

Supporting Information for

Thorium Metal–Organic Framework Crystallization for Efficient Recovery from Rare Earth Element Mixtures

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1. Materials

Caution! Thorium nitrate is a radioactive chemical containing ^{232}Th . Adhere to all necessary safety precautions when handling radioactive materials.

All chemicals were purchased from commercial suppliers and used without further purification, including: thorium nitrate tetrahydrate (98%, International Bio-Analytical Industries), lanthanum nitrate hexahydrate (99.99%, Sigma Aldrich), cerium nitrate hexahydrate (99.5%, Thermo Scientific), neodymium nitrate hexahydrate (99.9%, Sigma Aldrich), gadolinium nitrate hexahydrate (99.9%, Sigma Aldrich), dysprosium nitrate hydrate (99.9%, Sigma Aldrich), ytterbium nitrate pentahydrate (99.9%, Sigma Aldrich), trimesic acid (95%, Sigma Aldrich), benzoic acid (99.5%, Sigma Aldrich), 2-fluorobenzoic acid (97%, Sigma Aldrich), 4-fluorobenzoic acid (98%, Sigma Aldrich), acetic acid (glacial, Millipore Sigma), formic acid (96+%, Fisher), ethanol (anhydrous, Fisher), nitric acid (trace metal grade, Fisher), hydrogen peroxide (30% trace metal grade, GFS Chemicals), thorium ICP standard (1 g/L, Inorganic Ventures), and ICP standards for La, Ce, Nd, Gd, Dy, and Yb (1 g/L in nitric acid, Millipore Sigma). Ultrapure deionized water was obtained from a Millipore Milli-Q-Bioceel A10 instrument.

2. Instrumentation

2.1 Powder X-ray Diffraction (PXRD)

PXRD measurements were collected in transmission mode at room temperature using a Stoe STADI-P powder diffractometer equipped with a $\text{CuK}\alpha 1$ source ($\lambda = 1.54056 \text{ \AA}$) and a 1D silicon strip detector (MYTHEN2 1K from DECTRIS) at the IMSERC facility at Northwestern University. Samples were prepared by drop-casting powder slurries from solution onto flat plate transmission holders sealed with polyimide tape.

2.2 Single Crystal X-ray Diffraction (SCXRD)

Intensity data of a colorless, cubic single crystal of NU-2500 were collected at 100 K at the IMSERC facility at Northwestern University. A suitable single crystal with dimensions of $0.185 \times 0.101 \times 0.021 \text{ mm}^3$ was mounted on a MiTeGen loop with paratone oil on an XtaLAB Synergy diffractometer equipped with a micro-focus rotating-anode X-ray tube Rigaku (Cu) X-ray source and a Hybrid Pixel Array (HyPix) detector. The temperature of the crystal was controlled with an Oxford Cryosystems low-temperature device. Data reduction was performed with CrysAlisPro software using a multi-scan absorption correction. The structure was solved with the SHELXT¹ structure solution program using intrinsic phasing and by using Olex2² as the graphical interface. The model was refined with the SHELXL refinement package³ using least squares minimization. As BTC linkers are extremely disordered, the thermal parameters and geometry of carboxylate group in NU-2500 were restricted to a reasonable limit using EADP and DFIX instructions. The location of the counter $[\text{H}_3\text{O}]^+$ ions were not resolved due to the high disorder and strong overlapping with the BTC linker. Refinement results are summarized in Table S1. Crystallographic data in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2378389. The data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.).

The simulated PXRD pattern for NU-2500 was generated from the single crystal structure using Mercury.

2.3 Scanning Electron Microscopy (SEM)

SEM images were collected using a Hitachi SU8030 microscope at the NUANCE facility at Northwestern University. Prior to imaging, dried powder samples were adhered with carbon tape to aluminum SEM pin stub specimen mounts and coated with 9 nm of osmium using a Filgen OPC60A plasma coater.

2.4 Thermogravimetric Analysis (TGA)

TGA measurements of dried powder samples were measured on a Mettler Toledo TGA/DSC 1 Star System instrument. Samples were heated in air from 30 to 600 °C at a rate of 2 °C/minute. A background measurement collected by measuring an empty aluminum pan was subtracted from the sample data.

2.5 Microwave Digestion

Solid MOF samples were prepared for digestion by washing approximately 5 mg of the as-synthesized MOF powder 3 times with 10 mL portions of ethanol. After each wash, samples were centrifuged and the supernatants decanted. Following the final wash, samples were dried overnight in an 80 °C oven. To each dried sample, 3 mL trace-metal grade HNO₃ and 750 µL trace-metal grade 30% H₂O₂ was added. The samples were transferred to 55 mL MARSXpress PFA digestion vessels and digested in a CEM MARS6 microwave digestion system using the “Carbon” method.

2.6 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

ICP-OES analysis was performed with a Thermo iCAP 7600 spectrometer equipped with an ESI SC-2DX PrepFAST autosampler at the QBIC facility at Northwestern University.

To prepare digested MOF samples for ICP analysis, a 300 µL aliquot of the HNO₃ digest solution was diluted to a total volume of 10 mL with ultrapure water. To prepare supernatant samples for ICP analysis, a 120 µL aliquot of the supernatant was removed from the synthesis vial immediately upon removal from the oven following the crystallization reaction and diluted to a total volume of 12 mL with ultrapure water.

For quantification of metal contents in solid powder samples prepared from binary Th+La mixtures, a calibration curve with concentrations of 0 to 5 ppm La and 0 to 100 ppm Th was used. A calibration curve with concentrations of 0 to 75 ppm for both La and Th was used to quantify metal concentrations in supernatant solutions. For quantification of metal contents in solid powder samples prepared from mixtures of Th and additional REs (La, Ce, Nd, Gd, Dy, Yb), a calibration curve with concentrations of 0 to 5 ppm of each RE and 0 to 100 ppm Th was used. The spectral lines selected for analysis were as follows: La (379.478 and 412.323 nm), Ce (393.109, 404.076, and 535.353 nm), Nd (378.425, 401.225, and 430.358 nm), Gd (310.050, 335.047, and 364.619 nm), Dy (353.602 and 400.045 nm), Yb (211.667, 275.048, and 328.937 nm), and Th (283.231, 283.730, and 318.019 nm). Th was measured in radial plasma view; La, Ce, Nd, Gd, Dy, and Yb were measured in axial plasma view.

2.7 Thermal Activation

Prior to activation, as-synthesized NU-2500 powder was washed three times with 10 mL portions of EtOH, with at least 30 minutes between each wash, followed by an overnight soak in fresh EtOH. After washing, the EtOH was decanted and the sample was dried in an 80 °C oven to remove residual solvent. The powder was then degassed under vacuum at 120 °C for 18 hours using a Micromeritics Smart Vac Prep (SVP) instrument.

2.8 Adsorption Isotherms

Nitrogen sorption measurements were performed on approximately 80 mg of activated NU-2500 sample using a Micromeritics TriStar II Plus instrument. Nitrogen isotherms were collected at 77 K.

2.9 Optical Imaging

Optical images of NU-2500 single crystals were acquired with a Nikon SMZ1500 microscope.

3. Syntheses

3.1 Single Metal Trials for Modulator Screening

A 0.065 M lanthanum stock solution was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.7030 g, 1.624 mmol) and 25 mL H_2O . A 0.065 M thorium stock solution was prepared from $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.8964 g, 1.624 mmol) and 25 mL H_2O . A 0.065 M BTC stock solution was prepared from 1,3,5-benzenetricarboxylic acid (0.3416 g, 1.626 mmol) and 25 mL EtOH. Five 1 M modulator stock solutions were prepared separately as follows: benzoic acid (2.4422 g, 20.0 mmol) and 20 mL EtOH; 2-fluorobenzoic acid (2.8023 g, 20.0 mmol) and 20 mL EtOH; 4-fluorobenzoic acid (2.8022 g, 20.0 mmol) and 20 mL EtOH; acetic acid (1.14 mL) and 20 mL EtOH; formic acid (0.75 mL) and 20 mL EtOH.

To prepare each sample, 1 mL of the specified metal stock solution (either La or Th), 1 mL of BTC stock solution, and 1 mL of the specified modulator stock solution (benzoic acid, 2-fluorobenzoic acid, 4-fluorobenzoic acid, acetic acid, or formic acid) were added to a 1.5 dram screw-top glass vial. The samples were sealed and heated in a 60 °C oven for 16 hours. For trials synthesized with no modulator, 1 mL of pure EtOH was used in place of the modulator stock solution to maintain the same total volume.

3.2 NU-2500 Single Crystals

Stock solutions of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.065 M in H_2O) and BTC (0.065 M in EtOH) were prepared as described in section S3.1. To prepare single crystals of NU-2500 for X-ray diffraction, 1 mL of Th stock solution, 1 mL of BTC stock solution, and 1 mL of neat acetic acid were added to a 1.5 dram screw-top glass vial. The sample was sealed and heated in an 80 °C oven for 7 days. Crystals for X-ray diffraction were mounted directly from the mother liquor.

3.3 Single Metal Timepoint Trials

Stock solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.065 M in H_2O), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.065 M in H_2O), and BTC (0.065 M in EtOH) were prepared as described in section S3.1. An acetic acid stock solution was prepared from 14.3 mL acetic acid and 50 mL EtOH. To prepare each sample, 1 mL of the specified metal stock solution (either La or Th), 1 mL of BTC stock solution, and 1 mL of acetic acid stock solution were added to a 1.5 dram screw-top glass vial. Four identical replicates were prepared for both La and Th. The samples were sealed and heated in an 80 °C oven. Samples were removed from the oven after 30 minutes, 45 minutes, 1 hour, and 2 hours of heating, before further analysis by PXRD and ICP.

3.4 Binary La+Th Trials for Modulator Screening

A combined equimolar La+Th stock solution was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2815 g, 0.650 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.3585 g, 0.650 mmol) and 10 mL H_2O . Stock solutions of BTC (0.065 M in EtOH), benzoic acid (1 M in EtOH), 2-fluorobenzoic acid (1 M in EtOH), 4-fluorobenzoic acid (1 M in EtOH), acetic acid (1 M in EtOH), and formic acid (1 M in EtOH) were prepared as described in section S3.1.

To prepare each sample, 1 mL of the combined La+Th stock solution, 1 mL of BTC stock solution, and 1 mL of the specified modulator stock solution (benzoic acid, 2-fluorobenzoic acid, 4-fluorobenzoic acid, acetic acid, or formic acid) were added to a 1.5 dram screw-top glass vial. The samples were sealed and heated in a 60 °C oven for 4 hours before removal for further analysis by PXRD and ICP. For the trial synthesized with no modulator, 1 mL of pure EtOH was used in place of the modulator stock solution to maintain the same total volume.

3.5 Binary La+Th Trials with Varying Acetic Acid Concentration

A combined equimolar La+Th stock solution (0.065 M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.065 M $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in H_2O) was prepared as described in section S3.4. A stock solution of BTC (0.065 M in EtOH) was prepared as described in section S3.1. To prepare each sample, 1 mL of the combined La+Th stock solution, 1 mL of BTC stock solution, and 1 mL EtOH were added to a 1.5 dram screw-top glass vial. Five replicates were prepared, and varying volumes of acetic acid (0.06, 0.09, 0.11, 0.29, and 0.57 mL) were added to correspond to acetic acid concentrations of 1, 1.5, 2, 5, and 10 mmol, respectively. The samples were sealed and heated in an 80 °C oven for 2.5 hours before removal for further analysis by PXRD and ICP.

3.6 Binary La+Th Trials with Varying BTC Concentration

A combined equimolar La+Th stock solution (0.065 M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.065 M $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in H_2O) was prepared as described in section S3.4. Two BTC stock solutions were prepared: a 0.13 M solution was prepared from BTC (0.1094 g, 0.2589 mmol) and 4 mL EtOH; a 0.26 M solution was prepared from BTC (0.2186 g, 1.0403 mmol) and 4 mL EtOH. An acetic acid stock solution was prepared from 11.5 mL acetic acid and 40 mL EtOH.

To prepare each sample, 1 mL of the combined La+Th stock solution, 1 mL of the specified BTC stock solution (0.13 M or 0.26 M), and 1 mL of the acetic acid stock solution were added to a 1.5 dram screw-top glass vial. The samples were sealed and heated in an 80 °C oven for 2 hours before removal for further analysis by PXRD and ICP.

3.7 Binary La+Th Timepoint Trials

A combined equimolar La+Th stock solution was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.8445 g, 1.950 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (1.0775 g, 1.952 mmol) and 30 mL H_2O . A BTC stock solution was prepared from BTC (0.4097 g, 1.950 mmol) and 30 mL EtOH. An acetic acid stock solution was prepared from 8.59 mL acetic acid and 30 mL EtOH.

To prepare each sample, 1 mL of the combined La+Th stock solution, 1 mL of BTC stock solution, and 1 mL of acetic acid stock solution were added to a 1.5 dram screw-top glass vial. A total of 24 identical samples were prepared, sealed, and placed in an 80 °C oven. Samples were removed from the oven after heating for 8 specified time intervals (30 minutes, 1 hour, 2 hours, 3 hours, 6 hours, 8 hours, 24 hours, and 48 hours). Three replicate samples were removed at each time interval for further analysis by PXRD and ICP.

3.8 Thorium Soak Control Experiment

Stock solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.065 M in H_2O), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.065 M in H_2O), and BTC (0.065 M in EtOH) were prepared as described in section S3.1. An acetic acid stock solution was prepared from 2.86 mL acetic acid and 10 mL EtOH.

To prepare a sample of $\text{La}(\text{BTC})(\text{H}_2\text{O})_6$, 1 mL of the La stock solution, 1 mL of BTC stock solution, and 1 mL of acetic acid stock solution were added to a 1.5 dram screw-top glass vial. The sample was sealed and heated in an 80 °C oven for 2 hours. After heating, the sample was centrifuged and the supernatant was decanted. The solids were washed three times with 5 mL EtOH and soaked overnight in fresh EtOH. After centrifuging and decanting again, 1 mL of Th stock solution was added to the solids, and the sample was heated in an 80 °C oven for 2 hours. Following the second heating step, the sample was washed again before further analysis by PXRD and ICP.

3.9 Increased La:Th Ratios

A 3:1 La:Th stock solution was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1970 g, 0.455 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1241 g, 0.225 mmol) and 3.5 mL H_2O . A 6:1 La:Th stock solution was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4927 g, 1.138 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1253 g, 0.227 mmol) and 3.5 mL H_2O . A 15:1 La:Th stock solution was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.9853 g, 2.275 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1255 g, 0.227 mmol) and 3.5 mL H_2O . A BTC stock solution was prepared from BTC (0.2737 g, 1.302 mmol) and 20 mL EtOH. An acetic acid stock solution was prepared from 5.72 mL acetic acid and 20 mL EtOH. To account for the varying amounts of water in these hygroscopic metal salts, we note that the nominal concentrations of these solutions (3:1, 5:1, 15:1) are based on the metal concentrations in the initial stock solutions as determined by ICP-OES.

To prepare each sample, 1 mL of the specified La+Th stock solution (3:1, 6:1, or 15:1), 1 mL of BTC stock solution, and 1 mL of acetic acid stock solution were added to a 1.5 dram screw-top glass vial. Three replicate samples were prepared for each La:Th initial concentration. The samples were sealed and heated in an 80 °C oven for 2 hours before removal for further analysis by PXRD and ICP.

3.10 Additional Rare Earths

A combined Ce+Th stock solution was prepared from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.0993 g, 0.229 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1255 g, 0.227 mmol) and 3.5 mL H_2O . A combined Nd+Th stock solution was prepared from $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.0998 g, 0.230 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1259 g, 0.228 mmol) and 3.5 mL H_2O . A combined Gd+Th stock solution was prepared from $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1026 g, 0.230 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1261 g, 0.228 mmol) and 3.5 mL H_2O . A combined Dy+Th stock solution was prepared from $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1036 g, 0.230 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1250 g, 0.226 mmol) and 3.5 mL H_2O . A combined Yb+Th stock solution was prepared from $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1021 g, 0.230 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1149 g, 0.208 mmol) and 3.5 mL H_2O . A combined La+Nd+Gd+Dy+Yb+Th stock solution was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.0984 g, 0.227 mmol), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.0999 g, 0.230 mmol), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1030 g, 0.230 mmol), $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1042 g, 0.230 mmol), $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1016 g, 0.230 mmol), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.1257 g, 0.228 mmol), and 3.5 mL H_2O . Stock solutions of BTC (0.065 M in EtOH) and acetic acid (5 M in EtOH) were prepared as described in section S3.7.

To prepare each binary lanthanide/Th trial, 1 mL of the specified lanthanide+Th stock solution (Ce+Th, Nd+Th, Gd+Th, Dy+Th, or Yb+Th), 1 mL of BTC stock solution, and 1 mL of acetic acid stock solution were added to a 1.5 dram screw-top glass vial. Three replicate samples were prepared for each lanthanide. The samples were sealed and heated in an 80 °C oven for 2 hours before removal for further analysis by PXRD and ICP.

To prepare the senary La+Nd+Gd+Dy+Yb+Th trial, 1 mL of the La+Nd+Gd+Dy+Yb+Th stock solution, 1 mL of BTC stock solution, and 1 mL of acetic acid stock solution were added to a 1.5 dram screw-top glass vial. Three replicate samples were prepared. The samples were sealed and heated in an 80 °C oven for 2 hours before removal for further analysis by PXRD and ICP.

3.11 Large Batch NU-2500 Powder Synthesis

Stock solutions of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (0.065 M in H_2O) and BTC (0.065 M in EtOH) were prepared as described in section S3.1. A stock solution of acetic acid (5 M in EtOH) was prepared as described in section S3.7. To prepare NU-2500 powder, 5 mL of Th stock solution, 5 mL of BTC stock solution, and 5 mL of acetic acid stock solution were added to a 20 mL screw-top glass scintillation vial. The sample was sealed and heated in an 80 °C oven for 2 hours.

4. Supplementary Figures and Tables

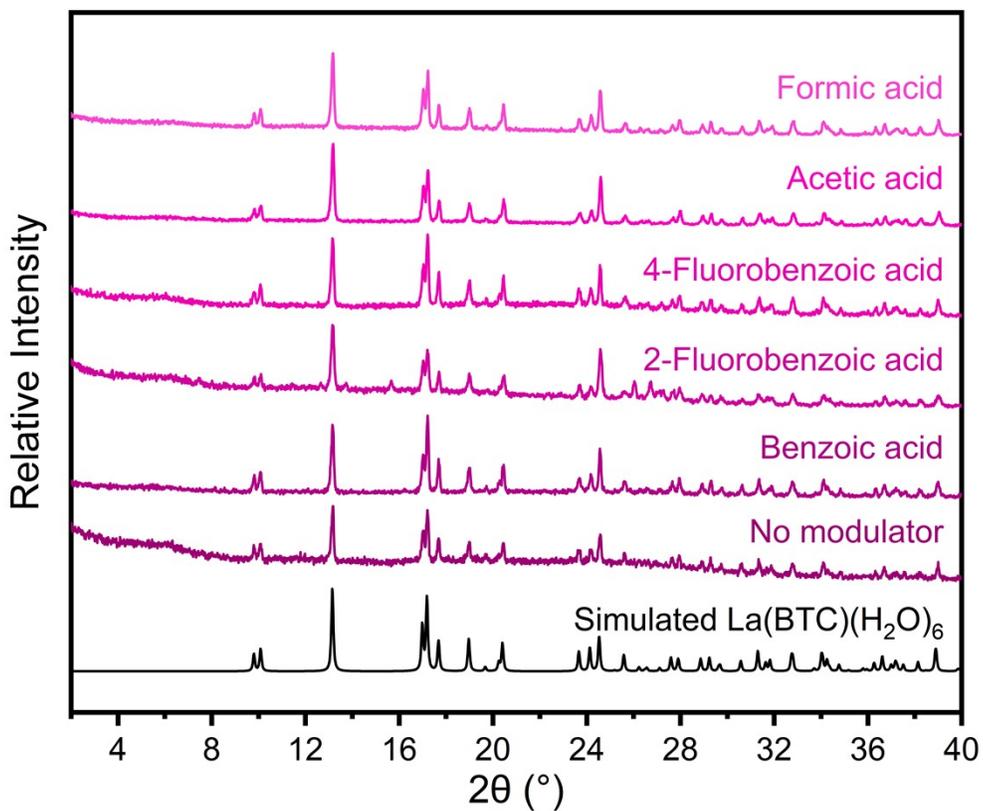


Figure S1. PXRD patterns of crystalline products resulting from single-metal syntheses with La, BTC linker, and specified modulators. The simulated pattern for $\text{La}(\text{BTC})(\text{H}_2\text{O})_6$ was generated from the reported single crystal structure.⁴



Figure S2. SEM image of $\text{La}(\text{BTC})(\text{H}_2\text{O})_6$.

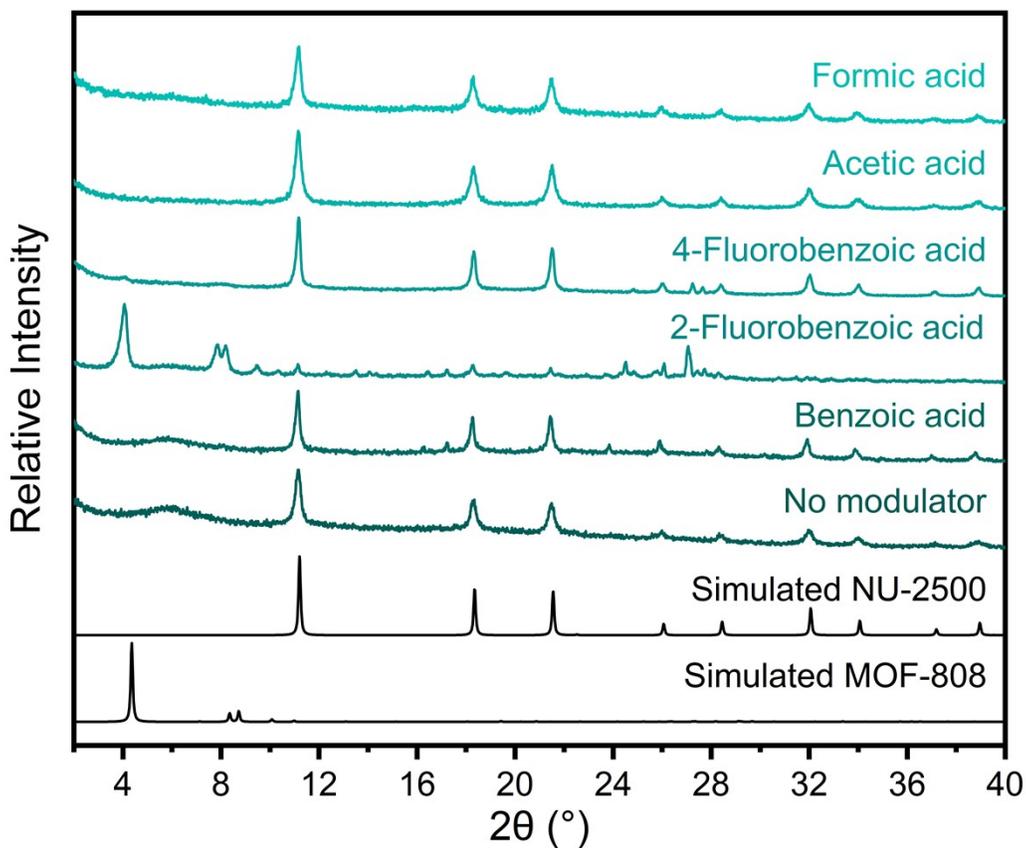


Figure S3. PXRD patterns of crystalline products resulting from single-metal syntheses with Th, BTC linker, and specified modulators. NU-2500 is the product for each of the modulators studied except 2-fluorobenzoic acid, which results in a mixture of Th-MOF-808 and NU-2500. The simulated patterns for NU-2500 and MOF-808⁵ were generated from the single crystal structures.

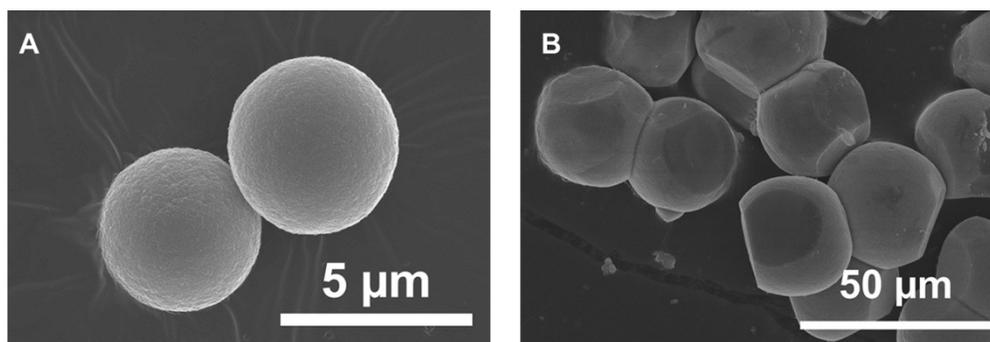


Figure S4. SEM images of A) NU-2500 powder and B) NU-2500 crystals.

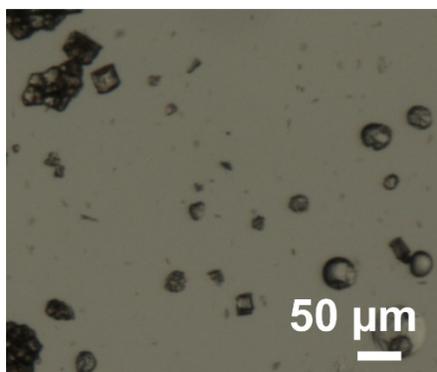


Figure S5. Optical image of NU-2500 single crystals.

Table S1. Summary of crystallographic data and structure refinement details for NU-2500.

| | |
|---|--|
| Empirical formula | $C_{27}H_9O_{18}Th_2$ |
| Formula weight | 1085.42 |
| Temperature/K | 100.00(10) |
| Crystal system | cubic |
| Space group | $Fd-3m$ |
| $a/\text{\AA}$ | 13.66820(8) |
| Volume/ \AA^3 | 2553.49(4) |
| Z | 4 |
| $\rho_{\text{calc}}/\text{g/cm}^3$ | 2.823 |
| μ/mm^{-1} | 38.207 |
| F(000) | 1980.0 |
| Crystal size/ mm^3 | $0.185 \times 0.101 \times 0.021$ |
| Radiation | $\text{CuK}\alpha$ ($\lambda = 1.54184$) |
| 2θ range for data collection/ $^\circ$ | 11.212 to 149.076 |
| Index ranges | $-17 \leq h \leq 17, -17 \leq k \leq 17, -16 \leq l \leq 17$ |
| Reflections collected | 23360 |
| Independent reflections | 155 [$R_{\text{int}} = 0.0418, R_{\text{sigma}} = 0.0054$] |
| Data/restraints/parameters | 155/1/17 |
| Goodness-of-fit on F^2 | 1.175 |
| Final R indexes [$I \geq 2\sigma(I)$] | $R_1 = 0.0394^{\text{a}}, wR_2 = 0.0965^{\text{b}}$ |
| Final R indexes [all data] | $R_1 = 0.0399, wR_2 = 0.0971$ |
| Largest diff. peak/hole / $e \text{\AA}^{-3}$ | 0.96/-0.56 |

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

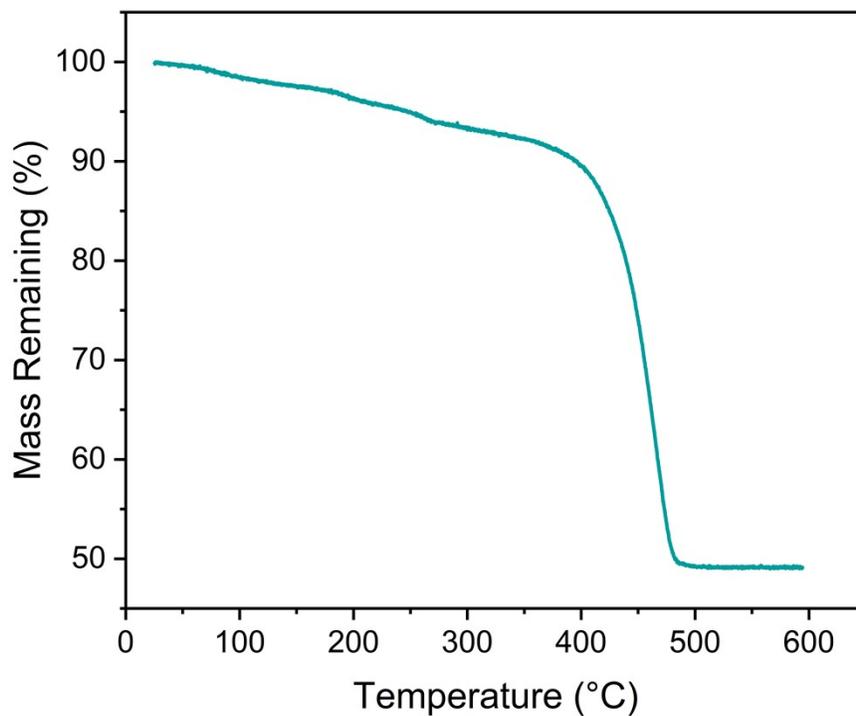


Figure S6. TGA of as-synthesized NU-2500 in air.

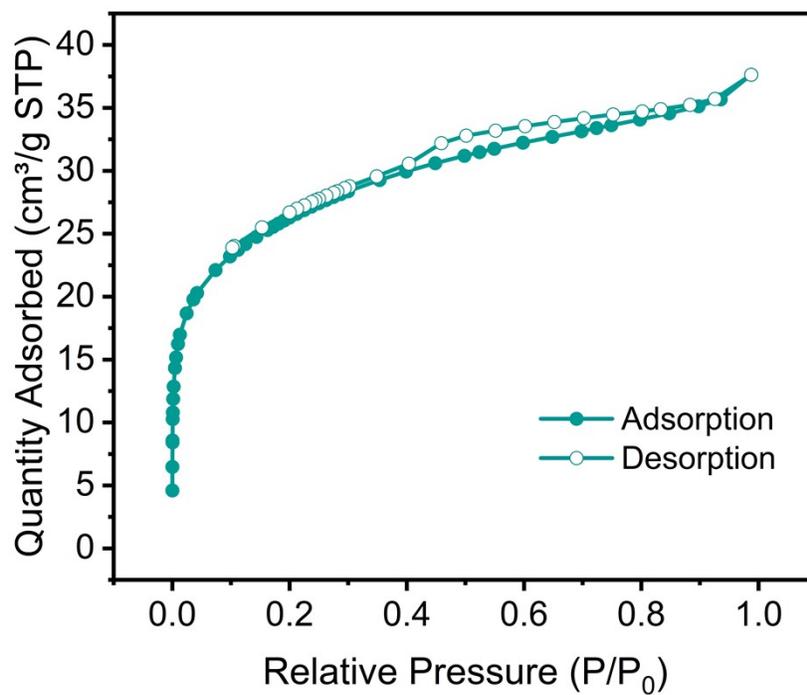


Figure S7. N₂ isotherm @ 77 K for NU-2500 activated at 120 °C.

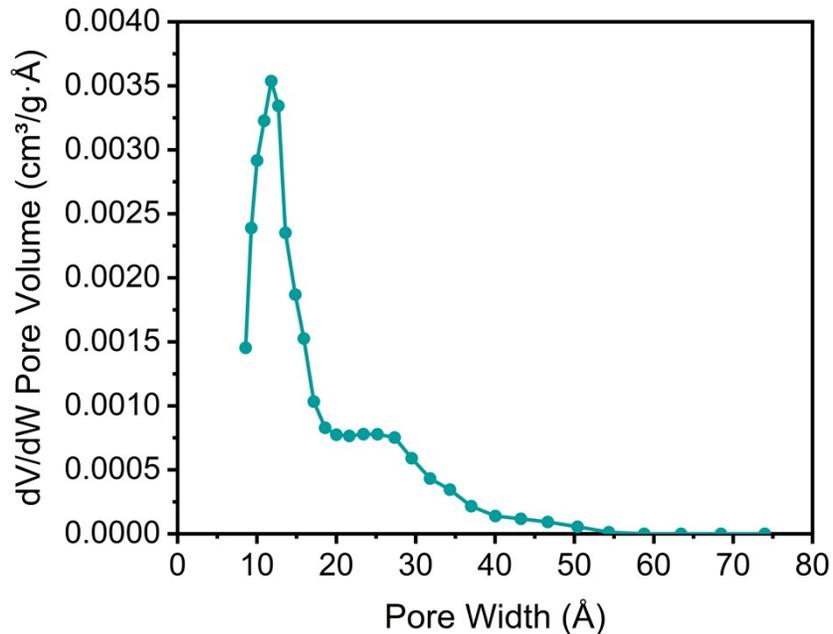


Figure S8. Experimental pore size distribution for NU-2500 derived from N₂ isotherm using N₂-DFT model with slit geometry.

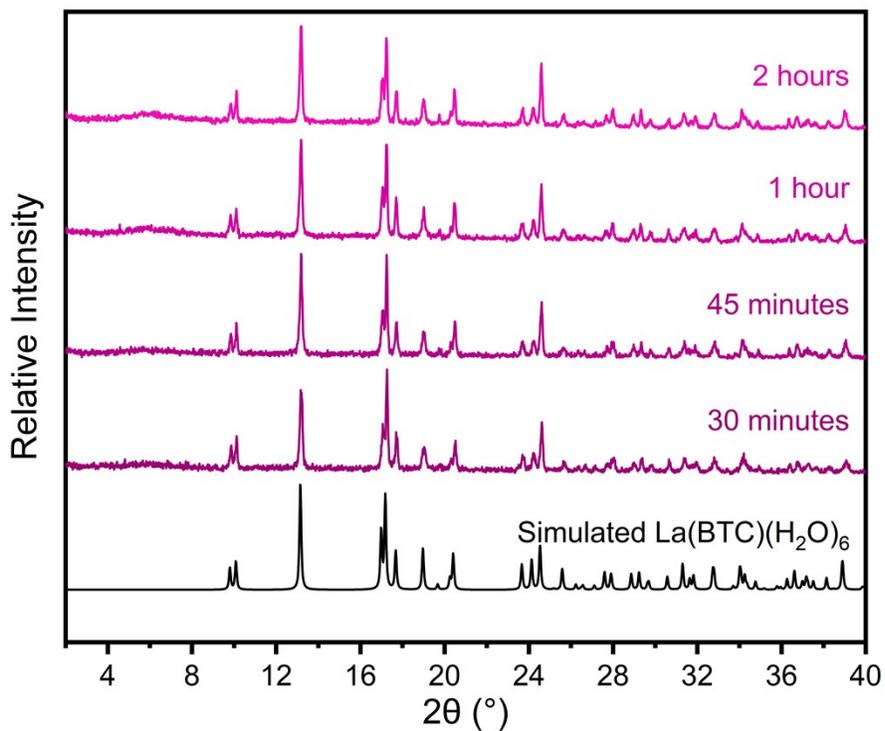


Figure S9. PXRD patterns of crystalline products resulting from single-metal syntheses with La, BTC linker, and acetic acid modulator after specified time intervals. The simulated pattern for La(BTC)(H₂O)₆ was generated from the reported single crystal structure.⁴

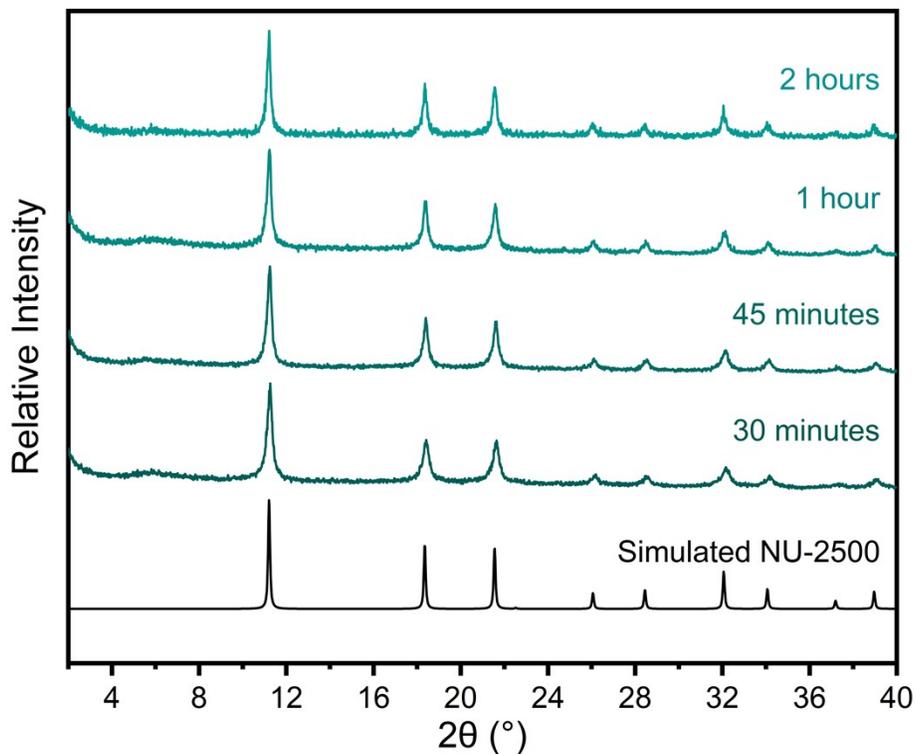


Figure S10. PXRD patterns of crystalline products resulting from single-metal syntheses with Th, BTC linker, and acetic acid modulator after specified time intervals. The simulated pattern for NU-2500 was generated from the single crystal structure.

| Modulator | Product Th:La Molar Ratio | Th Molar Fraction (%) | La Molar Fraction (%) |
|----------------------|---------------------------|-----------------------|-----------------------|
| None | 20.7 | 95.4 | 4.6 |
| Benzoic acid | 21.7 | 95.6 | 4.4 |
| 2-Fluorobenzoic acid | 23.4 | 95.9 | 4.1 |
| 4-Fluorobenzoic acid | 18.1 | 94.8 | 5.2 |
| Formic acid | 39.1 | 97.5 | 2.5 |
| Acetic acid | 45.2 | 97.8 | 2.2 |

Table S2. Metal contents of solid products resulting from crystallization trials with an equimolar initial solution of La+Th, BTC linker, and specified modulators as determined by ICP-OES.

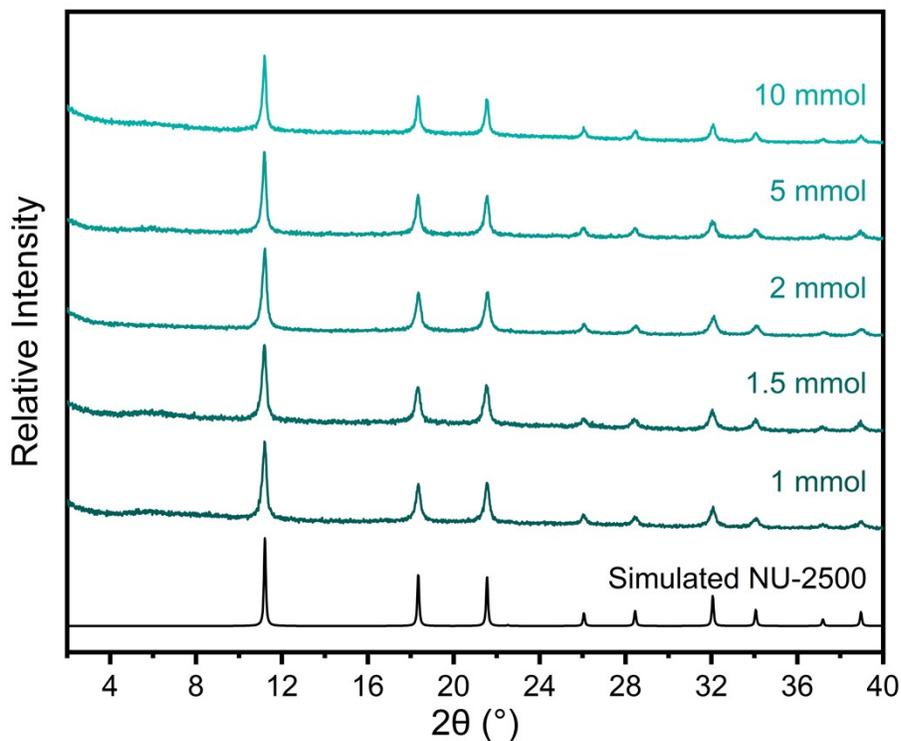


Figure S11. PXRD patterns of crystalline products resulting from binary trials with equimolar La+Th, BTC linker, and specified quantities of acetic acid modulator. The simulated pattern for NU-2500 was generated from the single crystal structure.

| Acetic Acid Concentration, mmol | Product Th:La Molar Ratio | Th Molar Fraction (%) | La Molar Fraction (%) |
|---------------------------------|---------------------------|-----------------------|-----------------------|
| 1 | 55.2 | 98.2 | 1.8 |
| 1.5 | 56.8 | 98.3 | 1.7 |
| 2 | 62.9 | 98.4 | 1.6 |
| 5 | 70.8 | 98.6 | 1.4 |
| 10 | 48.0 | 98.0 | 2.0 |

Table S3. Metal contents of solid products resulting from crystallization trials with an equimolar initial solution of La+Th, BTC linker, and specified concentrations of acetic acid modulator as determined by ICP-OES.

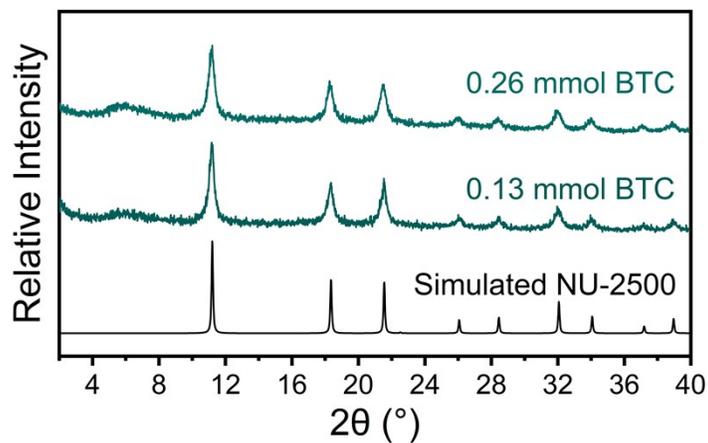


Figure S12. PXRD patterns of crystalline products resulting from binary trials with equimolar La+Th, acetic acid modulator, and specified quantities of BTC linker. The simulated pattern for NU-2500 was generated from the single crystal structure.

| BTC Quantity, mmol | Product Th:La Molar Ratio | Th Molar Fraction (%) | La Molar Fraction (%) |
|--------------------|---------------------------|-----------------------|-----------------------|
| 0.13 | 62.7 | 98.4 | 1.6 |
| 0.26 | 24.2 | 95.9 | 4.1 |

Table S4. Metal contents of solid products resulting from crystallization trials with an equimolar initial solution of La+Th, acetic acid modulator, and varying quantities of BTC linker as determined by ICP-OES.

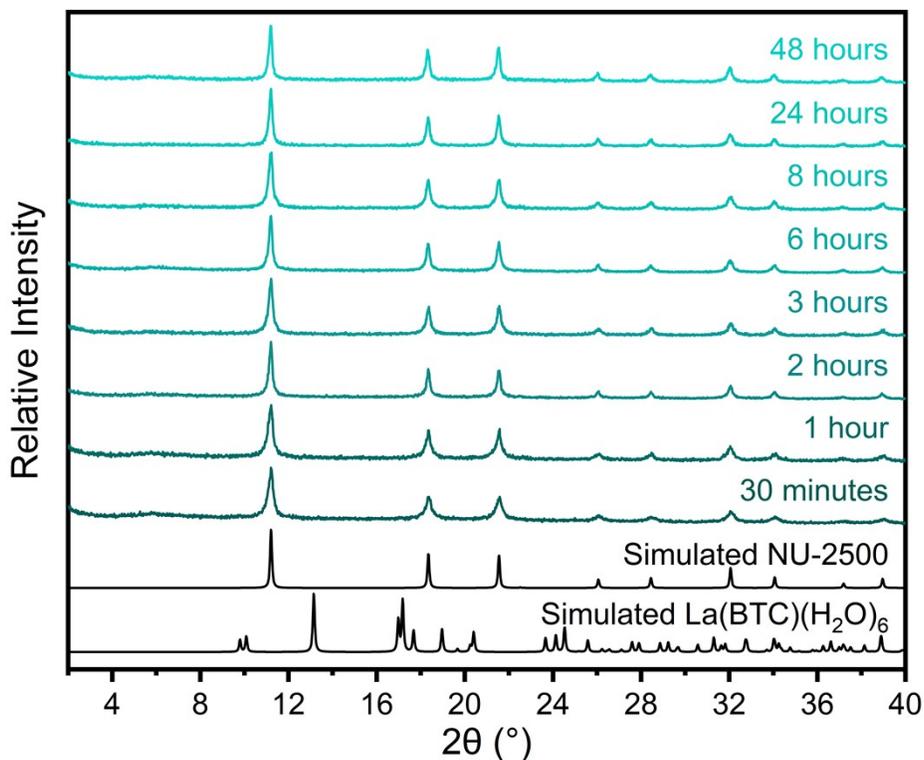


Figure S13. PXRD patterns of crystalline products resulting from binary trials with equimolar La+Th, BTC linker, and acetic acid modulator after heating for specified time interval. The simulated pattern for NU-2500 was generated from the single crystal structure.

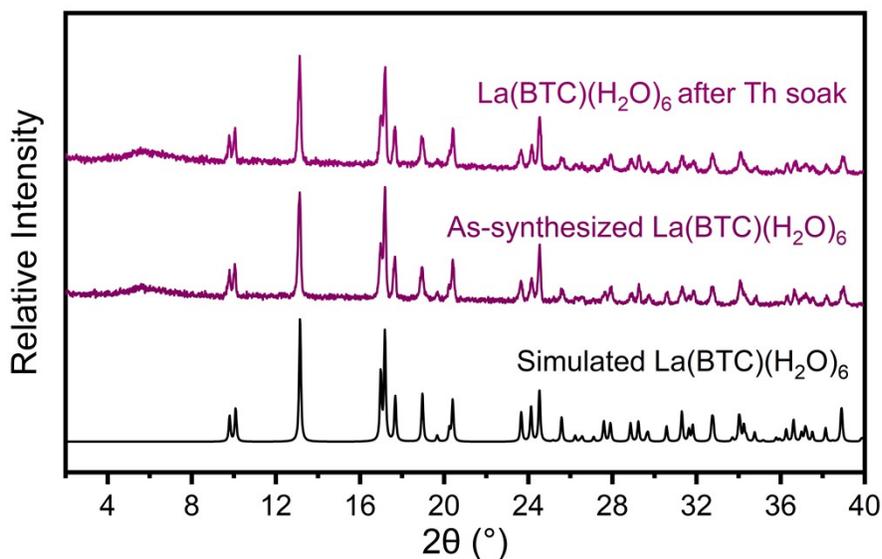


Figure S14. PXRD patterns of La(BTC)(H₂O)₆ before and after soaking in Th solution. The simulated pattern for La(BTC)(H₂O)₆ was generated from the reported single crystal structure.⁴

| Product La:Th Molar Ratio | La Molar Fraction (%) | Th Molar Fraction (%) |
|---------------------------|-----------------------|-----------------------|
| 31.5 | 96.9 | 3.1 |

Table S5. Metal contents of solid products resulting from control experiment soaking La(BTC)(H₂O)₆ in Th solution as determined by ICP-OES.

| Synthesis Time, hours | Product Th:La Molar Ratio | Average Th Molar Fraction (%) | Average La Molar Fraction (%) | Th/La Separation Factor |
|-----------------------|---------------------------|-------------------------------|-------------------------------|-------------------------|
| 0.5 | 77.6 ± 1.7 | 98.7 | 1.3 | 302.0 |
| 1 | 67.0 ± 0.3 | 98.5 | 1.5 | 309.5 |
| 2 | 64.1 ± 0.3 | 98.5 | 1.5 | 399.4 |
| 3 | 65.1 ± 1.6 | 98.5 | 1.5 | 524.0 |
| 6 | 67.5 ± 2.1 | 98.5 | 1.5 | 828.9 |
| 8 | 66.0 ± 1.9 | 98.5 | 1.5 | 889.3 |
| 24 | 65.8 ± 1.6 | 98.5 | 1.5 | 1279.3 |
| 48 | 58.0 ± 5.7 | 98.3 | 1.7 | 697.0 |

Table S6. Metal contents of solid products resulting from crystallization trials at specified timepoints with an equimolar initial solution of La+Th, BTC linker, and acetic acid modulator as determined by ICP-OES. The error on each molar ratio represents the standard deviation of three replicate crystallization trials. The separation factor for Th over La was calculated from metal concentrations using the following formula⁶, where R_c and R_m are the Th:La molar ratios in the crystalline products and in the mother liquor solution following crystallization, respectively:

$$S_{\text{Th/La}} = R_c/R_m = [(M_{\text{Th}})_c/(M_{\text{La}})_c] / [(M_{\text{Th}})_m/(M_{\text{La}})_m].$$

| Synthesis Time, hours | Supernatant La:Th Molar Ratio | Average Th Molar Fraction (%) | Average La Molar Fraction (%) |
|-----------------------|-------------------------------|-------------------------------|-------------------------------|
| 0.5 | 3.9 ± 0.3 | 20.4 | 79.6 |
| 1 | 4.6 ± 0.1 | 17.8 | 82.2 |
| 2 | 6.2 ± 0.1 | 13.8 | 86.2 |
| 3 | 8.1 ± 0.1 | 11.1 | 88.9 |
| 6 | 12.4 ± 0.5 | 7.5 | 92.5 |
| 8 | 13.5 ± 0.4 | 6.9 | 93.1 |
| 24 | 19.9 ± 2.7 | 4.9 | 95.1 |
| 48 | 15.8 ± 8.8 | 6.7 | 93.3 |

Table S7. Metal contents of supernatant solutions following crystallization trials at specified timepoints with an equimolar initial solution of La+Th, BTC linker, and acetic acid modulator as determined by ICP-OES. The error on each molar ratio represents the standard deviation of three replicate crystallization trials.

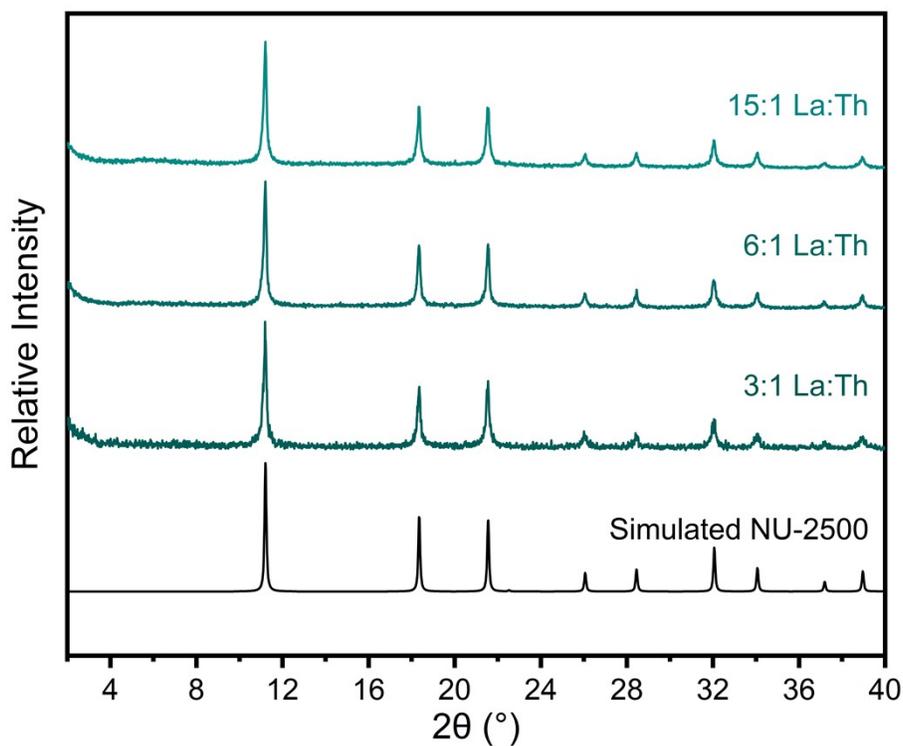


Figure S15. PXRD of crystalline products resulting from syntheses with elevated initial La:Th ratios.

| Nominal Initial Solution | Initial Th:La Molar Ratio | Product Th:La Molar Ratio | Average Th Molar Fraction (%) | Average La Molar Fraction (%) |
|--------------------------|---------------------------|---------------------------|-------------------------------|-------------------------------|
| 3:1 La:Th | 0.36 | 44.0 ± 0.8 | 97.8 | 2.2 |
| 6:1 La:Th | 0.14 | 23.9 ± 0.2 | 96.0 | 4.0 |
| 15:1 La:Th | 0.07 | 15.5 ± 0.2 | 93.6 | 6.4 |

Table S8. Metal contents of solid products resulting from crystallization trials with initial La+Th solutions of varying concentration, BTC linker, and acetic acid modulator as determined by ICP-OES. The error on each molar ratio represents the standard deviation of three replicate crystallization trials.

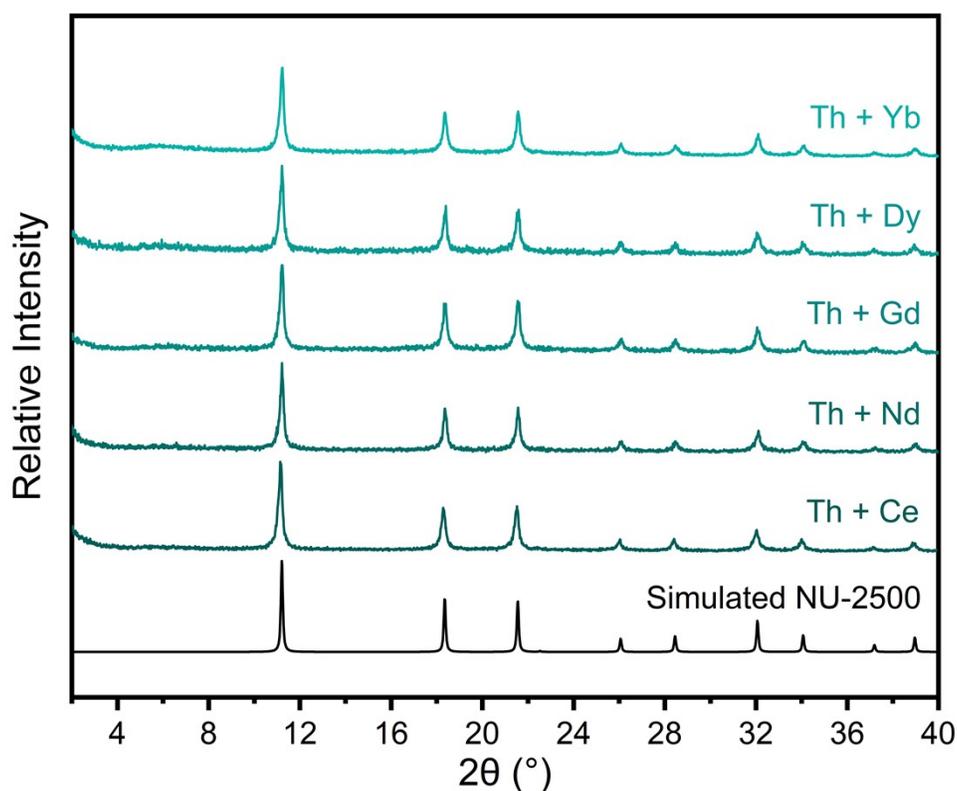


Figure S16. PXRD of crystalline products from binary metal trials with Th and specified trivalent rare earth ions (Ce, Nd, Gd, Dy, or Yb).

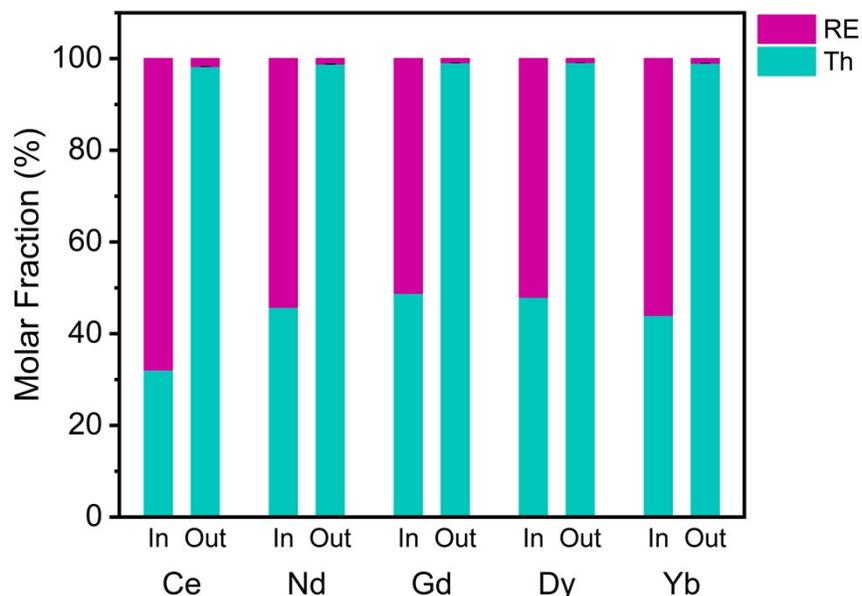


Figure S17. Molar fractions of metals present in binary crystallization trials with Th and additional specified trivalent REs (Ce, Nd, Gd, Dy, or Yb), BTC linker, and acetic acid modulator as determined by ICP-OES. The “in” bars represent the concentration of the initial binary metal solutions, and the “out” bars represent the contents of the crystalline products following synthesis. Error bars shown represent the standard deviation of three replicate crystallization trials.

| Rare Earth (RE) Identity | Initial Th:RE Molar Ratio | Product Th:RE Molar Ratio | Average Th Molar Fraction (%) | Average RE Molar Fraction (%) |
|--------------------------|---------------------------|---------------------------|-------------------------------|-------------------------------|
| Ce | 0.5 | 57.1 ± 1.0 | 98.3 | 1.7 |
| Nd | 0.8 | 81.9 ± 4.1 | 98.8 | 1.2 |
| Gd | 1.0 | 106.5 ± 1.9 | 99.1 | 0.9 |
| Dy | 0.9 | 111.2 ± 0.9 | 99.1 | 0.9 |
| Yb | 0.8 | 98.3 ± 1.4 | 99.0 | 1.0 |

Table S9. Metal contents of solid products resulting from crystallization trials with initial binary solutions of Th and specified trivalent REs (Ce, Nd, Gd, Dy, or Yb), BTC linker, and acetic acid modulator as determined by ICP-OES. The error on each molar ratio represents the standard deviation of three replicate crystallization trials.

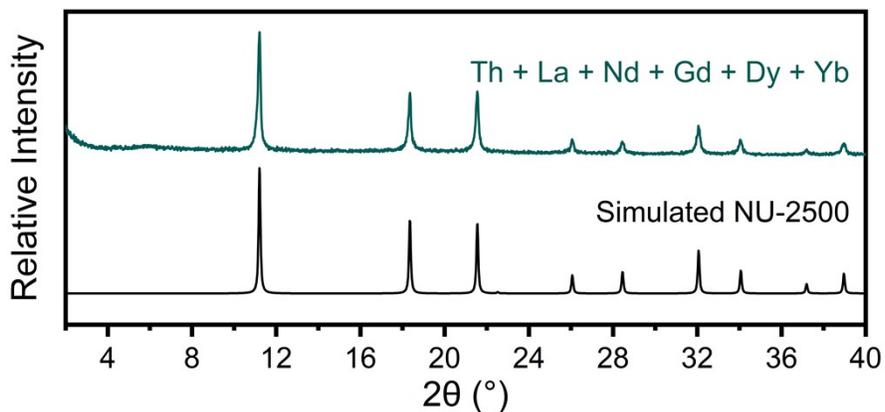


Figure S18. PXRD of crystalline products from mixed RE crystallization trial.

| Metal | Initial Solution Molar Fraction (%) | Product Molar Fraction (%) |
|-------|-------------------------------------|----------------------------|
| Th | 14.8 | 96.8 ± 0.1 |
| La | 16.9 | 1.0 ± 0.0 |
| Nd | 17.5 | 0.7 ± 0.0 |
| Gd | 16.4 | 0.5 ± 0.0 |
| Dy | 16.7 | 0.5 ± 0.0 |
| Yb | 17.7 | 0.5 ± 0.0 |

Table S10. Metal contents of initial senary solution (Th+La+Nd+Gd+Dy+Yb) and solid product resulting from crystallization trials with BTC linker and acetic acid modulator as determined by ICP-OES. The error on each molar fraction represents the standard deviation of three replicate crystallization trials.

5. References

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