (125 MHz, CD_3CN): δ = 171.7, 150.8, 146.1, 139.2, 138.1, 131.1, 130.9, 128.6, 65.7. HRMS (ESI): *m/z* calcd for $C_{78}H_{60}F_{24}N_{12}P_4$ $[M - 2PF_6]^{2+}$ 872.1810, found 872.1822.

AzaEx²Cage•6Cl, a water-soluble counterpart of **AzaEx²Cage**•$6PF_6$, was obtained by means of counterion exchange: Tetrabutylammonium chloride (TBACl, 200 mg) was added to a MeCN solution (5 mL) of **AzaEx²Cage**•$6PF_6$ (80 mg). The resulting yellow precipitate was collected by filtration and washed with MeCN to give the desired compound

AzaEx^{2}Cage•6Cl (53 mg, 99%) as a yellow powder. ^{1}H NMR (500 MHz, D_2O): δ = 9.19 (d, *J* = 6.5 Hz, 12H), 8.38 (d, *J* = 6.5 Hz, 12H), 8.31 (d, *J* = 7.5 Hz, 12H), 7.64 (d, *J* = 7.5 Hz, 12H), 5.92 (s, 12H). ^{13}C NMR (125 MHz, D_2O): δ = 170.6, 149.6, 145.1, 138.0, 136.0, 130.0, 139.5, 127.2, 64.7. HRMS (ESI): *m/z* calcd for $C_{78}H_{60}N_{12}$ $[M - 6Cl]^{6+}$ 194.0838, found 194.0828.

AzaEx^{2}Cage•6CF_3CO_2, another water-soluble counterpart of **AzaEx^{2}Cage**•6PF_6, was obtained by preparative reverse-phase HPLC (C_{18} column) starting with H_2O containing 0.1% TFA as eluent, and increasing to 50 % of MeCN / 0.1 % TFA. The fractions containing **AzaEx^{2}Cage**•6CF_3CO_2 were combined. After removing the solvent under vacuum, **AzaEx^{2}Cage**•6CF_3CO_2 was obtained (80% yield). ^{1}H NMR (500 MHz, CD_3CN): δ = 9.13 (d, *J* = 7.0 Hz, 12H), 8.72 (d, *J* = 8.0 Hz, 12H), 8.33 (d, *J* = 7.0 Hz, 12H), 7.82 (d, *J* = 8.5 Hz, 12H), 5.92 (s, 12H). ^{13}C NMR (125 MHz, CD_3CN): δ = 171.7, 160.5, 150.7, 146.3, 139.4, 138.1, 131.0, 130.9, 128.6, 65.6. HRMS (ESI): *m/z* calcd for $C_{86}H_{60}F_{12}N_{12}O_8$ $[M - 2CF_3CO_2]^{2+}$ 808.2227, found 808.2242.

3. NMR Spectra and HRMS Spectra

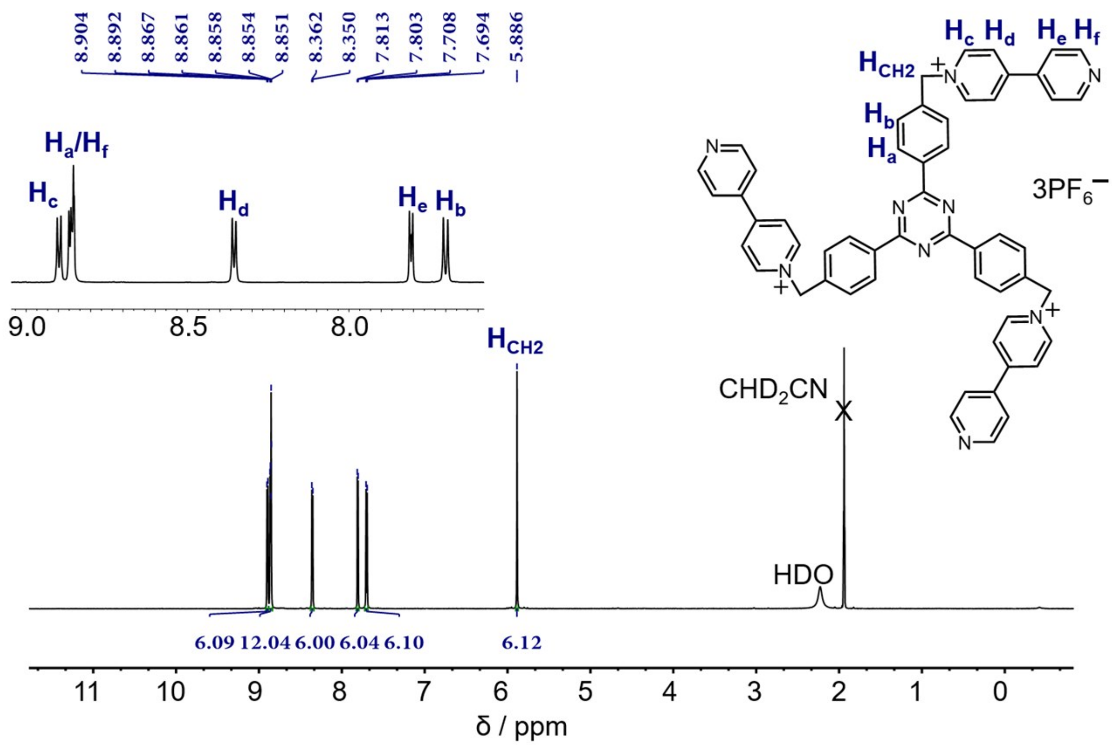


Figure S1. ^{1}H NMR Spectrum (600 MHz, CD_3CN, 298K) of **TBTP**•3PF_6.

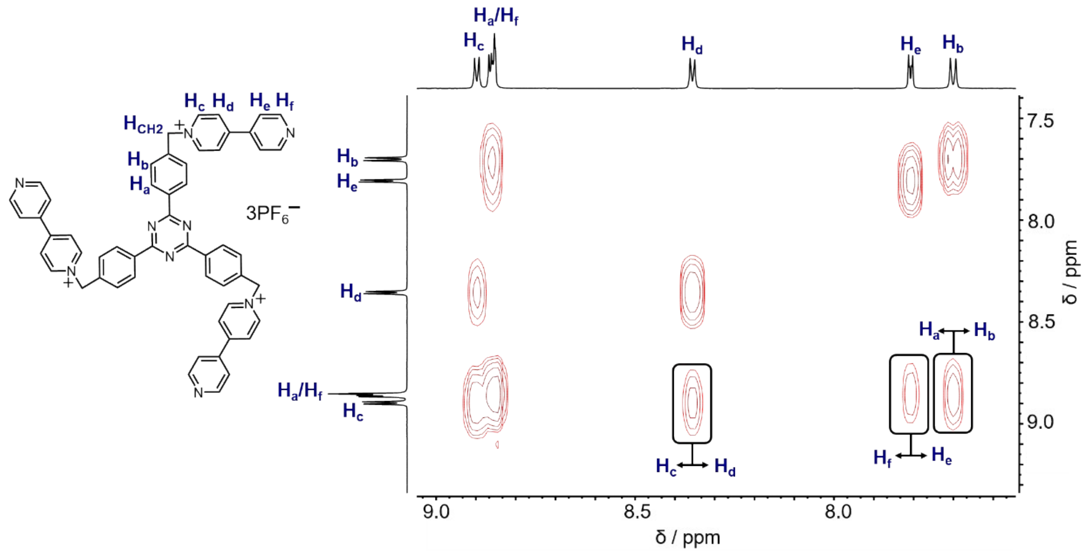


Figure S2. Partial ^1H–^1H Gradient-selected double-quantum filtered phase-sensitive COSY spectrum of **TBTP•**$3PF_6$ (600 MHz, CD_3CN, 298 K). Key correlation peaks are labeled in the spectrum.

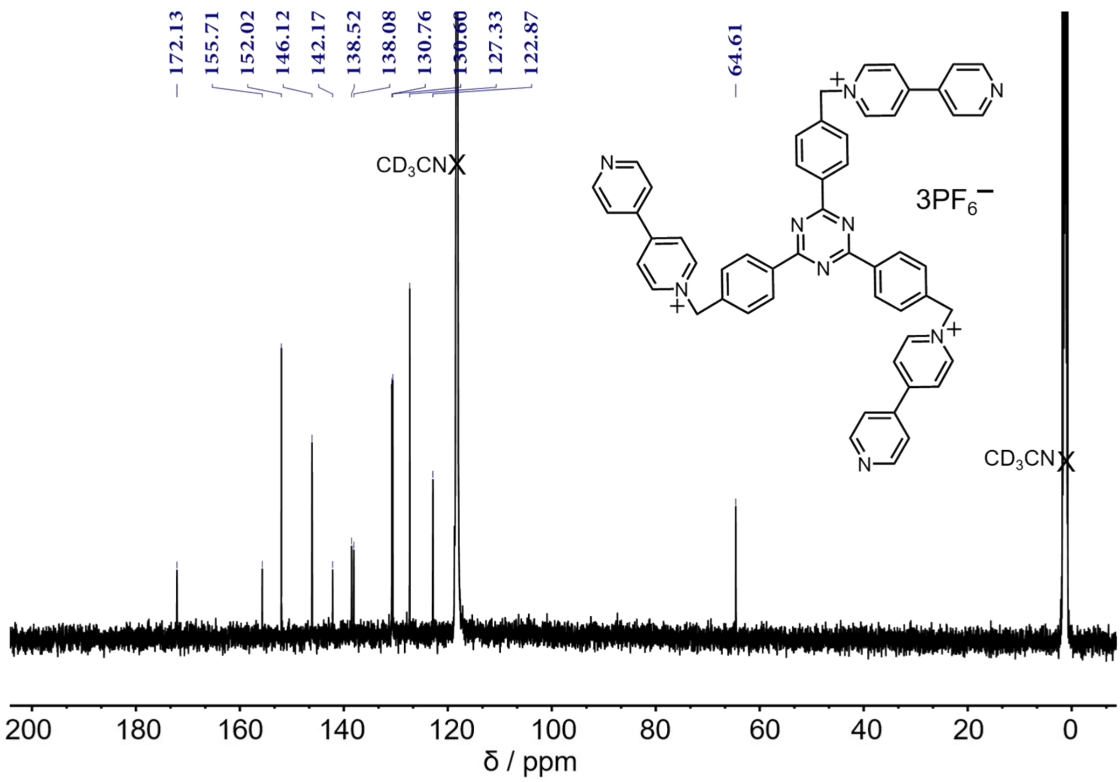


Figure S3. ^{13}C NMR Spectrum (125 MHz, CD_3CN, 298 K) of **TBTP•**$3PF_6$.

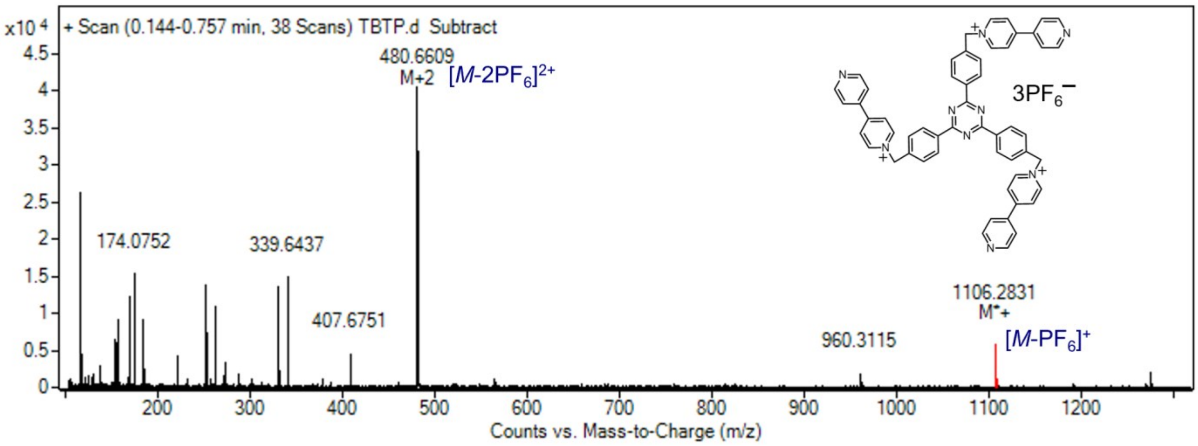


Figure S4. ESI-MS of **TBTP•**3PF_6. The signals labelled in the spectrum correspond to molecular cations that contain one or two charges by losing one or two PF_6^- counterions.

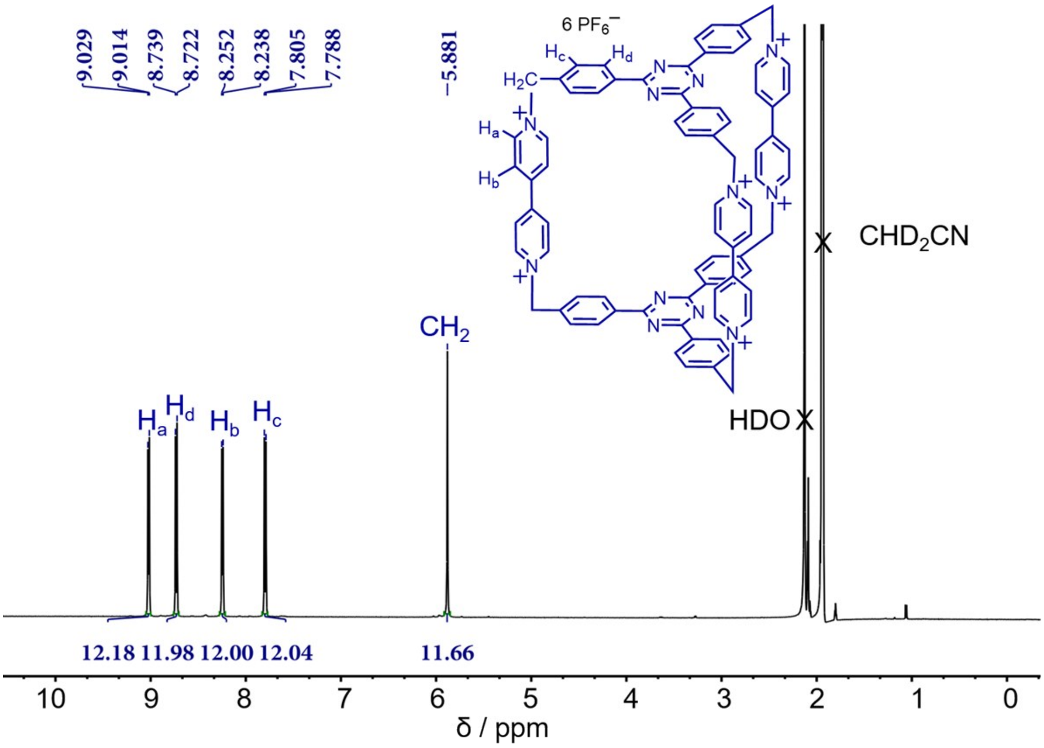


Figure S5. [1]H NMR Spectrum (500 MHz, CD_3CN, 298 K) of **AzaEx²Cage•**6PF_6.

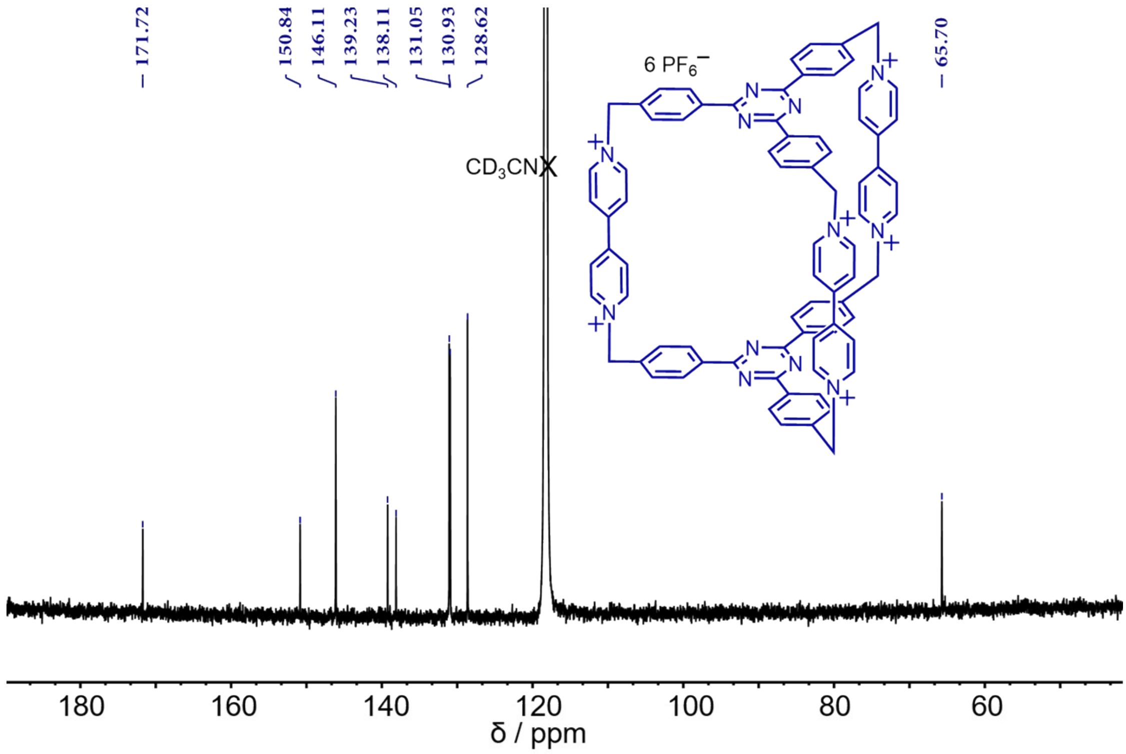


Figure S6. ^{13}C NMR Spectrum (125 MHz, CD_3CN, 298 K) of **AzaEx^{2}Cage**•$6PF_6$.

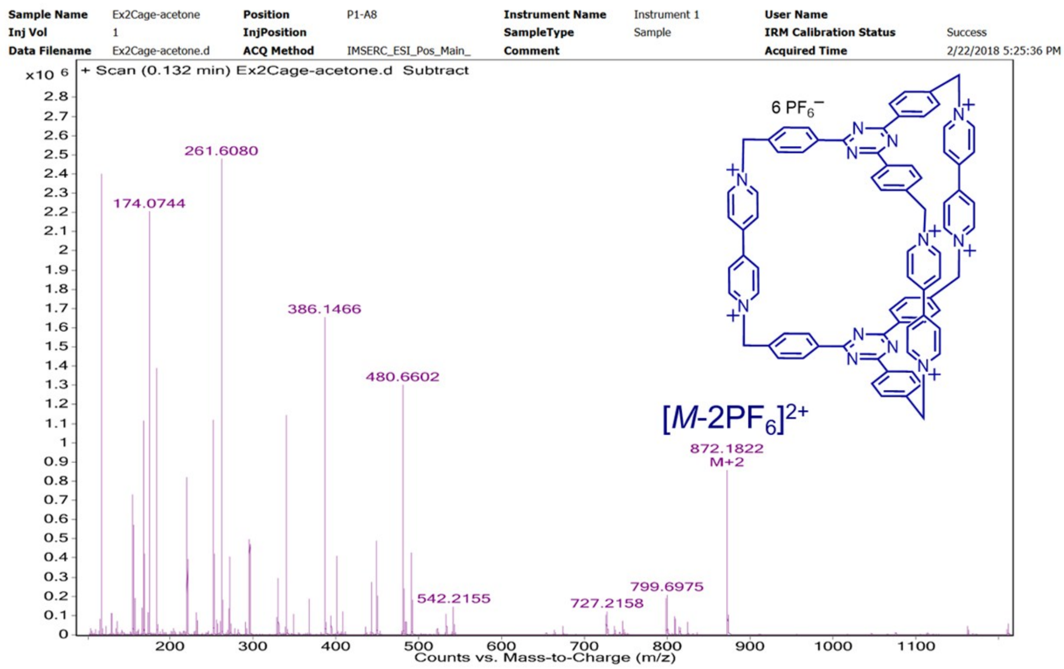


Figure S7. ESI-MS of **AzaEx^{2}Cage**•$6PF_6$. The signal labeled in the spectrum corresponds to molecular cation that contains two charges by losing two PF_6^- counterions.

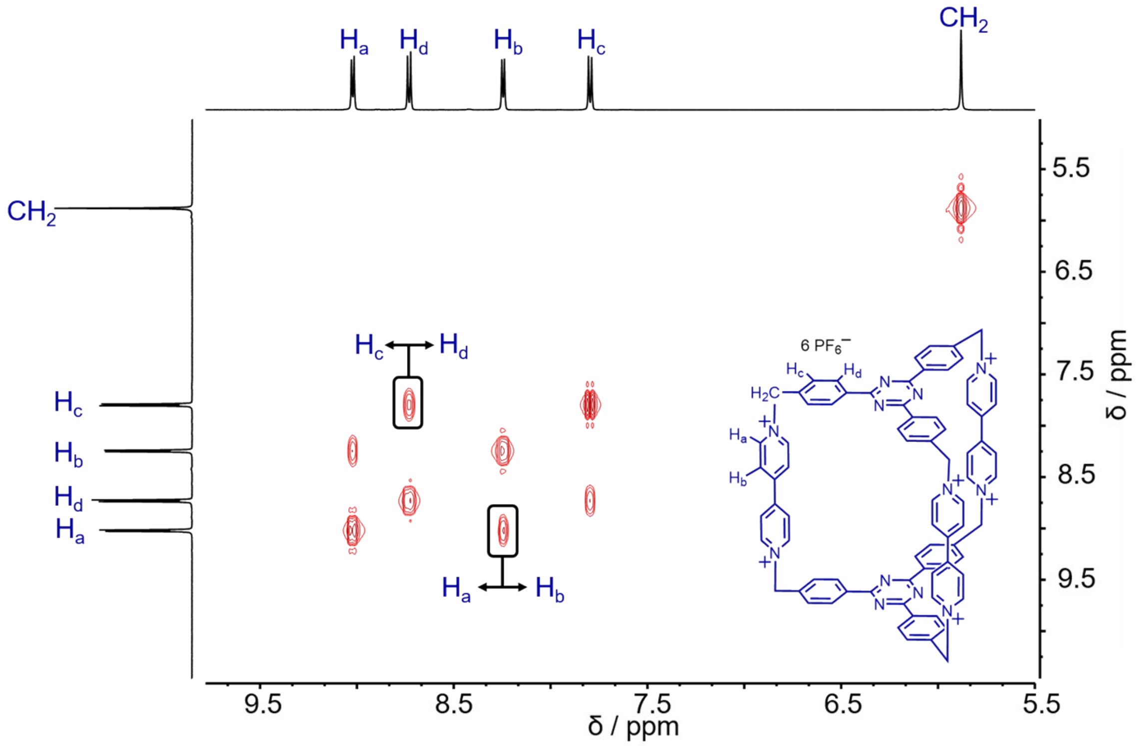


Figure S8. ^{1}H–^{1}H Gradient-selected double-quantum filtered phase-sensitive COSY spectrum of **AzaEx^{2}Cage**•6PF$_6$ (500 MHz, CD_3CN, 298 K). Key correlation peaks are labeled in the spectrum.

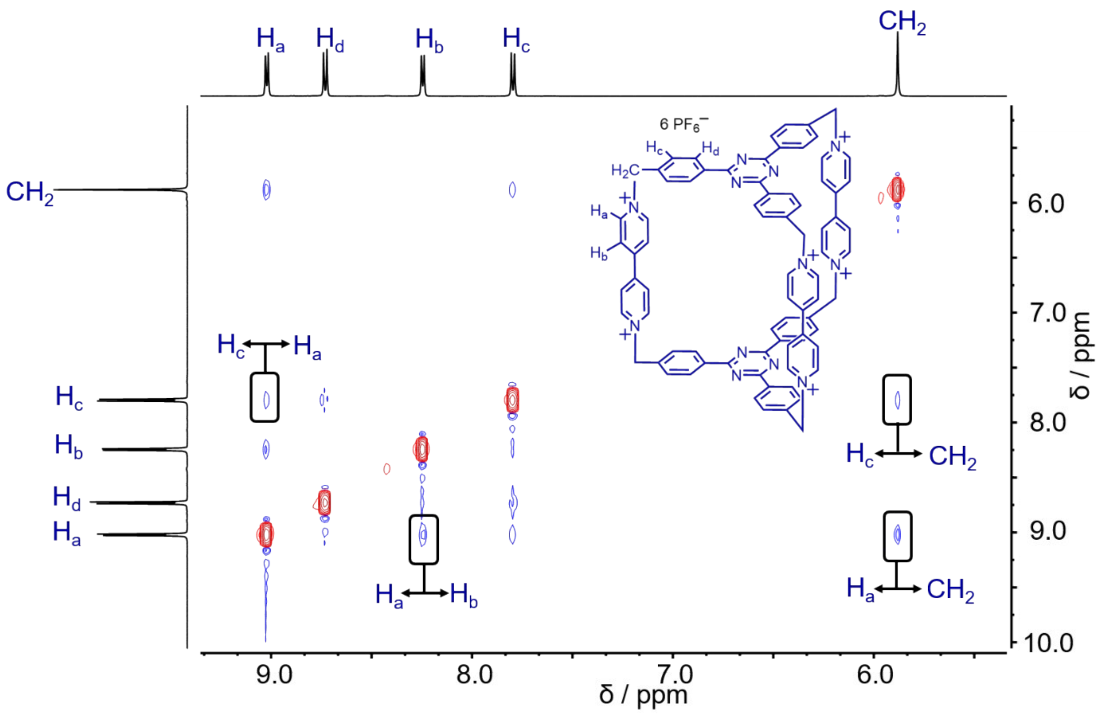


Figure S9. ^{1}H-^{1}H NOESY spectrum of **AzaEx^{2}Cage**•6PF$_6$ (500 MHz, CD_3CN, 298 K). Through-space proton couplings are labeled in the spectrum.

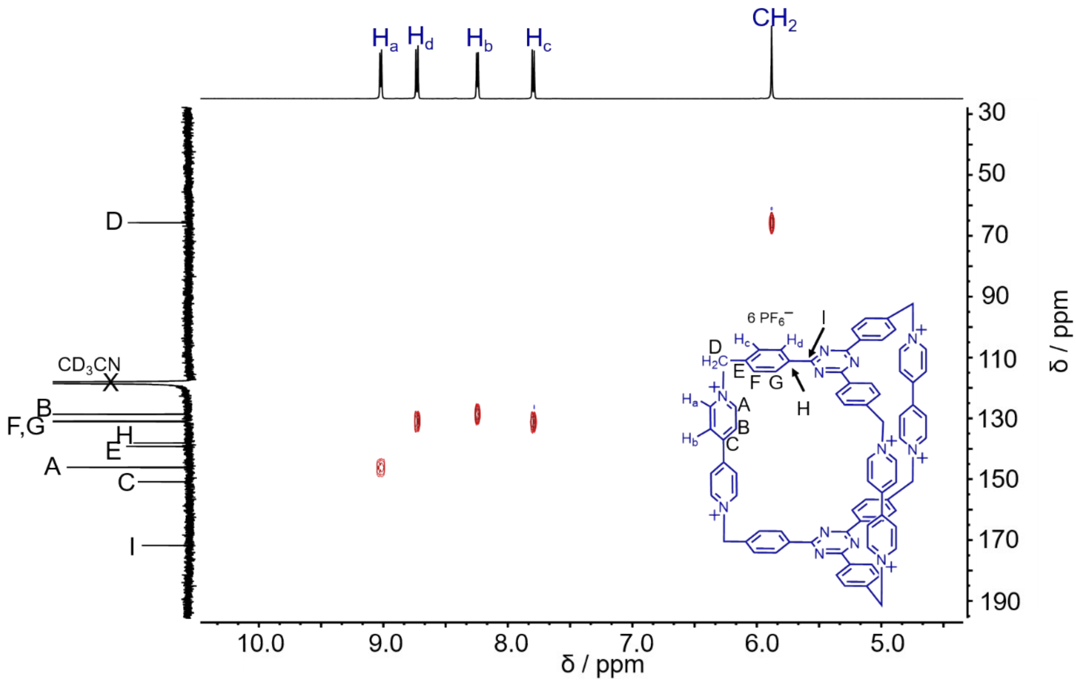


Figure S10. Part of the annotated [1]H–[13]C Heteronuclear Single Quantum Coherence (HSQC) spectrum (125 MHz, CD_3CN, 298 K) of **AzaEx[2]Cage**•$6PF_6$.

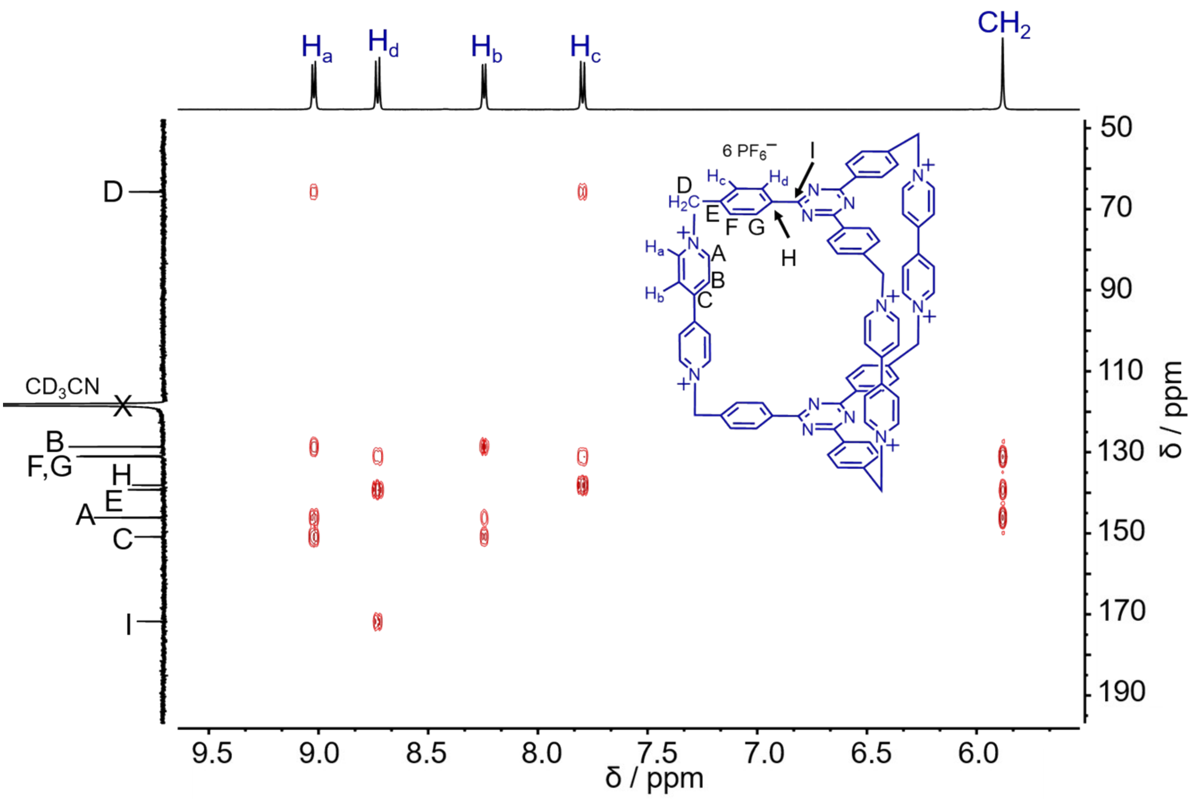


Figure S11. Part of the annotated [1]H – [13]C Heteronuclear Multiple Bond Coherence (HMBC) spectrum (125 MHz, CD_3CN, 298 K) of **AzaEx[2]Cage**•$6PF_6$.

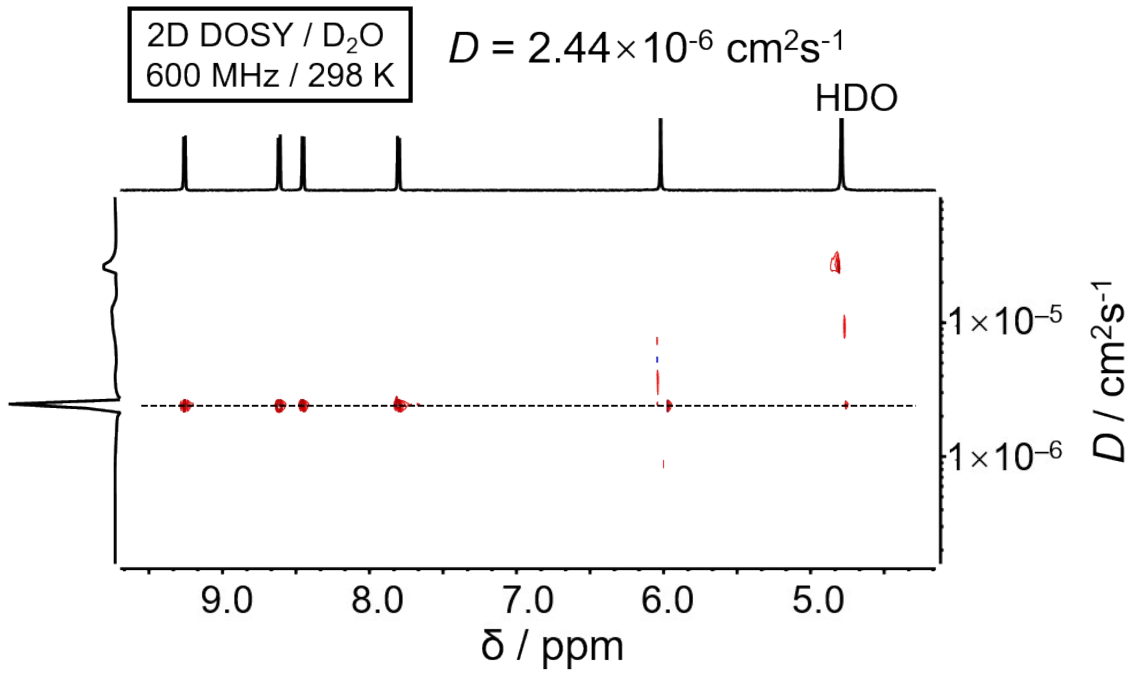


Figure S12. 2D DOSY spectrum (600 MHz, D_2O, 298 K) of **AzaEx^{2}Cage•**6Cl.

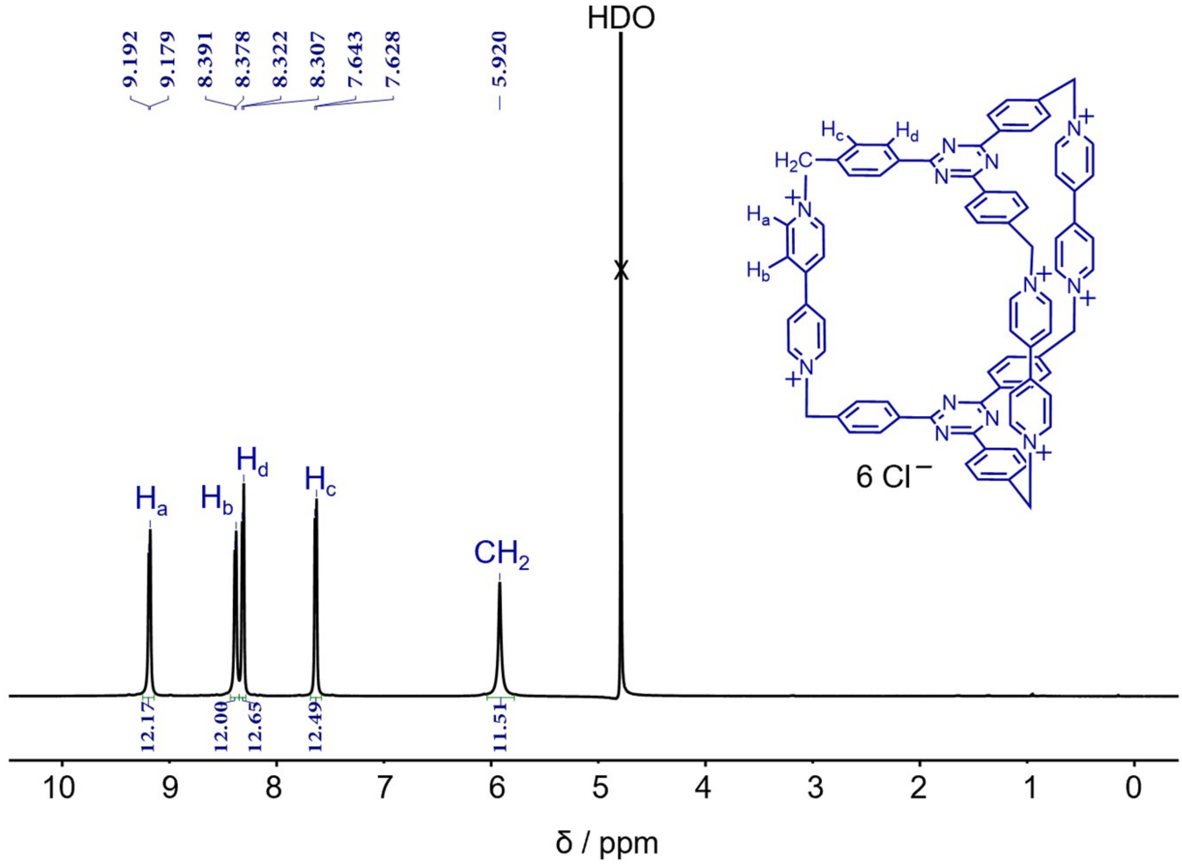


Figure S13. ^{1}H NMR Spectrum (500 MHz, D_2O, 298 K) of **AzaEx^{2}Cage•**6Cl.

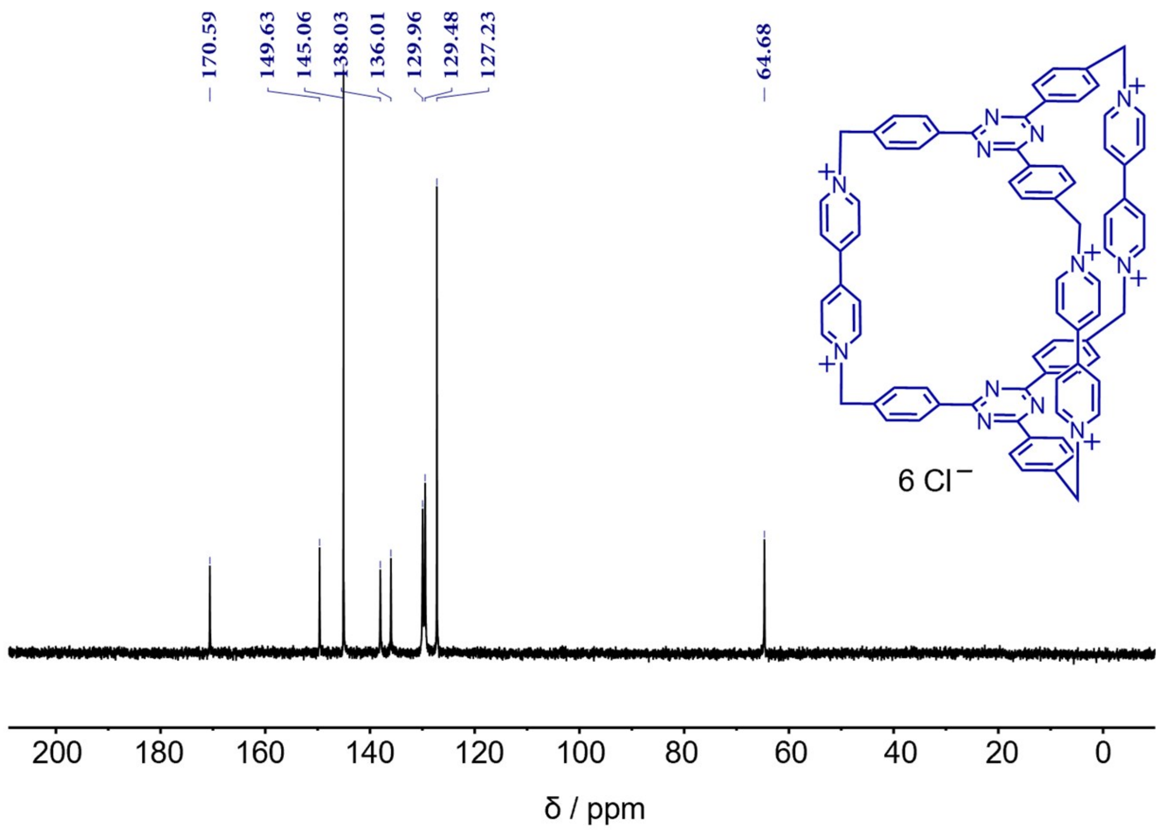


Figure S14. ^{13}C NMR Spectrum (125 MHz, D_2O, 298 K) of **AzaEx^{2}Cage•**6Cl.

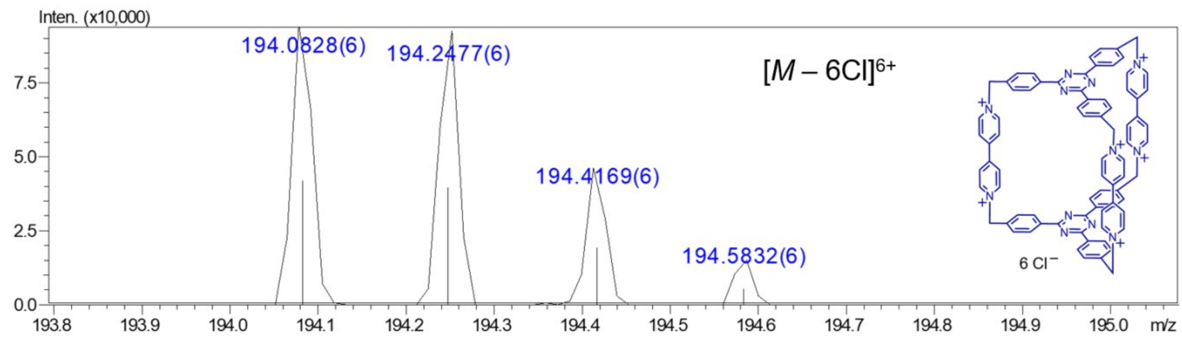


Figure S15. ESI-MS of **AzaEx^{2}Cage•**6Cl. The signal labeled in the spectrum corresponds to molecular cation that contains two charges by losing six Cl^- counterions.

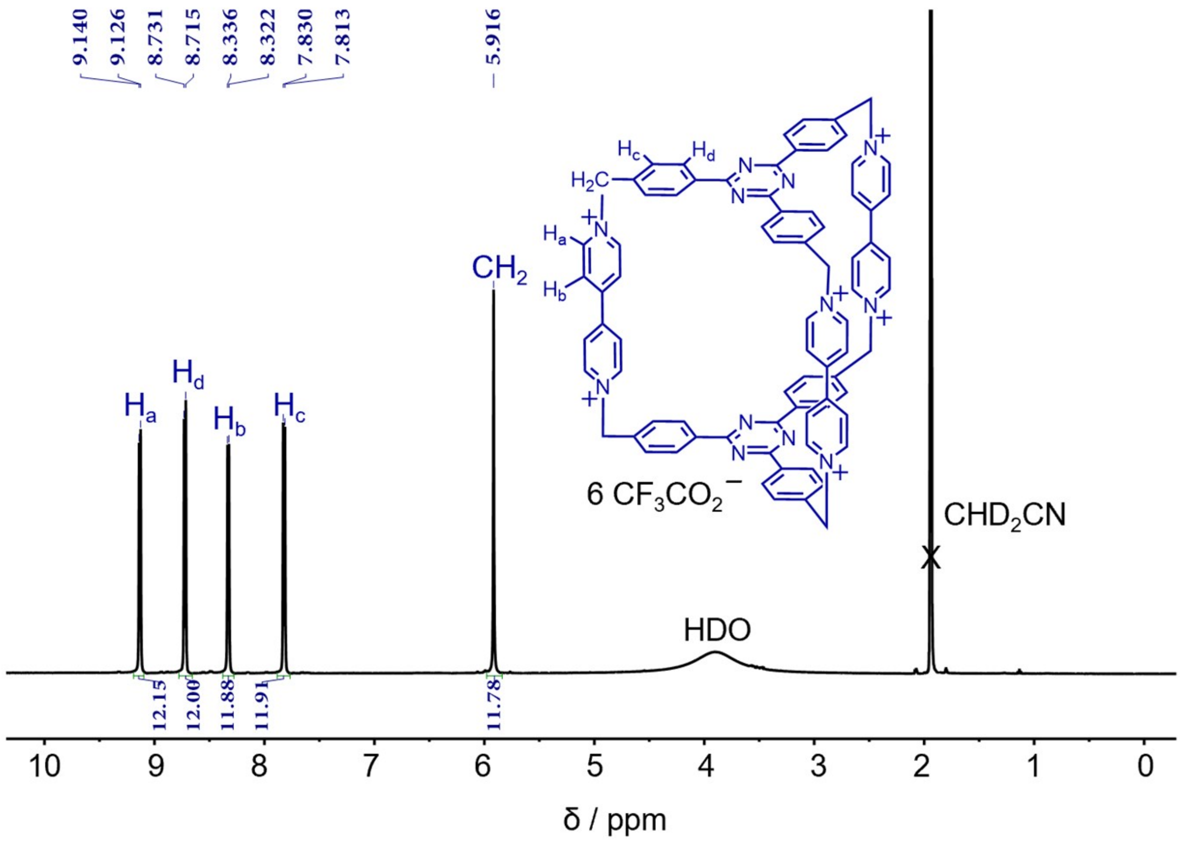


Figure S16. ^{1}H NMR Spectrum (500 MHz, CD_3CN, 298 K) of **AzaEx²Cage**•6CF_3CO_2.

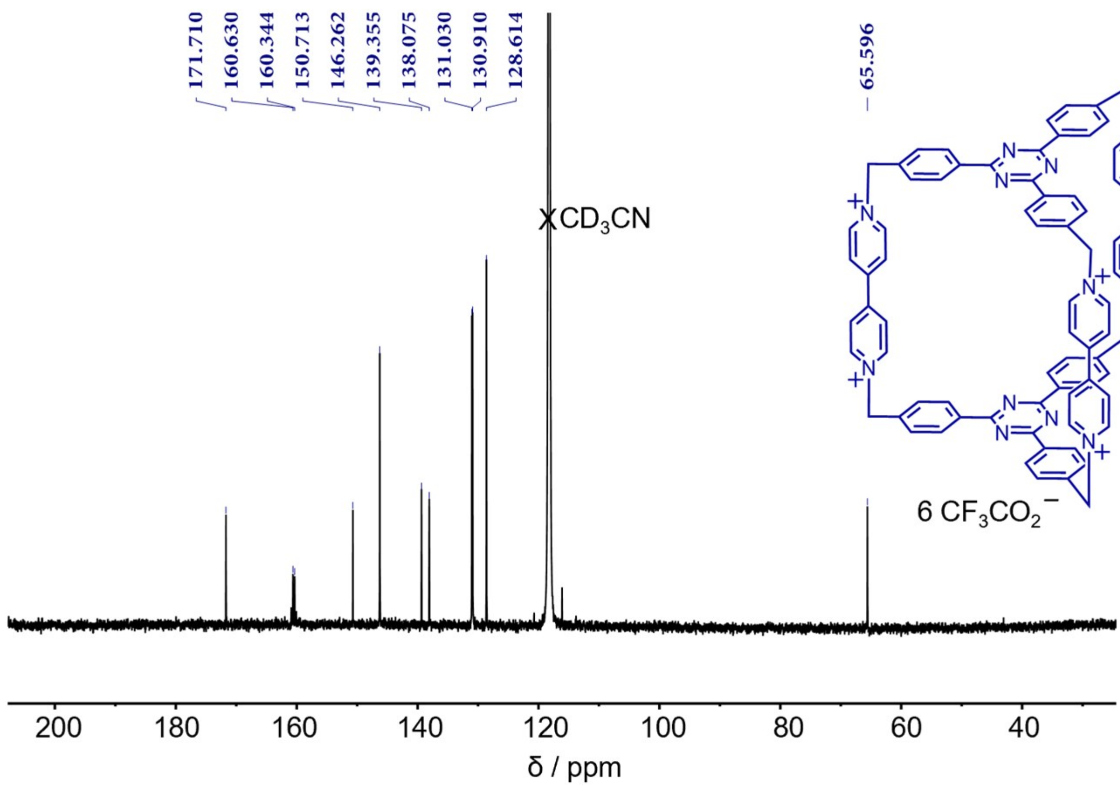


Figure S17. ^{13}C NMR Spectrum(125 MHz, CD_3CN, 298 K) of **AzaEx²Cage**•6CF_3CO_2.

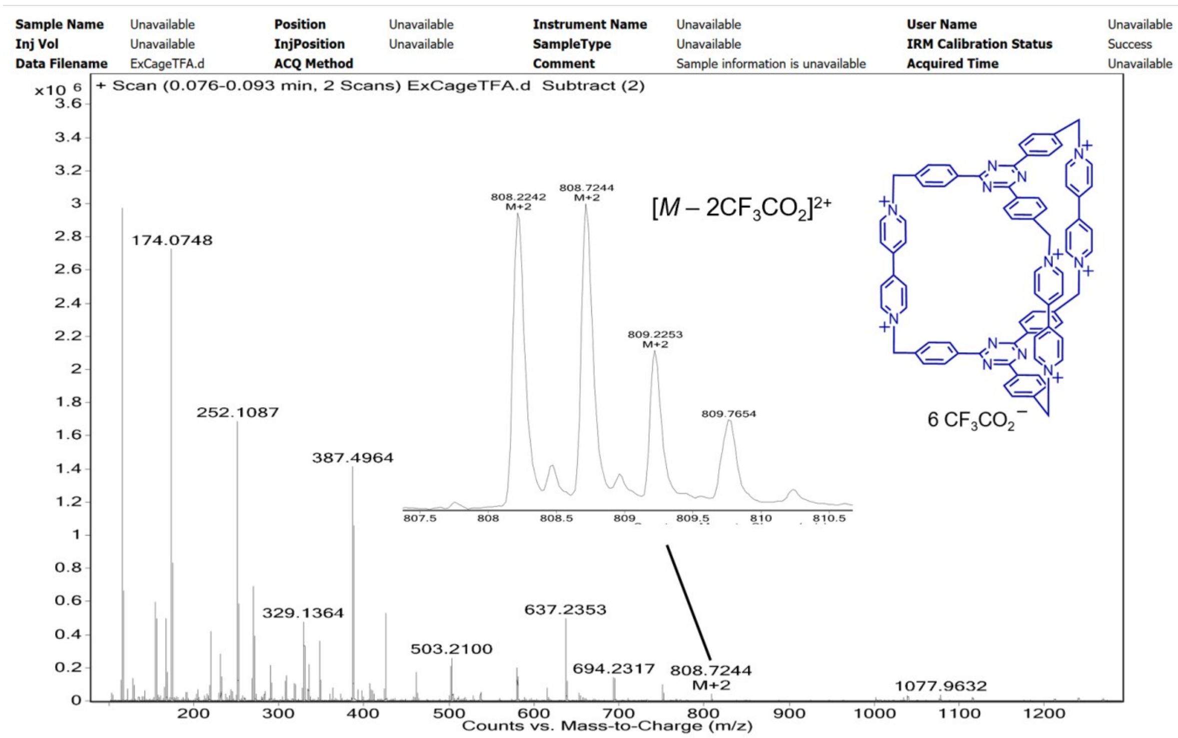


Figure S18. ESI-MS of **AzaEx²Cage•**6CF_3CO_2. The signal labeled in the spectrum corresponds to molecular cation that contains two charges by losing two $CF_3CO_2^-$ counterions.

4.Binding Studies and Characterization of Host-Guest Complex

General experimental procedure

A solution of **AzaEx²Cage**·6PF_6 in CD_3CN (approximately 1.0 × 10^{-3} M, 1 mL) was separated equally into two portions. An excess of solid-state guest (typically 20-50 equivalents relative to host **AzaEx²Cage**·6PF_6) was added to the first portion of the **AzaEx²Cage**·6PF_6 solution. This host-guest mixture solution was used to titrate the second portion solution of **AzaEx²Cage**·6PF_6, whose ^{1}H NMR spectra were recorded before and after the addition of the former mixture solution. All the spectra were recorded after shaking the NMR tube thoroughly, in order to allow the host-guest systems to reach the equilibrium. The upfield or downfield shifts (Δδ) of the corresponding proton resonances in **AzaEx²Cage**·6PF_6 upon addition of different amount of guest were recorded and used to fit to a 1:1 or 1:2 binding models using Bindfit[2].

1) Binding behavior between **PCA** and **AzaEx²Cage**·$6PF_6$

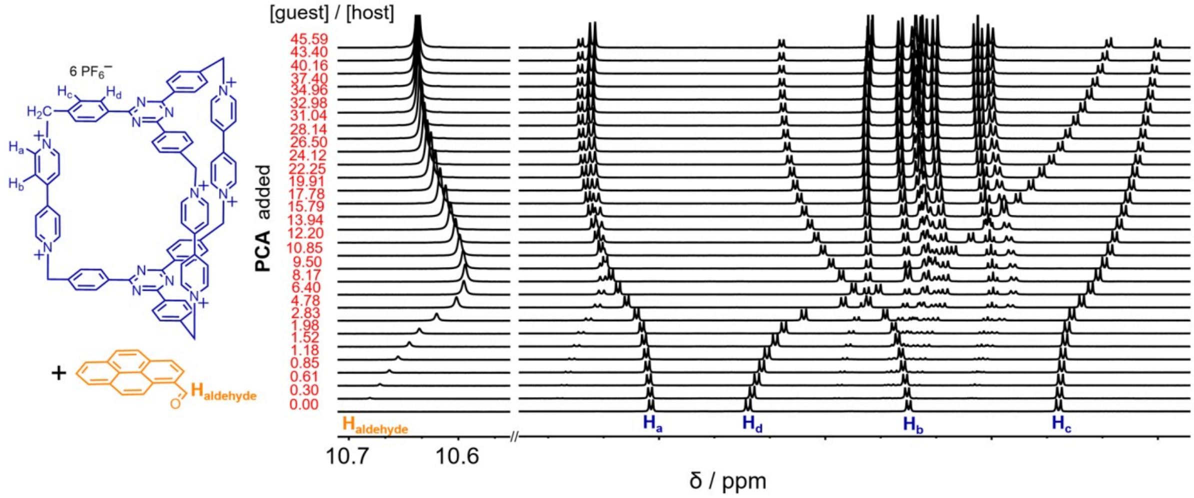


Figure S19. ¹H NMR spectra (600 MHz, 298 K) of **AzaEx²Cage•**$6PF_6$ (9.04×10^{-4} M) in CD_3CN after adding different amount (from 0 to 46 equiv) of 1-pyrenecarboxaldehyde (**PCA**) relatively to **AzaEx²Cage•**$6PF_6$.

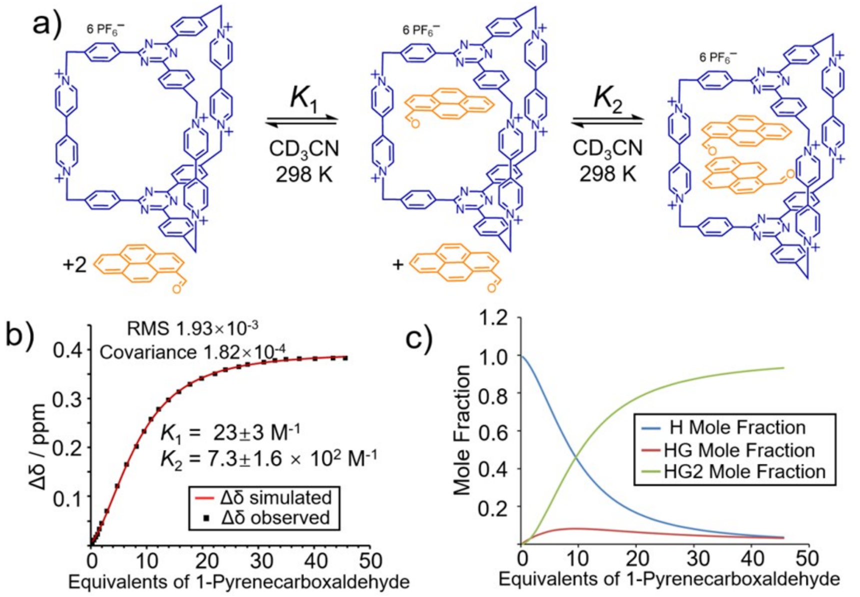


Figure S20. a) The 1:2 binding behavior between **AzaEx²Cage•**$6PF_6$ and **PCA**. b) Observed (dot) and calculated (red trace) binding curves of the downfield shifts of the resonance of proton H_b in **AzaEx²Cage•**$6PF_6$ versus [**PCA**]/[**AzaEx²Cage•**$6PF_6$]. By using a 2:1 binding model, the binding constants could be determined. c) Mole fraction based on the fitting results indicating that the concentration of the "free" host **AzaEx²Cage**$^{6+}$ undergoes continuous decrease (blue trace), while the concentration of $(\mathbf{PCA})_2\subset$**AzaEx²Cage**$^{6+}$ complex undergoes continuous increase (green trace). The half-occupied complex, namely (**PCA**)⊂**AzaEx²Cage**$^{6+}$ undergo concentration increase in the beginning of the titration, followed by decrease in concentration (red trace).

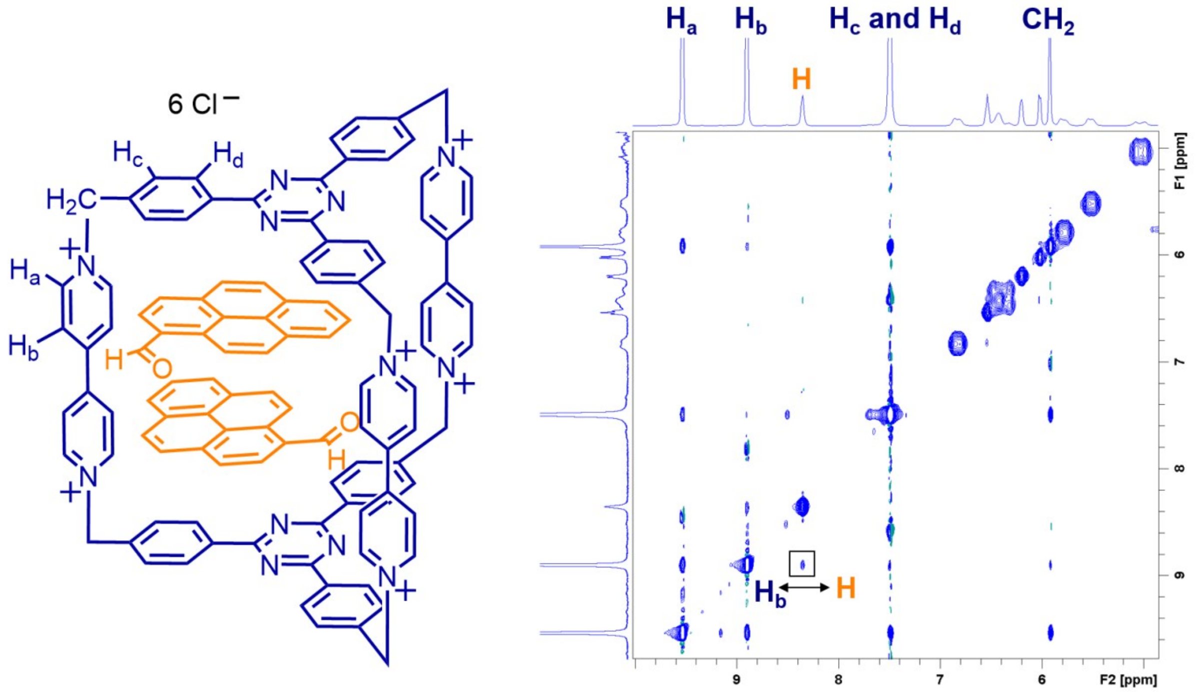


Figure S21. 2D NOESY spectrum (298 K, 500 MHz) of (**PCA**)$_2$ ⊂ **AzaEx^{2}Cage**·6Cl in D_2O. A NOESY cross-peak between the formyl proton in the guest and H_b in the host was observed and labeled in the spectrum.

2) Binding behavior between pyrene and **AzaEx^{2}Cage**·6PF$_6$

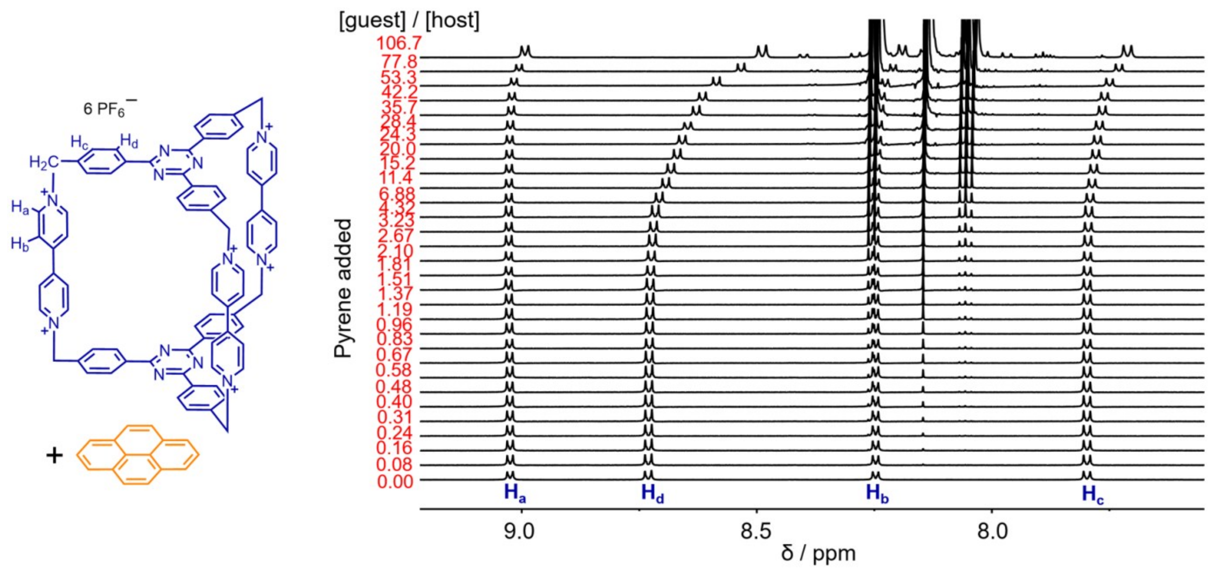


Figure S22. ^{1}H NMR spectra (500 MHz, 298 K) of **AzaEx^{2}Cage•**6PF$_6$ (0.49 × 10^{-3} M) in CD_3CN after adding different amount (from 0 to 107 equiv) of pyrene relative to **AzaEx^{2}Cage•**6PF$_6$. These spectra demonstrate that addition of pyrene leads to upfield shifts of the resonances of protons H_c and H_d in the phenyl residues of the host, while the protons H_a and H_b undergo very little shift, indicating that pyrene guest prefers to interact with the platforms of the cage.

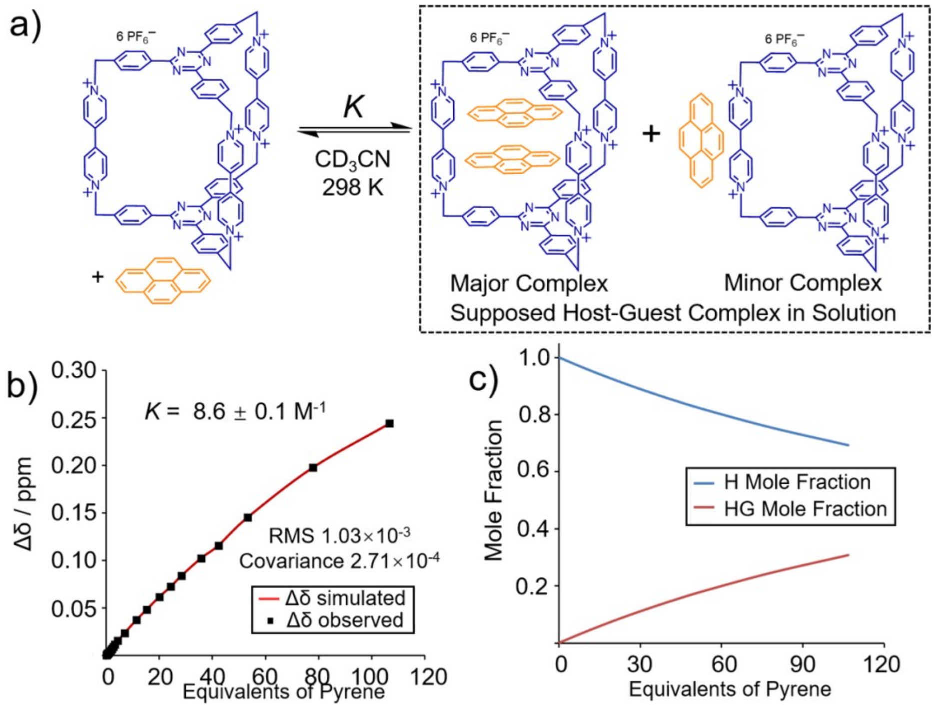


Figure S23. a) The binding behavior between **AzaEx²Cage•**6PF$_6$ and pyrene. b) Observed (dot) and calculated (red trace) binding curves of the upfield shifts of the resonance of proton H$_d$ in **AzaEx²Cage•**6PF$_6$ versus [pyrene]/[**AzaEx²Cage•**6PF$_6$]. By using a 1:1 binding model, the binding constant could be determined. c) Mole fraction based on the fitting results indicating that the concentration of the "free" host **AzaEx²Cage**$^{6+}$ undergoes continuous decrease (blue trace), while the concentration of complexes including either (pyrene)$_2$⊂**AzaEx²Cage**$^{6+}$ or pyrene⊂**AzaEx²Cage**$^{6+}$ undergoes continuous increase (red trace).

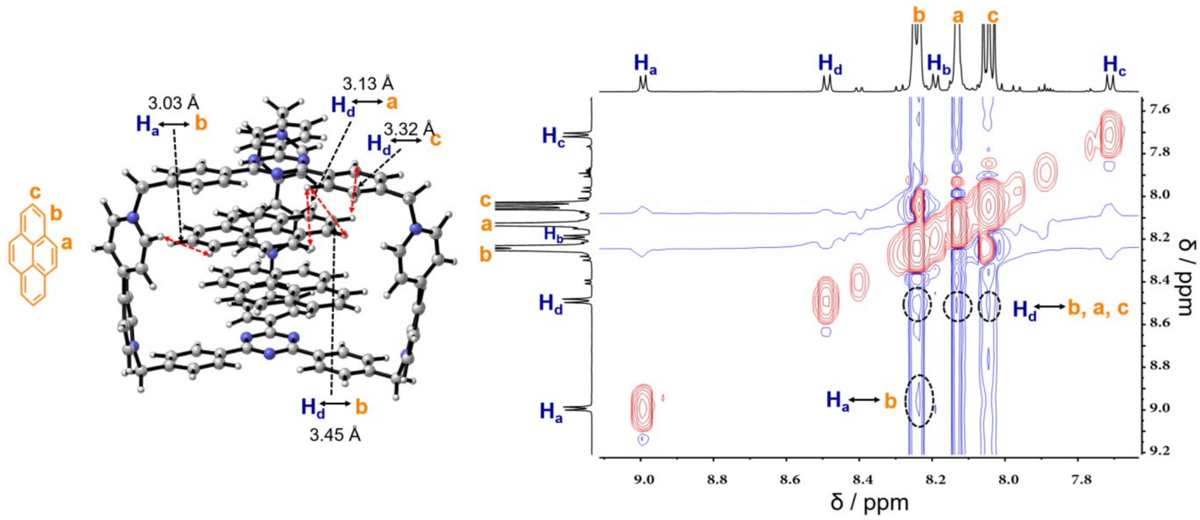


Figure S24. 2D NOESY spectrum (298 K, 500 MHz) of **AzaEx²Cage**·6PF$_6$ (0.49× 10^{-3} M) in CD$_3$CN after adding 107 equiv pyrene.

3) Binding behavior between **BH4EN** and **AzaEx²Cage**·$6PF_6$

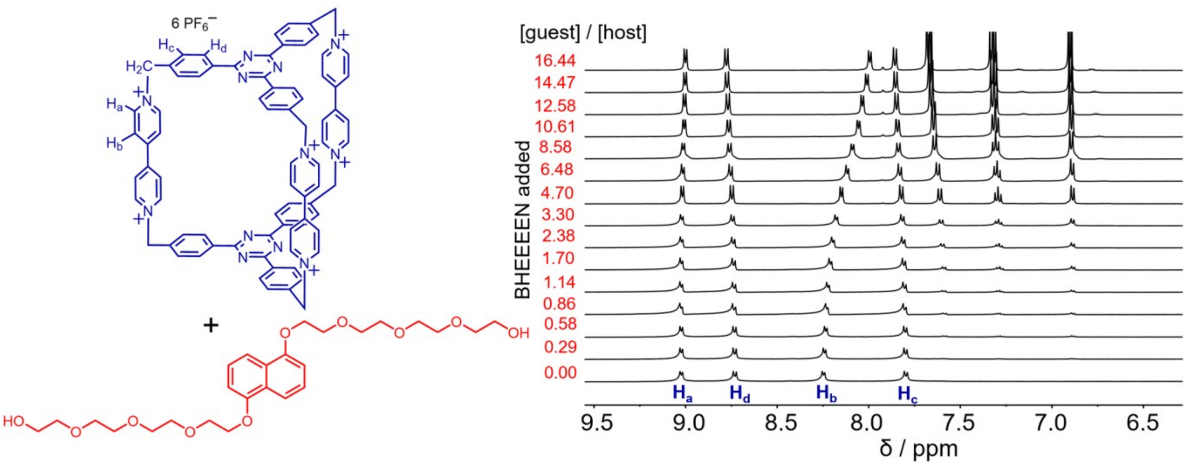


Figure S25. ^{1}H NMR spectra (500 MHz, 298 K) of **AzaEx²Cage•**$6PF_6$ (1.04×10^{-3} M) in CD_3CN after adding different amount (from 0 to 16 equiv) of **BH4EN** relative to **AzaEx²Cage•**$6PF_6$. These spectra demonstrate that addition of **BH4EN** leads to upfield shifts of the resonance of protons H_b in the pillars of the host, while the protons H_c and H_d undergo very little shift, indicating that **BH4EN** guest prefers to interact with the 4,4′-bipyridinium (**BIPY**$^{2+}$) pillars of the cage.

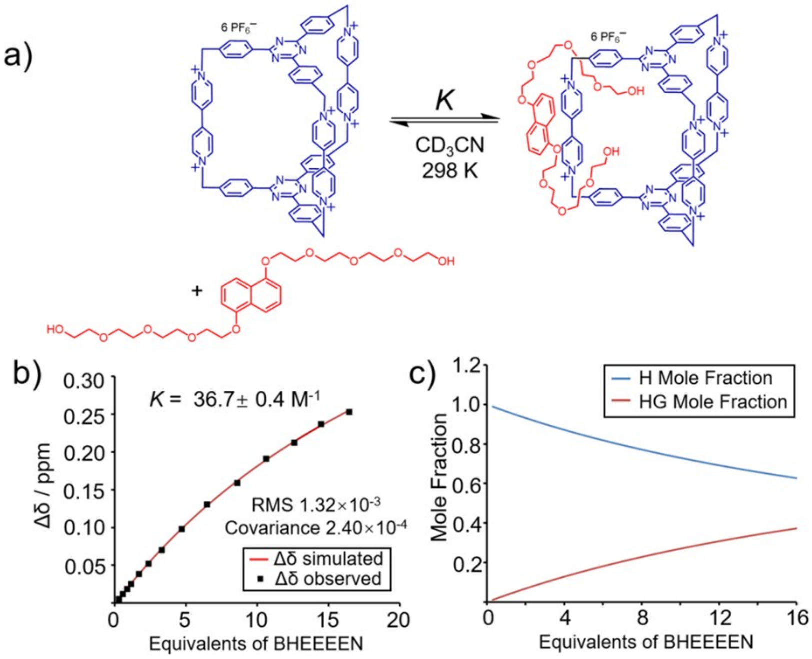


Figure S26. a) The binding behavior between **AzaEx²Cage•**$6PF_6$ and **BH4EN**.
b) Observed (dot) and calculated (red trace) binding curves of the upfield shifts of the resonance of proton H_b in **AzaEx²Cage•**$6PF_6$ versus [**BH4EN**] / [**AzaEx²Cage•**$6PF_6$]. By using a 1:1 binding model, the binding constant could be determined. c) Mole fraction based on the fitting results indicating that the concentration of the "free" host **AzaEx²Cage**$^{6+}$ undergoes continuous decrease (blue trace), while the concentration of complex undergoes continuous increase (red trace).

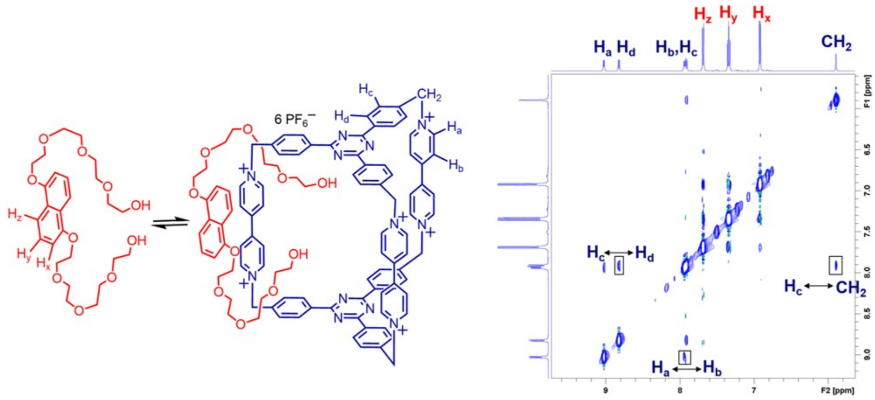


Figure S27. 2D NOESY spectrum (298 K, 500 MHz) of **BH4EN• AzaEx^{2}Cage**·6PF$_6$ in CD$_3$CN. NOESY cross-peaks between H$_c$ and H$_d$, H$_a$ and H$_b$, as well as H$_c$ and CH$_2$ were observed and labeled in the spectrum. However, no NOESY cross-peaks between host and guest were observed, indicating that the complexation might occur in a peripheral manner.

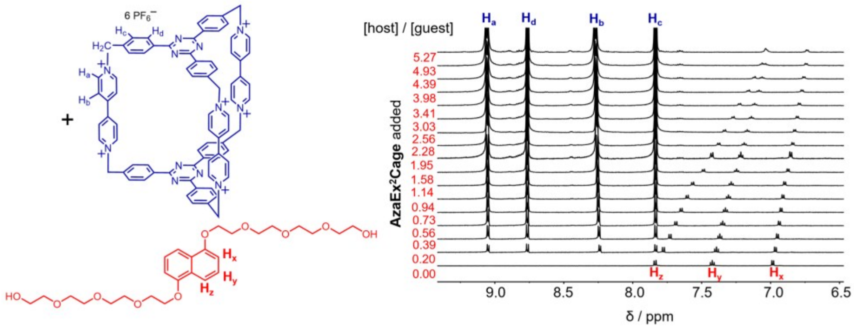


Figure S28. ^{1}H NMR spectra (500 MHz, 298 K) of **BH4EN** (1.13 × 10^{-3} M) in CD$_3$CN after adding different amount (from 0 to 6 equiv) of **AzaEx^{2}Cage•**6PF$_6$ relative to **BH4EN**.

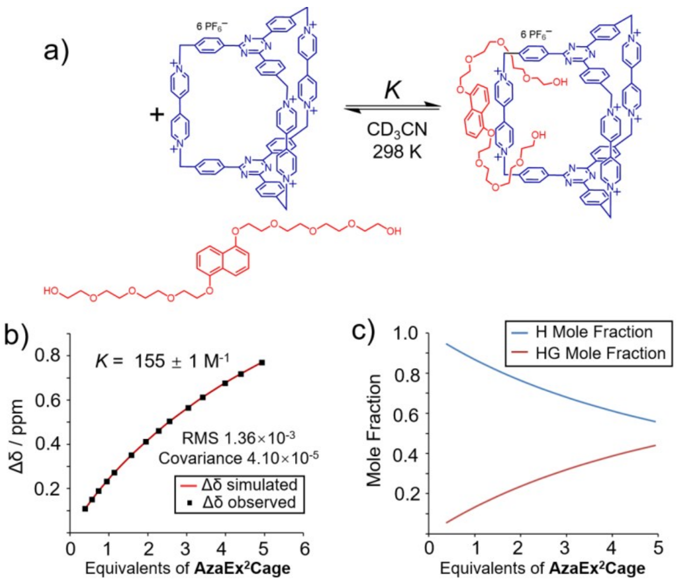


Figure S29. a) The binding behavior between **BH4EN** and **AzaEx^{2}Cage•**6PF$_6$.
b) Observed (dot) and calculated (red trace) binding curves of the upfield shifts of the resonance of proton H$_z$ in **BH4EN** versus [**BH4EN**] / [**AzaEx^{2}Cage•**6PF$_6$]. By using a

1:1 binding model, the binding constant could be determined. c) The curves of mole fractions of the **BH4EN** (blue trace) and the complex (red trace) versus the amount of cage **AzaEx²Cage•**6PF$_6$ added into the solution.

4) Binding behavior between **PCA** and **AzaEx²Cage**·6PF$_6$ in the presence of **BH4EN**.

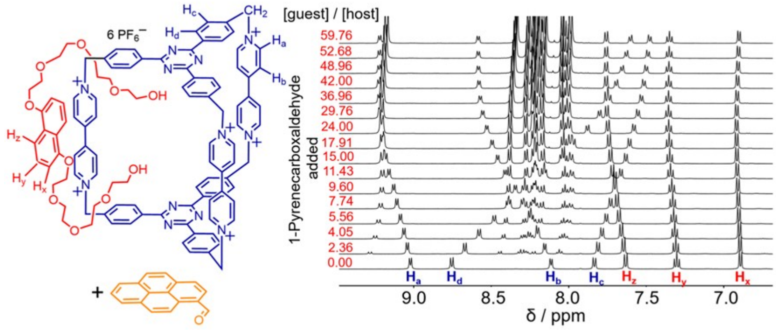


Figure S30. ^{1}H NMR spectra (500 MHz, 298 K) recorded after adding different amount of **PCA** (from 0 to 60 equiv relative to **AzaEx²Cage•**6PF$_6$) into **AzaEx²Cage•**6PF$_6$ (1.00 × 10^{-3} M) in the presence of **BH4EN** (7.81 × 10^{-3} M) in CD$_3$CN.

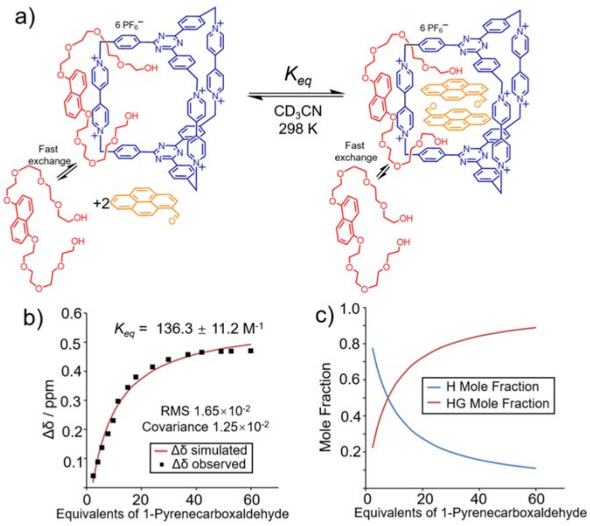


Figure S31. a) The binding behavior of a peripheral complex **BH4EN•AzaEx²Cage**·6PF$_6$ to accommodate two **PCA** guests. b) Observed (dot) and calculated (red trace) binding curves of the downfield shifts of the resonance of proton H$_b$ in **AzaEx²Cage•**6PF$_6$ versus [**PCA**]/[**AzaEx²Cage•**6PF$_6$] in the presence of 7.8 equiv **BH4EN** (relative to **AzaEx²Cage•**6PF$_6$). The trial to employ a 2:1 binding model to calculate the binding constants K_1 and K_2 is unsuccessful. By using a 1:1 binding model, the binding constants (136.3 ± 11.2 M^{-1}) could be determined, which is more or less the same as that of (**PCA**)$_2$⊂**AzaEx²Cage**$^{6+}$ complex calculated by using a 1:1 binding model. c) Mole fraction based on the fitting results indicating that the concentration of **BH4EN•AzaEx²Cage**·6PF$_6$ undergoes continuous decrease (blue trace), while the concentration of complex **BH4EN•**(**PCA**)$_2$ ⊂ **AzaEx²Cage**·6PF$_6$ undergoes continuous increase (red trace).

5) Binding behavior between **BH4EN** and **AzaEx²Cage**·$6PF_6$ with **PCA**.

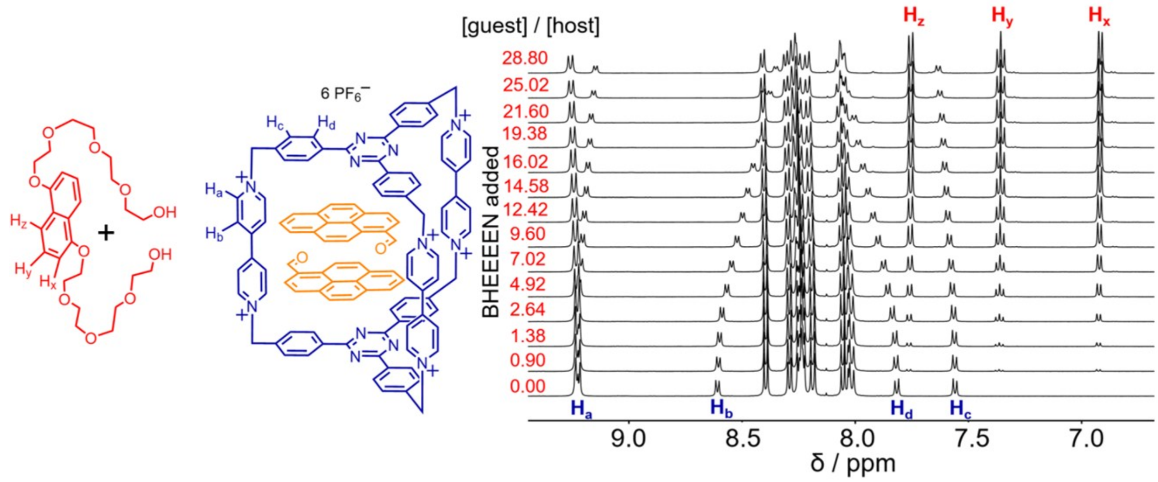


Figure S32. [1]H NMR spectra (500 MHz, 298 K) recorded after adding different amount of **BH4EN** (from 0 to 29 equiv relative to **AzaEx²Cage•**$6PF_6$) into **AzaEx²Cage•**$6PF_6$ (0.83×10^{-3} M) in the presence of **PCA** (2.21×10^{-2} M) in CD_3CN.

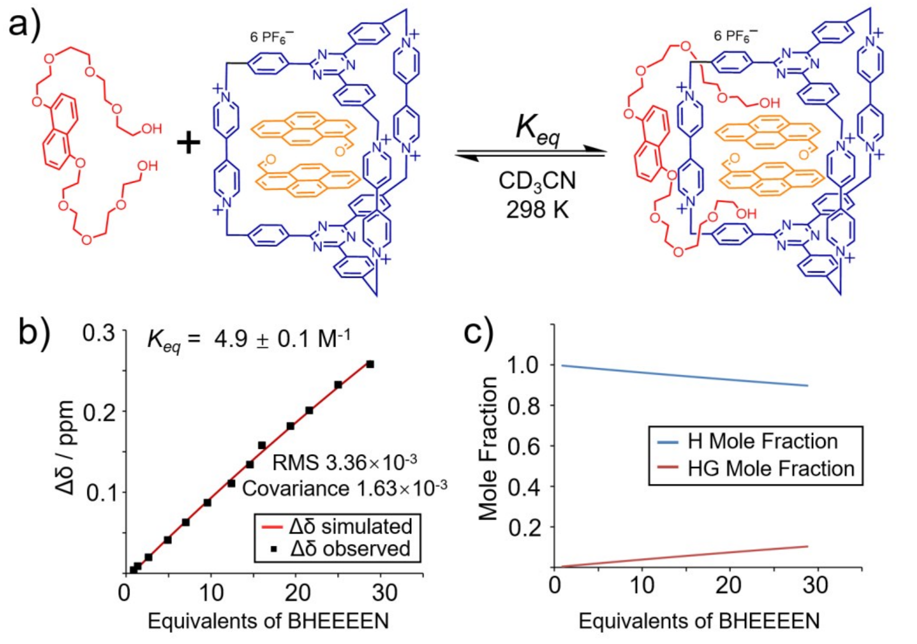


Figure S33. a) The binding behavior of an inclusion complex $(\mathbf{PCA})_2 \subset$ **AzaEx²Cage**·$6PF_6$ to bind **BH4EN** in a peripheral manner. b) Observed (dot) and calculated (red trace) binding curves of the upfield shifts of the resonance of proton H_b in **AzaEx²Cage•**$6PF_6$ versus [**BH4EN**]/[**AzaEx²Cage•**$6PF_6$] in the presence of 26.6 equiv **PCA** (relative to **AzaEx²Cage•**$6PF_6$). By using a 1:1 binding model, the binding constants could be determined. c) Mole fraction based on the fitting results indicating that the concentration of $(\mathbf{PCA})_2\subset$**AzaEx²Cage**·$6PF_6$ undergoes continuous decrease (blue trace), while the concentration of complex **BH4EN•**$(\mathbf{PCA})_2\subset$**AzaEx²Cage**·$6PF_6$ undergoes continuous increase (red trace).

6) Binding behavior between **BH4EN** and **MV**·$2PF_6$

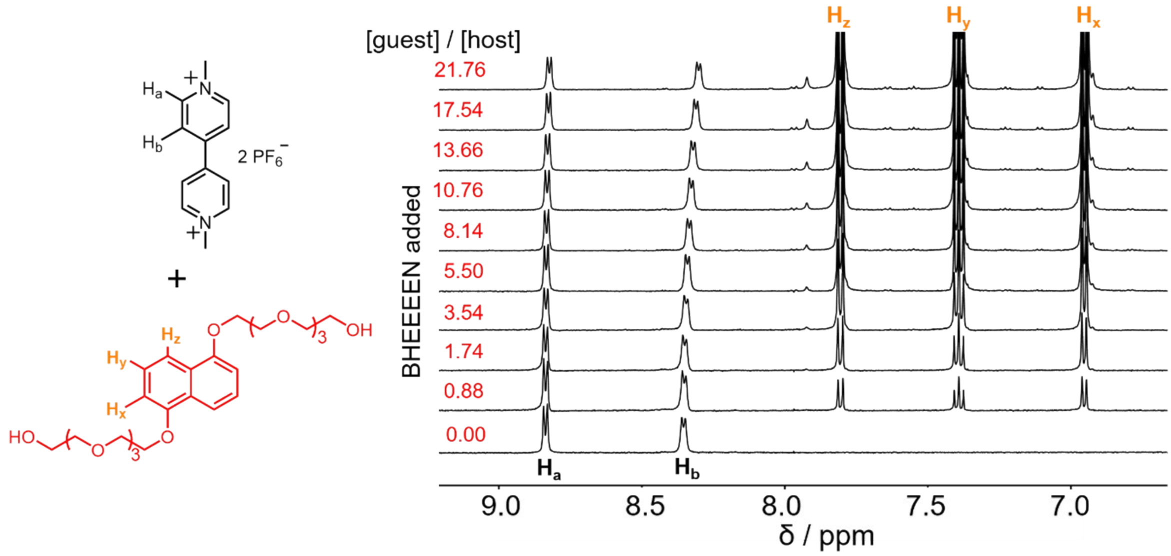


Figure S34. [1]H NMR spectra (500 MHz, 298 K) recorded after adding different amount of **BH4EN** (from 0 to 22 equiv relative to **MV•**$2PF_6$) into **MV•**$2PF_6$ (6.19×10^{-3} M) in CD_3CN.

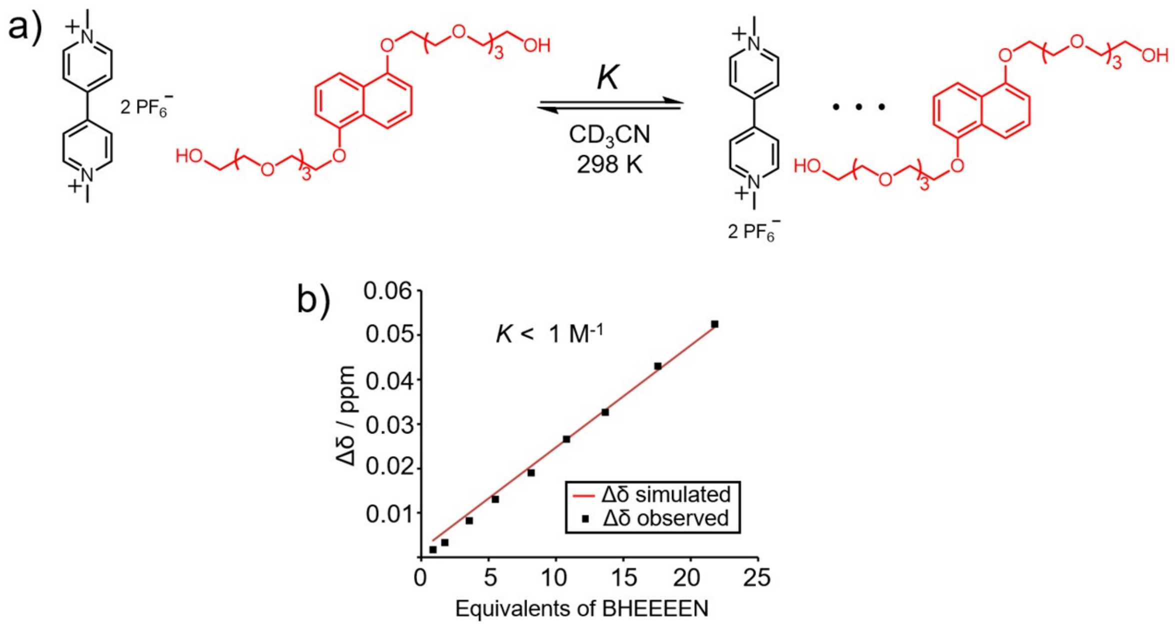


Figure S35. a) The binding behavior between **MV•**$2PF_6$ and **BH4EN**. b) Observed (dot) and calculated (red trace) binding curves of the upfield shifts of the resonance of proton H_b in **MV•**$2PF_6$ versus [**BH4EN**]/[**MV•**$2PF_6$]. By using a 1:1 binding model, the binding constants could be determined. This binding constant is lower than that of **BH4EN⊂AzaEx²Cage**·$6PF_6$, indicating that cage cavity could help to stabilize the supramolecular complexation.

5. Cyclic Voltammetry (CV) Analysis and UV-Vis-NIR Absorption spectrum of AzaEx²Cage·$6PF_6$.

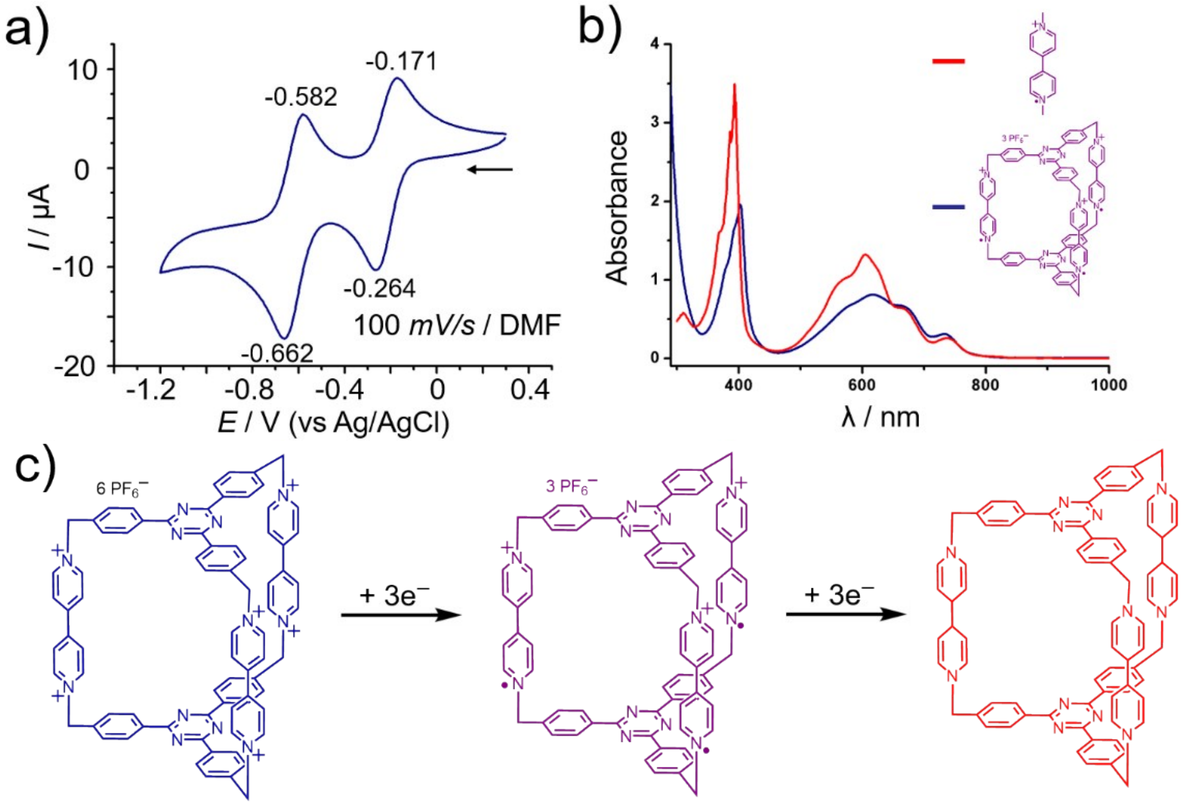


Figure S36. a) Cyclic voltammetry (CV) of **AzaEx²Cage•**$6PF_6$ (0.5 mM, DMF, 298 K) shows two three-electron redox processes, which correspond to the reduction of the **BIPY**$^{2+}$ pillars in the **AzaEx²Cage•**$6PF_6$. A glassy carbon working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode were used in the CV experiment, in which 0.1 M $TBAPF_6$ was used as the electrolyte. The scan rate is 100 mV s^{-1}. b) UV-Vis-NIR absorption spectrum of **AzaEx²Cage**$^{3(+\bullet)}$ (1.5×10^{-4} M^{-1}) recorded in MeCN at 298 K. The solution containing **AzaEx²Cage**$^{3(+\bullet)}$ was produced by adding Zn dust into a solution of **AzaEx²Cage•**$6PF_6$ in MeCN. The UV-Vis-NIR absorption spectrum (blue trace) is essentially the same as that of methyl-viologen (red trace). c) The schematic representation of the two-step reduction process of **AzaEx²Cage•**$6PF_6$.

6. X-ray Crystallography

1) AzaEx^{2}Cage•6CF_3CO_2

1.1) Methods

Single crystals of **AzaEx^{2}Cage**•6CF_3CO_2 were grown at room temperature by slow vapor diffusion of *i*Pr_2O into a solution of **AzaEx^{2}Cage**•6CF_3CO_2 in MeCN (2.0 mM). A suitable crystal was selected and was mounted on a MITIGEN holder in Paratone oil on a Bruker Kappa APEX CCD area detector diffractometer. Data collection was performed at 100 K. The structure was solved using Olex2[3] with the ShelXT[4] structure solution program relying on Intrinsic Phasing. Crystal structure refinement was performed by using a ShelXL[5] refinement package relying on Least Squares minimization.

1.2) Crystal data

$C_{39}H_{30}N_6$•$(C_2F_3O_2)_3$, M = 921.75, monoclinic, space group *P21/m* (no. 11), a = 13.6264(5) Å, b = 30.4112(12) Å, c = 14.0126(5) Å, β = 100.631(2)°, V = 5707.1(4) Å^3, Z = 4, T = 100 K, μ(CuKα) = 0.800 mm^{-1}, *Dcalc* = 1.073 g/mm^3, 30865 reflections measured (5.812 ≤ 2Θ ≤ 127.63), 9551 unique (R_{int} = 0.0274, R_{sigma} = 0.0266) which were used in all calculations. The final R_1 was 0.1063 (I > 2σ(I)) and wR_2 was 0.3680 (all data). CCDC number: 1858887

Distance restraints were imposed on the disordered anions as well as restraints on similar amplitudes separated by less than 1.7 Å. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 1871.5 Å^3 [32.7%] Total electron count / cell = 388.9.

1.3) Solid-state (super) structures

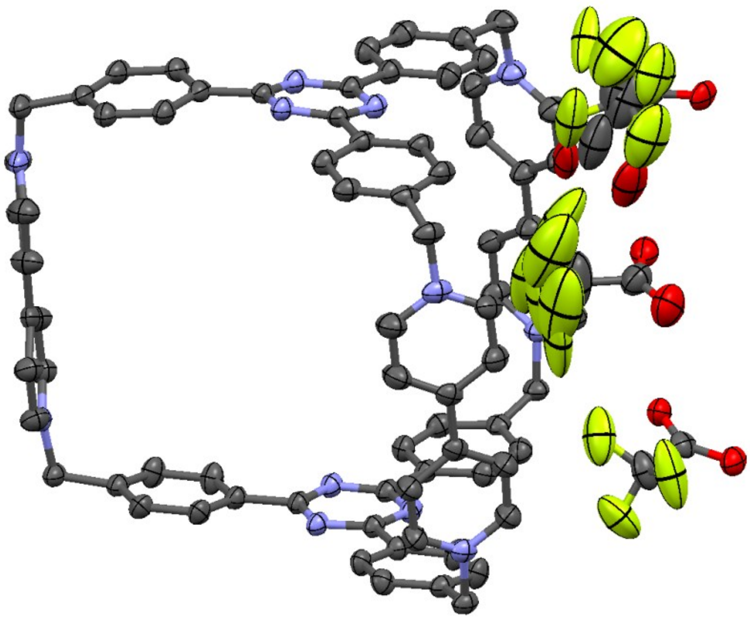


Figure S37. Thermal ellipsoids (50% probability) plot of **AzaEx^{2}Cage•**6CF_3CO_2.

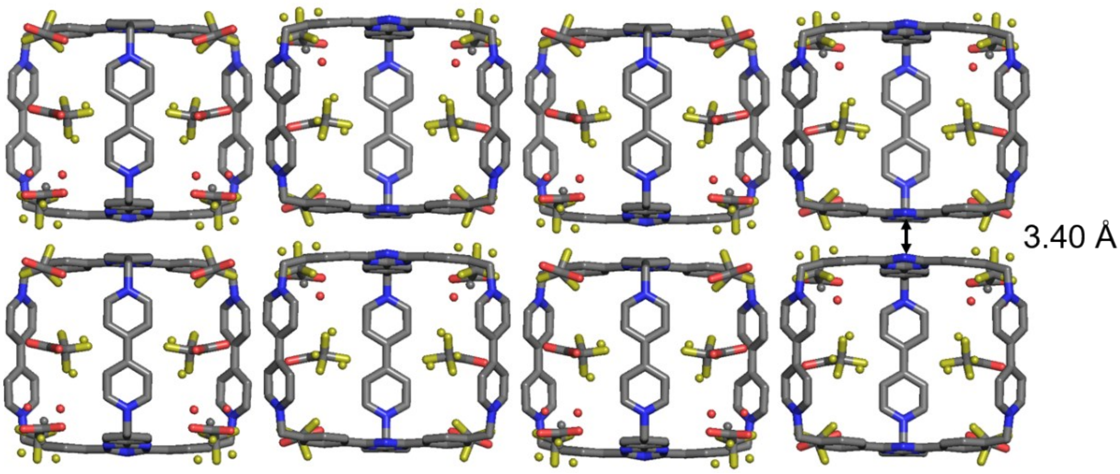


Figure S38. Side-on view along ***a*** axis of the long range packing of **AzaEx^{2}Cage•**6CF_3CO_2.

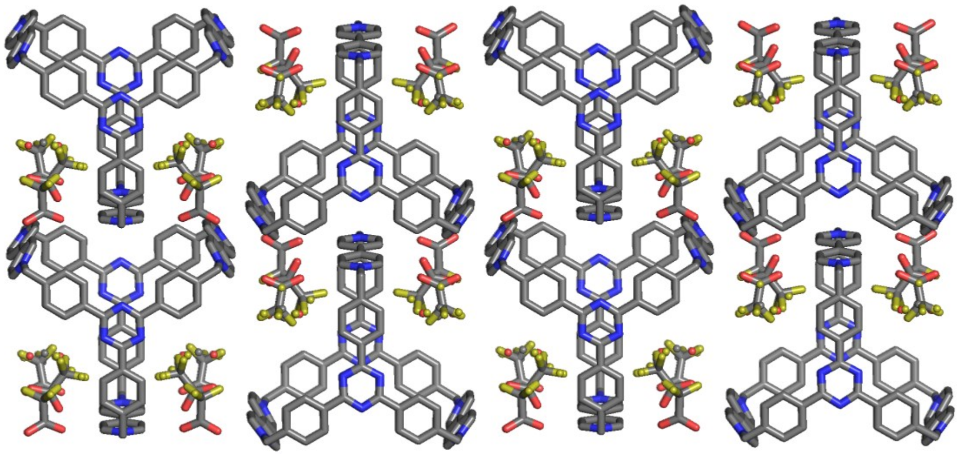


Figure S39. Side-on view along ***c*** axis of the long range packing of **AzaEx²Cage**•6CF_3CO_2.

2) AzaEx²Cage•6PF_6

2.1) Methods

Single crystals of **AzaEx²Cage**•6PF_6 were grown at 4 °C by slow vapor diffusion of *i*Pr_2O into a solution of **AzaEx²Cage**•6PF_6 in MeCN (2.0 mM). A suitable crystal was selected and was mounted on a MITIGEN holder in Paratone oil on a Kappa APEX 2 diffractometer. The crystal was kept at 100 K during data collection. The structure was solved using Olex2[3] with the ShelXT[4] structure solution program relying on Intrinsic Phasing. Crystal structure refinement was performed by using a ShelXL[5] refinement package relying on Least Squares minimization.

2.2) Crystal data

$C_{78}H_{60}N_{12}$•$(PF_6)_6$•$(C_2H_3N)_4$, M = 2199.41, triclinic, space group P (no.2), a = 13.9020(14) Å, b = 19.595(2) Å, c = 25.262(2) Å, α = 83.509(8)°, β = 84.344(8)°, γ = 85.297(8)°, V = 6786.9(12) Å^3, Z = 2, T = 100 K, μ(CuKα) = 1.525 mm^{-1}, $Dcalc$ = 1.076 g/mm^3, 13490 reflections measured (3.534 ≤ 2Θ ≤ 101.668), 13490 unique (R_{int} = ?, R_{sigma} = 0.1522) which were used in all calculations. The final R_1 was 0.2253 (I > 2σ(I)) and wR_2 was 0.5309 (all data). CCDC number: 1858888

The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied globally, as well as restraints on similar amplitudes separated by less than 1.7 Å. An ISOR restraint was imposed on N6 so that it would make it more isotropic. The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, and the data were processed using both orientation matrices with SAINT, the exact twin matrix identified by the integration program was found to be (–1.00035 0.00350 –0.00026 / –0.19461 1.00018 –0.16596 / 0.00008 –0.00192 –0.99983). The second domain is rotated from first domain by 180° about the real lattice b axis. The absorption correction was carried out using TWINABS V2008/4 to create an hklf5 file which was used in all refinements; the structure was solved using direct methods with only the non-overlapping reflections of component 1. The twin fraction refined to a value of 0.310(4). Diffuse, disordered solvent molecules could not be adequately modeled. The bypass procedure in Platon was used to remove the electronic contribution from these solvents. The total potential solvent accessible void volume was 2524 Å^3 and the electron count / cell = 807. As the exact solvent content is not known, the reported formula reflects only the atoms used in the refinement.

2.3) Solid-state (super) structures

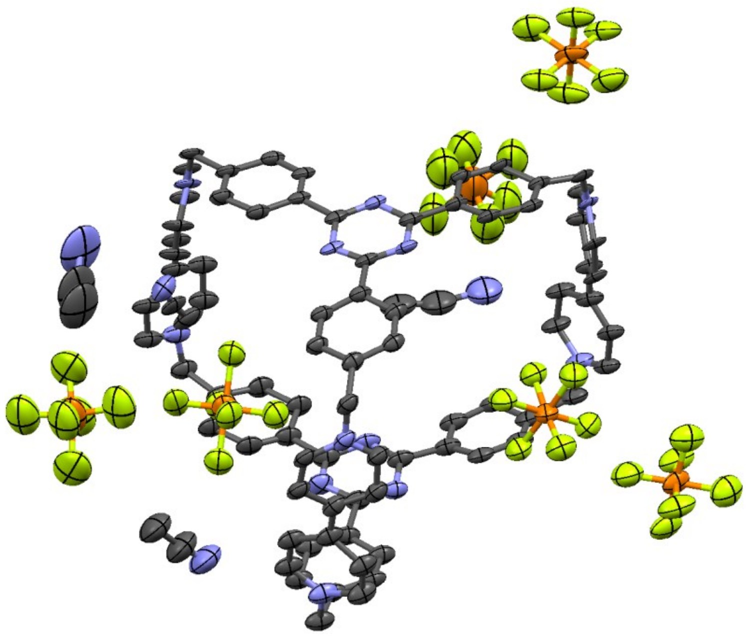


Figure S40. Thermal ellipsoids (50% probability) plot of **AzaEx^{2}Cage•**6PF_6.

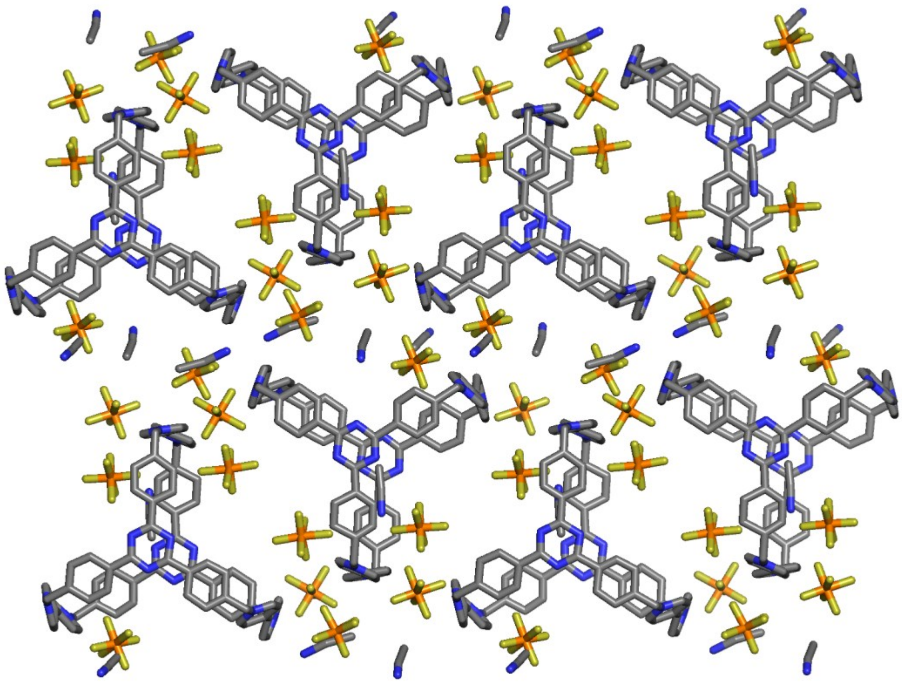


Figure S41. Side-on view along ***c*** axis of the long range packing of **AzaEx²Cage**·$6PF_6$.

3) (PCA)$_2$ ⊂ AzaEx²Cage·$6PF_6$

3.1) Methods

Solid **PCA** (1.0 mg, 1.6 µmol) was added to a solution of **AzaEx²Cage**•$6PF_6$ in MeCN (2.0 mM, 0.75 mL). After dissolving, the mixture was passed through a 0.45 µm filter and split equally into three 1 mL tubes. The tubes were placed together in one 20 mL vial containing *i*Pr_2O (~3 mL) and the vial was capped. Slow vapor diffusion of *i*Pr_2O into the solution of 1-pyrenecarboxaldehyde and **AzaEx²Cage**•$6PF_6$ in MeCN at 4 °C over the period of 3 d yielded yellow single crystals of (**PCA**)$_2$ ⊂ **AzaEx²Cage**•$6PF_6$. A suitable crystal was selected and was mounted on a MITIGEN holder in Paratone oil on a Bruker Kappa APEX CCD area detector diffractometer. The crystal was kept at 100 K during data collection. The structure was solved using Olex2[3] with the XM[6] structure solution program using Dual Space and refined with the XL[6] refinement package using Least Squares minimization.

3.2) Crystal data

$C_{78}H_{60}N_{12}$•$(C_{17}H_{10}O)_2$•$(PF_6)_{5.5}$•$(C_2H_3N)_1$•$(Br)_{0.5}$, M = 2504.22, orthorhombic, space group *Pnma* (no. 62), a = 27.3248(15) Å, b = 42.161(3) Å, c = 24.1600(16) Å, V = 27834(3) Å^3, Z = 8, T = 100 K, μ(CuKα) = 1.634 mm^{-1}, $Dcalc$ = 1.195 g/mm^3, 34207 reflections measured (5.314 ≤ 2Θ ≤ 100.866), 14398 unique (R_{int} = 0.1356, R_{sigma} = 0.1648) which were used in all calculations. The final R_1 was 0.1608 (I > 2σ(I)) and wR_2 was 0.4438 (all data). CCDC number: 1858889

Distance restraints were imposed on the **PCA** guest molecule. Rigid bond restraints were imposed on the displacement parameters as well as restraints on similar amplitudes separated by less than 1.7 Å. on the guest molecules. The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied on the cage. The guest molecules were restrained esd that their Uij components approximate to isotropic. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 7066.1 Å^3 [25.4%] Total electron count / cell = 1815.8.

3.3) Solid-state (super) structures

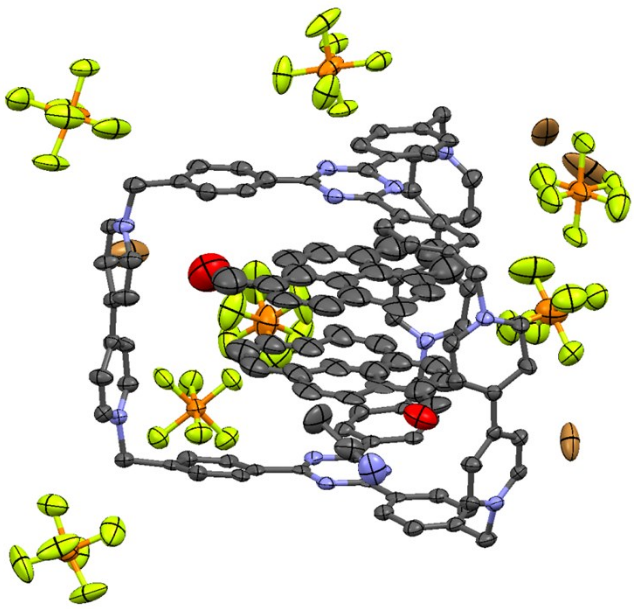


Figure S42. Thermal ellipsoids (30% probability) plot of (**PCA**)$_2$⊂**AzaEx^{2}Cage**•6PF$_6$.

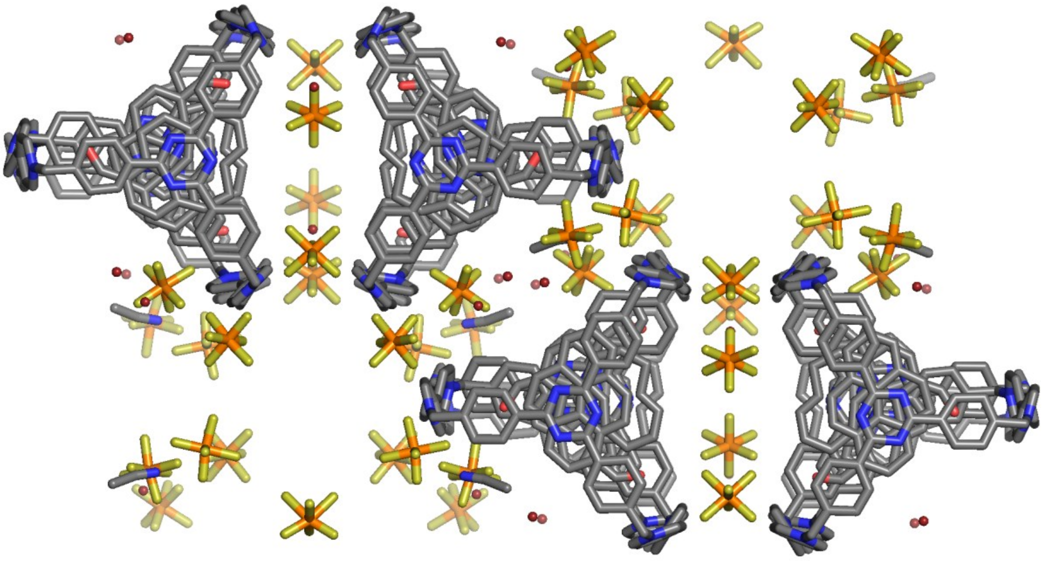


Figure S43. Side-on view along ***a*** axis of the long range packing of (**PCA**)$_2$ ⊂ **AzaEx^{2}Cage**•6PF$_6$.

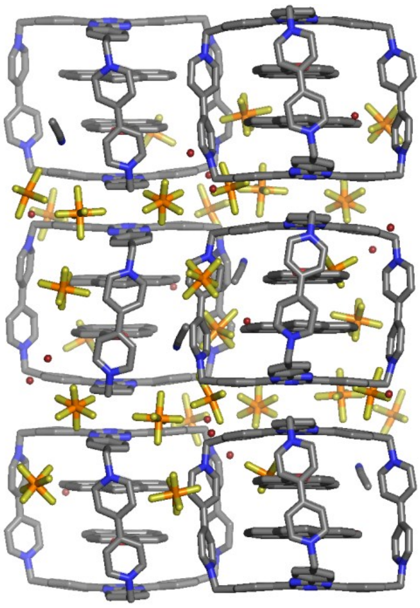


Figure S44. Side-on view along ***b*** axis of the long range packing of (**PCA**)$_2$ ⊂ **AzaEx^{2}Cage**·6PF$_6$.

4) BH4EN•AzaEx^{2}Cage·6PF$_6$

4.1) Methods

Single crystals of **BH4EN•AzaEx^{2}Cage**·6PF$_6$ were grown at room temperature by slow vapor diffusion of *i*Pr$_2$O into a 4:1 solution of **BH4EN** and **AzaEx^{2}Cage**·6PF$_6$ in MeCN (2.0 mM). A suitable crystal was selected and the crystal was mounted on a MITIGEN holder in

Paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 170 K during data collection. The structure was solved using Olex2[3] with the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXL[5] refinement package using Least Squares minimization.

4.2) Crystal data

$C_{78}H_{60}N_{12}\cdot(C_{26}H_{40}O_{10})_{0.5}\cdot(PF_6)_6\cdot(C_2H_3N)_4$, M = 2455.70, triclinic, space group *P (no. 2)*, a = 13.6331(5) Å, b = 20.6544(8) Å, c = 24.9241(10) Å, α = *72.715(3)°*, β = *85.475(3)°*, γ = *81.308(2)°*, V = 6620.0(5) Å^3, Z = 2, T = 170 K, μ(GaKα) = 1.060 mm^{-1}, *Dcalc* = 1.232 g/mm^3, 81234 reflections measured ($6.46 \leq 2\Theta \leq 109.932$), 25036 unique ($R_{int}$ = 0.0681, R_{sigma} = 0.0728) which were used in all calculations. The final R_1 was 0.1278 (I > 2σ(I)) and wR_2 was 0.4100 (all data). CCDC number: 1858890

Distance restraints were imposed on the guest molecule. The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied on O4, O5, C85 and C84. The contributions to the scattering factors due to disordered solvent molecules were removed by use of the utility SQUEEZE in PLATON.

4.3) Solid-state (super) structures

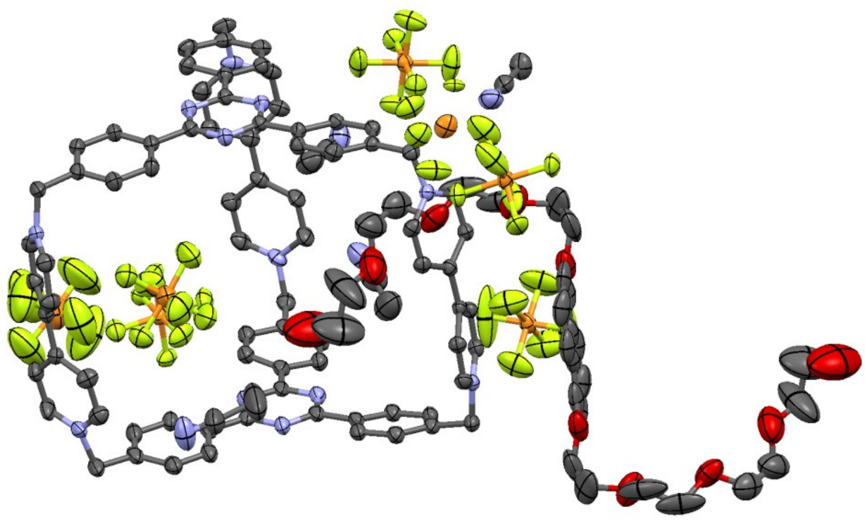


Figure S45. Thermal ellipsoids (30% probability) plot of **BH4EN•AzaEx^{2}Cage**•$6PF_6$.

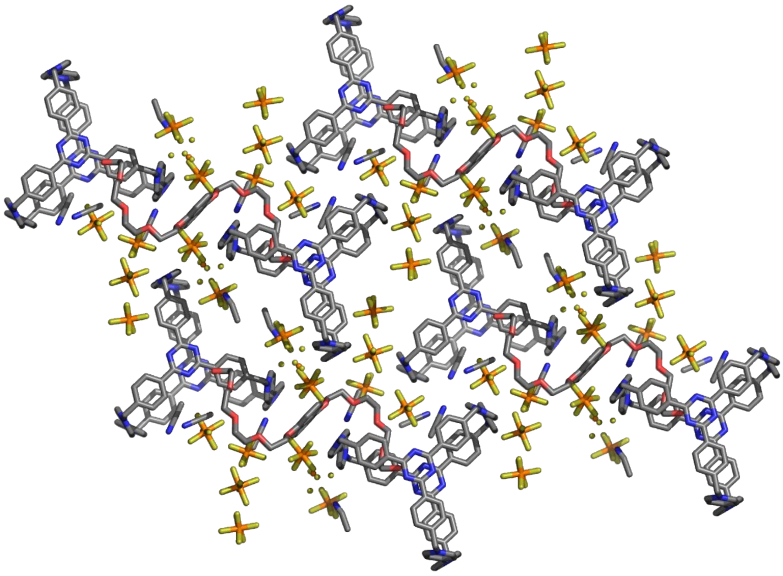


Figure S46. Side-on view along ***a*** axis of the long range packing of **BH4EN•AzaEx²Cage•**$6PF_6$.

5) BH4EN·(PCA)$_2$⊂AzaEx²Cage·$6PF_6$

5.1) Methods

Single crystals of **BH4EN·(PCA)$_2$⊂AzaEx²Cage**·$6PF_6$ were grown at room temperature by slow vapor diffusion of *i*Pr_2O into a 10:4:1 solution of **PCA**, **BH4EN** and **AzaEx²Cage**·$6PF_6$ in MeCN (2.0 mM). A suitable crystal was selected and the crystal was mounted on a MITIGEN holder in Paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 170 K during data collection. The structure was solved using Olex2[3] with the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXL[5] refinement package using Least Squares minimization.

5.2) Crystal data

$C_{78}H_{60}N_{12}\cdot(C_{17}H_{10}O)_3\cdot(C_{26}H_{40}O_{10})_{0.5}\cdot(PF_6)_6\cdot(C_2H_3N)_1\cdot(H_2O)_1$, M = 3041.30, triclinic, space group *P (no. 2)*, a = 13.9039(5) Å, b = 22.9522(9) Å, c = 23.8176(9) Å, α = *82.666(2)°*, β = *84.915(2)°*, γ = *85.037(2)°*, V = 7487.2(5) Å^3, Z = 2, T = 170 K, μ(GaKα) = 1.019 mm^{-1}, *Dcalc* = 1.349 g/mm^3, 81897 reflections measured (5.568 ≤ 2Θ ≤ 93.606), 20061 unique (R_{int} = 0.0646, R_{sigma} = 0.0653) which were used in all calculations. The final R_1 was 0.1575 (I >

2σ(I)) and wR_2 was 0.4621 (all data). CCDC number: 1858892

Distance restraints were imposed on the **PCA** guest molecule. The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied on the **PCA** and **BH4EN**. The guest molecules were restrained esd that their Uij components approximate to isotropic. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement.

5.3) Solid-state (super) structures

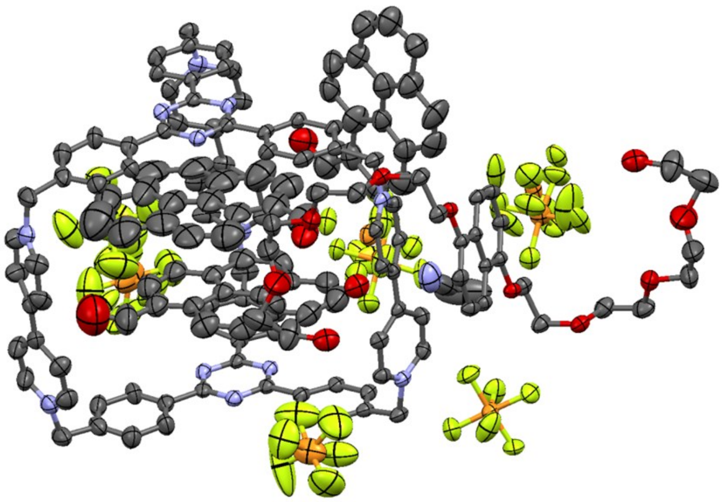


Figure S47. Thermal ellipsoids (30% probability) plot of **BH4EN · (PCA)**$_2$ ⊂ **AzaEx²Cage**·6PF$_6$.

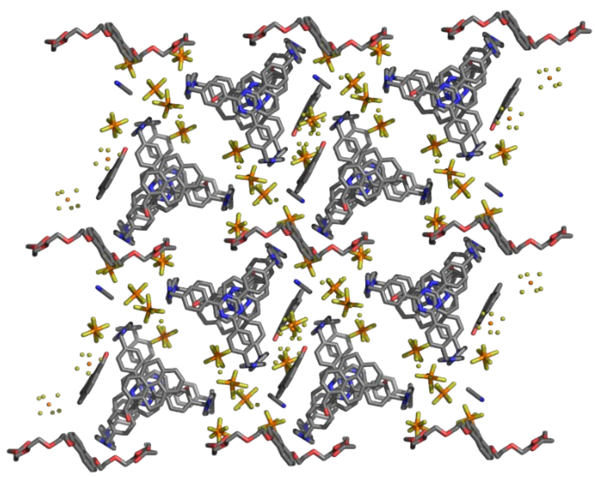


Figure S48. Side-on view along ***a*** axis of the long range packing of **BH4EN·(PCA)**$_2$**⊂AzaEx²Cage**·6PF$_6$.

6. Computational Analysis

6.1) Methods

All density functional theory (DFT) calculations were performed with Gaussian 09.[7] Geometry optimization of all the structures was carried out at the M06-2X level of theory[8,9] with 6-31G(d) basis set.[10] The vibrational frequencies of the optimized stationary points are calculated under the same level of theory, to obtain the zero-point vibrational energy (ZPVE) and thermal corrections at 298 K as well as verifying whether each of optimized stationary points is an energy minimum. The single-point energies and solvent effects in acetonitrile were computed at M06-2X level of theory with 6-311++G(d,p) basis set[10] for all the atoms, based on the gas-phase optimized structures. Solvation energies were evaluated by a self-consistent reaction field (SCRF) using the SMD model.[11] The reduced density gradient (RDG)[12] figure of (PCA)$_2$⊂**AzaEx**^{2}**Cage**$^{6+}$ was calculated by using the Multiwfn software[13] based on the DFT-optimized structure, and visualized by the Visual Molecular Dynamics (VMD) software.[14] The 3D diagrams of molecules were generated by using CYLView.[15]

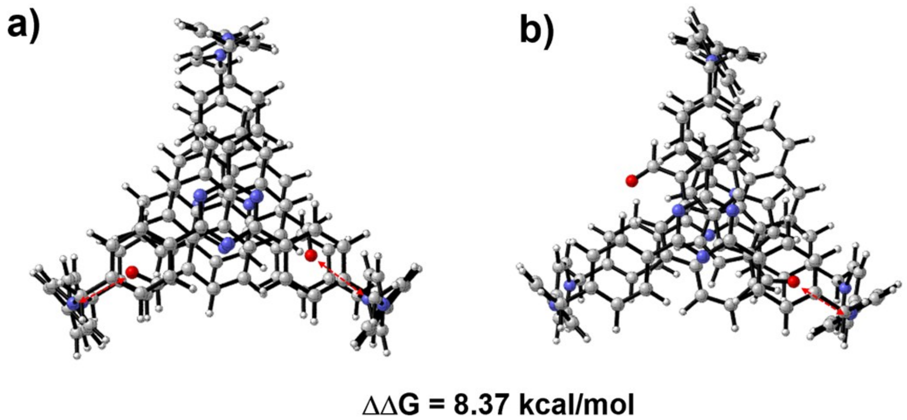


Figure S49. The DFT-optimized structure of a) (**PCA**)$_2$⊂**AzaEx**^{2}**Cage**$^{6+}$ with a conformation which is based on the single-crystal X-ray diffaction results, and b) a conformation in which the **PCA** guest undergoes a rotation by 60°, after which the carbonyl function of the guest is located in the middle between the two viologen pillars. DFT calculations indicate that the former conformation is more stable than the latter one by 8.37 kcal/mol, indicating the importance of the cation-dipole interactions.

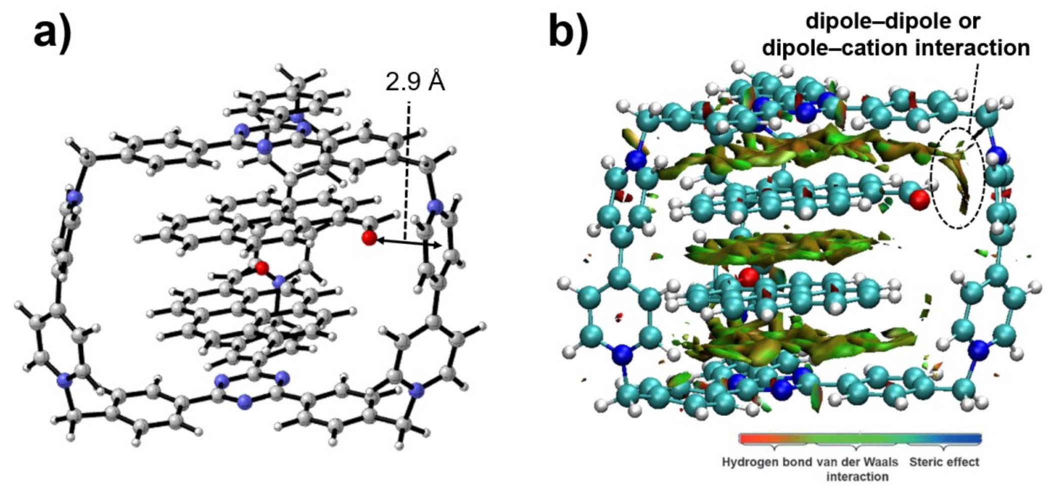


Figure S50. a) The DFT-optimized structure of (**PCA**)$_2$⊂**AzaEx^{2}Cage^{6+}**. b) Reduced density gradient (RDG) figure of (**PCA**)$_2$⊂**AzaEx^{2}Cage^{6+}**.

6.2) Detailed Computed Energies (in Hartees) of Optimized Structures

Structure	pyrene	**PCA**	**AzaEx^{2}Cage^{6+}**	(pyrene)$_2$⊂ **AzaEx^{2}Cage^{6+}**	**(PCA)$_2$⊂AzaEx^{2}Cage^{6+}**	**BH4EN• AzaEx^{2}Cage^{6+}**
ZPE	0.209262	0.219288	1.234570	1.655143	1.676172	1.901352
ΔE	0.219249	0.231263	1.302109	1.745138	1.769648	2.006777
ΔH	0.220193	0.232207	1.303053	1.746082	1.770592	2.007721
ΔG	0.174001	0.181361	1.126309	1.528369	1.547935	1.749909
E_{MeCN}	-615.459841	-728.766161	-3662.822653	-4893.798166	-5120.420894	-5428.957058
H_{MeCN}	-615.458897	-728.765217	-3662.821709	-4893.797222	-5120.419950	-5428.956114
G_{MeCN}	-615.505089	-728.816063	-3662.998453	-4894.014935	-5120.642607	-5429.213926
Imaginary Frequency (cm^{-1})	-	-	-	-	-	-

Table S1. Energies, enthalpies, and free energies (in Hartrees) of optimized structures calculated at the M06-2X/6-311++G(d,p), SMD(MeCN)//M06-2X/6-31G(d) level of theory.

6.3) Summary of Natural Population Analysis

AzaEx^{2}Cage^{6+}

Natural Population
Natural --------------------------------------

Atom No Charge Core Valence Rydberg Total

C 1 0.49034 1.99920 3.47777 0.03270 5.50966
C 2 -0.10338 1.99883 4.08546 0.01910 6.10338
N 3 -0.54681 1.99934 5.52626 0.02121 7.54681
C 4 -0.15879 1.99897 4.14395 0.01587 6.15879
C 5 -0.15903 1.99897 4.14439 0.01566 6.15903

N 6 -0.54692 1.99934 5.52638 0.02120 7.54692
C 7 0.48999 1.99920 3.47815 0.03266 5.51001
C 8 -0.20586 1.99912 4.18906 0.01768 6.20586
H 9 0.24463 0.00000 0.75364 0.00173 0.75537
C 10 -0.20320 1.99912 4.18649 0.01759 6.20320
H 11 0.24391 0.00000 0.75435 0.00175 0.75609
C 12 0.49035 1.99920 3.47779 0.03266 5.50965
C 13 -0.10495 1.99883 4.08707 0.01906 6.10495
N 14 -0.54658 1.99934 5.52599 0.02125 7.54658
C 15 -0.05854 1.99905 4.04379 0.01570 6.05854
H 16 0.23998 0.00000 0.75847 0.00155 0.76002
H 17 0.23851 0.00000 0.75989 0.00160 0.76149
C 18 -0.10454 1.99883 4.08664 0.01908 6.10454
C 19 -0.15849 1.99897 4.14367 0.01585 6.15849
C 20 -0.15843 1.99897 4.14376 0.01570 6.15843
C 21 -0.18276 1.99917 4.16327 0.02032 6.18276
C 22 -0.15841 1.99897 4.14357 0.01587 6.15841
C 23 -0.15858 1.99897 4.14392 0.01569 6.15858
C 24 -0.20545 1.99912 4.18863 0.01769 6.20545
H 25 0.24449 0.00000 0.75375 0.00175 0.75551
C 26 -0.20512 1.99912 4.18845 0.01755 6.20512
H 27 0.24426 0.00000 0.75399 0.00174 0.75574
N 28 -0.31498 1.99929 5.29878 0.01690 7.31498
H 29 0.25524 0.00000 0.74323 0.00153 0.74476
H 30 0.25451 0.00000 0.74403 0.00145 0.74549
C 31 -0.20547 1.99912 4.18860 0.01775 6.20547
H 32 0.24439 0.00000 0.75386 0.00175 0.75561
C 33 -0.20528 1.99912 4.18865 0.01751 6.20528
H 34 0.24415 0.00000 0.75411 0.00174 0.75585
C 35 -0.05530 1.99905 4.04081 0.01544 6.05530
H 36 0.23954 0.00000 0.75889 0.00157 0.76046
H 37 0.23878 0.00000 0.75962 0.00160 0.76122
C 38 0.12280 1.99920 3.85763 0.02037 5.87720
C 39 0.13198 1.99921 3.84841 0.02040 5.86802
C 40 -0.05598 1.99905 4.04139 0.01554 6.05598
H 41 0.23971 0.00000 0.75873 0.00156 0.76029
H 42 0.23878 0.00000 0.75963 0.00160 0.76122
C 43 -0.18273 1.99917 4.16317 0.02039 6.18273
C 44 -0.18501 1.99897 4.17141 0.01463 6.18501
H 45 0.26234 0.00000 0.73607 0.00160 0.73766
C 46 -0.18840 1.99897 4.17450 0.01492 6.18840
H 47 0.26411 0.00000 0.73464 0.00125 0.73589
C 48 -0.18248 1.99917 4.16295 0.02036 6.18248
N 49 -0.31519 1.99929 5.29892 0.01698 7.31519
H 50 0.25516 0.00000 0.74332 0.00152 0.74484
H 51 0.25466 0.00000 0.74387 0.00147 0.74534
C 52 0.01605 1.99907 3.96668 0.01819 5.98395
H 53 0.26972 0.00000 0.72873 0.00155 0.73028
H 54 0.27193 0.00000 0.72654 0.00153 0.72807
N 55 -0.31540 1.99929 5.29913 0.01697 7.31540
H 56 0.25526 0.00000 0.74322 0.00152 0.74474
H 57 0.25461 0.00000 0.74393 0.00146 0.74539
C 58 0.12418 1.99920 3.85615 0.02047 5.87582
C 59 0.12938 1.99921 3.85089 0.02052 5.87062
C 60 0.01699 1.99907 3.96573 0.01821 5.98301
C 61 0.12375 1.99920 3.85662 0.02043 5.87625
C 62 0.13029 1.99921 3.85002 0.02049 5.86971
C 63 -0.18506 1.99897 4.17142 0.01467 6.18506
H 64 0.26358 0.00000 0.73493 0.00149 0.73642
C 65 -0.18939 1.99897 4.17552 0.01490 6.18939
H 66 0.26436 0.00000 0.73436 0.00127 0.73564
C 67 -0.18915 1.99897 4.17528 0.01490 6.18915
C 68 -0.18488 1.99897 4.17125 0.01467 6.18488
C 69 -0.18496 1.99897 4.17134 0.01466 6.18496
H 70 0.26328 0.00000 0.73520 0.00152 0.73672
C 71 -0.18902 1.99897 4.17514 0.01490 6.18902
H 72 0.26432 0.00000 0.73441 0.00126 0.73568
C 73 0.01690 1.99907 3.96581 0.01822 5.98310
H 74 0.27013 0.00000 0.72833 0.00154 0.72987
H 75 0.27178 0.00000 0.72668 0.00153 0.72822
C 76 0.12928 1.99921 3.85098 0.02054 5.87072
H 77 0.27163 0.00000 0.72684 0.00153 0.72837
C 78 0.12408 1.99920 3.85623 0.02048 5.87592
H 79 0.26999 0.00000 0.72847 0.00154 0.73001
C 80 0.01687 1.99907 3.96580 0.01826 5.98313
H 81 0.26982 0.00000 0.72865 0.00153 0.73018
H 82 0.27192 0.00000 0.72656 0.00153 0.72808
C 83 0.01593 1.99907 3.96680 0.01820 5.98407
N 84 -0.31533 1.99929 5.29904 0.01699 7.31533
H 85 0.26438 0.00000 0.73435 0.00127 0.73562
H 86 0.26362 0.00000 0.73489 0.00149 0.73638
C 87 0.02176 1.99905 3.96150 0.01769 5.97824
C 88 -0.18879 1.99897 4.17488 0.01494 6.18879
C 89 -0.18487 1.99897 4.17126 0.01464 6.18487
C 90 -0.18255 1.99917 4.16301 0.02036 6.18255
C 91 -0.19962 1.99912 4.18599 0.01451 6.19962
C 92 -0.18480 1.99897 4.17103 0.01481 6.18480
C 93 0.13214 1.99921 3.84826 0.02040 5.86786

H 94 0.27213 0.00000 0.72634 0.00152 0.72787
C 95 0.12268 1.99920 3.85774 0.02039 5.87732
H 96 0.26960 0.00000 0.72884 0.00155 0.73040
C 97 -0.05541 1.99905 4.04090 0.01546 6.05541
H 98 0.25514 0.00000 0.74333 0.00153 0.74486
H 99 0.25477 0.00000 0.74376 0.00147 0.74523
C 100 0.13475 1.99920 3.84594 0.02012 5.86525
H 101 0.27245 0.00000 0.72612 0.00143 0.72755
C 102 0.12342 1.99920 3.85704 0.02034 5.87658
H 103 0.26976 0.00000 0.72873 0.00151 0.73024
N 104 -0.31515 1.99929 5.29899 0.01686 7.31515
H 105 0.26420 0.00000 0.73455 0.00125 0.73580
H 106 0.26259 0.00000 0.73580 0.00161 0.73741
C 107 -0.20545 1.99912 4.18881 0.01751 6.20545
C 108 -0.20539 1.99912 4.18853 0.01773 6.20539
N 109 -0.31439 1.99929 5.29874 0.01637 7.31439
H 110 0.26419 0.00000 0.73454 0.00126 0.73581
H 111 0.26292 0.00000 0.73553 0.00155 0.73708
C 112 -0.18230 1.99917 4.16283 0.02030 6.18230
C 113 -0.15843 1.99897 4.14376 0.01570 6.15843
H 114 0.23884 0.00000 0.75957 0.00160 0.76116
C 115 -0.15848 1.99897 4.14365 0.01586 6.15848
H 116 0.23957 0.00000 0.75886 0.00156 0.76043
C 117 -0.18263 1.99917 4.16302 0.02044 6.18263
C 118 -0.05858 1.99905 4.04375 0.01577 6.05858
H 119 0.25487 0.00000 0.74359 0.00153 0.74513
H 120 0.25472 0.00000 0.74383 0.00145 0.74528
C 121 -0.10484 1.99883 4.08693 0.01908 6.10484
H 122 0.24434 0.00000 0.75392 0.00175 0.75566
H 123 0.24430 0.00000 0.75395 0.00175 0.75570
C 124 -0.05755 1.99905 4.04287 0.01563 6.05755
H 125 0.25493 0.00000 0.74354 0.00153 0.74507
H 126 0.25475 0.00000 0.74379 0.00146 0.74525
C 127 -0.20356 1.99912 4.18688 0.01756 6.20356
C 128 -0.20574 1.99912 4.18893 0.01770 6.20574
C 129 0.49025 1.99920 3.47790 0.03266 5.50975
C 130 -0.20417 1.99912 4.18748 0.01756 6.20417
C 131 -0.20532 1.99912 4.18849 0.01771 6.20532
C 132 -0.15891 1.99897 4.14427 0.01566 6.15891
H 133 0.23866 0.00000 0.75974 0.00160 0.76134
C 134 -0.15869 1.99897 4.14384 0.01588 6.15869
H 135 0.24011 0.00000 0.75834 0.00155 0.75989
N 136 -0.54679 1.99934 5.52623 0.02123 7.54679
N 137 -0.54640 1.99934 5.52583 0.02122 7.54640
C 138 -0.15861 1.99897 4.14395 0.01569 6.15861
H 139 0.23854 0.00000 0.75986 0.00160 0.76146
C 140 -0.15848 1.99897 4.14365 0.01586 6.15848
H 141 0.23982 0.00000 0.75862 0.00156 0.76018
C 142 -0.10362 1.99883 4.08572 0.01907 6.10362
H 143 0.24413 0.00000 0.75413 0.00175 0.75587
H 144 0.24451 0.00000 0.75375 0.00175 0.75549
C 145 0.49048 1.99920 3.47764 0.03269 5.50952
C 146 0.49008 1.99920 3.47806 0.03267 5.50992
C 147 -0.10414 1.99883 4.08621 0.01910 6.10414
H 148 0.24397 0.00000 0.75428 0.00174 0.75603
H 149 0.24453 0.00000 0.75374 0.00173 0.75547
N 150 -0.54695 1.99934 5.52639 0.02122 7.54695
=======================================
==============================
* Total * 6.00010 179.91902 424.30161 1.77926
605.99990

Natural Population

Core 179.91902 (99.9550% of 180)
Valence 424.30161 (99.6013% of 426)
Natural Minimal Basis 604.22064 (99.7064% of 606)
Natural Rydberg Basis 1.77926 (0.2936% of 606)

BH4EN • AzaEx^{2}Cage^{6+}

Natural Population
Natural -------------------------------------

Atom No Charge Core Valence Rydberg Total

O 1 -0.57860 1.99971 6.55149 0.02739 8.57860
O 2 -0.63638 1.99977 6.61262 0.02398 8.63638
C 3 -0.10185 1.99893 4.07701 0.02591 6.10185
O 4 -0.63503 1.99978 6.61019 0.02506 8.63503
C 5 -0.24612 1.99911 4.22129 0.02572 6.24612
H 6 0.25717 0.00000 0.73918 0.00365 0.74283
C 7 -0.24077 1.99925 4.20681 0.03470 6.24077
H 8 0.22516 0.00000 0.77232 0.00252 0.77484
C 9 0.32302 1.99882 3.63668 0.04148 5.67698

C 10 -0.22921 1.99907 4.21484 0.01530 6.22921
H 11 0.23223 0.00000 0.76461 0.00316 0.76777
C 12 -0.05430 1.99917 4.03364 0.02149 6.05430
H 13 0.20134 0.00000 0.79699 0.00167 0.79866
H 14 0.19113 0.00000 0.80416 0.00471 0.80887
C 15 -0.03637 1.99921 4.01872 0.01844 6.03637
H 16 0.19412 0.00000 0.80397 0.00191 0.80588
H 17 0.18649 0.00000 0.81156 0.00194 0.81351
O 18 -0.77390 1.99980 6.75969 0.01440 8.77390
H 19 0.48862 0.00000 0.50699 0.00439 0.51138
C 20 -0.05033 1.99923 4.03371 0.01739 6.05033
H 21 0.18834 0.00000 0.80997 0.00169 0.81166
H 22 0.17764 0.00000 0.82035 0.00201 0.82236
C 23 -0.04722 1.99920 4.02799 0.02003 6.04722
H 24 0.19088 0.00000 0.80747 0.00165 0.80912
H 25 0.19496 0.00000 0.80275 0.00230 0.80504
O 26 -0.64511 1.99978 6.61244 0.03289 8.64511
C 27 -0.05548 1.99921 4.03708 0.01920 6.05548
H 28 0.18341 0.00000 0.81442 0.00216 0.81659
H 29 0.18429 0.00000 0.81401 0.00171 0.81571
C 30 -0.05896 1.99922 4.03927 0.02047 6.05896
C 31 -0.04450 1.99920 4.02337 0.02193 6.04450
H 32 0.18947 0.00000 0.80852 0.00200 0.81053
H 33 0.19439 0.00000 0.80344 0.00217 0.80561
C 34 -0.04263 1.99921 4.02327 0.02016 6.04263
O 35 -0.61965 1.99971 6.58450 0.03544 8.61965
O 36 -0.64520 1.99979 6.62056 0.02486 8.64520
C 37 -0.14208 1.99898 4.10791 0.03519 6.14208
O 38 -0.63670 1.99977 6.60957 0.02735 8.63670
C 39 -0.13675 1.99912 4.12032 0.01730 6.13675
H 40 0.23032 0.00000 0.76641 0.00327 0.76968
C 41 -0.24276 1.99927 4.21044 0.03305 6.24276
H 42 0.22898 0.00000 0.76877 0.00225 0.77102
C 43 0.36421 1.99870 3.60504 0.03204 5.63579
C 44 -0.27567 1.99905 4.25616 0.02046 6.27567
H 45 0.24550 0.00000 0.75284 0.00166 0.75450
C 46 -0.06474 1.99913 4.04379 0.02182 6.06474
H 47 0.19166 0.00000 0.80644 0.00190 0.80834
H 48 0.21332 0.00000 0.78270 0.00398 0.78668
C 49 -0.03549 1.99919 4.01672 0.01959 6.03549
H 50 0.18904 0.00000 0.80964 0.00132 0.81096
H 51 0.19307 0.00000 0.80526 0.00167 0.80693
O 52 -0.75886 1.99981 6.74471 0.01434 8.75886
H 53 0.47776 0.00000 0.51786 0.00438 0.52224
C 54 -0.04984 1.99919 4.03211 0.01854 6.04984
H 55 0.19012 0.00000 0.80835 0.00153 0.80988
H 56 0.18609 0.00000 0.81196 0.00195 0.81391
C 57 -0.04534 1.99920 4.02675 0.01940 6.04534
H 58 0.18859 0.00000 0.80969 0.00172 0.81141
H 59 0.18737 0.00000 0.81079 0.00184 0.81263
O 60 -0.64011 1.99976 6.61463 0.02572 8.64011
C 61 -0.03776 1.99920 4.02030 0.01826 6.03776
H 62 0.17990 0.00000 0.81798 0.00211 0.82010
H 63 0.18585 0.00000 0.81253 0.00161 0.81415
C 64 -0.04627 1.99926 4.02595 0.02105 6.04627
C 65 -0.04126 1.99921 4.02243 0.01962 6.04126
H 66 0.18234 0.00000 0.81592 0.00175 0.81766
H 67 0.18256 0.00000 0.81462 0.00282 0.81744
C 68 -0.05142 1.99924 4.03351 0.01867 6.05142
N 69 -0.29597 1.99934 5.25893 0.03770 7.29597
N 70 -0.54966 1.99934 5.52840 0.02191 7.54966
N 71 -0.54830 1.99934 5.52706 0.02190 7.54830
N 72 -0.31942 1.99929 5.30300 0.01713 7.31942
N 73 -0.55014 1.99934 5.52869 0.02210 7.55014
N 74 -0.55960 1.99934 5.52835 0.03191 7.55960
N 75 -0.55995 1.99934 5.52853 0.03208 7.55995
N 76 -0.54718 1.99934 5.52631 0.02153 7.54718
N 77 -0.31394 1.99929 5.29809 0.01657 7.31394
C 78 -0.14381 1.99912 4.11208 0.03261 6.14381
H 79 0.27439 0.00000 0.72025 0.00536 0.72561
N 80 -0.31522 1.99929 5.29846 0.01747 7.31522
N 81 -0.31539 1.99929 5.29907 0.01702 7.31539
C 82 -0.12678 1.99907 4.10907 0.01864 6.12678
C 83 -0.20524 1.99910 4.18963 0.01651 6.20524
H 84 0.27062 0.00000 0.72626 0.00311 0.72938
C 85 0.18246 1.99926 3.77993 0.03834 5.81754
H 86 0.26239 0.00000 0.72711 0.01049 0.73761
C 87 0.03150 1.99902 3.94722 0.02226 5.96850
C 88 -0.02586 1.99900 3.98557 0.04129 6.02586
C 89 -0.21135 1.99910 4.19348 0.01876 6.21135
H 90 0.26585 0.00000 0.73173 0.00242 0.73415
C 91 -0.04856 1.99905 4.03432 0.01519 6.04856
C 92 -0.20527 1.99912 4.18891 0.01724 6.20527
H 93 0.23848 0.00000 0.75998 0.00154 0.76152
C 94 -0.26494 1.99917 4.22611 0.03965 6.26494
H 95 0.24695 0.00000 0.74819 0.00486 0.75305
C 96 -0.06689 1.99904 4.03095 0.03689 6.06689
C 97 -0.15678 1.99896 4.14178 0.01604 6.15678

H 98 0.24700 0.00000 0.75172 0.00128 0.75300
C 99 -0.15492 1.99897 4.14040 0.01555 6.15492
H 100 0.24419 0.00000 0.75409 0.00172 0.75581
C 101 0.47164 1.99910 3.48269 0.04657 5.52836
C 102 -0.20652 1.99912 4.19063 0.01677 6.20652
H 103 0.23886 0.00000 0.75961 0.00154 0.76114
C 104 -0.11533 1.99902 4.09661 0.01969 6.11533
C 105 -0.07169 1.99924 4.05627 0.01618 6.07169
H 106 0.23237 0.00000 0.76425 0.00339 0.76763
C 107 0.50001 1.99901 3.46578 0.03520 5.49999
C 108 0.09331 1.99915 3.87363 0.03392 5.90669
H 109 0.25964 0.00000 0.73744 0.00292 0.74036
C 110 -0.17431 1.99916 4.15820 0.01696 6.17431
H 111 0.24509 0.00000 0.75316 0.00175 0.75491
N 112 -0.31305 1.99929 5.29822 0.01555 7.31305
C 113 0.11832 1.99915 3.85771 0.02482 5.88168
H 114 0.26879 0.00000 0.72919 0.00202 0.73121
C 115 0.50886 1.99901 3.46062 0.03151 5.49114
C 116 -0.06516 1.99908 4.04966 0.01642 6.06516
C 117 0.48933 1.99920 3.47872 0.03275 5.51067
C 118 -0.06345 1.99923 4.04262 0.02160 6.06345
C 119 -0.18609 1.99917 4.16660 0.02033 6.18609
H 120 0.25367 0.00000 0.74489 0.00144 0.74633
H 121 0.25424 0.00000 0.74420 0.00156 0.74576
C 122 0.49977 1.99901 3.46597 0.03524 5.50023
C 123 0.48945 1.99920 3.47858 0.03278 5.51055
C 124 -0.25174 1.99919 4.21452 0.03803 6.25174
H 125 0.23628 0.00000 0.76100 0.00272 0.76372
C 126 -0.23196 1.99919 4.19444 0.03833 6.23196
H 127 0.24815 0.00000 0.74911 0.00275 0.75185
H 128 0.26339 0.00000 0.72986 0.00675 0.73661
C 129 -0.06914 1.99924 4.05413 0.01577 6.06914
H 130 0.23467 0.00000 0.76199 0.00335 0.76533
C 131 -0.23367 1.99905 4.21507 0.01955 6.23367
H 132 0.29016 0.00000 0.70500 0.00483 0.70984
C 133 -0.15918 1.99897 4.14435 0.01586 6.15918
H 134 0.24488 0.00000 0.75340 0.00172 0.75512
C 135 -0.18984 1.99894 4.17386 0.01704 6.18984
H 136 0.23952 0.00000 0.75916 0.00132 0.76048
C 137 -0.18991 1.99893 4.17375 0.01722 6.18991
H 138 0.24086 0.00000 0.75786 0.00128 0.75914
C 139 -0.10312 1.99883 4.08513 0.01917 6.10312
C 140 -0.18231 1.99917 4.16280 0.02035 6.18231
H 141 0.25508 0.00000 0.74337 0.00155 0.74492
H 142 0.25456 0.00000 0.74391 0.00153 0.74544
C 143 -0.17452 1.99916 4.15838 0.01698 6.17452
H 144 0.24486 0.00000 0.75337 0.00177 0.75514
C 145 -0.11306 1.99902 4.09476 0.01928 6.11306
C 146 0.13254 1.99920 3.84818 0.02008 5.86746
H 147 0.26437 0.00000 0.73434 0.00130 0.73563
C 148 -0.19984 1.99914 4.18570 0.01500 6.19984
C 149 -0.20313 1.99912 4.18646 0.01754 6.20313
H 150 0.23863 0.00000 0.75977 0.00160 0.76137
C 151 -0.06964 1.99908 4.05366 0.01690 6.06964
C 152 0.12785 1.99919 3.85297 0.02000 5.87215
C 153 -0.05954 1.99905 4.04474 0.01574 6.05954
C 154 -0.15933 1.99897 4.14469 0.01567 6.15933
H 155 0.24379 0.00000 0.75449 0.00172 0.75621
C 156 0.04061 1.99885 3.94296 0.01758 5.95939
C 157 -0.20404 1.99915 4.18957 0.01533 6.20404
H 158 0.27222 0.00000 0.72641 0.00136 0.72778
C 159 -0.10449 1.99883 4.08654 0.01912 6.10449
C 160 0.01254 1.99910 3.97005 0.01831 5.98746
C 161 0.03517 1.99885 3.94770 0.01828 5.96483
C 162 -0.19560 1.99911 4.18199 0.01449 6.19560
H 163 0.27016 0.00000 0.72844 0.00140 0.72984
C 164 -0.18300 1.99917 4.16706 0.01676 6.18300
H 165 0.25325 0.00000 0.74577 0.00098 0.74675
C 166 -0.20562 1.99912 4.18887 0.01762 6.20562
H 167 0.23999 0.00000 0.75845 0.00155 0.76001
C 168 -0.18765 1.99894 4.17183 0.01689 6.18765
H 169 0.23874 0.00000 0.75985 0.00140 0.76126
C 170 0.02261 1.99905 3.96100 0.01734 5.97739
C 171 0.12660 1.99918 3.85426 0.01995 5.87340
H 172 0.26252 0.00000 0.73588 0.00160 0.73748
C 173 0.12961 1.99921 3.85068 0.02050 5.87039
H 174 0.26422 0.00000 0.73450 0.00128 0.73578
C 175 0.13563 1.99920 3.84517 0.02000 5.86437
H 176 0.26396 0.00000 0.73475 0.00129 0.73604
C 177 -0.18244 1.99917 4.16300 0.02027 6.18244
H 178 0.25513 0.00000 0.74326 0.00161 0.74487
H 179 0.25441 0.00000 0.74404 0.00155 0.74559
C 180 -0.20513 1.99912 4.18855 0.01747 6.20513
H 181 0.23874 0.00000 0.75966 0.00160 0.76126
C 182 -0.05644 1.99905 4.04189 0.01550 6.05644
C 183 -0.18253 1.99917 4.16294 0.02043 6.18253
H 184 0.25444 0.00000 0.74412 0.00144 0.74556
H 185 0.25503 0.00000 0.74347 0.00151 0.74497

C 186 -0.17457 1.99916 4.15833 0.01709 6.17457
H 187 0.24501 0.00000 0.75324 0.00175 0.75499
C 188 -0.19039 1.99893 4.17418 0.01728 6.19039
H 189 0.24139 0.00000 0.75735 0.00126 0.75861
C 190 -0.20529 1.99912 4.18849 0.01768 6.20529
H 191 0.23955 0.00000 0.75889 0.00156 0.76045
C 192 -0.15862 1.99897 4.14386 0.01578 6.15862
H 193 0.24474 0.00000 0.75353 0.00173 0.75526
C 194 -0.19967 1.99912 4.18581 0.01474 6.19967
H 195 0.27259 0.00000 0.72605 0.00137 0.72741
C 196 -0.18898 1.99898 4.17508 0.01493 6.18898
H 197 0.27171 0.00000 0.72674 0.00155 0.72829
C 198 -0.15880 1.99897 4.14414 0.01569 6.15880
H 199 0.24402 0.00000 0.75426 0.00172 0.75598
C 200 -0.20471 1.99915 4.19012 0.01544 6.20471
H 201 0.27255 0.00000 0.72605 0.00140 0.72745
C 202 -0.18242 1.99917 4.16286 0.02039 6.18242
H 203 0.25508 0.00000 0.74339 0.00153 0.74492
H 204 0.25462 0.00000 0.74391 0.00147 0.74538
C 205 0.13560 1.99920 3.84514 0.02006 5.86440
H 206 0.26411 0.00000 0.73466 0.00123 0.73589
C 207 0.12387 1.99920 3.85649 0.02044 5.87613
H 208 0.26330 0.00000 0.73518 0.00152 0.73670
C 209 -0.18536 1.99897 4.17170 0.01469 6.18536
H 210 0.27006 0.00000 0.72841 0.00153 0.72994
C 211 0.12280 1.99920 3.85773 0.02028 5.87720
H 212 0.26238 0.00000 0.73597 0.00165 0.73762
C 213 -0.18689 1.99898 4.17336 0.01455 6.18689
H 214 0.26956 0.00000 0.72888 0.00156 0.73044
C 215 0.12120 1.99918 3.85943 0.02018 5.87880
H 216 0.26030 0.00000 0.73826 0.00144 0.73970
H 217 0.19002 0.00000 0.80832 0.00166 0.80998
H 218 0.16781 0.00000 0.83016 0.00203 0.83219
H 219 0.18973 0.00000 0.80862 0.00166 0.81027
H 220 0.17558 0.00000 0.81998 0.00444 0.82442
H 221 0.18142 0.00000 0.81668 0.00190 0.81858
H 222 0.17458 0.00000 0.82159 0.00383 0.82542
H 223 0.18674 0.00000 0.81133 0.00193 0.81326
H 224 0.17849 0.00000 0.81943 0.00208 0.82151
H 225 0.27083 0.00000 0.72781 0.00136 0.72917
H 226 0.26367 0.00000 0.73485 0.00148 0.73633
=======================================
================================
* Total * 6.04503 251.89592 627.06408 2.99496
881.95497

Natural Population

Core 251.89592 (99.9587% of 252)
Valence 627.06408 (99.5340% of 630)
Natural Minimal Basis 878.96000 (99.6553% of 882)
Natural Rydberg Basis 2.99496 (0.3396% of 882)
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7. Cartesian Coordinates for the Optimized Structures

AzaEx^{2}Cage^{6+}

C -2.50609600 -0.25106100 4.60305900
C -1.41975700 -0.79011100 5.47047800
N -2.58764800 1.07378000 4.45386000
C -1.40456300 -2.14276900 5.81997300
C -0.41389700 0.05631700 5.95057600
N -3.32133800 -1.12894900 4.01221100
C -3.58996700 1.50726300 3.68381800
C -0.38706200 -2.64656600 6.62552200
H -2.20453400 -2.78981800 5.47755900
C 0.60812000 -0.45055800 6.74268100
H -0.44879500 1.11215500 5.70660600
C -4.28103200 -0.60114700 3.24734800
C -3.72935700 2.97774500 3.48260000
N -4.46087900 0.70910600 3.06052100
C 0.63361300 -1.80749600 7.07928300
H -0.41233100 -3.69147100 6.92725100
H 1.37443900 0.22174500 7.12185100
C -5.18800900 -1.53568800 2.52224500
C -4.79008100 3.48872300 2.73009100
C -2.79983300 3.85823900 4.04719900
C 1.76279000 -2.35913400 7.91930700
C -6.28936400 -1.04473800 1.81678100
C -4.93438800 -2.91197100 2.53207800
C -4.90555100 4.85972300 2.52226000

H -5.52943500 2.80791200 2.32388000
C -2.91188700 5.22615800 3.83153300
H -2.00112100 3.46229800 4.66427500
N 2.99108800 -2.56704000 7.06611600
H 2.05460800 -1.68039000 8.72306700
H 1.51817700 -3.32941100 8.35896700
C -7.11118500 -1.91549800 1.10691100
H -6.50570600 0.01740400 1.83855000
C -5.74968200 -3.77831900 1.81546500
H -4.09912500 -3.29239500 3.10930600
C -3.95828300 5.73575400 3.05768400
H -5.75870800 5.24483100 1.96806300
H -2.19362600 5.89997800 4.29336500
C 2.92317700 -3.46305100 6.06251600
C 4.10631000 -1.84023100 7.26103800
C -6.83595900 -3.28457200 1.08722000
H -7.98610300 -1.52452500 0.59217700
H -5.54901000 -4.84708600 1.84295400
C -4.04699100 7.22002100 2.78120500
C 3.96653000 -3.61077000 5.17165100
H 1.99732500 -4.02215000 5.98145000
C 5.18038000 -1.93663400 6.38834800
H 4.11295000 -1.17570700 8.11847800
C -7.68198400 -4.22421700 0.25750400
N -3.12767300 7.57233100 1.63892500
H -3.73503100 7.82596500 3.63402400
H -5.05188600 7.53110600 2.48664200
C 5.10678700 -2.80647600 5.29647700
H 3.85692100 -4.31936500 4.35813700
H 6.06085500 -1.33203000 6.58202500
N -6.96168400 -4.54026400 -1.02984300
H -7.86400900 -5.17840600 0.75585900
H -8.64556900 -3.78815000 -0.01656200
C -3.48303200 7.20893200 0.39169600
C -1.93014200 8.14029000 1.87262200
C 6.13366400 -2.82225100 4.21744900
C -6.83545300 -3.56441500 -1.95010800
C -6.37126100 -5.73565100 -1.21268300
C -2.60044500 7.33516900 -0.66322800
H -4.47399300 6.78364400 0.27746500
C -1.00042100 8.28104800 0.85470700
H -1.73161600 8.45832300 2.89068100
C 6.50248600 -4.00381200 3.56664900
C 6.67284100 -1.61728900 3.75029200
C -6.03820700 -3.73851500 -3.06362500
H -7.35932000 -2.63764600 -1.74276400
C -5.54865800 -5.96217200 -2.30511300
H -6.55762400 -6.49316500 -0.45885600
C -1.31155600 7.83056000 -0.43222000
H -2.91301300 6.99459000 -1.64435000
H -0.04505300 8.74265800 1.08326400
C 7.30324800 -3.94204100 2.43724900
H 6.17851200 -4.97708200 3.92104200
C 7.45766200 -1.61471200 2.61364300
H 6.44810500 -0.66949800 4.22736400
C -5.33380600 -4.93710000 -3.23173600
H -5.93381400 -2.91507300 -3.76170500
H -5.08900600 -6.93918800 -2.41551900
C -0.28312900 7.75459900 -1.50687400
N 7.72797100 -2.75888000 1.95665600
H 7.60326300 -4.82782100 1.88759600
H 7.85654400 -0.70394600 2.18046100
C -4.30416400 -5.04253000 -4.30289300
C -0.57990800 8.00362700 -2.84988600
C 1.00747700 7.31300700 -1.18826700
C 8.40547200 -2.67382000 0.61165800
C -4.48713500 -4.48489300 -5.57186500
C -3.06247600 -5.62109400 -4.01060300
C 0.37331800 7.73754400 -3.82222300
H -1.53932300 8.40477700 -3.16119600
C 1.91053500 7.05150700 -2.19788200
H 1.30366700 7.11776700 -0.16346700
C 7.41609700 -2.16060700 -0.41061100
H 8.76976600 -3.67654500 0.37951500
H 9.26653600 -2.01208600 0.73084800
C -3.42516300 -4.44781300 -6.46299800
H -5.44326600 -4.07975900 -5.88785600
C -2.03765600 -5.54446800 -4.93185600
H -2.86529900 -6.08819000 -3.05190100
N 1.57639100 7.23503000 -3.48997400
H 0.18791800 7.90597200 -4.87793600
H 2.90232700 6.65390200 -2.01183000
C 6.47602300 -3.02997800 -0.97143200
C 7.40656300 -0.81185700 -0.77344900
N -2.21889400 -4.93509000 -6.11977400
H -3.51470700 -4.01668900 -7.45450000
H -1.04260500 -5.92975100 -4.73713600
C 2.55994200 6.79609400 -4.54851400

C 5.52200800 -2.55272200 -1.86098800
H 6.49931700 -4.09082100 -0.73192400
C 6.44518800 -0.33000700 -1.65729600
H 8.16643100 -0.13443400 -0.39054100
C -1.01854400 -4.73997300 -7.01318400
C 2.78583000 5.30457300 -4.45392700
H 2.13559600 7.09472300 -5.50909500
H 3.47695800 7.36711200 -4.38249500
C 5.48789000 -1.19427800 -2.19504600
H 4.79957100 -3.22675500 -2.30718800
H 6.43951900 0.71556200 -1.94410800
C -0.04731900 -3.77741400 -6.36785400
H -1.39811800 -4.37259400 -7.96848500
H -0.57998700 -5.72794800 -7.17286300
C 1.82672000 4.41777200 -4.95349000
C 3.93991600 4.79973300 -3.85069400
C 4.42724800 -0.67430700 -3.10384300
C -0.29362100 -2.40148400 -6.40387700
C 1.09613600 -4.25352300 -5.72279600
C 2.00951700 3.04648400 -4.83225600
H 0.94250400 4.79770100 -5.46055000
C 4.11810800 3.42547600 -3.71656200
H 4.71977600 5.47629500 -3.50791800
N 3.61075000 -1.56103400 -3.67970500
N 4.33210000 0.64914700 -3.25805700
C 0.58223200 -1.51596100 -5.78929300
H -1.15921500 -2.01441300 -6.93716300
C 1.96886800 -3.36814000 -5.09619200
H 1.33087500 -5.31556000 -5.73557700
C 3.14874300 2.54082800 -4.19574400
H 1.27837300 2.35508200 -5.23562500
H 5.01678900 3.03190600 -3.25513800
C 2.64415900 -1.04561600 -4.44365800
C 3.32381500 1.06988900 -4.02669700
C 1.71268500 -1.99486900 -5.11759500
H 0.40694600 -0.44707600 -5.83628800
H 2.86486800 -3.73534300 -4.60827700
N 2.44585600 0.26262300 -4.62866700

(pyrene)$_2$ ⊂ **AzaEx^{2}Cage^{6+}**

C 1.24790000 0.30400300 1.26900100
C 1.61759300 -1.05632200 1.09373300
C 2.13589100 1.33701100 0.86420800
C 2.86757300 -1.35663400 0.54089700
C 0.69875900 -2.08302300 1.51075300
C -0.00844500 0.63250300 1.86309500
C 3.37453700 0.99161600 0.31037600
C 1.74257000 2.70603700 1.07533400
C 3.74021600 -0.34201100 0.16060600
H 3.15416900 -2.39913200 0.42328000
C -0.49634300 -1.77294000 2.07001600
H 0.98563900 -3.12091700 1.35669600
C -0.36533700 1.99226700 2.06670300
C -0.89318100 -0.40309700 2.27009900
H 4.06605400 1.78452400 0.03117500
C 0.55685900 3.01852400 1.65507600
H 2.43430100 3.48991400 0.77558100
H 4.71427600 -0.59379900 -0.24827700
H -1.18459300 -2.55700500 2.37582000
C -1.59473500 2.29107200 2.66767500
C -2.11815400 -0.06208800 2.85238700
H 0.28021200 4.05686900 1.82147400
C -2.46141100 1.27251000 3.04834200
H -1.85843500 3.33421400 2.83083300
H -2.79494400 -0.85563800 3.15951400
H -3.41239000 1.51497600 3.51943600
C -4.84726500 3.99113700 4.18028500
C -3.92381600 3.97779300 5.20585800
C -5.92622000 3.09784200 4.20809700
H -4.68534800 4.66130900 3.34287700
N -4.05582800 3.13143600 6.24502500
H -3.04134600 4.60803900 5.21021000
C -6.07955400 2.28467700 5.33468400
C -6.78815900 2.94757700 3.00461500
C -2.92633300 3.04675200 7.24133600
C -5.12725500 2.32450800 6.34189000
H -6.92866100 1.61815400 5.44902800
C -7.16151000 4.03769800 2.21272600
C -7.15053800 1.66462700 2.57589200
C -1.70429500 2.46645600 6.57050900
H -3.28471200 2.42981400 8.06757700
H -2.75800300 4.06006400 7.61434600
H -5.19309800 1.70521900 7.23021700
C -7.78272100 3.81489800 0.99352100

H -6.97650300 5.06131100 2.52286800
C -7.76255900 1.50281600 1.34978100
H -6.91376800 0.78161400 3.15936200
C -1.59401200 1.08635400 6.38886400
C -0.68500700 3.30672000 6.11326100
N -8.02834200 2.56397000 0.56424000
H -8.07333900 4.62428500 0.33204400
H -8.01624200 0.52923100 0.94520200
C -0.48133800 0.55037800 5.75123300
H -2.36607400 0.42053600 6.76850800
C 0.42463900 2.77251400 5.46876800
H -0.73317400 4.37784400 6.29830900
C -8.46380400 2.30518500 -0.85655600
C 0.53071700 1.39137100 5.28114500
H -0.38001300 -0.52160500 5.62128800
H 1.22886600 3.41618600 5.12968900
C -7.27697900 1.78237400 -1.63324100
H -8.84558600 3.24987400 -1.24806500
H -9.28758000 1.58889000 -0.81184300
C 1.73707700 0.82062100 4.62072400
C -6.32795300 2.67194000 -2.14711100
C -7.08908300 0.40777800 -1.79381500
N 2.64981200 1.67617900 4.15601300
N 1.84058400 -0.50982900 4.54494400
C -5.19431900 2.19212800 -2.79052900
H -6.48427300 3.74542400 -2.06558600
C -5.94997100 -0.07440000 -2.43218600
H -7.84677500 -0.29327800 -1.45016200
C 3.73735000 1.12079700 3.61618100
C 2.97055200 -0.96684500 4.00150000
C -4.99001700 0.81429000 -2.92211900
H -4.45729100 2.87648200 -3.19583300
H -5.79924500 -1.14027300 -2.56361900
C 4.77079700 2.03308000 3.05038100
N 3.95228700 -0.19288100 3.53020900
C 3.15283700 -2.44340400 3.91346800
C -3.75045900 0.29594300 -3.56571900
C 5.99203500 1.52546200 2.60070100
C 4.51004800 3.40315800 2.93914600
C 4.36615200 -2.97738200 3.47352000
C 2.11676600 -3.30542800 4.29091100
N -2.86044500 1.18179100 -4.01687400
N -3.60383900 -1.02886900 -3.64228700
C 6.93205000 2.37284900 2.02109000
H 6.20048800 0.46737700 2.71500800
C 5.44370400 4.24594700 2.34770800
H 3.57197000 3.79368600 3.31864100
C 4.54007200 -4.35723600 3.40238000
H 5.17554400 -2.30626100 3.20817800
C 2.28636100 -4.68132500 4.20641100
H 1.18620900 -2.88399600 4.65456700
C -1.75405000 0.65936400 -4.55374900
C -2.46684700 -1.45373700 -4.19551200
C 6.65634100 3.73484300 1.87532000
H 7.89373100 1.97215800 1.70799700
H 5.23557700 5.31170700 2.27874400
C 3.49773800 -5.21681000 3.75729400
H 5.50401500 -4.76095200 3.09969300
H 1.47977300 -5.34132800 4.51805700
C -0.74431200 1.60504300 -5.11081500
N -1.50088900 -0.64762800 -4.64899500
C -2.27134700 -2.92531600 -4.31940900
C 7.63760900 4.64455200 1.17088100
C 3.66293400 -6.71331200 3.63127400
C -1.04744500 2.96275000 -5.23523200
C 0.49211700 1.13097000 -5.56486900
C -3.27866400 -3.80188800 -3.90453900
C -1.09130500 -3.43940600 -4.86291900
N 7.16223700 4.86587700 -0.24347200
H 7.71277500 5.62955900 1.63567700
H 8.63945700 4.21342000 1.10719700
N 2.96626000 -7.19732900 2.38170700
H 3.21510800 -7.25536900 4.46634500
H 4.71087800 -7.01196300 3.54503700
C -0.13252800 3.83494900 -5.81985600
H -2.01512000 3.32236800 -4.90376100
C 1.40874600 2.00440500 -6.13655100
H 0.71221900 0.07237000 -5.48110000
C -3.09866600 -5.17603100 -4.01074500
H -4.20387300 -3.39693400 -3.50988600
C -0.91162500 -4.81420400 -4.96682000
H -0.32470100 -2.75331500 -5.20621300
C 7.20050400 3.82350800 -1.09556200
C 6.59851100 6.03128300 -0.60934100
C 3.36872100 -6.69126100 1.19988900
C 1.93078600 -8.05363800 2.44506300
C 1.10059900 3.36192500 -6.27362700
H -0.40489900 4.87848200 -5.96225500

H 2.35282900 1.61718600 -6.51376100
C -1.90830800 -5.69022700 -4.53209300
H -3.90485200 -5.84578900 -3.71923300
H 0.00449100 -5.20174000 -5.40767200
C 6.58276200 3.89288000 -2.32748400
H 7.69775600 2.92814800 -0.73842700
C 5.95316600 6.15504200 -1.83059500
H 6.65600400 6.84653000 0.10442500
C 2.68477500 -6.97813800 0.03799300
H 4.22124800 -6.02200800 1.23120900
C 1.19858800 -8.37035500 1.30908500
H 1.69312700 -8.46178800 3.42205100
C 2.09296400 4.30658900 -6.91326800
C -1.68352300 -7.18353000 -4.58689900
C 5.89093000 5.05517800 -2.69134100
H 6.59835400 3.01626900 -2.96558500
H 5.50435100 7.10970900 -2.08653200
C 1.54785700 -7.79584900 0.08446700
H 3.01373500 -6.51713800 -0.88701300
H 0.36656100 -9.06133600 1.40231100
N 3.17526800 4.66209100 -5.92562500
H 2.59303000 3.86407000 -7.77706900
H 1.63014000 5.24543000 -7.22713100
N -0.85840500 -7.59805600 -3.39477900
H -1.13077800 -7.49646200 -5.47478900
H -2.61575300 -7.75124800 -4.54142800
C 5.01512000 5.03646600 -3.89489700
C 0.70170400 -7.90839300 -1.13427400
C 2.83889200 5.40057000 -4.85023000
C 4.42375500 4.18013000 -6.06394800
C -1.44080600 -7.60795500 -2.18059000
C 0.45913200 -7.83595700 -3.52625700
C 5.36623000 4.35105700 -5.06150900
C 3.73974900 5.61182400 -3.82662200
C 1.26568900 -7.99437100 -2.41113000
C -0.68821500 -7.77365200 -1.03362500
H 1.82108600 5.77438400 -4.82367100
H 4.64109400 3.64209800 -6.98066000
H -2.51184200 -7.43735900 -2.15975200
H 0.84987800 -7.87269800 -4.53764300
H 6.36077000 3.94213800 -5.20872000
H 3.41775500 6.17870000 -2.96002000
H 2.32601000 -8.17492000 -2.55699100
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C -1.98272700 2.45357900 -0.89365100
C -2.46450400 0.08936500 -0.65241400
H -3.79581400 1.65983500 -0.04006700
C -0.74930600 2.16104700 -1.46684000
H -2.28367200 3.48904400 -0.76326800
C -1.20727000 -0.21557600 -1.23766900
C -3.33122800 -0.99534400 -0.27139100
C -0.33983400 0.83515400 -1.64164100
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C -0.81054600 -1.57639100 -1.40976100
C -2.96224900 -2.28838200 -0.44633900
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C 0.93152000 0.49689000 -2.22689500
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C -1.68010300 -2.62612500 -1.00961200
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H 1.58381500 1.30913900 -2.53816800
C 0.84417100 -3.21571000 -2.10361500
C -1.26040700 -3.95333000 -1.16630300
H 2.28161700 -1.03645000 -2.81383800
C -0.01072600 -4.23953100 -1.70404400
H 1.81387300 -3.44559500 -2.53924500
H -1.93180900 -4.75557100 -0.86705500
H 0.29889600 -5.27381600 -1.83692100

$(PCA)_2 \subset AzaEx^2Cage^{6+}$

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C -0.31289700 -1.09853700 2.07251800
C -0.32786600 1.35718300 2.04697900
C -1.52551600 -1.07612700 2.77555500
C 0.34139400 -2.32533300 1.72064000
C 1.53872900 0.12265900 0.99555800
C -1.53408300 1.33736500 2.75316300
C 0.30464600 2.59000500 1.66107100
C -2.12312500 0.12916200 3.11695500
H -1.98519600 -2.02032700 3.05751500
C 1.52024700 -2.33979100 1.04628600
H -0.13297000 -3.26144600 2.00620300
C 2.13893200 1.36296900 0.63508400
C 2.16188600 -1.11202400 0.65364800

H -2.00760700 2.28011600 3.01603800
C 1.47940900 2.59325100 0.98527400
H -0.18324200 3.52368700 1.93166900
H -3.05989600 0.13231000 3.66809200
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C 3.36475700 1.36204300 -0.04015100
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H 1.95728500 3.52769300 0.70146300
C 3.97619200 0.16372200 -0.36455600
H 3.83510100 2.30741900 -0.29515600
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H 4.93531000 0.17414300 -0.87829600
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H 4.12708700 -7.66187700 -1.24689700
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C 5.96623700 -1.62542500 2.23215300
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C 0.13042300 -1.28995000 -1.94617800
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H 1.68549100 -0.05557800 -2.82611100
C -3.01408100 -2.47175900 -0.24881800
H -4.57878200 -1.26957100 0.55402700
C 0.73970700 -2.52034700 -2.23225600
C -1.11353800 -3.71001300 -1.23985300
H -3.49770800 -3.41802700 -0.01848200
C 0.12218300 -3.71238200 -1.88086200
H 1.70226500 -2.52854400 -2.73885600
H -1.59739400 -4.64731600 -0.97725300
H 0.60838800 -4.65674100 -2.10033700

BH4EN • AzaEx^{2}Cage^{6+}

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O 6.20909500 -5.16501700 2.16828800
C 7.18002600 0.48800300 0.40075100
O 3.77759100 -5.66412400 1.09956200
C 7.59799400 0.32735400 -0.94884700
H 7.57630400 1.18853200 -1.60734700
C 8.14603300 -0.86663900 -1.34619900
H 8.54190500 -0.97200400 -2.35227000
C 7.79061700 -1.84447800 0.83269200
C 8.23359000 -1.97196700 -0.46732100
H 8.67918100 -2.89421100 -0.82006600
C 8.17075900 -4.13944500 1.34456700
H 9.26644900 -4.16182500 1.31735700
H 7.77595400 -4.38935000 0.35062000
C 7.61936500 -5.14010300 2.32939600
H 8.04921200 -6.12498800 2.10377800
H 7.88487100 -4.87301000 3.35965100
O 5.92539500 -3.36786000 -3.56489700
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H 5.85076100 -6.69019100 3.54340200
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$(PCA)_2 \subset AzaEx^2Cage^{6+}$ -2

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