Supporting information

**Reversible Reduction Drives Anion Ejection and C\textsubscript{60} Binding within a Fe\textsuperscript{II}\textsubscript{4}L\textsubscript{6} Cage**

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1. General Experimental Procedures

All the starting materials were purchased from commercial sources and used as received. Acetonitrile (99.9%, extra dry over molecular sieves) was bought from Acros and used as received. NMR solvents (CDCl$_3$, CD$_3$CN) were degassed (by 3 freeze-pump-thaw cycles) and dried over 3 Å molecular sieves. Air-sensitive compounds (For instance, reactions involving Cp$_2$Co) were handled under N$_2$ atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on a Bruker DRX-400, Bruker Avance 500 Cryo and Bruker 500 TCI-ATM Cryo. Chemical shifts (δ) for $^1$H NMR spectra are reported in parts per million (ppm) and are reported relative to the solvent residual peak. DOSY experiments were performed on a Bruker DRX-400 spectrometer. $^1$H and $^{13}$C NMR spectra are referenced to the residual solvent peak for CD$_3$CN ($^1$H: 1.94 ppm for CHD$_2$CN, $^{13}$C: 1.32 ppm for CD$_3$CN) and CDCl$_3$ ($^1$H: 7.26 ppm for CHCl$_3$, $^{13}$C: 77.16 ppm for CDCl$_3$). Low-resolution electrospray ionization mass spectra (ESI-MS) were obtained on a Micromass Quattro LC infused from a Harvard Syringe Pump at a rate of 10 µL per minute. High-resolution mass spectra were acquired using a Thermofisher LTQ Orbitrap XL.
2. Synthesis and characterization of subcomponent A

SP-01 was synthesized according to a literature procedure.¹

SP-02: A mixture of Na₂CO₃ (318 mg) in H₂O (2 mL) and DMF (8 mL) was degassed by bubbling N₂ for 30 min. Then 4-(N-tert-butoxycarbonyl)aminophenylboronic acid (378 mg, 1.59 mmol, 2.94 equiv), SP-01 (300 mg, 0.54 mmol, 1 equiv) and Pd(PPh₃)₄ (40 mg, 0.065 mmol, 0.12 equiv) were added to the mixture. The reaction mixture was then stirred at reflux in the dark under N₂ overnight. Then dichloromethane (100 mL) was added into the mixture for dilution, and the precipitate was removed by filtration, the organic layer was washed consecutively with water and brine before being dried over MgSO₄ and concentrated. The crude product was then purified by column chromatography flash silica gel, with DCM/Methanol (95 : 5) as eluent to afford the target product (SP-02, red solid, 170 mg, 41%).

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.63 (s, 2H), 7.52 (d, J₉H = 8 Hz, 4H), 7.39 (d, J₉H = 8 Hz, 4H), 6.62 (s, 2H, NH), 4.24 (t, J₉H = 6.6 Hz, 4H), 2.57 (t, J₉H = 6.6 Hz, 4H), 2.28 (s, 18H) ppm.
A: SP-02 (170 mg, 0.22 mmol, 1.0 equiv) and MeI (0.1 mL, 1.6 mmol, 7.2 equiv) were mixed in dry DMF (4 mL) at room temperature in a schlenk tube. The mixture was then stirred at 50 °C in an oil bath overnight. Then all the volatile compounds were removed under high vacuum. 50 mL H2O was added into the residue to obtain an orange solution. The solution was heated to reflux overnight resulting in a blue solution. An excess of LiNTf2 (248 mg, 0.88 mmol, 4 equiv) was added into the solution, and a blue solid precipitated immediately. The blue solid was obtained as the target compound (A, 124 mg, 48% over three steps) after filtration and dried under high vacuum.

1H NMR (500 MHz, CD3CN, 298 K): δ = 8.53 (s, 2H, H4), 7.29 (d, JHH = 10 Hz, 4H, H3), 6.76 (d, JHH = 10 Hz, 4H, H2), 4.49 (s, 4H, H1), 4.44 (t, JHH = 5 Hz, 4H, H5), 3.53 (t, JHH = 5 Hz, 4H, H6), 3.15 (s, 18H, H7) ppm.

13C NMR (126 MHz, CD3CN, 298 K): δ = 163.75, 163.74, 149.81, 148.49, 136.62, 131.29, 129.53, 128.29, 126.20, 125.58 (NTf2⁻, due to the C-F coupling), 123.03 (NTf2⁻), 122.19 (NTf2⁻), 119.64 (NTf2⁻), 114.94, 63.59, 59.29, 54.23 ppm.

HRMS (ESI) calcd. For [C36H40N6O4]2⁺ [C3F6NO2S2]⁻, Found 900.2163.
Figure S1. $^1$H and $^{13}$C NMR of subcomponent A in CD$_3$CN (500 MHz, 298 K).
3. Synthesis and characterization of cage 1.

Subcomponent A (50 mg, 0.042 mmol, 1 equiv), Fe(NTf₂)₂ (20 mg, 0.028 mmol, 0.69 equiv) and 2-formylpyridine (8.0 μL, 0.084 mmol, 2 equiv) were mixed in MeCN (3 mL) at room temperature. The solution was then stirred at 70 °C in an oil bath overnight. The crude product was purified by filtration through Celite and precipitation with diethyl ether. The resulting dark purple crystalline solid was collected by centrifugation, washed with excess diethyl ether and dried under vacuum (71 mg, 95%).

^1^H NMR (500 MHz, CD₃CN, 298 K): δ = 8.90 (s, 1H, H₅), 8.65 (d, J_HH = 10 Hz, 1H, H⁴), 8.46 (t, J_HH = 10 Hz, 1H, H³), 8.19 (s, 1H, H⁸), 7.83 (t, J_HH = 5 Hz, 1H, H²), 7.45 (m, 2H, H¹⁻¹), 7.01 (br s, 1H, H⁷), 6.07 (br s, 1H, H₆), 5.82 (br s, 1H, H⁵), 4.51 (m, 1H, H⁹) 4.31 (m, 1H, H⁹), 3.54 (m, 2H, H¹⁰), 3.16 (s, 9H, H¹¹) ppm.

^1^C NMR (126 MHz, CD₃CN, 298 K): δ = 175.07, 163.30, 163.20, 158.97, 150.86, 146.07, 141.51, 140.48, 135.73, 131.88, 130.58, 130.45, 129.91, 127.93, 126.27, 124.13, 123.52, 121.58, 63.47, 53.99, 35.09 ppm.

m/z (high resolution FT-ICR ESI-MS) calcd. For 1047.1176 [I(NTf₂)₁₂]8⁺, 1489.7954 [I(NTf₂)₁₄]6⁺, 1843.5365 [I(NTf₂)₁₅]5⁺, Found 1047.1142 [I(NTf₂)₁₂]8⁺, 1489.7901 [I(NTf₂)₁₄]6⁺, 1843.5306 [I(NTf₂)₁₅]5⁺.
Figure S2. $^1$H NMR (500 MHz, 298 K, CD$_3$CN) of 1 with assignments.

Figure S3. $^{13}$C NMR (126 MHz, 298 K, CD$_3$CN) of 1.
Figure S4. HSQC NMR of 1 (500 MHz, 298 K, CD$_3$CN).

Figure S5. $^1$H COSY NMR of cage 1 (500 MHz, 298 K, CD$_3$CN)
Figure S6. HMBC NMR of 1 (500 MHz, 298 K, CD$_3$CN).

Figure S7. $^1$H DOSY NMR of cage 1 (400 MHz, 298 K, CD$_3$CN). Vertical axis corresponds to diffusion coefficient D (in cm$^2$s$^{-1}$).
Figure S8. Low-resolution ESI-mass spectrum of 1·20NTf₂
Figure S9. High-resolution ESI-mass spectrum of 1·20NTf₂ showing the 5+ corresponding to the loss of 5 NTf₂⁻ anions.
Figure S10. High-resolution ESI-mass spectrum of 1·20NTf₂ showing the 6+ corresponding to the loss of 6 NTf₂⁻ anions.
Figure S11. High-resolution ESI-mass spectrum of 1·20NTf₂ showing the 8+ corresponding to the loss of 6 and 8 NTf₂⁻ anions.
4. **Encapsulation of C₆₀ within 1**

Cage 1 (20 mg, 0.0019 mmol, 1 equiv) and C₆₀ (5.4 mg, 0.0076 mmol, 4 equiv) were mixed in CD₃CN (0.5 mL). Cp₂Co (3.56 mg, 0.019 mmol, 10 equiv) was added into the mixture at room temperature. The reaction was kept at room temperature overnight. Then AgNTf₂ (11.1 mg, 0.029 mmol, 15 equiv) was added to the mixture, resulting in formation of C₆₀ ⊂ 1 which was characterized by NMR spectroscopy.

Figure S12-S17 are the data recorded 1 day after the addition of AgNTf₂.

Figure S18-S24 are the data recorded 10 days after the addition of AgNTf₂.

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**Figure S12.** ¹H NMR (500 MHz, 298 K, CD₃CN) of C₆₀⊂1. The sample was measured 1 day after the addition of AgNTf₂.
Figure S13. Expansion of the imine region of the $^1$H NMR (500 MHz, 298 K, CD3CN) of C$_{60}$⊂ 1. The signals are consistent with the presence of 1-$S_4$, 1-$C_3$ and 1-$T$ diastereomers in the mixture.
Figure S14. $^{13}$C NMR (126 MHz, 298 K, CD$_3$CN) of C$_{60}$⊂1. The sample was measured 1 day after the addition of AgNTf$_2$.

Figure S15. Aromatic region of the $^{13}$C NMR (126 MHz, 298 K, CD$_3$CN) of C$_{60}$⊂1. The sample was measured 1 day after the addition of AgNTf$_2$. 
Figure S16. $^1$H-$^1$H COSY spectrum (500 MHz, 298 K, CD$_3$CN) of [C$_{60}$ ⊂ 1]. The sample was measured 1 day after the addition of AgNTf$_2$.

Figure S17. HSQC spectrum (500 MHz, 298 K, CD$_3$CN) of [C$_{60}$ ⊂ 1]. The sample was measured 1 day after the addition of AgNTf$_2$. 
Figure S18. $^1$H NMR (500 MHz, 298 K, CD$_3$CN) of C$_{60}$$\subset$1. The sample was measured 10 days after the addition of AgNTf$_2$.

Figure S19. Aromatic region of the $^1$H NMR (500 MHz, 298 K, CD$_3$CN) of C$_{60}$$\subset$1. The sample was measured 10 days after the addition of AgNTf$_2$. 
Figure S20. $^{13}$C NMR (126 MHz, 298 K, CD$_3$CN) of C$_{60}$⊂I. The sample was measured 10 days after the addition of AgNTf$_2$.

Figure S21. Aromatic region of the $^{13}$C NMR (126 MHz, 298 K, CD$_3$CN) of C$_{60}$⊂I. The sample was measured 10 days after the addition of AgNTf$_2$. 
Figure S22. $^1$H-$^1$H COSY spectrum (500 MHz, 298 K, CD$_3$CN) of [C$_{60}$ ⊂ 1]. The sample was measured 10 days after the addition of AgNTf$_2$.

Figure S23. HSQC spectrum (500 MHz, 298 K, CD$_3$CN) of [C$_{60}$ ⊂ 1]. The sample was measured 10 days after the addition of AgNTf$_2$. 
Figure S24. $^1$H DOSY NMR (400 MHz, 298 K, CD$_3$CN) of C$_{60}$C$_1$. The sample was measured 10 days after the addition of AgNTf$_2$. Vertical axis corresponds to the diffusion coefficient $D$ (in cm$^2$s$^{-1}$).
5. Electrochemistry

Electrochemical experiments were performed with a SP-150 potentiostat manufactured by BioLogic. Measurements were conducted under Ar atmosphere with a glassy carbon working electrode (diameter 3 mm) and a platinum auxiliary electrode at a scan rate of 50 mV s$^{-1}$. A silver wire was used as reference electrode. All three electrodes were immersed in a CH$_3$CN solution (3 mL) containing TBAN$\text{F}_2$ (0.1 M) as a supporting electrolyte and Cage 1 or ligand A (0.001 M). In all cases, ferrocene was used as an internal standard, and all reduction potentials are reported with respect to the E$_{1/2}$ of the Fe/Fe$^+$ redox couple.

![Cyclic voltammetry](image)

**Figure S25.** Cyclic voltammetry (three scans) of ligand A in MeCN (0.1 M nBu$_4$N$^+$Tf$_2$N$^-$) at room temperature. The intensity of signals decreased after each cycle.
6. VOIDOO calculations

In order to determine the size of the inner cavity of 1, VOIDOO calculations based on the crystal structure of 1 were performed based on the crystal structure. A virtual probe with a radius of 1.4 Å (default, water-sized) was employed, and the following parameters were changed from their default settings:

- Maximum number of volume-refinement cycles: 30
- Minimum size of secondary grid: 3
- Grid for plot files: 0.2
- Primary grid spacing: 0.1
- Plot grid spacing: 0.1

![Figure S26. Void volume of 1 (1100 Å³) calculated by VOIDOO.](image-url)
7. Host-guest chemistry

Figure S27. Aromatic region of the $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) for pyrene (top), [Pyrene $\subset$ 1] (middle), cage 1 (bottom).

Figure S28. Aromatic region of the $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) for perylene (top), Perylene with 1 (middle), cage 1 (bottom).
**Figure S29.** Aromatic region of the $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) for coronene (top), Coronene with 1 (middle), cage 1 (bottom).

**Figure S30.** Aromatic region of the $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) for Corannulene (top), Corannulene with 1 (middle), cage 1 (bottom).
Figure S31. Aromatic region of the $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) for ortho-carborane with 1 (top), cage 1 (bottom).

Figure S32. Aromatic region of the $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) for C$_{60}$ with 1 (top), cage 1 (bottom).
8. Titrations

Figure S33. $^1$H NMR titration (400 MHz, 298 K) of KBF$_3$Ph into a solution of 1 (0.17 mM) in CD$_3$CN (equivalents of anion added are labelled on individual spectra)
Figure S34. $^1$H NMR titration (400 MHz, 298 K) of KBF$_3$Ph into a solution of 1 in CD$_3$CN (equivalents of anion are labelled on individual spectra)
Figure S35. $^{19}$F NMR titration (376 MHz, 298 K) of KBF$_3$Ph into a solution of 1 in CD$_3$CN, with hexafluorobenzene in a capillary as external standard. (Equivalents of anion are labelled on individual spectra).

Figure S36. Expansion of the triflimide signal during the $^{19}$F NMR titration (376 MHz, 298 K) of KBF$_3$Ph into a solution of 1 in CD$_3$CN.
Figure S37. Expansion of the KBF₃Ph signal of ¹⁹F NMR titration (376 MHz, 298 K) of KBF₃Ph into a solution of 1 in CD₃CN.
Figure S38. $^1$H NMR titration (400 MHz, 298 K) of TBABF$_4$ into a solution of 1 in CD$_3$CN (equivalents of anion are labelled on individual spectra)
Figure S39. $^1$H NMR titration (400 MHz, 298 K) of cesium carborane into a solution of 1 in CD$_3$CN (equivalents of anion are labelled on individual spectra)
Figure S40. $^1$H NMR titration (400 MHz, 298 K) of cesium carborane into a solution of 1 in CD$_3$CN (equivalents of anion are labelled on individual spectra)
9. **Redox-switching experiment of cage 1**

![Diagram showing redox-switching experiment of cage 1](image)

**Figure S41.** Control experiments of cage 1 upon the addition of Cp₂Co and AgNTf₂, showing loss of signals in the ¹H NMR spectrum (500 MHz, 298 K, CD₃CN) in the presence of Cp₂Co and the recovery of 1 with the addition of AgNTf₂.
10. **Phase transfer of cage 1 by anion exchange**

Cage 1 (1 mg, 0.094 mmol) was dissolved in CD$_3$CN (0.4 mL). Its $^1$H NMR spectrum was recorded. EtOAc (0.3 mL) was then added into the solution. This combined solution was then added to a Na$_2$SO$_4$ (0.5 mg, 2.6 mmol) solution in D$_2$O (0.6 mL) to form a bilayer (organic phase: red; water phase: colourless). After shaking, the red organic phase became light brown, and the water solution turned red. The presence of cage 1 was confirmed by $^1$H NMR in D$_2$O.

![Figure 42](image.png)

**Figure 42.** (a) the formation of bilayer phase; (b) phase-transfer after shaking.

![Figure S43](image.png)

**Figure S43.** $^1$H NMR (500 MHz) of cage 1 before phase transfer (bottom, in CD$_3$CN) and after phase transfer (top, in D$_2$O)
Cage 1 (2 mg, 0.00019 mmol, 1 equiv) and C\textsubscript{60} (0.5 mg, 0.00076 mmol, 4 equiv) were mixed in CD\textsubscript{3}CN (0.5 mL). Cp\textsubscript{2}Co (0.4 mg, 0.0019 mmol, 10 equiv) was added into the mixture at room temperature. The reaction was kept at room temperature overnight. Then AgNTf\textsubscript{2} (1.1 mg, 0.0029 mmol, 15 equiv) was added to the mixture, and the formation of C\textsubscript{60} ⊂ 1 was characterized by NMR spectroscopy. EtOAc (0.3 mL) was then added into the solution. This solution was then added to a Na\textsubscript{2}SO\textsubscript{4} (1 mg, 5.2 mmol) D\textsubscript{2}O (0.6 mL) solution to form a bilayer (organic phase: red; water phase: colorless). After shaking, the red organic phase became light brown, and the water solution turned red. The presence of cage 1 containing no C\textsubscript{60} was confirmed by \textsuperscript{1}H NMR in D\textsubscript{2}O (Figure S44). C\textsubscript{60} can be recovered by filtration of the bilayer liquid through a filter paper.

**Figure S44.** (a) The formation of bilayer phase for C\textsubscript{60} ⊂ 1; (b) phase-transfer after shaking.
Figure S45. $^1$H NMR (500 MHz) of $C_{60} \subset 1$ before phase transfer (bottom, in CD$_3$CN) and after phase transfer (top, in D$_2$O)
11. X-ray crystallography

Crystals of \([\text{Fe}_4\text{L}_6] \cdot 8\text{CB}_{11}\text{H}_{12} \cdot 3\text{NTf}_2 \cdot 4.5\text{CH}_3\text{CN} + 8.8\text{ anions + solvent}\) were grown by vapour diffusion of diethyl ether into an acetonitrile solution of \([\text{Fe}_4\text{L}_6] \cdot 20\text{NTf}_2\) containing excess \(\text{CsCB}_{11}\text{H}_{12}\). Data were collected at Beamline I19 of Diamond Light Source employing silicon double crystal monochromated synchrotron radiation (0.6889 Å) with \(\omega\) and \(\psi\) scans at 100(2) K. Data integration and reduction were undertaken with Xia2. Subsequent computations were carried out using the WinGX-32 graphical user interface. Multi-scan empirical absorption corrections were applied to the data using the AIMLESS tool in the CCP4 suite. The structure was solved by direct methods using SHELXT then refined and extended with SHELXL. In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary.

The crystals employed in this study were small and weakly diffracting, immediately losing solvent after removal from the mother liquor. Rapid handling prior to flash cooling in the cryostream was required to collect data. Despite these measures and the use of synchrotron radiation few reflections at greater than 0.95 Å resolution were observed and the data were trimmed accordingly. Nevertheless, the quality of the data is far more than sufficient to establish the connectivity of the structure. The asymmetric unit was found to contain one complete \([\text{Fe}_4\text{L}_6]\) assembly and associated counterions and solvent molecules.

Due to the less than ideal resolution, bond lengths and angles within pairs of organic ligands were restrained to be similar to each other and thermal parameter restraints (SIMU, RIGU, ISOR) were applied to all atoms except for iron. DFIX and DANG restraints were also applied to some atoms within the organic ligands.

The anions within the structure show significant evidence of disorder. Two triflimide anions were modelled as disordered over two locations and many anions were modelled with partial occupancy. The occupancies of the disordered anions were allowed to refine freely and then fixed at the obtained values. Some lower occupancy disordered atoms were modelled with isotropic thermal parameters and bond length restraints were applied to facilitate realistic modelling of the disordered triflimide anions. The \(\text{CB}_{11}\text{H}_{12}^-\) anions were modelled as rigid groups; for these anions the carbon site could not be clearly discerned from the electron density map so all atoms of the \(\text{CB}_{11}\text{H}_{12}^-\) anions were modelled as boron.

Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from disordered solvent and 8.8 unresolved anions per \(\text{Fe}_4\text{L}_4\) tetrahedron (required in order to achieve charge balance). Consequently the SQUEEZE function of PLATON was employed to remove the contribution of the electron density associated with these remaining anions and further highly disordered solvent, which gave a potential solvent accessible void of 12998 Å³ per unit cell (a total of approximately 3818 electrons). Since the
remaining anions could not be assigned conclusively to triflimide or CB$_{11}$H$_{12}^-$; they were not included in the formula. Similarly, diffuse solvent molecules could not be assigned to acetonitrile or diethyl ether. Consequently, the molecular weight and density given above are underestimated.

CheckCIF gives 6 A and 10 B level alerts. These alerts (both A and B level) result from the poor diffraction properties (low resolution) and thermal motion and/or unresolved disorder of some anions and solvent molecules (large average Ueqs, short contacts).

Crystallographic data have been deposited with the CCDC (CCDC 1935513).

Formula C$_{311.20}$H$_{387.90}$B$_{90.20}$F$_{18}$Fe$_4$N$_{55.50}$O$_{36}$S$_6$, $M$ 7214.87, Monoclinic, space group $C$ $c$ (#9), $a$ 33.3570(2), $b$ 32.3478(3), $c$ 45.8124(3) Å, $\beta$ 102.3200(10), $V$ 48294.4(6) Å$^3$, $D$$_c$ 0.992 g cm$^{-3}$, $Z$ 4, crystal size 0.040 by 0.030 by 0.030 mm, colour purple, habit block, temperature 100(2) Kelvin, $\lambda$(Synchrotron) 0.6889 Å, $\mu$(Synchrotron) 0.188 mm$^{-1}$, $T$(Analytical)$_{min,max}$ 0.9771-0.440761, 1.0, 2$\theta$$_{max}$ 42.52, $hkl$ range -34 32, -30 34, -48 47, $N$ 89539, $N$$_{ind}$ 51296 ($R$$_{merge}$ 0.0565), $N$$_{obs}$ 34171 ($I$ $> 2\sigma(I)$), $N$$_{var}$ 4647, residuals $^*$ $R1(F)$ 0.1030, $wR2(F^2)$ 0.2822, GOF(all) 1.027, $\Delta$$\rho$$_{min,max}$ -0.336, 0.610 e$^{-}$ Å$^{-3}$.

$^*$ $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ for $F_o \times 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2)/\Sigma(wF_c^2)^2)^{1/2}$ all reflections

$w=1/[\sigma^2(F_o^2)+(0.2000P)^2]$ where $P=(F_o^2+2F_c^2)/3$
12. Geometry optimized models

Cage $C_{60} \subset 1$ is comprised of four vertices with metal centers having either in $\Lambda$ or $\Delta$ stereochemical configuration. The mixture of $\Lambda$ and $\Delta$ configurations can give rise to five diastereomers including two pairs of enantiomers: $\Lambda\Lambda\Lambda\Lambda$ ($T$-symmetric), $\Lambda\Lambda\Lambda\Delta$ ($C_3$-symmetric), $\Lambda\Lambda\Delta\Delta$ ($S_4$-symmetric), $\Lambda\Delta\Delta\Delta$ ($C_3$-symmetric) and $\Delta\Delta\Delta\Delta$ ($T$-symmetric). PM3 geometry optimized models of three diastereomers ($\Delta\Delta\Delta\Delta$, $\Lambda\Delta\Lambda\Lambda$ and $\Lambda\Lambda\Delta\Lambda$) including $C_{60}$ are shown below (Figure S45 and Tables S1-S3). The $\Delta\Delta\Delta\Delta$ diastereomer is based on the free cage crystal structure while the other diastereomers were generated by inverting the stereo-configuration of one or two vertices from $\Delta$ to $\Lambda$. Note that modelling was performed in the absence of anions which led, in a first modelling attempt, to extreme ionic repulsion between the trimethylammonium moieties which is not observed in the crystal structure due to charge stabilization by counter-anions; therefore, the trimethylammonium moieties were replaced by tert-butyl moieties to avoid ionic repulsion and reduce calculation time.

Geometry optimized structures were modelled with semi-empirical methods using PM3 models using SCIGRESS software (Fujitsu Limited, Tokyo, Japan, 2013) version FJ 2.6 (EU 3.1.9) Build 5996.8255.20141202. The Cartesian coordinates for all models are given below.
Figure S46. PM3-optimized structures of the three diastereomers of C₆₀⊂₁. Fe⁺⁺ centers with Δ and Λ stereochemistry are colored orange and dark red, respectively.

Table S1. Cartesian coordinates (in Å) for the PM3 model of the tert-butyl derivative of C₆₀⊂₁-ΔΔΔΔ.

| Element | X  | Y  | Z  | H  | C  | N  | C  | H  | C  | H  | C  | H  | C  | H  | C  | H  | C  | H  |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Fe      | 12.223332 | 7.366899 | 28.651222 | H  | 15.150004 | 3.030149 | 29.695315 |
| Fe      | 2.833352 | 16.559087 | 14.474671 | C  | 14.533093 | 3.116423 | 27.617464 |
| Fe      | 21.839562 | 14.056179 | 13.605780 | H  | 15.013169 | 2.166092 | 27.343525 |
| Fe      | 14.501821 | 26.397077 | 26.245224 | C  | 13.831027 | 3.851390 | 26.658550 |
| O      | 8.291000 | 11.133352 | 25.446344 | H  | 13.751150 | 3.489175 | 25.624721 |
| O      | 4.274299 | 12.838143 | 24.122589 | C  | 13.222613 | 5.049335 | 27.031707 |
| O      | 9.538264 | 9.119409 | 18.774730 | C  | 12.433282 | 5.847152 | 26.082275 |
| O      | 6.351285 | 12.031637 | 17.340867 | H  | 12.360810 | 5.515822 | 25.017984 |
| N      | 13.308106 | 5.530192 | 28.326942 | C  | 11.003249 | 7.684246 | 25.642504 |
| N      | 11.840824 | 6.919255 | 26.549034 | C  | 9.664251 | 7.322492 | 25.468814 |
| N      | 2.762896 | 16.352427 | 16.639342 | H  | 9.230548 | 6.473123 | 26.011185 |
| N      | 1.403276 | 18.073675 | 15.044188 | C  | 8.875504 | 8.033978 | 24.570860 |
| N      | 6.253689 | 11.960438 | 24.868575 | H  | 7.827111 | 7.747835 | 24.420106 |
| N      | 8.009964 | 10.643627 | 18.021753 | C  | 9.422577 | 9.099787 | 23.854200 |
| C      | 6.258077 | 14.313117 | 27.963075 | C  | 10.756925 | 9.465835 | 24.048155 |
| C      | 8.310452 | 8.628206 | 14.722797 | H  | 11.180810 | 10.309988 | 23.488932 |
| C      | 13.990051 | 4.803689 | 29.247412 | C  | 11.553018 | 8.760998 | 24.943196 |
| H      | 14.019838 | 5.219889 | 30.264382 | H  | 12.611801 | 9.037675 | 25.070478 |
| C      | 14.611284 | 3.593645 | 28.920756 | C  | 4.879669 | 13.623533 | 19.088784 |
Table S2. Cartesian coordinates (in Å) for the PM3 model of the \textit{tert}-butyl derivative of C_{40}I-\Delta\Delta\Delta\Delta.

| Atom | X       | Y       | Z       | C   |
|------|---------|---------|---------|-----|
| Fe   | 12.340419 | 7.448859 | 28.67633 | C   |
| Fe   | 2.765935  | 16.363929 | 14.398839| C   |
| Fe   | 21.703489 | 14.010424 | 13.477607| C   |
| Fe   | 14.635139 | 26.610692 | 26.493994| C   |
| O    | 8.280665  | 11.306292 | 25.541767| H   |
| O    | 4.263658  | 13.025792 | 24.234938| H   |
| O    | 9.371727  | 9.128290  | 18.868611| H   |
| O    | 6.216581  | 12.065667 | 17.439976| H   |
| N    | 13.545781 | 7.504297  | 28.265265| C   |
| N    | 9.116261  | 7.097022  | 26.557076| H   |
| N    | 2.554923  | 16.170363 | 16.558361| H   |
| N    | 1.216079  | 17.797292 | 14.846830| H   |
| N    | 6.267380  | 12.189777 | 24.964124| C   |
| N    | 7.895292  | 10.706652 | 18.123340| H   |
| C    | 5.946390  | 14.241596 | 28.231626| H   |
| C    | 8.014502  | 8.909959  | 14.680823| H   |
| C    | 14.291765 | 4.976927  | 29.134082| H   |
| C    | 14.307445 | 5.334410  | 30.173150| H   |
| C    | 14.991663 | 8.358650  | 28.728841| H   |
| C    | 15.581887 | 3.268060  | 29.467718| C   |
| C    | 14.927544 | 4.340009  | 27.400361| H   |
| C    | 14.886756 | 4.166229  | 26.495526| H   |
| C    | 14.088676 | 3.861612  | 25.442258| C   |
| C    | 13.473527 | 5.293489  | 26.947363| H   |
| C    | 12.623302 | 6.086291  | 26.049292| H   |
| C    | 12.570853 | 5.789895  | 29.746034| H   |
| C    | 11.089554 | 7.857281  | 25.676137| C   |
| C    | 9.726965  | 7.540604  | 25.605522| H   |
| C    | 9.305981  | 6.726808  | 26.206512| H   |
| C    | 8.903693  | 8.247519  | 24.736369| C   |
| C    | 7.389480  | 7.990692  | 24.667783| C   |
| C    | 9.429373  | 9.271031  | 23.944585| H   |
| C    | 10.785801 | 9.594835  | 24.037533| C   |
| C    | 11.191599 | 10.405798 | 23.420391| H   |
| C    | 11.620387 | 8.889644 | 24.897260| O   |
| C    | 12.693542 | 9.173323  | 24.942644| H   |
| C    | 4.724219  | 13.632350 | 19.164836| C   |
| C    | 3.458554  | 13.247644 | 18.716145| H   |
| C    | 3.022283  | 12.297680 | 19.490945| H   |
| C    | 2.742277  | 14.072813 | 17.854822| H   |
| C    | 1.741227  | 17.767229 | 17.528286| C   |
| C    | 3.299344  | 15.286748 | 17.440966| H   |
| C    | 4.570388  | 15.671470 | 17.874770| H   |
| C    | 5.009643  | 16.632039 | 15.764011| H   |
| C    | 5.278109  | 14.841236 | 18.736336| O   |
| C    | 6.269566  | 15.148235 | 19.089513| O   |
| C    | 1.652424  | 16.960084 | 17.084801| O   |
| C    | 1.428174  | 16.999775 | 18.161422| C   |
| C    | 0.888263  | 17.838508 | 16.189338| N   |
| C    | -0.130930 | 16.882156 | 15.736872| C   |
| C    | -0.357377 | 18.675805 | 17.738311| N   |
| C    | -0.841637 | 19.458151 | 15.765079| N   |
| C    | -1.653156 | 20.108701 | 16.122460| C   |
| C    | -0.517054 | 19.419276 | 14.414315| N   |
| C    | -0.165314 | 20.024658 | 13.684185| C   |
| C    | 0.515255  | 18.573640 | 13.982565| C   |
| C    | 0.802681  | 18.499119 | 12.924270| C   |
| C    | 5.347118  | 12.567112 | 23.925267| H   |
| C    | 7.452105  | 11.457150 | 24.654047| H   |
| C    | 8.858584  | 9.973759  | 22.957683| H   |
| C    | 8.810972  | 9.623395  | 21.600437| H   |
| C    | 9.566997  | 8.843904  | 21.376857| C   |
| C    | 8.155499  | 10.258014 | 20.577891| H   |
| C   | 13.365794 | 12.936664 | 18.956454 | C   | 11.849002 | 19.172470 | 21.599213 |
|-----|-----------|-----------|-----------|-----|-----------|-----------|-----------|
| C   | 13.339430 | 14.654327 | 24.153127 | C   | 12.416043 | 19.369254 | 20.352370 |
| C   | 12.212520 | 15.568837 | 24.284649 | C   | 11.799632 | 18.781066 | 19.169968 |
| C   | 11.001937 | 15.266764 | 23.686637 | C   | 12.865305 | 18.343798 | 18.277003 |
| C   | 15.565529 | 15.036192 | 23.175898 | C   | 15.896369 | 17.341936 | 22.382679 |
| C   | 14.553267 | 15.450482 | 24.023608 | C   | 14.830503 | 17.779087 | 23.275653 |
| C   | 15.822153 | 15.517248 | 18.697409 | C   | 14.072338 | 18.821739 | 22.596131 |
| C   | 16.531316 | 15.372994 | 21.050627 | C   | 14.669043 | 19.028890 | 21.282621 |
| C   | 16.439424 | 16.105825 | 19.880000 | C   | 13.862513 | 19.295031 | 20.190265 |
| C   | 16.254514 | 16.006273 | 22.333717 | C   | 14.140028 | 18.661338 | 18.907742 |
| C   | 12.725201 | 17.173065 | 17.552873 | C   | 15.209747 | 17.792462 | 18.782194 |
| C   | 10.647307 | 18.025095 | 19.294285 | C   | 16.059017 | 17.511538 | 19.932617 |
| C   | 12.698568 | 18.891482 | 22.749990 | C   | 15.795001 | 18.113271 | 21.150659 |
Table S3. Cartesian coordinates (in Å) for the PM3 model of the tert-butyl derivative of C_{60}I-ΛΛΔΔ.

| Element | X        | Y        | Z        | Charge |
|---------|----------|----------|----------|--------|
| Fe      | 12.489452| 7.389133 | 28.822045| C      |
| Fe      | 2.851060 | 16.199874| 14.290209| C      |
| Fe      | 21.862734| 26.204790| 13.462460| C      |
| Fe      | 14.278866| 26.769517| 26.393248| C      |
| O       | 6.754625 | 11.082151| 26.196631| C      |
| O       | 3.279626 | 13.009765| 23.979602| H      |
| O       | 9.728136 | 9.434283 | 19.939325| C      |
| O       | 6.594459 | 11.922187| 17.774758| C      |
| N       | 11.308341| 5.598182 | 28.579099| C      |
| N       | 12.925461| 6.813522 | 25.758738| C      |
| N       | 2.659758 | 16.007540| 16.441474| H      |
| N       | 1.310676 | 17.644188| 14.746224| H      |
| N       | 5.052352 | 12.094780| 25.142752| C      |
| N       | 8.223107 | 10.746920| 18.828341| H      |
| C       | 5.006831 | 14.259307| 28.158767| C      |
| C       | 9.208382 | 8.908704 | 15.553104| C      |
| C       | 10.533629| 4.970950 | 29.499178| C      |
| H       | 10.465886| 5.453392 | 30.484799| C      |
| C       | 9.865818 | 3.775786 | 29.212849| H      |
| C       | 9.250238 | 3.294610 | 29.961612| C      |
| C       | 9.993035 | 2.370704 | 27.950384| H      |
| C       | 9.477130 | 2.266843 | 27.707757| H      |
| C       | 10.790478 | 3.583771 | 26.992932| C      |
| H       | 10.910502 | 3.403165 | 25.991149| C      |
| C       | 11.440596| 5.026817 | 27.327572| H      |
| C       | 12.315650| 7.518557 | 26.373705| H      |
| C       | 12.433626| 5.277893 | 26.376933| H      |
| C       | 13.812839| 7.451170 | 25.799645| C      |
| C       | 15.021981| 6.839052 | 25.452058| C      |
| C       | 15.347740| 5.911030 | 25.938201| C      |
| C       | 15.801179| 7.386942 | 24.439268| C      |
| C       | 16.735266| 6.891320 | 24.138825| C      |
| C       | 15.370875| 8.535301 | 23.769378| H      |
| C       | 14.206815| 9.188634 | 24.182468| C      |
| C       | 13.890670| 10.113343| 23.628472| C      |
| C       | 13.419771| 8.646634 | 25.193584| C      |
| C       | 12.471450| 9.132728 | 25.470530| C      |
| C       | 4.674242 | 13.438948| 19.136981| C      |
| C       | 3.478734 | 13.025726| 18.543554| H      |
| C       | 3.058218 | 12.057141| 18.811649| H      |
| C       | 2.827467 | 13.854397| 17.635843| H      |
| C       | 1.871735 | 15.535605| 17.292607| H      |
| C       | 3.380581 | 15.099224| 17.319700| H      |
| C       | 4.607733 | 15.491541| 17.859591| H      |
| C       | 5.056063 | 16.463779| 17.602985| C      |
| C       | 5.250200 | 16.657374| 18.768290| O      |
| C       | 6.199464 | 14.974146| 19.215274| O      |
| C       | 1.778456 | 16.811413| 16.979758| C      |
| C       | 1.568985 | 16.856675| 18.062169| O      |
| C       | 1.013303 | 17.022929| 16.094939| N      |
| C       | 0.017493 | 18.545583| 16.578682| N      |
| C       | -0.020757| 18.575764| 17.663735| C      |
| C       | -0.002046| 19.342652| 15.694196| N      |
| C       | -1.945211| 20.008956| 16.062620| N      |
| C       | -0.410587| 19.277814| 14.336064| N      |
| C       | -0.968378| 19.888347| 13.612084| C      |
| C       | 0.600469 | 18.420495| 13.899636| C      |
| C       | 0.862417 | 18.330943| 12.826087| C      |
| C       | 4.384097 | 12.498216| 23.924513| H      |
| C       | 6.235983 | 11.372979| 25.121270| C      |
| C       | 6.672664 | 11.003812| 23.066378| H      |
| C       | 8.019101 | 10.227074| 23.735546| H      |
| C       | 8.584733 | 9.916516 | 22.473038| C      |
| C       | 9.473366 | 9.269039 | 22.439219| C      |
| C       | 8.054403 | 10.423815| 21.310696| H      |
| C     | 13.123138 | 12.987734 | 19.144533 | C     | 12.080866 | 19.165641 | 22.131773 |
|-------|-----------|-----------|-----------|-------|-----------|-----------|-----------|
| C     | 13.317397 | 14.430937 | 24.423111 | C     | 12.634490 | 19.388412 | 20.883254 |
| C     | 12.256854 | 15.410809 | 24.623099 | C     | 11.956552 | 18.904070 | 19.687448 |
| C     | 11.016962 | 15.221149 | 24.039222 | C     | 12.972080 | 18.444143 | 18.748671 |
| C     | 15.543094 | 14.716549 | 23.410983 | C     | 16.011942 | 17.033750 | 22.726806 |
| C     | 14.578715 | 15.152132 | 24.302578 | C     | 14.995796 | 17.493343 | 23.665234 |
| C     | 15.740447 | 15.411167 | 18.957908 | C     | 14.295630 | 18.617515 | 23.057178 |
| C     | 16.486102 | 15.098453 | 21.283127 | C     | 14.878302 | 18.852497 | 21.742077 |
| C     | 16.419478 | 15.895607 | 20.153602 | C     | 14.069159 | 19.227080 | 20.683811 |
| C     | 16.278386 | 15.681511 | 22.602674 | C     | 14.277295 | 18.643365 | 19.365034 |
| C     | 12.739126 | 17.324368 | 17.969747 | C     | 15.283960 | 17.713934 | 19.171121 |
| C     | 10.759063 | 18.219950 | 19.800792 | C     | 16.135828 | 17.318883 | 20.285380 |
| C     | 12.932900 | 18.769708 | 23.246183 | C     | 15.938029 | 17.873100 | 21.537939 |
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