Modulation of Crystal Growth and Structure within Cerium-Based Metal–Organic Frameworks

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I) Materials

All chemicals and solvents were obtained from commercial suppliers and used without further purification. Ammonium cerium nitrate (≥98.5%), glycine (≥99%), sodium chloride (≥99.5%), benzoic acid (≥99.5%), terephthalic acid (98%), 2,6-naphthalenedicarboxylic acid (99%), and N,N-dimethylformamide (99%) were purchased from Sigma-Aldrich. 2-naphthoic acid (98%) was purchased from Combi-Blocks. Acetone (99.8%) was purchased from Fischer Chemical. Deionized water was used as the water source.

II) Materials and Characterization

$[Ce_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(NH_3CH_2COO)_8(NO_3)_4(H_2O)_6]Cl_8 \cdot 8H_2O$ (**Ce₆ precursor**) was synthesized according to literature procedure.[1,2]
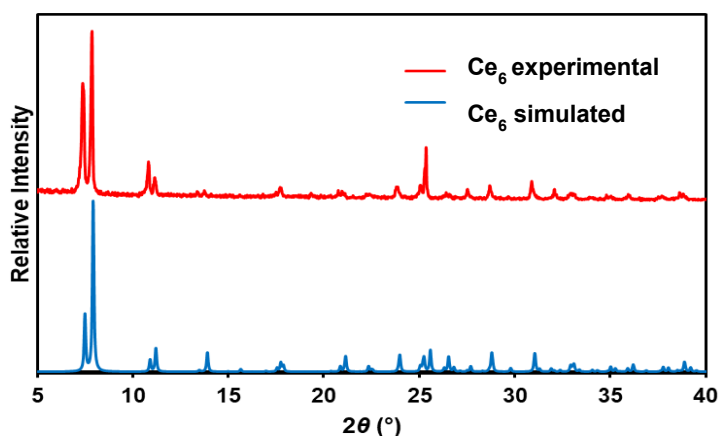

Figure S1: PXRD patterns ($\lambda = 1.5406$ Å) of experimentally synthesized and simulated patterns of **Ce₆ precursor**.

Ce-MOF Modulation Protocols with Benzoic Acid

63 mg of **Ce₆ precursor** was placed in 3.5 mL of DMF and sonicated until dispersed. 500 µL of this solution was then placed in seven 1.5-dram vials. Next, the following amounts of benzoic acid were massed out and placed in the separate vials: 4.7 mg, 23.5 mg, 47 mg, 70.5 mg, 94 mg, 117.5 mg, 141 mg, 188 mg. Next, 70 mg of 2,6-naphthalenedicarboxylic acid was placed in 3.5 mL of DMF and sonicated. 500 µL of this solution was then placed in each of the vials. The vials were then placed in a 100 °C oven for 18 hours. Upon reaction completion, the vials were removed from the oven and cooled to room temperature. The mixtures were placed in 1.5 mL centrifuge tubes and centrifuged for five minutes to remove the supernatant. Then, the resultant product was washed with N,N-dimethylformamide (1.5 mL×2) and acetone (1.5 mL×2). The material was then dried in a vacuum oven at 80 °C for 1 hour.

Ce-MOF Modulation Protocols with Trifluoroacetic Acid

81 mg of **Ce₆ precursor** was placed in 4.5 mL of DMF and sonicated until dispersed. 500 µL of this solution was then placed in nine 1.5-dram vials. Next, the following amounts of trifluoroacetic acid were added to the separate vials: 3 µL, 7.4 µL, 10.3 µL, 14.7 µL, 19.1 µL, 23.5 µL, 29.5 µL, 44.2 µL, and 58.9 µL. Next, 90 mg of 2,6-naphthalenedicarboxylic acid was placed in 4.5 mL of DMF and sonicated. 500 µL of this solution was then placed in each of the vials. The vials were then placed in a 100 °C oven for 18 hours. Upon reaction completion, the vials were removed from the oven and cooled to room temperature. The mixtures were placed in 1.5 mL centrifuge tubes and centrifuged for five minutes to remove the supernatant. Then, the resultant product was washed with N,N-dimethylformamide (1.5 mL×2) and acetone (1.5 mL×2). The material was then dried in a vacuum oven at 80 °C for 1 hour.

NU-350 Synthesis

9 mg of **Ce₆ precursor** was placed in 0.5 mL of DMF inside a 1.5 dram vial and sonicated until dispersed. Next, 3 µL of trifluoroacetic acid was added. Lastly, 10 mg of 2,6-naphthalenedicarboxylic acid was solubilized in 0.5 mL of DMF which was then added to the Ce solution. The reaction was placed in a 100 °C oven for 18 hours. Upon reaction completion, the vial was removed from the oven and cooled to room temperature. The mixture was placed in 1.5 mL centrifuge tubes and centrifuged for five minutes to remove the supernatant. Then, the resultant product was washed with N,N-dimethylformamide (1.5 mL×2) and acetone (1.5 mL×2). The material was then dried in a vacuum oven at 80 °C for 1 hour.

Ce-UiO-NDC Bulk Synthesis

70 mg of **Ce₆ precursor** was added to 3.5 mL of DMF in an 8-dram vial and sonicated until dispersed. Next, 1.5 g of benzoic acid was added to this vial which was then sonicated. Separately, 100 mg of 2,6-naphthalenedicarboxylic acid was added to 5 mL of DMF which was then sonicated. This 5 mL linker solution was then added to the starting node solution. The vial was then transferred to a 100 °C oven for 18 hours. Upon reaction completion, the vial was removed from the oven and cooled to room temperature. The resulting product was then into a 15 mL centrifuge tube and washed with DMF (5 mL x 3) and acetone (5 mL x 3). The material soaked in acetone overnight, followed by additional washing with acetone (5 mL x 3). The material was then dried in the vacuum oven for 1 hour at 80 °C. The material was then activated by heating at 100 ˚C for overnight under high vacuum on a Micromeritics Smart Vacprep.

Ce-UiO-66 Bulk Synthesis

156 mg of **Ce₆ precursor** was added to 2 mL of water in a 100 mL VWR glass jar. Separately, 4 g of benzoic acid was sonicated in 9 mL of DMF which was then added to the VWR jar. 132 mg of terephthalic acid was added to 9 mL of DMF in a separate vial which was then sonicated. The resulting linker solution was then added to the glass jar. Then, the glass jar was transferred to a 100 °C oven for 18 hours. Upon reaction completion, the vial was removed from the oven and cooled to room temperature. The resulting product was then into a 15 mL centrifuge tube and washed with DMF (5 mL x 3) and acetone (5 mL x 3). The material soaked in acetone overnight, followed by additional washing with acetone (5 mL x 3). The material was then dried in the

vacuum oven for 1 hour at 80 °C. The material was then activated by heating at 100 °C for overnight under high vacuum on a Micromeritics Smart Vacprep.

III) Methods for Material Characterization
Single Crystal X-Ray Diffraction Analysis

Table S1: Crystallographic details of NU-350

	NU-350
Empirical formula	$C_{64.5} H_{59} Ce_3 N_{4.5} O_{24.5}$
Formula weight	1709.52
Temperature/K	200
Crystal System	Triclinic
Space Group	$P–1$
a/Å	13.2389 (6)
b/Å	14.3168(7)
c/Å	19.909(1)
α/°	71.557(4)
β/°	74.917(4)
γ/°	75.843(3)
Volume/Å^3	3401.7(3)
Z	2
ρ_{calc}g/cm^3	1.669
μ/mm^{-1}	15.943
$F(000)$	1665
Crystal size/mm^3	0.015×0.015×0.015
Radiation / Å	1.54178
2θ range for data collection/°	2.387–59.296
Index ranges	3.51–58.72
Reflections collected	18978
Independent reflections	9628
Data/restraints/parameters	9628/223/932
Goodness-of-fit on F^2	1.017 ($I \geq 2\sigma(I)$), 1.012 (all data)
Final R indexes [$I \geq 2\sigma (I)$]	$R_1 = 0.0527$, $wR_2 = 0.1235$
Final R indexes [all data]	$R_1 = 0.0729$, $wR_2 = 0.1338$
CCDC deposition number	2017725

Refinement Details of NU-350

      For single-crystal X-ray diffraction measurements, one crystal of NU-350 was mounted on MicroMesh (MiTeGen) in paratone oil and transferred to the cold gas stream (200 K) of a Bruker APEX II CCD area detector equipped with a Cu Kα (λ = 1.54178 Å) I μS micro-source with MX optics. Data integration and reduction were performed using Bruker SAINT program in APEX2. Absorption correction was performed by multi-scan method using SADABS.[3] Space groups were determined using XPREP program implemented in APEX2. The structure was determined by intrinsic phasing methods (SHELXT 2014/5)[4] and refined by full-matrix least-squares refinement on F^2 (SHELXL-2018/3)[5] using the Yadokari-XG software package.[6] 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 CCDC-2017725. 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.).

Responses to B level checkcif alert for NU-350 single crystal:

Alert level B

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575
      Calculated sin(theta_max)/wavelength =   0.5577

Response: Diffraction spots from high angles were weak for this material despite several attempts at data collection. This may be because there is a large amount of disorder in the structure, especially for the coordinated solvent species.

PLAT220_ALERT_2_B NonSolvent   Resd 1 C   Ueq(max)/Ueq(min) Range   9.0 Ratio

Response: This may be because there is a large amount of disorder in the structure, especially for the coordinated solvent species.

Powder X-ray Diffraction Analysis

Powder X-ray diffraction (PXRD) patterns of the samples were measured by a STOE-STADI MP powder diffractometer operating at 40 kV voltage and 40 mA current with Cu-Kα1 X-ray radiation (λ = 1.5406 Å) in transmission geometry.

N_2 Sorption Isotherm Measurements

N_2 adsorption and desorption isotherms on activated materials were measured on a Micromeritics Tristar (Micromeritics, Norcross, GA) instrument at 77 K. Around 30 mg of sample was used in each measurement. Prior to N_2 isotherm measurements, the samples were placed under high vacuum at 100 °C on a Micromeritics Smart Vacprep for 18 h. The specific surface areas were determined using the Brunauer−Emmett−Teller model from the N_2 sorption data in the region P/P_0 = 0.005–0.05. Pore size distributions were obtained using DFT calculations using a carbon slit-pore model with a N_2 kernel.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy measurements were carried out on a Thermo Scientific ESCALAB 250 Xi equipped with an electron flood gun and a scanning ion gun. Analysis used the Thermo Scientific Avantage Data System software, and C1s peak (284.8 eV) peak was used as the reference. Oxidation states of Ce were assigned by comparison to previously published data.[7]

Scanning Electron Microscopy Imaging

Prior to observation, the samples were coated with OsO_4 (~9 nm) in a Denton Desk III TSC Sputter Coater. Scanning electron microscopy (SEM) images were acquired from a Hitachi SU8030 scanning electron microscope.

High Resolution Transmission Electron Microscopy Imaging

Transmission electron microscopy (TEM) images were collected at Northwestern University's EPIC/NUANCE facility using a TEM JEOL ARM300F equipped with a Gatan OneView-IS camera (CMOS electron sensor) at an acceleration voltage of 300 kV and an emission current of 15 µA. The samples were prepared with Lacey carbon copper mesh girds and loaded onto a single tilt TEM holder. The cumulative electron dose was around 5 $e^-/Å^2$.

Thermogravimetric Analysis

Sample weight loss data was measured on a Mettler Toledo TGA/DSC 1 Star System instrument. Samples were heated in air from 30°C to 600°C at a rate of 5°C/minute. The sample was held at 600°C for 60 minutes.
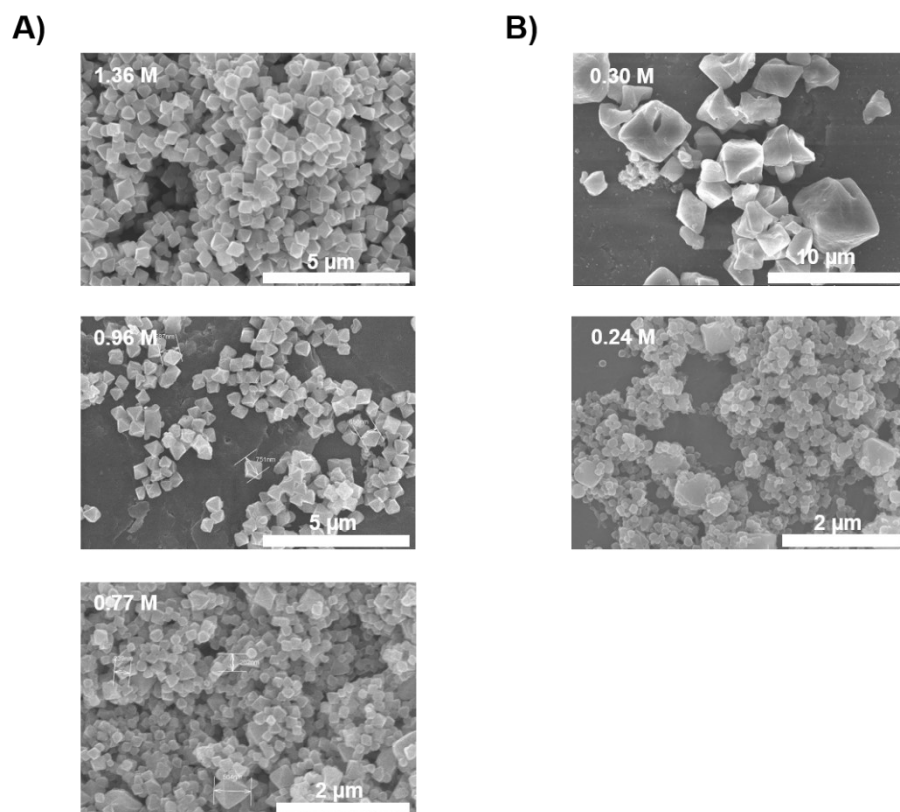
IV) SEM Images

Figure S2: Scanning electron microscope (SEM) images of Ce-UiO-NDC under specified concentrations of either (A) benzoic acid or (B) trifluoroacetic acid.
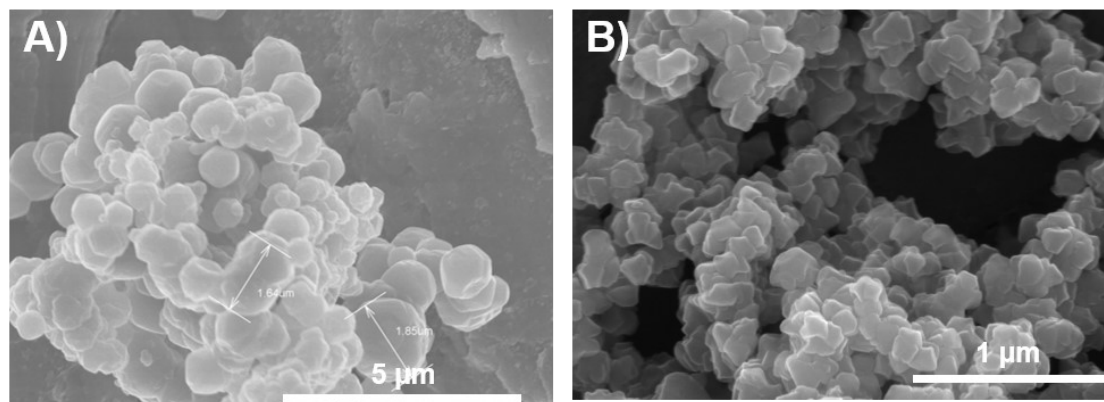

Figure S3: Scanning electron microscope (SEM) images of (A) Ce-UiO-NDC and (B) Ce-UiO-66 following syntheses reported from previously reported protocols.[8]
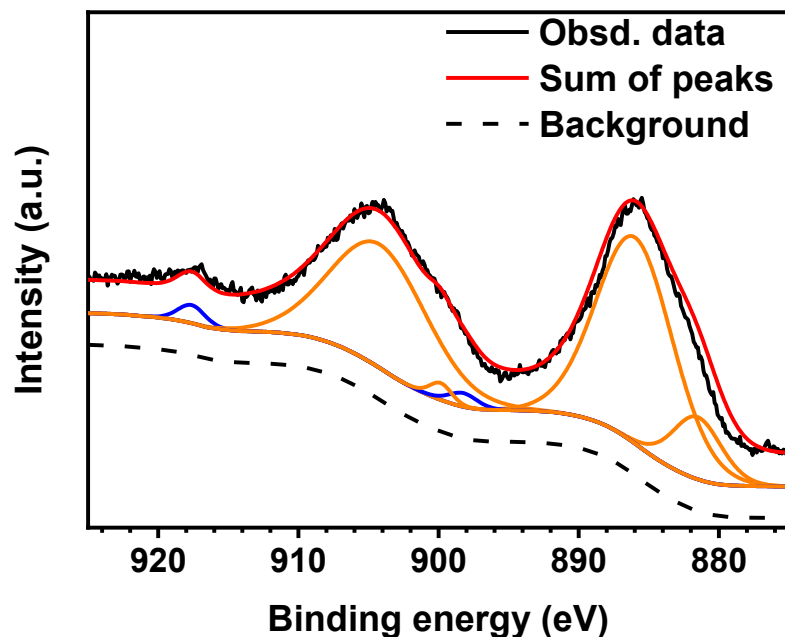
V)   XPS Data

Figure S4: Observed Ce 3d XPS (solid black line) and sum of fitted data (red line) for NU-350. The observed data were fitted by Gaussian/Lorentzian functions with deconvoluted peaks in blue corresponding to Ce^{4+} and orange deconvoluted peaks corresponding to Ce^{3+}.
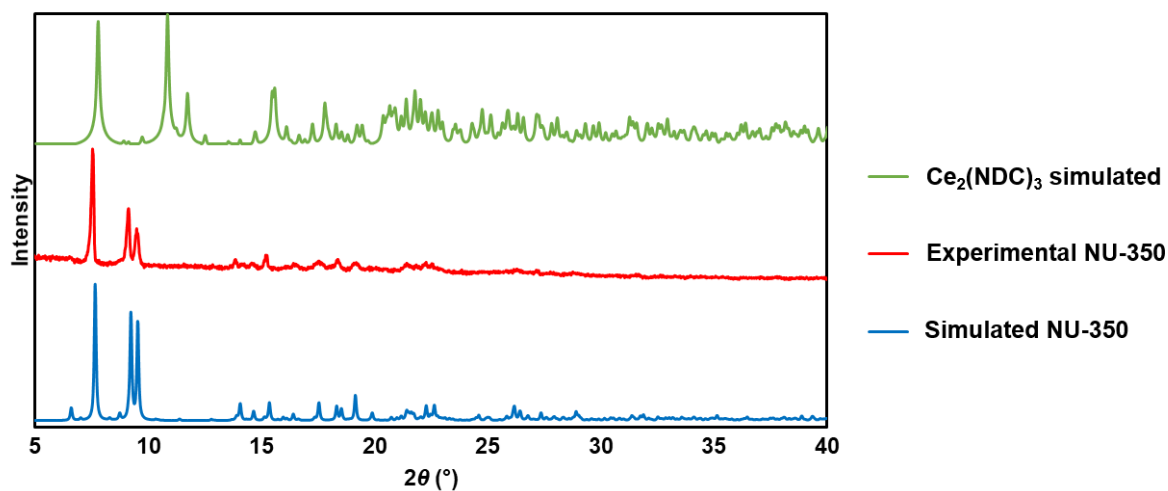
VI)   PXRD Patterns

Figure S5: Overlaid PXRD patterns of simulated and experimentally observed NU-350 in this study as well as a simulated pattern of a similar $Ce_2(NDC)_3$ framework reported in literature.[9]
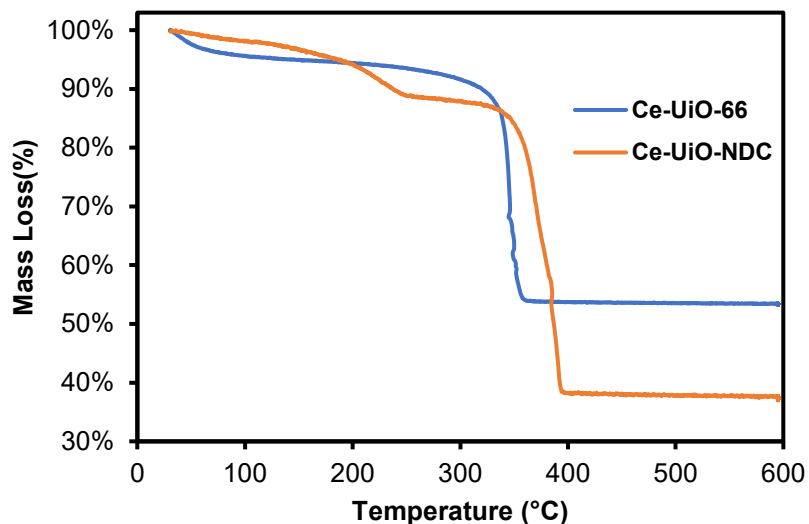
VII) TGA Data

Figure S6: TGA data of Ce-UiO-66 and Ce-UiO-NDC large batch syntheses. The mass loss of ~39% corresponds to ~1.4 missing linkers per node in Ce-UiO-66. The mass loss of ~50% corresponds to ~0.8 missing linkers per node in Ce-UiO-NDC.

VIII) References

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