Supporting Information for

An fcu Th-MOF Constructed from In Situ Coupling of Monovalent Ligands

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S1. Methods

X-ray Crystallography. Single-crystal XRD data were collected on a Bruker D8 Venture single-crystal X-ray diffractometer (Mo Kα radiation, λ = 0.71073 Å). The data were collected and integrated to 0.85 Å by Bruker program SAINT[1], empirical absorption correction was applied using program SADAB[1]. The structure was solved with direct method using SHELXT[2] and refined by full-matrix least-squares on F^2 using SHELXL[3] in Olex2[4]. All non-H atoms were located easily and refined anisotropically. Idealized atom positions were calculated for H atoms. Details of the refinement were given in **Table S1**.

Table S1 Crystal data and structure refinement details for SUM-5.

CCDC deposition number	2085727
Compound name	st025401
Formula	$C_{84}H_{48}N_{12}O_{38}Th_6$
Formula weight	3225.58
Temperature/K	293.25
habit	octahedral
Crystal system	Cubic
Space group	Fm-3m
a,b,c/Å	30.5859(19)
α, β,γ/°	90
Volume/Å^3	28613(5)
Z	4
ρ_{calcd}/cm^3	0.749
μ/mm^{-1}	3.129
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.766 to 49.614
Index ranges	-35 ≤ h ≤ 36, -36 ≤ k ≤ 36, -36 ≤ l ≤ 36
Reflections collected	173850

Independent reflections	1290 [R_{int} = 0.2321, R_{sigma} = 0.0299]
Goodness-of-fit on F^2	1.120
Final R indexes [I>=2σ (I)]	R_1 = 0.0622, wR_2 = 0.1696
Final R indexes [all data]	R_1 = 0.0777, wR_2 = 0.1881
Largest diff. peak/hole / e $Å^{-3}$	1.63/-1.18

Level A alerts:
PLAT430_ALERT_2_A Short Inter D...A Contact N1 ..N1 . 0.64 Ang.
1-x,1/2-z,1/2-y = 43_655 Check
PLAT430_ALERT_2_A Short Inter D...A Contact N1 ..N1 . 1.13 Ang.
x,1/2-y,1/2-z = 28_555 Check
Response: Due to the symmetry of the crystals, the azo moiety is disordered at two positions of equivalent probabilities, causing the short interatomic distances.
PLAT973_ALERT_2_A Check Calcd Positive Resid. Density on Th01 2.19 eA-3
Response: The atom type is correct, and no twinning. The crystal showed strong diffuse scattering between Bragg peaks. This is believed to be the source of the high electron density on Th. The structural model is unaffected.

Powder X-ray diffraction (PXRD). PXRD data were collected on Rigaku MiniFlex600 at 40 kV, 40 mA for Cu Kα (λ = 1.54178 Å) with a scan speed of 10º/min from 3 to 50º at a step size of 0.01º. The simulated PXRD pattern was produced from the CIF of **SUM-5** using Mercury 2020.2.0 (Build 290188).

Fourier Transform Infrared (FT-IR) Spectroscopy. The FT-IR spectrum was collected in the range of 400-4000 cm^{-1} on a Spectrum Two Li10014 infrared spectrometer using KBr pellet.

N_2 Sorption and Brunauer-Emmett-Teller (BET) Analysis. After solvothermal synthesis, **SUM-5** crystals were removed from the mother liquor and washed copiously with fresh DMF. Then the crystals were soaked in 20 mL of DCM three times over 1 h (20 min each) and subsequently immersed in 20 mL n-hexane three times over 1h (20 min each). Finally, after removal of most of the n-hexane, the crystals were transferred to a round-bottom flask on a Schlenk vacuum line and evacuated for 3 h before activated at the degas station under vacuum at ambient temperature for 24 h before N_2 uptake measurement taking place on BELSORP MAX.

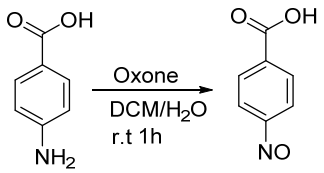
Thermogravimetric Analysis (TGA). **SUM-5** crystals were washed with DMF/DCM (as described above) and then briefly dried in a N_2 flow. The experiment was performed in a constant N_2 flow (100 mL/min) at a heating rate of 5°C /min from room temperature (~27°C) to 900 °C.

S2. Syntheses

Caution! Th-232 used in this study is an α emitter with daughter of radioactive Ra-228 and γ-emitter with daughter of radioactive Tl-208. All thorium compounds used and investigated were operated in an authorized laboratory designed for actinide element studies. Standard precautions with suitable care and specific protection against α and γ radiation for handling radioactive

materials should be followed.

Synthesis of 4-nitrosobenzoic acid, L1. 4-aminobenzoic acid (1 g, 7.3 mmol) was suspended in DCM (12 mL). A solution of Oxone (8.97 g, 14.6 mmol) dissolved in water (45 mL) was added to the DCM solution and the mixture was continuously stirred under nitrogen atmosphere at room temperature for 1 hour. The yellow precipitate was then collected and washed with pure water and dried in vacuum at 30 °C for 2 days. Yield: 1.07 g, 98%. ^{1}H NMR (DMSO-d_6, 400 MHz): 13.667(br, 1H), 8.26-8.28(d, *J*=8.0 Hz, 2H), δ= 8.05-8.03(d, *J*=8.0 Hz, 2H).



Scheme S1. Synthesis of **L1.**

Synthesis of SUM-5. L1 (10 mg), $Th(NO_3)_4 \cdot xH_2O$ (10 mg) were ultrasonically dissolved in 1.0 mL DMF in a 4 ml Pyrex vial sealed tightly. The mixture was heated in an oven at 120 ℃ for 48 hours. Orange single crystals were filtered, washed with fresh DMF (3x1ml). Alternative synthetic protocol: **L1** (10 mg), $Th(NO_3)_4 \cdot xH_2O$ (10 mg) and formic acid (0.2 ml) were ultrasonically dissolved in 1.3 mL DMF in a 4 ml Pyrex vial sealed tightly. The vial was placed in an autoclave and heated in an oven at 150℃ for 48 hours. After cooling down to room temperature, orange octahedral crystals were collected and washed with fresh DMF (3x1ml). Yield, 50% based on **L1**. For ^{1}H NMR, the crystals soaked in DMF were exchanged with DCM (3x1ml) and dried in vacuum, digested in a mixture of DMSO-d_6 (0.5 mL) and DCl in D_2O (20%, 0.02 mL) before transferring the clear solution into an NMR tube. ^{1}H NMR (DMSO-d_6, 400MHz): δ=8.09-8.12 (m, 4H), δ=7.94-7.97 (m, 4H). FT-IR (KBr, 400-4000 cm^{-1}): 2987cm^{-1}, 2923cm^{-1}, 1652cm^{-1}, 1595cm^{-1}, 1547cm^{-1}, 1412cm^{-1}, 1098cm^{-1}, 1011cm^{-1}, 873cm^{-1}, 792cm^{-1}, 707cm^{-1}, 544cm^{-1}.

Modulated synthesis of SUM-5. L1 (10 mg), $Th(NO_3)_4 \cdot xH_2O$ (10 mg) and nitrosobenzene (10 mg) were ultrasonically dissolved in 1.0 mL DMF in a 4 ml Pyrex vial sealed tightly. The mixture was heated in an oven at 100 ℃ for 48 hours. Orange to yellow single crystals were collected.

S3. Figures and Tables

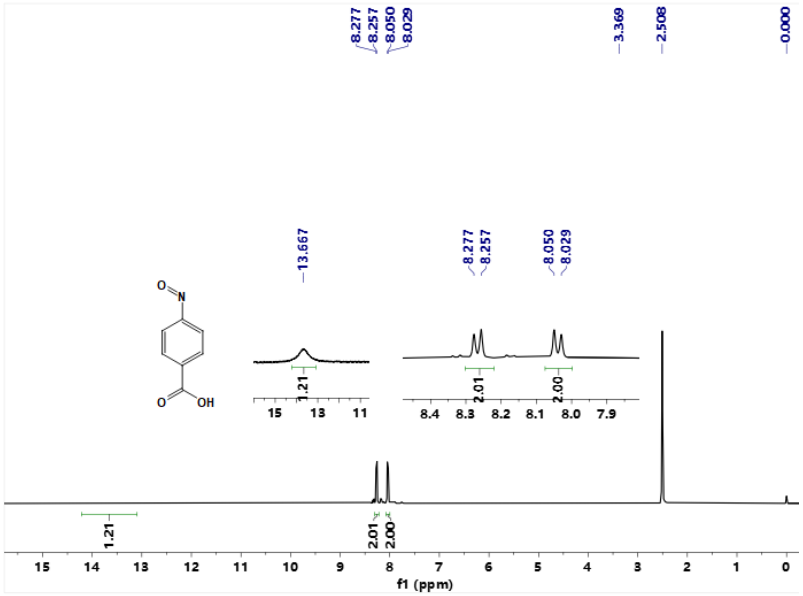


Figure S1. ^{1}H NMR spectrum of **L1** in DMSO-d_6.

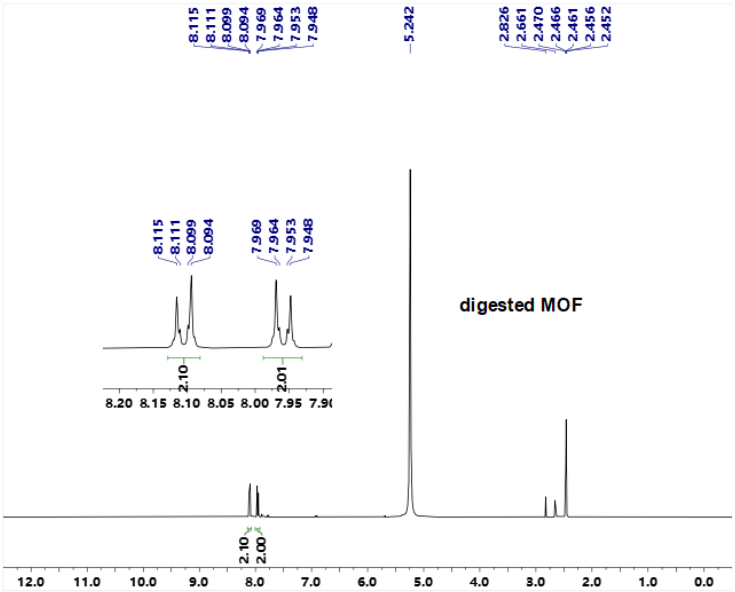


Figure S2. ^{1}H NMR spectrum of digested **SUM-5** in DMSO-d_6.

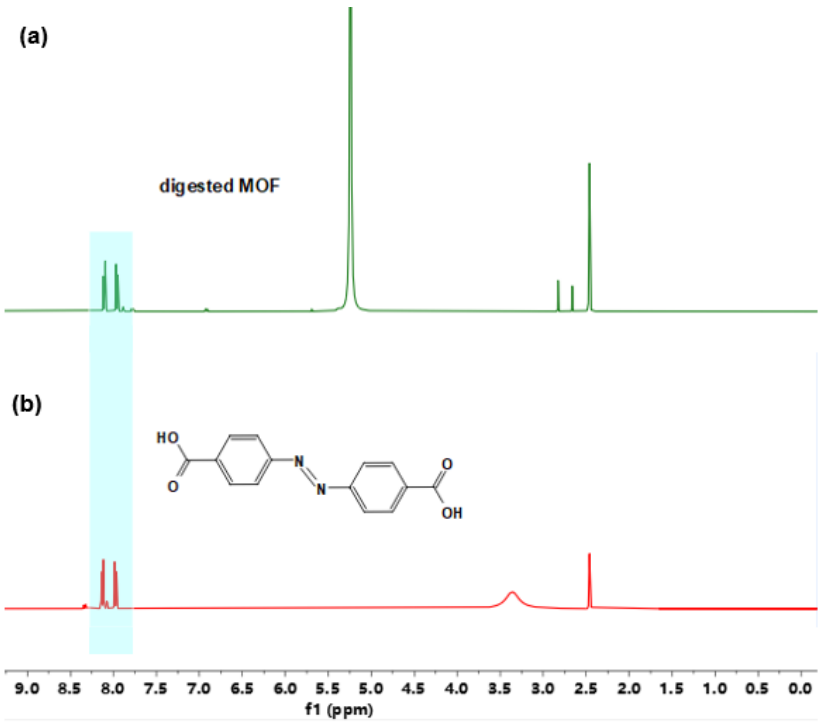


Figure S3. ^{1}H NMR spectra comparison of (a) digested **SUM-5** and (b) azobenzene dicarboxylic acid in DMSO-d_6.

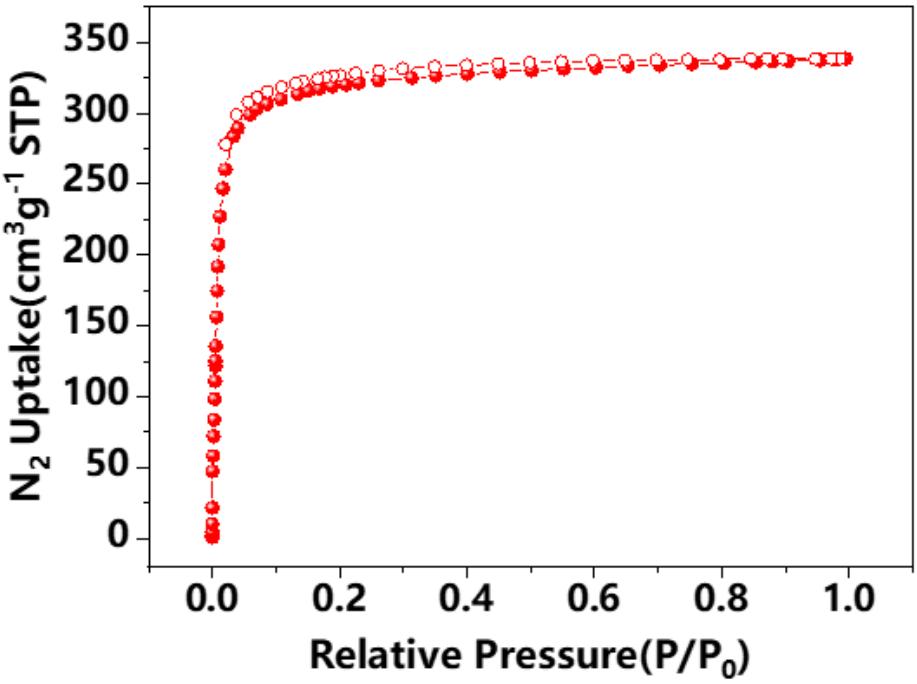


Figure S4. N_2 sorption isotherm of **SUM-5** (adsorption: filled circles; desorption: open circles).

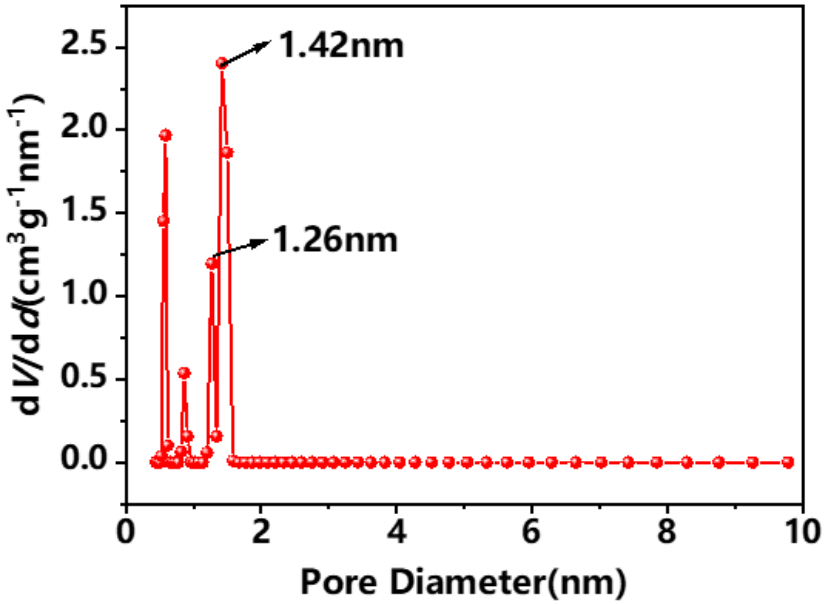


Figure S5. Pore size distribution plot of **SUM-5**.

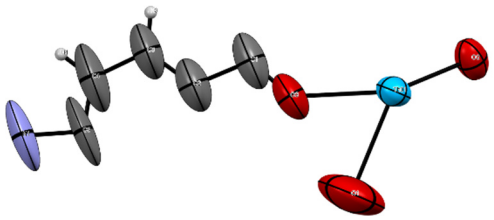


Figure S6. ORTEP diagram of the asymmetric unit of **SUM-5** (50% probability factor for the thermal ellipsoids), generated in Mercury 2020.2.0 (Build 290188)[5].

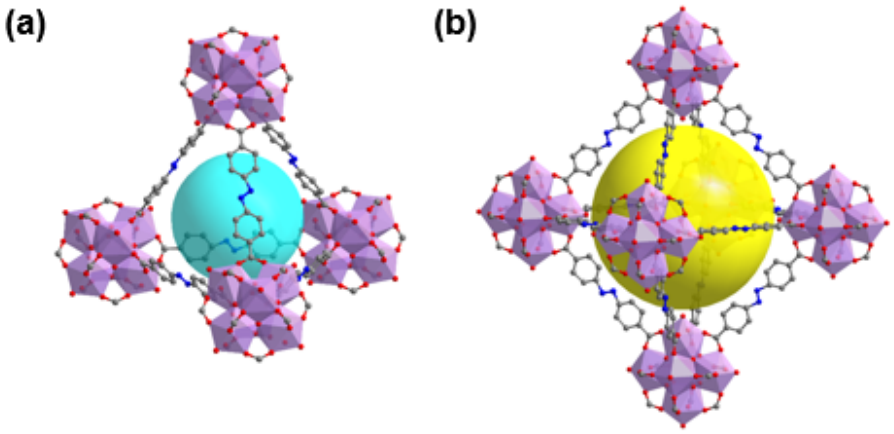


Figure S7. Crystal structure of **SUM-5**, showing (a) tetrahedral cage and (b) octahedral cage. Cyan sphere and yellow sphere represent the tetrahedral and octahedral cavity, respectively. Atom colors: Th,

purple polyhedra; C, grey spheres; N, blue spheres; O, red spheres. H atoms are omitted for clarity.

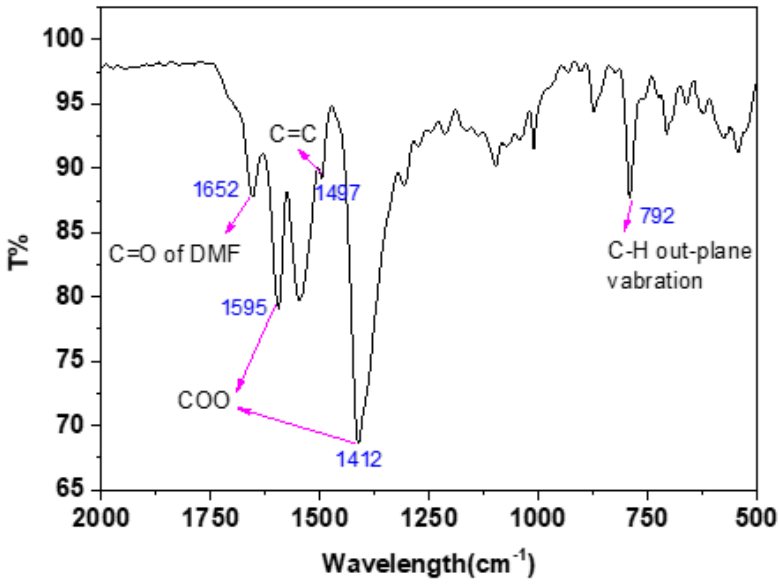


Figure S8. FT-IR spectrum of **SUM-5**.

S4. References

1. APEX2, SAINT, and SADABS ed.; Bruker AXS Inc.: Madison WI, USA, **2014**.
2. Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst. Section A.* **2015**, *71*, 3-8.
3. Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Cryst. Section C.* **2015**, *71*, 3-8.
4. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
5. Macrae, C.F.; Bruno, I.J.; Chisholm, J.A.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A. Mercury CSD 2.0-new features for the visualization and investigation of crystal structures. *J. Appl. Cryst.* **2008**, *41*, 466-470.