Single-Crystal Synthesis and Diverse Topologies of Hexanuclear Ce^{IV}-based Metal-Organic Frameworks

Yu-Feng Zhang,[a] Qian Wang,[a] Dong-Xu Xue,*[a] and Junfeng Bai*[a,b]

[a]Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China

[b]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Corresponding authors:

Email: xuedx@snnu.edu.cn
Email: bjunfeng@nju.edu.cn, bjunfeng@snnu.edu.cn.

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Section 1. Materials and Methods.

All reagents were obtained from commercial sources and used without further purification. PXRD measurements were performed on a Rigaku MiniFlex 600 diffractometer with Cu Kα (λ = 1.5406 Å), and the X-ray tube was operated at 40 kV and 15 mA. High resolution thermogravimetric analysis (TGA) were performed under a continuous N_2 flow and recorded on a Q600SDT thermal analyzer with a heating rate of 5°C per minute. Fourier-transform infrared (FT-IR) spectrum (4000-400 cm^{-1}, KBr pellet) was collected in the solid state on a Bruker Tensor 27 FT-IR spectrometer. The morphologies of the samples were obtained on a Desktop Scanning Electron Scanning Electron Microscope (TM300).

Section 2. Synthetic Procedure for SC-Ce-MOF-1−4.

Synthesis of SC-Ce-MOF-1: Terephthalic acid (7.2 mg, 0.0435 mmol), $(NH_4)_2Ce(NO_3)_6$•$6H_2O$ (23.85 mg, 0.0435 mmol), DMF (1.5 mL), C_2H_5OH (0.5 mL), 2-fluorobenzoic acid DMF solution (0.5 mL, 3.48 mol L^{-1}) were combined in a 20 mL scintillation vial, sealed and heated to 105 °C for 36 h and cooled to room temperature. The yellow hexagonal prism crystals were collected and DMF washed. CHN elemental analysis (%) for SC-Ce-MOF-1, $[Ce_6(OH)_4(O)_4(C_8H_4O_4)_6(H_2O)_6]\cdot(C_3H_7ON)_3(H_2O)_{16}$: Calculated C (26.61), H (3.64), N (1.63); Found C (26.42), H (3.01), N (1.61).

Synthesis of SC-Ce-MOF-2: 2-Fluoroterephthalic acid (8.0 mg, 0.0435 mmol), $(NH_4)_2Ce(NO_3)_6$•$6H_2O$ (23.85 mg, 0.0435 mmol), DMF (1.5 mL), C_2H_5OH (0.5 mL), 2-fluorobenzoic acid DMF solution (0.7 mL, 3.48 mol L^{-1}) were combined in a 20 mL scintillation vial, sealed and heated to 105 °C for 36 h and cooled to room temperature. The extremely fine yellow hexagonal prism crystals were collected and DMF washed. CHN elemental analysis (%) for SC-Ce-MOF-2, $[Ce_6(OH)_4(O)_4(C_8H_3FO_4)_6(H_2O)_6]\cdot(C_3H_7ON)_{3.5}(H_2O)_{22}$: Calculated C (24.87), H (3.66), N (1.74); Found C (24.80), H (3.26), N (1.77).

Synthesis of SC-Ce-MOF-3: 2-Aminoterephthalic acid (7.9 mg, 0.0435 mmol), $(NH_4)_2Ce(NO_3)_6$•$6H_2O$ (47.7 mg, 0.087 mmol), DMF (2.0 mL), C_2H_5OH (0.5 mL), 2-fluorobenzoic acid DMF solution (0.4 mL, 3.48 mol L^{-1}) were combined in a 20 mL scintillation vial, sealed and heated to 105 °C for 48 h and cooled to room temperature. The light brown polyhedral crystals were collected and DMF washed. CHN elemental analysis (%) for SC-Ce-MOF-3, $[Ce_6(OH)_4(O)_4(C_8H_5NO_4)_6(H_2O)_6](C_3H_7ON)_5(H_2O)_{40}$: Calculated C (23.34), H (5.01), N (4.75); Found C (22.94), H (4.75), N (4.84).

Synthesis of SC-Ce-MOF-4: Naphthalene-2,6-dicarboxylic acid (9.4 mg, 0.0435 mmol), $(NH_4)_2Ce(NO_3)_6$•$6H_2O$ (23.85 mg, 0.0435 mmol), DMF (2.0 mL), C_2H_5OH (0.5 mL), 2-fluorobenzoic acid DMF solution (0.6 mL, 3.48 mol L^{-1}) were combined in a 20 mL scintillation vial, sealed and heated to 105 °C for 36 h and cooled to room temperature. The yellow polyhedral crystals were collected and DMF washed. CHN elemental analysis (%) for SC-Ce-MOF-4, $[Ce_6(OH)_4(O)_4(C_{12}H_6O_4)_6(H_2O)_6]\cdot(C_3H_7ON)_{10}(H_2O)_{25}$: Calculated C (34.54), H (4.89), N (3.95); Found C (34.23), H (4.18), N (4.23).

Section 3. Additional Structural Figures.

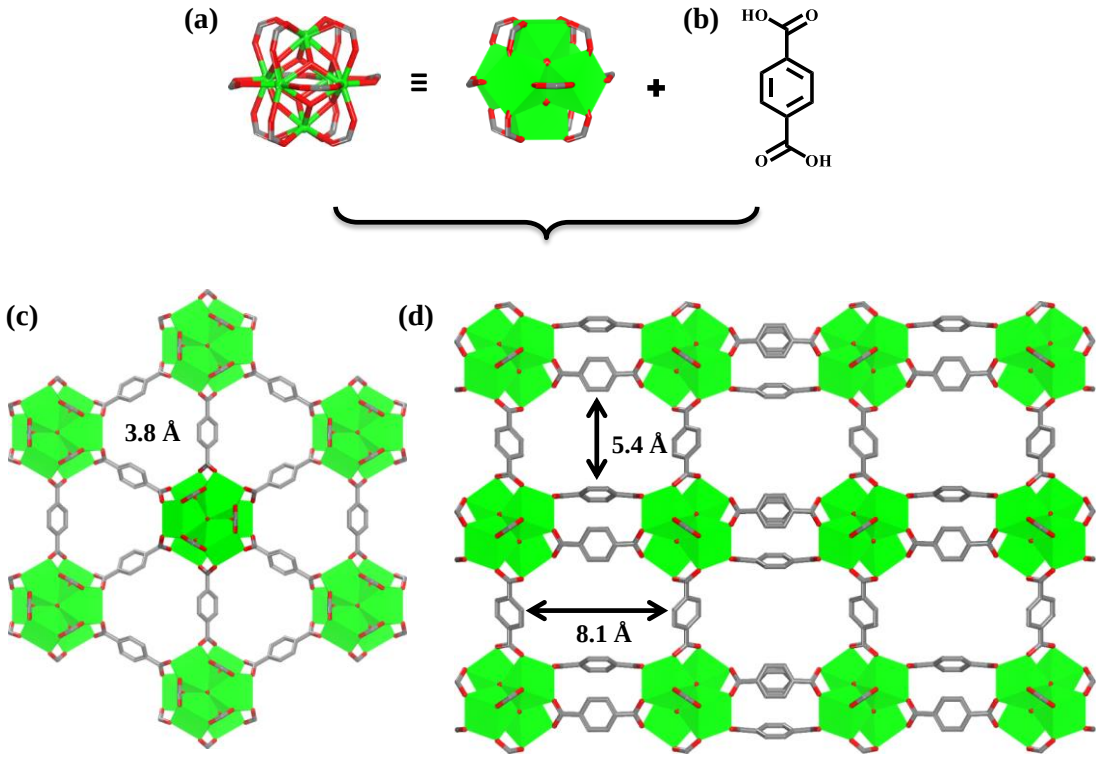

Figure S1. Schematic representations of SC-Ce-MOF-1 constructed from the assembly of hexanuclear Ce(IV)-based MBB and the organic linker of H_2BDC (b) to produce a 3-periodic net along *c*-axis (c) and *b*-axis (d) associated with the channel sizes of 3.8 Å, 5.4 × 8.1 $Å^2$, respectively. Hydrogen atoms and coordinated water molecules are omitted for clarity. Ce = green, C = gray, O =red.

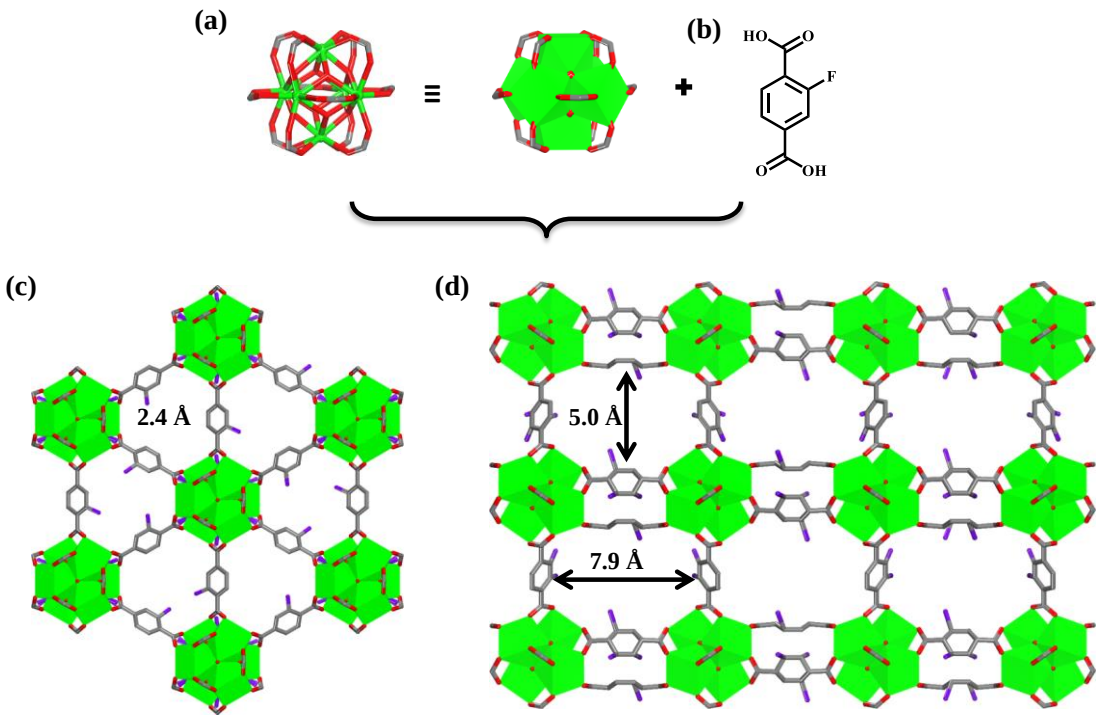

Figure S2. Schematic representations of SC-Ce-MOF-2 constructed from the assembly of hexanuclear Ce(IV)-based MBB (a) and the organic linker of H_2FBDC (b) to generate a 3-periodic net along *c*-axis (c) and *b*-axis (d) associated with the channel sizes of 2.4 Å, 5.0 × 7.9 $Å^2$, respectively. Hydrogen atoms and coordinated water molecules are omitted for clarity. Ce = green, C = gray, O =red, F = purple.

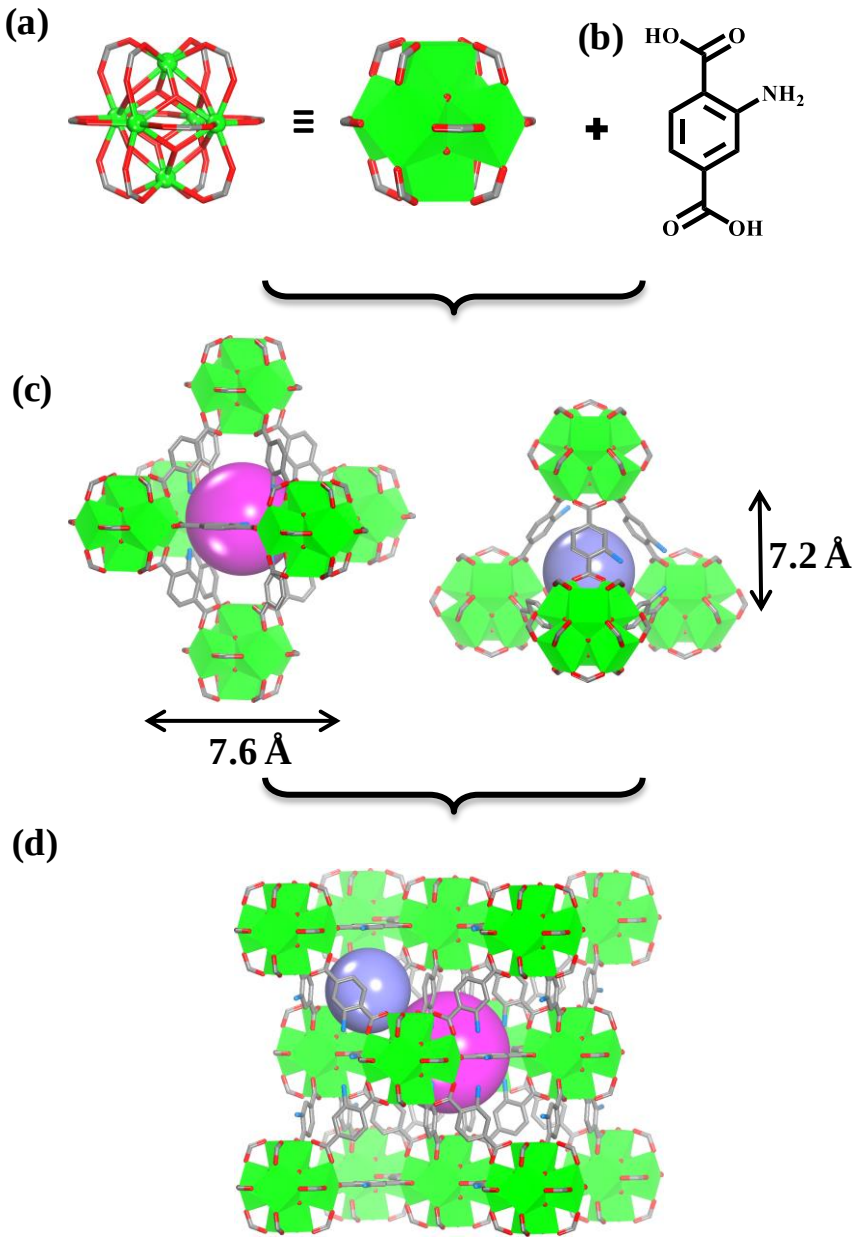

Figure S3. Schematic representations of SC-Ce-MOF-3 constructed from the assembly of hexanuclear Ce(IV)-based MBB and the organic linker of H_2ABDC to generate a 3-periodic **fcu** net, and the cages are: 7.6 Å and 7.2 Å, respectively**.** Hydrogen atoms and coordinated water molecules are omitted for clarity. Ce = green, C = gray, O =red, N = blue.

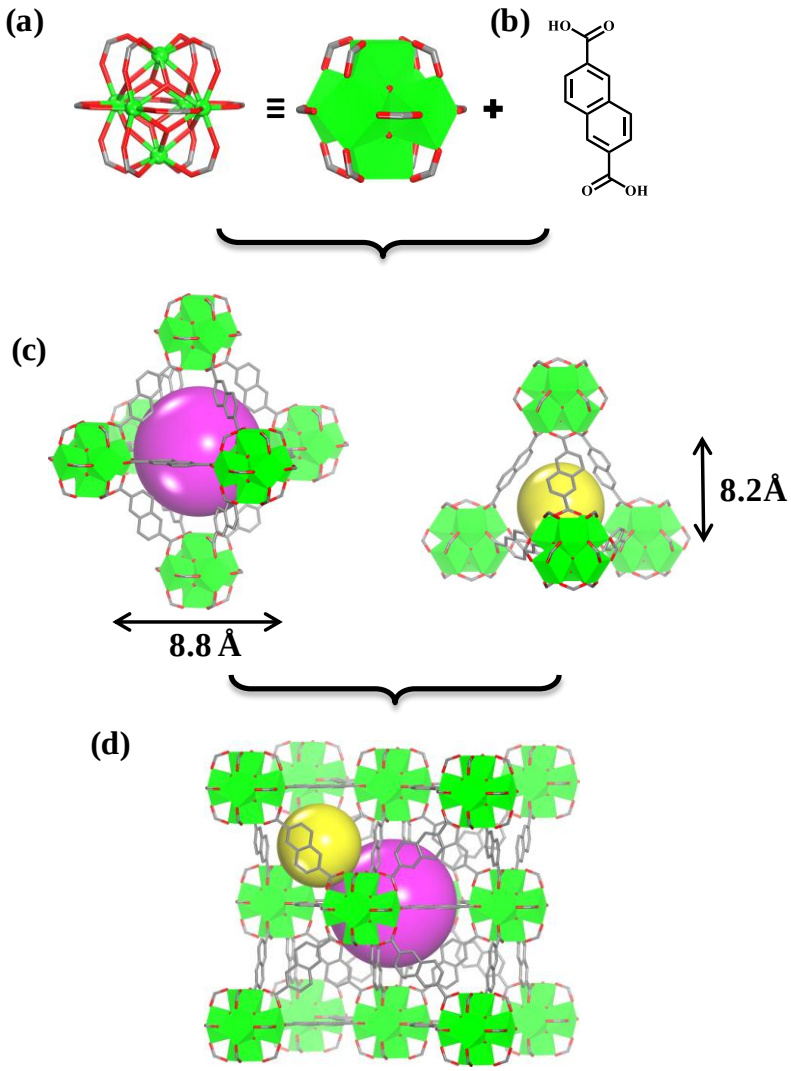

Figure S4. Schematic representations of SC-Ce-MOF-4 constructed from the assembly of hexanuclear Ce(IV)-based MBB and the organic linker of H_2NDC to generate a 3-periodic **fcu** net, and the two cages are: 8.8 Å and 8.2 Å. Hydrogen atoms and coordinated water molecules are omitted for clarity. Ce = green, C = gray, O =red.

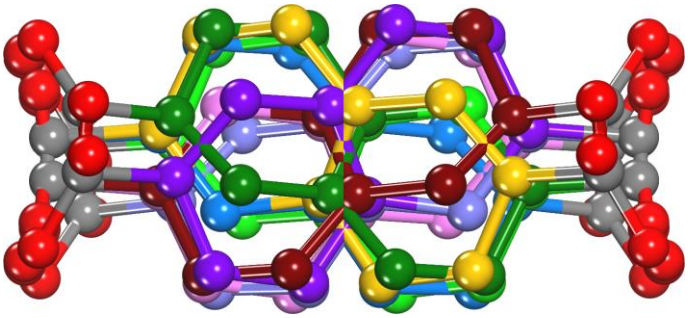

Figure S5. Highly disordered 2,6-NDC molecule in the SC-Ce-MOF-4.

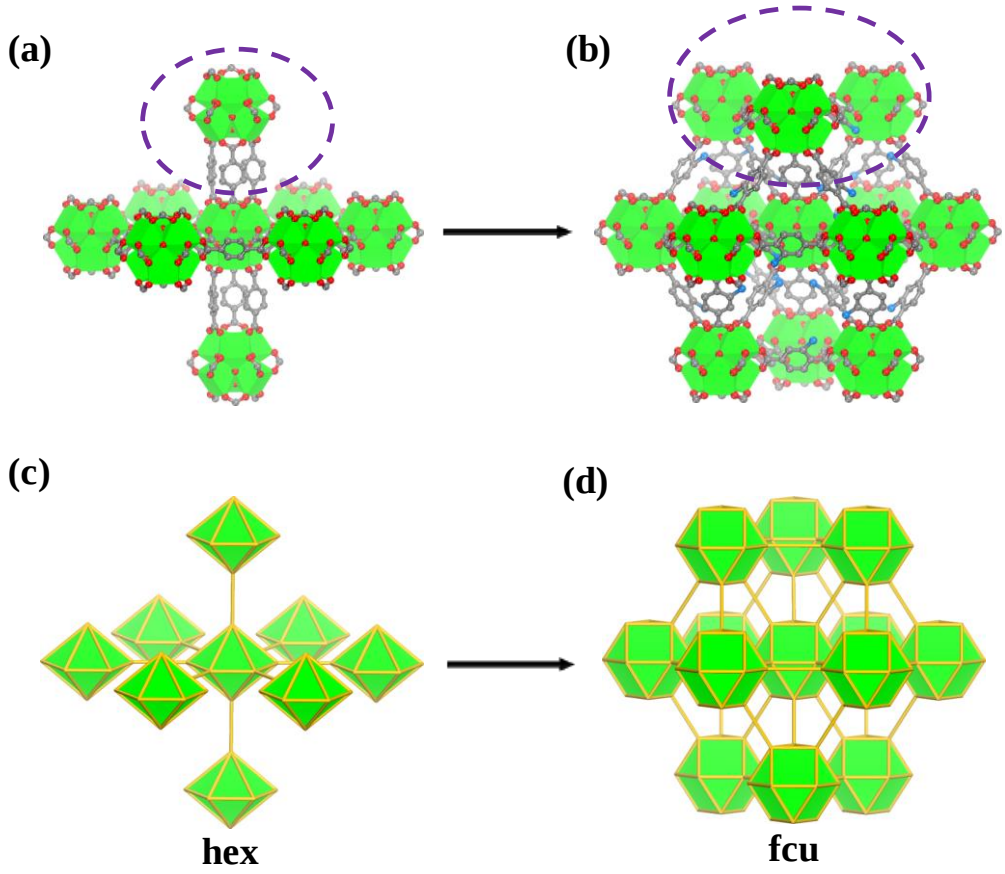

Figure S6. Schematic representations of the detailed structural differences surrounding the MBBs in SC-Ce-MOF-1 (a) and SC-Ce-MOF-3 (b) and topological analysis of SC-Ce-MOF-1 (c) and SC-Ce-MOF-3 (d), respectively. Hydrogen atoms and coordinated water molecules are omitted for clarity. Ce = green, C = gray, O = red, N = blue.

Section 4. PXRD, TGA plots and FT-IR spectra.

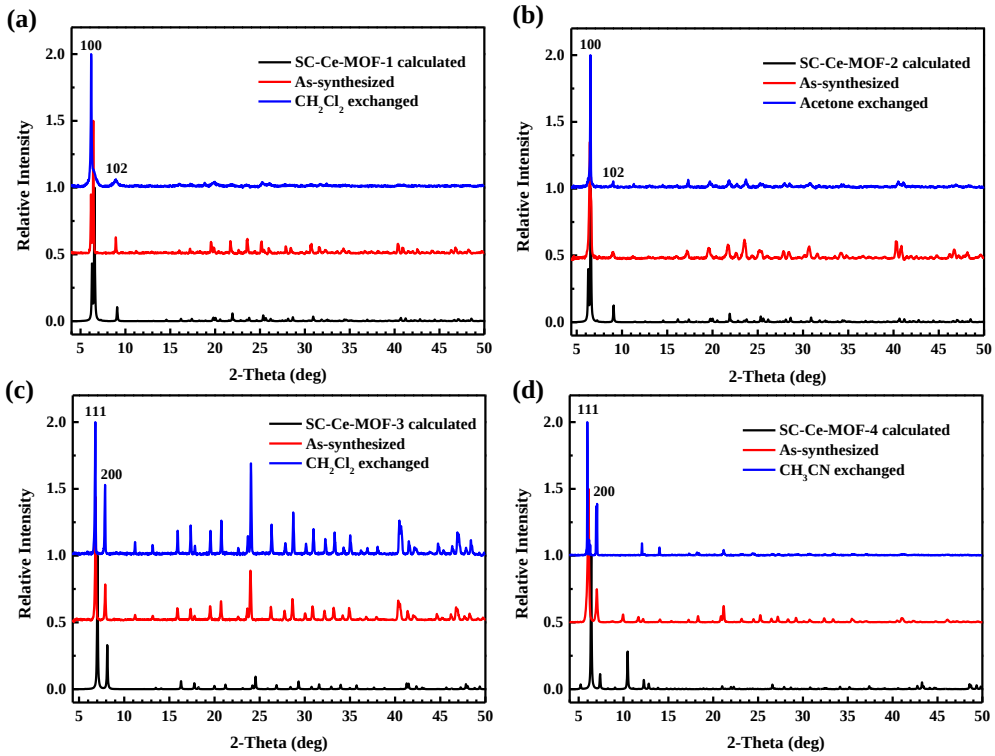

Figure S7. Powder X-ray diffraction (PXRD) patterns of the calculated, as-synthesized, and solvent-exchanged compounds of SC-Ce-MOF-1 (a), SC-Ce-MOF-2 (b), SC-Ce-MOF-3 (c) and SC-Ce-MOF-4 (d)**.**

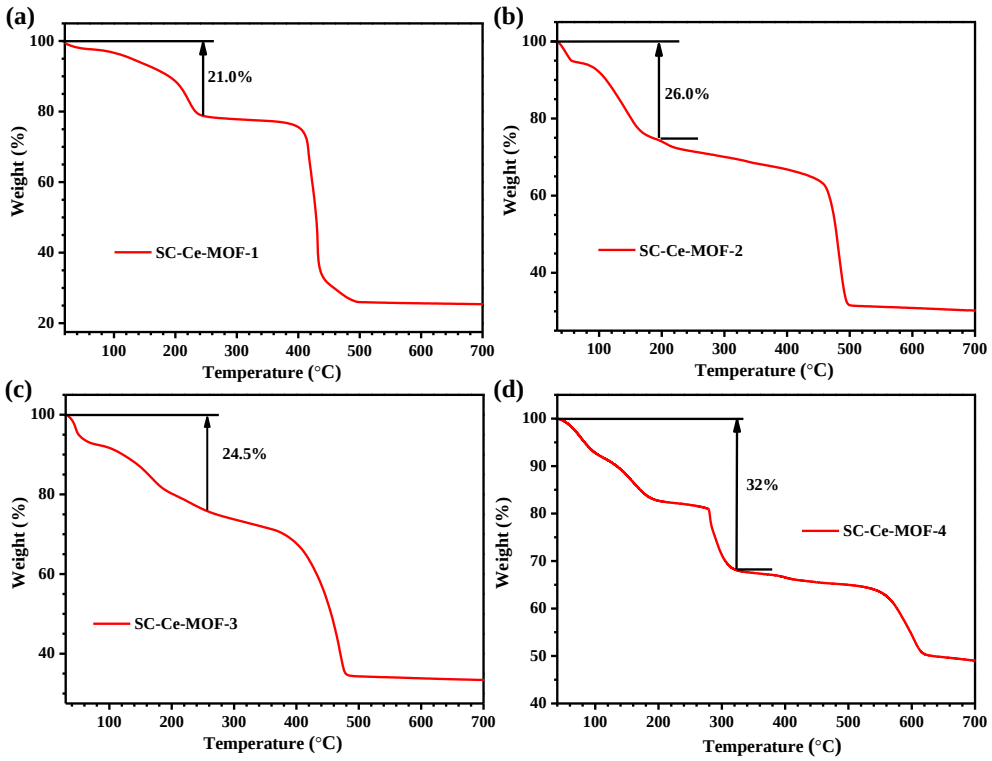

Figure S8. TGA plots of the as-synthesized SC-Ce-MOF-1 (a): <230℃, Loss of free/surface/coordinated solvent/water; >390 ℃, framework degradation. SC-Ce-MOF-2 (b): <194℃, Loss of free/surface/coordinated solvent/water; >450 ℃, framework degradation. SC-Ce-MOF-3 (c): <255℃, Loss of free/surface/coordinated solvent/water; >374 ℃, framework degradation. SC-Ce-MOF-4 (d): <323℃, Loss of free/surface/coordinated solvent/water; >530 ℃, framework degradation.

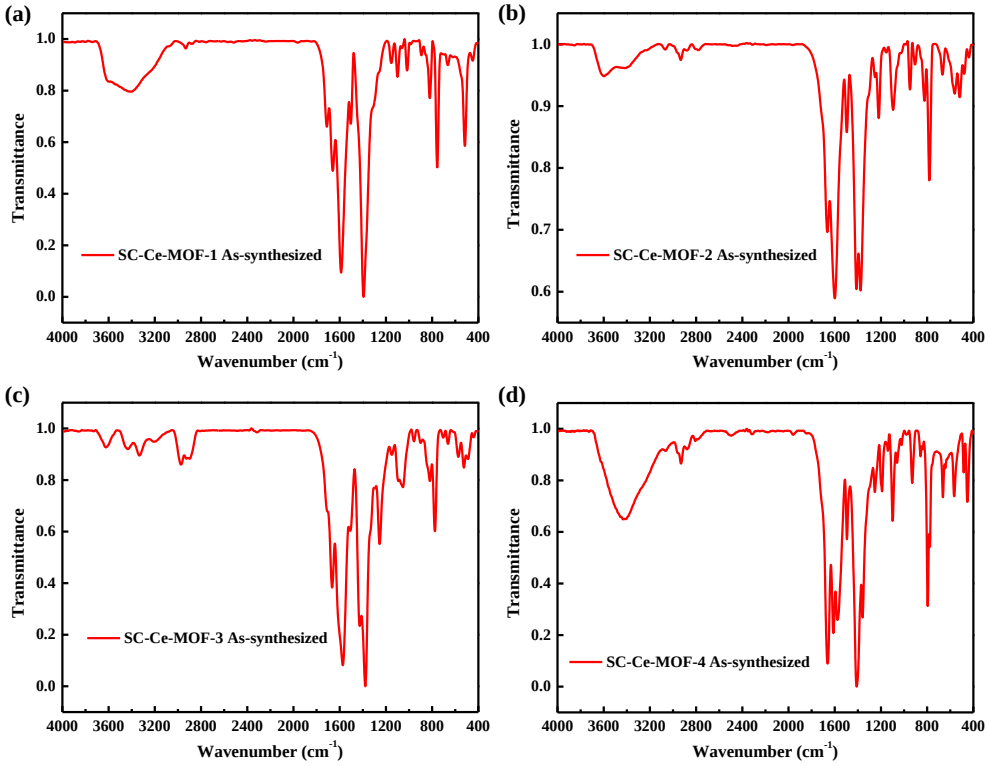

Figure S9. FT-IR spectra of the as-synthesized SC-Ce-MOF-1 (a), SC-Ce-MOF-2 (b), SC-Ce-MOF-3 (c) and SC-Ce-MOF-4 (d).

Section 5. Low-Pressure Gas Sorption Measurements.

Gas Sorption. Gas adsorption studies were conducted on a fully automated micropore gas analyzer Autosorb-iQ3 (Quantachrome Instruments) at relative pressures up to 1 atm. The cryogenic temperature was controlled using liquid nitrogen at 77 K. The bath temperature for the CH_4 and CO_2 sorption measurements was controlled using a recirculating bath containing an ethylene glycol/H_2O mixture. The apparent surface areas were determined from the nitrogen adsorption isotherms collected at 77 K by applying the BET models. Pore size analyses were performed using a cylindrical/spherical NLDFT pore model system by assuming an oxidic (zeolitic) surface. After exchanged with solvents, all of the samples were activated at 80 ^{o}C, 80 ^{o}C, 30 ^{o}C and 100 ^{o}C for 12 hours (30 ^{o}C for 4 hours and then heated to higher temperatures for 8 hours, and the heating rate is 1 ^{o}C/minute), under vacuum prior to N_2 sorption measurements, respectively.

Isosteric Heat of Adsorption. The isosteric heat of adsorption represents the strength of the interactions between adsorbate molecules and the adsorbent lattice atoms and can be used as a measurement of the energetic heterogeneity of a solid surface. The isosteric heat of adsorption at a given amount can be calculated by the Clausius−Clapeyron equation as

$$Q_{\mathrm{st}} = -RT^2 \left(\frac{\partial \ln P}{\partial T}\right) n_a$$

where Q_{st} is the isosteric heat of adsorption (kJ mol^{-1}), P is the pressure (kPa), T is the temperature, R is the gas constant, and n_a is the adsorption amount (mmol g^{-1}).

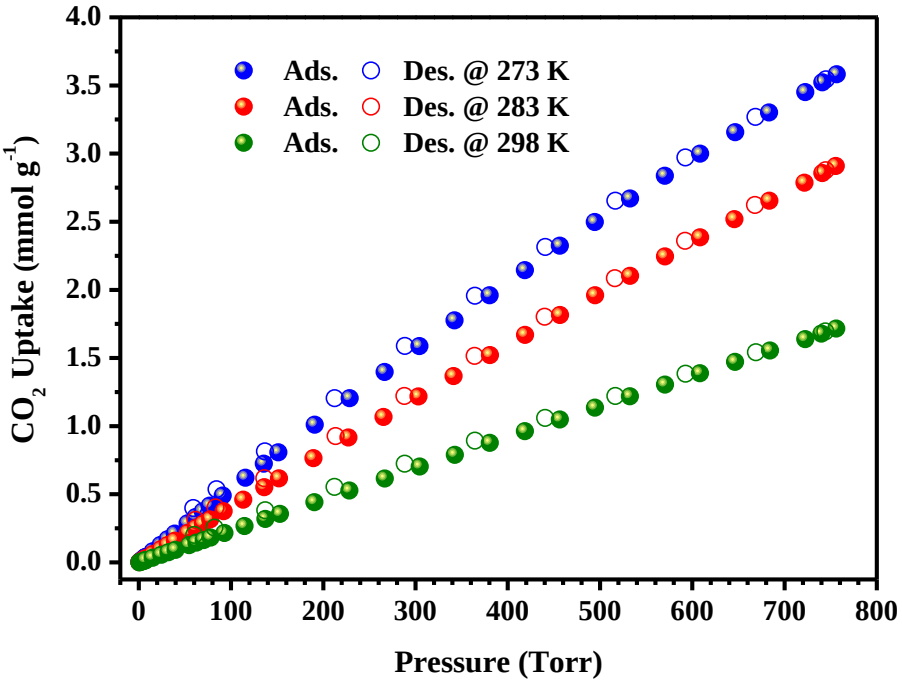

Figure S10. Variable-temperature CO_2 sorption isotherm for SC-Ce-MOF-1.

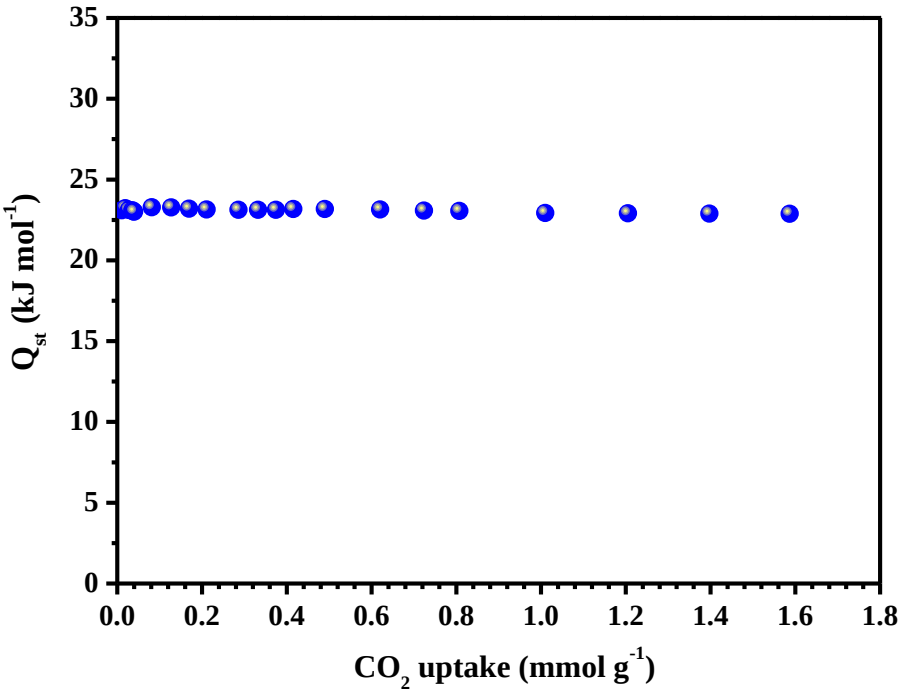

Figure S11. Isosteric heat of CO_2 adsorption of SC-Ce-MOF-1.

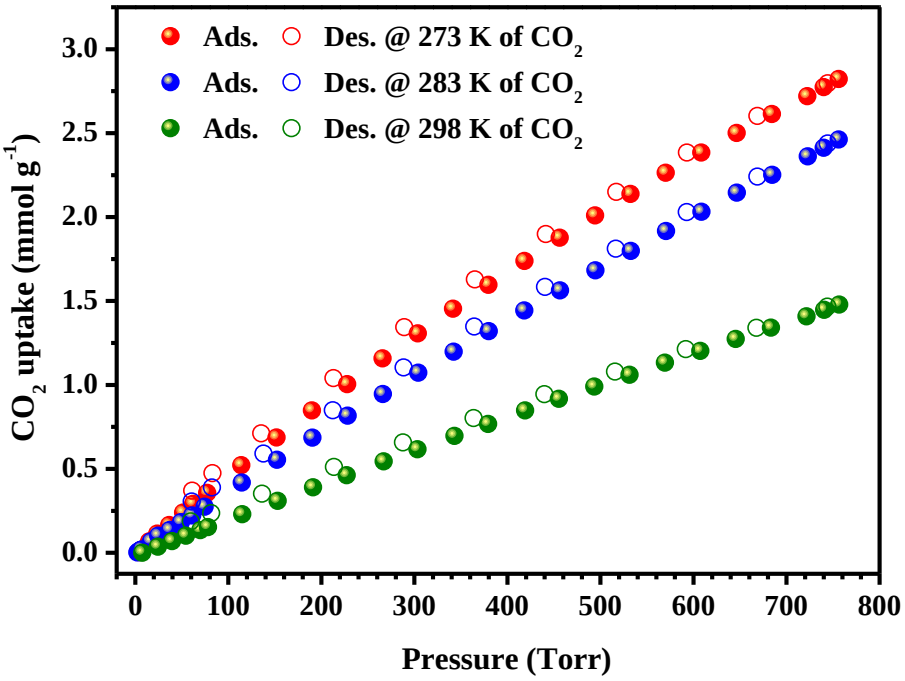

Figure S12. Variable-temperature CO_2 sorption isotherm for SC-Ce-MOF-2.

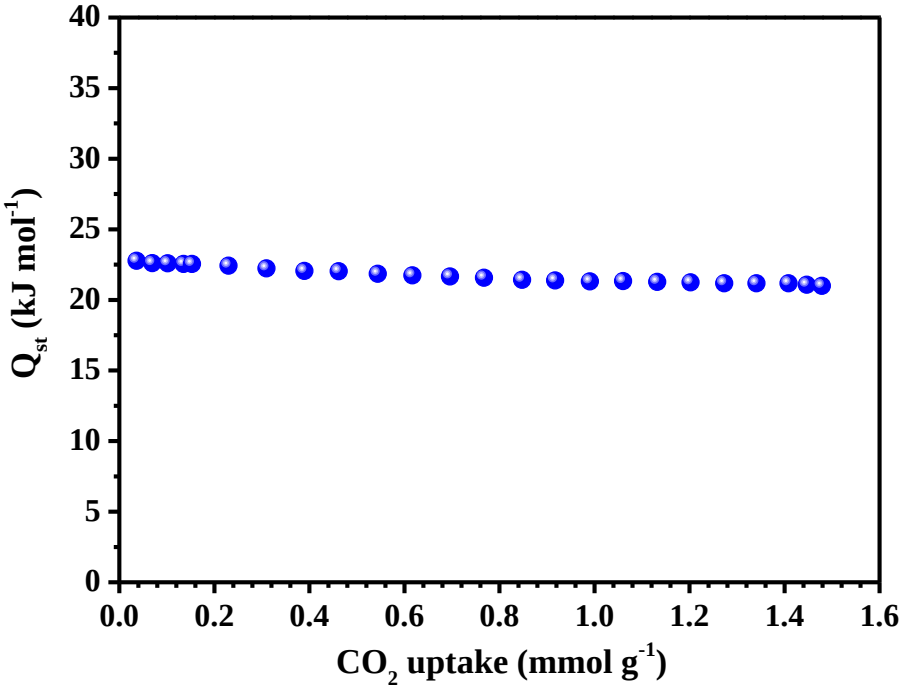

Figure S13. Isosteric heat of CO_2 adsorption of SC-Ce-MOF-2.

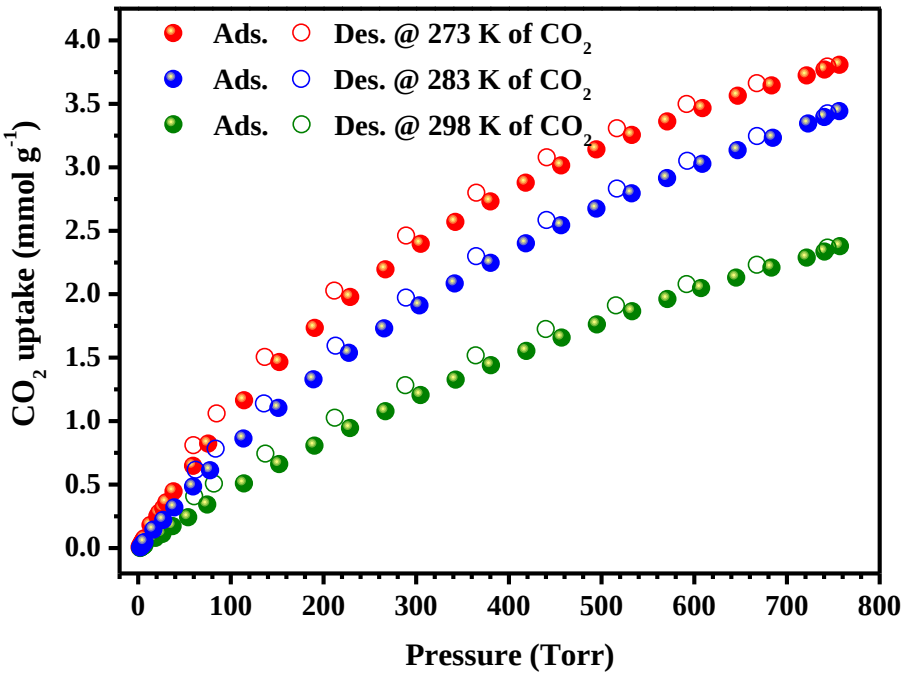

Figure S14. Variable-temperature CO_2 sorption isotherm for SC-Ce-MOF-3.

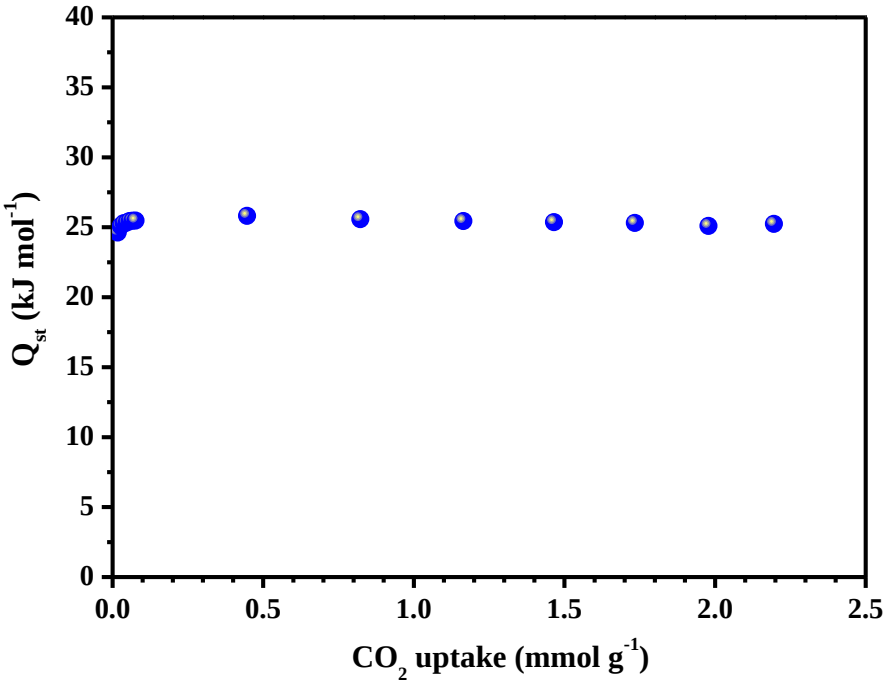

Figure S15. Isosteric heat of CO_2 adsorption of SC-Ce-MOF-3.

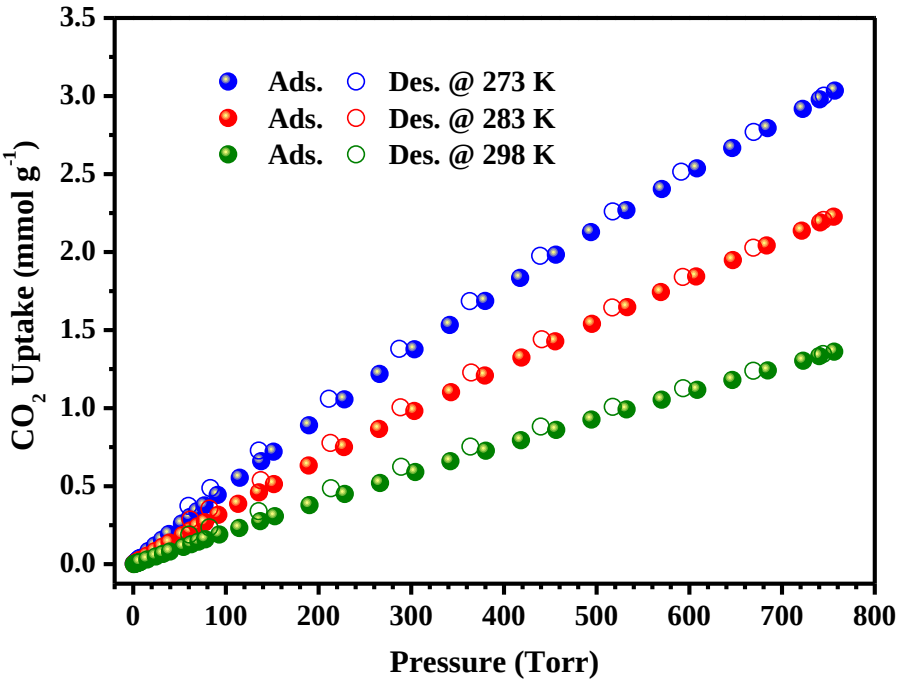

Figure S16. Variable-temperature CO_2 sorption isotherm for SC-Ce-MOF-4.

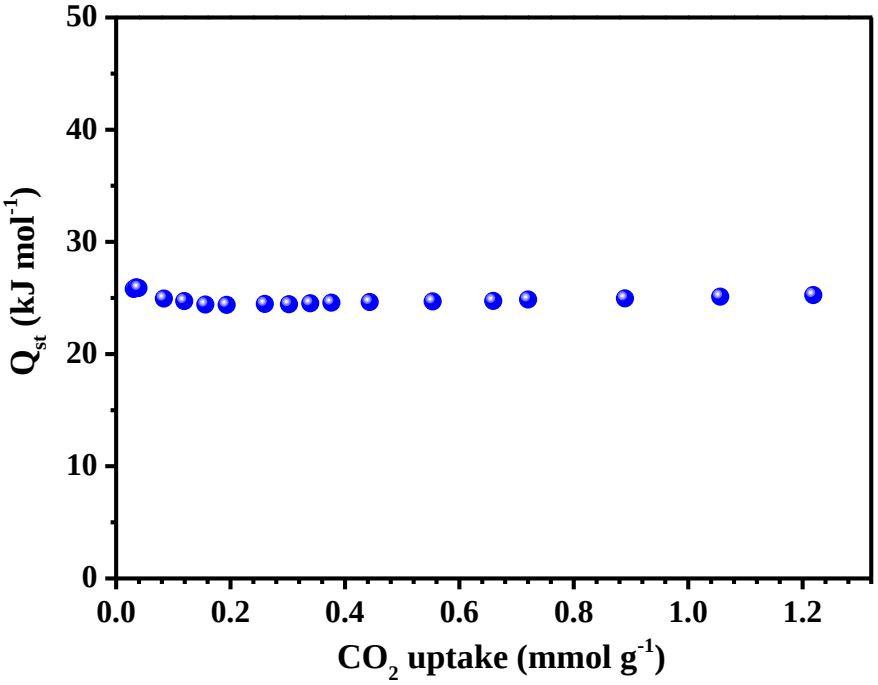

Figure S17. Isosteric heat of CO_2 adsorption of SC-Ce-MOF-4.

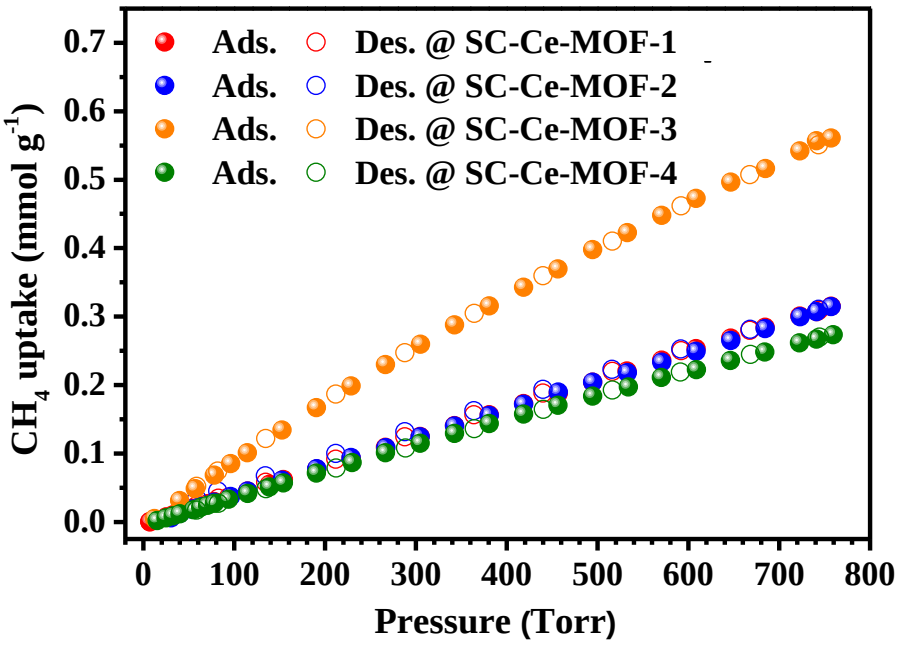

Figure S18. CH_4 sorption isotherms of SC-Ce-MOF-1−4 at 298 K.

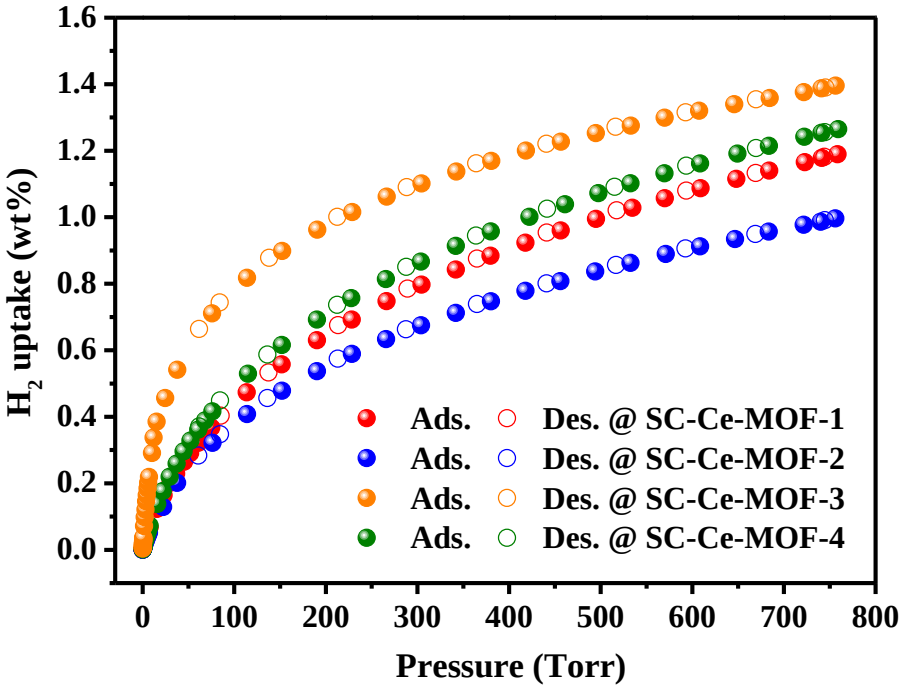

Figure S19. H_2 adsorption isotherms at 77 K of SC-Ce-MOF-1−4.

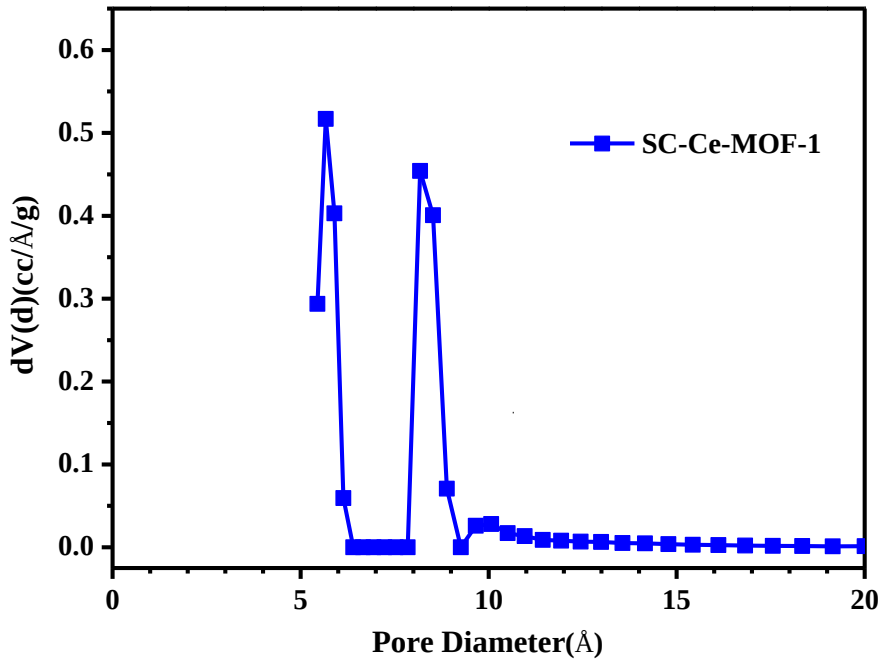

Figure S20. Pore size distribution of SC-Ce-MOF-1.

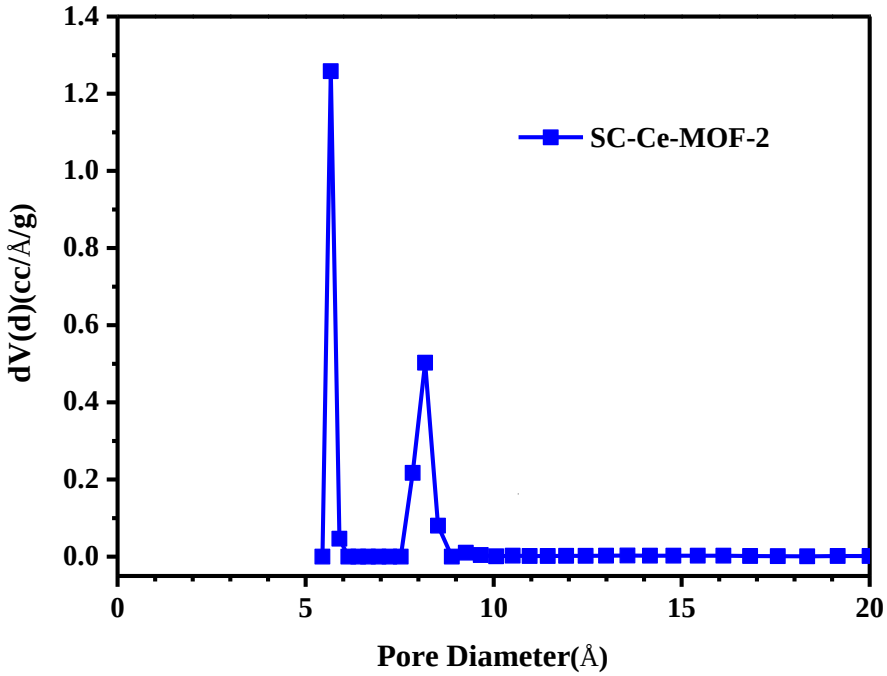

Figure S21. Pore size distribution of SC-Ce-MOF-2.

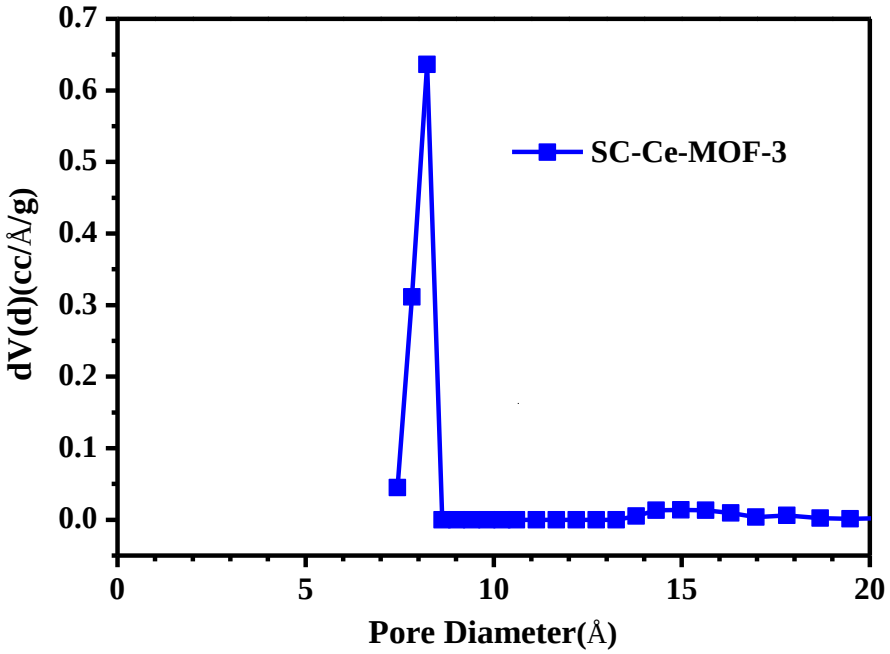

Figure S22. Pore size distribution of SC-Ce-MOF-3.

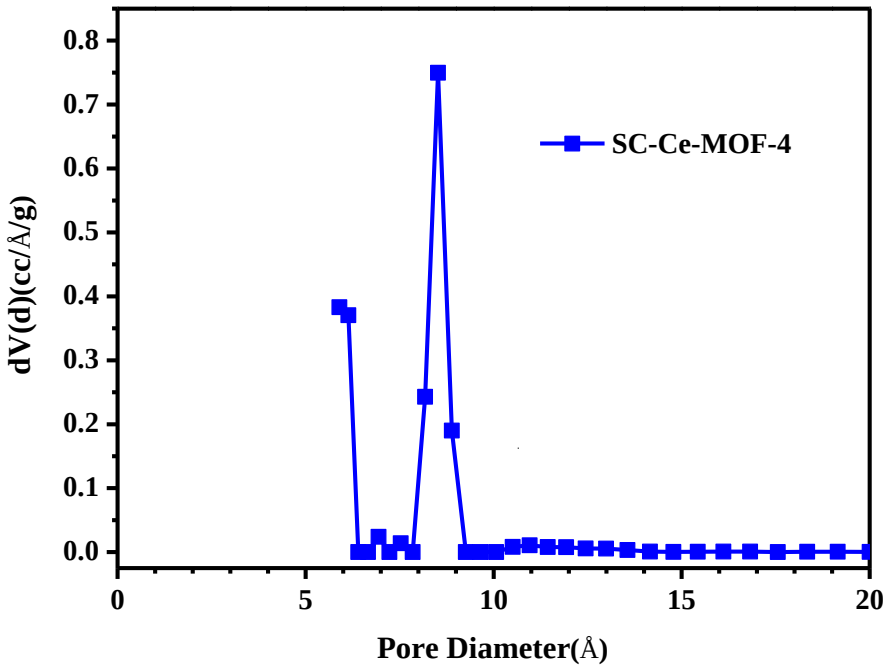

Figure S23. Pore size distribution of SC-Ce-MOF-4.

Section 6. Crystal Images.

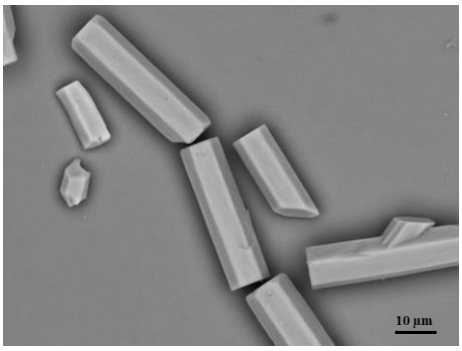

Figure S24. SEM image for SC-Ce-MOF-2, showing the hexagonal prism morphology.

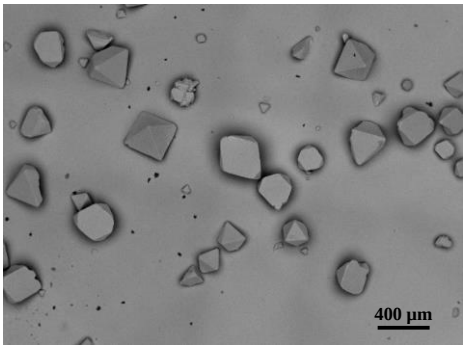

Figure S25. SEM image for SC-Ce-MOF-4, showing the octahedron morphology.

Section 7. Single-Crystal X-Ray Crystallography.

Single-crystal X-ray diffraction data for SC-Ce-MOF-1 and SC-Ce-MOF-3 were collected on a Bruker D8 quest diffractometer (Mo/*K*α, λ = 0.71073 Å) and SC-Ce-MOF-2 and SC-Ce-MOF-4 was collected on a Bruker D8 venture diffractometer (Cu/*K*α, λ = 1.5418 Å) at 153 K, respectively. Indexing was performed using APEX2 (Difference Vectors method).[1] Data integration and reduction were performed using SaintPlus 6.01.[2] Absorption correction was performed by multi-scan method implemented in SADABS.[3] Space groups were determined using XPREP implemented in APEX2. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXT[4] package or refined using SHELXL-2014 (full-matrix least-squares on F^2) contained in Olex2.[5] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. For all compounds, the contributions of heavily disordered solvent molecules were treated as diffuse using Squeeze procedure implemented in Platon program.[6-7] Crystal data and refinement conditions are shown in Tables S1-4.

Table S1. Crystal data and structure refinement for SC-Ce-MOF-1.

Identification code	SC-Ce-MOF-1
Empirical formula	$C_{48}H_{24}Ce_6O_{38}$
Formula weight	2049.39
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	$P6_3/mmc$
Unit cell dimensions	a = 15.5561(2) Å α = 90°
	b = 15.5561(2) Å β = 90°
	c = 28.1098(6) Å γ = 120°
Volume	5891.0(2) $Å^3$
Z	2
Density (calculated)	1.155 Mg/m^3
Absorption coefficient	2.322 mm^{-1}
F(000)	1928
Crystal size	0.100 x 0.100 x 0.060 mm^3
Theta range for data collection	2.648 to 25.995°
Index ranges	-19<=h<=19, -19<=k<=19, -34<=l<=34
Reflections collected	61525
Independent reflections	2193 [R(int) = 0.0444]
Completeness to theta = 25.242°	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2193 / 0 / 85
Goodness-of-fit on F^2	1.107
Final R indices [I>2sigma(I)]	R_1 = 0.0351, wR_2 = 0.0826
R indices (all data)	R_1 = 0.0409, wR_2 = 0.0861
Largest diff. peak and hole	1.162 and -1.310 $e.Å^{-3}$

Table S2. Crystal data and structure refinement for SC-Ce-MOF-2.

Identification code	SC-Ce-MOF-2	
Empirical formula	C3.84 H0 Ce0.48 F0.48 O3.04	
Formula weight	171.14	
Temperature	153(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_3/mmc$	
Unit cell dimensions	a = 15.5719(4) Å	α = 90°
	b = 15.5719(4) Å	β = 90°
	c = 28.1777(7) Å	γ = 120°
Volume	5917.2(3) $Å^3$	
Z	25	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	18.017 mm^{-1}	
F(000)	1988	
Crystal size	0.120 x 0.030 x 0.030 mm^3	
Theta range for data collection	3.633 to 70.126°.	
Index ranges	-11<=h<=18, -17<=k<=16, -34<=l<=26	
Reflections collected	29089	
Independent reflections	2147 [R(int) = 0.0371]	
Completeness to theta = 67.679°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2147 / 2 / 89	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R_1 = 0.0311, wR_2 = 0.0937	
R indices (all data)	R_1 = 0.0324, wR_2 = 0.0951	
Extinction coefficient	0.00002(2)	
Largest diff. peak and hole	0.959 and -0.542 e.$Å^{-3}$	

Table S3. Crystal data and structure refinement for SC-Ce-MOF-3.

Identification code	SC-Ce-MOF-3
Empirical formula	$C_{24}Ce_3N_3O_{19}$
Formula weight	1012.60
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	*Fm*-3*m*
Unit cell dimensions	a = 22.1418(2) Å α = 90°
Volume	10855.2(3) $Å^3$
Z	8
Density (calculated)	1.239 Mg/m^3
Absorption coefficient	2.520 mm^{-1}
F(000)	3760
Crystal size	0.040 x 0.040 x 0.040 mm^3
Theta range for data collection	2.602 to 27.487°
Index ranges	-28<=h<=25, -26<=k<=26, -28<=l<=20
Reflections collected	9867
Independent reflections	689 [*R*(int) = 0.0401]
Completeness to theta = 25.242°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	689 / 0 / 33
Goodness-of-fit on F^2	1.193
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0487, wR_2 = 0.1209
R indices (all data)	R_1 = 0.0518, wR_2 = 0.1223
Extinction coefficient	0.00012(3)
Largest diff. peak and hole	1.574 and -1.026 $e.Å^{-3}$

Table S4. Crystal data and structure refinement for SC-Ce-MOF-4.

Identification code	SC-Ce-MOF-4
Empirical formula	$C_{24}H_{12}CeO_{10.33}$
Formula weight	605.79
Temperature	153(2) K
Wavelength	1.54178 Å
Crystal system	Cubic
Space group	*Fm*-3*m*
Unit cell dimensions	a = 25.0373(5) Å α = 90°
Volume	15695.0(9) $Å^3$
Z	24
Density (calculated)	1.538 Mg/m^3
Absorption coefficient	13.916 mm^{-1}
F(000)	7120
Crystal size	0.090 x 0.070 x 0.050 mm^3
Theta range for data collection	4.996 to 65.039°
Index ranges	-27<=h<=28, -23<=k<=19, -29<=l<=9
Reflections collected	6450
Independent reflections	721 [*R*(int) = 0.0239]
Completeness to theta = 65.039°	98.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	721 / 340 / 154
Goodness-of-fit on F^2	1.327
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.1187, wR_2 = 0.3302
R indices (all data)	R_1 = 0.1188, wR_2 = 0.3302
Extinction coefficient	0.00037(10)
Largest diff. peak and hole	1.782 and -1.167 e.$Å^{-3}$

Section 8. References.

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