Electronic Supplementary Material (ESI) for ChemComm.

Supplemental Information

Synthesis, Characterization, and Solid State Elucidation of Unusual Pyridine Donor Uranyl Complexes

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Experimental Details

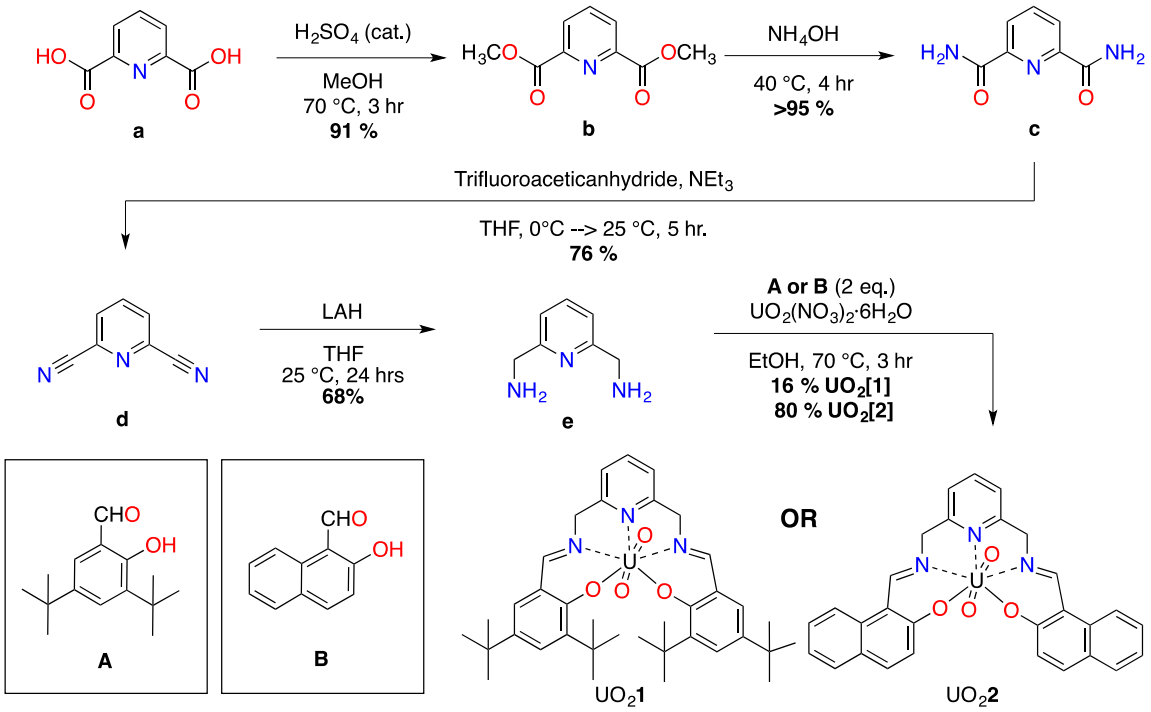
General considerations

Caution! The $UO_2(NO_3)_2$•$6H_2O$ used in this study contained depleted uranium, standard precautions for handling radioactive materials or heavy metals, such as uranyl nitrate, were followed.

All solvents not specifically mentioned were ACS grade from EMD and used as received with no further purification. Reagents methanol (HPLC grade, EMD), ethanol (200 proof, ACS grade, Pharmco-aaper), 2,6-pyridinedicarboxylic acid (99%, Acros), sulfuric acid (95-98%, Sigma Aldrich), sodium bicarbonate (EMD), sodium chloride (Macron), ammonium hydroxide (BDH), trifluoroacetic anhydride (>99%, Sigma Aldrich), palladium 5% on carbon, dry, type 87L (Alpha Aesar), celite (Alpha Aesar), 3,5-di-tert-butylsalicyaldehyde (98%, TCI), 2-hydroxynapthaldehyde (98%, Alpha Aesar), hydrochloric acid (ACS grade, Fischer Scientific), sodium hydroxide (ACS grade, EMD), copper (II) acetate hydrate (>98%, MC/B), zinc (II) acetate dihydrate (Sigma Aldrich),vanadium (IV) bis(acetylacetonato)oxide (98%, STREM), iron (III) acetylacetonate hydrate (99%, STREM), cobalt (II) acetate tetrahydrate (Mallinckrodt), nickel (II) acetate tetrahydrate (Sigma Aldrich), and dysprosium (III) acetate hydrate (99.9%, STREM) were used as received without further purification. Anhydrous dichloromethane (BDH) and tetrahydrofuran (Macron) were purchased, stored under argon, and dispensed from a solvent purification system. Triethylamine (99%, Alpha Aesar) was distilled and stored under argon until use. $UO_2(NO_3)_2$•$6H_2O$ (98%, J. T. Baker) was recrystallized from a nitric acid solution and stored under hexanes until use.

NMR Spectroscopy: ^1H NMR spectra were recorded with a Bruker AC400 spectrometer at 400 or 600 MHz. ^{13}C NMR spectra were recorded with a Bruker AC400 spectrometer at 100 or 151 MHz. NMR spectroscopic data were collected using deuterated chloroform ($CDCl_3$), deuterated dimethylsulfoxide (D_6-DMSO) or deuterated acetonitrile (CD_3CN).

X-ray Diffraction: Suitable crystals were selected and mounted on a glass fiber using paratone-n oil and data collection was completed on a 'Bruker APEX CCD' diffractometer. The crystal was kept at 180(2) K during unit cell and data collection. The structure was solved with the ShelXS structure solution program using Direct Methods[1] and refined with the ShelXL refinement package using Least Squares minimization[2], or refined with the olex2.refine[3] refinement package using Gauss-Newton minimisation. Projections were created on Olex2 software.[4]



Scheme 1. Synthesis of $UO_2$1 and $UO_2$2

Dimethyl-2,6-pyridinedicarboxylate (b)
Methanol (320 mL) and 2,6-pyridinedicarboxylic acid (8.195 g, 49.03 mmol) were added to a round bottom flask, charged with a stir bar and gently warmed to 30 °C to aid in dissolution. Sulfuric acid (10 mL) was added slowly, followed by heating the flask to reflux for 4 hours. The reaction solution was quenched with $HNaCO_3$ until a neutral pH was attained, followed by the extraction of the ester into dichloromethane (DCM). The ester was washed twice with brine solution and remaining solvent was removed under reduced pressure yielding a white powder (8.681 g, 44.48 mmol, 91 %). 1H NMR (400 MHz, $CDCl_3$) δ 4.37 (s, 6H), 8.041 (t, 1H, *J* = 7.8 Hz), 8.332 (d, 2H, *J* = 7.6 Hz); TOF MS (ESI) m/z (M^+ + 1) Cald 196.0532, Found 196.0597.

2,6-pyridinedicarboxamide (c)
Ammonium hydroxide (50 mL) and dimethyl-2,6-pyridinedicarboxylate (3.053 g, 15.64 mmol) were added to a round bottom flask, charged with a stir bar and heated to 40 °C for 8 hours. Resulting white powder was filtered using cold deionized water. Product was dried at 60 °C overnight in a vacuum oven, yielding a matte white solid in quantitative yield (2.583g, 15.64 mmol). ^{1}H NMR (400 MHz, D_6-DMSO) δ 7.717 (s, 2NH) 8.117-8.198 (m, 3H) 8.881 (s, 2NH); MS (ESI) m/z (M^+ + 1) Cald 166.0538, Found 166.0642.

2,6-pyridinedicarbonitrile (d)
Dry THF (25 mL), 2,6-pyridinedicarboxamide (3.517 g, 21.29 mmol) and freshly distilled triethylamine (7 mL) were added to a round bottom flask, charged with a stir bar and cooled to 0 °C. Trifluoroacetic anhydride (8.75 mL) was added dropwise with stirring. Reaction vessel was stirred for 30 minutes in ice, and then allowed to warm to room temperature. Reaction was allowed to continue until judged

complete, for 4 hours, and quenched with saturated sodium bicarbonate solution. Solution was filtered and washed with cold deionized water, yielding a shiny white solid (2.075 g, 16.08 mmol, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.924 (d, 2H, J = 8.0 Hz), 8.067 (t, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.41, 131.07, 135.40, 138.78; TOF MS (ESI) m/z (M^+ + 1) Cald 130.0327, Found 130.0420.

2,6-(dimethylamino)pyridine (e)

2,6-pyridinedicarbonitrile (0.989 g, 7.67 mmol) and dry tetrahydrofuran (100 mL) were added to a flame dried round bottom flask charged with a stir bar and allowed to dissolve. Lithium Aluminum Hydride (3.5 eq., 1.034 g, 27.2 mmol) was added to the reaction vessel slowly and allowed to stir at room temperature for 22 hours. The resulting solution was quenched slowly using cold isopropanol (60 mL), while stirring in an ice bath. The solution was stirred at room temperature for 2 additional hours and then filtered over celite to remove excess aluminum salts, and solvent was removed from resulting filtrate under reduced pressure to yield a thick yellow oil (0.7239 g, 5.284 mmol, 69%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.676 (s, 4H), 3.967 (s, 4H), 7.145 (d, 2H, J = 7.8 Hz), 7.613 (t, 1H, J = 7.5Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 47.96, 119.48, 137.31, 161.56; TOF MS (ESI) m/z (M^+ + 1) Cald 138.0953, Found 138.0748.

2,6-bis[1-[(2-hydroxy-3,5-ditert-butylphenyl)imino]ethyl]pyridine (1)

Ethanol (60 mL), 3,5-ditertbutylsalicylaldehyde (1.948 g, 8.325 mmol), 2,6-(dimethylamino)pyridine (0.5766 g, 4.209 mmol), trifluoroacetic acid (1 drop), and magnesium sulfate (1 g) were added to round bottom flask charged with a stir bar. The reaction vessel was heated to reflux for 18 hours until it was judged complete by TLC. Magnesium sulfate was removed via hot filtration, and the solvent was removed from the resulting filtrate under reduced pressure to yield a crude yellow oil. Crude product was purified with column chromatography with a gradient of 5% ethyl acetate in hexanes solution, followed by a 10% ethyl acetate in hexanes solution. The product was collected and concentrated under reduced pressure to yield a bright yellow solid (0.3404 g, 0.5982 mmol, 14.42%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.312 (s, 18H), 1.449 (s, 18H), 4.930 (s, 4H), 7.146 (s, 2H), 7.285 (d, 2H, *J* = 7.2 Hz), 7.408 (s, 2H), 7.686 (t, 1H, *J* = 7.5 Hz), 8.549 (s, 2H), 13.657 (s, 2OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.604, 31.684, 34.314, 35.219, 65.204, 118.077, 120.587, 126.376, 127.413, 136.896, 137.850, 140.381, 158.164, 158.232, 168.179; TOF MS (ESI) m/z (M^+ + 1) Cald 570.3981, Found 570.3319.

UO_2[2,6-bis[1-[(2-hydroxy-3,5-ditert-butylphenyl)imino]ethyl]pyridine] ($UO_2$1)

Ethanol (50 mL) was added to 2,6-(dimethylamino)pyridine (0.3116 g, 2.258 mmol) in a round bottom flask charged with a stir bar, and stirred until dissolved with gentle warming. Magnesium sulfate and 3,5-ditert-butylsalicylaldehyde (1.949 g, 8.329 mmol) were added to the reaction vessel and heated to reflux for 18 hours. The resulting solution was filtered to remove the magnesium sulfate and transferred to a round bottom flask. Uranyl nitrate hexahydrate (1.082 g, 2.16 mmol) and trimethylamine (660 uL) were added to the reaction vessel and gently warmed to 40 °C for 3 hours, until the reaction was judged complete by TLC. The crude red solid, attained by removal of solvent through rotary evaporation, was

purified using column chromatography and DCM as eluent to produce a dark red solid (0.309g, 0.369 mmol, 16.3 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.315 (s, 18H), 1.821 (s, 18H), 5.668 (s, 4H), 7.284 (s, 2H), 7.538 (d, 2H, *J* = 8.4 Hz), 7.741 (s, 2H), 7.942 (t, 1H, *J* = 7.5 Hz), 9.427 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.90, 31.74, 33.88, 35.93, 69.67, 120.19, 122.83, 127.87, 130.29, 139.29, 140.77, 160.96, 166.76, 169.75; ^{1}H NMR (400 MHz, CD_3CN) δ 1.344 (s, 18H), 1.764 (s, 18H), 5.771 (s, 4H), 7.485 (d, 2H, J = 2.3 Hz), 7.681 (d, 2H, *J* = 2.8 Hz), 7.792 (s, 1H), 7.812 (s, 1H), 8.192 (t, 1H, *J* = 7.6 Hz), 9.427 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 31.481, 32.211, 34.877, 36.969, 70.476, 122.188, 124.503, 129.769, 131.071, 140.353, 141.418, 124.564, 162.222, 167.512, 171.399; MS (ESI) m/z (M^+ + 1) Cald 838.4231, Found 838.4254. Single crystals of UO_2**1** [Emily021716_1_0m] were grown from slow evaporation of a concentrated solution of UO_2**1** in acetonitrile.

UO_2[2,6-bis[1-[(2-hydroxy-napthyl)imino]ethyl]pyridine] ($UO_2$2)

Ethanol (50 mL) was added to 2,6-(dimethylamino)pyridine (0.143 g, 1.04 mmol) in a round bottom flask charged with a stir bar, and stirred until dissolved with gentle warming. 2-hydroxynapthaldehyde (0.385 g, 2.24 mmol) were added to the reaction vessel and heated to reflux for 9 hours. Uranyl nitrate hexahydrate (0.5126 g, 1.021 mmol) and trimethylamine (400 uL) were added to the reaction vessel and gently warmed to 40 °C for 12 hours, until the reaction was judged complete. The resulting solution was placed in ice to precipitate an orange solid was separated via vacuum filtration (0.5891 g, 0.826 mmol, 79.5 %). ^{1}H NMR (400 MHz, d_6-DMSO) δ 6.154 (s, 4H), 7.305 (t, 2H, *J*= 7.3 Hz), 7.424 (d, 2H, *J*= 9.0 Hz), 7.585 (t, 2H, *J*= 7.6 Hz), 7.893 (d, 2H, *J*= 8.0 Hz), 7.990 (d, 2H, *J*= 7.8 Hz), 8.213 (d, 2H, *J*= 9.0 Hz), 8.353-8.382 (m, 3H), 10.581 (s, 2H); ^{13}C NMR (150 MHz, d_6-DMSO) δ 69.074, 113.220, 121.487, 121.802, 123.255, 124.771, 127.753, 127.980, 129.102, 134.566, 136.351, 142.096, 161.565, 165.044, 170.347; TOF MS (ESI) m/z (M^+ + 1) Cald 714.2040, Found 714.2008 . Single crystals of UO_2**2** [Emily051916_1_0mFINAL] were grown from slow diffusion of hexanes into a concentrated solution of UO_2**2** in DCM.

Electronic Spectroscopy

Titration Procedure

Serial titrations of **1** were completed by introducing a known amount of various $UO_2(NO_3)_2$ and $Zn(C_2H_3O_2)$ to a solution of free base in indicated solvent. Solutions were 2 mL of 0.123 mM ligand, with approximately 30 µL of 1.5 mM metal salt. The actual volumes and concentrations varied depending on stock solutions, but 1/5 equivalent of metal salt was added per addition. Serial titrations were completed in DCM, EtOH and MeOH. The solutions were shaken for 3 seconds and replaced in the spectrometer and the absorbance spectrum or fluorescence spectrum was collected. This was repeated until an excess of metal salt was present.

Absorbance Spectroscopy: All absorbance spectra were collected on a VARIAN Cary 50 WinUV Spectrometer with a xenon lamp with absorbance spectra from 200 nm to 900 nm with a 1 cm width quartz cuvette.

Fluorescence Spectroscopy: All fluorescence spectra were collected on a Shimadzu RF-5301 PC fluorospectrophotometer with a xenon lamp and a 1 cm width quartz cuvette with an excitation of 365 nm and an emission spectrum of 375–900 nm. Slit widths were set so that the maximum emission of the ligand could be seen.

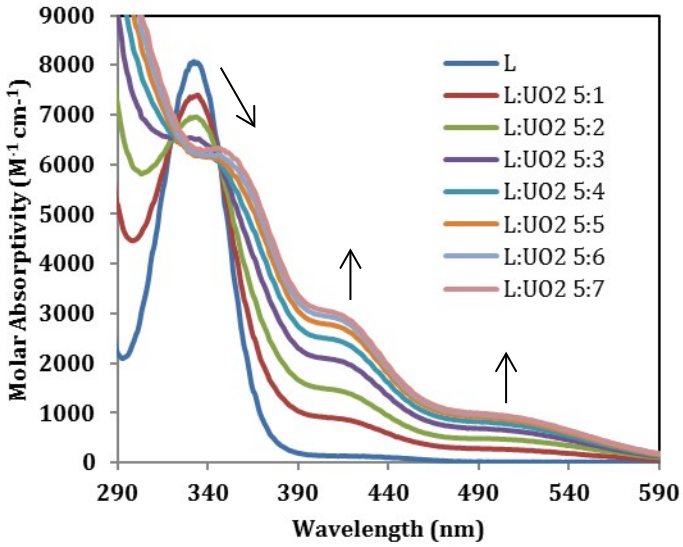


Figure SI1. Absorbance spectrum of a serial titration completed via the general procedure of **1** in ethanol solution with an increasing ratio of $UO_2(NO_3)_2 \bullet 6H_2O$, from 5:1 to 5:7 **1**:$UO_2$.

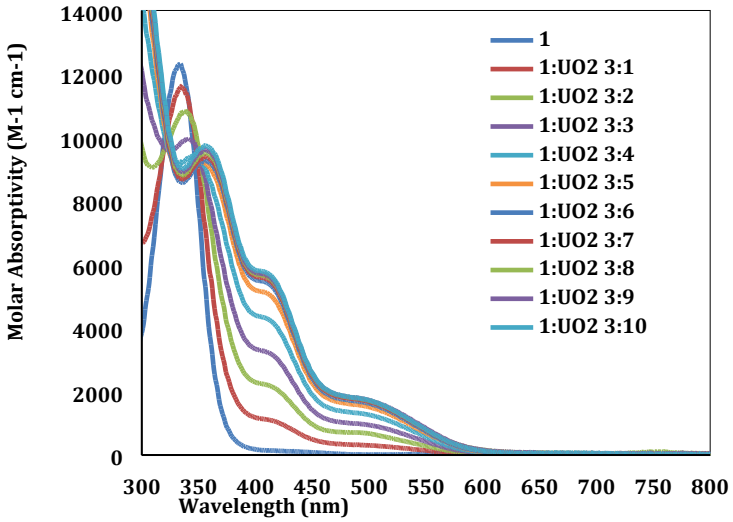


Figure SI2. Absorbance spectrum of a serial titration completed via the general procedure of UO_2**1** in dichloromethane solution with an increasing ratio of $UO_2(NO_3)_2 \bullet 6H_2O$, from 3:1 to 3:10 **1**:UO_2.

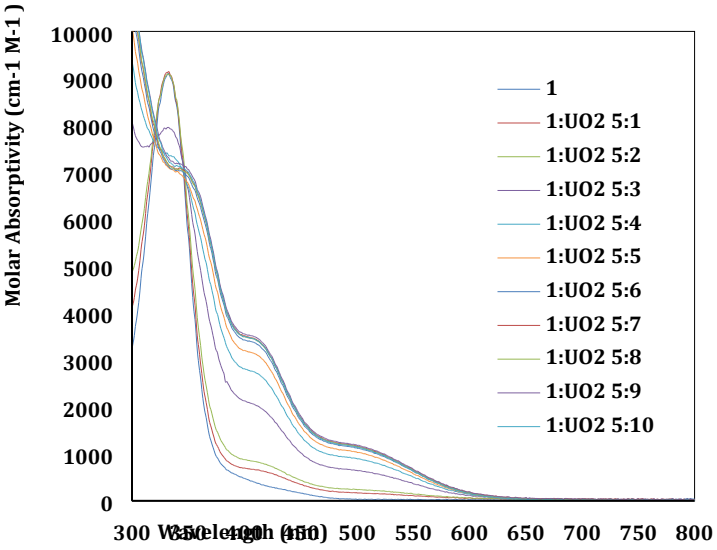


Figure SI3. Absorbance spectrum of a serial titration completed via the general procedure of UO_2**1** in methanol solution with an increasing ratio of $UO_2(NO_3)_2 \bullet 6H_2O$, from 5:1 to 5:10 **1**:UO_2.

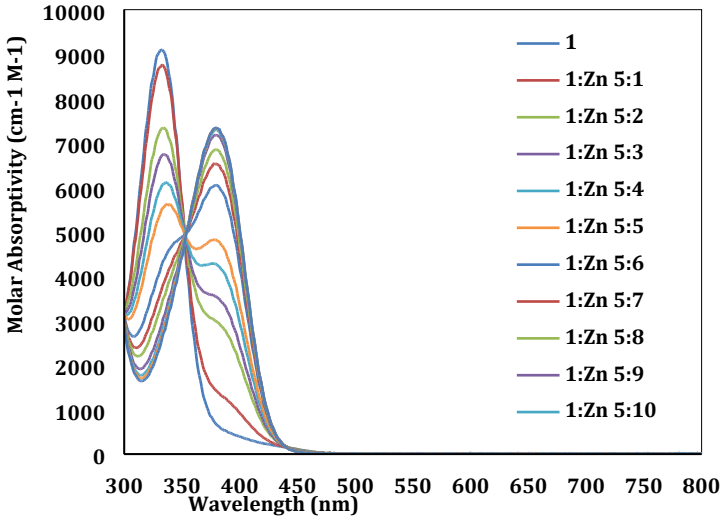


Figure SI4. Absorbance spectrum of a serial titration completed via the general procedure of free base **1** in methanol solution with an increasing ratio of $Zn(C_2H_3O_2)_2 \bullet 4H_2O$, from 5:1 to 5:10 **1**:Zn.

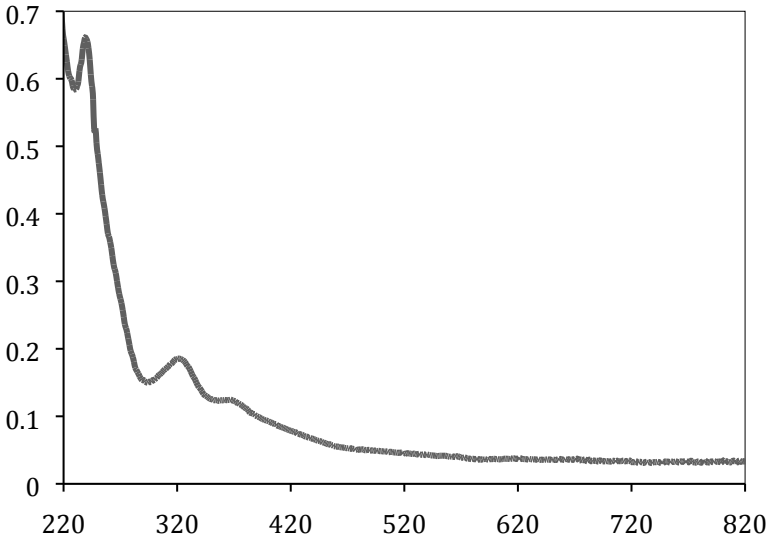


Figure SI5. Absorbance spectrum of UO_2**2** in dichloromethane.

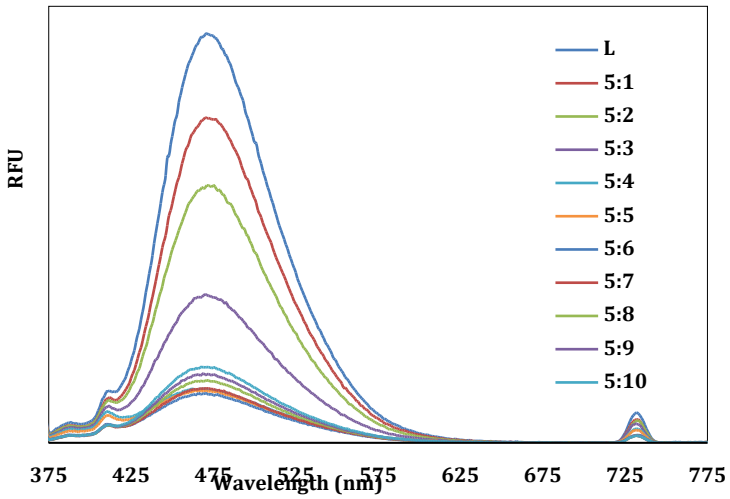


Figure SI6: Emission spectrum of a serial titration completed via the general procedure of **1** in methanol solution with an increasing ratio of $UO_2(NO_3)_2 \bullet 6H_2O$, from 5:1 to 5:10 **1**:UO_2 excited at 365 nm.

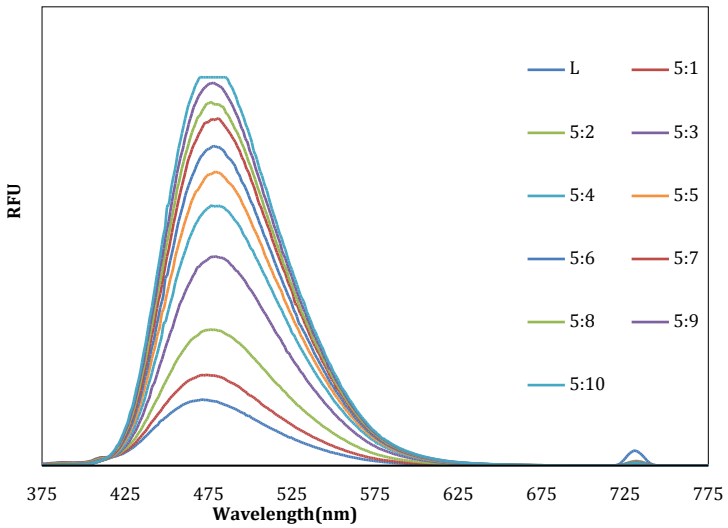


Figure SI7: Emission spectrum of a serial titration completed via the general procedure of **1** in methanol solution with an increasing ratio of $Zn(C_2H_3O_2)_2 \bullet 2H_2O$, from 5:1 to 5:10 **1**:Zn excited at 365 nm.

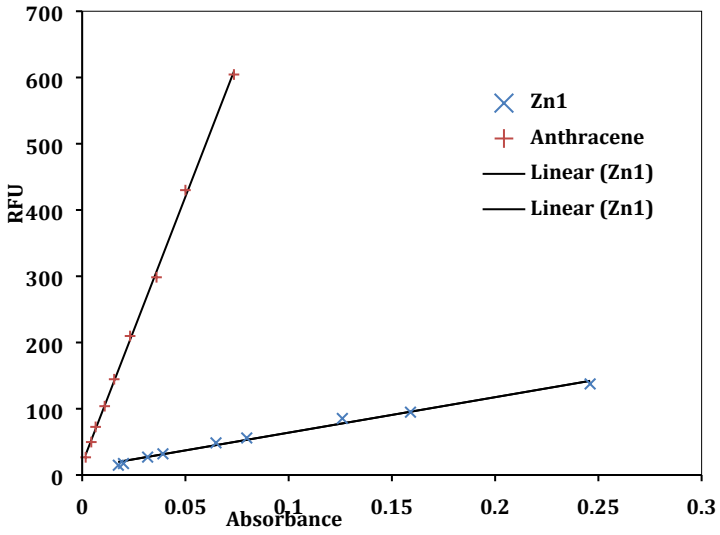


Figure SI8: Zn**1** fluorescence at 473 nm after excitation at 365 nm vs. absorbance value at 365 nm of 116, 87, 58, 43.5, 29.2, 21.8, 14.5, 10.9, 7.2, 5.5, 3.6, 2.7 uM solutions in methanol and Anthracene fluorescence at 422 nm after excitation at 365 nm vs. absorbance value at 365 nm of 35.7, 23.8, 15.8, 10.6, 7.1, 4.7, 3.1, 2.0, 1.0 uM solutions in methanol.

Quantum Yield was calculated via **equation 1**

$$\Phi_X = \Phi_{ST}\left(\frac{Slope_X}{Slope_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right) \qquad \textbf{(1)}$$

Where the subscripts ST and X denote standard and unknown respectively, Φ is the fluorescence quantum yield, Slope is the slope from the plot of fluorescence intensity vs absorbance, and η the refractive index of the solvent. In this case the solvent was constant, and Φ_{ST} was equal to 0.24 (24 %).[5] The quantum yield of Zn**1** was calculated to be 0.016 (1.6 %).

Crystallographic Tables

Table SI1 Crystal data and structure refinement for Emily021716_1_0m

Identification code	Emily021716_1_0m
Empirical formula	$C_{40}H_{52}N_3O_4U$
Formula weight	876.87
Temperature/K	180(2)
Crystal system	orthorhombic
Space group	Pccn
a/Å	13.9974(3)
b/Å	23.5111(5)
c/Å	23.6244(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7774.7(3)
Z	8
ρ_{calc}mg/mm^3	1.498
m/mm^{-1}	4.217
F(000)	3496.0
Crystal size/mm^3	0.06 × 0.06 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.386 to 61.054°
Index ranges	-19 ≤ h ≤ 19, -23 ≤ k ≤ 33, -32 ≤ l ≤ 33
Reflections collected	93148
Independent reflections	11882 [R_{int} = 0.0538, R_{sigma} = 0.0376]
Data/restraints/parameters	11882/0/446
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0619
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.0699
Largest diff. peak/hole / e Å^{-3}	1.37/-0.74

Table SI2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Emily021716_1_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
U1	6576.3(2)	3772.4(2)	2540.7(2)	20.73(3)
O1	5726.4(13)	3283.4(8)	3189.2(7)	25.9(4)
O2	5323.3(13)	4029.0(8)	1993.8(7)	27.0(4)
O3	6737.5(13)	3175.0(8)	2089.2(8)	29.4(4)
O4	6506.5(13)	4379.8(8)	2995.7(8)	27.6(4)
N1	7681.9(15)	3246.6(10)	3208.1(9)	25.0(5)
N2	7136.6(16)	4464.9(9)	1804.3(9)	25.5(5)
N4	6545(3)	5110(2)	5271.0(18)	97.0(15)
N3	8415.1(15)	3971.3(11)	2461.0(8)	23.9(4)
C17	9050(2)	3616.3(12)	2710.9(11)	26.8(6)
C16	8620.7(19)	3097.4(13)	2975.2(12)	30.0(6)
C15	7535(2)	3152.6(12)	3734.6(11)	26.7(6)
C14	6639.3(19)	3223.7(12)	4035.3(11)	25.5(6)
C13	6676(2)	3201.3(12)	4635.3(11)	29.4(6)
C8	5863(2)	3225.5(12)	4959.0(11)	29.0(6)
C7	4995(2)	3246.4(12)	4666.7(12)	29.4(6)
C2	4901.5(19)	3260.7(11)	4080.5(11)	24.8(5)
C1	5749.7(19)	3263.8(11)	3751.0(11)	24.2(6)
C3	3917(2)	3276.1(13)	3797.5(12)	30.3(6)
C4	3808(2)	3843.7(14)	3471.6(15)	42.1(8)
C6	3104(2)	3249.5(16)	4232.8(14)	41.7(8)
C5	3802(2)	2771.4(13)	3393.1(12)	33.1(7)
C12	5871(2)	3199.1(15)	5611.7(12)	39.9(8)
C10	5233(4)	3671(2)	5849.8(17)	97.4(19)
C9	5508(4)	2625(2)	5801.8(15)	93.2(19)
C11	6854(3)	3303(2)	5847.8(15)	77.1(15)
C18	10034(2)	3734.4(14)	2711.6(14)	38.3(8)
C19	10329(2)	4239.4(17)	2470.1(12)	43.1(8)
C20	9688(2)	4599.4(14)	2222.1(12)	36.3(7)
C21	8732(2)	4448.1(12)	2215.3(11)	27.4(6)
C22	7983(2)	4806.9(13)	1932.6(12)	31.5(6)
C23	6818(2)	4486.4(12)	1296.1(11)	27.9(6)
C24	5961(2)	4216.6(12)	1082.3(11)	26.6(6)
C37	5223(2)	4017.3(12)	1435.2(10)	25.0(5)
C32	4361(2)	3830.4(12)	1170.9(11)	28.6(6)
C31	4324(2)	3823.5(12)	582.1(11)	30.3(6)
C26	5074(2)	4000.5(12)	227.4(11)	28.7(6)
C27	4970(2)	3960.5(13)	-418.3(12)	33.8(7)

C29	4041(3)	4250.5(16)	-608.0(14)	50.4(9)
C28	5809(3)	4240.4(16)	-725.3(12)	46.9(9)
C30	4921(3)	3325.3(14)	-577.9(12)	43.3(8)
C25	5875(2)	4205.8(12)	489.0(11)	28.6(6)
C33	3499(2)	3641.5(17)	1524.6(13)	41.3(8)
C36	3754(3)	3123.8(18)	1879.7(14)	53.9(10)
C34	2630(2)	3482(2)	1155.3(15)	66.7(13)
C35	3182(2)	4136(2)	1907.1(16)	61.5(12)
C38	6078(4)	4773(2)	4275.1(17)	77.8(14)
C39	6357(3)	4965.9(18)	4832.1(18)	57.7(10)

Table SI3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Emily021716_1_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	20.01(5)	17.24(5)	24.94(5)	-0.96(4)	-0.56(3)	-1.05(4)
O1	23.1(10)	25.3(11)	29.3(9)	4.0(8)	0.9(7)	-1.8(8)
O2	23.1(10)	29.9(11)	27.9(9)	-2.4(8)	-3.9(7)	-0.6(9)
O3	31.1(11)	24.5(11)	32.5(10)	-6.4(8)	3.1(8)	-2.0(9)
O4	31.7(11)	22.3(10)	28.8(9)	-5.0(8)	-2.7(8)	2.5(9)
N1	21.9(12)	19.6(12)	33.7(11)	4.3(9)	1.6(9)	0.1(9)
N2	28.4(12)	17.6(12)	30.4(11)	1.1(9)	-4.7(9)	-5(1)
N4	120(4)	96(4)	75(3)	-20(3)	-34(3)	14(3)
N3	24.4(11)	21.8(11)	25.5(10)	-3.0(8)	0.0(9)	-4.9(9)
C17	26.0(14)	28.2(16)	26.2(12)	-2.9(11)	3.1(10)	0.1(12)
C16	23.6(15)	26.9(16)	39.5(15)	2.2(12)	3.4(11)	5.3(12)
C15	23.7(14)	20.7(15)	35.7(14)	3.1(11)	-1.9(11)	-1.7(11)
C14	25.6(14)	19.4(14)	31.5(13)	4.2(11)	1.2(11)	-2.5(12)
C13	27.6(15)	26.9(16)	33.7(13)	3.7(12)	-3.0(11)	-4.1(12)
C8	31.5(15)	24.6(15)	31.0(13)	2.8(12)	2.5(11)	-6.8(13)
C7	30.1(16)	20.4(15)	37.7(14)	1.9(12)	7.7(11)	-4.3(12)
C2	24.7(14)	13.8(13)	35.8(13)	1.6(11)	2.5(11)	-0.3(11)
C1	25.7(14)	15.3(13)	31.5(13)	2.5(11)	0.9(10)	-2.3(11)
C3	21.9(14)	25.7(16)	43.1(15)	5.8(13)	0.7(12)	-0.4(12)
C4	32.4(17)	31.4(19)	62(2)	9.8(16)	-8.8(15)	2.9(14)
C6	24.7(16)	47(2)	53.1(19)	-2.4(16)	3.7(14)	-0.8(15)
C5	25.7(15)	31.9(17)	41.8(15)	3.2(13)	-2.7(12)	-7.8(13)
C12	39.8(18)	50(2)	30.2(14)	0.3(14)	2.4(13)	-12.6(16)
C10	106(4)	142(5)	44(2)	-29(3)	5(2)	30(4)
C9	145(5)	93(4)	42(2)	27(2)	-17(2)	-73(4)
C11	69(3)	127(4)	35.4(18)	4(2)	-9.8(18)	-45(3)
C18	28.6(16)	47(2)	39.5(15)	2.7(14)	-5.8(12)	2.7(16)
C19	21.8(15)	62(2)	45.7(17)	5.8(17)	-0.3(13)	-11.8(15)
C20	33.9(17)	37.3(19)	37.8(15)	2.1(13)	0.4(13)	-13.2(14)
C21	31.9(15)	23.5(15)	26.6(12)	-3.8(11)	-0.8(11)	-8.1(12)
C22	36.5(17)	22.5(16)	35.6(14)	2.5(12)	-6.3(12)	-10.9(13)
C23	32.6(15)	21.8(15)	29.2(13)	2.1(11)	-1.3(11)	-1.4(12)
C24	26.2(14)	21.3(15)	32.2(13)	0.1(11)	-6.5(11)	0.4(12)
C37	26.1(14)	20.6(14)	28.3(12)	-3.8(11)	-3.9(11)	4.8(12)
C32	25.0(14)	27.4(16)	33.4(13)	-6.0(12)	-3.8(10)	3.6(12)
C31	28.2(15)	27.7(16)	35.0(14)	-8.4(12)	-7.2(11)	2.5(12)
C26	36.6(16)	20.3(14)	29.2(13)	-1.4(11)	-7.8(11)	3.8(12)
C27	46.5(19)	26.4(16)	28.7(13)	-2.7(12)	-9.2(12)	-3.4(14)

C29	58(2)	47(2)	46.9(18)	3.2(17)	-23.4(17)	4.9(19)
C28	63(2)	49(2)	28.8(14)	0.8(15)	-5.9(15)	-13.5(19)
C30	62(2)	34.3(19)	33.8(15)	-7.5(14)	-1.0(15)	-5.6(17)
C25	33.0(16)	24.2(16)	28.6(13)	2.1(11)	-3.5(11)	-0.9(12)
C33	23.7(15)	63(2)	37.3(15)	-15.5(15)	0.9(12)	-4.0(16)
C36	48(2)	71(3)	43.0(18)	-4.5(18)	9.6(16)	-26(2)
C34	31.3(19)	117(4)	52(2)	-21(2)	-1.1(16)	-24(2)
C35	30.4(19)	95(4)	59(2)	-31(2)	3.2(16)	17(2)
C38	119(4)	57(3)	57(2)	-17(2)	-9(3)	6(3)
C39	67(3)	48(2)	59(2)	-8(2)	-7(2)	6(2)

Table SI4 Bond Lengths for Emily021716_1_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
U1	O1	2.2548(18)	C3	C4	1.548(4)
U1	O2	2.2603(18)	C3	C6	1.535(4)
U1	O3	1.7780(19)	C3	C5	1.532(4)
U1	O4	1.7901(18)	C12	C10	1.531(6)
U1	N1	2.532(2)	C12	C9	1.511(5)
U1	N2	2.508(2)	C12	C11	1.505(5)
U1	N3	2.623(2)	C18	C19	1.381(5)
O1	C1	1.328(3)	C19	C20	1.366(5)
O2	C37	1.327(3)	C20	C21	1.385(4)
N1	C16	1.467(3)	C21	C22	1.502(4)
N1	C15	1.280(3)	C23	C24	1.447(4)
N2	C22	1.464(3)	C24	C37	1.409(4)
N2	C23	1.282(3)	C24	C25	1.407(4)
N4	C39	1.122(5)	C37	C32	1.427(4)
N3	C17	1.355(4)	C32	C31	1.392(4)
N3	C21	1.338(4)	C32	C33	1.534(4)
C17	C16	1.497(4)	C31	C26	1.407(4)
C17	C18	1.404(4)	C26	C27	1.535(4)
C15	C14	1.451(4)	C26	C25	1.368(4)
C14	C13	1.419(4)	C27	C29	1.536(4)
C14	C1	1.418(4)	C27	C28	1.529(4)
C13	C8	1.372(4)	C27	C30	1.542(4)
C8	C7	1.398(4)	C33	C36	1.521(5)
C8	C12	1.543(4)	C33	C34	1.543(4)
C7	C2	1.391(4)	C33	C35	1.538(5)
C2	C1	1.420(4)	C38	C39	1.445(5)
C2	C3	1.532(4)			

Table SI5 Bond Angles for Emily021716_1_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	U1	O2	96.61(6)	O1	C1	C2	121.8(2)
O1	U1	N1	69.53(7)	C14	C1	C2	118.3(2)
O1	U1	N2	165.27(7)	C2	C3	C4	109.0(2)
O1	U1	N3	131.10(7)	C2	C3	C6	111.9(2)
O2	U1	N1	163.87(7)	C6	C3	C4	107.2(3)
O2	U1	N2	70.91(7)	C5	C3	C2	110.4(2)
O2	U1	N3	132.29(7)	C5	C3	C4	110.3(3)
O3	U1	O1	94.12(8)	C5	C3	C6	108.0(2)
O3	U1	O2	88.07(8)	C10	C12	C8	109.5(3)
O3	U1	O4	175.83(9)	C9	C12	C8	109.3(3)
O3	U1	N1	84.86(8)	C9	C12	C10	110.1(4)
O3	U1	N2	93.27(8)	C11	C12	C8	111.7(3)
O3	U1	N3	88.47(8)	C11	C12	C10	106.2(4)
O4	U1	O1	88.28(8)	C11	C12	C9	110.0(3)
O4	U1	O2	95.05(8)	C19	C18	C17	117.6(3)
O4	U1	N1	92.80(8)	C20	C19	C18	120.9(3)
O4	U1	N2	85.16(8)	C19	C20	C21	118.7(3)
O4	U1	N3	87.38(8)	N3	C21	C20	122.0(3)
N1	U1	N3	62.09(7)	N3	C21	C22	115.6(2)
N2	U1	N1	123.90(7)	C20	C21	C22	122.3(3)
N2	U1	N3	61.81(7)	N2	C22	C21	110.4(2)
C1	O1	U1	133.14(17)	N2	C23	C24	126.7(3)
C37	O2	U1	130.17(16)	C37	C24	C23	123.2(2)
C16	N1	U1	115.51(16)	C25	C24	C23	115.3(3)
C15	N1	U1	126.26(19)	C25	C24	C37	121.4(2)
C15	N1	C16	117.8(2)	O2	C37	C24	120.2(2)
C22	N2	U1	117.78(16)	O2	C37	C32	122.1(2)
C23	N2	U1	124.48(19)	C24	C37	C32	117.6(2)
C23	N2	C22	117.0(2)	C37	C32	C33	121.0(2)
C17	N3	U1	120.18(18)	C31	C32	C37	118.2(3)
C21	N3	U1	120.37(18)	C31	C32	C33	120.8(3)
C21	N3	C17	119.2(2)	C32	C31	C26	124.3(3)
N3	C17	C16	114.9(2)	C31	C26	C27	120.2(3)
N3	C17	C18	121.5(3)	C25	C26	C31	116.5(2)
C18	C17	C16	123.7(3)	C25	C26	C27	123.3(3)
N1	C16	C17	108.7(2)	C26	C27	C29	110.1(3)
N1	C15	C14	126.5(3)	C26	C27	C30	107.9(2)
C13	C14	C15	117.0(2)	C29	C27	C30	108.7(3)
C1	C14	C15	122.3(2)	C28	C27	C26	111.8(2)
C1	C14	C13	120.5(2)	C28	C27	C29	108.7(3)

C8	C13	C14	121.7(3)	C28	C27	C30	109.6(3)
C13	C8	C7	116.5(2)	C26	C25	C24	121.8(3)
C13	C8	C12	123.3(3)	C32	C33	C34	112.5(3)
C7	C8	C12	120.1(3)	C32	C33	C35	109.1(3)
C2	C7	C8	125.0(3)	C36	C33	C32	110.3(3)
C7	C2	C1	117.8(2)	C36	C33	C34	107.6(3)
C7	C2	C3	121.3(2)	C36	C33	C35	110.4(3)
C1	C2	C3	120.8(2)	C35	C33	C34	106.8(3)
O1	C1	C14	119.8(2)	N4	C39	C38	177.7(5)

Table SI6 Hydrogen Bonds for Emily021716_1_0m.

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
C23	H23	N4[1]	0.95	2.71	3.642(5)	167.5
C38	H38B	O4	0.98	2.61	3.217(4)	120.4
C38	H38B	O4	0.98	2.61	3.217(4)	120.4
C38	H38B	O4	0.98	2.61	3.217(4)	120.4
C38	H38B	O4	0.98	2.61	3.217(4)	120.4

[1]3/2-X,+Y,-1/2+Z

Table SI7 Torsion Angles for Emily021716_1_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
U1	O1	C1	C14	-45.0(4)	C7	C2	C3	C4	116.1(3)
U1	O1	C1	C2	137.3(2)	C7	C2	C3	C6	-2.3(4)
U1	O2	C37	C24	-44.9(4)	C7	C2	C3	C5	-122.5(3)
U1	O2	C37	C32	138.0(2)	C1	C14	C13	C8	-0.9(4)
U1	N1	C16	C17	49.9(3)	C1	C2	C3	C4	-63.5(3)
U1	N1	C15	C14	13.1(4)	C1	C2	C3	C6	178.1(3)
U1	N2	C22	C21	41.9(3)	C1	C2	C3	C5	57.8(3)
U1	N2	C23	C24	14.3(4)	C3	C2	C1	O1	0.4(4)
U1	N3	C17	C16	5.3(3)	C3	C2	C1	C14	-177.3(2)
U1	N3	C17	C18	-175.2(2)	C12	C8	C7	C2	-178.8(3)
U1	N3	C21	C20	172.5(2)	C18	C17	C16	N1	145.8(3)
U1	N3	C21	C22	-7.5(3)	C18	C19	C20	C21	-0.2(5)
O2	C37	C32	C31	-179.0(3)	C19	C20	C21	N3	2.4(4)
O2	C37	C32	C33	1.0(4)	C19	C20	C21	C22	-177.6(3)
N1	C15	C14	C13	-168.2(3)	C20	C21	C22	N2	159.0(3)
N1	C15	C14	C1	17.2(5)	C21	N3	C17	C16	179.7(2)
N2	C23	C24	C37	17.7(5)	C21	N3	C17	C18	-0.8(4)
N2	C23	C24	C25	-167.3(3)	C22	N2	C23	C24	-175.7(3)
N3	C17	C16	N1	-34.7(3)	C23	N2	C22	C21	-128.8(3)
N3	C17	C18	C19	2.8(4)	C23	C24	C37	O2	-5.6(4)
N3	C21	C22	N2	-21.0(3)	C23	C24	C37	C32	171.6(3)
C17	N3	C21	C20	-1.9(4)	C23	C24	C25	C26	-175.4(3)
C17	N3	C21	C22	178.1(2)	C24	C37	C32	C31	3.8(4)
C17	C18	C19	C20	-2.3(5)	C24	C37	C32	C33	-176.2(3)
C16	N1	C15	C14	-174.4(3)	C37	C24	C25	C26	-0.2(4)
C16	C17	C18	C19	-177.7(3)	C37	C32	C31	C26	-1.4(4)
C15	N1	C16	C17	-123.4(3)	C37	C32	C33	C36	-62.4(4)
C15	C14	C13	C8	-175.6(3)	C37	C32	C33	C34	177.5(3)
C15	C14	C1	O1	-5.5(4)	C37	C32	C33	C35	59.1(4)
C15	C14	C1	C2	172.2(3)	C32	C31	C26	C27	178.3(3)
C14	C13	C8	C7	2.9(4)	C32	C31	C26	C25	-1.9(4)
C14	C13	C8	C12	179.6(3)	C31	C32	C33	C36	117.6(3)
C13	C14	C1	O1	-179.9(2)	C31	C32	C33	C34	-2.6(5)
C13	C14	C1	C2	-2.2(4)	C31	C32	C33	C35	-120.9(3)
C13	C8	C7	C2	-1.9(4)	C31	C26	C27	C29	52.0(4)
C13	C8	C12	C10	132.7(4)	C31	C26	C27	C28	173.0(3)
C13	C8	C12	C9	-106.6(4)	C31	C26	C27	C30	-66.5(4)
C13	C8	C12	C11	15.4(5)	C31	C26	C25	C24	2.7(4)
C8	C7	C2	C1	-1.1(4)	C27	C26	C25	C24	-177.5(3)
C8	C7	C2	C3	179.3(3)	C25	C24	C37	O2	179.6(3)

C7	C8	C12	C10	-50.7(4)	C25	C24	C37	C32	-3.1(4)
C7	C8	C12	C9	70.0(4)	C25	C26	C27	C29	-127.8(3)
C7	C8	C12	C11	-168.0(3)	C25	C26	C27	C28	-6.8(4)
C7	C2	C1	O1	-179.3(2)	C25	C26	C27	C30	113.7(3)
C7	C2	C1	C14	3.1(4)	C33	C32	C31	C26	178.6(3)

Table SI8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Emily021716_1_0m.

Atom	*x*	*y*	*z*	U(eq)
H16A	8551	2794	2688	36
H16B	9042	2955	3281	36
H15	8066	3023	3950	32
H13	7279	3169	4817	35
H7	4425	3251	4885	35
H4A	3874	4163	3736	63
H4B	3177	3858	3292	63
H4C	4304	3870	3180	63
H6A	3151	2895	4449	63
H6B	2488	3263	4036	63
H6C	3153	3574	4491	63
H5A	4336	2766	3125	50
H5B	3200	2809	3185	50
H5C	3796	2416	3611	50
H10A	5254	3662	6264	146
H10B	4575	3613	5722	146
H10C	5463	4041	5715	146
H9A	5910	2325	5639	140
H9B	4847	2574	5674	140
H9C	5533	2602	6216	140
H11A	6825	3305	6262	116
H11B	7091	3672	5714	116
H11C	7286	3001	5721	116
H18	10479	3476	2872	46
H19	10987	4338	2476	52
H20	9894	4947	2057	44
H22A	7804	5126	2185	38
H22B	8244	4969	1578	38
H23	7181	4702	1033	33
H31	3754	3690	408	36
H29A	3496	4072	-417	76
H29B	3968	4210	-1019	76
H29C	4064	4655	-509	76
H28A	5831	4646	-629	70
H28B	5726	4197	-1135	70
H28C	6406	4058	-608	70
H30A	5496	3132	-441	65
H30B	4881	3288	-990	65
H30C	4355	3153	-404	65

H25	6387	4345	264	34
H36A	3980	2818	1632	81
H36B	3188	2995	2087	81
H36C	4259	3225	2149	81
H34A	2792	3153	918	100
H34B	2459	3805	914	100
H34C	2088	3385	1400	100
H35A	2640	4015	2140	92
H35B	2991	4460	1672	92
H35C	3714	4249	2153	92
H38A	5820	4386	4301	117
H38B	6637	4774	4025	117
H38C	5589	5028	4122	117

Crystal Data for $C_{40}H_{52}N_3O_4U$ (M =876.87): orthorhombic, space group Pccn (no. 56), a = 13.9974(3) Å, b = 23.5111(5) Å, c = 23.6244(5) Å, V = 7774.7(3) Å^3, Z = 8, T = 180(2) K, μ(MoKα) = 4.217 mm^{-1}, *Dcalc* = 1.498 g/mm^3, 93148 reflections measured (3.386 ≤ 2Θ ≤ 61.054), 11882 unique (R_{int} = 0.0538, R_{sigma} = 0.0376) which were used in all calculations. The final R_1 was 0.0305 (I > 2σ(I)) and wR_2 was 0.0699 (all data).

Single crystals of $C_{40}H_{52}N_3O_4U$ [Emily021716_1_0m] were grown from slow evaporation of ACN. A suitable crystal was selected and mounted using paratone-n oil and data collection was completed on a 'Bruker APEX CCD' diffractometer. The crystal was kept at 180(2) K during data collection. The structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [2] refinement package using Least Squares minimisation. Projections were created on Olex2 software.[3]

Table SI9 Crystal data and structure refinement for Emily051916_0maFINAL.

Identification code	Emily051916_0maFINAL
Empirical formula	$C_{29}H_{21}N_3O_4U$
Formula weight	713.54
Temperature/K	180.45
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.8062(10)
b/Å	7.2736(3)
c/Å	14.7805(6)
α/°	90
β/°	97.3343(5)
γ/°	90
Volume/Å^3	2431.78(18)
Z	4
ρ_{calc}mg/mm^3	1.9488
m/mm^{-1}	6.720
F(000)	1320.2
Crystal size/mm^3	0.12 × 0.12 × 0.04
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	3.6 to 63.04°
Index ranges	-33 ≤ h ≤ 33, -10 ≤ k ≤ 10, -21 ≤ l ≤ 21
Reflections collected	61345
Independent reflections	8098 [R_{int} = 0.0473, R_{sigma} = 0.0295]
Data/restraints/parameters	8098/0/333
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0726
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.0755
Largest diff. peak/hole / e Å^{-3}	3.18/-5.58

Table SI10 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Emily051916_0maFINAL. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
U1	2665.70(6)	6702.81(17)	3444.78(8)	11.33(4)
O2	2136.0(12)	7009(4)	2047.1(18)	17.0(5)
N1	3348.1(15)	7175(4)	4877(2)	15.4(6)
N2	1903.7(14)	4179(4)	3165(2)	13.1(5)
N3	2567.2(14)	4501(4)	4773(2)	12.7(5)
C16	2222.4(16)	1657(5)	5326(2)	15.1(6)
C12	3100.6(18)	6796(5)	5724(2)	17.6(7)
C10	4217.0(17)	8071(5)	4181(3)	15.8(7)
C13	2784.3(16)	4964(5)	5633(2)	13.6(6)
C17	2290.3(16)	2866(5)	4620(2)	12.5(6)
C15	2440.4(18)	2166(6)	6211(3)	18.4(7)
C14	2723.0(18)	3845(5)	6371(2)	16.9(7)
C9	4855.3(18)	8040(5)	4312(3)	18.6(7)
C6	6105(2)	8122(6)	4530(4)	31.4(10)
C2	4239(2)	9706(6)	2745(3)	24.1(8)
C11	3904.7(18)	7518(5)	4933(3)	16.3(7)
C1	3909.9(18)	8868(5)	3394(3)	17.9(7)
C4	5168.0(19)	8844(6)	3631(3)	21.7(8)
C3	4840(2)	9677(6)	2857(3)	25.2(9)
C7	5804(2)	7308(6)	5196(4)	29.6(10)
C8	5193.4(19)	7258(6)	5080(3)	22.8(8)
C5	5795(2)	8846(6)	3757(3)	28.1(9)
C20	1173.9(17)	5694(5)	2060(3)	16.3(7)
C18	2084.2(18)	2459(5)	3636(3)	15.9(7)
C19	1398.8(16)	4216(5)	2666(2)	15.3(7)
C21	556.4(17)	5688(6)	1688(3)	20.0(7)
C28	1348(2)	8183(7)	1038(3)	30.9(10)
C29	1566.0(17)	6964(5)	1745(3)	16.2(7)
C27	775(2)	8159(6)	656(3)	30.4(10)
C25	-238(2)	6881(7)	564(3)	30.1(10)
C26	358.6(19)	6932(6)	967(3)	23.6(8)
C24	-629(2)	5666(8)	862(4)	34.7(11)
O4	3167.7(12)	5102(4)	3040.0(18)	17.9(5)
O3	2151.1(13)	8170(4)	3898(2)	19.6(5)
C22	131.8(19)	4501(7)	1993(3)	29.2(10)
C23	-446(2)	4490(8)	1590(4)	34.6(11)
O1	3322.6(13)	8957(4)	3251(2)	20.7(6)

Table SI11 Anisotropic Displacement Parameters (Å^2×10^3) for Emily051916_0maFINAL. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}

U1	13.96(6)	9.98(6)	9.63(6)	-0.66(5)	-0.14(4)	1.18(5)
O2	14.8(12)	21.6(14)	13.9(12)	-1.3(10)	-0.8(9)	5.2(10)
N1	21.7(16)	12.1(13)	12.3(13)	-3.5(11)	1.0(12)	-0.6(10)
N2	18.3(15)	11.1(13)	9.9(13)	-1.6(11)	2.0(11)	-0.4(10)
N3	14.6(14)	12.0(13)	11.2(13)	0.2(11)	0.4(10)	-0.4(10)
C16	16.2(16)	12.8(15)	15.9(15)	-1.1(13)	0.1(12)	3.0(13)
C12	24.8(18)	17.6(16)	10.2(15)	-2.5(15)	0.9(13)	-1.6(13)
C10	20.0(17)	12.3(16)	14.8(15)	-4.3(13)	1.5(13)	-0.2(12)
C13	14.5(15)	14.8(15)	11.4(14)	2.0(13)	1.2(12)	-0.5(12)
C17	14.0(15)	10.6(14)	12.8(15)	0.8(11)	1.4(12)	1.2(11)
C15	21.1(18)	20.8(17)	14.0(16)	-0.9(14)	4.7(14)	5.2(13)
C14	20.3(18)	20.6(17)	10.0(15)	0.9(14)	2.4(13)	1.0(13)
C9	21.8(18)	12.7(16)	21.2(18)	-2.0(13)	1.6(14)	-5.0(13)
C6	17.2(19)	27(2)	50(3)	2.3(16)	4.9(19)	-14(2)
C2	33(2)	22.2(19)	17.2(17)	-9.2(17)	1.9(16)	2.9(15)
C11	22.4(18)	11.0(15)	14.4(16)	-1.8(13)	-2.2(13)	1.1(12)
C1	19.7(18)	15.4(16)	17.8(17)	-6.5(14)	-1.1(14)	1.0(13)
C4	23(2)	16.7(17)	26(2)	-4.9(15)	5.9(16)	-7.5(15)
C3	31(2)	26(2)	20.7(19)	-10.6(17)	8.7(16)	-2.2(16)
C7	22(2)	22(2)	43(3)	5.5(16)	-4.1(19)	-6.3(19)
C8	22.8(19)	14.8(17)	30(2)	-1.8(14)	-1.9(16)	-1.5(15)
C5	25(2)	24(2)	38(2)	-5.0(17)	11.7(19)	-10.5(18)
C20	14.9(16)	18.1(16)	15.5(16)	1.0(13)	0.1(13)	0.3(13)
C18	24.2(19)	8.5(15)	14.2(16)	0.3(13)	-0.8(13)	1.6(12)
C19	14.1(16)	18.1(16)	13.3(15)	-1.5(13)	0.5(12)	2.0(13)
C21	14.8(17)	25.1(19)	19.3(18)	4.4(15)	-1.1(14)	-1.6(15)
C28	31(2)	32(2)	28(2)	-1.6(19)	-5.0(18)	14.4(19)
C29	16.6(17)	17.5(17)	13.5(15)	1.6(13)	-2.1(12)	0.3(13)
C27	29(2)	25(2)	34(2)	3.9(18)	-8.6(18)	11.2(18)
C25	22(2)	36(3)	30(2)	10.3(18)	-6.7(17)	-1.4(19)
C26	18.0(18)	26(2)	25(2)	6.4(15)	-4.0(15)	0.6(16)
C24	15(2)	49(3)	38(3)	7.3(19)	-3.6(18)	-8(2)
O4	15.0(12)	22.4(13)	15.6(12)	1.8(11)	-0.5(9)	-0.8(11)
O3	22.9(14)	15.6(12)	20.6(13)	3.0(11)	3.7(11)	-1.1(11)
C22	17.3(19)	41(3)	29(2)	-3.1(18)	1.1(16)	5.6(19)
C23	17(2)	47(3)	39(3)	-2.1(19)	3.0(18)	1(2)
O1	21.6(14)	20.1(13)	19.1(13)	-6.1(11)	-3.2(11)	7.6(11)

Table SI12 Bond Lengths for Emily051916_0maFINAL.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
U1	O2	2.267(3)	C9	C4	1.430(6)
U1	N1	2.486(3)	C9	C8	1.409(6)
U1	N2	2.525(3)	C6	C7	1.401(7)
U1	N3	2.565(3)	C6	C5	1.369(8)
U1	O4	1.789(3)	C2	C1	1.428(5)
U1	O3	1.780(3)	C2	C3	1.360(6)
U1	O1	2.264(3)	C1	O1	1.331(5)
O2	C29	1.320(5)	C4	C3	1.421(6)
N1	C12	1.464(5)	C4	C5	1.419(6)
N1	C11	1.286(5)	C7	C8	1.382(6)
N2	C18	1.465(5)	C20	C19	1.450(5)
N2	C19	1.286(5)	C20	C21	1.445(5)
N3	C13	1.348(4)	C20	C29	1.406(5)
N3	C17	1.352(4)	C21	C26	1.426(6)
C16	C17	1.388(5)	C21	C22	1.414(6)
C16	C15	1.389(5)	C28	C29	1.412(6)
C12	C13	1.513(5)	C28	C27	1.356(7)
C10	C9	1.444(6)	C27	C26	1.421(7)
C10	C11	1.451(5)	C25	C26	1.415(6)
C10	C1	1.404(5)	C25	C24	1.367(8)
C13	C14	1.382(5)	C24	C23	1.396(8)
C17	C18	1.501(5)	C22	C23	1.375(6)
C15	C14	1.387(6)			

Table SI13 Bond Angles for Emily051916_0maFINAL.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	U1	O2	164.84(10)	C18	C17	C16	123.5(3)
N2	U1	O2	69.31(10)	C14	C15	C16	119.9(3)
N2	U1	N1	125.66(10)	C15	C14	C13	118.4(3)
N3	U1	O2	132.07(10)	C4	C9	C10	119.0(4)
N3	U1	N1	62.70(10)	C8	C9	C10	123.6(4)
N3	U1	N2	62.99(9)	C8	C9	C4	117.5(4)
O4	U1	O2	92.78(11)	C5	C6	C7	120.2(4)
O4	U1	N1	90.97(11)	C3	C2	C1	121.3(4)
O4	U1	N2	85.90(11)	C10	C11	N1	125.5(3)
O4	U1	N3	88.38(11)	C2	C1	C10	118.9(4)
O3	U1	O2	89.08(12)	O1	C1	C10	122.5(3)
O3	U1	N1	88.15(12)	O1	C1	C2	118.5(4)
O3	U1	N2	91.39(12)	C3	C4	C9	118.8(4)
O3	U1	N3	87.69(11)	C5	C4	C9	119.5(4)
O3	U1	O4	175.94(13)	C5	C4	C3	121.6(4)
O1	U1	O2	95.60(10)	C4	C3	C2	121.6(4)
O1	U1	N1	69.84(10)	C8	C7	C6	120.0(5)
O1	U1	N2	163.42(10)	C7	C8	C9	121.9(4)
O1	U1	N3	132.31(10)	C4	C5	C6	120.9(4)
O1	U1	O4	88.10(12)	C21	C20	C19	118.9(3)
O1	U1	O3	95.31(12)	C29	C20	C19	120.1(3)
C29	O2	U1	133.9(2)	C29	C20	C21	120.4(4)
C12	N1	U1	115.8(2)	C17	C18	N2	109.0(3)
C11	N1	U1	126.0(3)	C20	C19	N2	126.1(3)
C11	N1	C12	117.8(3)	C26	C21	C20	118.9(4)
C18	N2	U1	113.4(2)	C22	C21	C20	123.6(4)
C19	N2	U1	128.8(3)	C22	C21	C26	117.5(4)
C19	N2	C18	117.8(3)	C27	C28	C29	122.0(4)
C13	N3	U1	120.6(2)	C20	C29	O2	123.0(3)
C17	N3	U1	120.4(2)	C28	C29	O2	118.2(4)
C17	N3	C13	119.0(3)	C28	C29	C20	118.6(4)
C15	C16	C17	118.5(3)	C26	C27	C28	121.5(4)
C13	C12	N1	108.7(3)	C24	C25	C26	120.9(4)
C11	C10	C9	118.6(3)	C27	C26	C21	118.6(4)
C1	C10	C9	120.3(3)	C25	C26	C21	119.6(4)
C1	C10	C11	120.5(4)	C25	C26	C27	121.8(4)
C12	C13	N3	114.7(3)	C23	C24	C25	120.0(4)
C14	C13	N3	122.4(3)	C23	C22	C21	121.6(5)
C14	C13	C12	122.9(3)	C22	C23	C24	120.4(5)
C16	C17	N3	121.8(3)	C1	O1	U1	127.9(2)
C18	C17	N3	114.6(3)				

Table SI14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Emily051916_0maFINAL.

Atom	*x*	*y*	*z*	U(eq)
H16	2031.1(16)	506(5)	5206(2)	18.2(7)
H12a	3420.9(18)	6759(5)	6243(2)	21.2(8)
H12b	2819.9(18)	7781(5)	5840(2)	21.2(8)
H15	2396.0(18)	1366(6)	6705(3)	22.1(9)
H14	2870.9(18)	4217(5)	6973(2)	20.3(8)
H6	6525(2)	8172(6)	4615(4)	37.6(12)
H2	4034(2)	10295(6)	2224(3)	28.9(10)
H11	4130.7(18)	7398(5)	5516(3)	19.6(8)
H3	5045(2)	10227(6)	2407(3)	30.2(10)
H7	6020(2)	6790(6)	5727(4)	35.5(12)
H8	4995.8(19)	6680(6)	5532(3)	27.4(10)
H5	6003(2)	9356(6)	3299(3)	33.7(11)
H18a	1746.6(18)	1594(5)	3587(3)	19.1(8)
H18b	2407.7(18)	1880(5)	3350(3)	19.1(8)
H19	1149.7(16)	3177(5)	2697(2)	18.3(8)
H28	1611(2)	9045(7)	822(3)	37.1(12)
H27	649(2)	8980(6)	170(3)	36.5(12)
H25	-369(2)	7702(7)	81(3)	36.1(12)
H24	-1026(2)	5622(8)	573(4)	41.7(13)
H22	248.4(19)	3692(7)	2488(3)	35.1(12)
H23	-722(2)	3678(8)	1809(4)	41.6(13)

Crystal Data for $C_{29}H_{21}N_3O_4U$ (*M* =713.54): monoclinic, space group $P2_1/c$ (no. 14), *a* = 22.8062(10) Å, *b* = 7.2736(3) Å, *c* = 14.7805(6) Å, *β* = 97.3343(5)°, *V* = 2431.78(18) Å^3, *Z* = 4, *T* = 180.45 K, μ(Mo Kα) = 6.720 mm^{-1}, *Dcalc* = 1.9488 g/mm^3, 61345 reflections measured (3.6 ≤ 2Θ ≤ 63.04), 8098 unique (R_{int} = 0.0473, R_{sigma} = 0.0295) which were used in all calculations. The final R_1 was 0.0359 (I>=2u(I)) and wR_2 was 0.0755 (all data).

Single crystals of C29H21N3O4U [Emily051916_0maFINAL] were grown from slow diffusion of hexanes into DCM. A suitable crystal was selected mounted using paratone-n oil and data collection was completed on a 'Bruker APEX CCD' diffractometer. The crystal was kept at 180.45 K during data collection. The structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

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