A Robust Calcium-Organic Framework for Effective Separation of Xenon and Krypton

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Experimental

Materials and reagents

The ligand of H_4TBAPy was purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co.,Ltd. All other reagents and solvents including Ca $(NO_3)_2 \cdot 4H_2O$, hydrochloric (HCl), N, N-Dimethylformamide (DMF), and methanol were purchased from commercial sources without further purification.

Synthesis of ECUT-50a

The bulk **ECUT-50** were immersed into methanol for three days. The methanol was changed three times every day. After that, the products were evacuated at 180 °C under vacuum condition (**ECUT-50a**).

Single Crystal X-ray diffraction

After synthesis, one yellow crystal with suitable size was selected from the mother liquor and mounted on the tip of glass fibre. The data collection of the single crystal was performed on a Bruker-AXS SMART Breeze CCD diffractometer using graphite monochromated Mo Kα radiation (λ =0.71073 Å). The structure was solved by direct method and refined by full-matrix least-squares using SHELXTL program package.2.7. The selected crystallographic data and refinement parameters for the single crystal are summarized in Table S1. Selected bond lengths and angles for **ECUT-50** are listed in Table S2. Crystallographic data for the structure of **ECUT-50** have been deposited in CIF format in Cambridge Crystallographic Data Center with CCDC 1974915.

Physical Measurements

The powder X-ray diffraction (PXRD) patterns were recorded using Cu Kα radiation (λ= 1.5406 Å) on AXSD8 Discover powder diffractometer at 40 kV, 40 mA at room temperature in the range of 5-50 degree (2 theta). Thermal gravimetric analysis (TGA) was carried out using a TGA Q500 thermal analysis system and the sample was heated from 30 to 800 °C under N_2 atmosphere with a heating rate of 10 °C/min. The data analysis was carried out using the TA Universal Analysis software package.

Gas adsorption experiments and calculations

The gas sorption isotherms were collected on a Belsorp-max. Ultrahigh purity grade Xe (99.99%) and Kr (99.99%) were used for the measurements. To maintain the experimental temperatures, liquid nitrogen (77 K) and temperature-programmed water bath (273 and 298 K) were used, respectively. A roughly 100 mg of **ECUT-50a** were taken for the nitrogen adsorption experiments at 77 K. The adsorption isotherms for Xe/Kr were obtained at temperature of 273 K and 298 K, respectively. The isosteric heats of adsorption (Q_{st}) were calculated based on Clausius-Clapeyron equation using dual-site Langmuir-Freundlich model with the following equation.

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \qquad (1)$$

The adsorption selectivity was established by the Ideal Adsorbed Solution Theory (IAST) for Xe/Kr (20:80) at 298 K. The adsorption selectivity was calculated from

$$S_{ads} = \frac{q_A / q_B}{y_A / y_B} \qquad (2)$$

where the q_A, and q_B represent the molar loadings in **ECUT-50** that is in equilibrium with a bulk fluid mixture with mole fractions y_A, and $y_B = 1 - y_A$. The molar loadings, also called gravimetric uptake capacities, are expressed in mol kg^{-1}. The IAST calculations for the mixtures were

performed at 298 K, taking the mole fractions $y_A = 0.2$ and $y_B = 1 - y_A = 0.8$.

Breakthrough experiment

The breakthrough experiments were carried out at 298 K. The powder of **ECUT-50a** were packed into column. Firstly, the pure helium gas (100 ml/min) flow through the column for 30 min. Then the Xe/Kr gas mixture (20/80) passed through the fixed bed column with a flow rate of 2 mL/min. The effluent gases from the column were monitored by a gas chromatography (TCD-Thermal Conductivity Detector, detection limit 0.1%).

Table S1. Crystal structure information for **ECUT-50**.

Compound	**ECUT-50**
Formula	$C_{22}H_{13}CaO_5$
Formula weight	397.40
Color	light yellow
Crystal system	orthorhombic
Space group	*Pbam*
a(Å)	20.371(6)
b(Å)	6.895(2)
C (Å)	16.506(5)
α	90.00
β	90.00
γ	90.00
Volume ($Å^3$)	2318.4
Z	4
Temperature for data collection (K)	296
Range for data collection θ(º)	1.234 to 25
No. of measured reflections	11208
No. of unique reflections	2124
No. of parameters	138
No. of restraints	1
Goodness-of-fit on F^2	1.173
Final R indexes[I≥2σ(I)]	R_1=0.1112, wR_2=0.3026
Final R indexes [all data]	R_1=0.1440,

wR_2=0.3258

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

Table S2 Selected bond length (Å) and angles (°)for **ECUT-50**

Bond length			
Ca(1)-O(2)#1	2.312(4)	Ca(1)-O(1)	2.506(6)
Ca(1)-O(2)#2	2.312(4)	Ca(1)-O(2)	2.511(4)
Ca(1)-O(3)#3	2.423(4)	Ca(1)-O(2)#3	2.511(4)
Ca(1)-O(3)	2.423(4)	Ca(1)-O(1)#4	2.54037(6)

Symmetrical code: #1 -X,3-Y,+Z; #2 1/2-X,-1/2+Y,-Z; #3 1/2-X,-1/2+Y,+Z; #4 +X,+Y,-Z;

Bond angles			
O(2)#1-Ca(1)-O(2)#2	79.2(2)	O(1)-Ca(1)-O(2)	132.94(12)
O(2)#1-Ca(1)-O(3)#3	86.68(19)	O(2)#1-Ca(1) -O(2)#3	98.18(15)
O(2)#2-Ca(1)-O(3)#3	153.00(17)	O(2)#2-Ca(1)-O(2)#3	153.02 (11)
O(2)#1-Ca(1)-O(3)	153.00(17)	O(3)#3-Ca(1)-O(2)#3	51.54(14)
O(2)#2-Ca(1)-O(3)	86.68(19)	O(3)-Ca(1)-O(2)#3	104.60(18)
O(3)#3-Ca(1)-O(3)	96.2(3)	O(1)-Ca(1)-O(2)#3	132.94(12)
O(2)#1-Ca(1)-O(1)	72.27(14)	O(2)-Ca(1)-O(2)#3	71.93(18)
O(2)#2-Ca(1)-O(1)	72.27(14)	O(2)#1-Ca(1)-O(1)#4	84.40(15)
O(3)#3-Ca(1)-O(1)	81.57(15)	O(2)#2-Ca(1)-O(1)#4	4.40(15)
O(3)-Ca(1)-O(1)	81.57(15)	O(3)#3-Ca(1)-O(1)#4	117.23(14)
O(2)#1-Ca(1)-O(2)	153.02(11)	O(3)-Ca(1)-O(1)#4	117.23(14)
O(2)#2-Ca(1)-O(2)	98.18(15)	O(1)-Ca(1)-O(7)	149.4(2)
O(3)#3-Ca(1)-O(2)	104.60(18)	O(2)-Ca(1)-O(1)#4	68.63(14)
O(3)-Ca(1)-O(2)	51.54(14)	O(2)-Ca(1)-O(1)#4	68.63(14)

Symmetrical code: #1 1/2-X,-1/2+Y,-Z; #2 1/2-X,-1/2+Y,+Z; #3 +X,+Y,-Z; #4 1/2-X,1/2+Y,+Z

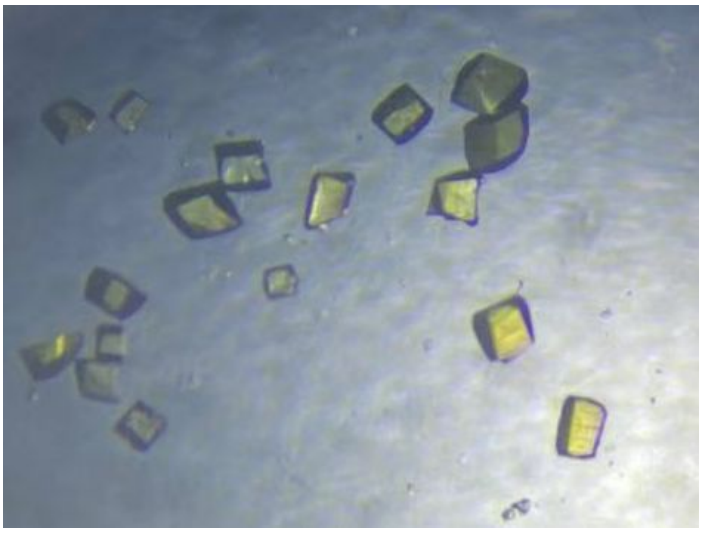

Figure S1. The optical microscope image of **ECUT-50**

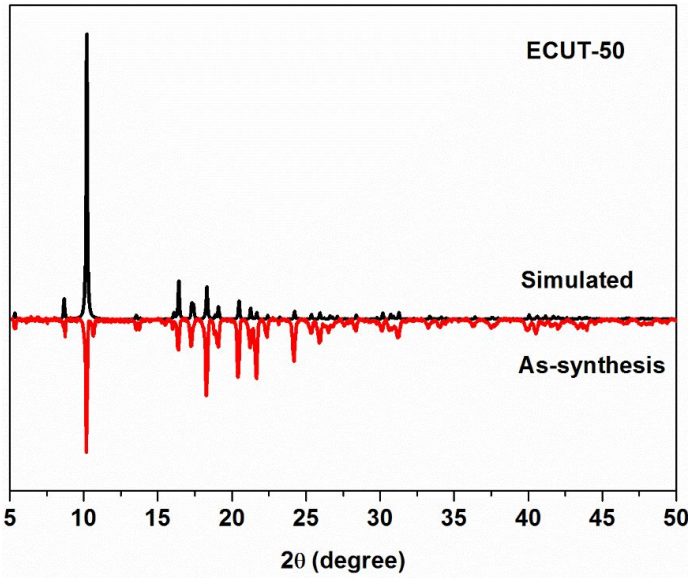

Figure S2. The PXRD patterns of **ECUT-50** with as-synthesized samples and the PXRD patterns simulated from single crystal data.

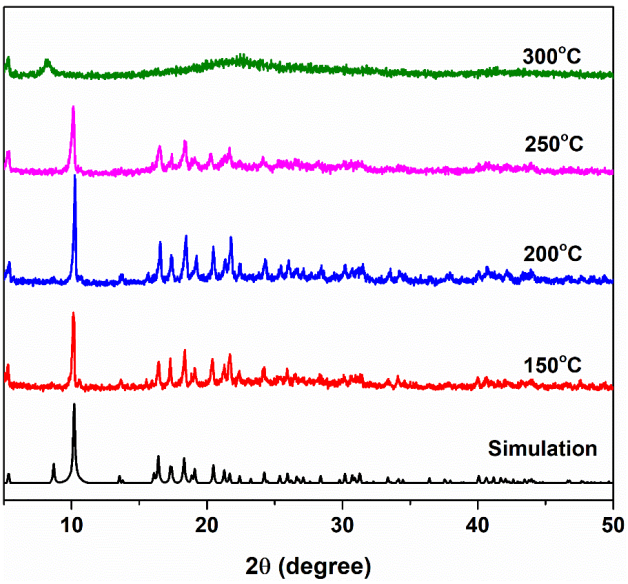

Figure S3. Thermal stability from 150°C to 300°C of **ECUT-50** including the simulated result.

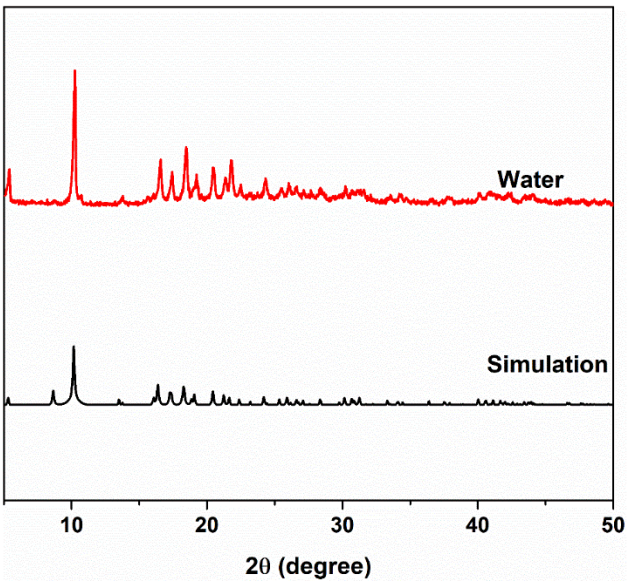

Figure S4. PXRD patterns of **ECUT-50** after immersed into water including the simulated result.

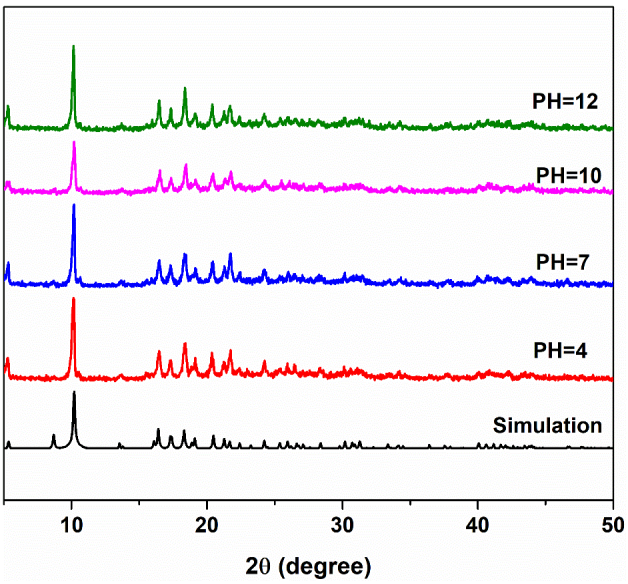

Figure S5. PXRD patterns of **ECUT-50** after soaking in different pH values including the simulated result.

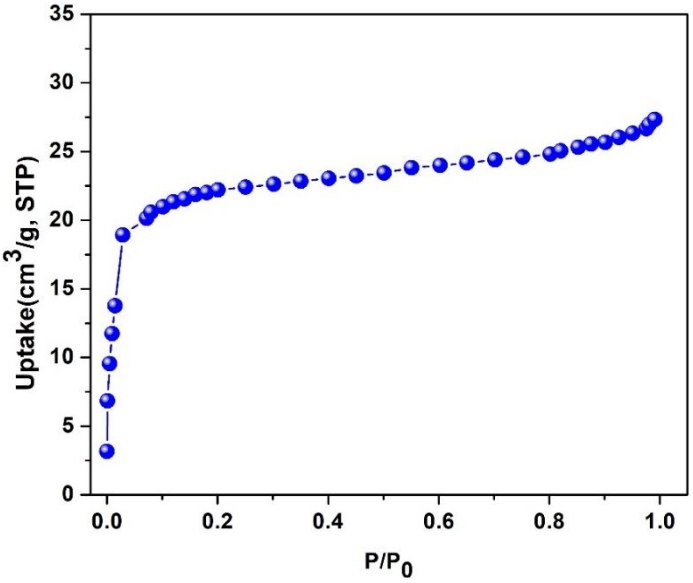

Figure S6. N2 adsorption isotherms of **ECUT-50a** at 77 K.

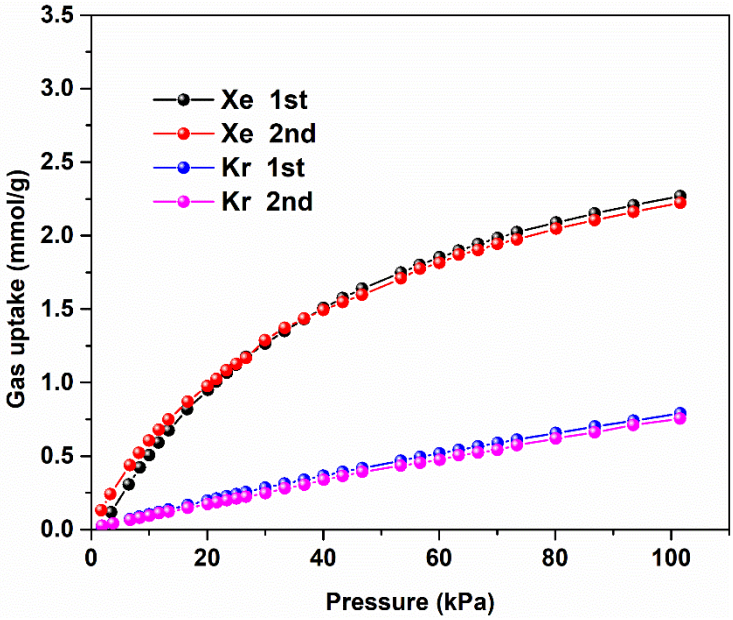

Figure S7. Two cycles adsorption isotherms for Xe and Kr.

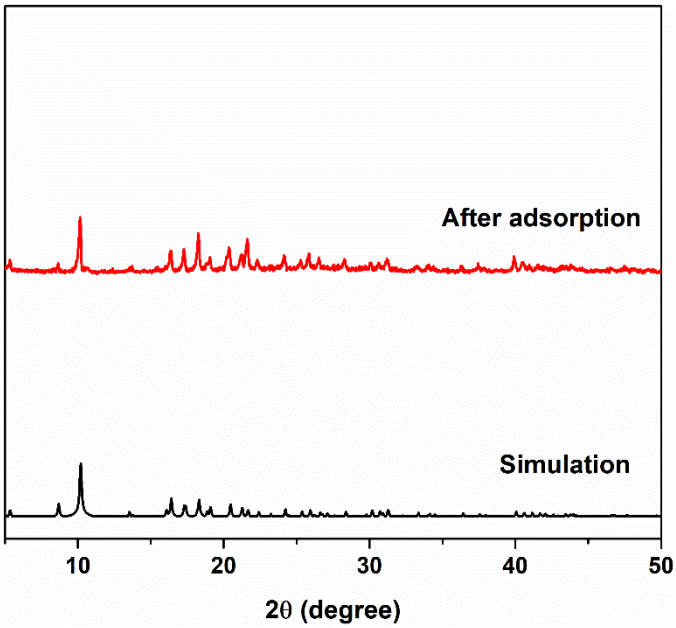

Figure S8. PXRD patterns of **ECUT-50** after two cycles adsorption including simulated result.

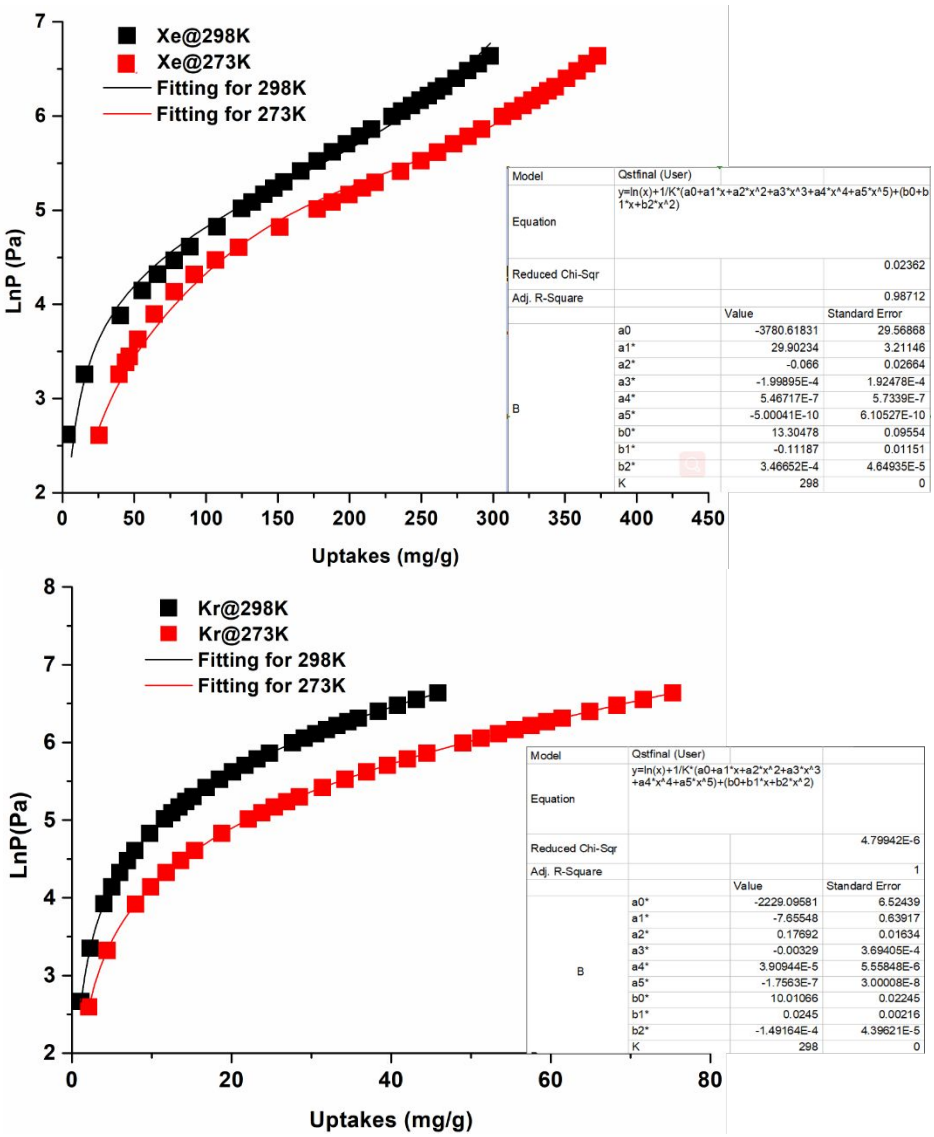

Figure S9. The fitting curves for adsorption isotherms of **ECUT-50** for Xe and Kr

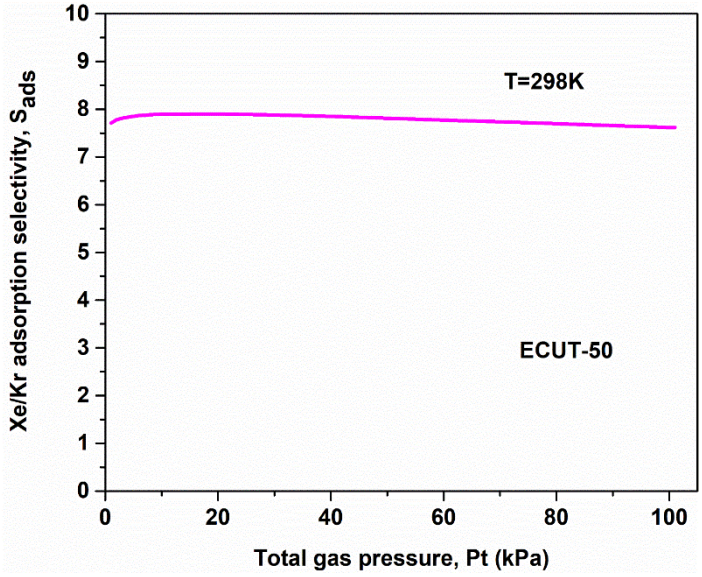

Figure S10. The calculated IAST selectivity for Xe/Kr (20/80) of **ECUT-50** at 298 K

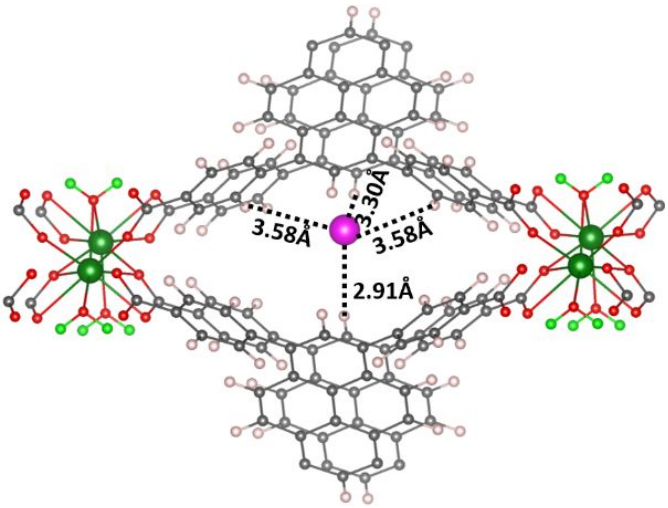

Figure S11. The binding sites of Xe in **ECUT-50**