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Two-electron oxidation of a homoleptic U(III) guanidinate complex by diphenyldiazomethane

Nicholas S. Settineri, Angela A. Shiau and John Arnold*

Department of Chemistry, University of California, Berkeley, and Chemical Sciences Division,
Lawrence Berkeley Laboratory, Berkeley, California, 94720, United States

E-mail: arnold@berkeley.edu

Supporting Information

A. Experimental Details

General Considerations. Unless otherwise stated, all reactions were performed under an atmosphere of dry N_2 using standard Schlenk line techniques or in an MBraun N_2 atmosphere glovebox (<1.0 ppm of O_2/H_2O). Toluene, *n*-hexane, *n*-pentane, THF, and diethyl ether were dried and degassed using a commercially available Phoenix SDS from JC Meyer Solvent Systems. Hexamethyldisiloxane (HMDSO) was distilled from sodium/benzophenone, degassed by sparging with nitrogen, and stored over molecular sieves. All glassware, syringes, and cannulas were stored in a 140 °C oven for a minimum of 16 h prior to use. Deuterated solvents (C_6D_6, tol-d_8) were vacuum-transferred from a flask containing sodium/benzophenone, degassed with three freeze−pump−thaw cycles, and stored over molecular sieves. UCl_4,[1] Li(TIG)(THF),[2] UI_3(1,4-dioxane)$_{1.5}$,[3] N_2CPh_2,[4] and *p*-tolyl azide[5] were prepared according to previously reported literature procedures. Pyridine *N*-oxide was sublimed prior to use. All other reagents were purchased from commercial sources and used as received. Unless otherwise stated, NMR spectra were collected at ambient temperature on an AV-600 spectrometer. ^1H NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks. Melting points were determined on an Optimelt SRS instrument using capillary tubes sealed under dry N_2. UV-visible spectra were collected on a Varian Cary 50 UV-visible spectrophotometer using a Schlenk-adapted 1 cm quartz cell at ambient temperature. Cyclic voltammograms were recorded using a Gamry Instruments Reference 600 potentiostat and Gamry Framework software. Elemental analysis samples were sealed under vacuum and analyzed at either the London Metropolitan University or the University of California, Berkeley. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 FTIR spectrophotometer using Nujol mulls pressed between KBr plates. Solution magnetic moments were obtained by Evans Method.

Synthesis of UCl(TIG)$_3$ (1): UCl_4 (0.939 g, 2.47 mmol) was added to a 250 mL Schlenk flask containing a magnetic stir-bar and dissolved in 30 mL of THF. A THF solution (50 mL) of Li(TIG)(THF) (2.26 g, 7.40 mmol) was added to the dark green solution. Over the course of 4 h, the reaction mixture became a suspension of a light green precipitate in a brown-green solution. Volatiles were removed under reduced pressure and the resulting solid was extracted into toluene (50 mL). A gray-green solid was filtered away, and the brown-green solution was concentrated to 20 mL. Storage of this solution at -40 °C yielded **1** as analytically pure, green crystals (2.18 g, 92.8%) ^1H NMR (600 MHz, tol-d_8): δ 21.69, 18.47, 4.37, 2.95, 0.99. Anal. Calcd for $C_{39}H_{84}N_9ClU$ (952.6): C, 49.17; H, 8.89; N, 13.23. Found: C, 49.42; H, 8.78; N, 12.99. Mp: 168 °C (decomp). FTIR(Nujol): 1408 (w), 1378 (w), 1308 (s), 1212 (s), 1178 (w), 1156 (w), 1133 (m), 1061 (s), 1014 (m), 976 (m), 940 (w), 862 (m), 815 (w), 722 (w), 681 (w), 666 (m), 576 (w), 507 (w), 458 (w), 416 (w). $\mu_{eff} = 2.93\ \mu_B$. Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated *n*-hexane solution stored at -35 °C for 16 h.

Synthesis of U(TIG)$_3$ (2): UI_3(1,4-dioxane)$_{1.5}$ (0.500 g, 0.666 mmol) was added to a 20 mL scintillation vial containing a magnetic stir-bar and suspended in 4 mL of THF, resulting in a dark blue-purple suspension. A solution of Li(TIG)(THF) (0.626 g, 2.05 mmol) in THF (12 mL) was added to the reaction mixture; the dark blue solution was stirred at ambient temperature for 3 h. Volatiles were removed under reduced pressure, and the sticky blue-gray solid was triturated with *n*-hexane (2 x 2 mL). The blue-gray solid was then extracted with 8 mL of *n*-hexane and filtered away from the gray precipitate. Volatiles were removed under reduced pressure, resulting in dark blue and yellow solids. HMDSO (8 mL) was used to extract the blue solid. The solution was filtered, concentrated to 3 mL, and stored at -35 °C to yield **2** as analytically pure, dark blue, block crystals (0.445 g, 72.9%). ^{1}H NMR (600 MHz, C_6D_6): δ 30.04 (s, C*H*Me$_2$, 6H), 9.36 (m, C*H*Me$_2$, 6H), 4.72 (d, CHC*H*$_3$CH$_3$, 18 H), 4.09 (d, CHC*H*3CH3, 18 H), 0.71 (s, CHC*H*3CH3, 18H), -10.01 (s, CHC*H*$_3$CH$_3$, 18H). Anal. Calcd for $C_{39}H_{84}N_9U$ (917.2): C, 51.07; H, 9.23; N, 13.74. Found: C, 50.74; H, 9.25; N, 13.54. Mp: 165 – 170 °C. FTIR (Nujol): 1631 (w), 1404 (w), 1377 (s), 1362 (m), 1314 (s), 1212 (s), 1133 (m), 1058 (s), 1017 (m), 971 (w), 863 (w), 722 (m), 666 (w), 574 (w), 450 (w). $\mu_{eff} = 3.34\ \mu_B$. UV-Vis: 614 nm (ε = 323 L/mol·cm). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated HMDSO solution stored at -35 °C for 16 h.

Alternative synthesis of 2: Solid **1** (0.698 g, 0.733 mmol) was added to a 100 mL Schlenk flask containing a magnetic stir-bar and was dissolved in 40 mL of THF. KC$_8$ (0.107 g, 0.792 mmol) was added to this green solution. The color of the reaction mixture immediately turned dark teal, then dark blue. This solution was stirred at ambient temperature for 2 h. Volatiles were removed under reduced pressure, and the solid was extracted with HMDSO (20 mL). The solution was filtered through Celite, concentrated to ~3 mL, and stored at -35 °C for 16 h, resulting in dark blue crystals of **2** (0.544 g, 81.0%).

Synthesis of U(N$_2$CPh$_2$)(TIG)$_3$ (3): Solid **2** (0.300 g, 0.327 mmol) was added to a 20 mL scintillation vial containing a magnetic stir-bar and dissolved in *n*-hexane (5 mL). A magenta solution of diphenyldiazomethane (0.063 g, 0.324 mmol) in *n*-hexane (2 mL) was added slowly to the dark blue U(TIG)$_3$ solution. Immediately upon the addition, the dark blue solution becomes dark red-brown. The reaction mixture was stirred at ambient temperature for 16 h. Volatiles were removed under reduced pressure, resulting in a sticky red-brown solid. Recrystallization of this solid from 2 mL of *n*-pentane yielded **3** as analytically pure, dark red-brown crystals (0.263 g, 72.4%). ^{1}H NMR (600 MHz, C_6D_6): δ 20.99, 9.74, 8.16, -2.82. Anal. Calcd for $C_{52}H_{94}N_{11}U$ (1110.4): C, 56.20; H, 8.53; N, 13.86. Found: C, 56.01; H, 8.61; N, 13.53. Mp: 129 – 132 °C. FTIR (Nujol): 1596 (w), 1493 (w), 1405 (m), 1378 (m), 1362 (m), 1317 (m), 1209 (s), 1175 (m), 1158 (w), 1132 (m), 1060 (s), 1015 (w), 974 (m), 935 (w), 863 (w), 768 (m), 758 (m), 723 (w), 698 (m), 681 (w), 666 (m), 507 (m), 456 (w). $\mu_{eff} = 2.68\ \mu_B$. UV-Vis: 467 nm (ε = 1,268 L/mol·cm). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated *n*-pentane solution stored at -35 °C for 16 h.

Synthesis of U(N-*p*tolyl)(TIG)$_3$ (4): Solid **2** (0.216 g, 0.236 mmol) was added to a 20 mL scintillation vial containing a magnetic stir bar and dissolved in *n*-hexane (6 mL). In a smaller vial, *p*-tolyl azide was weighed out (0.034 g, 0.255 mmol) and dissolved in 0.5 mL of *n*-hexane. When the azide solution was added slowly to the U(TIG)$_3$ solution, bubbling occurred and the solution color immediately changed from dark blue to dark red-brown. The reaction was then stirred at ambient temperature for 3 h. Volatiles were removed under reduced pressure, resulting in a foamy brown solid. This solid was dissolved in *n*-pentane, concentrated, and stored at -35 °C for 48 h, resulting in red-brown block crystals **4** (0.182 g, 75.6%). ^{1}H NMR (600 MHz, C_6D_6): δ 20.30, 19.89, 10.07, 6.12, 3.62, -1.97. Anal. Calcd for $C_{46}H_{91}N_{10}U$ (1022.3): C, 54.04; H, 8.97; N, 13.70. Found: C, 53.67; H, 8.97; N, 13.48. Mp: 132 – 139 °C. FTIR (Nujol): 1631 (w), 1377 (w), 1362 (m), 1315 (m), 1259 (m), 1211 (s), 1171 (m), 1131 (m), 1057 (s), 973 (w), 901 (w), 859 (w), 813 (m), 722 (m), 681 (w), 665 (w), 506 (w). $\mu_{eff} = 2.67\ \mu_B$. UV-Vis: 473 nm (ε = 2,842 L/mol·cm). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated *n*-pentane solution stored at -35 °C for 16 h.

Synthesis of U(O)(TIG)$_3$ (5): Solid **2** (0.199 g, 0.217 mmol) was added to a 20 mL scintillation vial containing a magnetic stir bar and dissolved in toluene (2 mL). To this stirred solution was added a solution of pyridine *N*-oxide (0.022 g, 0.231 mmol) in toluene (4 mL), resulting in an immediate color change from dark blue to dark red. The reaction was stirred at ambient temperature for 15 min. Volatiles were removed under reduced pressure, and the resulting red solid was triturated with *n*-hexane (4 mL), extracted into *n*-pentane (6 mL), filtered through Celite, concentrated to ~1 mL and stored at -35 °C for 16 h, resulting in red block crystals of **5** (0.180 g, 88.9%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.88, -1.52, -1.71. Mp: 158-162 °C. FTIR (Nujol): 1378 (s), 1363 (s), 1315 (s), 1211 (s), 1174 (m), 1156 (m), 1132 (m), 1060 (m), 1011 (w), 974 (w), 862 (w), 782 (m), 723 (w), 683 (w), 666 (w), 499 (w). $\mu_{eff} = 2.31\ \mu_B$. UV-Vis: 486 nm (ε = 874 L/mol·cm) Anal. Calcd for $C_{39}H_{84}N_9OU$ (933.2): C, 50.20; H, 9.07; N, 13.51. Found: C, 49.90; H, 8.72; N, 13.43. Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated *n*-pentane solution stored at -35 °C for 72 h.

Synthesis of U(N$_3$)(TIG)$_3$ (6): In a 20 mL scintillation vial containing a magnetic stir bar, NaN_3 (0.010 g, 0.154 mmol) was suspended in 3 mL of THF. A light green, THF solution (10 mL) of **1** (0.151 g, 0.159 mmol) was added to the stirring suspension, and the reaction mixture was stirred at ambient temperatures for two days. The reaction mixture became cloudy. Volatiles were removed under reduced pressure and the pale green solid was extracted into diethyl ether. A white precipitate was filtered away, and the pale green solution was concentrated and stored at -35 °C, yielding green crystals of **6** (0.099 g, 65.3%). ^{1}H NMR (600 MHz, C_6D_6): δ 17.40, 16.45, 10.78, 5.86, 1.81, 0.14, -1.02, -2.43, -6.19. Anal. Calcd for $C_{39}H_{84}N_{12}U$ (959.2): C, 48.83; H, 8.83; N, 17.52. Found: C, 49.14; H, 8.62; N, 17.23. Mp: 225 °C (decomp). FTIR (Nujol): 2088 (s), 1377 (m), 1309 (w), 1210 (s), 1181 (m), 1158 (m), 1132 (m), 1061 (m), 1013 (w), 975 (w), 863 (w), 722 (w), 682 (w), 665 (w), 505 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated *n*-pentane solution stored at -35 °C for 24 h.

B. NMR Spectra

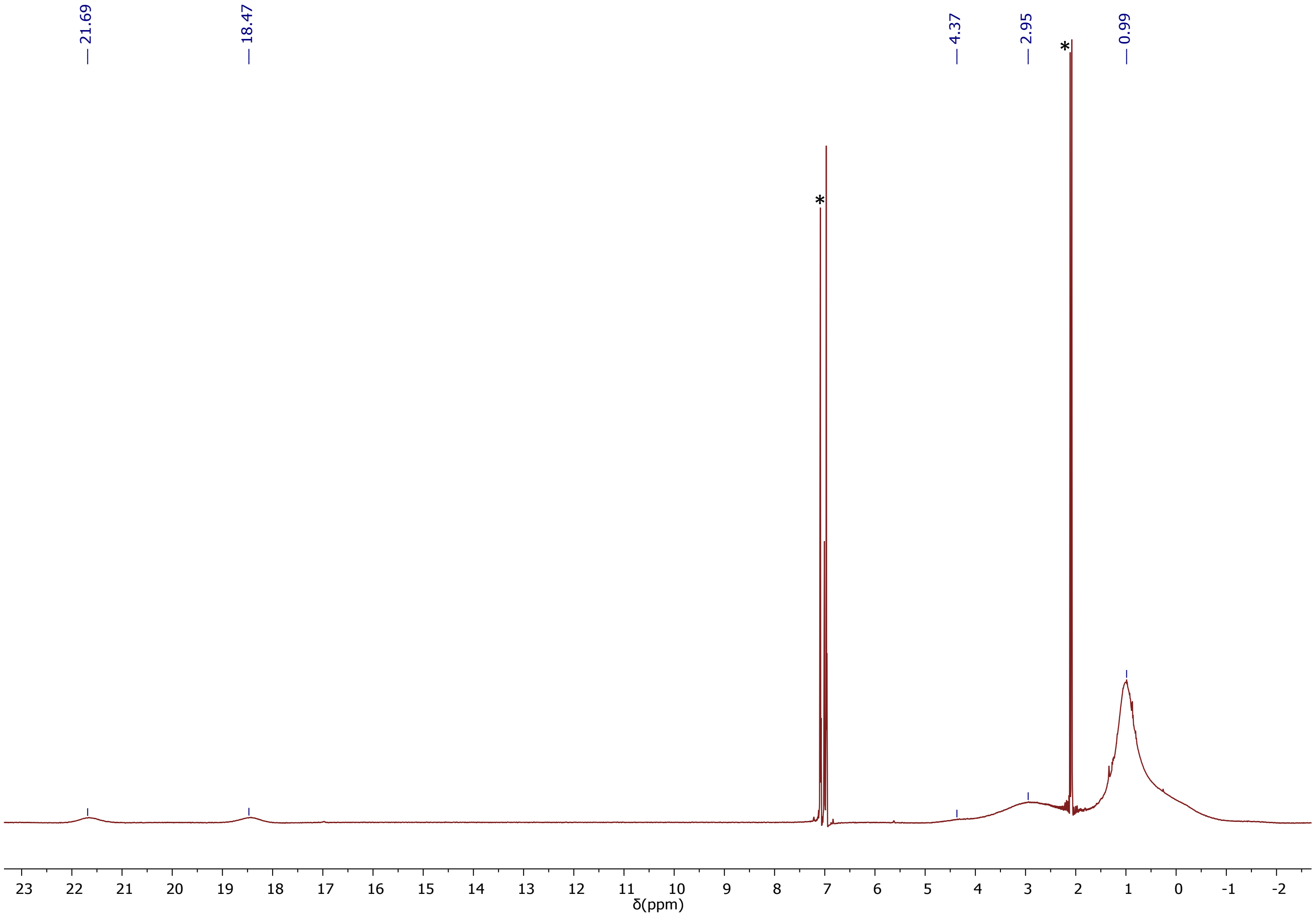

Figure S1. ^{1}H NMR spectrum of UCl(TIG)$_3$ (**1**) at 298 K in tol-d_8. *Toluene

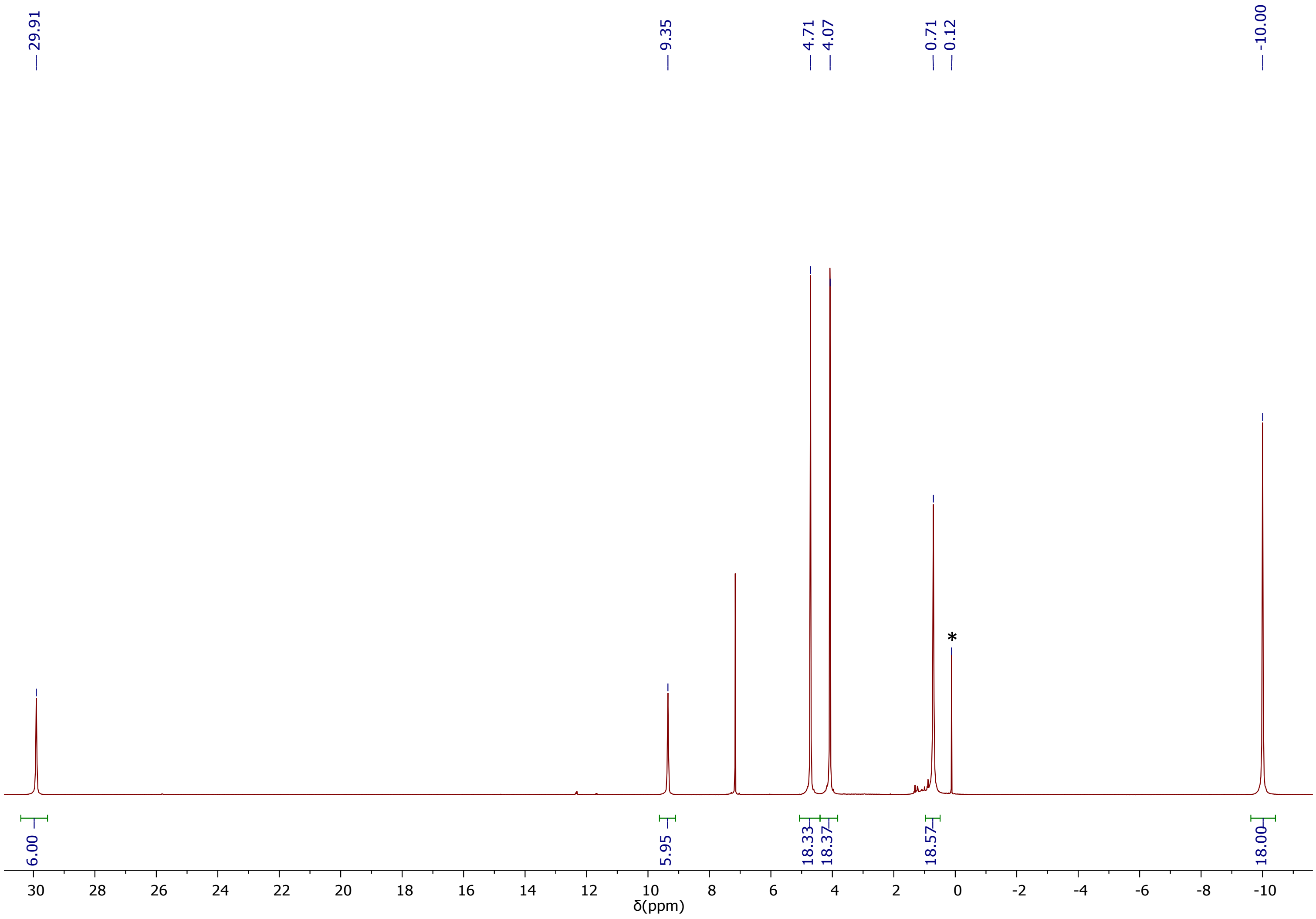

Figure S2. ^{1}H NMR spectrum of U(TIG)$_3$ (**2**) at 298 K in C_6D_6. *HMDSO

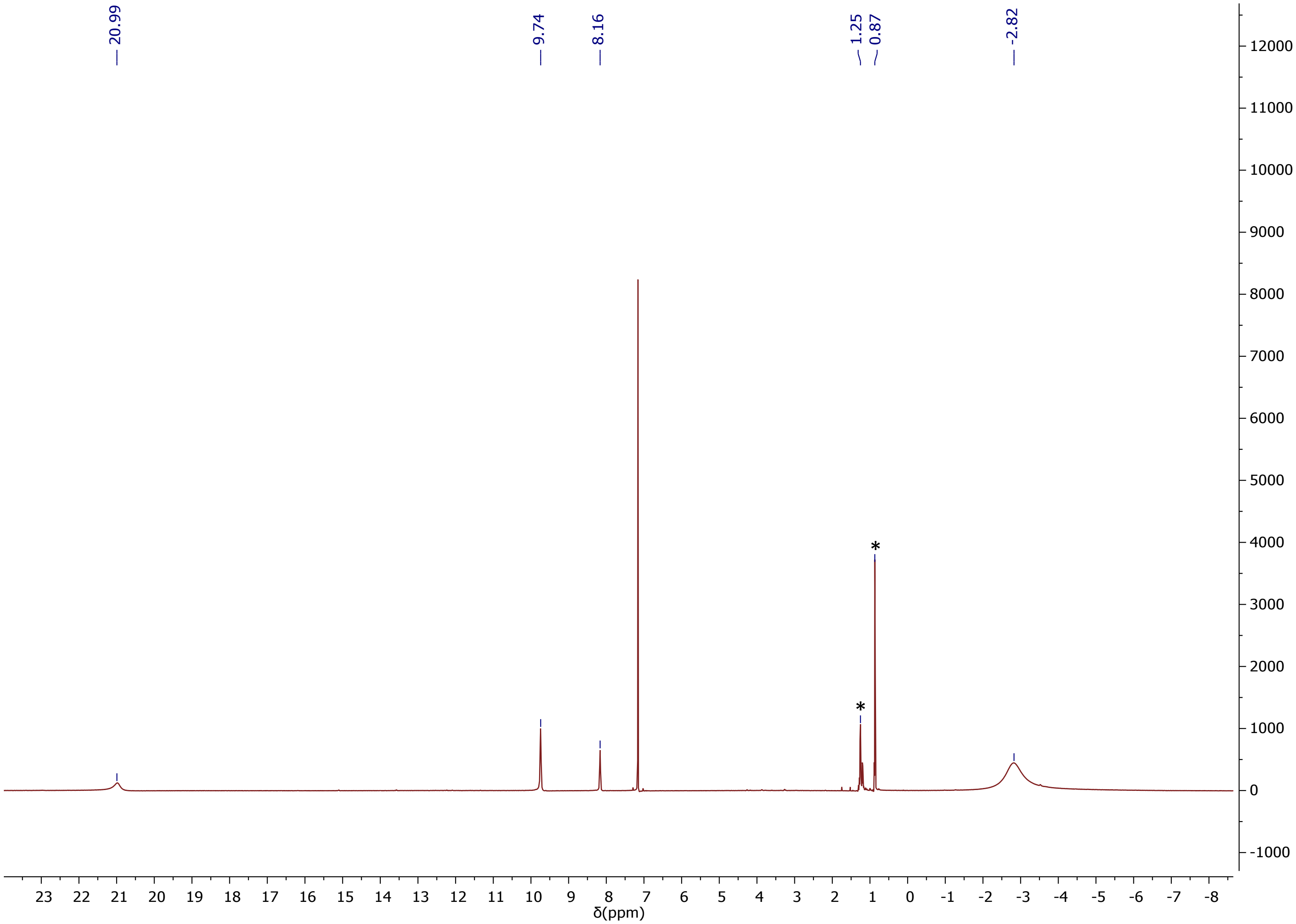

Figure S3. ^{1}H NMR spectrum of U(N_2CPh_2)(TIG)$_3$ (**3**) at 298 K in C_6D_6. *Pentane

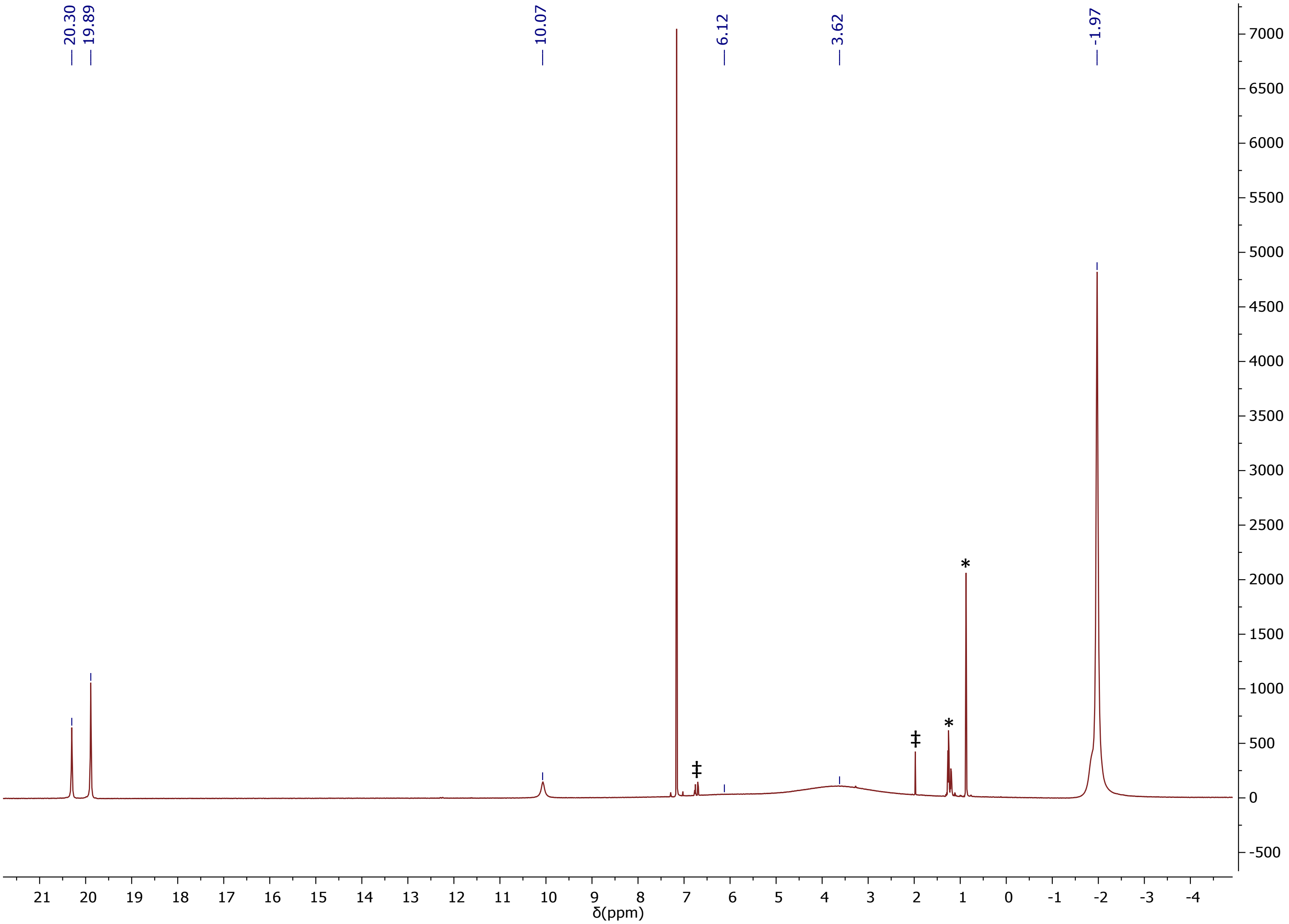

Figure S4. ^{1}H NMR spectrum of U(N-*p*tolyl)(TIG)$_3$ (**4**) at 298 K in C_6D_6. *Pentane. ‡*p*-tolyl azide

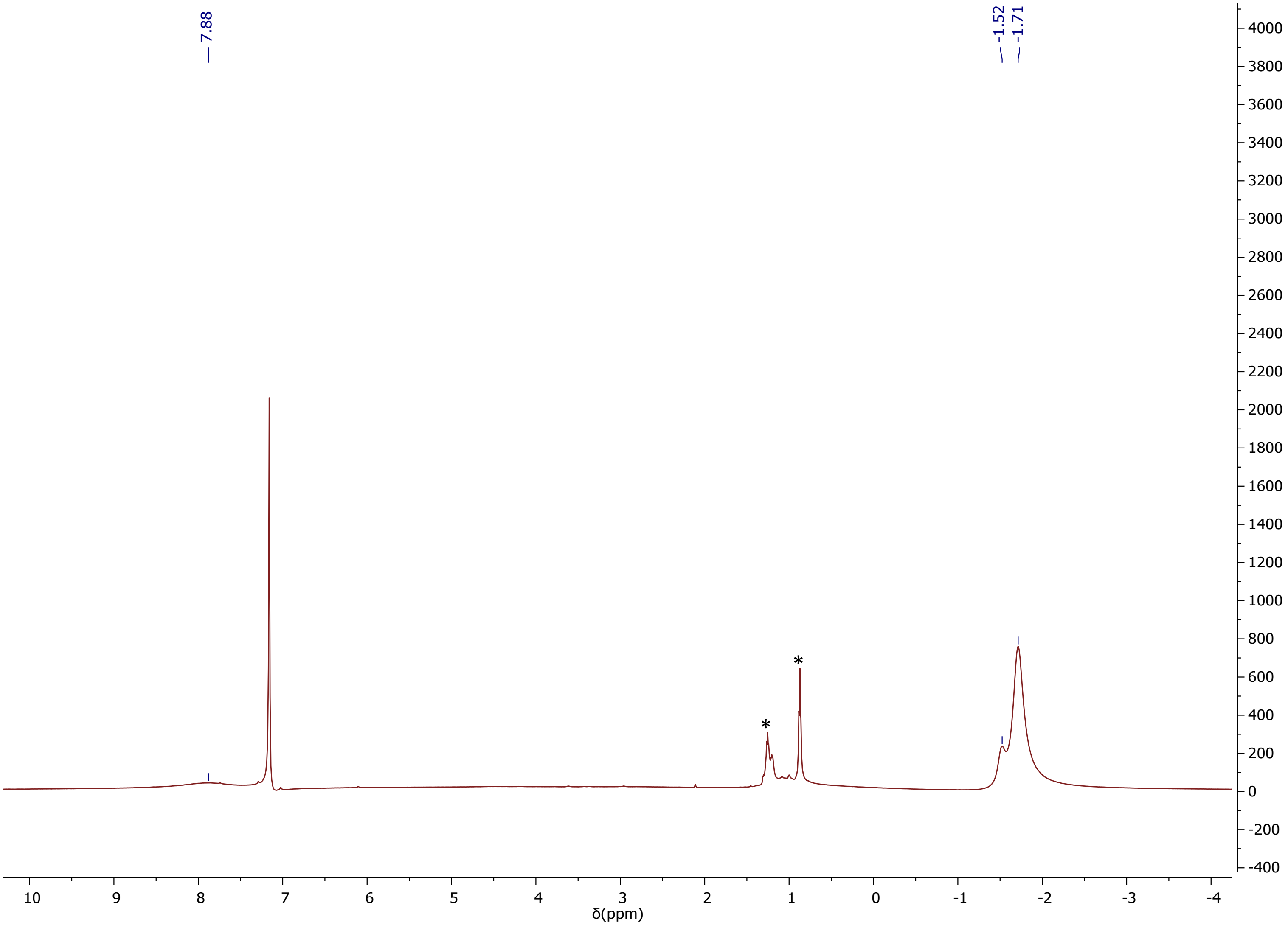

Figure S5. ^{1}H NMR spectrum of U(O)(TIG)$_3$ (**5**) at 298 K in C_6D_6. *Hexane

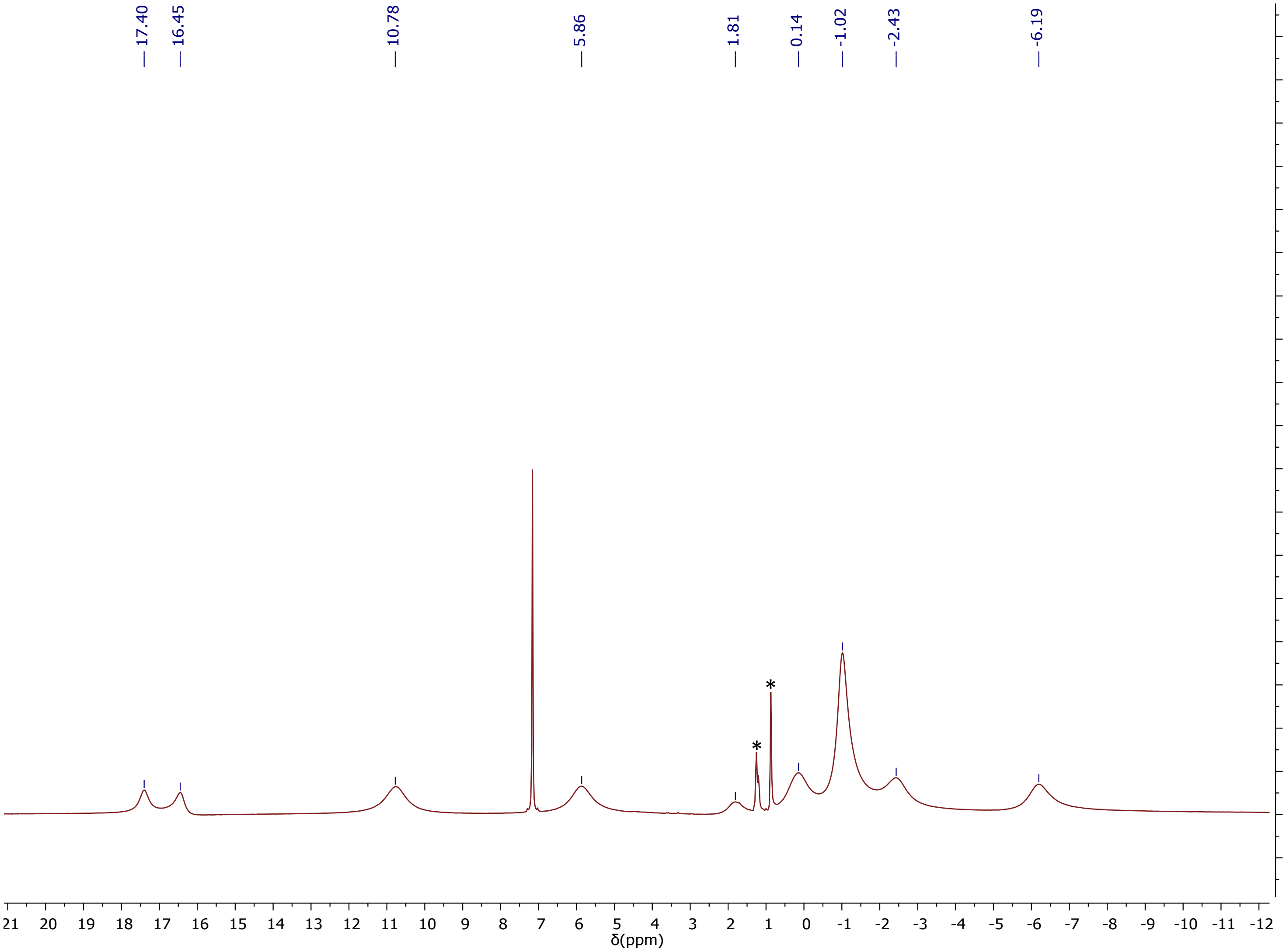

Figure S6. ^{1}H NMR spectrum of U(N_3)(TIG)$_3$ (**6**) at 298 K in C_6D_6. *Hexane

C. IR Spectra

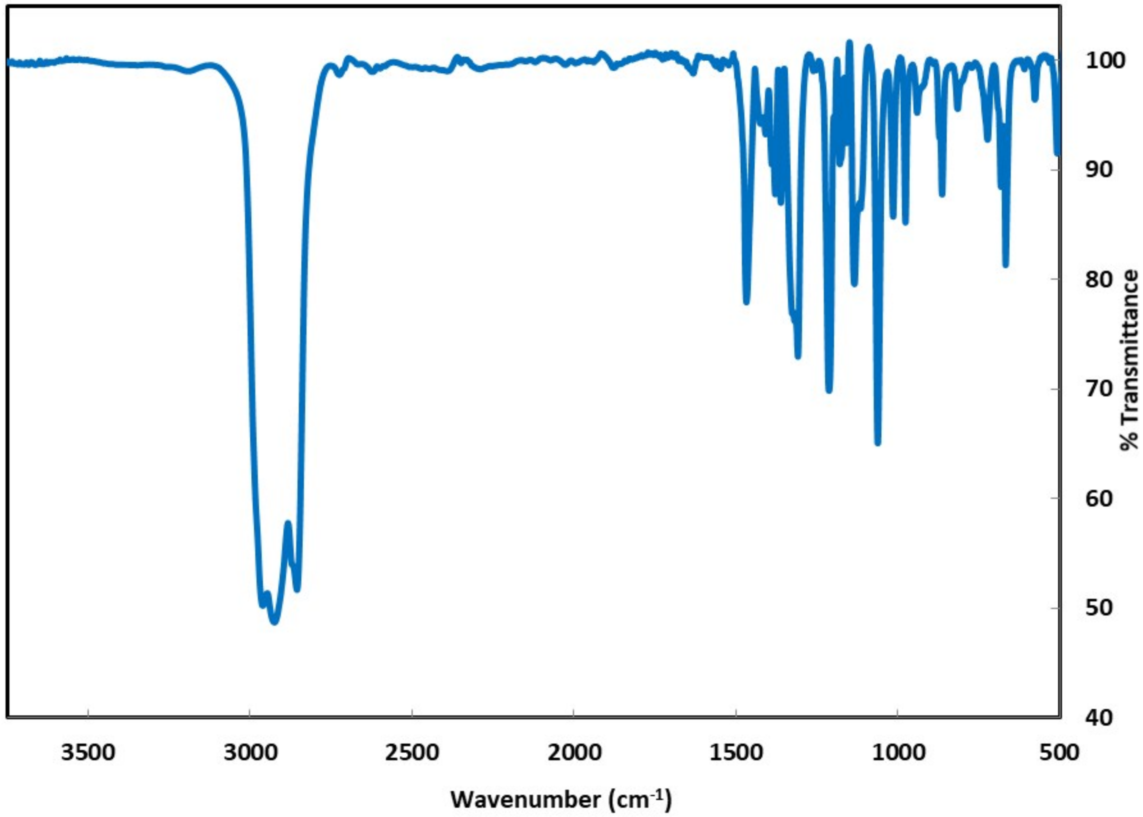

Figure S7. Infrared spectrum of $UCl(TIG)_3$

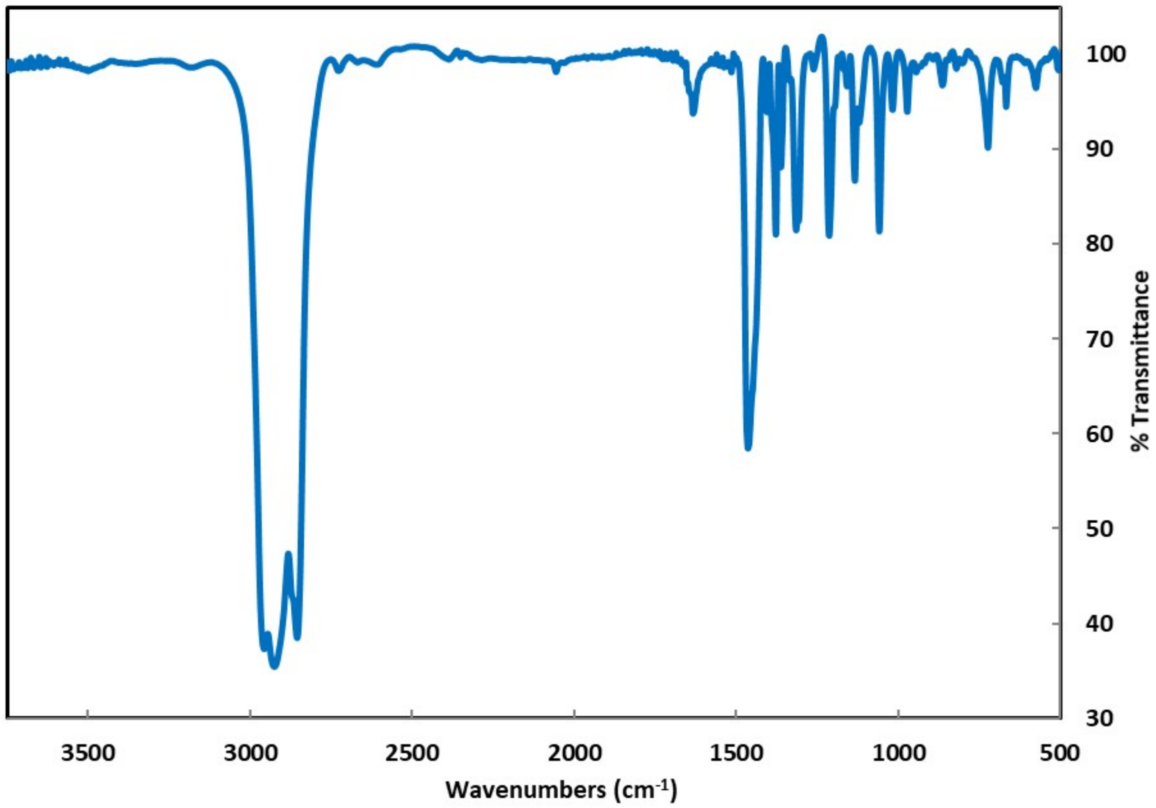

Figure S8. Infrared spectrum of U(TIG)$_3$

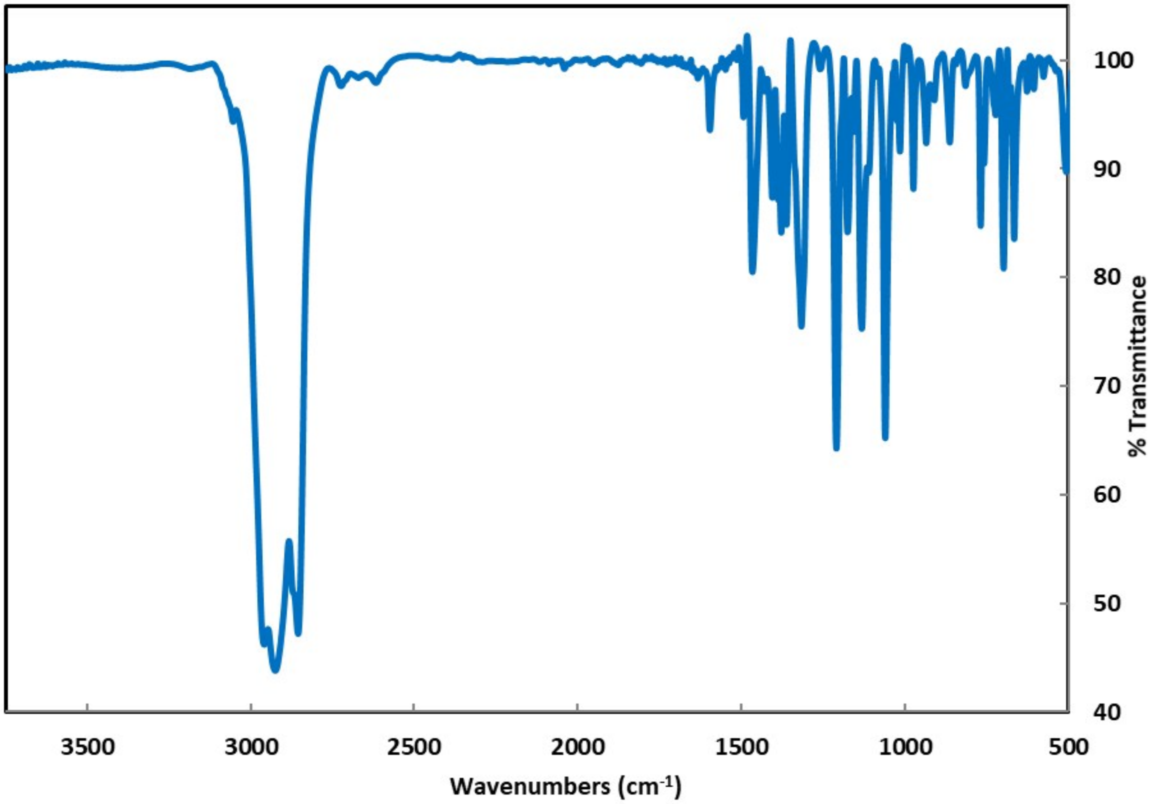

Figure S9. Infrared spectrum of U(N_2CPh_2)(TIG)$_3$

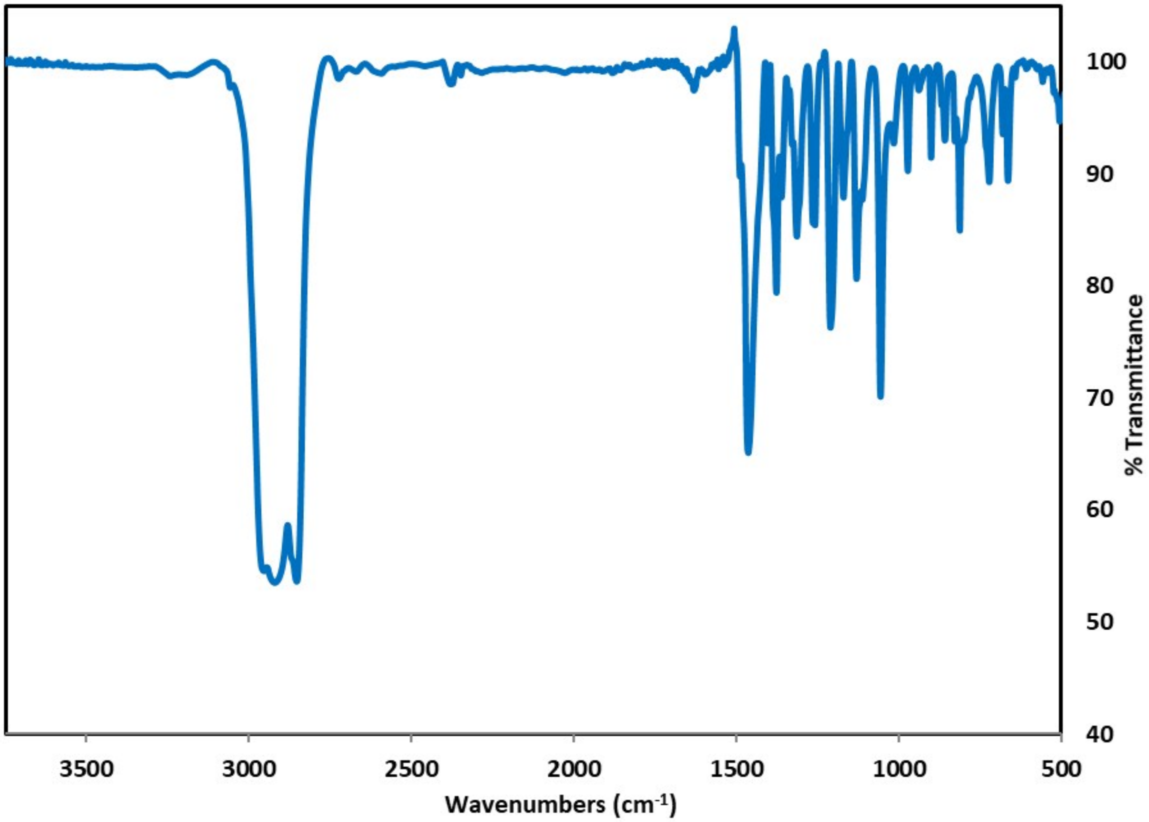

Figure S10. Infrared spectrum of U(N-ptolyl)(TIG)$_3$

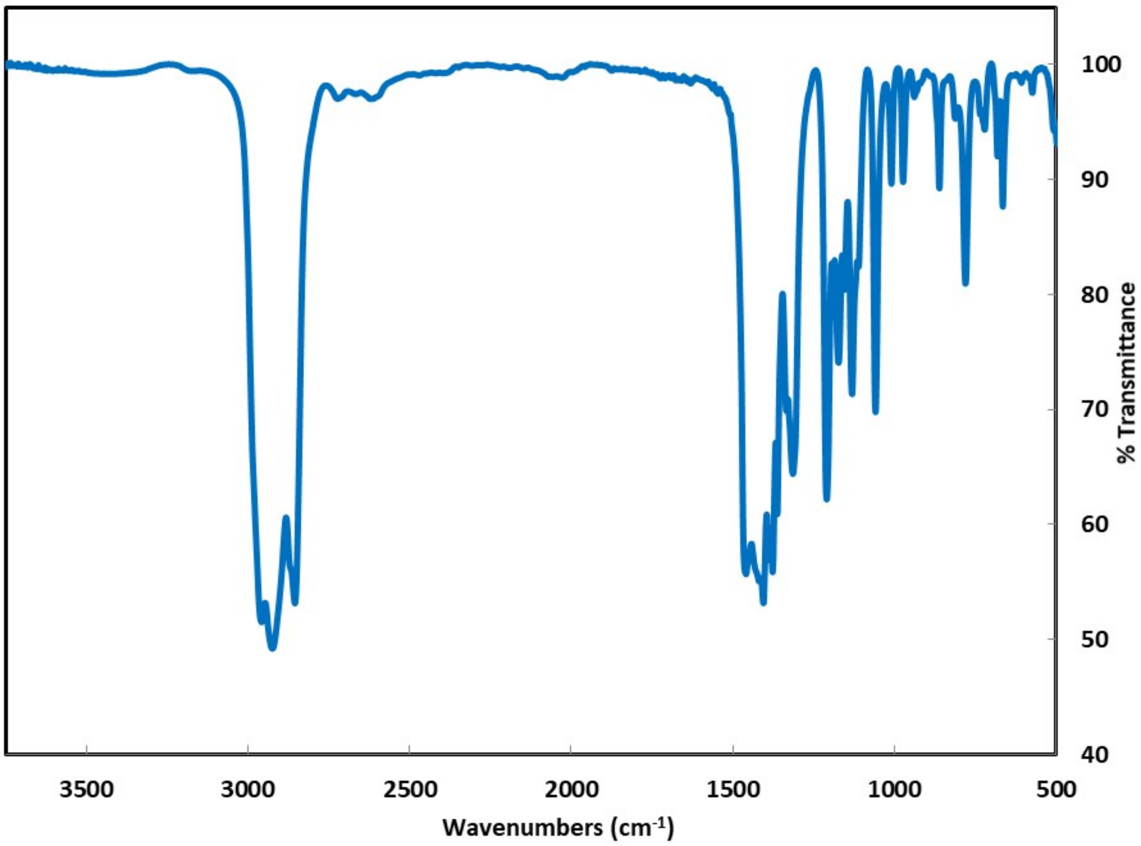

Figure S11. Infrared spectrum of U(O)(TIG)$_3$

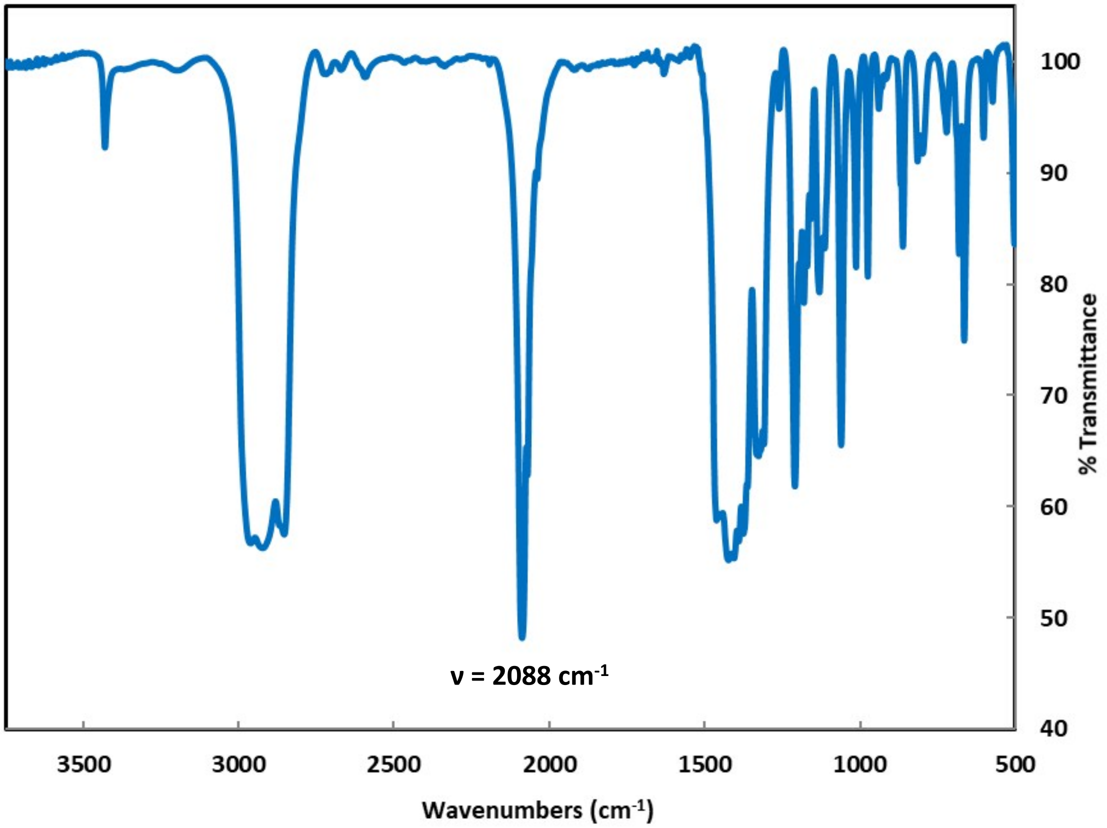

Figure S12. Infrared spectrum of U(N_3)(TIG)$_3$

D. UV-Vis Spectra

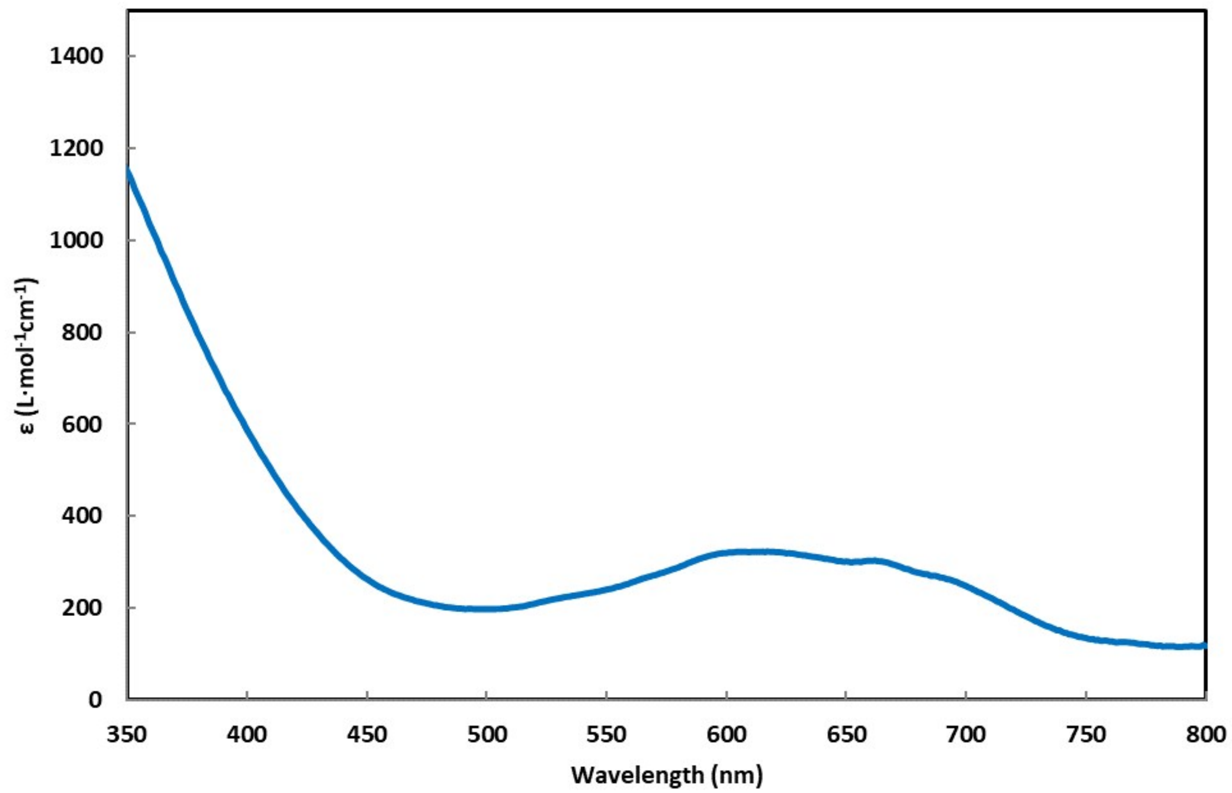

Figure S13: UV-Vis spectrum 3.94×10^{-4}M of U(TIG)$_3$ in toluene
Broad peak at 614 nm (ε=323 L/mol·cm)

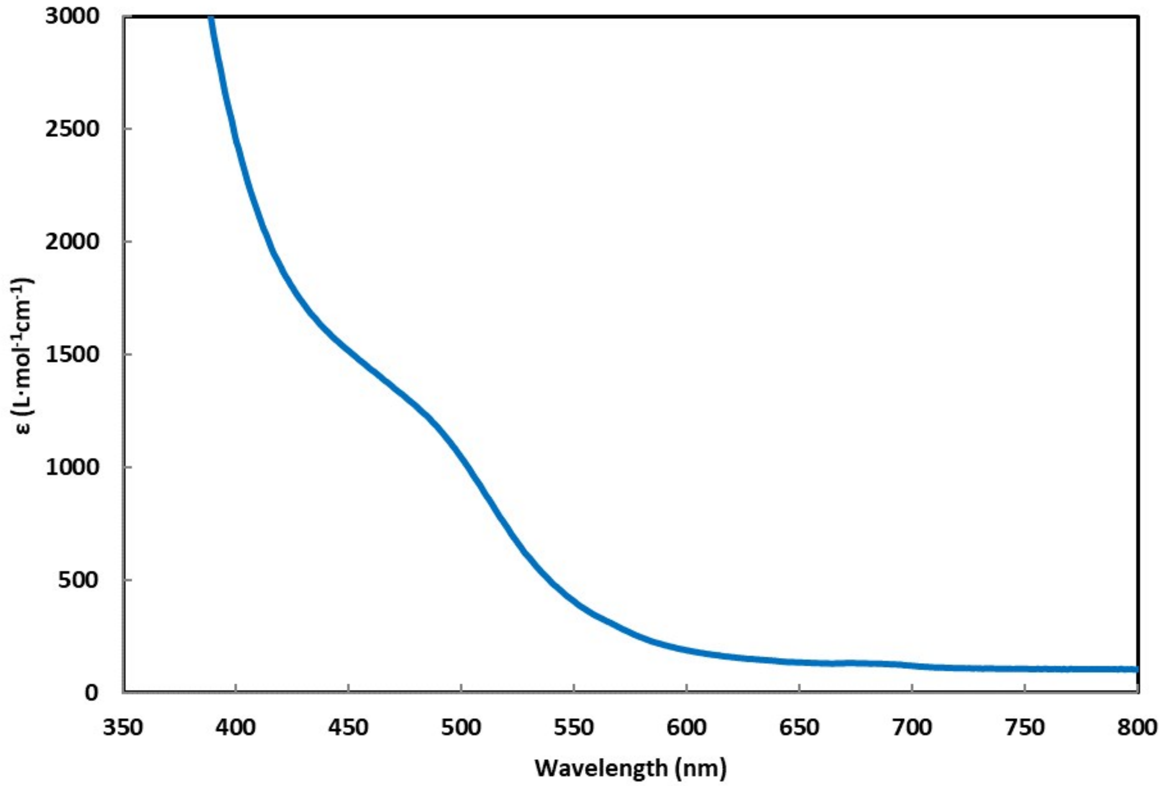

Figure S14: UV-Vis spectrum of 5.42x10^{-4}M of U(N_2CPh)$_2$(TIG)$_3$ in toluene
Broad peak at around 467 nm (ε=1,268 L/mol·cm)

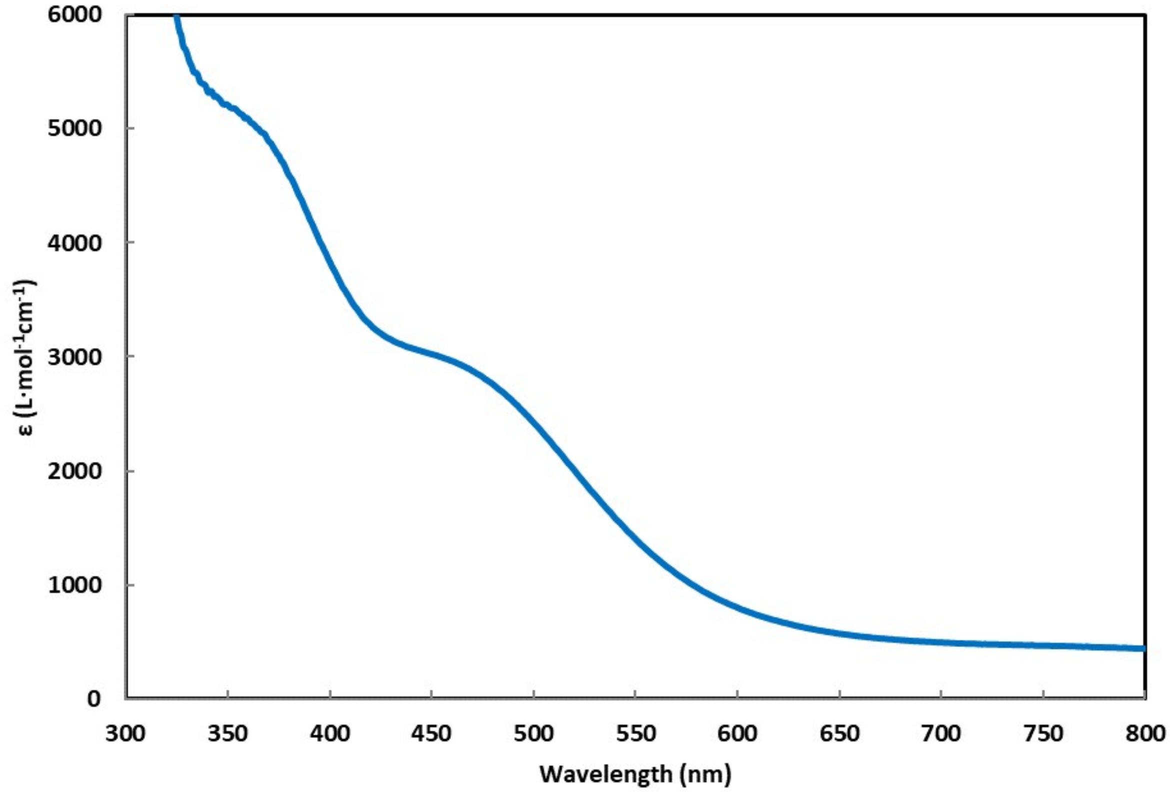

Figure S15: UV-Vis spectrum of 3.45×10^{-4}M of U(N-*p*tolyl)$(TIG)_3$ in toluene. Broad peak at 473 nm (ε=2,842 L/mol·cm)

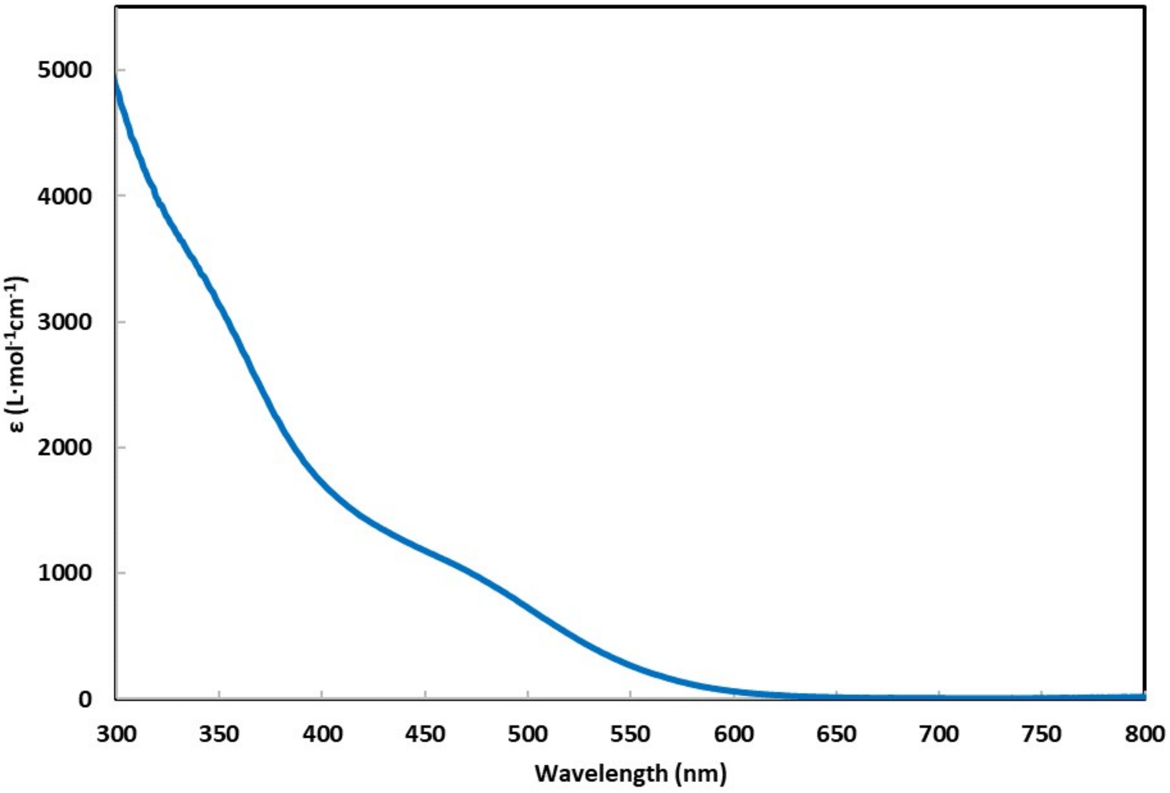

Figure S16: UV-Vis spectrum of 4.50x10^{-4}M of U(O)(TIG)$_3$ in toluene.
Broad peak at 486 nm (ε=874 L/mol·cm)

E. Cyclic Voltammetry

General. All cyclic voltammograms were recorded in dichloromethane with 0.1 M TBAP ($[NBu_4][PF_6]$) as a supporting electrolyte. A glassy carbon working electrode was used, along with a Pt-gauze counter electrode and a Pt-wire quasi-reference electrode.

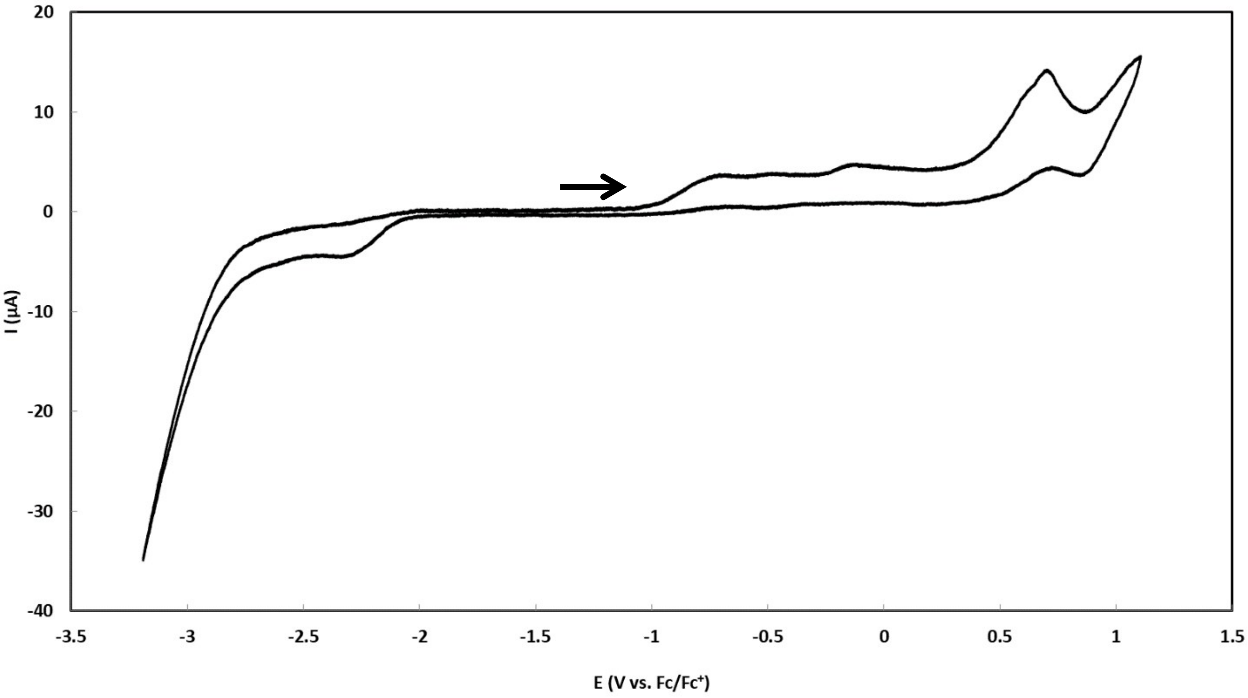

Figure S17. Cyclic voltammogram of $U(N_2CPh_2)(TIG)_3$. The scan rate was 100 mV/s. All redox events do not become reversible once studied in isolation.

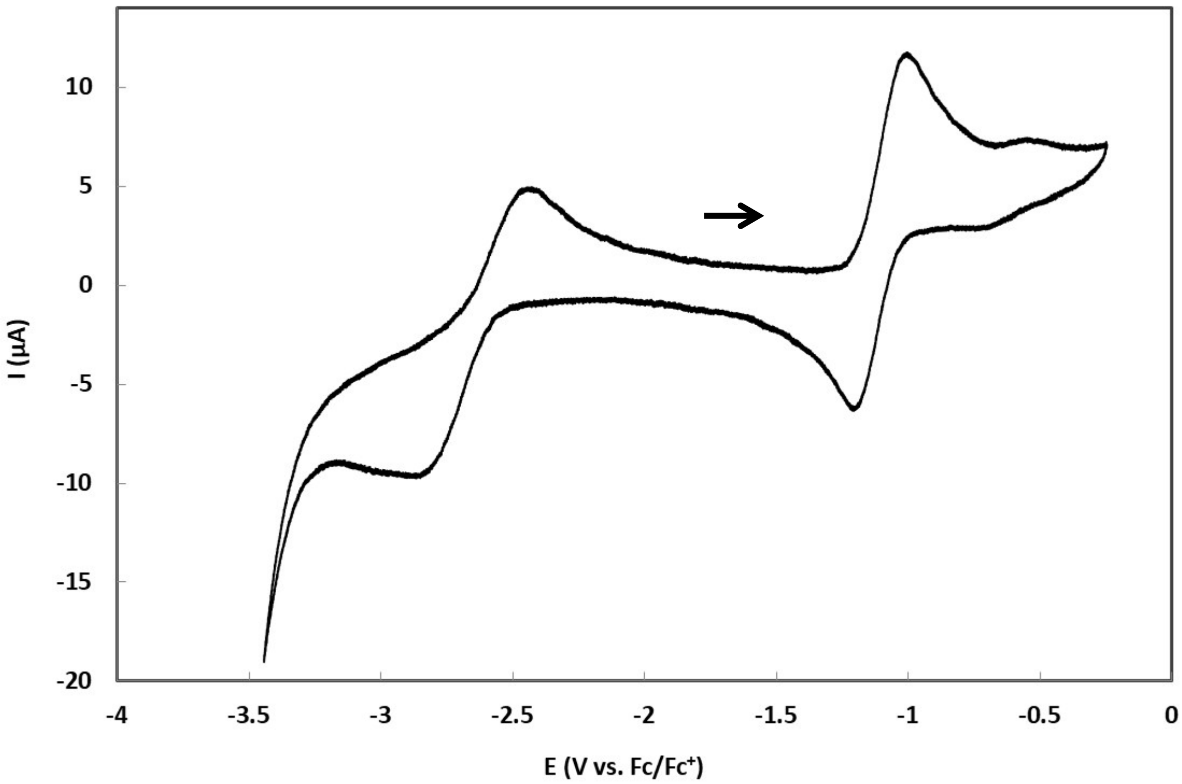

Figure S18. Cyclic voltammogram of U(N-*p*tolyl)(TIG)$_3$. The scan rate is 100 mV/s. Studies of isolated events are shown below (Figure S29).

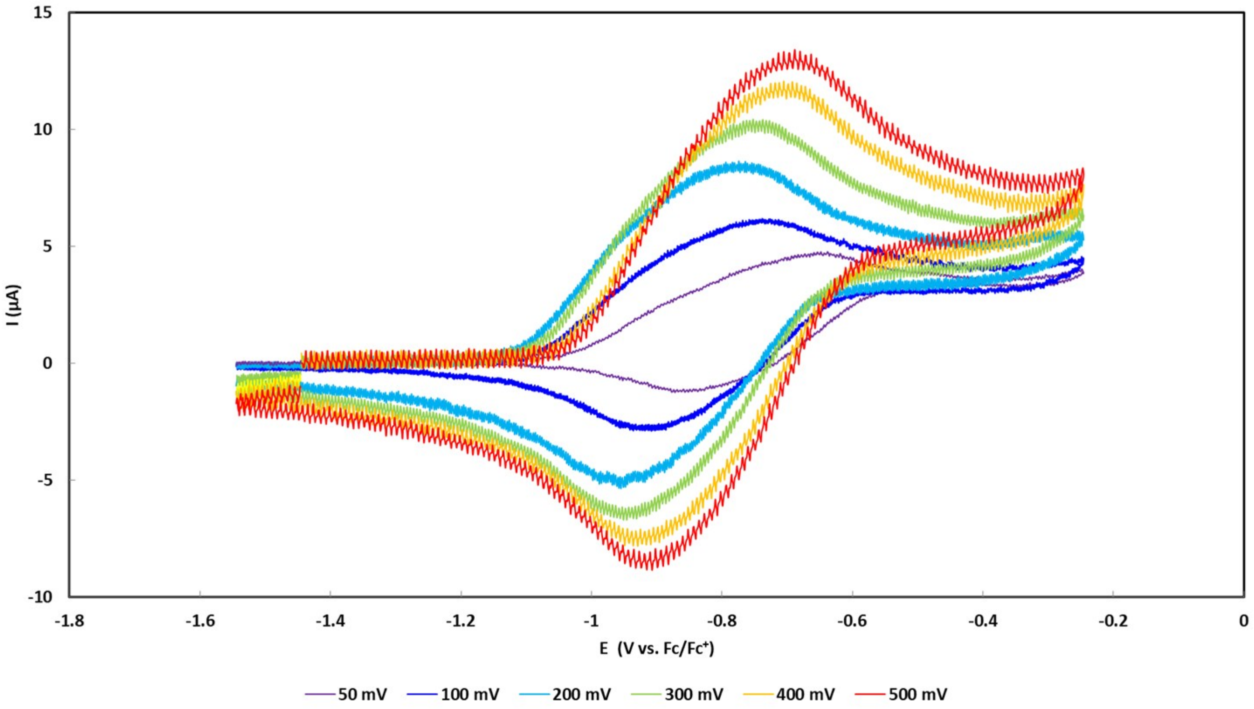

Figure S19. $U^{V/VI}$ couple at -0.829 V vs. Fc/Fc^+ at various scan rates (50 mV/s, 100 mV/s, 200 mV/s, 300 mV/s, 400 mV/s, 500 mV/s).

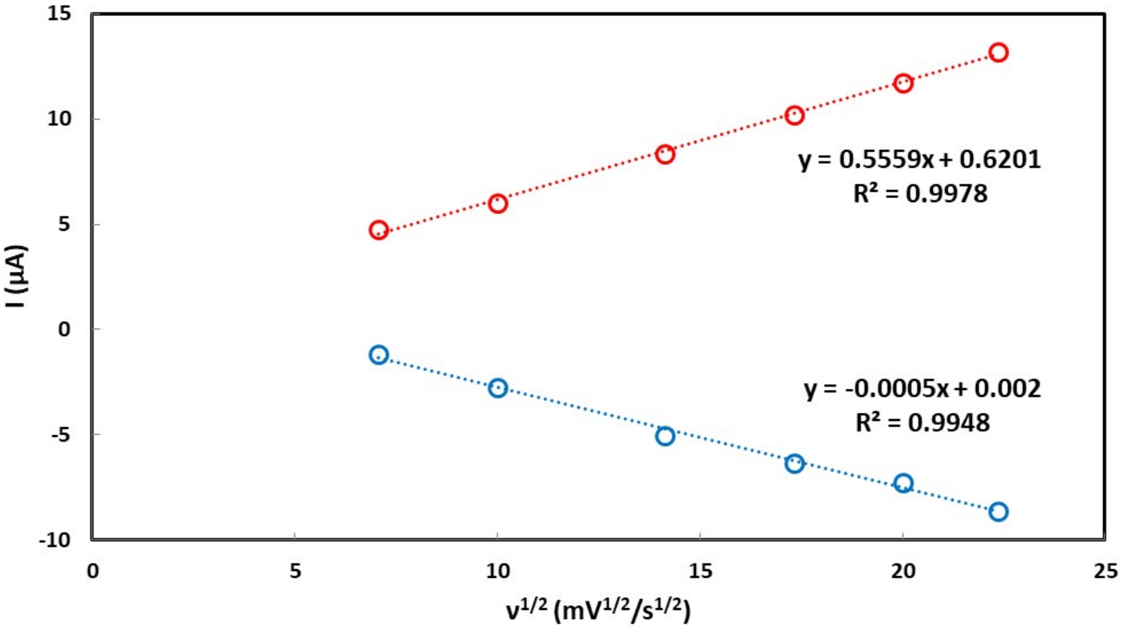

Figure S20. Scan rate dependence studies of $U^{V/VI}$ couple. Linearity of these lines suggests reversibility of this redox event.

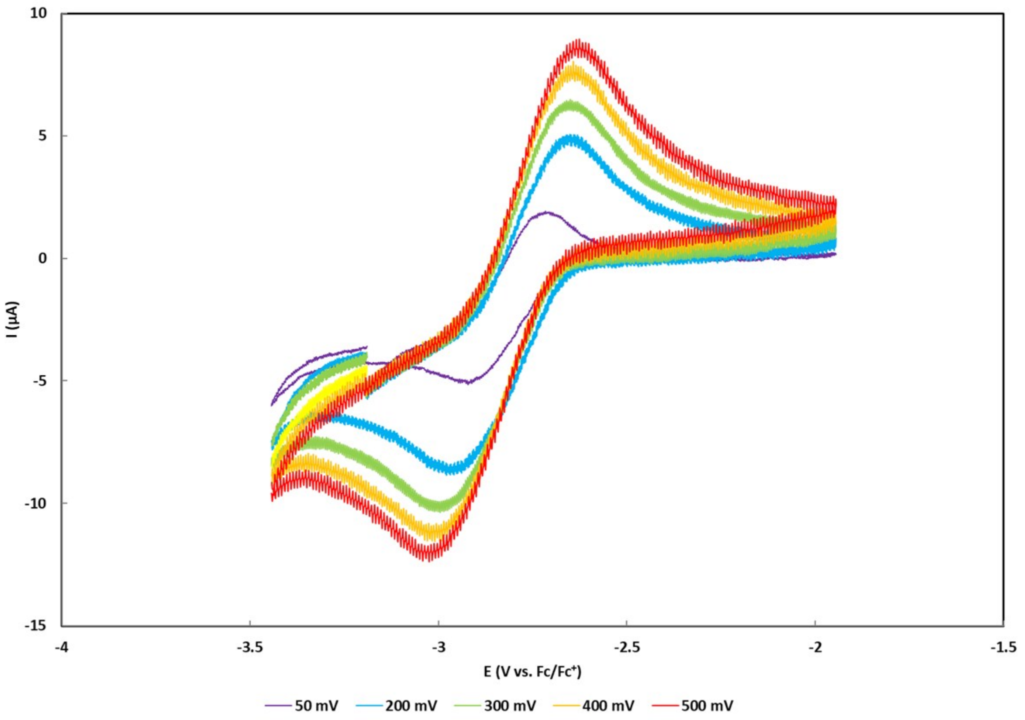

Figure S21. $U^{IV/V}$ couple at -2.702 V vs. Fc/Fc^+ at various scan rates (50 mV/s, 200 mV/s, 300 mV/s, 400 mV/s, 500 mV/s).

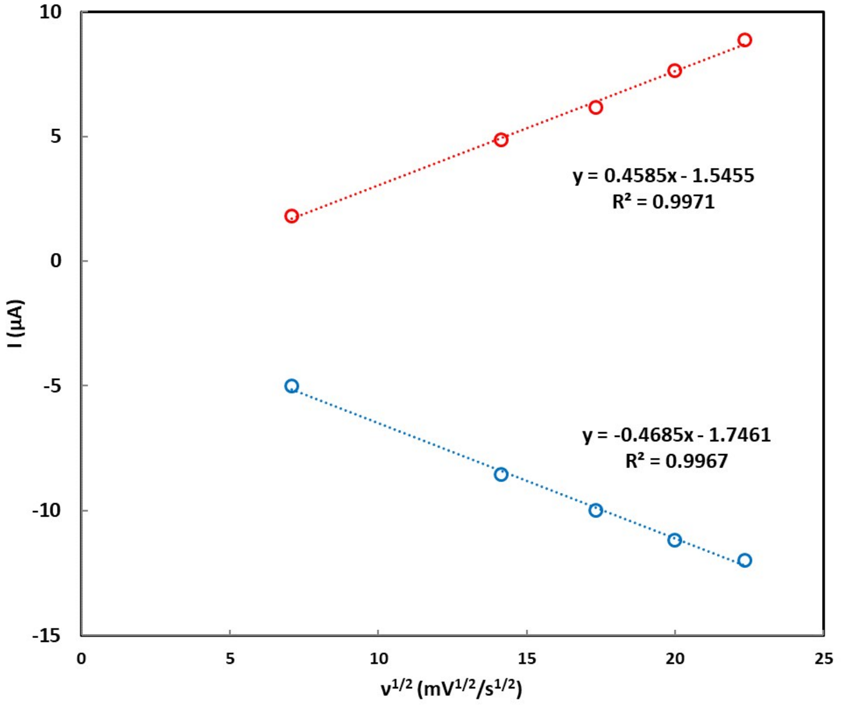

Figure S22. Scan rate dependence studies of $U^{IV/V}$ couple. Linearity of these lines suggests reversibility of this redox event.

F. X-ray Crystallography

Single-crystal X-ray diffraction experiments were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements for compounds **1**, **6** were performed on a Rigaku XtaLAB P200 rotating anode equipped with a Pilatus 200K hybrid pixel array detector. Data were collected using Mo Kα radiation (λ = 0.71073 Å). Crystals were kept at 100(2) K throughout collection. Data collection was performed with CrysAlis^{Pro}.[6] Data processing was done using CrysAlis^{Pro} and included a multi-scan absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlis^{Pro}. Measurements for compounds **2-5** were performed on a Bruker APEX-II area detector using Mo Kα radiation (λ = 0.71073 Å). Crystals were kept at 100(2) K throughout collection. Data collection was performed with Bruker APEX2 software (v. 2014.11). Data refinement and reduction were performed with Bruker SAINT (V8.34A). All structures were solved with SHELXT.53.[7] Structures were refined with SHELXL-2014.[8] Molecular graphics were computed with Mercury 3.10. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were either included at the geometrically calculated positions and refined using a riding model or located as Q peaks in the Fourier difference map. Compounds **3**, **4**, and **6** contained highly disordered outer sphere solvent molecules that could not be accurately modeled; the data for these structures were treated with the SQUEEZE routine included in PLATON.[9]

	1	**2**	**3**	**4**	**5**	**6**
Chemical formula	$C_{39}H_{84}N_9ClU \cdot 1.5(C_6H_{14})$	$C_{39}H_{84}N_9U$	$C_{52}H_{94}N_{11}U \cdot C_5H_{12}$	$C_{46}H_{91}N_{10}U \cdot 0.5(C_6H_{14})$	$C_{39}H_{84}N_9OU$	$C_{39}H_{84}N_{12}U$
Formula weight	1081.88	917.18	1183.55	1065.40	933.19	959.21
Colour, habit	Green, block	Blue, block	Brown, block	Brown, block	Red, block	Green, block
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P 21/c	P 21/c	P-1	C 2/c	P 21/c	P-1
a (Å)	11.6454(4)	13.2890(11)	12.3599(6)	39.246(4)	19.9133(19)	13.0981(2)
b (Å)	37.8373(10)	19.9565(16)	12.6609(6)	14.3692(16)	12.7998(16)	13.2024(2)
c (Å)	13.3431(4)	18.7099(14)	21.0290(11)	19.965(2)	19.1902(16)	17.7597(2)
α (°)	90	90	88.8639(11)	90	90	96.1010(10)
β (°)	109.795(3)	110.091(3)	77.3174(11)	109.062(9)	109.856(4)	103.8660(10)
γ (°)	90	90	79.3741(11)	90	90	119.6380(10)
V ($Å^3$)	5532.0(3)	4659.9(6)	3154.7(3)	10641(2)	4600.5(8)	2497.88(7)
Z	4	4	2	8	4	2
Densitiy (Mg m^{-3})	1.299	1.307	1.246	1.330	1.347	1.275
F(000)	2260	1892	1234	4432	1924	988
Radiation Type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
μ (mm^{-1})	3.020	3.517	2.614	3.091	3.566	3.286
Crystal size (mm^3)	0.40 x 0.20 x 0.10	0.05 x 0.05 x 0.05	0.12 x 0.10 x 0.10	0.05 x 0.05 x 0.05	0.25 x 0.13 x 0.08	0.18 x 0.17 x 0.15
Meas. Refl.	61124	246388	50668	88992	109654	58226
Indep. Refl.	11297	8549	11131	9820	9404	12188
R(int)	0.0816	0.0714	0.0338	0.0457	0.0492	0.0589
Final R indices [$I > 2\sigma(I)$]	R = 0.0395 R_w = 0.0830	R = 0.0295 R_w = 0.0589	R = 0.0315 R_w = 0.0726	R = 0.0424 R_w = 0.0987	R = 0.0184 R_w = 0.0404	R = 0.0232 R_w = 0.0515
Goodness-of-fit	1.042	1.089	1.115	1.070	1.031	1.041
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	1.855, -1.469	3.202, -1.116	3.501, -0.778	1.850, -1.266	0.682, -0.347	0.798, -0.540
CCDC	1860829	1860831	1860826	1860827	1860830	1860828

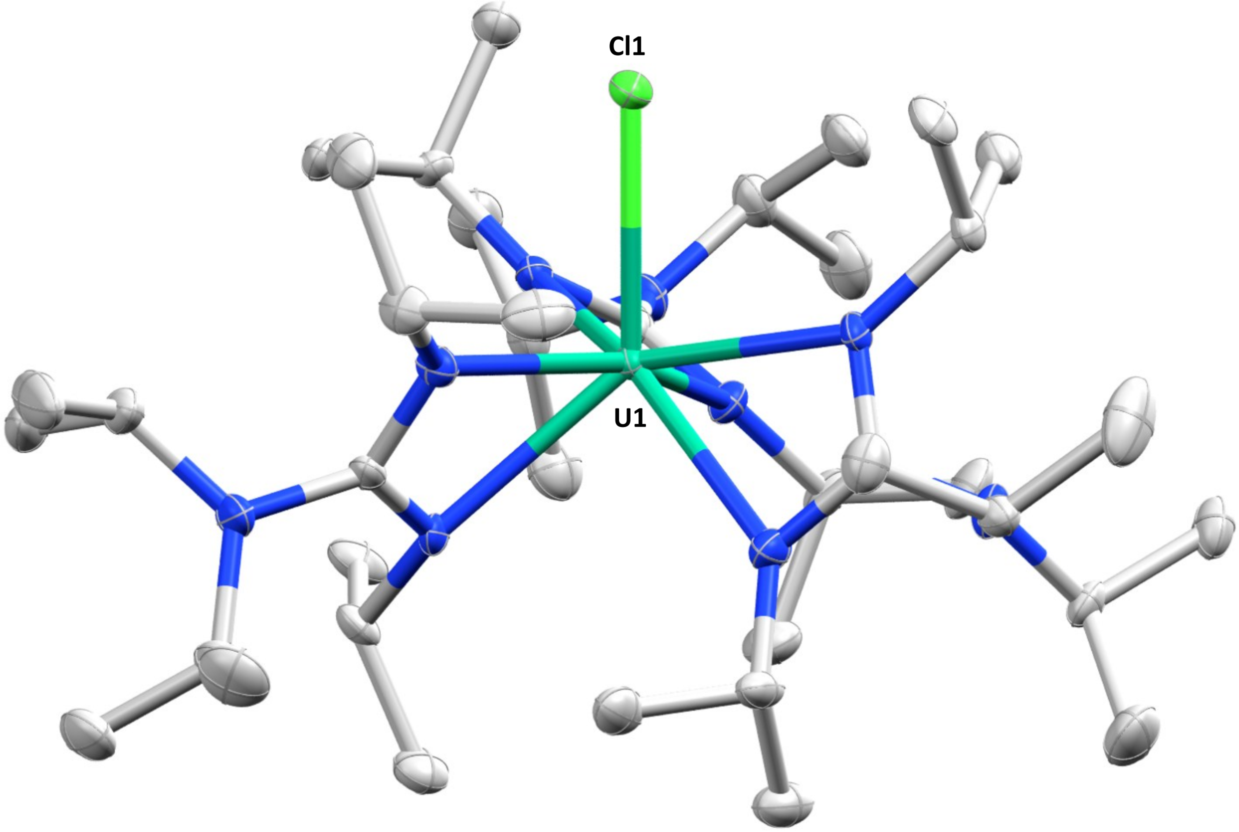

Figure S23. Molecular structure of **1** (thermal ellipsoids drawn at the 50% probability level). Hexane solvent molecules and hydrogen atoms omitted for clarity.

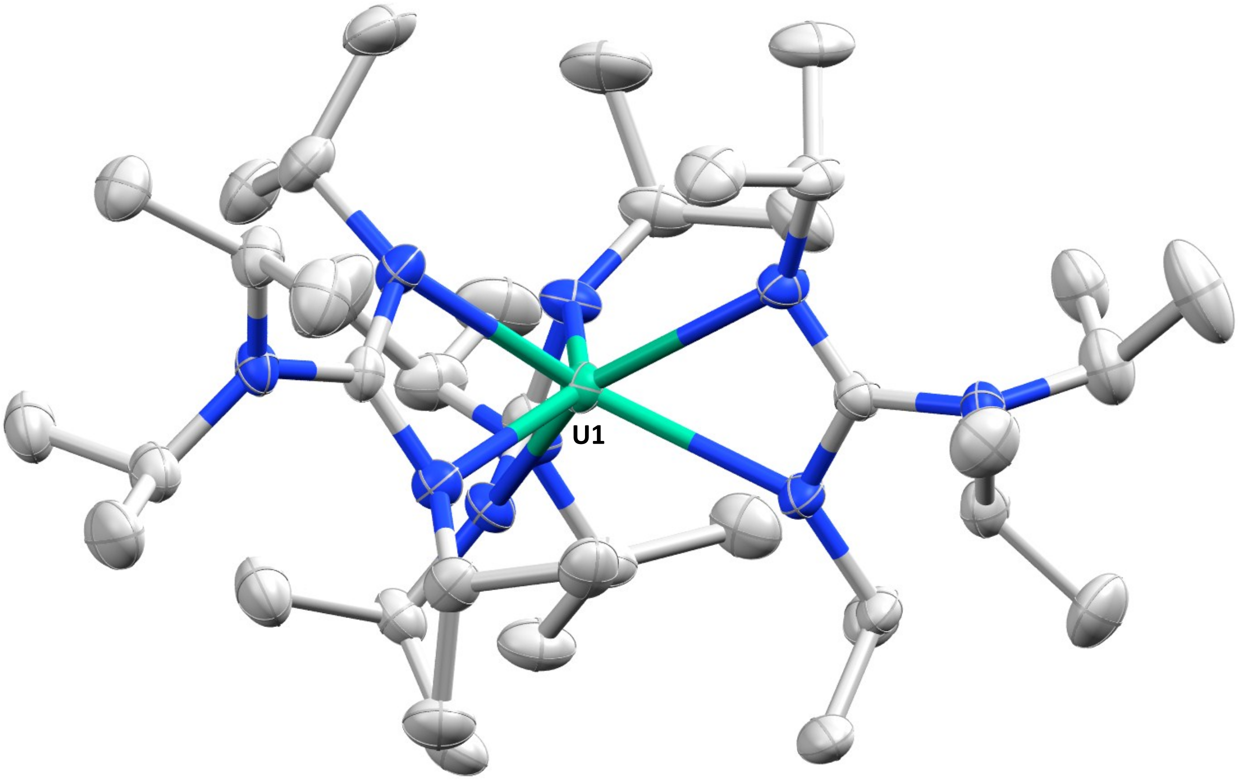

Figure S24. Molecular structure of **2** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms omitted for clarity.

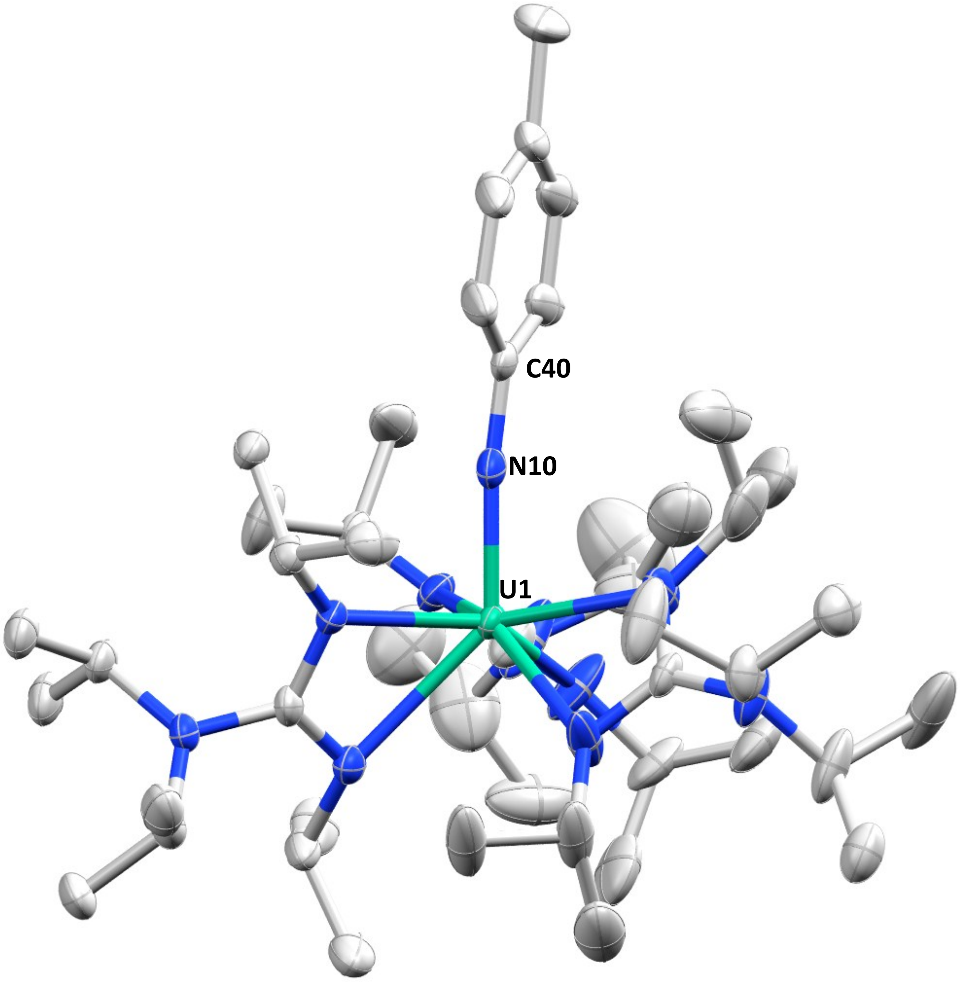

Figure S25. Molecular structure of **4** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms and hexane solvent molecule omitted for clarity.

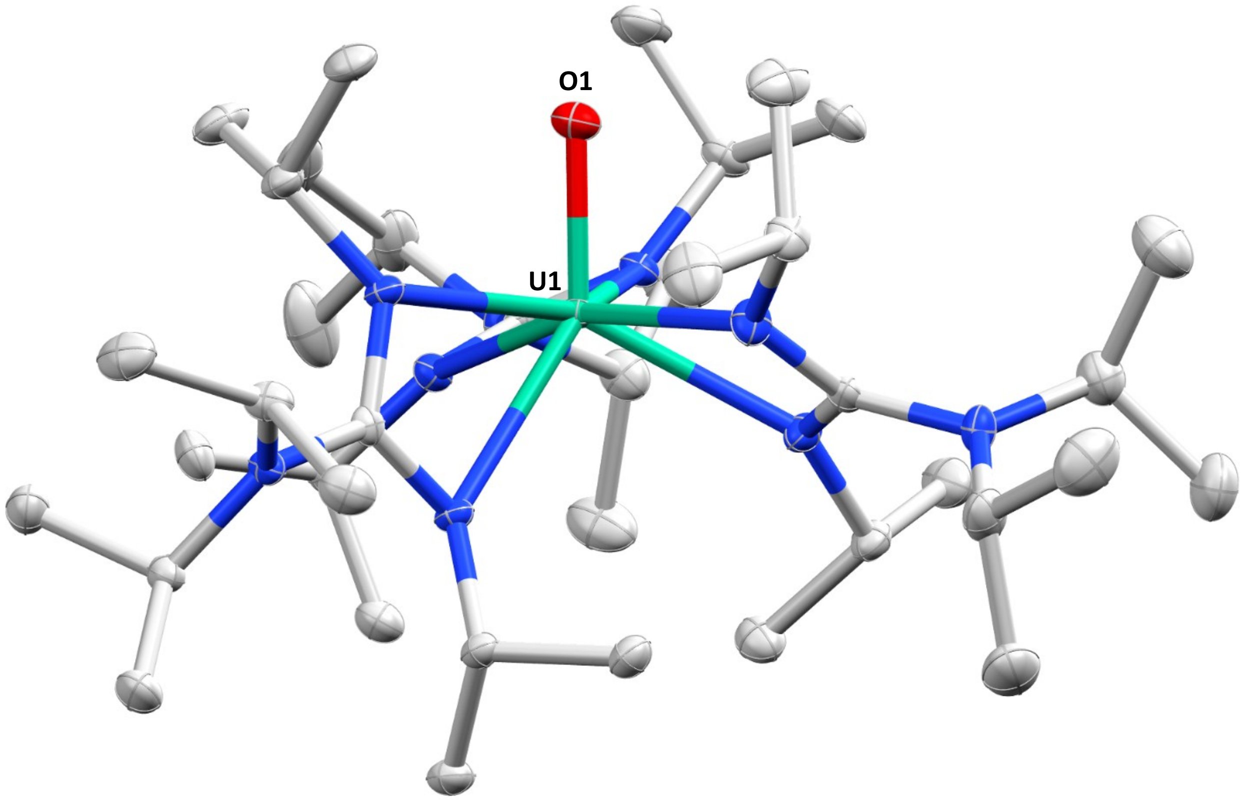

Figure S26. Molecular structure of **5** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms omitted for clarity.

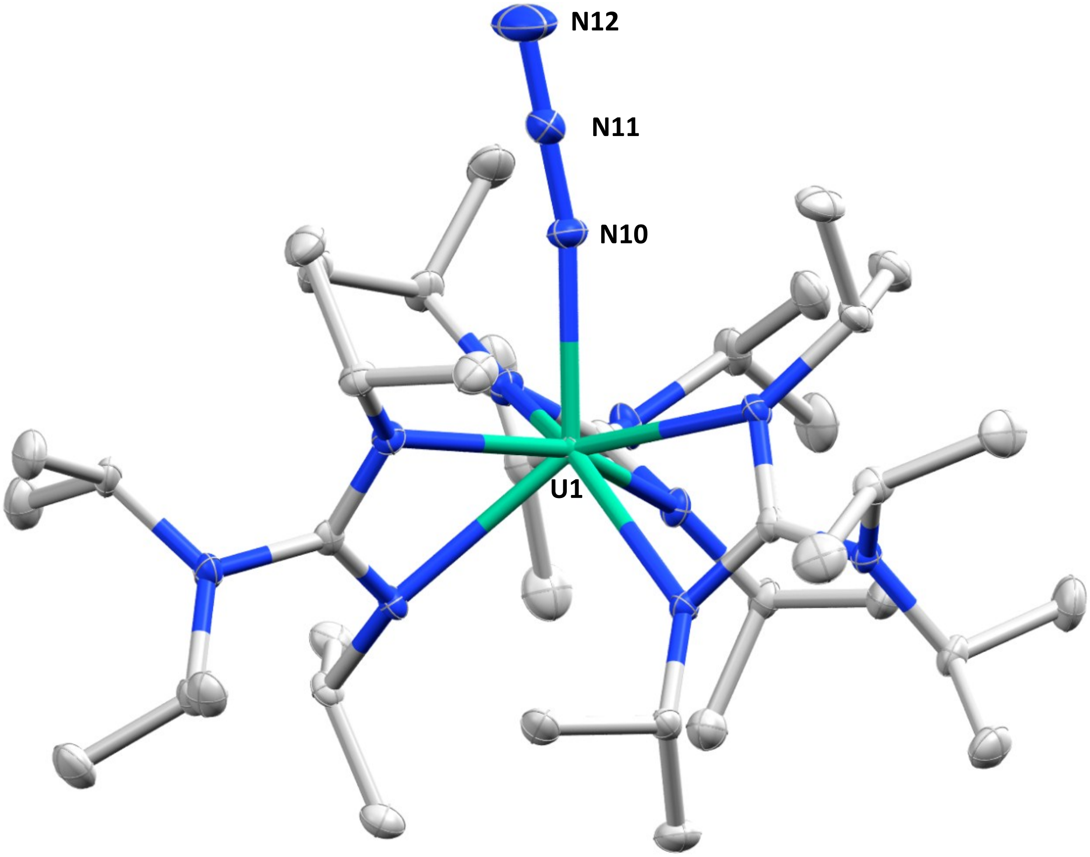

Figure S27. Molecular structure of **6** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms omitted for clarity.

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