Supporting Information

A microporous Ce-based MOF with the octahedron cage for highly selective adsorption towards xenon over krypton

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Table S1. Crystallographic Data for Ce-SINAP-1.

| Code                  | Ce-SINAP-1                                      |
|-----------------------|-------------------------------------------------|
| **CCDC number**       | 2085724                                         |
| **Formula**           | C_{29}H_{16}O_{8}Ce                              |
| **Mass**              | 632.54                                          |
| **Habit**             | Triclinic                                       |
| **Space Group**       | P-1                                             |
| **a (Å)**             | 12.1829(10)                                     |
| **b (Å)**             | 14.9798(13)                                     |
| **c (Å)**             | 15.5382(13)                                     |
| **α (°)**             | 67.680(3)                                       |
| **β (°)**             | 69.005(3)                                       |
| **γ (°)**             | 67.206(3)                                       |
| **V (Å³)**            | 2343.1(4)                                       |
| **Z**                 | 2                                               |
| **T (K)**             | 100                                             |
| **λ (Å)**             | 0.71073                                         |
| **Max. 20 (°)**       | 55.152                                          |
| **ρ_{calc} (g·cm⁻³)** | 0.897                                           |
| **μ (mm⁻¹)**          | 0.999                                           |
| **F (000)**           | 624.0                                           |
| **Crystal size (mm³)**| 0.2*0.18*0.1                                    |
| **GoF on F²**         | 1.081                                           |
| **Radiation**         | MoKα                                            |
| **R_1, ωR_2 [I>2σ(I)]**| 0.0434, 0.1213                                 |
| **R_1, ωR_2 (all data)**| 0.0480, 0.1235                                 |
| **(Δρ)_{max}, (Δρ)_{min} / e (Å⁻³)** | 2.167, -1.619                                 |
| **Reflections collected** | 38851                                          |
| Assignment | Bond length(Å) | Assignment | Bond length(Å) |
|------------|----------------|------------|----------------|
| Ce1-O1     | 2.452(3)       | Ce1-O5     | 2.462(3)       |
| Ce1-O1a    | 2.898(3)       | Ce1-O6     | 2.572(3)       |
| Ce1-O2     | 2.579(3)       | Ce1-O7     | 2.490(3)       |
| Ce1-O3     | 2.567(3)       | Ce1-O8     | 2.515(3)       |
| Ce1-O4     | 2.410(3)       |            |                |

| Assignment | Bond angles(°) | Assignment | Bond angles(°) |
|------------|----------------|------------|----------------|
| O1-Ce1-O1a | 78.66(9)        | O3-Ce1-O6  | 50.90(9)       |
| O1-Ce1-O2  | 89.33(9)        | O3-Ce1-O7  | 71.08(10)      |
| O1-Ce1-O3  | 155.47(10)      | O3-Ce1-O8  | 73.60(10)      |
| O1-Ce1-O4  | 75.19(10)       | O4-Ce1-O1a | 70.87(9)       |
| O1-Ce1-O5  | 75.95(9)        | O4-Ce1-O5  | 133.19(9)      |
| O1-Ce1-O6  | 144.79(10)      | O4-Ce1-O6  | 75.24(9)       |
| O1-Ce1-O7  | 125.83(9)       | O4-Ce1-O7  | 90.75(11)      |
| O1-Ce1-O8  | 82.21(10)       | O4-Ce1-O8  | 136.28(11)     |
| O2-Ce1-O1a | 159.97(9)       | O5-Ce-O1a  | 67.87(9)       |
| O2-Ce1-O3  | 78.97(9)        | O5-Ce1-O6  | 139.16(9)      |
| O2-Ce1-O4  | 90.70(10)       | O5-Ce1-O7  | 77.42(10)      |
| O2-Ce1-O5  | 78.97(9)        | O5-Ce1-O8  | 73.65(10)      |
| O2-Ce1-O6  | 72.38(9)        | O6-Ce1-O1a | 108.85(9)      |
| O2-Ce1-O7  | 143.83(9)       | O6-Ce1-O7  | 73.11(9)       |
| O2-Ce1-O8  | 51.66(10)       | O6-Ce1-O8  | 107.00(9)      |
| O3-Ce1-O1a | 117.90(9)       | O7-Ce1-O1a | 47.64(8)       |
| O3-Ce1-O4  | 125.89(9)       | O7-Ce1-O8  | 132.39(12)     |
| O3-Ce1-O5  | 93.07(9)        | O8-Ce1-O1a | 140.07(9)      |

Figure S1. Single unit of **Ce-SINAP-1** with labels.
Figure S2. Structure of Ce-SINAP-1.

Thermogravimetric Analysis (TGA) Plot
Figure S3. TGA curves of as-synthesized **Ce-SINAP-1** before and after activation.

**PXRD Patterns**

Figure S4. PXRD patterns of **Ce-SINAP-1**, simulated, as-synthesized, activated and after γ-ray irradiation.
Figure S5. PXRD patterns of Ce-SINAP-1 with different temperatures.

BET and pore size distribution
1. BET Analysis

\[ y = a + b \times x \]

Adj. R-Square: 0.99995
Slope: 0.00947
Standard Error: 2.64274E-5

Figure S6. Brunauer-Emmet-Teller (BET) and the Langmuir surface areas were calculated to be 459.4 m²/g and 490.1 m²/g for Ce-SINAP-1.
2. Pore Size Use NLDFT Model

![Diagram](image)

Figure S7. Pore size distribution for Ce-SINAP-1 samples using Non-Local Density Functional Theory (NLDFT) model.

**Single Component Isotherm:**

The adsorption isotherms for Xe, Kr and Ar in Ce-SINAP-1 were measured at 273 K, 293 K and 313 K. The single-component isotherm data were fitted with the Single-site Langmuir-Freundlich model for Xe, Kr and Ar. Here, $P$ is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), $q$ is the adsorbed amount per mass of adsorbent (mol/kg), $q_{sat}$ is the saturation capacities of site (mol/kg). $b_a$ is affinity coefficient of site (1/kPa), and $v_a$ represents the deviations from an ideal homogeneous surface.

$$q = q_{a, \text{sat}} \frac{b_ap^{v_a}}{1 + b_ap^{v_a}}$$

1. Kr Adsorption Isotherms
Figure S8. Kr adsorption isotherms for Ce-SINAP-1 at different temperatures (273 K, 293 K, 313 K).

2. Xe Adsorption Isotherm
3. Ar Adsorption Isotherm

Figure S10. Ar adsorption isotherms for Ce-SINAP-1 at different temperatures (273K, 293K, 313K).

Table S3. The fitting parameters of single-site Langmuir-Freundlich model at
293 K.

| Adsorbent  | Adsorbates | $q_{a,sat}$ (mmol/g) | $b_a$ (kPa$^{-1}$) | $v_a$ |
|------------|------------|----------------------|-------------------|--------|
| Ce-SINAP-1 | Xe         | 3.77792              | 0.02002           | 0.85889|
|            | Kr         | 2.77311              | 0.00267           | 1.04838|
|            | Ar         | 2.67065              | 0.00161           | 1.09001|

**Henry’s Constant Fitting**

The Henry’s constant of Ce-SINAP-1 were obtained from a linear fit in low pressure of the adsorption isotherm as the following function.$^1$

$$H(\text{mmol}\cdot\text{g}^{-1}\text{bar}^{-1}) = \frac{q(\text{mmol/g})}{P(\text{bar})}$$

Figure S11. Henry coefficient fitting of Xe adsorption isotherm at 293 K.
Figure S12. Henry coefficient fitting of Kr adsorption isotherm at 293 K.

Figure S13. Henry coefficient fitting of Ar adsorption isotherm at 293 K.

Table S4. The Henry coefficient of Xe/Kr, Xe/Ar and Kr/Ar at 293K.

| Adsorbate | Henry Coefficient | Xe/Kr selectivity | Xe/Ar Selectivity | Kr/Ar Selectivity |
|-----------|------------------|-------------------|-------------------|------------------|
| Xe        | 6.76             |                   |                   |                  |
| Kr        | 0.82             |                   |                   |                  |
| Ar        | 0.23             |                   |                   |                  |

S11
**Isosteric Heat of Adsorption**

Isosteric heat of adsorption ($Q_{st}$) is used to evaluate the adsorption affinity and strength of interaction between the adsorbates and the adsorbents. The Clausius-Clapeyron equation and Langmuir-Freundlich method are used to signify the $Q_{st}$. It defined as:

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

Where $n_a$ (mmol/g) is the amount of adsorbed gas, $T$ (K) is the temperature, $P$ (kPa) is the pressure, $Q_{st}$ (kJ/mol) is the isosteric heat of adsorption. Integration of the equation gives:

$$\ln P = \frac{Q_{st}}{RT} + C$$

In this study, adsorption equilibrium data at 273k, 293 K and 313 K were used to calculated the heat of adsorption that was obtained at a given uptake from the slopes of the isosteres according to the equations as mentioned. The fitting parameters of Langmuir-Freundlich model were displayed in Table S3.

**IAST Calculation of Adsorption Selectivity**

The adsorption selectivity was calculated by the Ideal Adsorbed Solution Theory (IAST)\textsuperscript{2} for Xe/Kr (20/80, v/v) and Xe/Ar (1/99, v/v), two binary mixtures in Ce-SINAP-1. The adsorption selectivity, $S_{12}$, is defined by the following equation:

$$S_{12} = \frac{x_1/x_2}{y_1/y_2}$$

Where $x_1$ and $x_2$ are the equilibrated adsorption capacity of component 1 and 2 in adsorbents, respectively; and $y_1$ and $y_2$ are the molar fractions of component 1 and 2 in gas phase, respectively.\textsuperscript{3-5}

**Breakthrough experiments**

The adsorption capacity was estimated from the breakthrough curves using the following equation:

$$n_{adsi} = FC_i t_i$$

Where $n_{adsi}$ is the adsorption capacity of the gas i, $F$ is the total molar flow, $C_i$ is the concentration of the gas i entering the column and the $t_i$ is the time corresponding to the gas i, which is estimated from the breakthrough profile.
Figure S14. Flowchart of the dynamic breakthrough experiment.

1,2,3-Helium, Mixture Gas (Ar Kr Xe), Argon
4-Gas Mixer, 5-Gas Flowmeter, 6,9-Pressure Gauge
7-Temperature Controlled Chamber
8- Packed Bed, 10-Gas Filter, 11-Gas Chromatograph

Figure S15. Density of states of different elements in Ce-SINAP-1.

Table S5. List of the adsorption performance of MOFs adsorbents for Xe/Kr under different radiation condition

| adsorbents   | Xe uptake (mmol/g at 1.0 bar) | Xe Qst (kJ/mol) | γ-ray Irradiation Resistance (kGy) | Xe/Kr Selectivity |
|--------------|-------------------------------|-----------------|-----------------------------------|-------------------|
| UiO-66(Zr)   | 2.0<sup>a</sup>               | 24.6            | 2                                 | 7.7<sup>c</sup>   |
| Zr-Fum-Me    | 1.9<sup>a</sup>               | 30.9            | 8                                 | 15.8<sup>c</sup>  |
| SIFSIX-3-Cu  | 2.1<sup>a</sup>               | -               | 50                                | 4.81<sup>e</sup>  |
| SIFSIX-3-Fe  | 2.45<sup>a</sup>              | 27.4            | 10                                | around 6<sup>c</sup> |
| Ce-SINAP-1   | 2.02<sup>b</sup>              | 24.2            | 20                                | 8.24<sup>d</sup>  |

<sup>a</sup> Ref. [1], <sup>b</sup> Ref. [2], <sup>c</sup> Ref. [3], <sup>d</sup> Ref. [4], <sup>e</sup> Ref. [5]
a. Xe uptake at 298K  
b. Xe uptake at 293K  
c. Henry’s separation at 298K  
d. Henry’s separation at 293K  
e. Xe/Kr selectivity at 298K with 400 ppm Xe and 40 ppm Kr, balanced with dry air.

References

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