Electronic Supporting Information for

Tetrahedral metal-organic cages with cube-like cavities for selective encapsulation of fullerene guests and their spincrossover properties

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1. Experimental Section

All reagents and solvents were reagent grade, purchased from commercial sources and used without further purification.

Infrared spectra were measured with a Nicolet 6700 FT-IR spectrophotometer with ATR attachment in the range of 500-4000 cm⁻¹ region. Nuclear magnetic resonance (NMR) spectra were recorded on AVANCE III (400 MHz) instrument at 298 K using standard Bruker software, and chemical shifts were reported in parts per milion (ppm) downfield from tetramethylsilane. UV/vis absorbance spectra were collected on Shimadzu UV-2101 PC scanning spectrophotometer. The thermogravimetric analysis (TGA) were carried out by using TGA/1100SF thermograbinetric analyzer with a heating rate of 15 °C·min⁻¹ from 25 to 900 °C under N₂ atmosphere. Variabletemperature magnetic susceptibilities were performed on a Quantum Design MPMS-XL-7 SQUID magnetometer with an applied magnetic field of 1000 Oe over the temperature range of 2-400 K. The host-guest complexes were prepared by the equilibration of C₆₀ and cage compounds in CH₃CN at 50 °C for 1 week and filtered. The empty cages and the encapsulated cages can be separated by fractional crystallization, due to faster crystallization rate of the encapsulated cages. Diethyl ether was added dropwise to the filtrate, and the first part of the precipitate was collected, which was confirmed as the complete encapsulated cages by HRMS. The molar susceptibility was corrected for diamagnetic contributions using Pascal's constants and the increment method. Samples were restrained with petroleum jelly to prevent decomposing of the crystallites. High-resolution mass spectra (HRMS) were obtained on a Quadrupole-time-of-flight (Q-TOF) mass spectrometer and the fragment voltage was set at 175 V. General procedure for the host-guest investigations: crystalline samples of cage 1 or 2 (about 20 mg) were completely dissolved in 0.6 mL CD₃CN in an NMR tube, and the fullerene guest molecules (about 5 equiv.) were added as a solid. The mixture was sonicated for 5 min and allowed to equilibrate at 50 °C for at least 24 hours before the measurement of NMR and mass spectra. The Raman spectra of the samples deposited on a glass slide were obtained from Invia Raman spectra (Reinshaw England) with 785 nm excitation line.

2. Synthesis

2.1 Synthesis of 1,4-bis(2-bromoethoxy)benzene



A mixture of hydroquinone (3.303 g, 30 mmol) and anhydrous potassium carbonate (11.056 g, 80 mmol) in a 250 mL three round bottom flask containing 80 mL acetone was stirred under nitrogen atmosphere at 60 °C for two hours. Then, excess 1,2-dibromoethane (40 mL) was added. The reaction mixture was further stirred under N₂ atmosphere at 60 °C for 24 h and filtered. The filtrate was evaporated with a rotary evaporator to removed 1,2-dibromoethane and solvent. The residue was dissolved in 100 mL chloroform, and washed with sodium hydroxide solution (3×50mL), water (2×50 mL). And the extracting solution was dried over anhydrous MgSO₄. After CHCl₃ was removed and dried under vacuum in 40 °C to give 1,4-bis(2-bromoethoxy)benzene as a pale brown powder (Yield: 35 %). ATR-FTIR (*v* cm⁻¹): 3050, 2944, 2927, 1505, 1459, 1429, 1283, 1220, 1029, 927, 820, 746. ¹H NMR (400 MHz: CDCl₃, δ ppm): 6.89 (s, 4H¹), 4.25-4.28 (t, 4H²), 3.62-3.65 (t, 4H³).



Figure. S1. ATR FT-IR spectrum of 1,4-bis(2-bromoethoxy)benzene.





2.2 Synthesis of 1,4-bis(2-bromoethoxy)naphthalen



1,4-bis(2-bromoethoxy)naphthalene was prepared in a manner analogous to that of 1,4-bis(2-bromoethoxy)benzene except that 1,4-dihydroxynaphthalene (4.805 g, 30 mmol) was used instead of hydroquinone (Yield: 23 %). ATR-FTIR (v cm⁻¹): 3059, 2966, 2919, 1628, 1591, 1450, 1416, 1375, 1240, 1221, 1100, 764, 739. ¹H NMR (400 MHz: CDCl₃, δ ppm): 8.28-8.30 (m, 2H¹), 7.55-7.58 (m, 2H²), 6.72 (s, 2H³), 4.43-4.46 (t, 4H⁴), 3.77-3.81 (t, 4H⁵).



Figure. S3. ATR FT-IR spectrum of 1,4-bis(2-bromoethoxy)naphthalene.



2.3 Synthesis of 1,4-bis(2-(1-(imidazole-2-carbaldehyde))bromoethoxy)benzene



Imidazole-2-carboxaldehyde (1.35 g, 14 mmol), 1,4-bis(2-bromoethoxy)benzene (1.62 g, 5 mmol), and potassium carbonate (1.38 g, 10 mmol) were added to a 50 mL flask containing 20 mL DMF in nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 3 days and then filtered. The filtrate was extracted with ethyl acetate (4×15 mL), collecting the organic phase, washed with saturated aqueous solution of potassium chloride, dried with anhydrous magnesium sulfate, removed the solvent on a rotary evaporator and dried under vacuum in 40 °C to give the desired product as yellow crystals (Yield: 56 %). ATR-FTIR (ν cm⁻¹): 3086, 2930, 2829, 1681, 1511, 1477, 1456, 1410, 1364, 1283, 1230, 1157, 1084, 1048, 810, 777. ¹H NMR (400 MHz: CD₃CN, δ ppm): 9.73 (s, 2H¹), 7.45 (d, 2H²), 7.25 (d, 2H³), 6.79 (s, 4H⁴), 4.74-4.76 (t, 4H⁵), 4.21-4.24 (t, 4H⁶).



carbaldehyde))bromoethoxy)benzene.



Figure. S6. ¹H NMR spectrum of 1,4-bis(2-(1-(imidazole-2-carbaldehyde))bromoethoxy)benzene.

2.4Synthesisof1,4-bis(2-(1-(imidazole-2-
carbaldehyde))bromoethoxy)naphthalene



Imidazole-2-carboxaldehyde (1.35 g, 14 mmol), 1,4-bis(2bromoethoxy)naphthalene (1.87 g, 5 mmol), and potassium carbonate (1.38 g, 10 mmol) were added to a 50 mL flask containing 20 mL DMF in nitrogen atmosphere.

The reaction mixture was stirred at 50 °C for 3 days and then filtered. The filtrate was extracted with ethyl acetate (4×15 mL), collecting the organic phase, washed with saturated aqueous solution of potassium chloride, dried with anhydrous magnesium sulfate, removed the solvent on a rotary evaporator and dried under vacuum in 40 °C to give the desired product as yellow crystals (Yield: 51 %). ATR-FTIR ($v \text{ cm}^{-1}$): 3112, 2923, 2845, 1686, 1596, 1473, 1457, 1407, 1332, 1274, 1241, 1107, 804, 763. ¹H NMR (400 MHz: CD₃CN, δ ppm): 9.77 (s, 2H¹), 8.03-8.05 (m, 2H²), 7.59 (s, 2H³), 7.51-7.53 (m, 2H⁴), 7.27 (s, 2H⁵), 6.76 (s, 2H⁶), 4.91-4.93 (t, 4H⁷), 4.40-4.42 (t, 4H⁸).



Figure. S7. ATR FT-IR spectrum of 1,4-bis(2-(1-(imidazole-2-carbaldehyde))bromoethoxy)naphthalene.



2.5 Synthesis of cage 1



1,4-bis(2-(1-(imidazole-2-carbaldehyde))bromoethoxy)benzene (0.0708 g, 0.2 mmol), (*R*)-1-(naphthalen-2-yl)ethanamine (0.0685 g, 0.4 mmol) and Fe(OTf)₂ (0.0472 g, 0.133 mmol) were added to a flask with 20 mL of acetonitrile in N₂ atmosphere. The solution was stirred and heated at 80 °C for 2 h, cooled to room temperature. Then, the resulting purple solution was filtered. Cage **1** was precipitated as dark purple crystals through slow diffusion of diethyl ether into the filtrate at room temperature. Yield: 48 %. Formula: $C_{260}H_{240}F_{24}S_8Fe_4N_{36}O_{36}\cdot C_4H_{10}O$. ATR-FTIR (*v* cm⁻¹): 3121, 2973, 2925, 1601, 1573, 1506, 1440, 1256, 1151, 1028, 824, 748, 636.

2.6 Synthesis of cage 2



1,4-bis(2-(1-(imidazole-2-carbaldehyde))bromoethoxy)naphthalene (0.0809g, 0.2 mmol), (*R*)-1-(naphthalen-2-yl)ethanamine (0.0685 g, 0.4 mmol) and Fe(OTf)₂ (0.0472 g, 0.133 mmol) were added to a flask with 20 mL of acetonitrile in nitrogen atmosphere. The solution was stirred and heated at 80 °C for 8 h, cooled to room temperature. Then, the resulting purple solution was filtered. Cage **2** was precipitated as dark purple crystals through slow diffusion of diethyl ether into the filtrate at room temperature. Yield: 57 %. Formula: $C_{284}H_{252}F_{24}S_8Fe_4N_{36}O_{36}\cdot55(C_4H_{10}O)\cdot3(C_2H_3N)$. ATR-FTIR (*v* cm⁻¹): 3118, 2972, 2923, 1596, 1572, 1485, 1458, 1440, 1258, 1152, 1028, 819, 747, 636.

3. IR, UV-Vis and TGA characterization of cages 1-2



Figure. S9. IR spectra of (a) cage 1 and (b) cage 2.



Figure. S10. UV-Visible spectra of (a) cage 1 and (b) cage 2 in MeCN (10⁻⁵ M).



Figure. S11. Thermogravimetric analysis (TGA) curves of (a) cage 1 and (b) cage 2.

The weight of the two cages (1 and 2) were nearly a constant following the increasing temperature until 289 °C for cage 1, 300 °C for cage 2, and then the complex started to decompose. Further heated to 900 °C, there were approximate 25 and 34 percent of weight residual for these two cages, which possibly corresponded to the iron oxides.

4. NMR spectroscopy of cage 1



Figure. S12. The ¹H NMR (400 MHz, 298 K, CD₃CN) of cage 1.

The ¹H NMR signals outside of the usual chemical shift range for diamagnetic compounds, consistent with the presence of mixed spin-state iron(II) centers.



Figure. S13. The ¹³C NMR (400 MHz, 298 K, CD₃CN) of cage **1**.



Figure. S14. The ¹³C-DEPT135-NMR (400 MHz, 298 K, CD₃CN) of cage 1.



Figure. S15. Aromatic region of ¹H-¹H COSY spectrum (400 MHz, 298 K, CD₃CN) of cage 1.



Figure. S16. Aromatic region of ¹H-¹H NOESY spectrum (400 MHz, 298 K, CD₃CN) of cage 1.

5. NMR spectroscopy of cage 2



Figure. S17. The ¹H NMR (400 MHz, 298 K, CD₃CN) of cage **2**.

The ¹H NMR signals outside of the usual chemical shift range for diamagnetic compounds, consistent with the presence of mixed spin-state iron(II) centers.



Figure. S18. The ¹³C NMR (400 MHz, 298 K, CD₃CN) of cage **2**.



Figure. S19. The ¹³C-DEPT135-NMR (400 MHz, 298 K, CD₃CN) of cage 2.



Figure. S20. Aromatic region of ¹H-¹H COSY spectrum (400 MHz, 298 K, CD₃CN) of cage **2**.



Figure. S21. Aromatic region of ¹H-¹H NOESY spectrum (500 MHz, 298 K, CD₃CN) of cage 2.

6. High-resolution mass spectra of cage 1



Figure. S22. High resolution mass spectrum of cage 1 showing the +2, +3 and +4 peaks.



Figure. S23. Observed and calculated isotope patterns of $[1(OTf)_6]^{2+}$.



Figure. S24. Observed and calculated isotope patterns of $[1(OTf)_5]^{3+}$.



Figure. S25. Observed and calculated isotope patterns of $[1(OTf)_4]^{4+}$.

7. High-resolution mass spectra of cage 2



Figure. S26. High resolution mass spectrum of cage **2** showing the +2, +3 and +4 peaks.



Figure. S27. Observed and calculated isotope patterns of $[2(OTf)_6]^{2+}$.



Figure. S28. Observed and calculated isotope patterns of $[2(OTf)_5]^{3+}$.



Figure. S29. Observed and calculated isotope patterns of $[2(OTf)_4]^{4+}$.

8. X-ray structures of cages 1-2



Figure. S30. (a) One of C_3 -symmetric iron coordinate vertex, (b) intramolecular π - π interactions (green dashed lines) of cage 1. All H atoms and anions have been removed for clarity. (C: Grey; N: blue; O: red; Fe: purple).



Figure. S31. (a) One of C_3 -symmetric iron coordinate vertex, (b) intramolecular π - π interactions (green dashed lines) of cage 2. All H atoms and anions have been removed for clarity. (C: Grey; N: blue; O: red; Fe: purple).



Figure. S32. Four benzene moieties were in the state of "face to face", while another two benzene moieties were in the state of "edge to edge".



Figure. S33. All the naphthalene moieties were in the state of almost "edge to edge".

9. NMR spectroscopy of the host-guest complexes



Figure. S34. Comparison of ¹³C NMR (400 MHz, 298 K, CD₃CN) in host-guest complex $C_{60} \subset \mathbf{1}$ (top) and empty cage 1 (bottom).



complex $C_{60} \subset 1$ (top) and empty cage 1 (bottom).



Figure. S36. Aromatic region of ¹H-¹H COSY spectrum (400 MHz, 298 K, CD₃CN) of $C_{60} \subset 1$.



Figure. S37. Aromatic region of ¹H-¹H NOESY spectrum (400 MHz, 298 K, CD₃CN) of $C_{60} \subset 1$.



Figure. S38. Comparison of ¹³C NMR (400 MHz, 298 K, CD₃CN) in host-guest complex $C_{60} \subset 2$ (top) and empty cage 2 (bottom).



Figure. S39. Comparison of ¹³C-DEPT135-NMR (400 MHz, 298 K, CD₃CN) in host-guest complex $C_{60} \subset 2$ (top) and empty cage 2 (bottom).



Figure. S40. Aromatic region of ¹H-¹H COSY spectrum (400 MHz, 298 K, CD₃CN) of $C_{60} \subset 2$.



Figure. S41. Aromatic region of ¹H-¹H NOESY spectrum (400 MHz, 298 K, CD₃CN) of $C_{60} \subset 2$.



Figure. S42. Partial ¹H NMR spectra (400 MHz, 298 K, CD₃CN) of a mixture of cage 1 and C_{70} (about 5 equiv.), allowed to equilibrate at 50 °C for 0 hours and one week.



Figure. S43. Partial ¹H NMR spectra (400 MHz, 298 K, CD₃CN) of a mixture of cage **2** and C_{70} (about 5 equiv.), allowed to equilibrate at 50 °C for 0 hours and one week.



10. High-resolution mass spectra of the host-guest complex [C_{60} \subset 1]

Figure. S44. High resolution mass spectrum of cage C_{60} cage 1 showing the +3, +4 and +5 peaks.



Figure. S45. Observed and calculated isotope patterns of $C_{60} \subset [1(OTf)_5]^{3+}$.



Figure. S46. Observed and calculated isotope patterns of $C_{60} \subset [1(OTf)_4]^{4+}$.



Figure. S47. Observed and calculated isotope patterns of $C_{60} \subset [1(OTf)_3]^{5+}$.



11. High-resolution mass spectra of the host-guest complex [C_{60} \subset 2]

Figure. S48. High resolution mass spectrum of cage C_{60} cage 2 showing the +3, +4 and +5 peaks.



Figure. S49. Observed and calculated isotope patterns of $C_{60} \subset [2(OTf)_5]^{3+}$.



Figure. S50. Observed and calculated isotope patterns of $C_{60} \subset [2(OTf)_4]^{4+}$.



Figure. S51. Observed and calculated isotope patterns of $C_{60} \subset [2(OTf)_3]^{5+}$.

12. Variable temperature solid-state magnetic susceptibility measurements



Figure. S52. Plots of $\chi_{\rm M}T$ versus *T* for cage 1.



Figure. S53. Plots of $\chi_{\rm M}T$ versus *T* for cage **2**.



Figure. S54. Plots of $\chi_M T$ versus *T* for [C₆₀ \subset 1].



Figure. S55. Plots of $\chi_M T$ versus *T* for [C₆₀ \subset **2**].

The samples were quickly cooled from room temperature down to 2 K, and the magnetic susceptibility measurements were first measured in the warming mode from 2 to 400 K. The following magnetic data were again recorded in cooling mode from 400 to 2 K. As shown in Figure S52-S55, distinct SCO properties between the warming mode and cooling mode were observed for cage 1, cage 2, host-guest complexes $[C_{60}\subset 1]$ and $[C_{60}\subset 2]$, respectively. The estimated transition temperature of cage 1 was $T_{1/2}\uparrow=344$ K in warming and $T_{1/2}\downarrow=311$ K in cooling. The spin transition behavior of cage 2 was abrupt with $T_{1/2}\uparrow=328$ K in the warming mode and $T_{1/2}\downarrow=284$ K in the cooling mode. For host-guest complex $[C_{60}\subset 1]$, in the warming mode, the estimated value of $T_{1/2}\uparrow=312$ K, while the estimated $T_{1/2}\downarrow=209$ K responded to host-guest complex $[C_{60}\subset 2]$ in the warming and cooling mode, respectively.

13. Variable temperature UV-Vis spectra



Figure. S56. Variable temperature UV-Vis spectra for (a) cage 1 and (b) $[C_{60} \subset 1]$.



Figure. S57. Variable temperature UV-Vis spectra for (a) cage 2 and (b) $[C_{60} \subset 2]$.

14. Raman spectra



Figure. S58. Raman spectra for (a) cage 1, (b) cage 2, (c) $[C_{60} \subset 1]$ and (d) $[C_{60} \subset 2]$.

15. Variable temperature ¹H NMR



Figure. S59. Variable temperature ¹H NMR (400 MHz, CD₃CN) for cage 1.



Figure. S60. Variable temperature ¹H NMR (400 MHz, CD₃CN) for cage 2.

Variable temperature ¹H NMR measurements over a limited temperature range resulted in a clear change in the spectrum. As shown in Fig. S59-S60, the broad peaks observed at ambient temperature were further broadened, the ¹H chemical shift values of the signals attributed to cages **1-2** were observed to increase with temperature, respectively. The imine peak showed the largest increase due to its proximity to the iron(II) metal center. This shift was consistent with an increase in the high-spin population of iron(II) ions.



Figure. S61. Variable temperature ¹H NMR (400 MHz, CD₃CN) for $[C_{60} \subset 1]$.



Figure. S62. Variable temperature ¹H NMR (400 MHz, CD₃CN) for $[C_{60} \subset 2]$.

Variable temperature ¹H NMR measurements over a limited temperature range resulted in a clear change in the spectrum. As shown in Fig. S61-S62, the broad peaks observed at ambient temperature were further broadened, the ¹H chemical shift values of the signals attributed to the host-guest compounds [C_{60} ⊂1] and [C_{60} ⊂2] were observed to increase with temperature, respectively. The imine peak showed the largest increase due to its proximity to the iron(II) metal center. This shift was consistent with an increase in the high-spin population of iron(II) ions.

16. X-ray Crystallography

The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were retrieved using SMART software and refined using SAINT^[1] on all observed reflections. The highly redundant data sets were reduced using SAINT^[1] and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS^[2] supplied by Bruker. Structures were solved by direct methods using the 2014 version of SHELXL program.^[3] All of the non-hydrogen atoms except the anions were refined with anisotropic thermal displacement coefficients. Hydrogen atoms of organic ligands were located geometrically and refined in a riding model, whereas those of solvent molecules were not treated during the structural refinements. Disorder was modeled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. For cage 1, six 1-(naphthalen-2yl)ethanamine groups (C10K/C10P-C21K/C21P, occupancy 0.684 and 0.316; C10W/C10D-C21W/C21D, occupancy 0.235 and 0.765; C10J/C10Q-C21J/C21Q, occupancy 0.568 and 0.432; C10V/C10E-C21V/C21E, occupancy 0.235 and 0.765; C10Z/C10A-C21Z/C21A, occupancy 0.394 and 0.606; C10C/C10X-C21C/C21X, occupancy 0.749 and 0.251) in the structure are disorder over two unequal positions. For cage 2, three 1-(naphthalen-2-yl)ethanamine groups (C12W/C12D-C23W/C23D, C12Q/C12J-C23Q/C23J, occupancy 0.365 and occupancy 0.159 and 0.841; 0.635; C13B/C13Y-C23B/C23Y; occupancy 0.748 and 0.252) in the structure are disorder over two unequal positions. Final crystallographic data for cages 1-2 are listed in Table S1, and the selected bond distances [Å] and angles [°] are listed in Table S2.

Specific details: the crystals decayed rapidly out of solvent, despite rapid handling and long exposure times, the data collected was less than ideal quality. The diffraction of the crystal was very weak. No diffraction was observed past 0.94 Å although the explosure time was increased to 100s per degree, and the data was trimmed. Reflecting the instability of the crystals, there was a large area of smeared electron density present in the lattice. Despite many attempts to model this region of disorder as a combination of some solvent molecules and anions no reasonable fit could be found. Accordingly, the SQUEEZE^[4] function of PLATON^[5] was employed to remove this contribution from the model and it was included in the formula weight calculations as one diethyl ether solvent molecules and three OTf⁻ anions per unit cell for cage 1, three acetonitrile, fifty-five diethyl ether solvent molecules and one OTf⁻ anion per unit cell for cage 2.

	cage 1		
Wavelength (Å)	0.71073		
Crystal system	triclinic		
Space group	P_1		
a , <i>b</i> , <i>c</i> (Å)	20.1550(11), 20.4279(11), 20.6157(10)		
α, β, γ (°)	114.452(2), 109.4720(10), 91.124(2)		
$T(\mathbf{K})$	173(2)		
Tot., Uniq. Data, R(int)	54473, 37843, 0.078		
$\operatorname{GOF}(F^2)$	1.054		
R_1^a , $wR_2^b(I \ge 2\sigma(I))$	0.0638, 0.1297		
R_1^a , wR_2^b (all data)	0.1468, 0.1545		
	Calculated	Reported	
Formula	$C_{252}H_{240}Fe_4N_{36}O_{12},$ 5(CF ₃ SO ₃)[+solvent]	$C_{252}H_{240}Fe_4N_{36}O_{12}, \\ 8(CF_3SO_3), C_4H_{10}O$	
Fw	4933.54	5430.85	
$V(Å^3)$	7160.9(7)	7160.9(7)	
Ζ	1	1	
D_{calc} (Mg/m ³)	1.144	1.259	
$\mu (\mathrm{mm}^{-1})$	0.308	0.343	
<i>F</i> (000)	2569.0	2818.0	
	-23<= <i>h</i> <=23	-23<= <i>h</i> <=23	
Index ranges	-21<= <i>k</i> <=23	-21<= <i>k</i> <=23	
	-23<= <i>l</i> <=24	-23<= <i>l</i> <=24	

Table S1. Summary of crystallographic data for cages 1-2.

 $\overline{R_{l}^{a} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma F_{o}|} \cdot wR_{2}^{b} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})]^{1/2}.$

cage 2			
Wavelength (Å)	0.71073		
Crystal system	trigonal		
Space group		P_{32}	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.7520(11), 23.7520(11), 49.776(5)		
α, β, γ (°)	9	0, 90, 120	
$T(\mathbf{K})$		173(2)	
Tot., Uniq. Data, R(int)	11134	0, 39566, 0.064	
$\operatorname{GOF}(F^2)$	1.192		
R_1^a , $wR_2^b(I \ge 2\sigma(I))$	0.0788, 0.1966		
R_1^a , wR_2^b (all data)	0.1366, 0.2439		
	Calculated	Reported	
Formula	C ₂₇₆ H ₂₅₂ Fe ₄ N ₃₆ O ₁₂ , 7(CF ₃ SO ₃)[+solvent]	$C_{276}H_{252}Fe_4N_{36}O_{12},8(CF_3SO_3),$ 55(C ₄ H ₁₀ O),3(C ₂ H ₃ N)	
Fw	5531.98	9880.81	
$V(Å^3)$	24319(4)	24319(3)	
Ζ	3	3	
D_{calc} (Mg/m ³)	1.133	1.133	
$\mu (\mathrm{mm}^{-1})$	0.296	0.364	
<i>F</i> (000)	8613.0	15960.0	
	-25<= <i>h</i> <=25	-25<= <i>h</i> <=25	
Index ranges	-25<= <i>k</i> <=25	-25<= <i>k</i> <=25	
	-51<= <i>l</i> <=52	-51<= <i>l</i> <=52	

 $\overline{R_1^a = \Sigma ||F_0| - |F_c|| / \Sigma F_0|} \cdot wR_2^b = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)]^{1/2}.$

Table S2. Selected bond lengths [Å] and angles [°] for cages 1-2.

cage 1				
	Fe1-N1A	1.954(7)	Fe3-N1D	1.961(9)
	Fe1-N1C	1.901(9)	Fe3-N1H	1.938(9)
	Fe1-N1E	1.896(11)	Fe3-N1I	1.943(7)
	Fe1-N3A	1.975(7)	Fe3-N3D	1.995(9)
	Fe1-N3C	2.012(9)	Fe3-N3H	1.994(7)
	Fe1-N3E	1.987(7)	Fe3-N3I	1.991(9)
	Fe2-N1B	1.968(7)	Fe4-N1F	1.945(9)
	Fe2-N1G	1.914(9)	Fe4-N1J	1.922(7)
	Fe2-N1L	1.915(8)	Fe4-N1K	1.935(8)
	Fe2-N3B	1.988(7)	Fe4-N3F	1.984(7)
	Fe2-N3G	1.971(7)	Fe4-N3J	2.006(8)

Fe2-N3L	2.011(9)	Fe4-N3K	1.990(9)
N1A-Fe1-N1C	90.8(3)	N1D-Fe3-N1H	91.8(4)
N1A-Fe1-N1E	92.3(3)	N1D-Fe3-N1I	91.6(3)
N1A-Fe1-N3A	82.1(3)	N1D-Fe3-N3D	81.3(4)
N1A-Fe1-N3C	92.0(3)	N1D-Fe3-N3H	90.9(3)
N1C-Fe1-N1E	89.4(4)	N1H-Fe3-N1I	90.1(3)
N1C-Fe1-N3C	81.0(4)	N1H-Fe3-N3H	81.8(3)
N1C-Fe1-N3E	91.5(3)	N1H-Fe3-N3I	90.6(4)
N1E-Fe1-N3A	92.3(4)	N1I-Fe3-N3D	94.0(3)
N1E-Fe1-N3E	81.1(3)	N1I-Fe3-N3I	81.5(3)
N3A-Fe1-N3C	97.8(4)	N3D-Fe3-N3H	94.4(3)
N3A-Fe1-N3E	95.7(3)	N3D-Fe3-N3I	96.8(4)
N3C-Fe1-N3E	95.0(3)	N3H-Fe3-N3I	96.3(3)
N1B-Fe2-N1G	90.8(3)	N1F-Fe4-N1J	92.7(3)
N1B-Fe2-N1L	93.9(3)	N1F-Fe4-N1K	88.8(4)
N1B-Fe2-N3B	80.8(3)	N1F-Fe4-N3F	81.2(3)
N1B-Fe2-N3L	94.9(3)	N1F-Fe4-N3J	92.5(4)
N1G-Fe2-N1L	89.5(4)	N1J-Fe4-N1K	92.0(3)
N1G-Fe2-N3B	92.7(4)	N1J-Fe4-N3J	80.8(3)
N1G-Fe2-N3G	81.5(3)	N1J-Fe4-N3K	90.8(3)
N1L-Fe2-N3G	89.2(3)	N1K-Fe4-N3F	92.2(3)
N1L-Fe2-N3L	81.1(4)	N1K-Fe4-N3K	81.4(4)
N3B-Fe2-N3G	96.3(3)	N3F-Fe4-N3J	95.0(3)
N3B-Fe2-N3L	97.1(4)	N3F-Fe4-N3K	96.0(3)
N3G-Fe2-N3L	93.2(3)	N3J-Fe4-N3K	97.6(4)
cage 2			
Fe1-N1A	1.979(10)	Fe3-N1D	1.908(14)
Fe1-N1C	1.941(13)	Fe3-N1H	1.929(15)
Fe1-N1E	1.962(11)	Fe3-N1K	1.992(14)
Fe1-N3A	1.996(11)	Fe3-N3D	1.982(12)
Fe1-N3C	1.987(10)	Fe3-N3H	2.006(14)
Fe1-N3E	2.032(13)	Fe3-N3K	2.052(16)
Fe2-N1B	1.957(14)	Fe4-N1F	1.979(11)
Fe2-N1G	1.927(12)	Fe4-N1J	1.993(14)
Fe2-N1I	1.938(13)	Fe4-N1L	1.981(13)
Fe2-N3B	2.009(11)	Fe4-N3F	1.999(16)
Fe2-N3G	2.028(15)	Fe4-N3J	2.017(10)
Fe2-N3I	1.991(11)	Fe4-N3L	2.021(15)
N1A-Fe1-N1C	91.9(5)	N1D-Fe3-N1H	90.0(6)
N1A-Fe1-N1E	90.9(4)	N1D-Fe3-N1K	91.4(6)

N1A-Fe1-N3A	80.5(4)	N1D-Fe3-N3D	80.1(6)
N1A-Fe1-N3E	92.5(5)	N1D-Fe3-N3K	92.8(6)
N1C-Fe1-N1E	91.0(5)	N1H-Fe3-N1K	92.2(6)
N1C-Fe1-N3A	93.2(5)	N1H-Fe3-N3D	91.2(5)
N1C-Fe1-N3C	81.1(5)	N1H-Fe3-N3H	83.6(6)
N1E-Fe1-N3C	94.0(4)	N1K-Fe3-N3H	91.3(6)
N1E-Fe1-N3E	80.1(5)	N1K-Fe3-N3K	77.0(6)
N3A-Fe1-N3C	95.0(4)	N3D-Fe3-N3H	97.5(5)
N3A-Fe1-N3E	96.4(5)	N3D-Fe3-N3K	99.9(5)
N3C-Fe1-N3E	95.2(5)	N3H-Fe3-N3K	94.0(6)
N1B-Fe2-N1G	93.8(5)	N1F-Fe4-N1J	91.8(5)
N1B-Fe2-N1I	92.5(5)	N1F-Fe4-N1L	90.3(5)
N1B-Fe2-N3B	79.4(5)	N1F-Fe4-N3F	82.1(5)
N1B-Fe2-N3G	92.8(5)	N1F-Fe4-N3J	91.3(4)
N1G-Fe2-N1I	91.3(5)	N1J-Fe4-N1L	94.6(5)
N1G-Fe2-N3G	79.1(5)	N1J-Fe4-N3J	79.8(5)
N1G-Fe2-N3I	89.9(5)	N1J-Fe4-N3L	91.6(6)
N1I-Fe2-N3B	90.6(5)	N1L-Fe4-N3F	90.6(5)
N1I-Fe2-N3I	79.9(5)	N1L-Fe4-N3L	80.9(6)
N3B-Fe2-N3G	99.5(5)	N3F-Fe4-N3J	95.2(5)
N3B-Fe2-N3I	97.2(4)	N3F-Fe4-N3L	95.3(6)
N3G-Fe2-N3I	95.3(5)	N3J-Fe4-N3L	97.8(5)

17. Theory calculations

In order to further investigated the association of fullerene C_{60} in cages 1-2, preliminary theory calculations were carried out. We performed DFT calculations with no symmetry constraints to investigate the optimized geometries on the $[C_{60} \subset 1]$ and $[C_{60} \subset 2]$, the original coordinates of were based on the crystal structure of cage 1 and cage 2. Full optimizations on all conformations of possible complexes studied were performed at the semi-empirical Parameterized Model (PM6) with Gaussian 09 programs.^[6] Possible orientations of C_{60} molecules in the $[C_{60} \subset 1]$ and $[C_{60} \subset 2]$ were shown in Figure S63. Some relatively stable minima's by PM6 were then subjected to geometry optimization at the ONIOM(B3LYP/6-31G*:PM6) level of theory. We employed the density functional theory (DFT) with no symmetry constraints to investigate the optimized geometries.



Figure. S63. DFT-optimized structure of (a) $[C_{60} \subset 1]$, (b) partial structure of $[C_{60} \subset 1]$ highlighting the π -stacking interactions between the O-benzene moieties and C_{60} guest. (c) $[C_{60} \subset 2]$, (b) partial structure of $[C_{60} \subset 2]$ highlighting the π -stacking interactions between the O- naphthalene moieties and C_{60} guest. All H atoms have been omitted for clarity. Atom colors: C, grey; N, blue; O, red; Fe, purple. The C_{60} guest molecule is demonstrated in purple.

The calculated host-guest complex $[C_{60} \subset 1]$ thus provided insight into the guest recognition occurred through π -stacking interactions between the O-benzene moieties and C_{60} molecule. The "face to face" π - π interactions were generated between four Obenzene moieties and the π -electron surface of C_{60} , while another two O-benzene moieties generated "edge to face" π -stacking interactions with the C_{60} guest (Figure. S63 a-b). Comparison of the single crystal structure of cage 2 and the calculated hostguest complex [$C_{60} \subset 2$], the O-naphthalene units were slightly rotated to provide favorable π -stacking interactions for forming the stable host-guest complexes (Figure. S63 c-d).

18. References

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