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Supporting Information

Synthesis of an Iron-Based Metal-Organic Framework with Octahedral Cage for the Selective Capture of Sulfur Hexafluoride

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1. Materials and general procedures

Materials

Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$), *N*, *N*-dimethylformamide (DMF) were purchased from *Bidepharm*. Unless otherwise noted, all commercial chemicals were used without further purification.

Characterization

Fourier transform infrared (FT-IR) spectra were collected using a ThermoFisher iS50 FT-IR spectrometer. Nitrogen sorption isotherms at 77 K were measured using a Micromeritics 3Flex volumetric gas sorption instrument equipped with liquid nitrogen containers. ^1H NMR spectra were recorded on a Bruker Avance DMX-500 (500 MHz for ^1H NMR). The deuterated solvents used are indicated in the experimental part, chemical shifts are given in ppm from TMS with residual solvent resonances as internal standards. Powder X-ray diffraction (PXRD) of MOFs were measured on a Rigaku smartlab X-ray diffractometer operating at 40 kV/30 mA using the Cu Kα line ($\lambda = 1.5418$Å). Data were measured over the range of 3-30° in 13°/min steps over two minutes.

Crystal Structure Determination. Single crystal data of **Fe-cage-MOF** was collected using a Bruker D8 Venture diffractometer equipped with a Mo Kα ($\lambda = 0.71073$ Å) radiation, and a highly sensitive CPAD Photon II detector, coupled with a CryoStream 800 Plus (Oxford Cryosystems) temperature controller. Data reduction and cell parameter refinement were performed using Apex software with included SAINT and SADABS programs. Intensities of reflections for the sample absorption were corrected using multi-Fean method. Structures were solved by intrinsic phasing method and refined anisotropically with weighted full-matrix least squares on F^2 using SHELXT 6 and SHELXL 7 programs with Olex 2 graphic interface. All non-hydrogen atoms were refined anisotropically with restraints (DFIX, ISOR, SIMU and DELU) on DMF molecules and partially phenyl groups. Hydrogen atoms within structures were placed in idealized positions and refined using riding coordinate model. A solvent mask procedure was further performed dues to highly disordered interstitial solvent molecules. Crystal data and structure refinement parameters are summarized in **Table S1**. Crystal structures are deposited in CCDC data base. The deposition number is 2325370.

2. Synthesis of ligands

Synthetic protocols for 4,4'-(1,10-phenanthroline-2,9-diyl) dibenzoic acid

The compound was synthesized according to the previously reported literatures

Synthesis of $[Fe_3O(CH_3COO)_6(H_2O)_3]\ Cl\cdot 6H_2O$ (Fe_3)

The Fe_3 cluster was synthesized according to the reported procedure with slight modifications.[1] $FeCl_3\cdot 6H_2O$ (8.11 g, 0.03 mol) and $CH_3COONa\cdot 3H_2O$ (8.16 g, 0.06 mol) were separately dissolved in 10 ml hot water (50 °C). The resulting solutions were mixed together and keep stirring at 50 °C for 10 minutes. Then the solution was allowed to cool down to the room temperature and stay in air for crystallization. After several days, dark red crystals were obtained. The crystals were filtered off and washed with a small amount of ethanol and diethyl ether.

Synthesis of single crystals of Fe-cage-MOF

A DMF solution of PHDC (5.0 mg, 1.0 ml) and DMF solution of Fe_3 (8.0 mg, 1.0 ml) were combined in a 15 mL vial. Then, acetic acid (0.1 mL) was added. The mixture was sonicated for 2 min and sealed and heated to 150 °C for 2 days. Single crystals were formed and used for single crystal X-ray diffraction measurements.

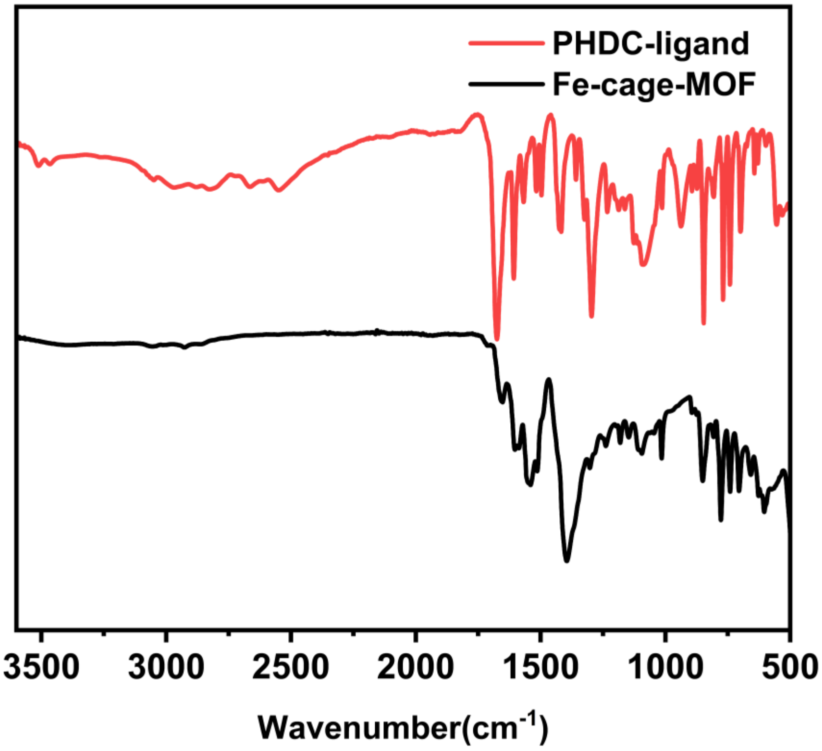

Figure S1. FT-IR spectra of **Fe-cage-MOF** and PHDC ligand

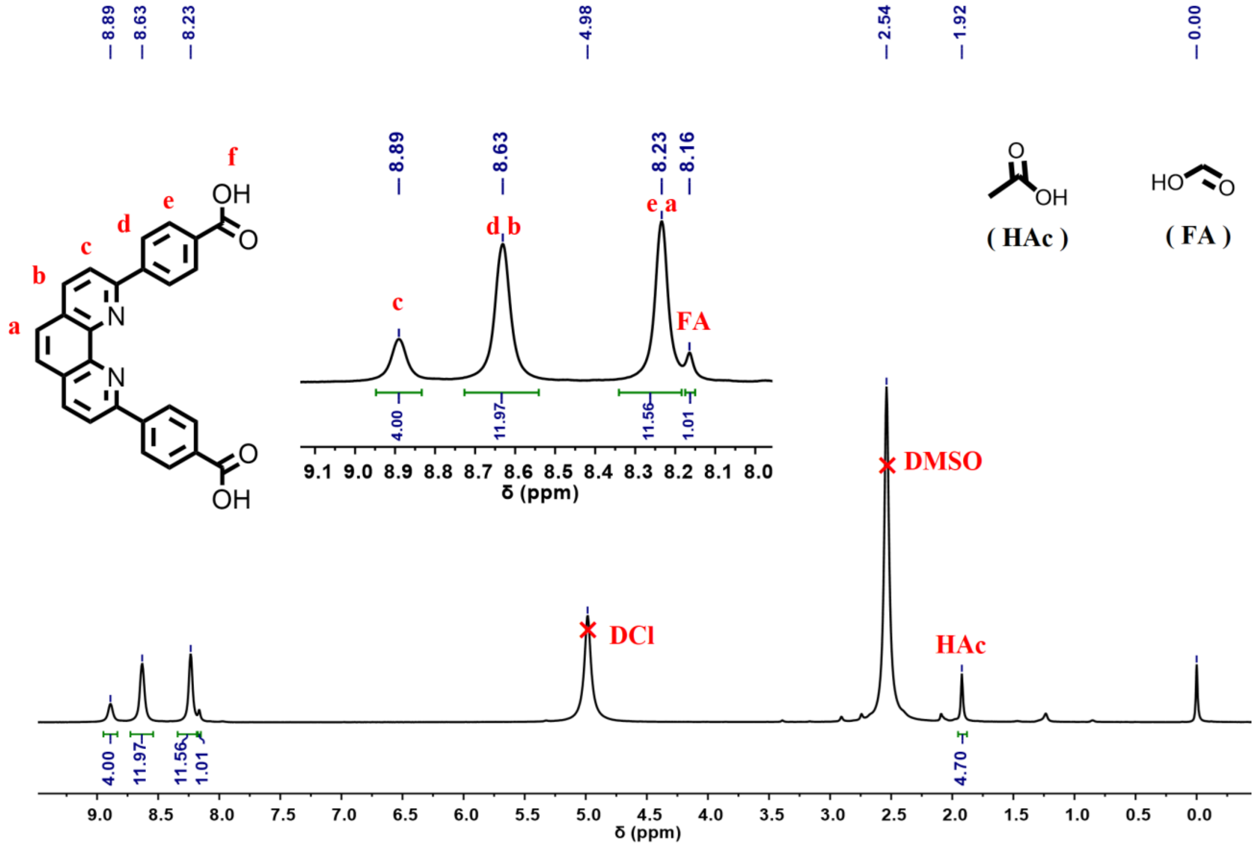

Figure S2. ^{1}H NMR spectrum of the digested **Fe-cage-MOF** reveals the FA: HAc: PHDC = 1: 2 :2

4. Single Crystal X-ray Data

Table S1. Crystallographic data of **Fe-cage-MOF**

	Fe-Cage-MOF
Empirical formula	$C_{81}H_{93}Fe_3N_{12}O_{24}$
Formula weight	1786.22
Temperature/K	173
Crystal system	monoclinic
Space group	$C2/c$
a/Å	34.238(2)
b/Å	16.0211(9)
c/Å	33.7881(17)
α/°	90
β/°	91.0780 (10)
γ/°	90
Volume/Å^3	18530.6(18)
Z	8
Calcd Density (g/cm^3)	0.861
μ (mm^{-1})	0.507
F(000)	4904.0
Crystal size (mm^3)	0.2×0.1×0.1
Radiation	MoKα (λ = 0.71073)
Total reflection	113259
R_{int}	0.0676
Goodness-of-fit	1.029
R_1 [$I>2\sigma(I)$]	$R_1 = 0.0673$, $wR_2 = 0.1948$
wR_2 (all reflection)	$R_1 = 0.0814$, $wR_2 = 0.2118$
Largest diff. peak/hole	0.96/-0.72
CCDC-number	2325370

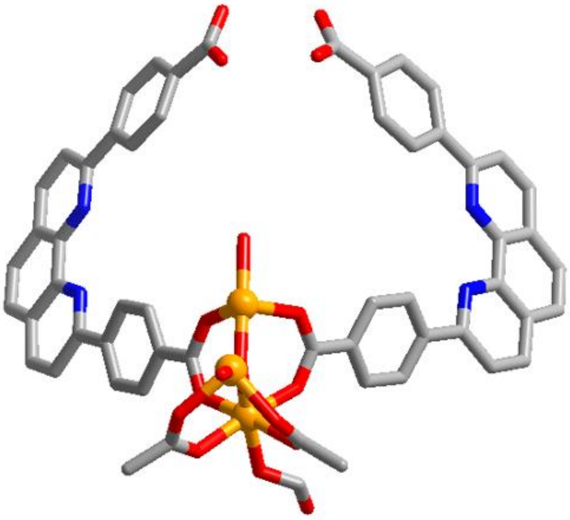

Figure S3. The asymmetric unit of **Fe-cage-MOF**. Atom color code: Fe (yellow), O (red), N (blue), C (gray). Hydrogen atoms are omitted for clarity.

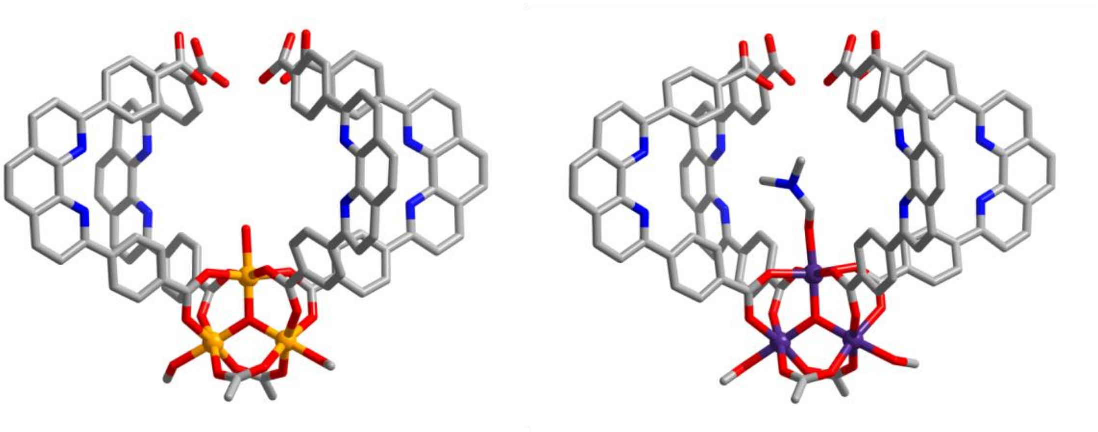

Figure S4. Comparison of coordination environments of the trinuclear clusters of **Fe-cage-MOF** (left) and **Sc-cage-MOF** (right).

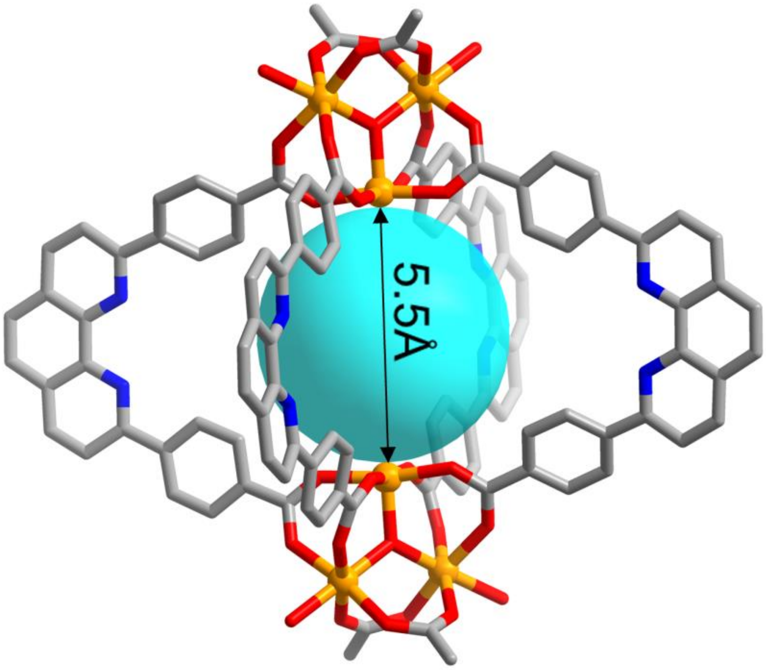

Figure S5. The illustration of the octahedron cage. Atom color code: Fe (yellow), O (red), N (blue), C (gray), Hydrogen atoms are omitted for clarity.

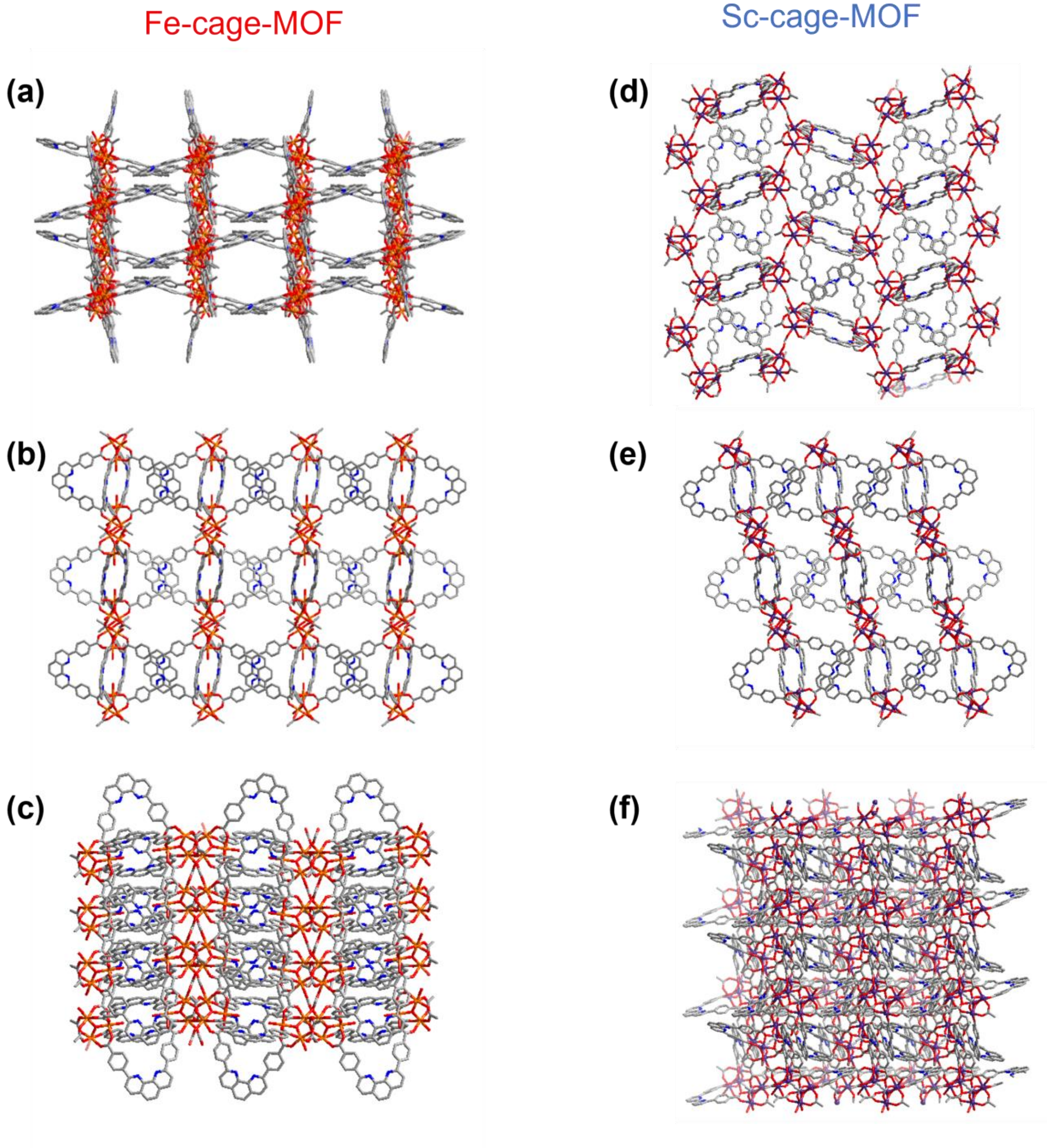

Figure S6. The stacking structure of **Fe-cage-MOF** and **Sc-cage-MOF** along with *a* (a,d), *b* (b,e) and *c* (c,f) crystallography direction.

5. N_2 and SF_6 Sorption

5.1 Sample activation and N_2 sorption isotherm

Prior to gas sorption, the as-synthesized samples (~ 40 mg) were washed 2 times with DMF and then sequentially immersed in acetone for 2 days, during which time the acetone was replaced three times. The solids were then activated at 120 °C under vacuum for 12 h.

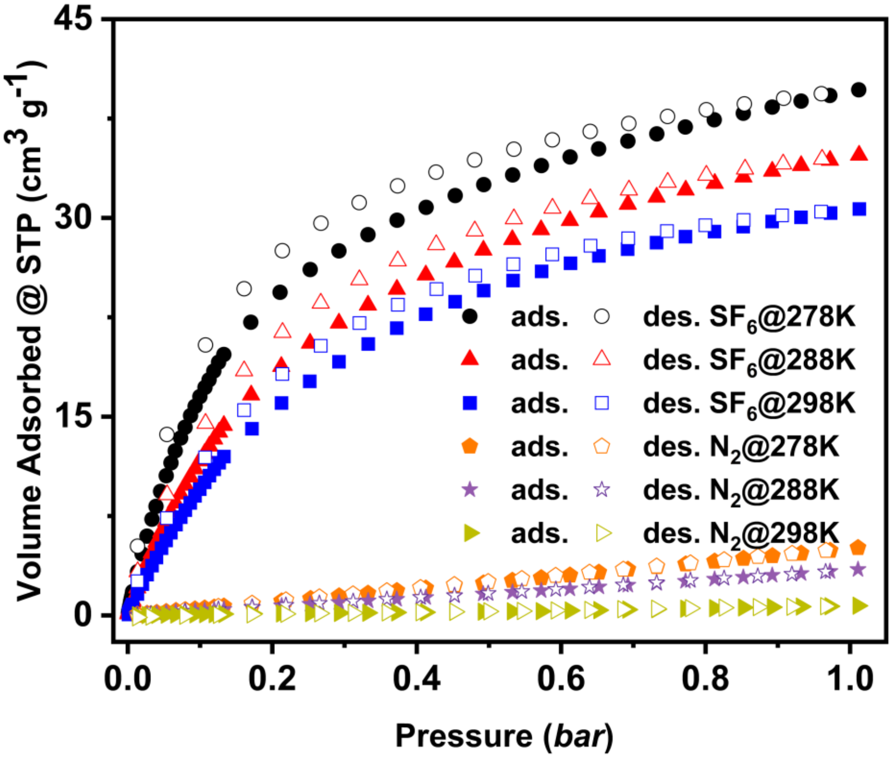

Figure S7. The N_2 and SF_6 adsorption-desorption isotherms of **Fe-cage-MOF** at 278 K, 288 K and 298 K.

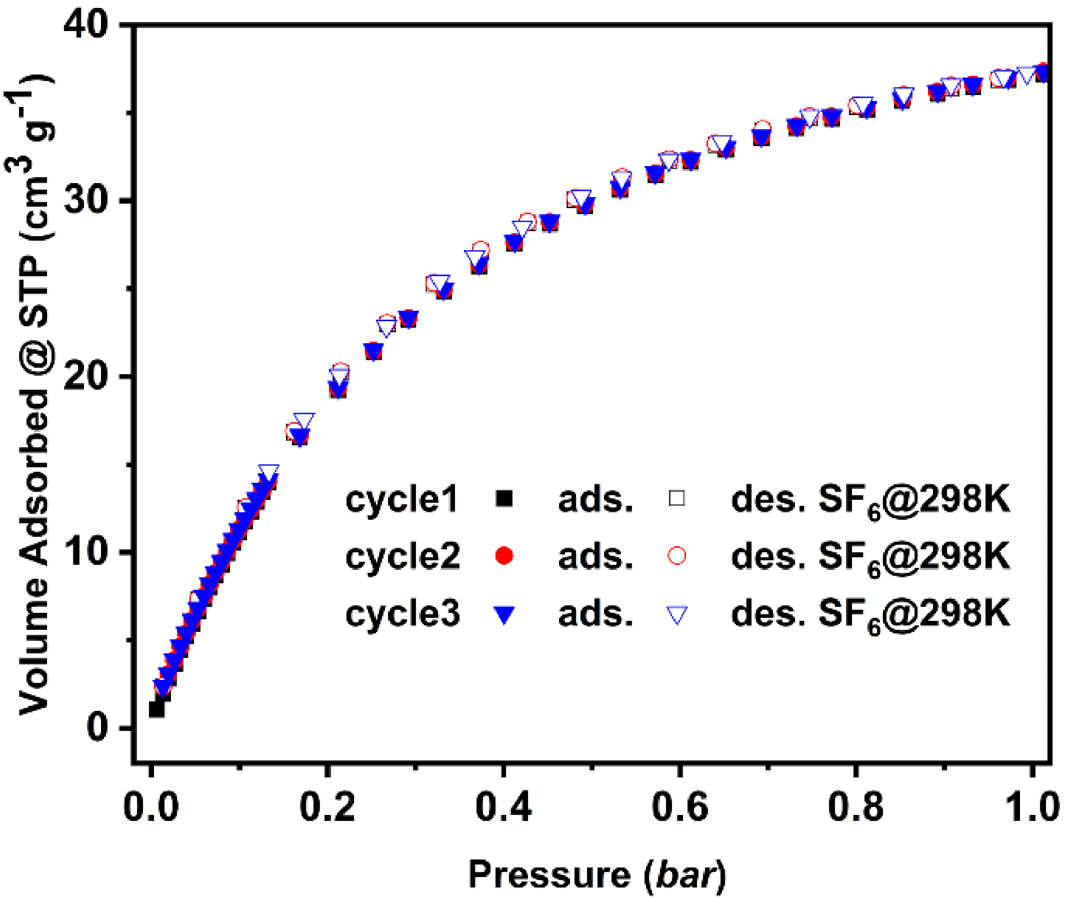

Figure S8. Adsorption-desorption cycle tests for SF_6 at room temperature.

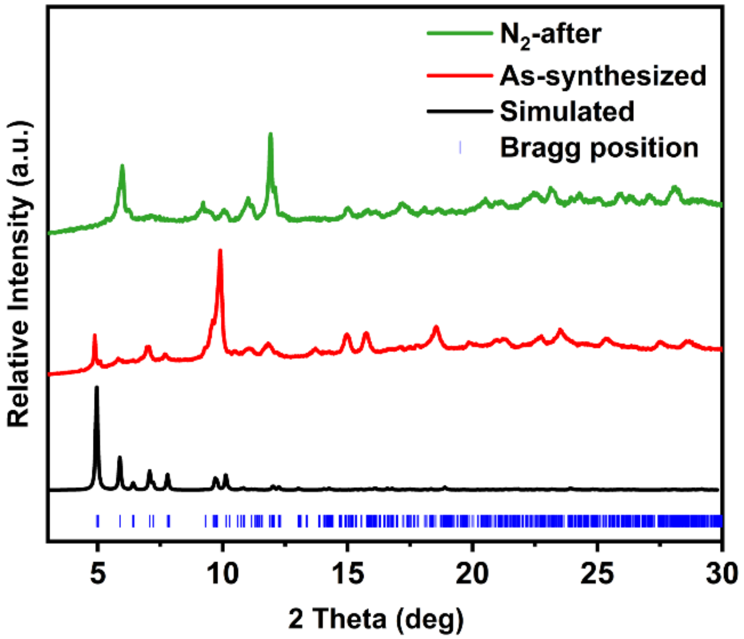

Figure S9. PXRD patterns for **Fe-cage-MOF** before and after gas sorption.

6. IAST Calculations

Prediction of multicomponent gas adsorption Ideal Adsorption Solution Theory (IAST)

The Ideal Adsorption Solution Theory (IAST) proposed by Mayer and Prausnitz (1965)[2] uses pure gas adsorption isotherms to predict the mixture adsorption equilibrium at the temperature of interest. For IAST application, the main condition to be fulfilled is the availability of (i) good quality single component adsorption data of different gases, and (ii) an excellent curve fitting model for such data (Chen and Sholl, 2007;[3] Bae et al., 2008[4]). In the current work, Dual-Site Langmuir-Freundlich model was used to fit the pure gas isotherms.
The most important equations used in the IAST calculation are listed hereafter:

$$f_i = x_i f_i^0(\pi) \quad (1)$$

$$\frac{\pi A}{RT} = \int_0^{f_i^0} n_i d \ln f_i \quad (2)$$

$$\frac{1}{n_t} = \sum_i \frac{x_i}{n_i^0} \quad (3)$$

$$S_{SF_6-i} = \frac{x_{SF_6}/x_i}{y_{SF_6}/y_i} \quad (4)$$

where f_i is the fugacity of component i in the gas phase; f_i^0 is the standard-state fugacity (i.e., the fugacity of pure component i at the equilibrium spreading pressure of the mixture, π); x_i and y_i are the mole fractions of component i in the adsorbed and gas phase, respectively; A is the surface area of the adsorbent; n_i is the number of moles adsorbed of pure component i (i.e., the pure-component isotherm); and n_i^0 is the number of moles adsorbed of pure component i at the standard-state pressure.

Equation (1) is the central equation of IAST, specifying the equality of the chemical potential of component i in the gas and the adsorbed phase (which is assumed to be ideal in the sense of Raoult's law). Equation (2) allows the calculation of the spreading pressure from the pure component adsorption isotherm. The total amount adsorbed of the mixture, n_t, and the selectivity of SF_6 with respect to i, S_{SF_6-i}, are given by equations (3) and (4), respectively. The selectivity S_{SF_6-i}, reflects the efficiency of SF_6 separation.

Dual-Site Langmuir Model for single gas sorption fitting

In the current work, the Dual-Site Langmuir (DSL) model was used to fit the pure gas isotherms and its simple formulation as expressed by equation (5).

$$q = q_{A,\ sat}\,\frac{b_A\,p}{1+b_A\,p} + q_{B,\ sat}\,\frac{b_B\,p}{1+b_B\,p} \qquad (5)$$

where q is the adsorption quantity, q_{sat} is the saturate adsorption quantity, b is the coefficients. The subscripts A and B indicate the parameters for the adsorption sites A and B, respectively.

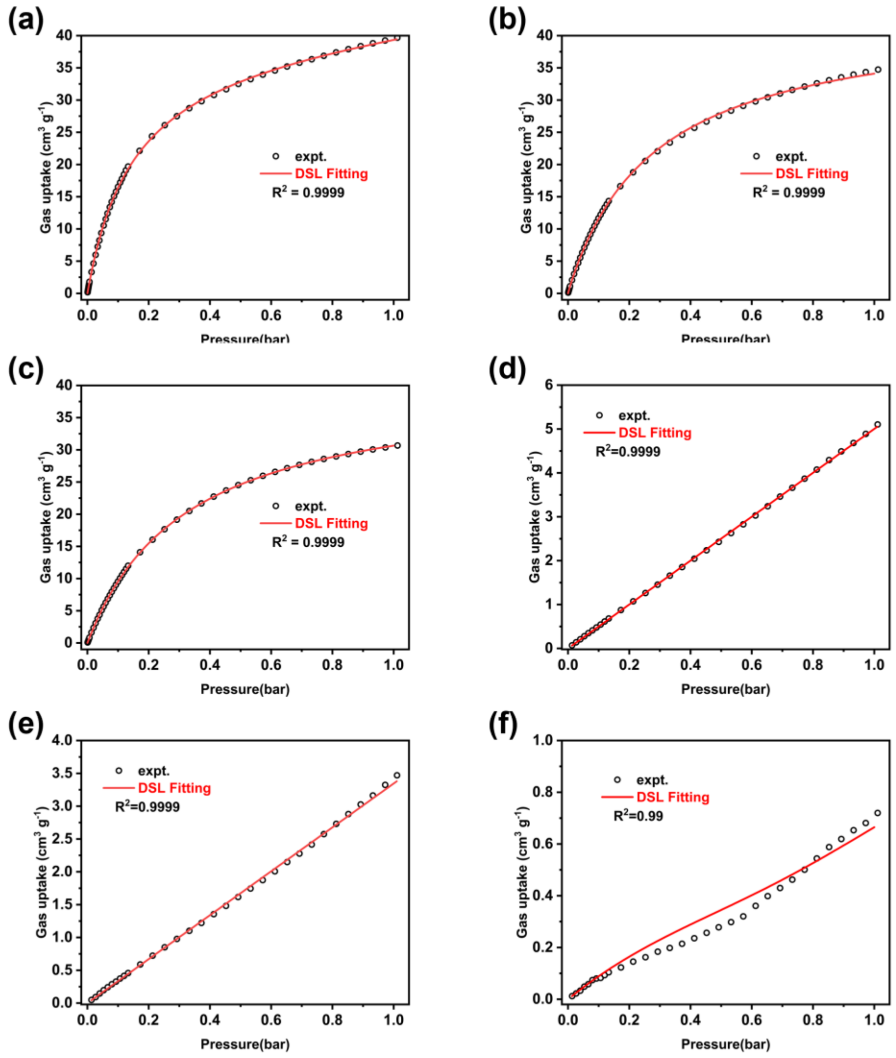

Figure S10. (a-c) The DSL model for fitting SF_6 isotherms of **Fe-cage-MOF** at 278, 288 and 298 K. (d-f) The DSL model for fitting N_2 isotherms of **Fe-cage-MOF** at 278, 288 and 298 K.

Table S2. The fitted parameters by using the DSL model based on the single-component isotherms data of SF_6 and N_2 in **Fe-cage-MOF** at 278, 288 and 298 K.

	Gas	$q_{A,sat}$	b_A	$q_{B,sat}$	b_B
278K	SF_6	38.9758	0.0686349	3320.23	1.60435e-05
	N_2	6926.09	4.26889e-06	1650.68	1.24124e-05
288K	SF_6	43.3499	0.0352217	0.347362	0.665677
	N_2	3.79607e-20	1.2362e-15	1101.62	3.04172e-05
298K	SF_6	22.064	0.0308089	18.5334	0.0308089
	N_2	0.0022092	10000	60.996	0.000106253

7. References

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3. H. Chen and D. S. Sholl, *Langmuir*, 2007, **23**, 6431-6437.
4. Y. S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp and R. Q. Snurr, *Langmuir*, 2008, **24**, 8592-8598.