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Single crystal structure and photocatalytic behavior of grafted uranyl on the Zr-node of a pyrene-based metal-organic framework

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Experimental

Chemicals

Caution! Uranyl acetate dihydrate contains depleted uranium; necessary precautions should always be taken when handling this chemical.

All chemicals were used as purchased. Uranyl acetate dihydrate (≥98%) was purchased from International Bio-Analytical Industries, Inc. Methanol (99%) and N,N-dimethylformamide (DMF) (99%) were purchased from Fisher Chemical. Acetonitrile-d_3 (98%) was purchased from ACROS Organics and 4-methoxybenzyl alcohol (99%) from TCI America. Methyl acetate (99%) was purchased from Fisher.

Synthesis of NU-1000-U

NU-1000 was prepared according to the literature.[1] 93 μL of a 10 mg/mL stock solution of uranyl acetate in DMF were added to 10 mg of NU-1000 in a 1.5 dram glass vial. The total volume was diluted to 1 mL with fresh DMF. The suspension was sonicated for 5 minutes and subsequently placed into a sand bath within a convection oven at 75 °C for 24 hours. The resulting yellow powder was washed 3 times with 1 mL of fresh DMF each time.

Synthesis of Single Crystal NU-1000-U

Single crystal NU-1000-U was prepared according to the literature,[1] with some alterations. Half the amount of all the starting materials (excluding TFA and solvents) was used. 2 mL of a 10 mg/mL stock solution of uranyl acetate dihydrate in DMF were added to 50 μg of solvated single crystal NU-1000 in 2 mL of DMF 1.5-dram glass vial. The vial was sealed and placed into a sand bath within a convection oven at 75 °C for 2 days. The vial was removed, the solvent was carefully decanted so that the crystals always remained solvated, and the crystals were soaked overnight in fresh DMF.

Synthesis of 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H_4TABy)

H_4TABy was synthesized according to the literature.[2]

Synthesis of NU-1200

NU-1200 was synthesized according to the literature.[3]

Characterization Techniques

Powder X-Ray Diffraction (PXRD). PXRD patterns were obtained on a STOE-STADI P powder diffractometer at 40 kV voltage and 40 mA current with Cu-Kα1 X-ray radiation ($\lambda = 0.154056$ nm) in transmission geometry.

Inductively Coupled Optical Emission Spectroscopy (ICP-OES). Uranium loading was confirmed *via* ICP-OES measurements taken on a Thermo iCap7600 ICP-OES spectrometer at Northwestern University. Samples were prepared by adding approximately 2 mg of material to a 2 – 5 mL Biotage microwave vial and subsequently adding 2 mL of concentrated HNO_3. Samples were heated in a Biotage SPX microwave reactor (software version 2.3, build 6250) at 150 °C for 15 minutes. 300 μL of the digested material was added to a 15 mL centrifuge tube, diluted to 10 mL with Millipore H_2O, and analyzed for U (385.958 nm, 409.014 nm, 367.007 nm, axial) and Zr (343.823 nm, 327.305 nm, 339.198 nm, axial) compared to standard solutions. The concentrations calculated by the spectrometer were subsequently divided by the stoichiometric coefficients (6 for Zr_6, 1 for UO_2^{2+}) and then by the atomic mass of each atom. Finally, the quantity of U calculated was divided by the quantity of Zr calculated to get the ratio of U:Zr.

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). Samples were loaded on carbon tape placed on an aluminum stub and coated with 9 nm o Au/Pd (composition 80/20) prior to the experiment. The measurements were performed on Phenom ProX equipped with fully integrated EDS detector applying acceleration voltage of 15 kV.

Brunauer–Emmett–Teller (BET) Surface Area and Pore Size Analysis. All MOFs samples were placed in a vacuum oven for 2 hours before being activated under ultrahigh vacuum at 150 °C for 18 h on a Micrometrics Smart Vac Prep. N_2 isotherms were measured on a Micrometrics Tristar II 3020 instrument at 77 K. Nitrogen isotherms were analyzed with Brunauer–Emmett–Teller (BET) theory and pore size distributions were calculated using density functional theory (DFT).

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Spectra were collected on a Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with an MCT detector and a Harrick praying mantis accessory. All samples were activated before measurement. Resolution was 1 cm^{-1} and the background was KBr.

Raman Spectroscopy. Raman spectra were collected on a DXR SmartRaman at Los Alamos National Laboratory, using a 780 nm laser with 25 sec exposure and 50 μm pinhole. Data was averaged over 10 runs.

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 N_2 flow.

Nuclear Magnetic Resonance (NMR) spectroscopy. ^1H NMR spectra were collected on a Bruker Avance III 600 MHz at room temperature. Kinetics NMR spectra were collected in acetonitrile-d_3. MOF base digestion NMR spectra were collected by dissolving approximately 0.5 mg of MOF in 3 drops of NaOD (40% by weight), 100 μL of DMSO-d_6, and 900 μL and D_2O. Acetate on the node was calculated by integrating the acetate peak (1.85 ppm, 3H) relative to the two linker within the unit cell of NU-1000 (7.53 ppm, 8H) and dividing the integration of the acetate peak by 3.

Single Crystal X-Ray Diffraction (SCXRD).

Single-crystal X-ray diffraction (SCXRD) data of **NU-1000-U** was collected at 200 K on a 'Bruker APEX-II CCD' diffractometer with a CuKα (λ = 1.54184 Å) microfocus X-ray source. The single crystals were mounted on MicroMesh (MiTeGen) with paratone oil. The structures were determined by intrinsic phasing (SHELXT 2018/2)[4] and refined by full-matrix least-squares refinement (SHELXL-2018/3)[5] using the Olex2[6] software packages. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were added using a riding model. The disordered non-coordinated solvents were removed using the PLATON SQUEEZE program.[7] The refinement results are summarized in Table S1. Crystallographic data for the **NU-1000-U** structure has been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-1971894. 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.).

Photocatalysis Experiments

60 mg of NU-1000-U by mass was placed in a 2-5 mL Biotage microwave vial with a micro stir bar. 2 mL of CD_3CN and 74 μL of 4-methoxybenzyl alcohol were also added, as well as 25 μL of methyl acetate as an internal standard. The vial was sealed and purged with O_2 gas for 15 minutes. A balloon filled with oxygen was attached to the vial *via* a needle. The vial was placed on a stirplate and stirred consistently. A cardboard box with cutouts for an LED light was placed around the outside of the vial to prevent light contamination, and a blue LED light was shone on the vial. 50 uL aliquots were collected hourly after temporarily turning off the light and piercing the septum of the microwave cap with a needle. The aliquots were then diluted to 1 mL using acetonitrile-d_3; ^{1}H NMR spectra were then collected.

Brief Discussion of Luminescence

Upon visual inspection with UV glasses under blue light irradiation, we observed weaker luminescence by **NU-1000-U** as compared to NU-1000. Furthermore, the strong luminescence of NU-1000 made it difficult to collect Raman spectra. Once uranyl acetate was deposited, it was far easier to collect Raman spectra.

Table S1. Crystallographic data of **NU-1000-U.**

	NU-1000-U
Empirical formula	$C_{44}H_{22}O_{16.3}U_{0.27}Zr_3$
Formula weight	1148.95
Temperature/K	200(2)
Crystal system	hexagonal
Space group	*P6/mmm*
a/Å	39.5261(3)
b/Å	39.5261(3)
c/Å	16.52780(10)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	22362.1(4)
Z	6
ρ_{calc}g/cm^3	0.512
μ/mm^{-1}	2.680
F(000)	3367.0
Crystal size/mm^3	0.12 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.472 to 136.274
Index ranges	$-42 \leq h \leq 45$, $-45 \leq k \leq 26$, $-19 \leq l \leq 19$
Reflections collected	98944
Independent reflections	7483 [R_{int} = 0.0616, R_{sigma} = 0.0237]
Data/restraints/parameters	7483/232/194
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1863

Final R indexes [all data]	$R_1 = 0.0591$, $wR_2 = 0.1916$
Largest diff. peak/hole / e Å^{-3}	1.14/-0.77
CCDC number	1971894

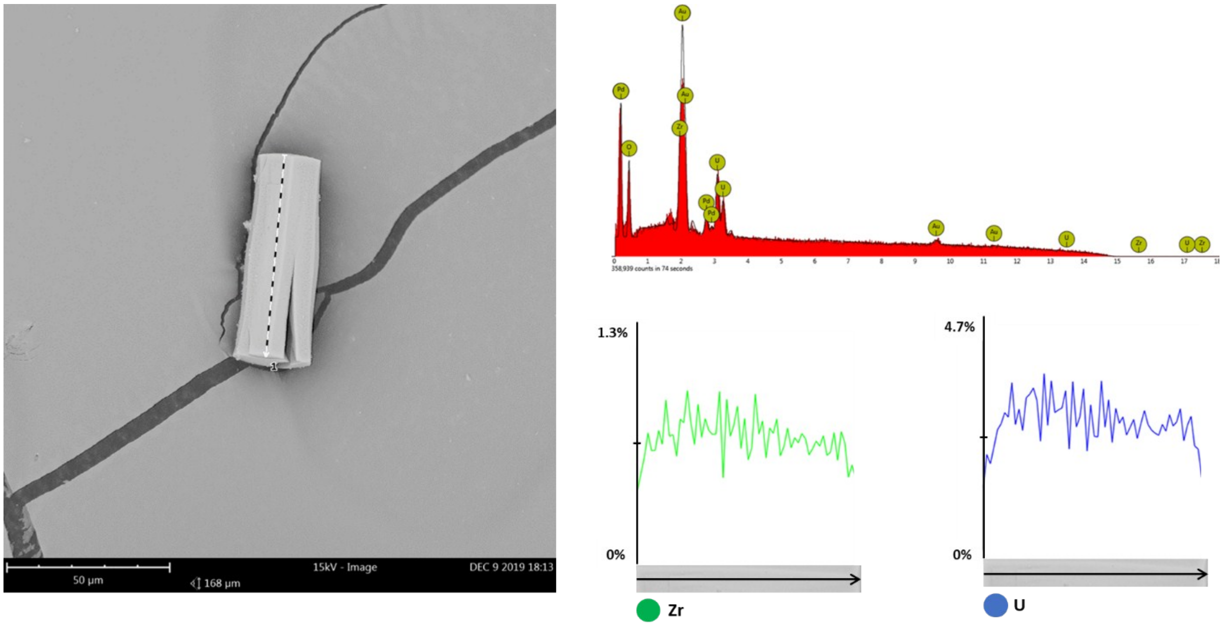

Figure S1. SEM (left) and EDS images (right) of NU-1000-U indicating consistent loading of uranyl. The cracks observed are from beam exposure; analysis of sample within crack shows the same composition as surface. The EDS mapping (bottom right) of uranium has a very similar overall shape to the zirconium mapping, indicating distribution of uranium throughout the entire length of the particle.

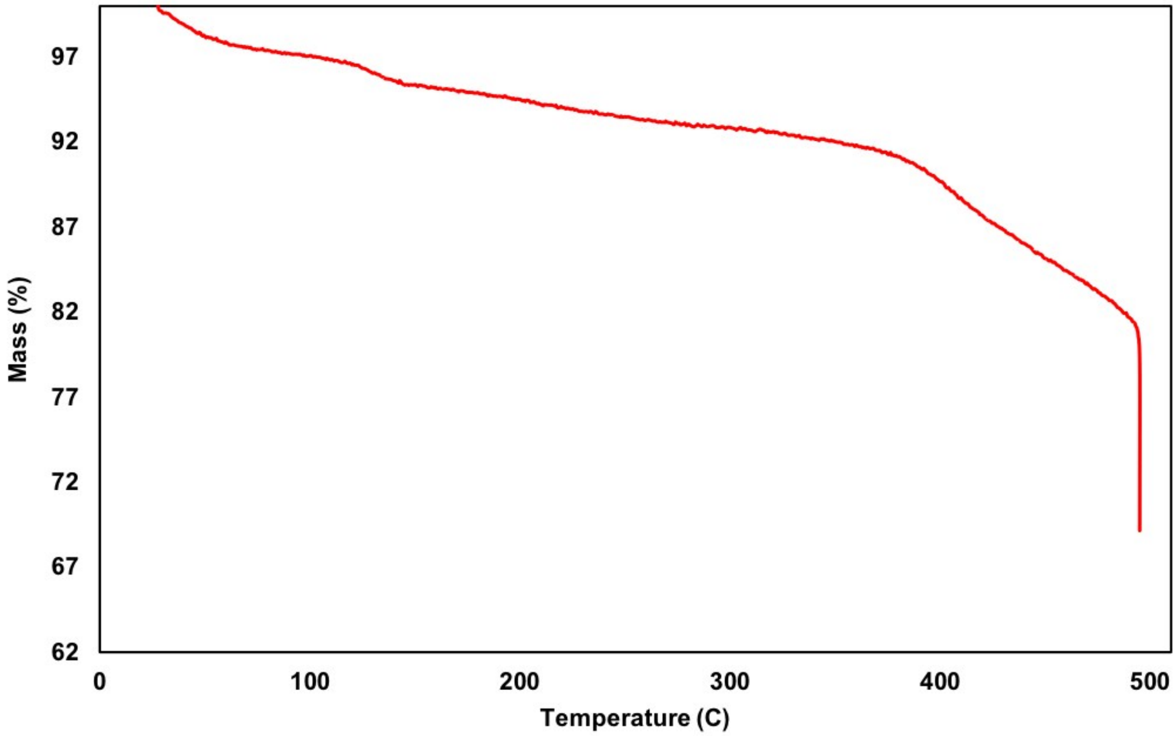

Figure S2. TGA curve up to 500 °C of **NU-1000-U**. The slight decrease following 100 °C is the removal of water from the MOF. The drop-off starting at 400 °C is the decomposition of the framework.

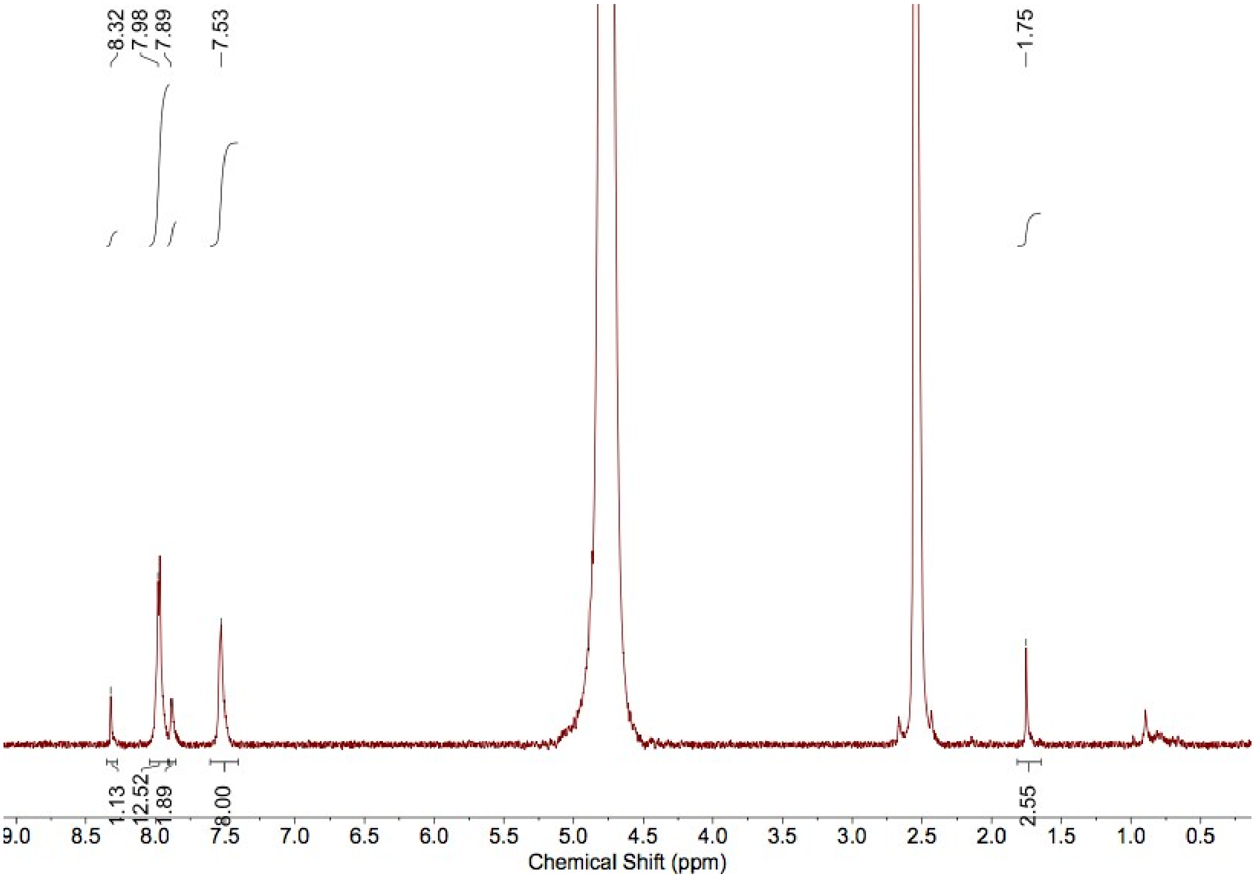

Figure S3. ^{1}H NMR spectra of base-digested NU-1000-U, with acetate peak (1.85 ppm).

	0 hrs	**8 hrs**	**24 hrs**
NU-1200	0%	0%	2%
	0 hrs	**6.5 hrs**	**24 hrs**
UO_2^{2+}/H_4TBAPy (5%:1% relative to MBA)	0%	5%	9%

Table S2. Kinetics data for NU-1200 and UO_2^{2+}/H_4TBAPy.

References

1. Islamoglu, T., Otake, K., Li, P., Buru, C.T., Peters, A.W., Akpinar, I., Garibay, S.J., Farha, O.K., *CrystEngComm.* **2018,** *20*, 5913 - 5918.
2. Wang, T., Vermeulen, N., Kim, I., Martinson, A.B.F., Stoddart, J.F., Hupp, J.T., Farha, O.K., *Nat. Protoc.* **2016,** *11*, 149 - 162.
3. Wang, X., Zhang, X., Li, P., Otake, K., Cui, Y., Lyu, J., Krzyaniak, M.D., Buru, C.T., Islamoglu, T., Wasielewski, M.R., Li, Z., Farha, O.K., *J. Am. Chem. Soc.* **2019,** *141*, 8306 - 8314.
4. Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr A* **2015,** *71* (1), 3-8.
5. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallographica Section C* **2015,** *71* (1), 3-8.
6. 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. Crystallogr.* **2009,** *42* (2), 339-341.
7. Spek, A., PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallographica Section C* **2015,** *71* (1), 9-18.