

Supplementary Information

Enhanced Xe/Kr separation via the pore size confinement effect of a microporous thorium-based metal-organic framework

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S1. Materials and characterizations. Caution! Th-232 used in this study is an α emitter with the daughter of radioactive Ra-228. All thorium compounds used and investigated were operated in an authorized laboratory designed for actinide element studies. Standard precautions for handling radioactive materials should be performed. All reagents and solvents were purchased from commercial suppliers and used without further purification. PXRD data were collected from 5 to 50° on a Bruker D8 advance diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with a Lynxeye one-dimensional detector. The solid-state luminescence and UV-vis-NIR spectra were recorded on a Craic Technologies microspectrophotometer. The infrared spectra were recorded in the range of 4000-450 cm^{-1} on a Thermo Nicolet 6700 spectrometer. Elemental analyses (C, H, N) were executed with a Vario EL CHNOS elemental analyzer. The thermalgravimetric analysis was carried out on a NETZSCH STA 449F5 instrument in the range of 30-900 °C under an argon flow at a heating rate of 10 °C/ min.

S2. Synthesis. A mixture of Th(NO₃)₄·6H₂O (29.4 mg, 0.05 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (11.2 mg, 0.05 mmol) and 0.3 ml ethanol was dissolved in a mixture of 2.7 mL DMF and 150 μL trifluoroacetic acid. The resulting solution was sealed in a 10 mL glass vial and heated at 120 °C for 3 days. The reaction system was then cooled naturally to room temperature. The colorless crystal product was filtered and washed with DMF and ethanol. The resulting product was activated under a dynamic vacuum at room temperature for 6 hours and then at 120 °C for 6 hours. Yield: ca. 18 % (based on Th(NO₃)₄·6H₂O). Anal. Calcd for C_{26.5}H_{29.5}N_{4.5}ThO_{14.5}: C, 36.37; H, 3.40; N, 7.20. Found: C, 35.47; H, 2.29; N, 6.80.

S3. X-ray crystallography. Data collection was performed on a Bruker D8-Quest diffractometer with a Turbo X-ray Source (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) adopting the direct drive rotating anode technique and a CMOS detector at room temperature. The data frames were collected using the program APEX3 and processed using the program SAINT routine in APEX3. The structures were solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXTL-2018 program¹. All

non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and included as riding atoms. Crystallographic and refinement details are summarized in **Table S1**. The solvent molecules in **Th-BPYDC-I** are highly disordered and impossible to refine using conventional discrete-atom models. To resolve this issue, the contribution of solvent-electron density was removed using the SQUEEZE routine in PLATON,² thereby producing a set of solvent-free diffraction intensities. The OMIT command was used to ignore the unreasonable diffraction points to make Fobs vs Fcalc plot more reasonable. The final formula was calculated from the SQUEEZE results in combination with elemental analysis and TGA.

Table S1. Crystallographic data for **Th-BPYDC-I** (after squeeze)

Formula	C ₂₄ H ₁₂ N ₄ O ₈ Th
MM [g mol ⁻¹]	716.42
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.2224(9)
<i>b</i> (Å)	14.7467(13)
<i>c</i> (Å)	14.9219(16)
<i>V</i> (Å ³)	1690.3(3)
<i>Z</i>	2
<i>D_c</i> (g cm ⁻³)	1.408
μ (mm ⁻¹)	4.456
<i>F</i> (000)	676
<i>T</i> (K)	293
^a <i>R</i> ₁ , ^b <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0593,0.1495
^a <i>R</i> ₁ , ^b <i>wR</i> ₂ (all data)	0.0652,0.1548

$${}^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|. {}^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

S4. Stability measurements. Stability measurements of **Th-BPYDC-I** were studied by activation at 120 °C in a vacuum environment (less than 200 Torr).

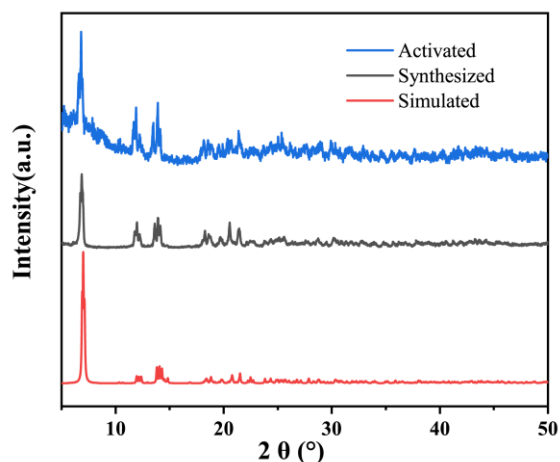


Figure S1. Simulated (red), synthesized (black) and activated (blue) PXRD patterns for Th-BPYDC-I.

S5. Thermogravimetric analysis. Thermogravimetric analysis (TGA) curves were recorded on an STA 449 F3 Jupiter. Dried as-synthesized samples of Th-BPYDC-I were heated at a constant rate of 10 K min^{-1} in nitrogen from $30 \text{ }^\circ\text{C}$ to $900 \text{ }^\circ\text{C}$. The total weight loss of about 18.39 % from 30 to $310 \text{ }^\circ\text{C}$ (cal.18.13 %) suggests the departure of free ethanol, water and DMF. The collapse of the framework occurred at ca. $310 \text{ }^\circ\text{C}$.

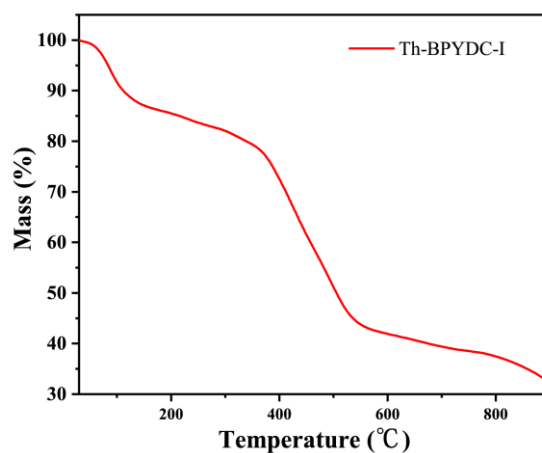


Figure S2. The TGA curves of Th-BPYDC-I measured from $30 \text{ }^\circ\text{C}$ to $900 \text{ }^\circ\text{C}$.

S6. Kr and Xe adsorption measurements. Ultrahigh purity grade Kr (99.999%) and Xe (99.999%) were used for all measurements. The adsorption measurements of krypton and xenon were studied at room temperature. The Xe/Kr selectivity is the ratio of the Henry coefficients (KH). The low-pressure regime of the adsorption isotherm

exhibits almost linear behavior. A line with zero intercept to these data was fitted to identify the K_H of Xe and Kr in the material.

The isosteric heat of Xe adsorption, Q_{st} , defined as

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

were determined by using pure component isotherm fits the Clausius-Clapeyron equation. Q_{st} (kJ mol^{-1}) is the isosteric heat of adsorption, T (K) is the temperature, P (bar) is the pressure, R is the gas constant, and q (mmol g^{-1}) is the adsorbed amount³.

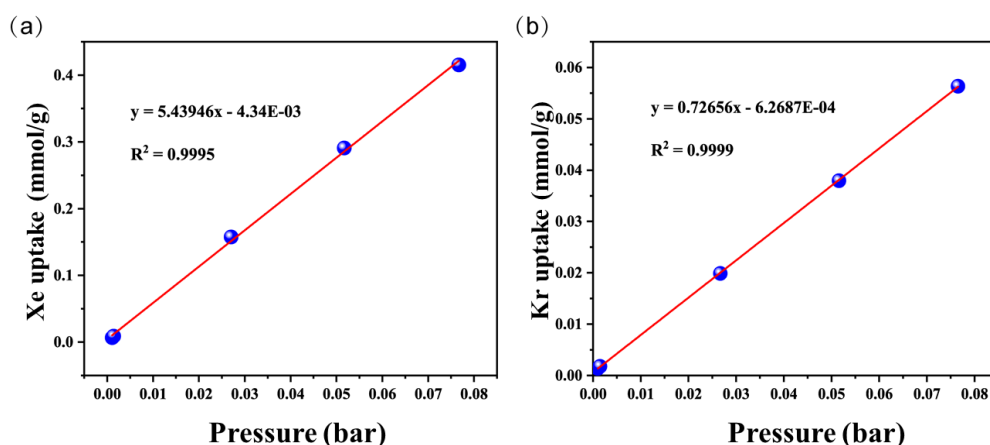


Figure S3. The Henry coefficient fit isotherms for (a) Xe and (b) Kr for Th-BPYDC-I at 298 K.

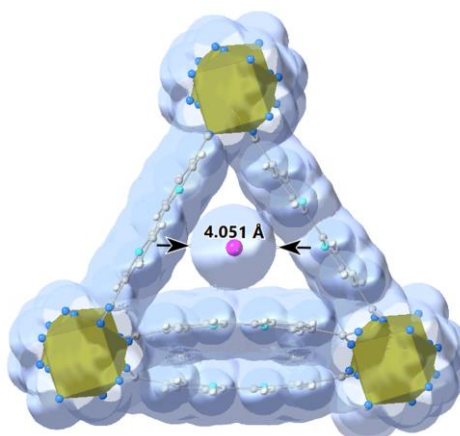


Figure S4. The effective pore size of Th-BPYDC-I after considering the influence of van der Waals force.

S7. N₂ adsorption measurements. Gas adsorption measurements of N₂ (77 K) were carried out on a Quantachrome Autosorb Gas Sorption analyser IQ2. Methanol was added every 8 h, and the extract was discarded. The sample was soaked for 3 days to remove solvent molecules. After decanting the methanol extract, the treated Th-BPYDC-I sample was activated by using the “outgas” function of the surface area analyser for 12 h at 120 °C.

S8. Spectroscopic characterizations.

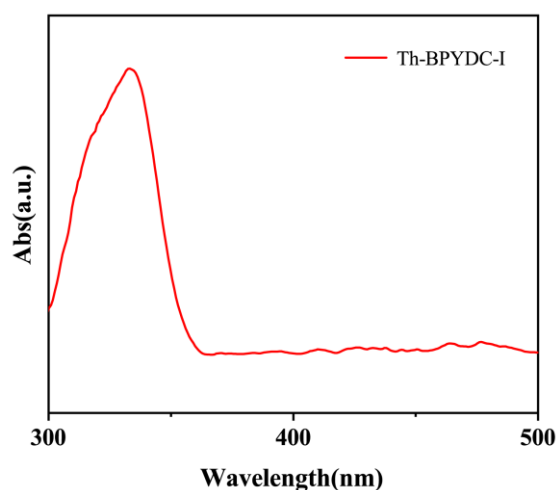


Figure S5. The UV-Vis absorption spectra for Th-BPYDC-I measured at 298 K.

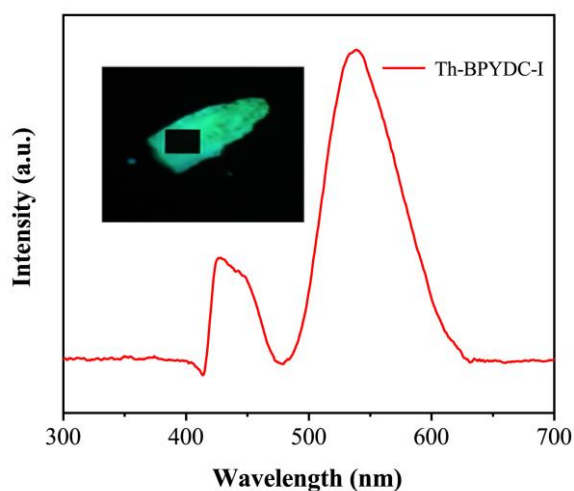


Figure S6. The emission spectra for Th-BPYDC-I measured at 298 K under excitation of 365 nm's UV light.

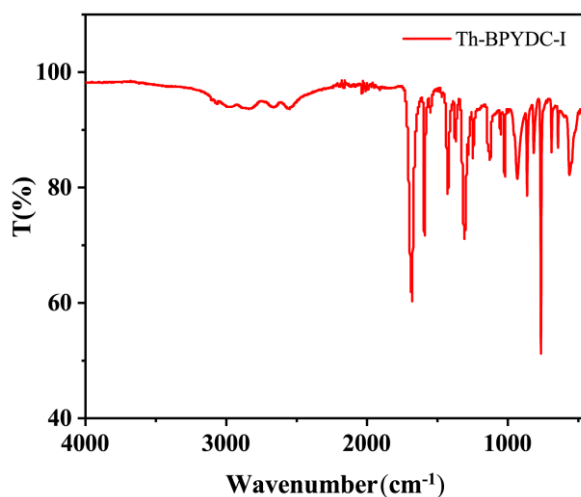


Figure S7. The IR spectra for **Th-BPYDC-I** measured at 298 K.

Table S2. Summary and comparison of Xe Adsorption Capacity and Xe/Kr Selectivity for selected materials

Materials	Xe (mmol/g)	Selectivity	Ref.
Th-BPYDC-I	2.15 ^a	7.49 ^b	This work
UiO-66	1.58 ^a	3.8 ^c	<i>J. Hazard. Mater.</i> 2016 , 320, 513–520
Zn-MOF-74	3.88 ^a	5.6	<i>J. Phys. Chem. C</i> 2014 , 118, 11685–11698
Ni-MOF-74	4.19 ^a	7.3	<i>Langmuir</i> 2012 , 28, 11584–11589
Mg-MOF-74	5.58 ^a	5.92	<i>J. Phys. Chem. C</i> 2014 , 118, 11685–11698
MOF-505	2.2 ^a	8 ^c	<i>Aiche J.</i> 2011 , 57, 1759–1766
PCN-14	7.1 ^a	6.5 ^d	<i>J. Phys. Chem. C.</i> 2014 , 118, 11685–11698
MOF-303	4.14 ^a	6.6 ^c	<i>Angew. Chem. Int. Ed.</i> 2021 , 133, 3459–3463
SCU-11	3.15 ^a	5.7 ^b	<i>Angew. Chem. Int. Ed.</i> 2018 , 130, 5885–5889
MOF-5	2.19 ^a	2.4	<i>J. Mater. Chem.</i> 2006 , 16, 626–636

^aAt 298 K and 1 bar.

^bHenry's constant based on a single-component isotherm.

^cFrom breakthrough experiment (Xe/Kr 20/80).

^dFrom IAST calculation (Xe/Kr 10/90).

References

- 1 Sheldrick, G. M. SHELXTL; Siemens Analytical X-ray Instruments: Madison, WI, **2001**.
- 2 Spek, A. Structure validation in chemical crystallography. *Acta Crystallogr., Sect. D.* **2009**, *65*, 148-155.
- 3 Tóth, J. State Equation of the Solid-Gas Interface Layers. *Acta Chim. Acad. Sci. Hung.* **1971**, *69*, 311–317.