Supporting Information

for:

Formation of uranium disulfide from a uranium thioamidate single-source precursor

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A. Experimental Section

Methods and Materials

General Considerations: Unless otherwise noted, all reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen, or in an MBraun inert atmosphere glovebox under an atmosphere of nitrogen or argon. Glassware, Celite, and cannulae were stored in an oven at *ca*. 160 °C for at least 4 h prior to use. 3 Å and 4 Å molecular sieves were activated by heating under vacuum at 300 °C for 24 h. NMR spectra were recorded at 298 K unless otherwise noted on Bruker AV-300, AVB-400, AVQ-400, and AV-500 spectrometers. ^{1}H chemical shifts were calibrated relative to residual solvent peaks and are recorded in units of parts per million (ppm). FTIR samples were prepared as Nujol mulls pressed between KBr plates, and the data were collected with a Nicolet iS10 FT-IR spectrometer. A solution phase UV-vis electronic absorption spectrum was collected at ambient temperature using a Varian Cary 5G UV-Vis-NIR spectrophotometer in 1 cm quartz cuvettes (Agilent Technologies, Inc). Melting points were determined using sealed capillaries prepared under nitrogen on an OptiMelt automated melting point system. Elemental analysis was determined at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley.

Materials: *n*-Hexane, *n*-pentane, toluene, and tetrahydrofuran were purified by passage through a column of activated alumina prior to use. Deuterated solvents were dried using sodium/benzophenone, degassed with three freeze-pump-thaw cycles, and vacuum-transferred or distilled before being stored over 4 Å molecular sieves in a glovebox. UCl_4,[1] $UI_4(dioxane)_2$,[2] 2-methyl-N-(2-methyl-2-propanyl)propanthioamide (H(ITTA)),[3] and K(ITTA)[4,5] were synthesized according to literature procedures. All other chemicals were purchased from commercial sources and used as received.

U(ITTA)$_4$: *Method 1* – A THF solution (50 mL) of UCl_4 (0.968 g, 2.55 mmol) was added dropwise to a stirred THF solution (70 mL) of K(ITTA) (2.0160 g, 10.212 mmol) cooled to 0 °C. The cold bath was removed and the solution was stirred for 18 h, by which time the color had turned from dark green to brown-green and cloudy. The solvent was removed *in vacuo,* and the product was extracted into hexane (150 mL), filtered, and concentrated (*ca*. 80 mL). The resulting bright green solution was cooled to −40 °C overnight, resulting in green crystals (1.405 g, 60% yield). *Method 2* – A THF solution (3 mL) of $UI_4(dioxane)_2$ (52.4 mg, 0.057 mmol) was added dropwise to a stirred THF solution (8 mL) of K(ITTA) (45.8 mg, 0.232 mmol) cooled to 0 °C. After addition of the $UI_4(dioxane)_2$ solution was complete, the cold bath was removed, and the solution was stirred for 18 h. After stirring was complete, the solution had turned from red to brown-yellow and cloudy. The solvent was removed *in vacuo,* and the product was extracted into pentane (10 mL), filtered, and concentrated (*ca*. 4 mL). The resulting bright green solution was cooled to -40 °C overnight, resulting in green crystals (21 mg, 42 % yield). Mp *ca*. 210 °C (decomp); ^{1}H NMR (500 MHz, 298K, tol-d8): δ 9.52 (s, CH(C*H*$_3$)$_2$, 12H), 1.13 (s, C(C*H*$_3$)$_3$, 9H), 1.13 (s, CH(C*H*$_3$)$_2$, 12H)*, 1.11 (s, CH(C*H*$_3$)$_2$, 6H), -1.63 (s, CH(C*H*$_3$)$_2$, 6H), -6.25 (s, C(C*H*$_3$)$_3$, 9H), -8.89 (s, C*H*(CH$_3$)$_2$, 4H), -9.09 (s, C(C*H*$_3$)$_3$, 36H).; ^{13}C NMR (300 MHz, tol-d8): δ 27.01, 26.67(CH(*C*H$_3$)$_2$), 25.47(CH(*C*H$_3$)$_2$), 22.54(CH(*C*H$_3$)$_2$), 18.18(C(*C*H$_3$)$_3$), 16.04(C(*C*H$_3$)$_3$), 15.17, 12.66(CH(CH$_3$)$_2$), 12.33(*C*H(CH$_3$)$_2$), -60.31.; IR (Nujol mull on KBr): 1527 (s), 1172 (m), 1098 (w), 1029 (w), 973 (s), 891 (w), 722 (w), 688 (w), 542 (w), 440 (w) cm^{-1}. Anal. Calc'd (%) for $US_4N_4C_{32}H_{64}$

($U(ITTA)_4$): C, 44.00; H, 7.40; N, 6.40; S, 14.70. Found: C, 43.67; H, 7.25; N, 6.21; S, 14.39. *Assignments for the 1.13 ppm ^1H NMR peaks based on exchange seen in EXSY spectrum below.

NMR Decomposition Study: $U(ITTA)_4$ (10 mg) was added to a J-Young NMR tube inside a nitrogen glovebox. The tube was brought out of the glovebox and the bottom of the tube containing the sample was heated to 300 °C in an aluminum heating block for 16 h. After cooling to room temperature, the tube was brought back into the glovebox and placed in a liquid nitrogen-cooled well for 15 minutes to condense volatile decomposition products. A solution of hexamethylbenzene (1.0 mg) in C_6D_6 (0.50 mL) was quickly added to the tube. The tube was then capped and allowed to warm to room temperature before collecting the NMR spectrum (Figure S9).

Pyrolysis of U(ITTA)$_4$: *Method 1 (1-US$_2$, non-annealed)*– $U(ITTA)_4$ (*ca*. 100 mg) was added to a quartz tube fitted with a Schlenk adapter inside an argon glovebox. The tube was brought out of the glovebox, transferred onto the Schlenk line, and then placed in a Thermo Scientific Lindberg Blue M single zone tube furnace under flow of argon. The sample was heated to 250 °C for 1 h, then held at 250 °C for 2 h. The sample was allowed to cool in the furnace before bringing back into the glovebox to collect the black powder. *Method 2 (2-US$_2$, annealed)* – $U(ITTA)_4$ (*ca*. 100 mg) was added to a quartz tube fitted with a Schlenk adapter inside an argon glovebox. The tube was brought out of the glovebox, transferred onto the Schlenk line, and then placed in the tube furnace under flow of argon. The sample was heated to 250 °C for 1 h, then held at 250 °C for 1 h, heated to 850 °C for 1.5 h, and held at 850 °C for 5 h. This yielded a shiny, black solid. Anal. Calc'd (%) for 1-US_2: C, 0.00; H, 0.00; N, 0.00; S, 22.00. Found: C, 2.33; H, 0.39; N, 0.79; S, 21.40.

X-Ray Diffraction:

Single Crystal X-ray Diffraction: Samples of single crystals for $U(ITTA)_4$ were coated in Paratone-N oil for transport to the Advanced Light Source (ALS). Crystals were mounted on a MiTeGen 10 μm aperture Dual-Thickness MicroMount loop. X-ray diffraction data was collected at the ALS, Lawrence Berkeley National Lab, Berkeley, CA, station 12.2.1 using a silicon monochromated beam of 17 keV (λ = 0.7288 Å) synchrotron radiation. Data was collected at 100 K, with the crystals cooled by a stream of dry nitrogen. Bruker APEX3 software was used for the data collections, Bruker SAINT v8.37A or V8.38A software was used to conduct the cell refinement and data reduction procedures,[6] and absorption corrections were carried out by a multi-scan method utilizing the SADABS program.[6] Initial structure solutions were found using direct methods (SHELXT),[7] and refinements were carried out using SHELXL-2014,[8] as implemented by Olex2.[9] Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically. Thermal ellipsoid plots were made using CrystalMaker 10. The $U(ITTA)_4$ structure was deposited to the Cambridge Crystallographic Data Centre (CCDC), with deposition number: 2353086.

Powder X-ray Diffraction (PXRD): PXRD samples were prepared by dispersing particles in toluene and drop casting onto a silicon zero background plate, which was then covered with an acrylic dome. Patterns were measured with a Cu source (45 kV, 40 mA) by using a Panalytical X'Pert Pro Diffractometer with continuous scans with a 0.02° 2θ step size.

U L_3-edge X-ray Absorption Spectroscopy

$U(ITTA)_4$ and pyrolyzed samples of $U(ITTA)_4$ were ground using a mortar and pestle in an argon filled glovebox and diluted with BN (9-13 wt%). The diluted samples were then packed into aluminum holders sealed with indium wire.[10] Due to the air and water sensitivity of the samples, they were stored under argon in three layers of aluminized mylar bags until measurement. Samples were measured using a liquid He-cooled cryostat at 30 K at the U L_3-edge (17.166 keV) at Beamline 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a Si 220 monochromator detuned to 50%. The sealed holders were transferred into the cryostat at the beamline and quickly cycled under vacuum with an He backfill. Data were collected in both transmission and fluorescence mode, using a 100 Element Canberra Ge Fluorescence detector (sample at 45° from the incident beam and fluorescence detector). No photoreduction of the sample was observed over time in the X-ray beam. Data were internally edge-energy calibrated using the first inflection point against a UO_2 (17.171 keV) reference collected simultaneously. A slit height for the sample was chosen to be less than 0.7 mm, such that the data resolution would be core-hole lifetime limited.[11] Fluorescence data were also corrected for dead time. Data were reduced and analyzed using the RSXAP software package.[11,12] Data were fit in r-space using EXAFS standards calculated using FEFF8L and error bars calculated using a profiling method.[11,13] The number of parameters used in the fit were limited to be fewer than the number of independent points.

For the 1-US_2 data, the fitting range is 1.90-5.50 Å. The k^3 weighted data are transformed between 2.50-13.00 $Å^{-1}$ and are Gaussian narrowed by 0.30 $Å^{-1}$. Errors were calculated using the "Stern" method. The data have 26.1 independent data points, and 22.1 degrees of freedom.

For the 2-US_2 data, the fitting range is 1.95-5.50 Å. The k^3 weighted data are transformed between 2.50-13.00 $Å^{-1}$ and are Gaussian narrowed by 0.30 $Å^{-1}$. Errors were calculated using the "Stern" method. The data have 25.7 independent data points, and 8.7 degrees of freedom.

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images were captured through an FEI Apreo VolumeScope SEM equipped with EDAX and EBSD detector. The samples for SEM imaging were prepared by dispersing the sample in hexanes and drop-casting 10 μL of the respective sample dispersions on ultra-flat silicon wafers. Solvent was evaporated overnight in a desiccator.

Simultaneous Thermal Analysis

Simultaneous thermal analysis (STA), which performs thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in tandem, measurements were performed on $U(ITTA)_4$ to study material thermal decomposition. Samples of ~20 mg were transferred and loaded in a positive pressure argon glovebox, which is dedicated only for STA measurements. Prior to sample analysis, the instrument was temperature and weight calibrated with a series of metal calibrants. STA measurements were performed on a NETZSCH STA 449F1-Jupiter. The sample chamber was purged and flushed with argon three times to ensure inert atmosphere prior to sample heating. Samples were heated to 850 °C in Al_2O_3 crucibles at a constant heating rate of 5 °C/min. TG mass loss and DSC heat output curves were generated using NETZSCH 6.1.0 Proteus® software.

B. Spectroscopy

NMR Spectroscopy for U(ITTA)$_4$:

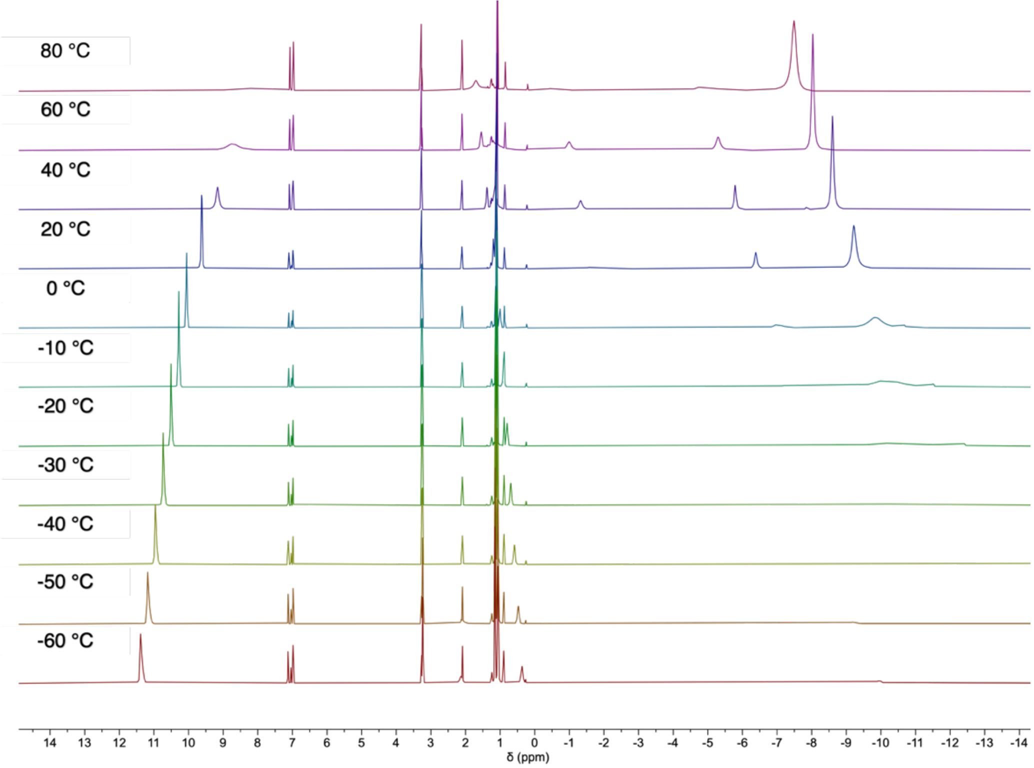

Figure S1. Variable temperature ^{1}H NMR spectra for U(ITTA)$_4$ in toluene-d$_8$ (213-353 K, 500 MHz).

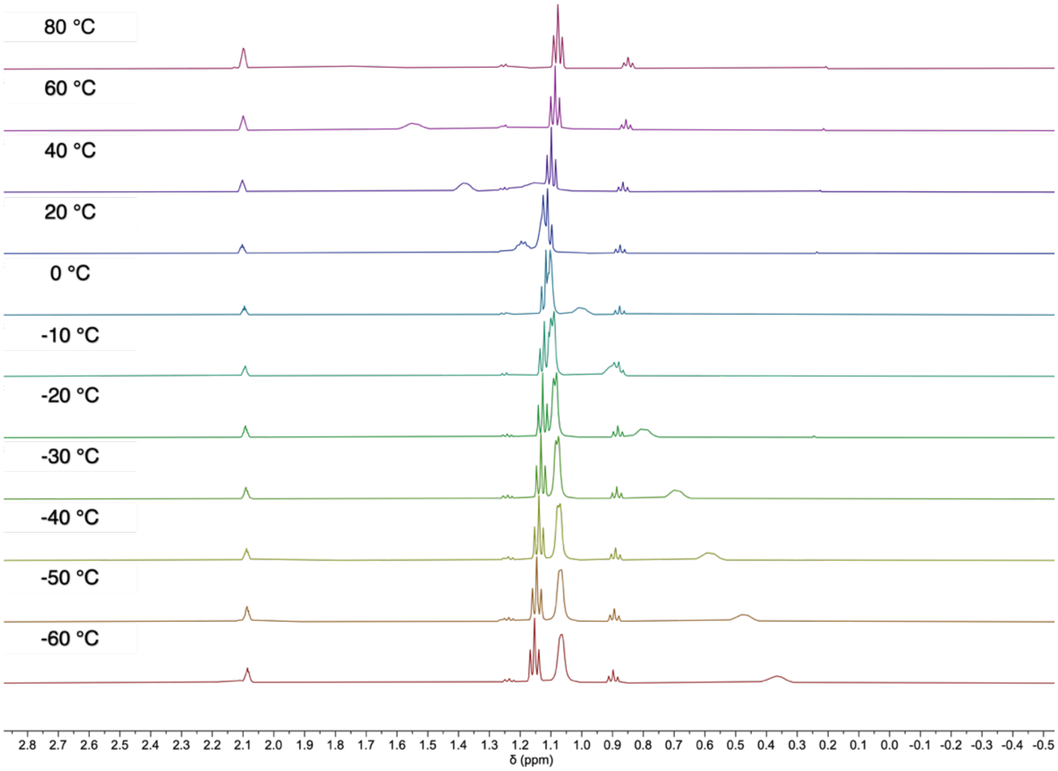

Figure S2. Variable temperature ^{1}H NMR spectra for U(ITTA)$_4$ in toluene-d$_8$ (213-353 K, 500 MHz), zoomed in for clarity.

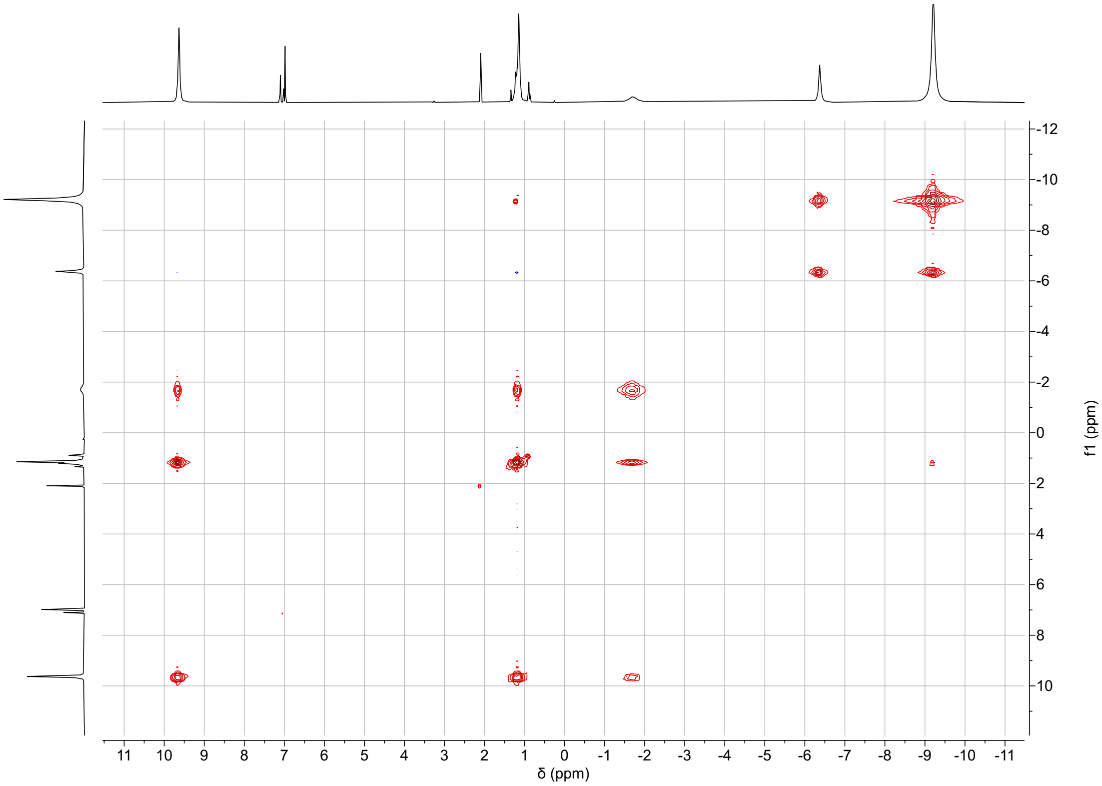

Figure S3. ^1H-^1H *EXSY NMR of U(ITTA)$_4$ in toluene-d$_8$ (298K, 300 MHz).*

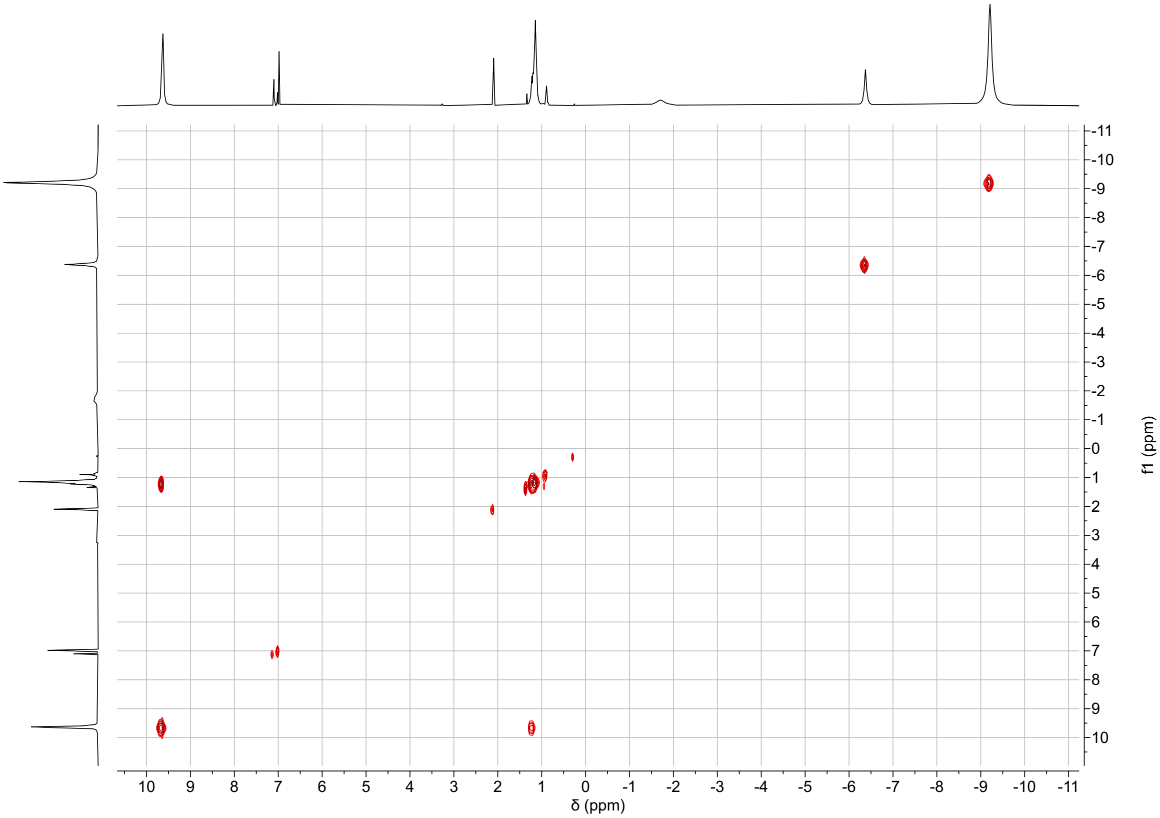

Figure S4. ^1H-^1H *COSY NMR spectrum of U(ITTA)$_4$ in toluene-d$_8$ (298K, 300 MHz).*

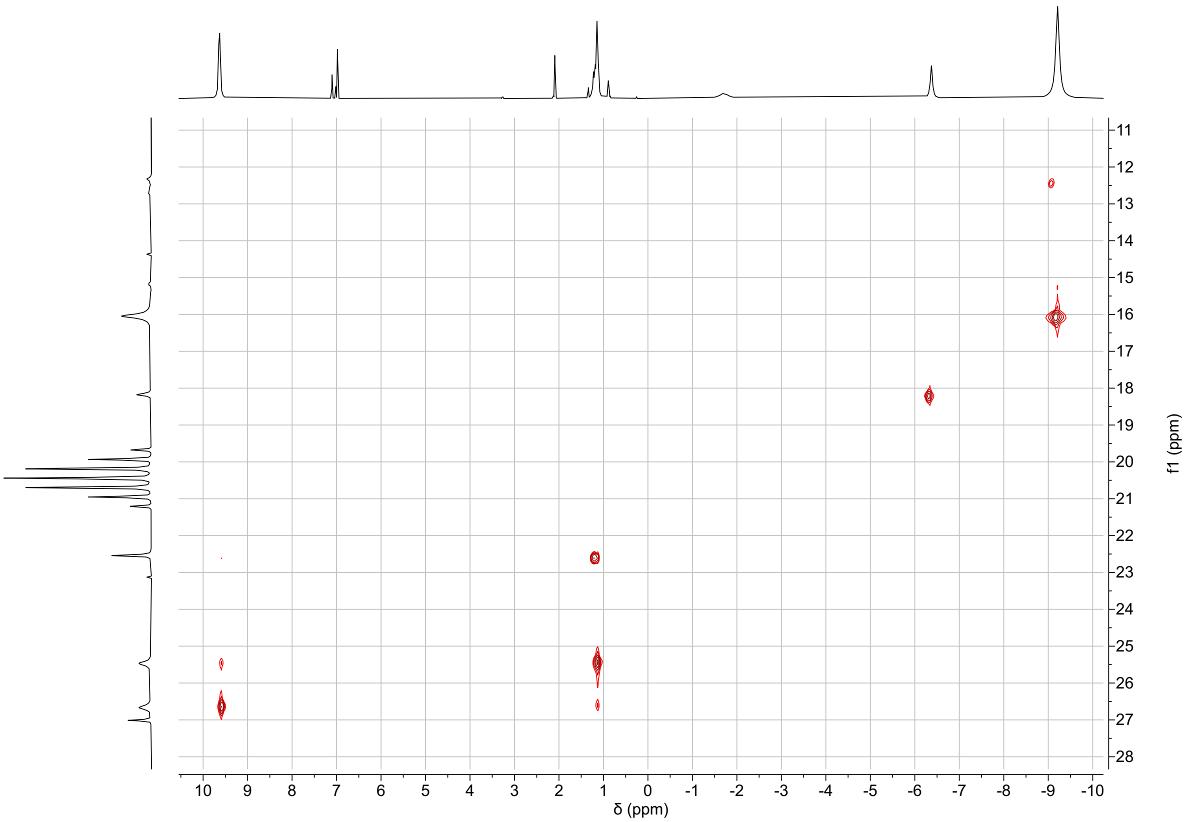

Figure S5. ^{1}*H-*^{13}*C HSQC NMR spectrum of U(ITTA)*$_4$ *in toluene-d8 (298K, 300 MHz).*

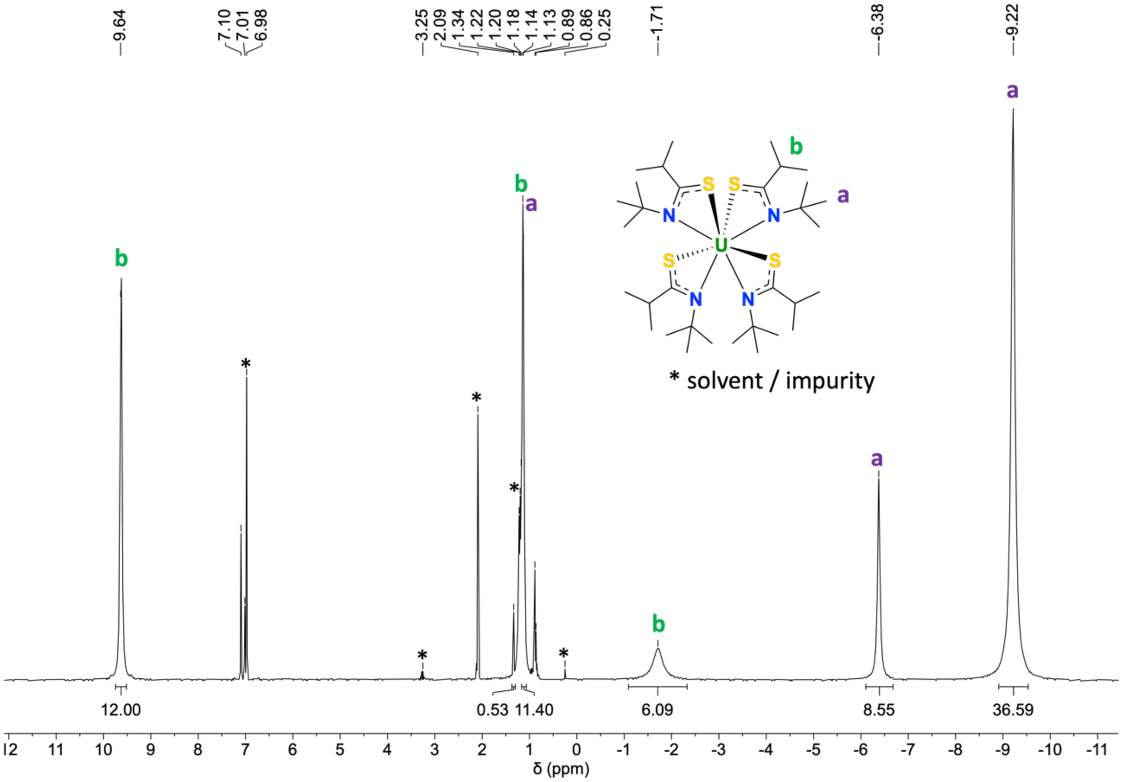

Figure S6. ^{1}*H NMR spectra for U(ITTA)*$_4$ *in toluene-d*$_8$ *(298 K, 500 MHz). Assignments for the tertbutyl hydrogens are marked with a purple a, isopropyl methyl hydrogens are marked with a green b, and solvent peaks are marked with black asterisk.*

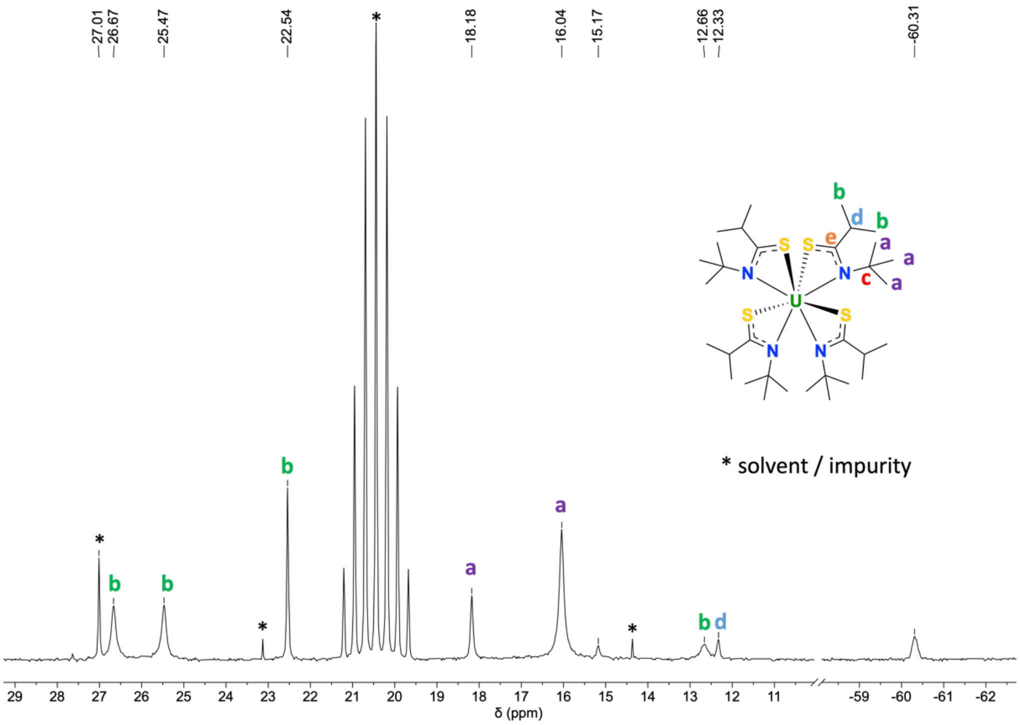

Figure S7. ^{13}C NMR spectra for U(ITTA)$_4$ in toluene-d$_8$ (298 K, 300 MHz). Assignments for the tertbutyl carbons are marked with a purple a, isopropyl methyl carbons are marked with a green b, and the isopropyl methine carbon is marched with a blue d. The solvent peaks are marked with black asterisks. Additional peaks at 27.01, 15.17, and -60.31 ppm likely belong to carbons c and e, but do not have cross peaks in HSQC and so are ambiguous.

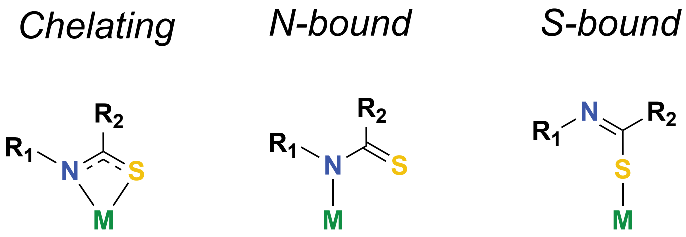

Figure S8. Binding modes of thioamidates to the metal center, generating the three possible isomers for U(ITTA)$_4$: κ^2-S,N, κ^1-S, or κ^1-N.

NMR Spectroscopy for the Pyrolysis of U(ITTA)$_4$

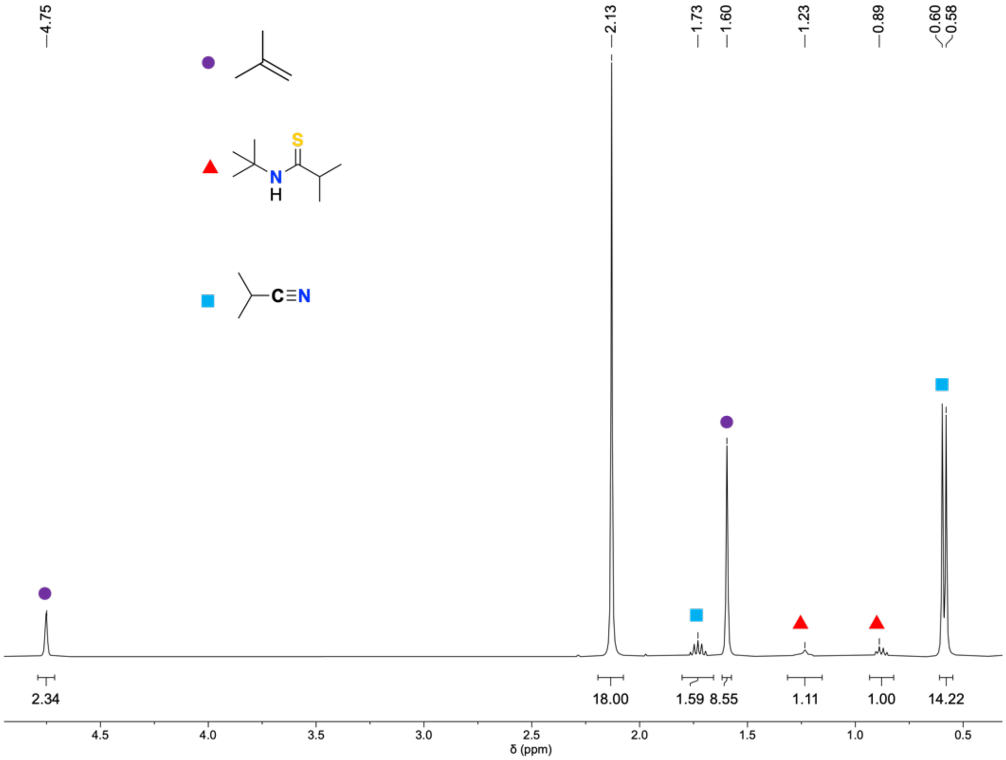

Figure S9. ^{1}H NMR spectrum for pyrolysis of U(ITTA)$_4$ in C_6D_6 (298K, 400 MHz). Expected byproducts are labeled. The unlabeled peak at 2.13 is hexamethylbenzene, added as an internal standard.

FT-IR Spectroscopy

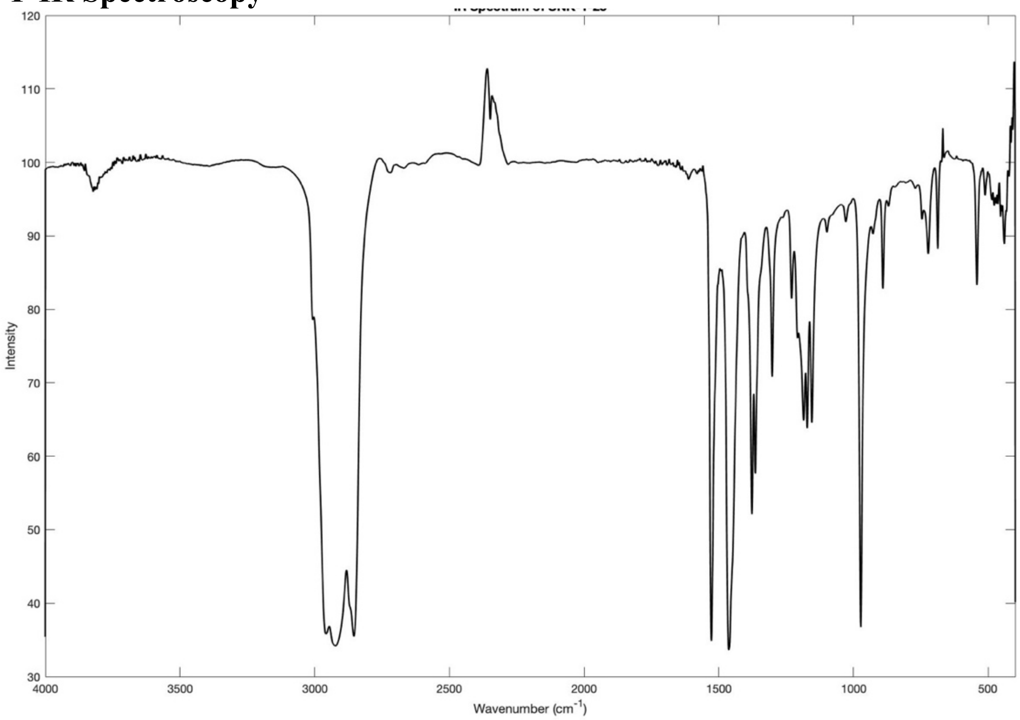

Figure S10. FT-IR spectrum of U(ITTA)$_4$ (KBr, Nujol).

UV-Vis Spectroscopy

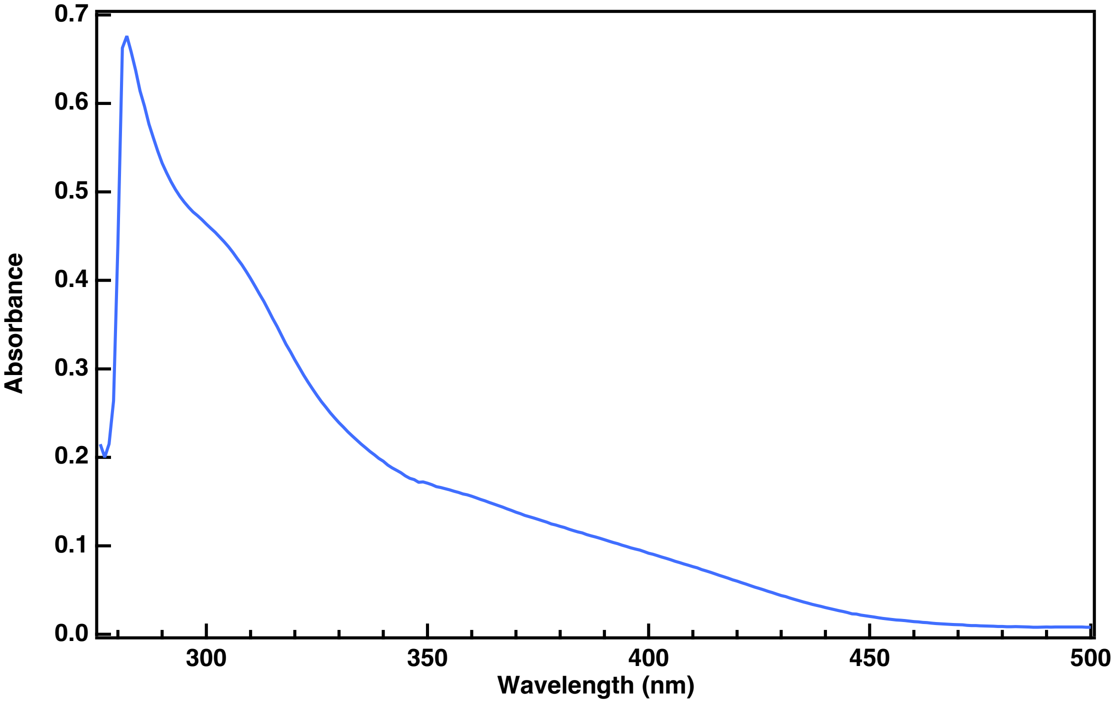

Figure S11. UV-Visible spectrum of U(ITTA)$_4$ in toluene.

X-Ray Absorption Spectroscopy

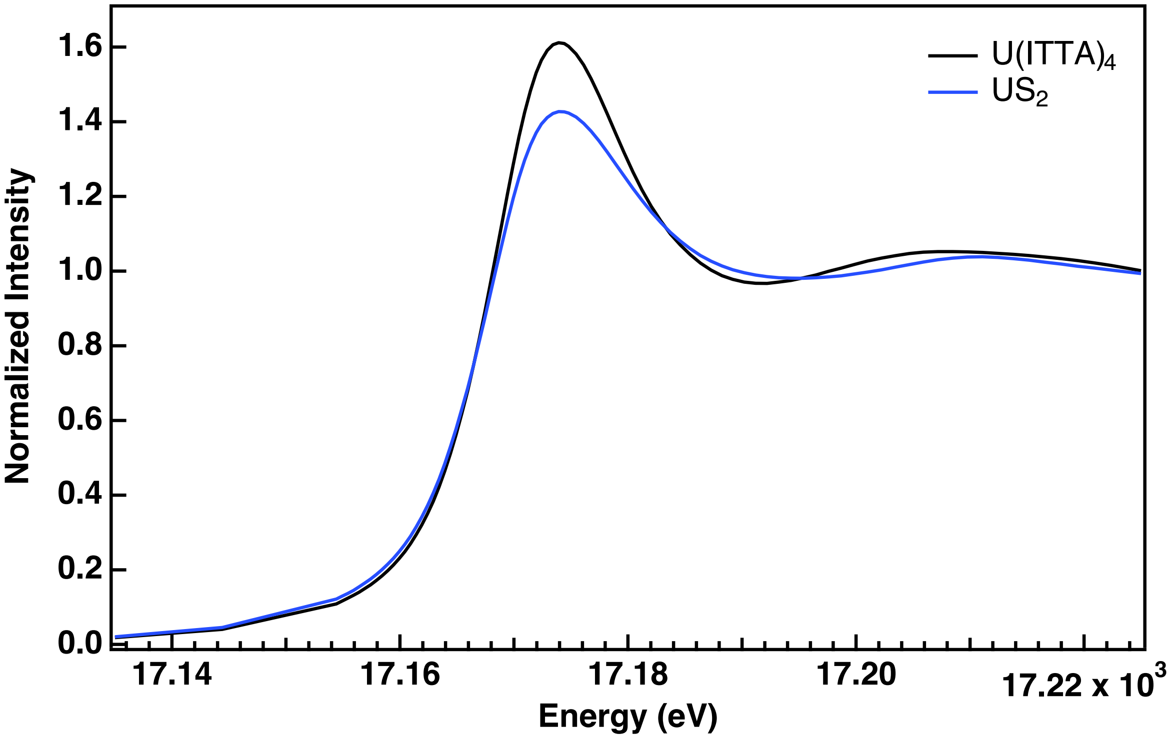

Figure S12. XANES of U(ITTA)$_4$ (black) compared to bulk US$_2$ (blue)..

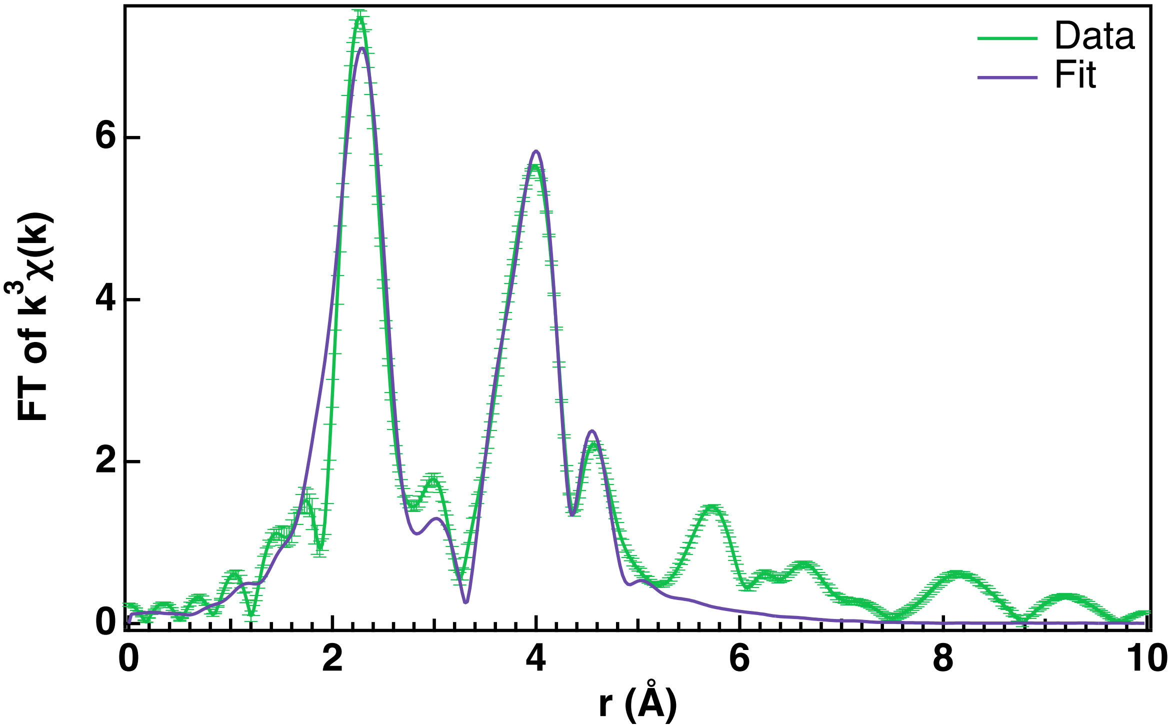

Figure S13. EXAFS U L_3-edge spectrum of bulk β-US_2, including fit. Fit range between 1.90 and 5.50 Å. The k^3 weighted data are transformed between 2.50-13.00 Å^{-1} and are Gaussian narrowed by 0.30 Å^{-1}. Errors were calculated using the "Stern" method. The data have 26.1 independent data points and 11.1 degrees of freedom.

Table S1. EXAFS derived fitting parameters for bulk β-US_2. The coordination number (N) for all paths were constrained to their crystallographic values.

Sample	**Path**	**ΔE (eV)**	**N**	**R (Å)**	**σ^2 (Å^2)**
β-US₂	U – S′	-1.9(2)	6	2.74(1)	0.0112(8)
	U – S′	-1.9(2)	2	3.15(2)	0.009(3)
	U – U	-1.9(2)	4	4.105(9)	0.0025(4)
	U – S″	-1.9(2)	6	4.43(5)	0.02(1)
	U – U	-1.9(2)	2	4.65(3)	0.007(3)

C. Scanning Electron Microscopy

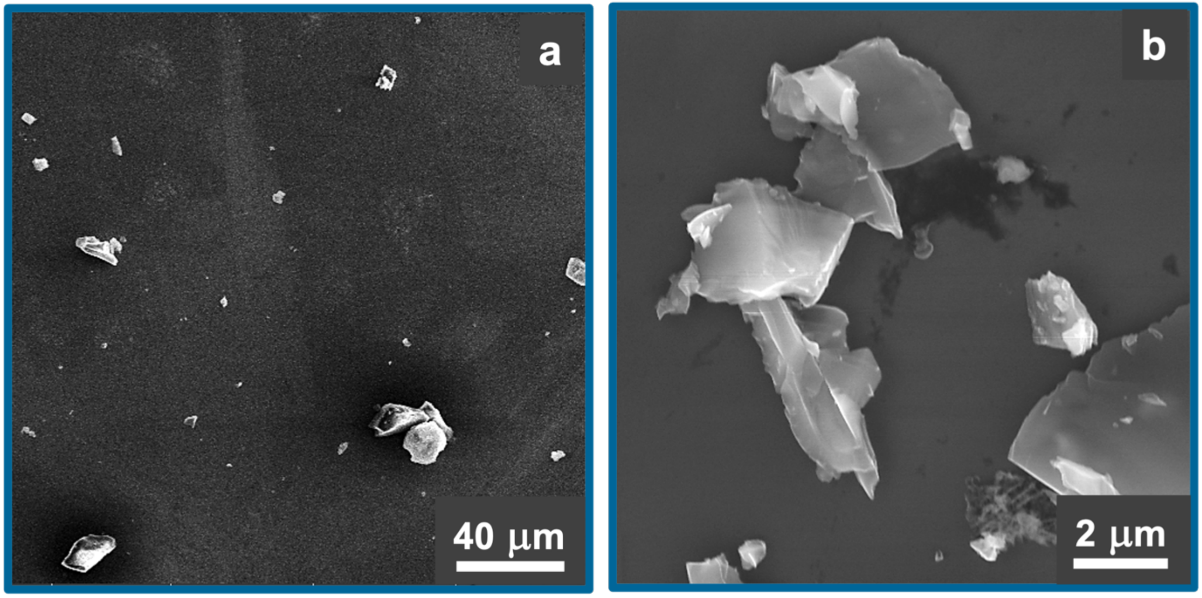

Figure S14. Scanning electron microscopy images of U(ITTA)$_4$, demonstrating particle sizes and the sheet-like morphology of the precursor.

D. Simultaneous Thermal Analysis

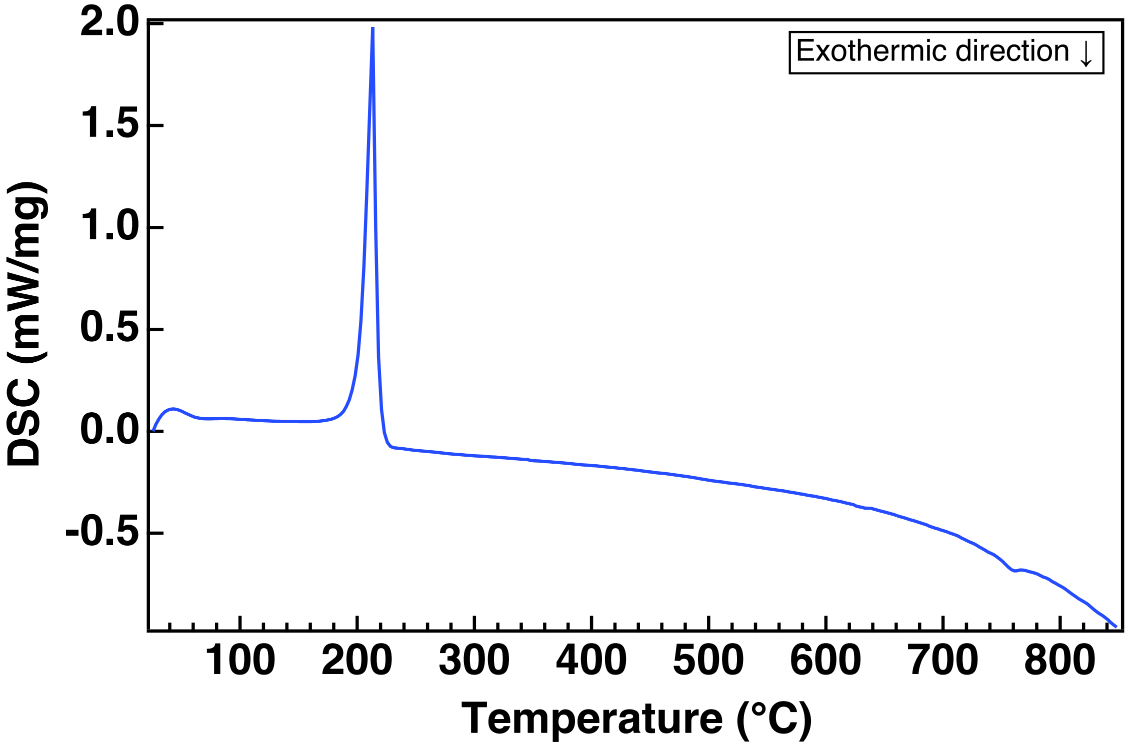

Figure S15. Differential scanning calorimetry for U(ITTA)$_4$, demonstrating that the onset of decomposition of is at 202(5) °C, and the peak at 213(5) °C, which is consistent with visual melting point experiments. The exothermic change for DSC on this instrument is in the negative direction.

E. X-Ray Crystallography

Table S2: Crystal Data for U(ITT)₄

	U(ITTA)₄
Chemical formula	$C_{32}H_{64}N_4S_4U$
M_r	871.14
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	21.6654(2)
b (Å)	11.61050(10)
c (Å)	15.62010(10)
α (°)	90
β (°)	96.2840(10)
γ (°)	90
V (Å^3)	3905.57(6)
Z	4
Density (g/cm^3)	1.482
F(000)	1760.0
Radiation Type	synchrotron (λ = 0.7288)
μ (mm^{-1})	13.877
2Θ range for data collection/°	8.212 to 154.926
Index ranges	$-27 \leq h \leq 27$, $-14 \leq k \leq 14$, $-18 \leq l \leq 19$
Abs. corr. T_{max}	0.491
Crystal size (mm)	0.06 × 0.05 × 0.03
Reflections collected	79768
Independent reflections	8264
R_{int}	0.0469
Data/restraints/parameters	8264/0/390
Goodness-of-fit on F^2	1.103
R_1 / wR_2 [$I \geq 2\sigma(I)$]	0.0227 / 0.0586
R_1 / wR_2 [all data]	0.0252 / 0.0599
Largest diff. peak/hole / e Å^{-3}	1.37/-1.36
CCDC	2353086

Table S3: Bonds (Å) and Angles (deg)

Atoms	**U(ITTA)₄**
U1 – S1	2.7758(7)
U1 – S2	2.7766(6)
U1 – S3	2.7683(6)
U1 – S4	2.7734(6)
U1 – N1	2.588(2)
U1 – N2	2.599(2)
U1 – N3	2.598(2)

U1 – N4	2.590(2)
C1 – S1	1.754(3)
C2 – S2	1.758(3)
C3 – S3	1.755(3)
C4 – S4	1.756(3)
C1 – N1	1.298(4)
C2 – N2	1.297(3)
C3 – N3	1.296(3)
C4 – N4	1.296(3)
S1 – C1 – N1	116.3(2)
S2 – C2 – N2	116.67(19)
S3 – C3 – N3	116.19(19)
S4 – C4 – N4	116.42(19)

F. Powder X-Ray Diffraction

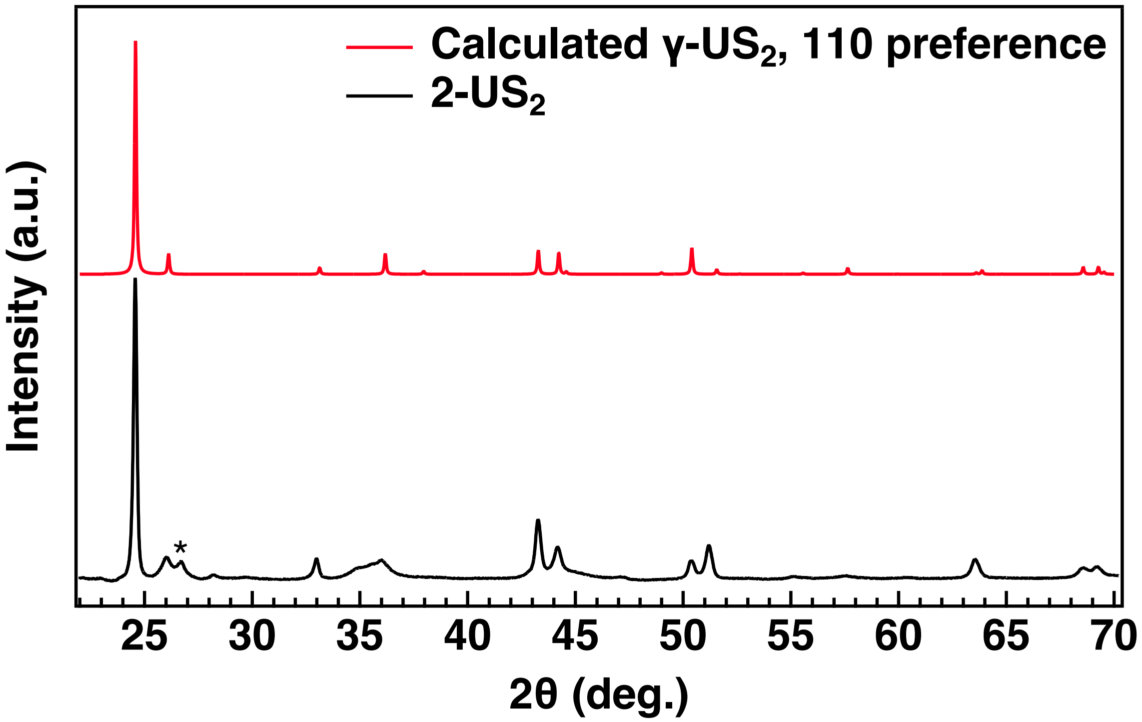

Figure S16. Powder X-ray diffraction pattern for 2-US2 (black, bottom), and calculated γ-US$_2$[14] (top, pink) with a 110 preferred orientation. The March-Dollase parameter was set to 0.46 for the calculated pattern.

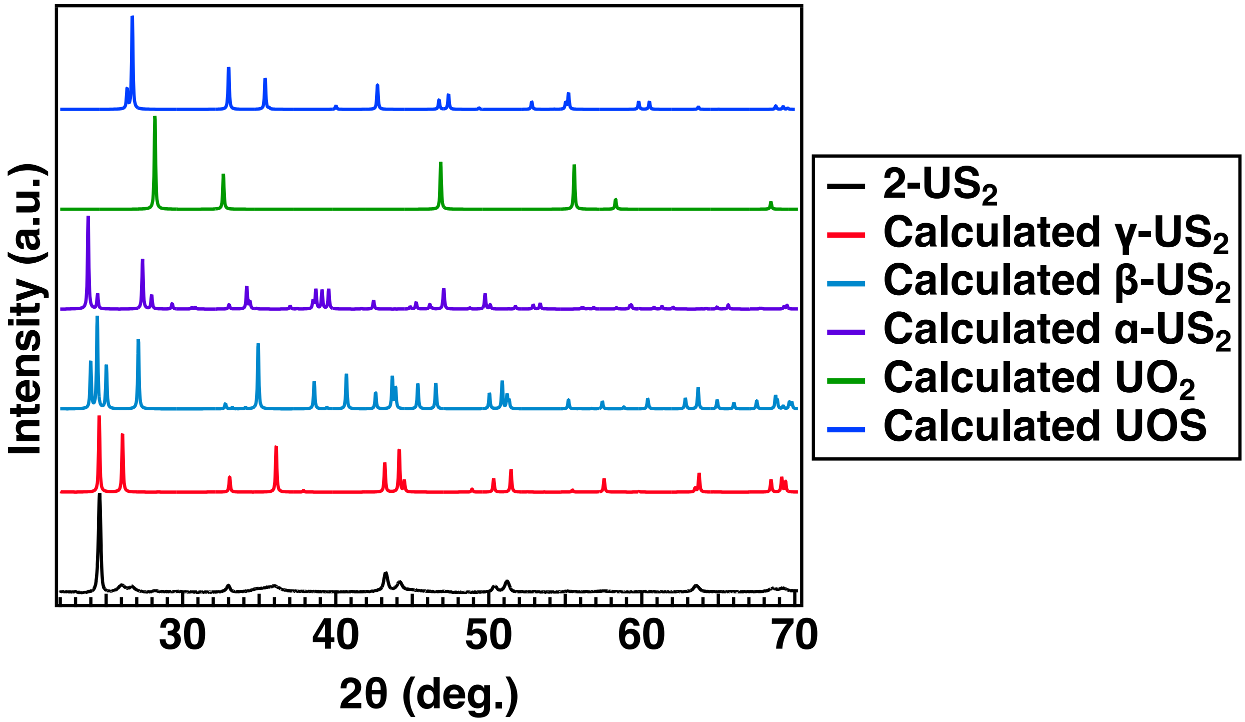

Figure S17. Powder X-ray diffraction pattern of 2-US$_2$ (bottom, black) compared to calculated patterns: for γ-US$_2$[14] (pink), β-US$_2$[15] (light blue), α-US$_2$[16] (purple), UO$_2$[17] (green), and UOS[18] (dark blue).

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