

Supporting Information for

Electron Transitions in a Ce(III)-Catecholate Metal-Organic Framework

Julia G. Knapp, Debmalya Ray, Paul B. Calio, Megan C. Wasson, Thais R. Scott, Laura Gagliardi,
Omar K. Farha

Table of Contents

Materials and Synthesis	S2
Characterization Methods	S2
Computational Work	S4
Table S1. Magnetic Moment at various Ce centers of NU-1701	S4
Table S2. Crystallographic Details for NU-1701	S5
Figure S1. Experimental and simulated PXRD patterns of NU-1701	S6
Figure S2. SEM image of NU-1701	S7
Figure S3. NMR spectra following base digestion of NU-1701	S8
Figure S4. TGA curve of NU-1701	S9
Figure S5. N ₂ isotherm at 77K of NU-1701	S9
Figure S6. Pore Size Distribution of NU-1701	S10
Figure S7. PXRD pattern of NU-1701 following activation.....	S10
Figure S8. DRIFTS of NU-1701	S11
Figure S9. XPS spectra of NU-1701	S11
Figure S10. Solid-State UV-Vis spectra of NU-1701	S12
Figure S11. DoS calculations for Ce-UiO-66 framework.....	S12
Table S3. Full catalytic results for NU-1701 dehydroxymethylation.....	S13
Figure S12. PXRD pattern of NU-1701 following catalysis.....	S13
References	S14

Materials and Methods

Materials.

All materials were used as purchased. Cerium acetate trihydrate, tetrabutylammonium bromide, 1,3-dimethyl-2-imidazolidinone (DMI), sodium deuterioxide (40% wt), deuterium oxide, cyclohexanemethanol, and diethylmalonate were purchased from Aldrich. 2,3,6,7,10,11-hexahydroxytriphenylene was purchased from TCI America. Acetonitrile- d_3 was purchased from Cambridge Isotope Laboratories.

Synthesis of NU-1701.

Cerium acetate trihydrate (100 mg), hexahydroxytriphenylene hydrate (50 mg) and tetrabutylammonium bromide (100 mg) were combined in the 23 mL Teflon liner of an acid digestion vessel (Parr Instruments). A 3:2 mixture of deionized water (3 mL) and 1,3-dimethyl-2-imidazolidinone (2 mL) was added to the liner, and the vessel was sealed. The vessel was placed in an isothermal oven for 24 hours at 120 °C. Upon removal and cooling to slightly above room temperature, the vessel was opened, and black truncated octahedral crystals were present at the bottom of the liner. The crystals were washed 3 times (with 5 minute soaks) with water. The crystals were soaked for one week in ethanol (30 mL) with solvent exchanges between 1-3 times per day.

Characterization Methods

Powder X-ray Diffraction (PXRD).

PXRD patterns were collected at room temperature on a STOE-STADI-P powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK α 1 radiation, $\lambda = 1.54056$ Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. Powder was packed in a 3 mm mask and sandwiched between 2 layers of acetate tape. Intensity data from 3 to 40 degrees two theta were collected over a period of 25 mins. Instrument was calibrated against a NIST Silicon standard (640d) prior the measurement.

Single-Crystal X-ray Diffraction.

Intensity data of NU-1701 were collected at 100 K. A suitable single crystal was mounted on a MiTeGen loop with paratone oil on an XtaLAB Synergy diffractometer equipped with a micro-focus sealed X-ray tube PhotonJet (Mo) X-ray source and a Hybrid Pixel Array Detector (HyPix) detector. Temperature of the crystal was controlled with an Oxford Cryosystems low-temperature device. Data reduction was performed with the CrysAlisPro software using an empirical absorption correction. The structure was solved with the ShelXT¹ structure solution program using the Intrinsic Phasing method and by using Olex2 as the graphical interface.² The model was refined with ShelXL³ using least squares minimization. A solvent mask was calculated using SQUEEZE within Olex2; 1009 electrons were found in a volume of 23754 Å³ in 1 void per unit cell. This is consistent with the presence of 0.727[C₅H₁₀N₂O]

(dimethylimidazolidinone) per unit cell, which account for 992 electrons per unit cell. The rest of the electrons may be attributed to water. The structure was deposited into the Cambridge Crystallography Data Centre under deposition number 2122281.

Activation Procedures.

NU-1701 was activated using supercritical CO₂ in a Tousimis drier and subsequently placed on a Micromeritics SmartVacPrep under vacuum at room temperature for 24 hours.

Brunauer–Emmett–Teller (BET) Surface Area and Pore Size Analysis.

Nitrogen isotherms were measured on a Micrometrics Tristar II 3020 instrument at 77 K. and were analyzed with Brunauer–Emmett–Teller (BET) theory. Pore size distributions were calculated using density functional theory (DFT) modeling N₂ as a slit.

Solid State UV-Vis Spectroscopy.

UV-Vis spectra were collected on a Shimadzu UV-2600 spectrometer with barium sulfate as background.

X-ray Photoelectron Spectroscopy (XPS).

XPS data were collected on a Thermo Scientific ESCALAB 250Xi equipped with an electron flood gun and a scanning ion gun. Data were analyzed using Thermo Scientific Advantage Data System software and with the C1s peak (284.8 eV) as reference.

Thermogravimetric Analysis (TGA).

TGA experiments were carried out on a TGA/DCS 1 system (Mettler-Toledo AG) with STARe software. Samples were heated from 25 °C to 500 °C at 10 °C/minute under N₂ flow in an aluminum pan.

Scanning Electron Microscopy (SEM).

SEM images were collected on a Hitachi S4800-II cFEG microscope.

Nuclear Magnetic Resonance (NMR).

Approximately 1 mg of material was dissolved in a solution of D₂O and two drops of NaOD (40% by weight). ¹H spectra of digestions to determine acetate content were completed on a Bruker A600 NMR spectrometer.

¹H and ¹³C{¹H} spectra for photocatalysis yield quantification were collected on a Bruker Avance III HD equipped with a TXO Prodigy probe.

Photocatalysis Experiments.

All photocatalysis experiments were performed on dry or activated materials. To a 5 mL Biotage microwave vial, catalyst (relative to diethylmalonate) was added to 0.5 mL of acetonitrile-d₃.

Subsequently, 48 μL of cyclohexanemethanol and 219 μL of diethylmanolante were added via micropipette to the mixture, along with a micro stir-bar. The vial was capped and then purged with Ar for 10 minutes. The vial was then placed 5 cm away from a purple LED light (390 nm). The light and vial were surrounded by cardboard. The reaction was left to stir for 12 hours. Afterwards, via syringe, 100 μL of reaction mixture was transferred to an NMR tube, along with 400 μL of acetonitrile- d_3 and 30 μL of methyl acetate as an internal standard. In the cases where there was a heterogeneous catalytic phase, the reaction mixture, acetonitrile- d_3 , and methyl acetate were centrifuged in a microcentrifuge tube to remove the heterogeneous phase.

Computational Work.

Starting from the experimental unit cell of **NU-1701** we constructed a primitive cell of **NU-1701** that contains 24 Ce(III) centers and 4 hexameric building units. Each hexameric unit contains 5 hydroxyl groups, 1 water group, and 1 nitrate group and is connected to 6 HTTP linkers.

The periodic structure for **NU-1701** was optimized using the VASP software package.⁴⁻⁷ We used the projected augmented wavefunction (PAW) pseudopotentials^{8,9} with the PBE exchange-correlation functional^{10,11} with Hubbard U correction and Grimme D3 dispersion correction¹² and Becke Johnson damping. A Hubbard U value of 4 eV was used for the Ce 4f orbitals. The periodic calculations were performed at Γ -point with a planewave energy cutoff of 520 eV. The geometry optimization was performed using an energy convergence criterion of 10^{-5} eV and a force convergence criterion of $0.05 \text{ eV } \text{\AA}^{-1}$. In **NU-1701**, each Ce is in the +3-oxidation state, meaning each Ce has one 4f electron. This makes our DFT calculation extremely challenging as 24 unpaired 4f electrons can rise to systems with spin multiplicities between (1 and 25). In terms of magnetic configurations there is a total of 2^{24} magnetic configuration possible for this system. Thus, to simplify our calculation we used the “NUPDOWN” keyword in VASP and optimized the periodic structure for the highest spin only (i.e., where all the Ce centers are in a ferromagnetic configuration). Further, these density of state (DOS) calculations were performed on the optimized structure using the HSE06 exchange correlation functional.¹³⁻¹⁵

Ce Center	Magnetic Moment (μ_B)	Ce Center	Magnetic Moment (μ_B)	Ce Center	Magnetic Moment (μ_B)	Ce Center	Magnetic Moment (μ_B)
1	0.976	7	0.981	13	0.975	19	0.982
2	0.979	8	0.983	14	0.980	20	0.978
3	0.979	9	0.980	15	0.981	21	0.980
4	0.975	10	0.982	16	0.978	22	0.981
5	0.979	11	0.980	17	0.980	23	0.980
6	0.981	12	0.976	18	0.981	24	0.980

Table S1. Magnetic Moment at various Ce centers of NU-1701 (optimized using PBE+U(=4 eV) level of theory) using HSE06 level of theory.

Table 2. Crystallographic Details

Empirical formula	C ₃₂ H ₁₆ Ce _{4.36} N _{2.18} O _{21.46}
Formula weight	1302.70
Temperature/K	100.15
Crystal system	cubic
Space group	Fd-3m
a/Å	34.9097(6)
b/Å	34.9097(6)
c/Å	34.9097(6)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	42544(2)
Z	22
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.119
μ/mm^{-1}	2.557
F(000)	13264.0
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.87 to 58.652
Index ranges	$-45 \leq h \leq 46$, $-39 \leq k \leq 41$, $-42 \leq l \leq 46$
Reflections collected	41838
Independent reflections	2561 [$R_{\text{int}} = 0.0712$, $R_{\text{sigma}} = 0.0303$]
Data/restraints/parameters	2559/2/83
Goodness-of-fit on F^2	1.084
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0415$, $wR_2 = 0.1167$
Final R indexes [all data]	$R_1 = 0.0419$, $wR_2 = 0.1194$
Largest diff. peak/hole / e Å ⁻³	1.48/-0.65

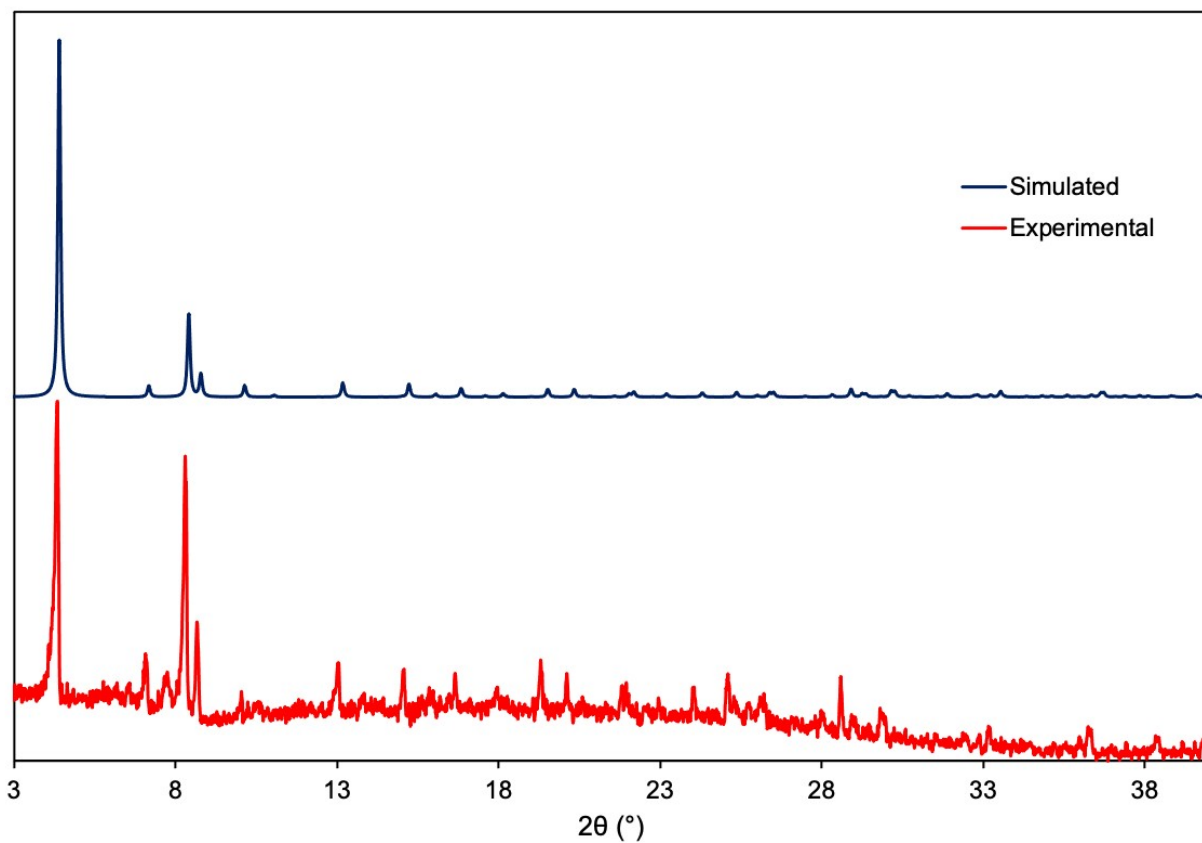


Figure S1. PXRD patterns of **NU-1701** simulated from the single crystal structure (top) and as synthesized (bottom).

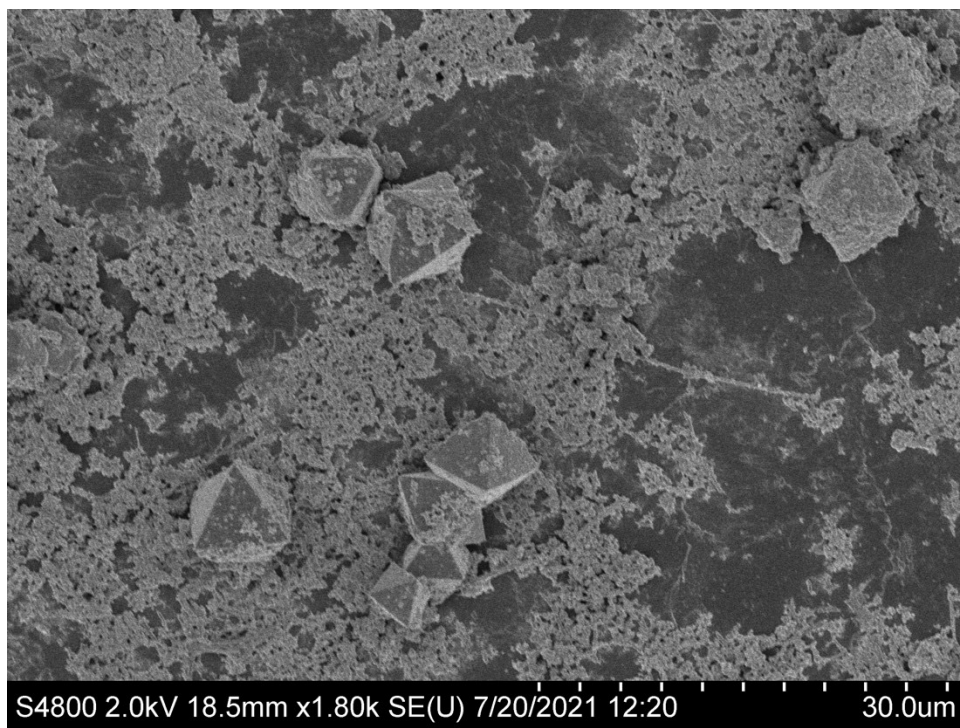


Figure S2. SEM image of octahedral crystals of NU-1701.

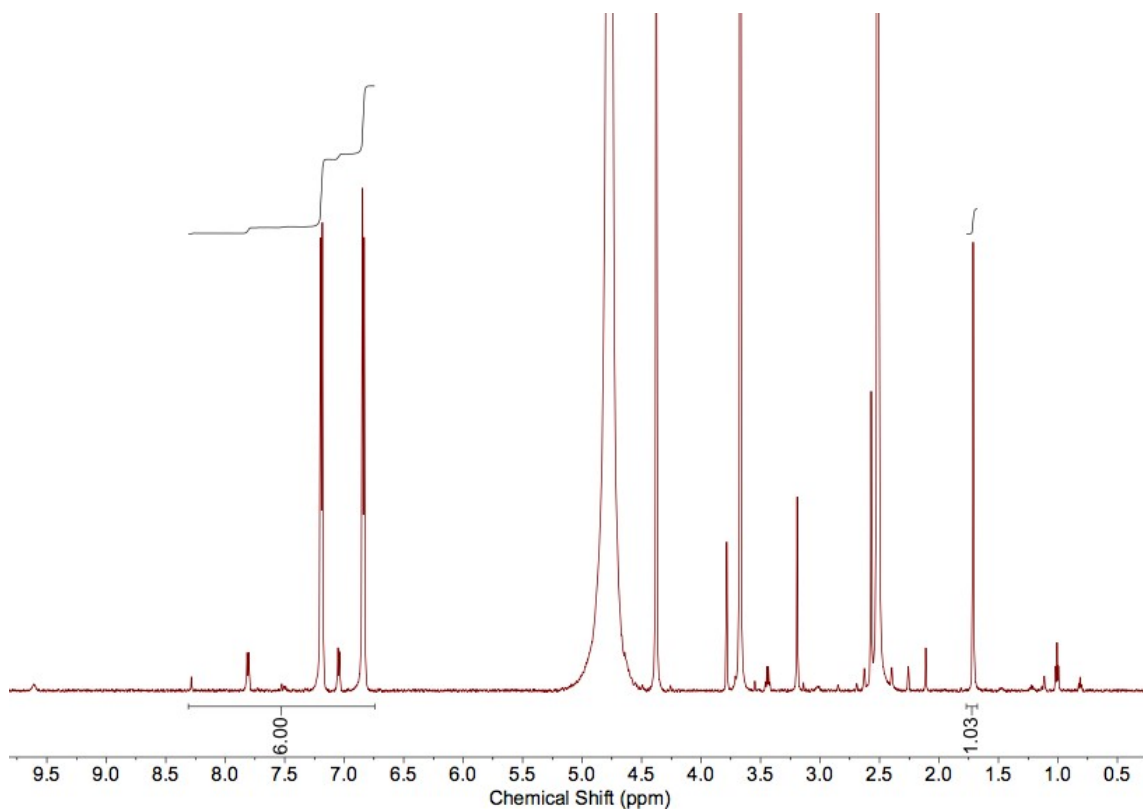


Figure S3. NMR spectra following base digestion of **NU-1701**. All peaks between 6.8 ppm and 8.3 ppm were integrated as HHTP linkers, as these peaks shift depending on linker oxidation state. The acetate peak is at 1.78 ppm.

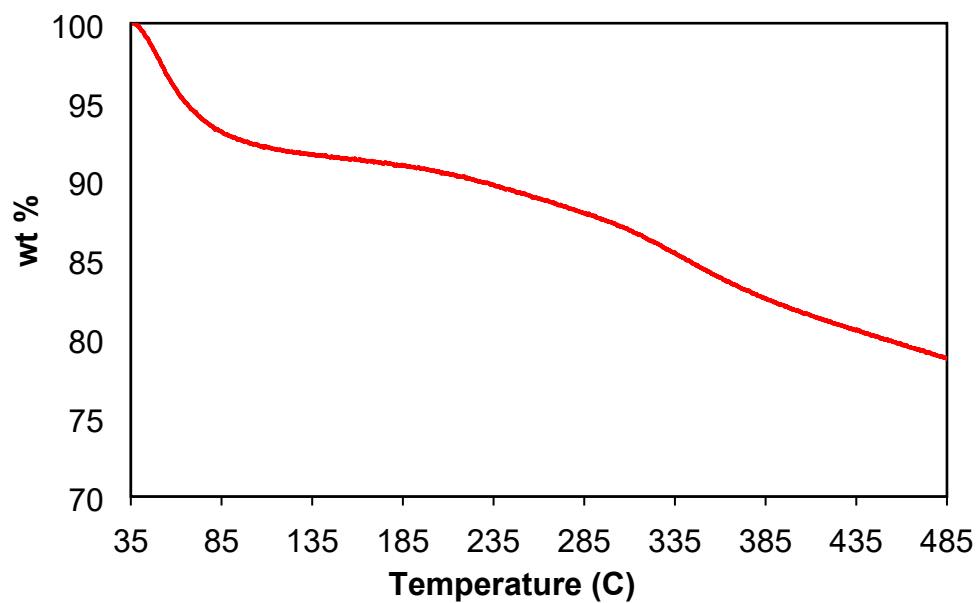


Figure S4. TGA curve of NU-1701.

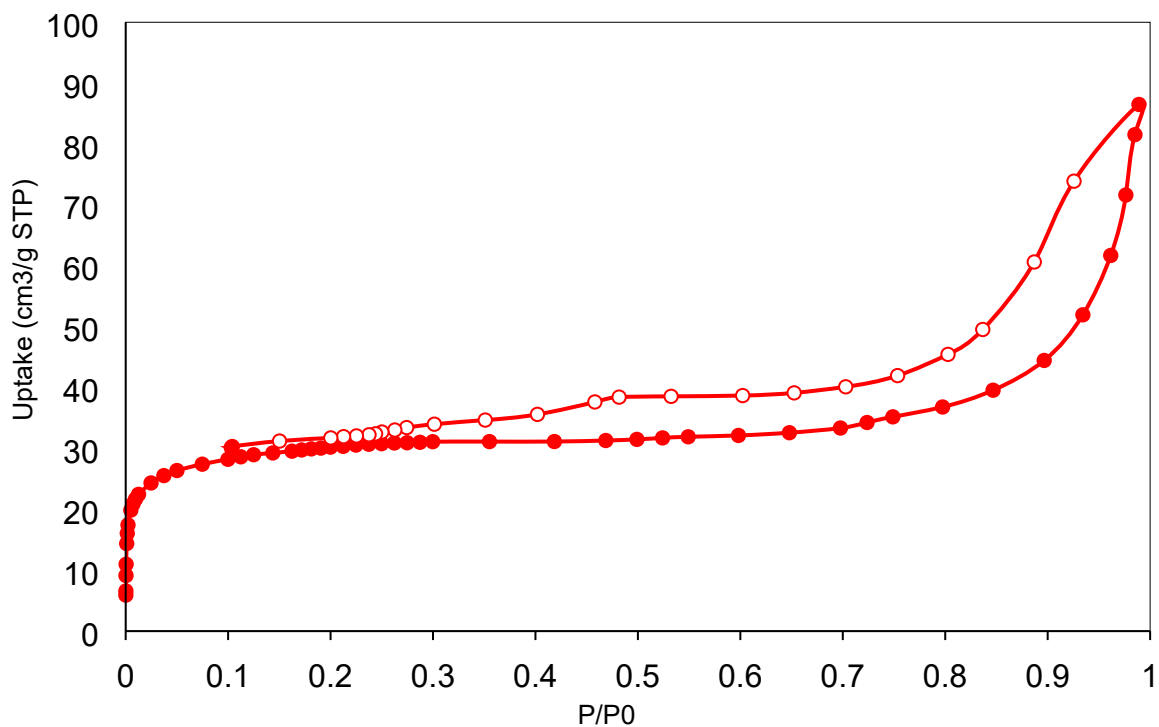


Figure S5. N₂ isotherm at 77K of NU-1701. Adsorption represented by filled circles, desorption by open circles.

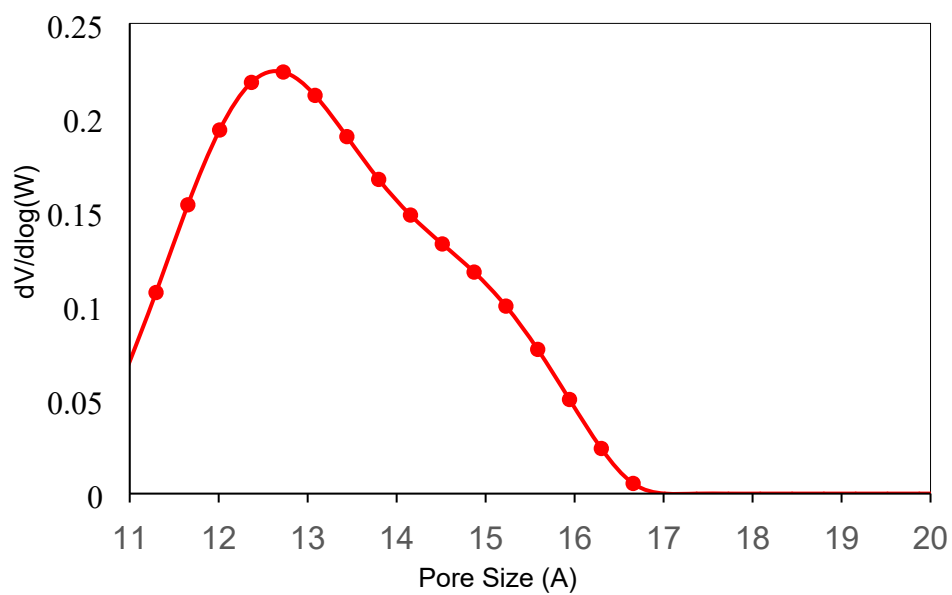


Figure S6. Pore Size Distribution of NU-1701.

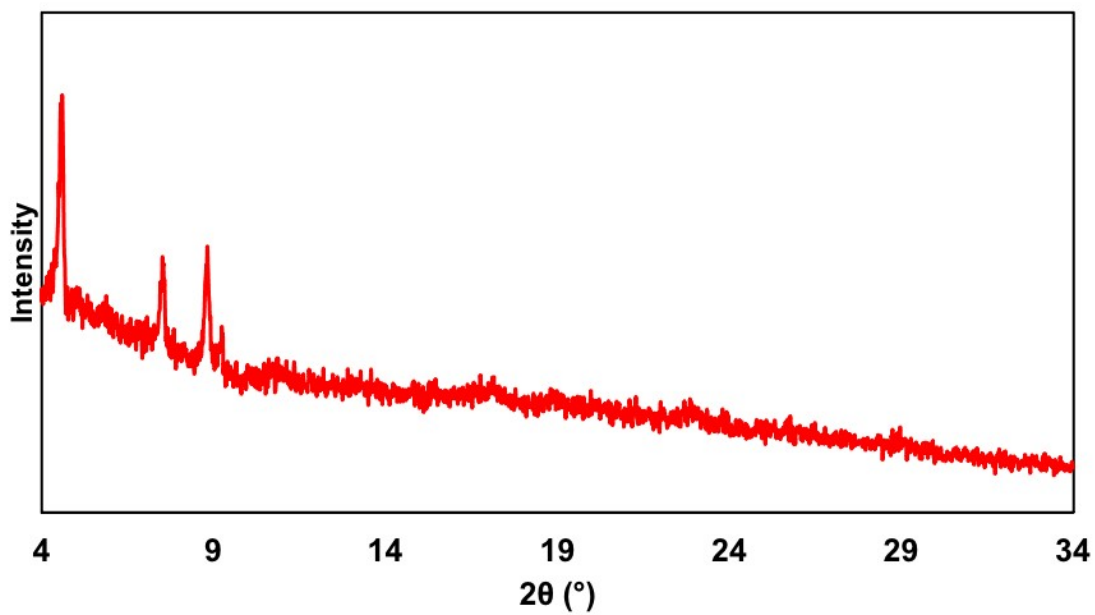


Figure S7. PXRD pattern of NU-1701 following activation.

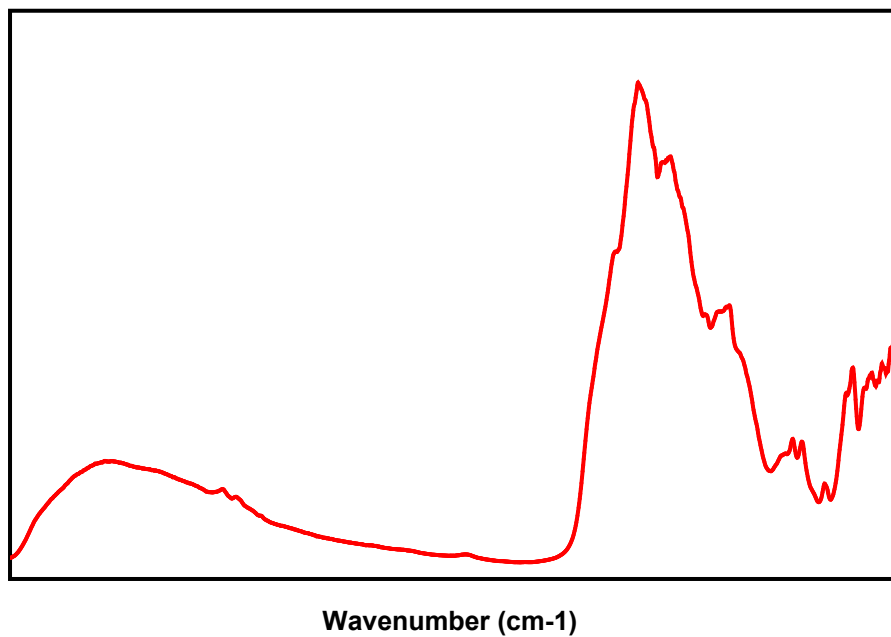


Figure S8. DRIFTS of NU-1701.

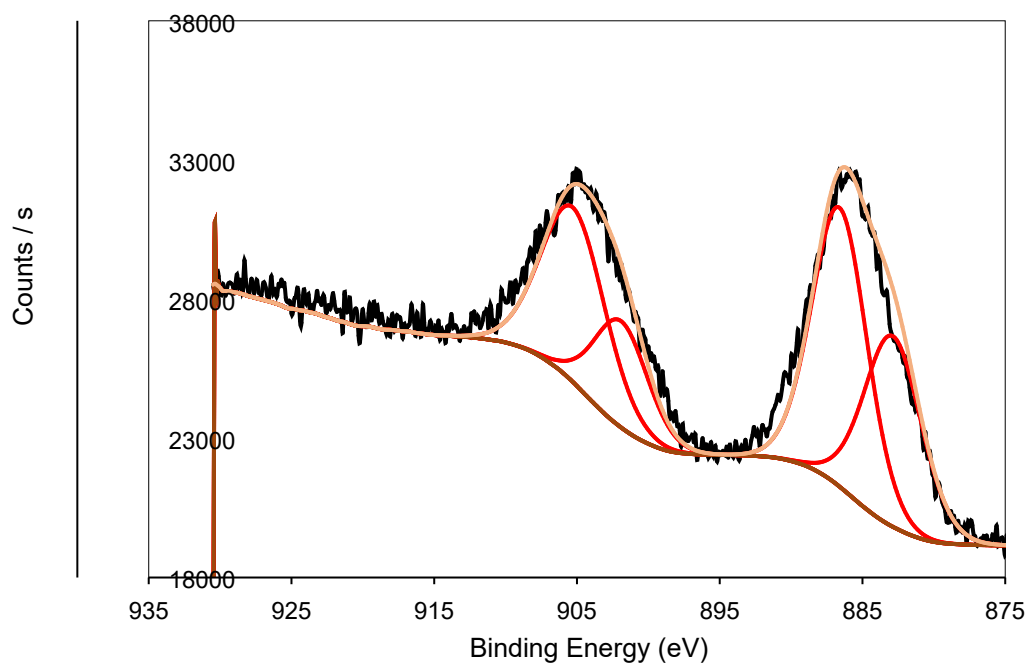


Figure S9. Observed Ce 3d XPS (solid black line), background (brown line), fitted data (red lines), and sum of fitted data (orange line) for NU-1701. The observed data were fitted by Gaussian/Lorentzian functions.

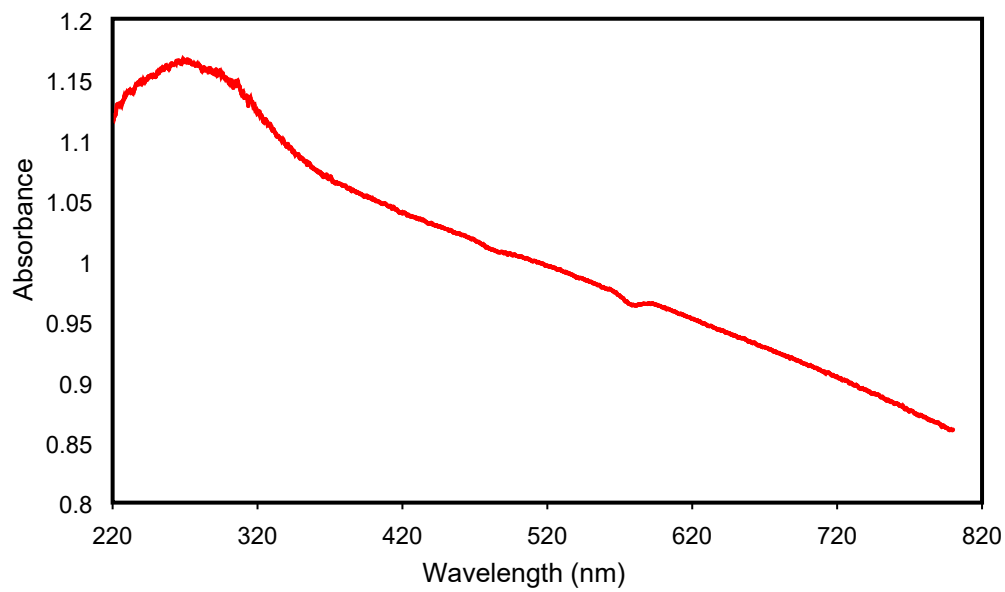


Figure S10. Solid-State UV-Vis spectra of NU-1701.

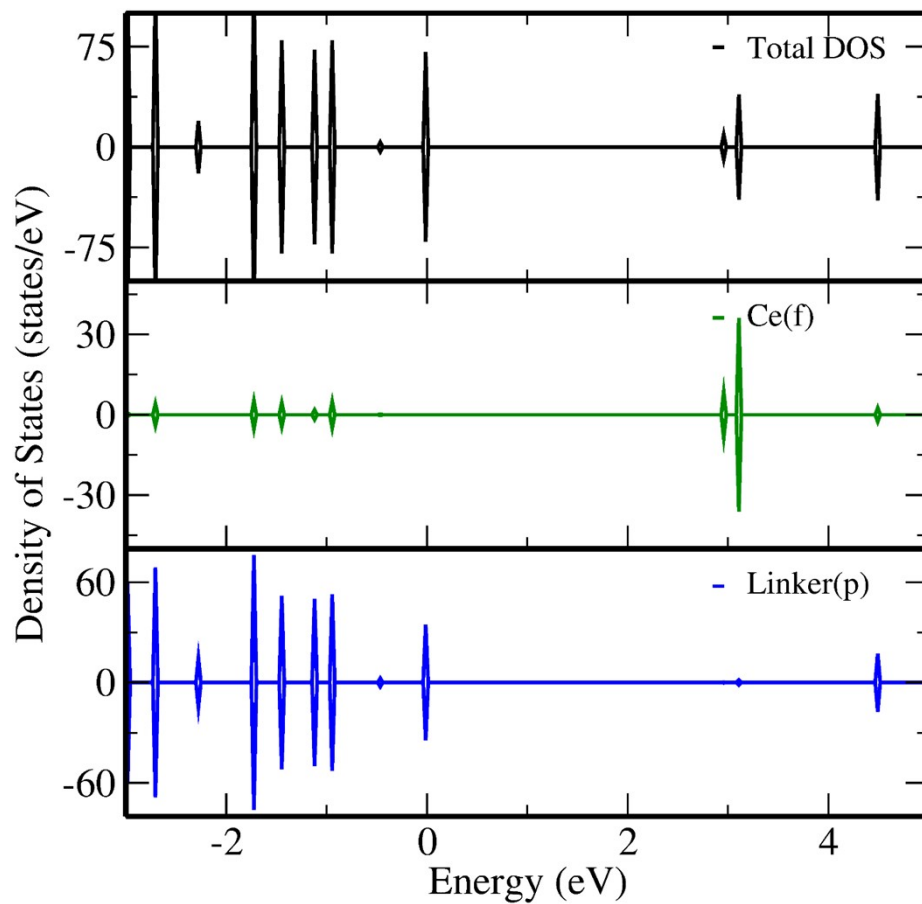


Figure S11. DOS calculations using HSE06 functional for Ce-UiO-66 framework (black), Ce of the Ce_6 nodes (green), and C, O of the 1,4-benzenedicarboxylate linker (blue).

Reaction	Trial 1	Trial 2	Trial 3	Average
5% CeCl ₃	10%	10%	7%	9% ± 2%
5% CeCl ₃ , 5% HHTP	8%	7%	7%	7% ± 0.0%
5% NU-1701	11%	15%	10%	12% ± 3%
5% CeCl ₃ , 15% NBu ₄ Br	26%	19%	10%	18% ± 8%
5% CeCl ₃ , 5% HHTP, 15% NBu ₄ Br	8%	19%	14%	14% ± 6%
5% NU-1701, 15% NBu ₄ Br	13%	4%	8%	8% ± 4%

Table S3. Dehydroxymethylation reaction yields including all trials and control experiments.

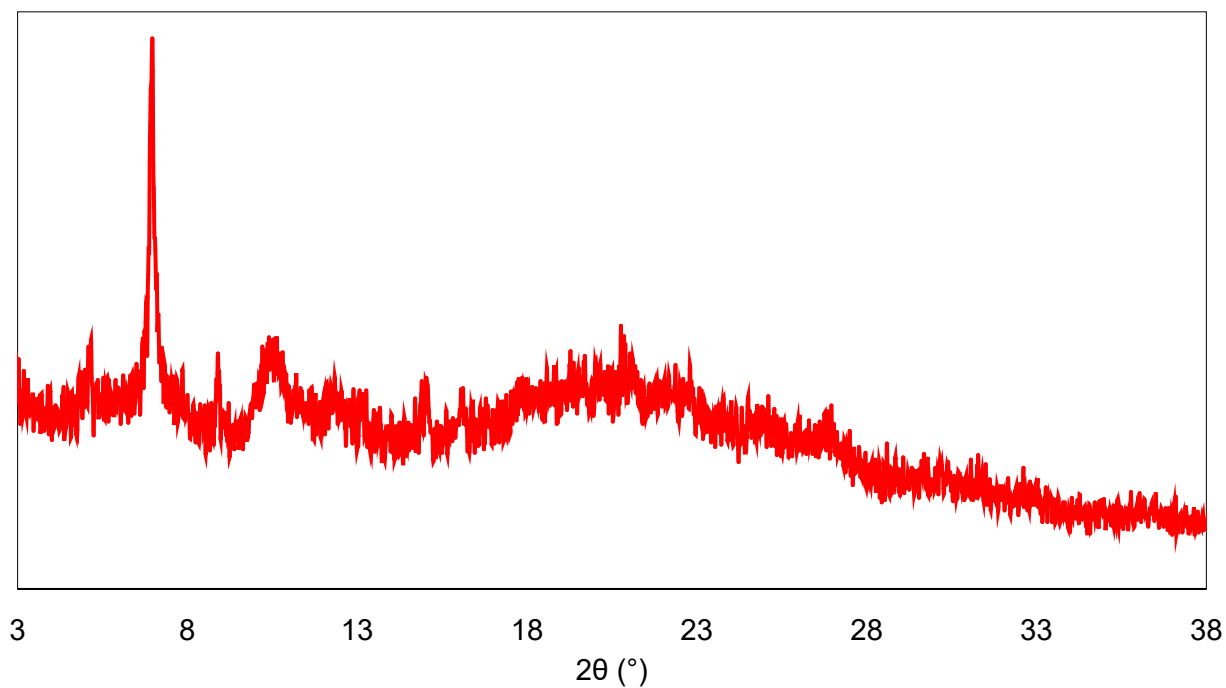


Figure S13. Representative PXRD pattern of NU-1701 following catalysis.

References

1. Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst. A* **2015**, 71 (1), 3-8.
2. O. V. Dolomanov; L. J. Bourhis; R. J. Gildea; J. A. K. Howard; H. Puschmann. "OLEX2: a complete structure solution, refinement and analysis program". *J. Appl. Cryst.* **2009**, 42, 339-341.
3. Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Crystal. C* **2015**, 71 (1), 3-8
4. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, 54 (16), 11169–11186.
5. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, 6 (1), 15–50.
6. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 47 (1), 558– 561.
7. Kresse, G.; Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 49 (20), 14251–14269.
8. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 50 (24), 17953–17979.
9. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, 59 (3), 1758–1775.
10. Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, 45 (23), 13244–13249.
11. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865– 3868.
12. Becke, A. D.; Johnson, E. R. A density-functional model of the dispersion interaction. *J. Chem. Phys.* **2005**, 123 (15), 154101.
13. Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: "Hybrid Functionals Based on a Screened Coulomb Potential" [J. Chem. Phys. 118, 8207 (2003)]. *J. Chem. Phys.* **2006**, 124 (21), 219906.
14. Heyd, J.; Peralta, J. E.; Scuseria, G. E.; Martin, R. L. Energy band gaps and lattice parameters evaluated with the Heyd-ScuseriaErnzerhof screened hybrid functional. *J. Chem. Phys.* **2005**, 123 (17), 174101.
15. Heyd, J.; Scuseria, G. E. Assessment and validation of a screened Coulomb hybrid density functional. *J. Chem. Phys.* **2004**, 120 (16), 7274–7280.