Nine isomorphous lanthanide-uranyl f-f bimetallic materials with 2-thiophenecarboxylic acid and terpyridine: structure and concomitant luminescent properties

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Supporting Information

I. Powder X-ray Diffraction Patterns

The bulk reaction products of all complexes are impure and typically a mixture of two phases; the title complexes and the recently reported Ln^{3+} dimer complexes, $[Ln_2(TPY)_2(C_5H_3O_2S)_4(\mu\text{-}C_5H_3O_2S)_2(H_2O)_2]\cdot nH_2O$ (Ln = La–Ho, excluding Pm).[1] In all patterns presented below, the calculated powder patterns of the title complexes are provided as well as the calculated patterns of the Ln^{3+} only dimer phases. All nomenclature associated with complexes presented in the paper by Knope *et al.* was used to reference the materials herein.[1]

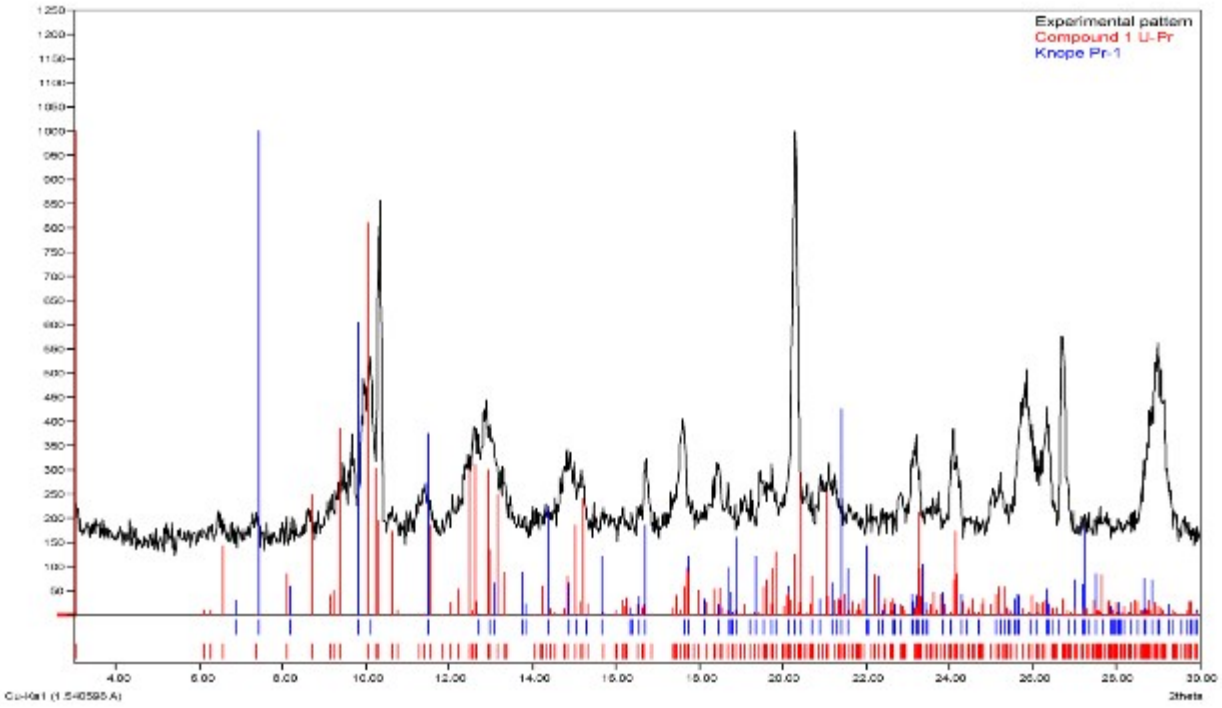


Figure S1: The PXRD pattern of the bulk product of complex **1** with the calculated pattern overlaid in red. The calculated pattern of the Pr^{3+} only phase from Knope *et al.* is given in blue.[1]

[1] R. J. Batrice, J. A. Ridenour, R. L. Ayscue III, J. A. Bertke, K. E. Knope, CrystEngComm, 2017, 19, 5300-5312.

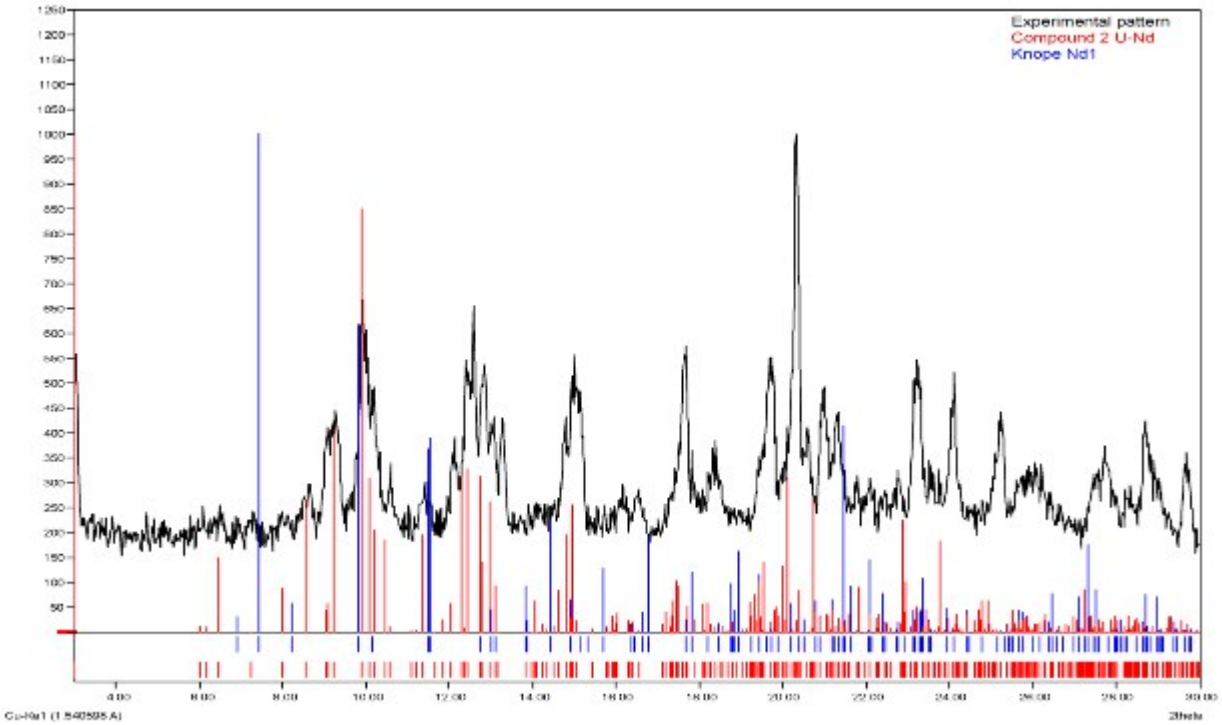


Figure S2: The PXRD pattern of the bulk product of complex **2** with the calculated pattern overlaid in red. The calculated pattern of the Nd^{3+} only phase from Knope *et al.* is given in blue.

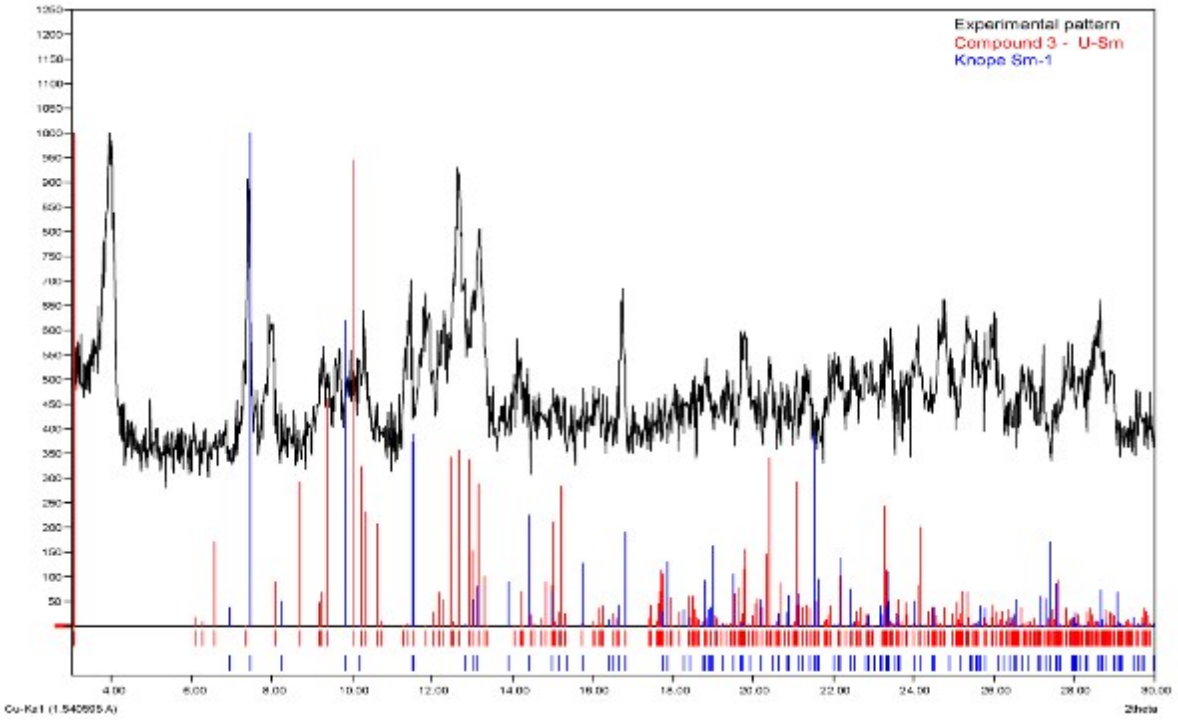


Figure S3: The PXRD pattern of the bulk product of complex **3** with the calculated pattern overlaid in red. The calculated pattern of the Sm^{3+} only phase from Knope *et al.* is given in blue. Unaccounted for peaks in the diffraction pattern correspond to an unknown impurity.

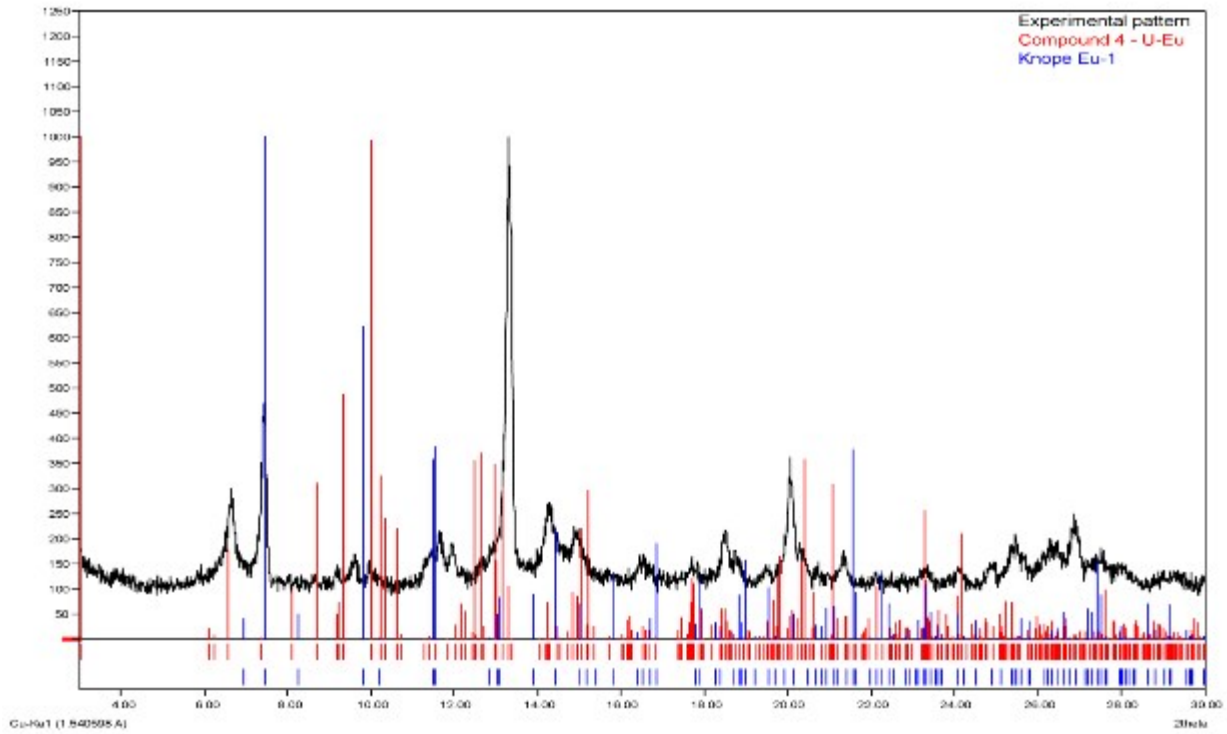


Figure S4: The PXRD pattern of the bulk product of complex **4** with the calculated pattern overlaid in red. The calculated pattern of the Eu^{3+} only phase from Knope *et al.* is given in blue.

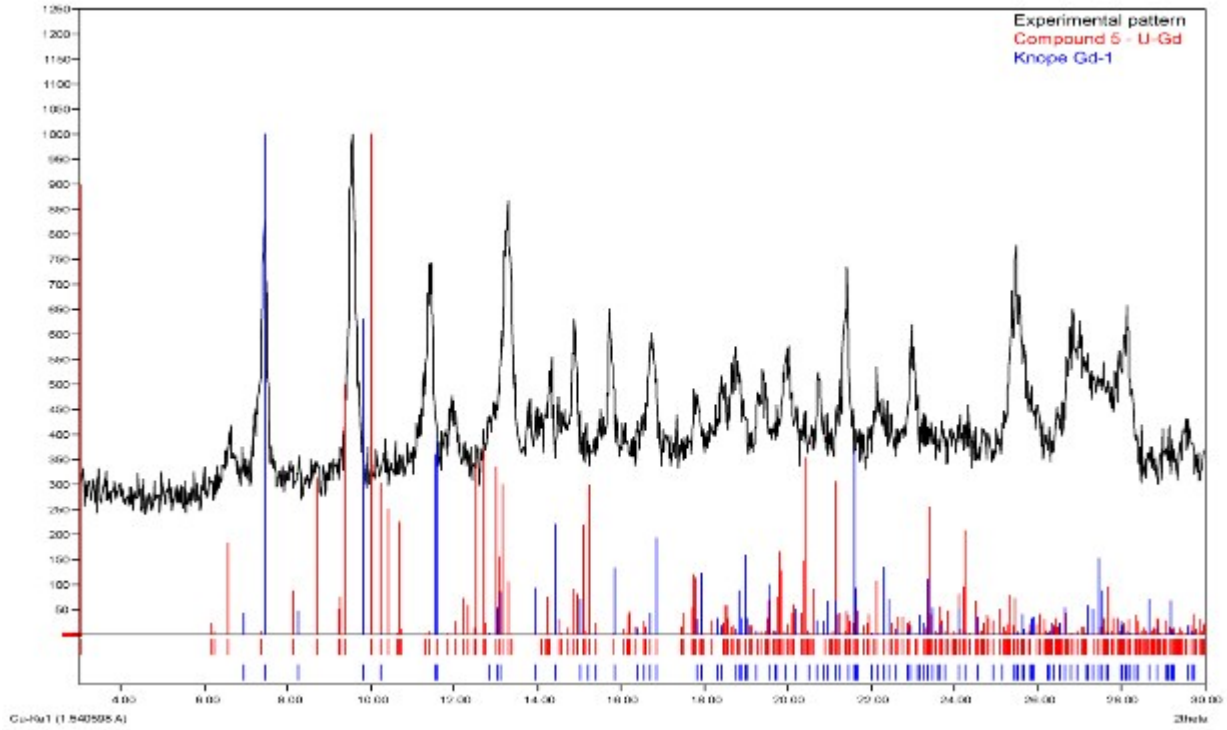


Figure S5: The PXRD pattern of the bulk product of complex **5** with the calculated pattern overlaid in red. The calculated pattern of the Gd^{3+} only phase from Knope *et al.* is given in blue.

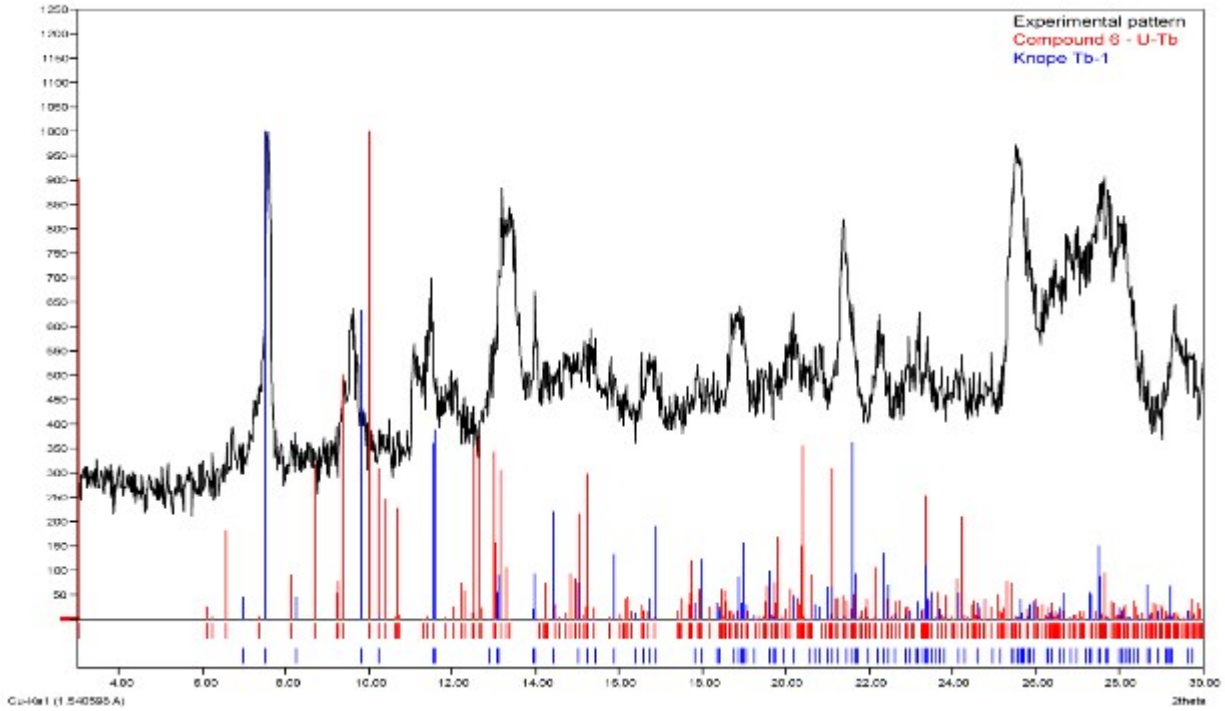


Figure S6: The PXRD pattern of the bulk product of complex **6** with the calculated pattern overlaid in red. The calculated pattern of the Tb^{3+} only phase from Knope *et al.* is given in blue.

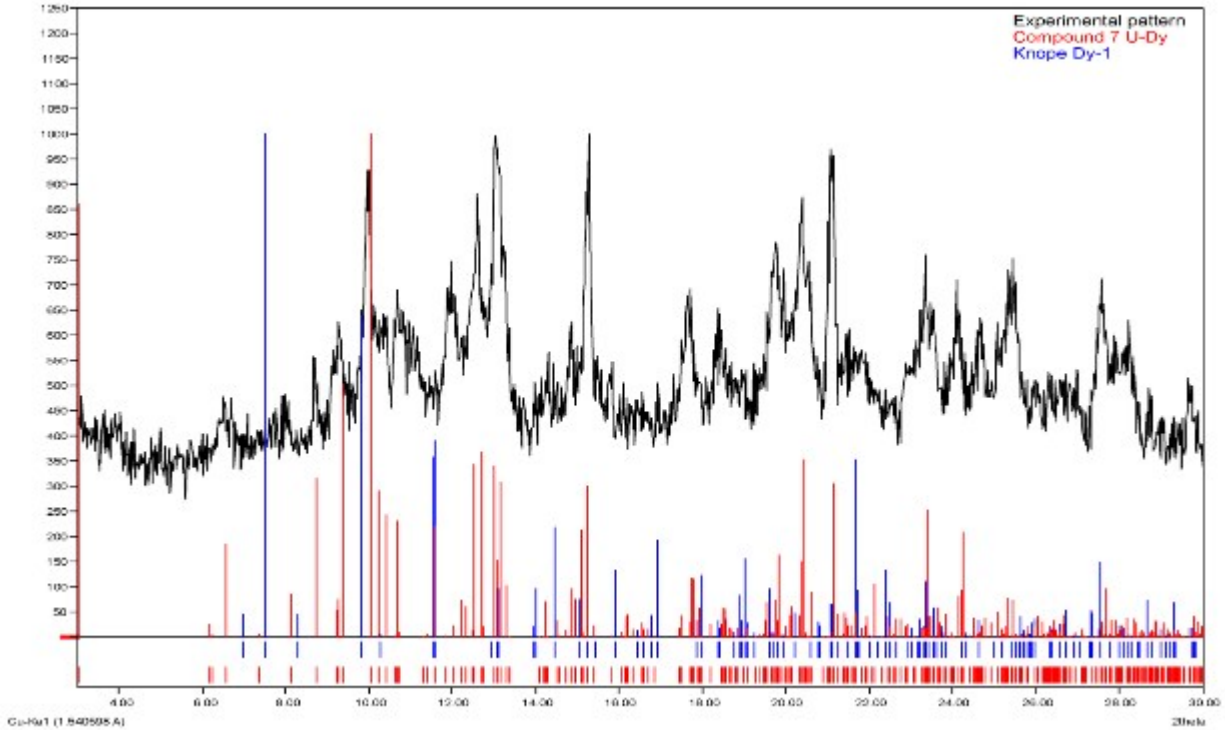


Figure S7: The PXRD pattern of the bulk product of complex **7** with the calculated pattern overlaid in red. The calculated pattern of the Dy^{3+} only phase from Knope *et al.* is given in blue.

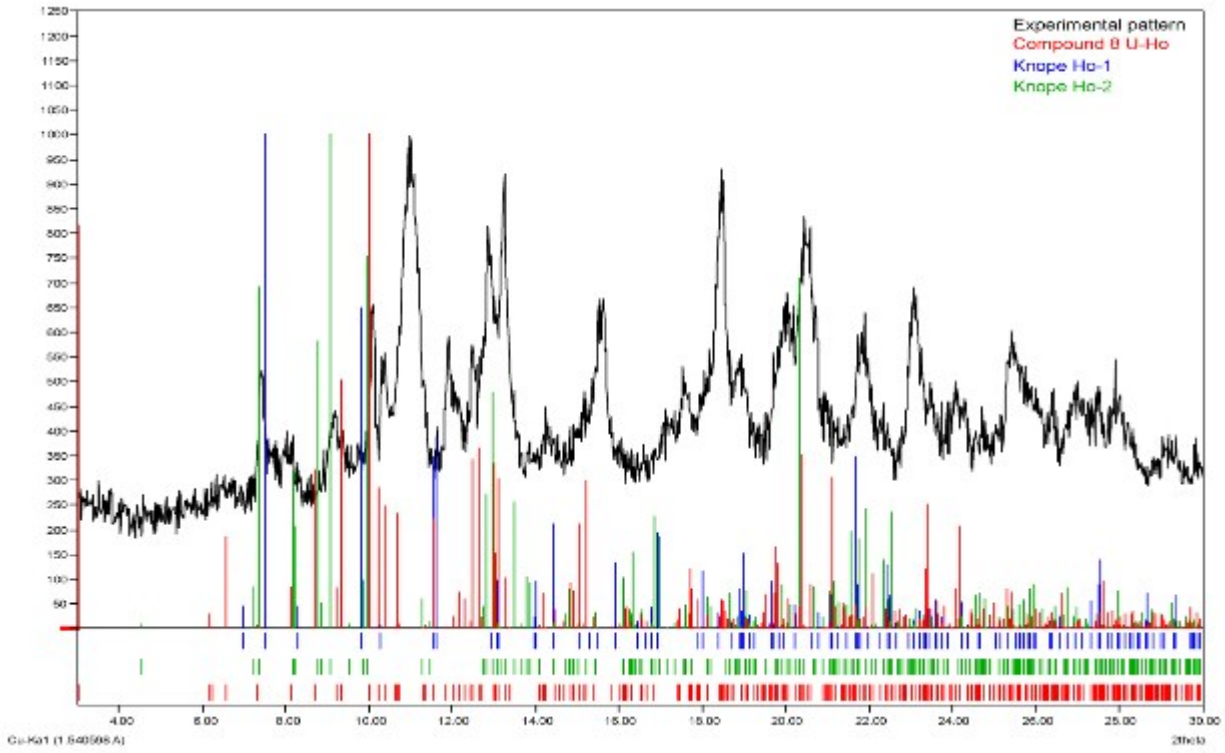


Figure S8: The PXRD pattern of the bulk product of complex **8** with the calculated pattern overlaid in red. The calculated patterns of Ho^{3+} phases from Knope *et al.* are in blue and green.

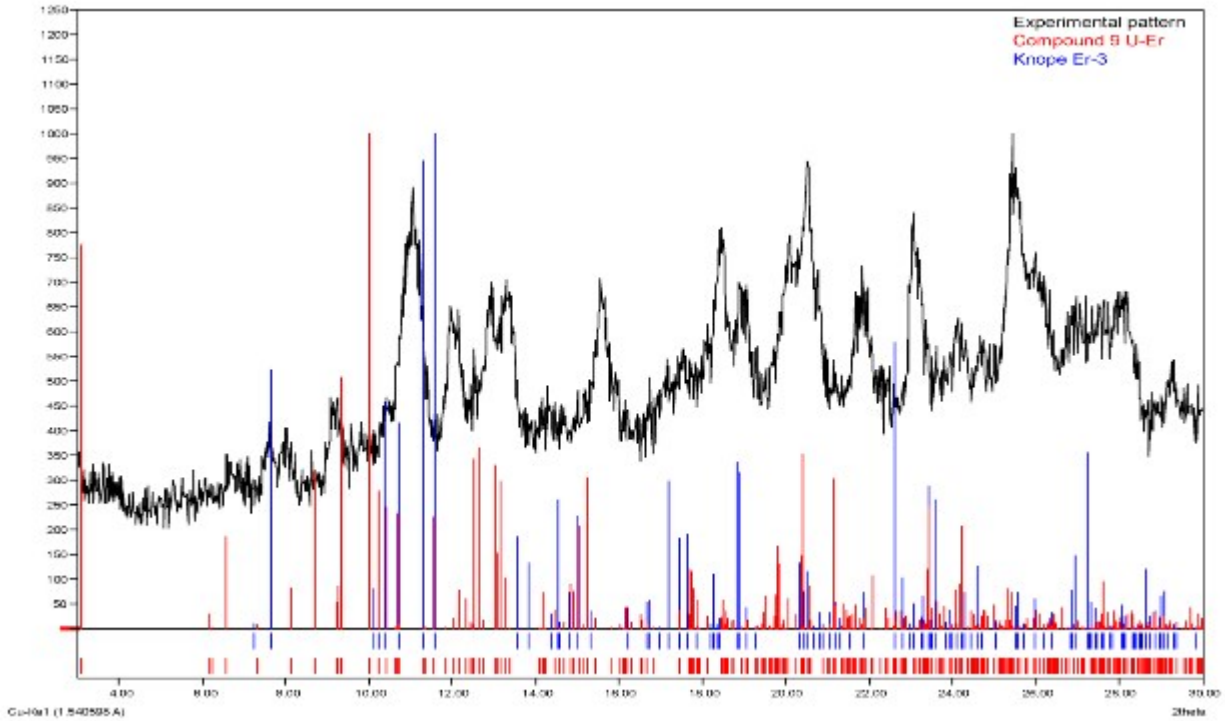


Figure S9: The PXRD pattern of the bulk product of complex **9** with the calculated pattern overlaid in red. The calculated pattern of the Er^{3+} only phase from Knope *et al.* is given in blue.

II. Thermal Ellipsoid Plots

The thermal ellipsoid plots provided below have, sometimes, been split up into multiple images for ease of viewing all atoms in each asymmetric unit due to the complexity of the three molecular units.

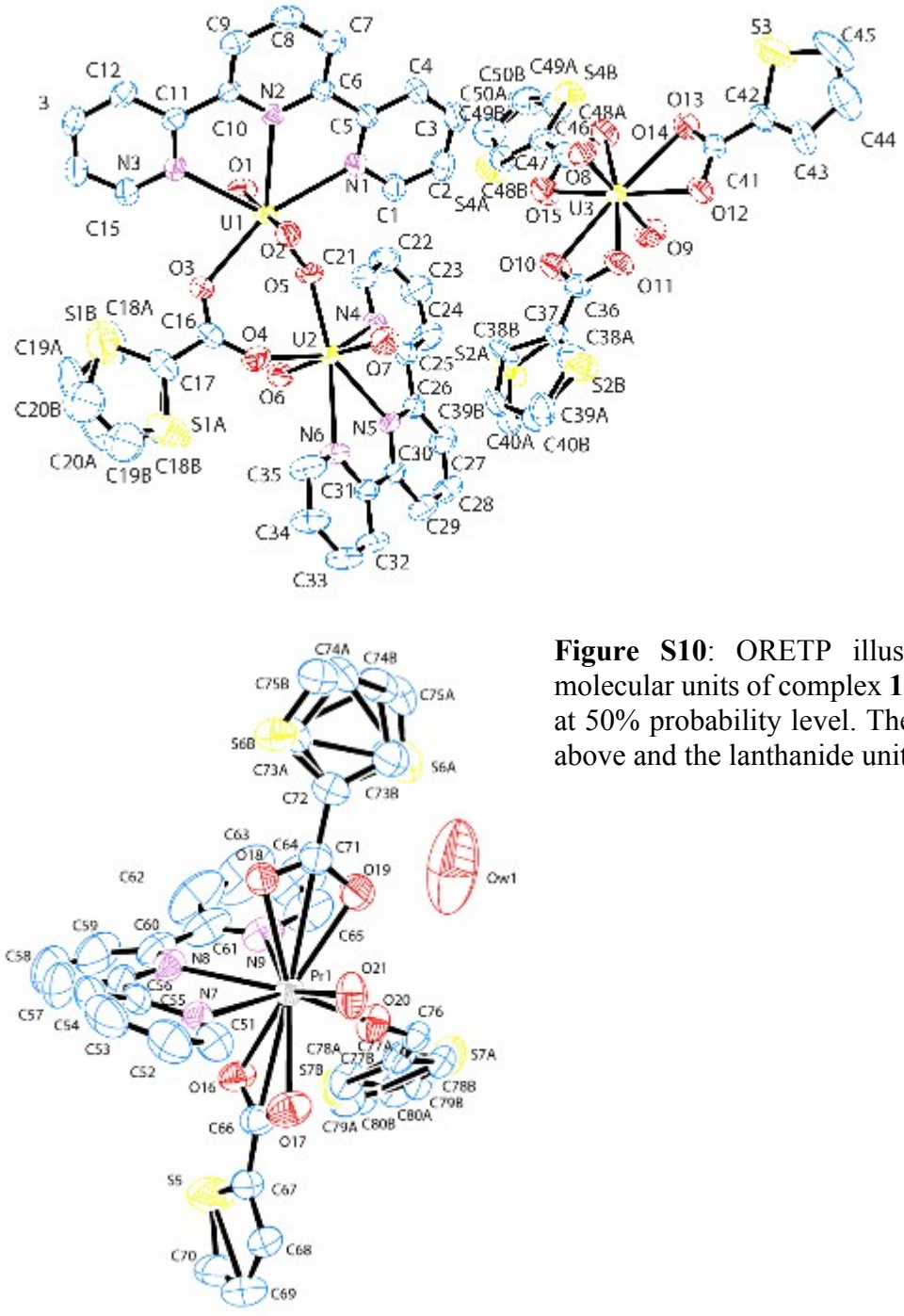


Figure S10: ORETP illustration of the three molecular units of complex **1**. Ellipsoids are shown at 50% probability level. The two uranyl units are above and the lanthanide unit is to the left.

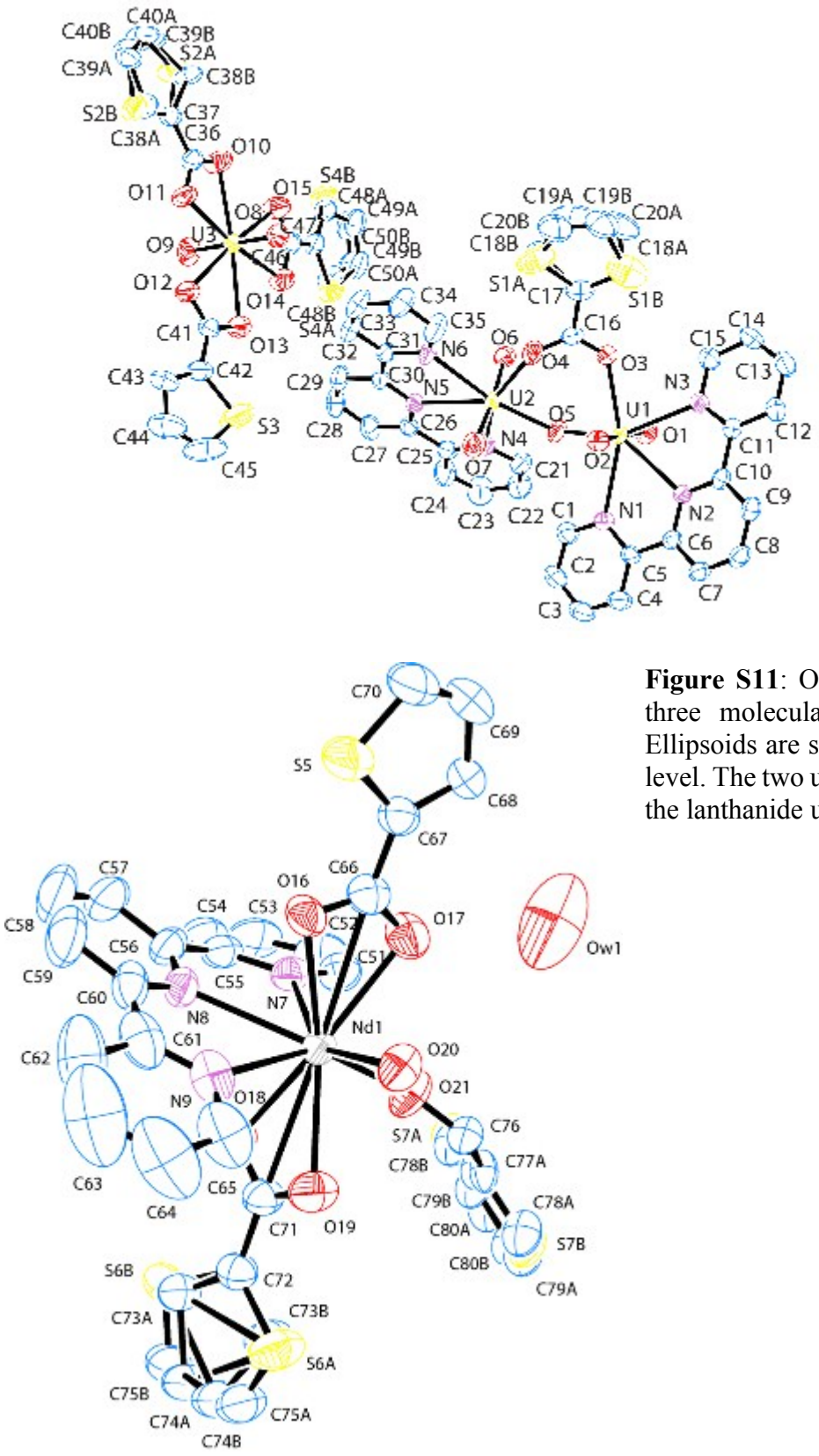
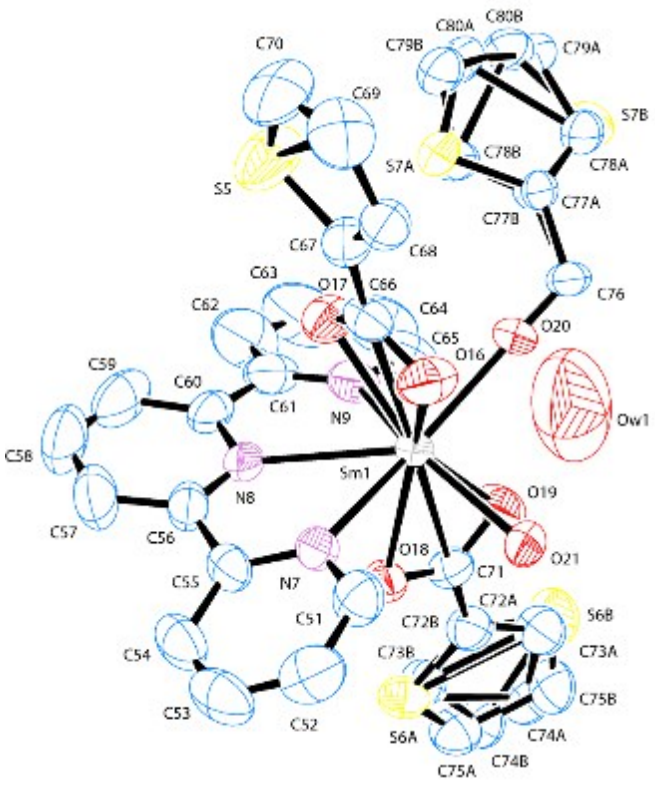


Figure S11: ORETP illustration of the three molecular units of complex **2**. Ellipsoids are shown at 50% probability level. The two uranyl units are above and the lanthanide unit is to the left.



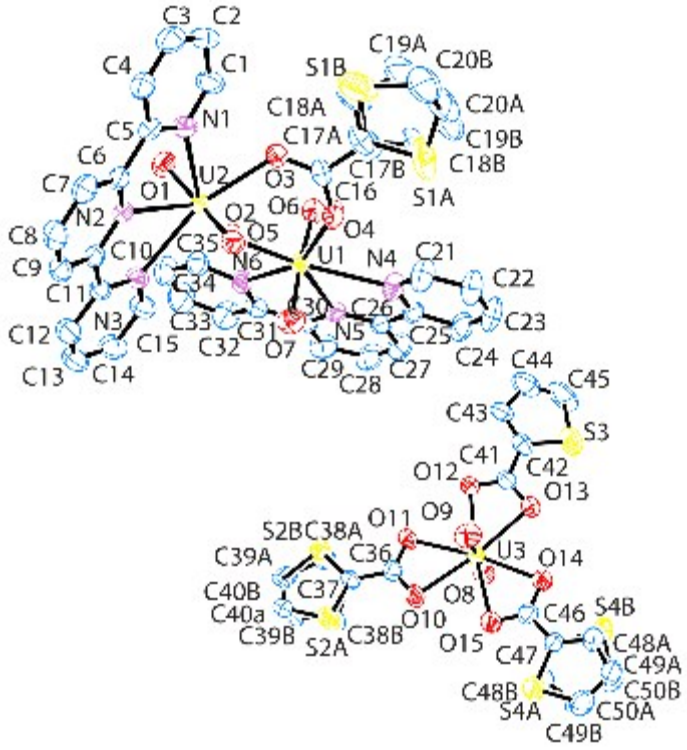


Figure S12: ORETP illustration of the three molecular units of complex **3**. Ellipsoids are shown at 50% probability level. The two uranyl units are above and the lanthanide unit is to the left.

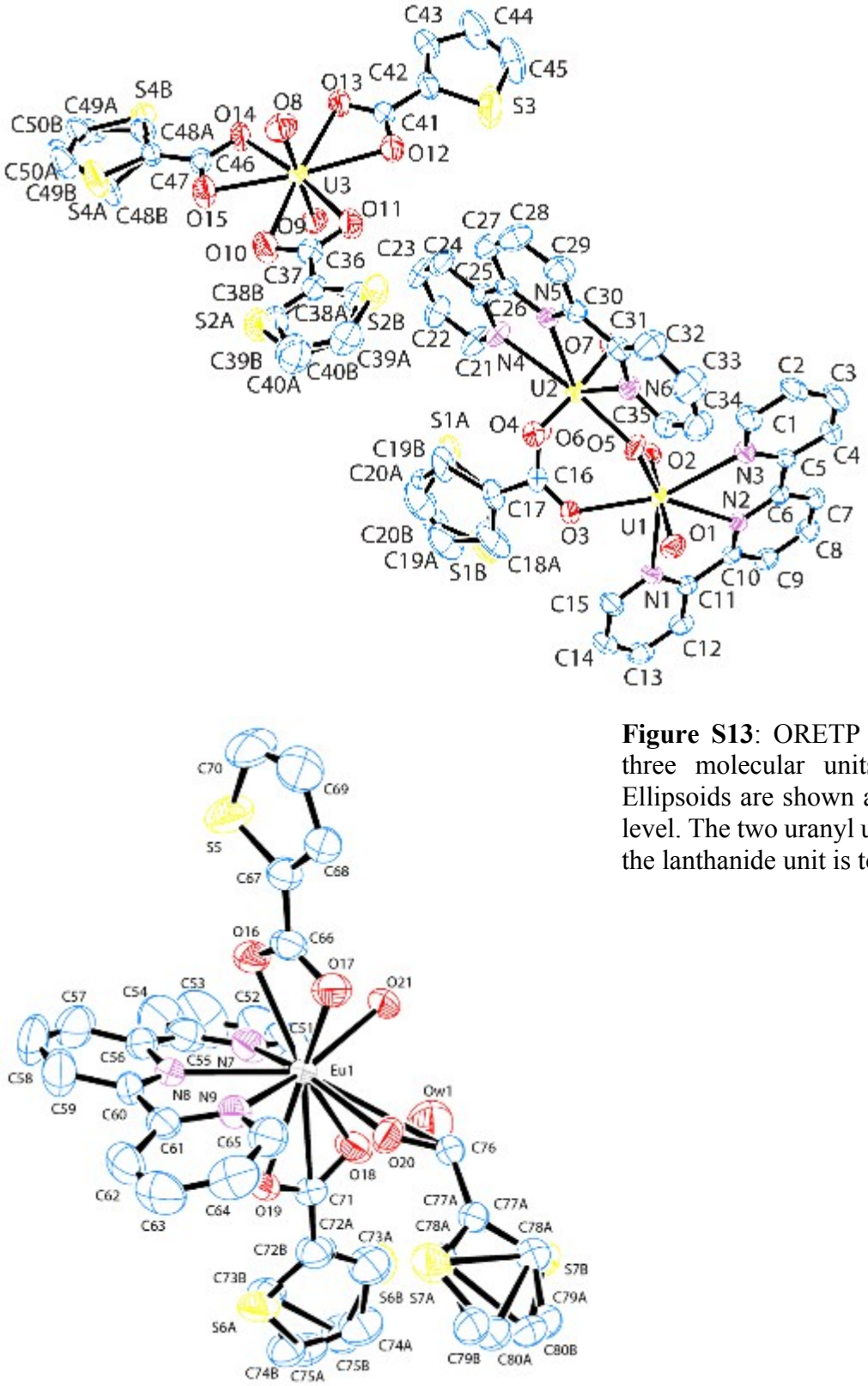


Figure S13: ORETP illustration of the three molecular units of complex **4**. Ellipsoids are shown at 50% probability level. The two uranyl units are above and the lanthanide unit is to the left.

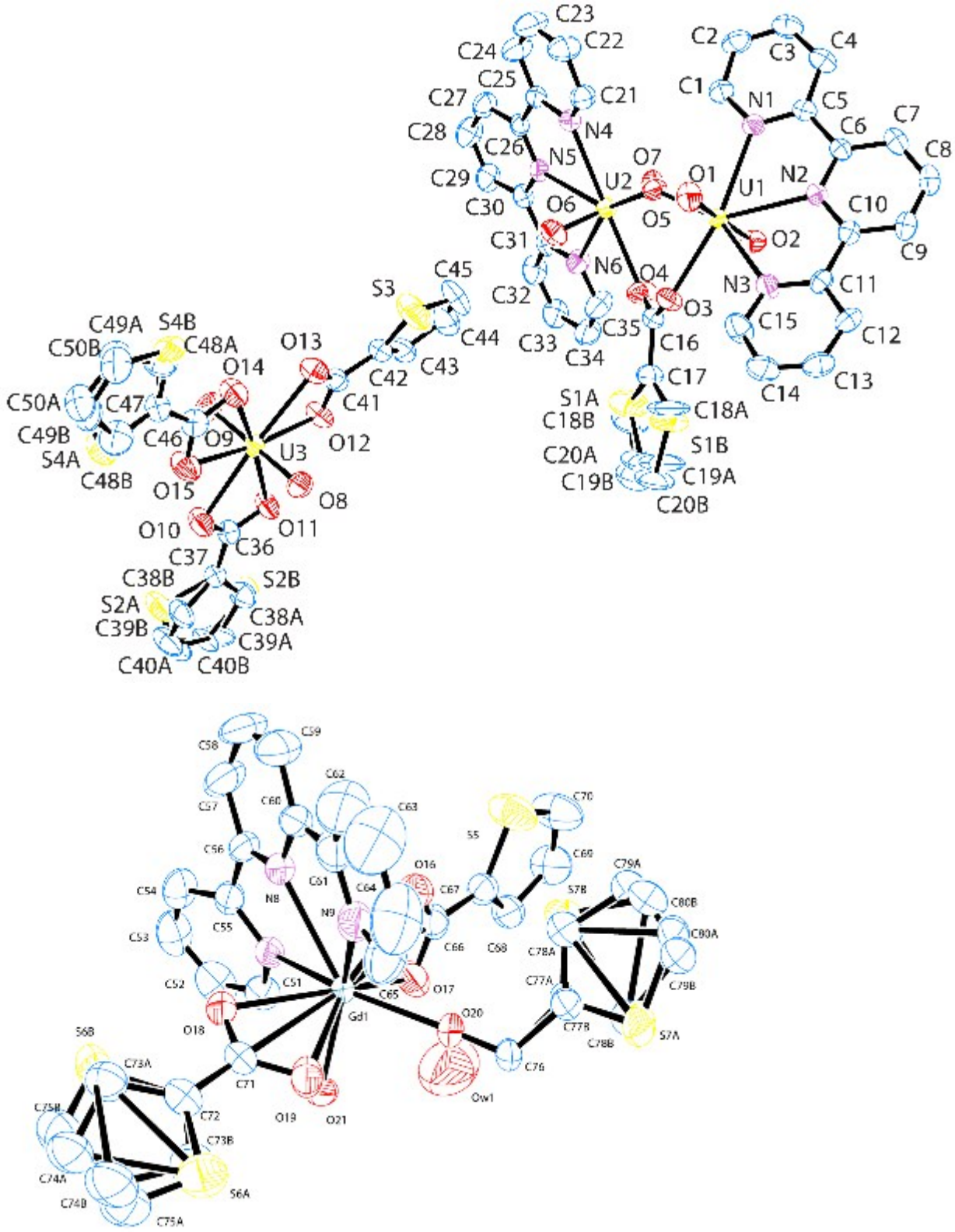


Figure S14: ORETP illustration of the three molecular units of complex **5**. Ellipsoids are shown at 50% probability level. The two uranyl units are on top and the lanthanide unit is on the bottom.

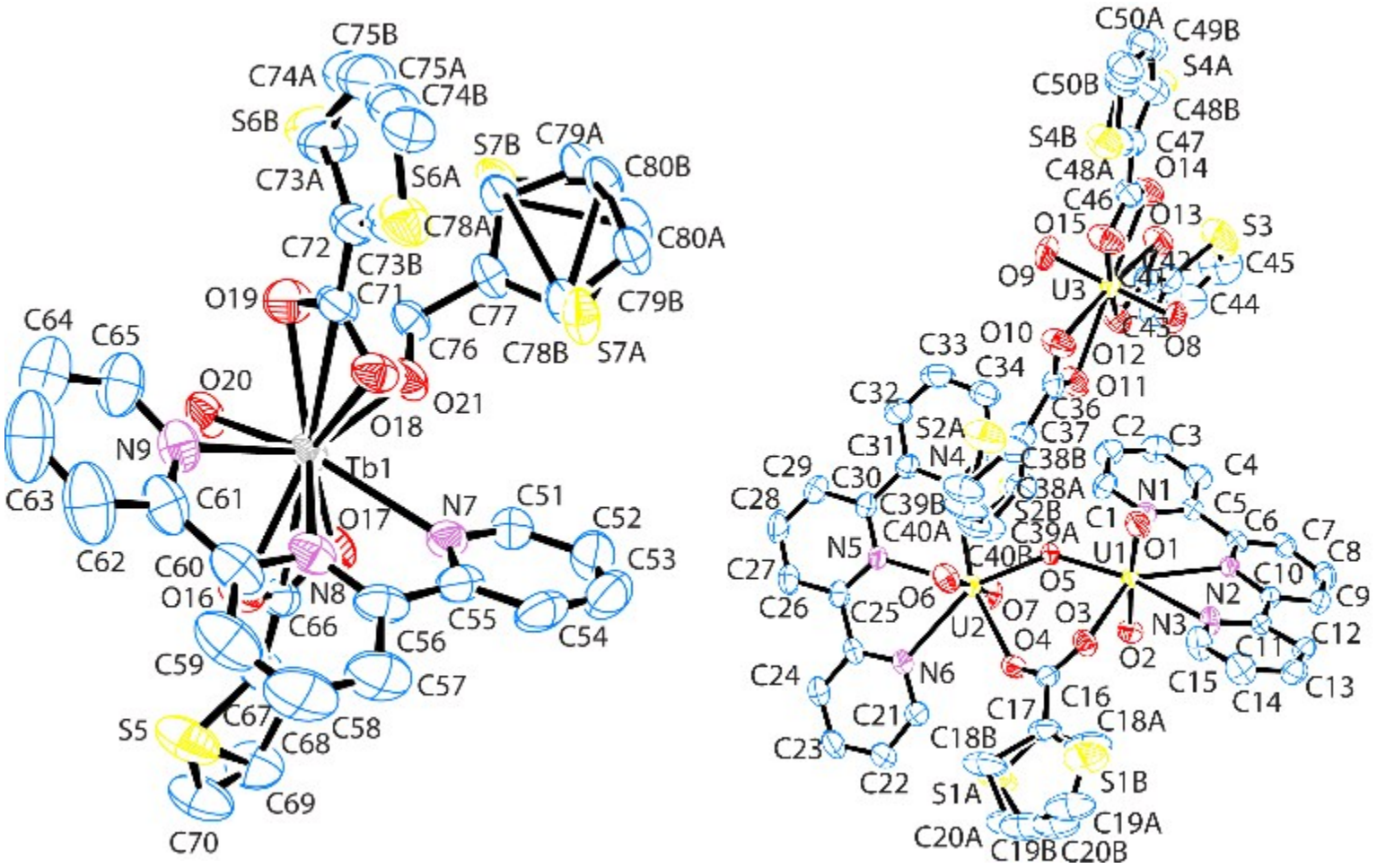


Figure S15: ORETP illustration of the three molecular units of complex **6**. Ellipsoids are shown at 50% probability level.

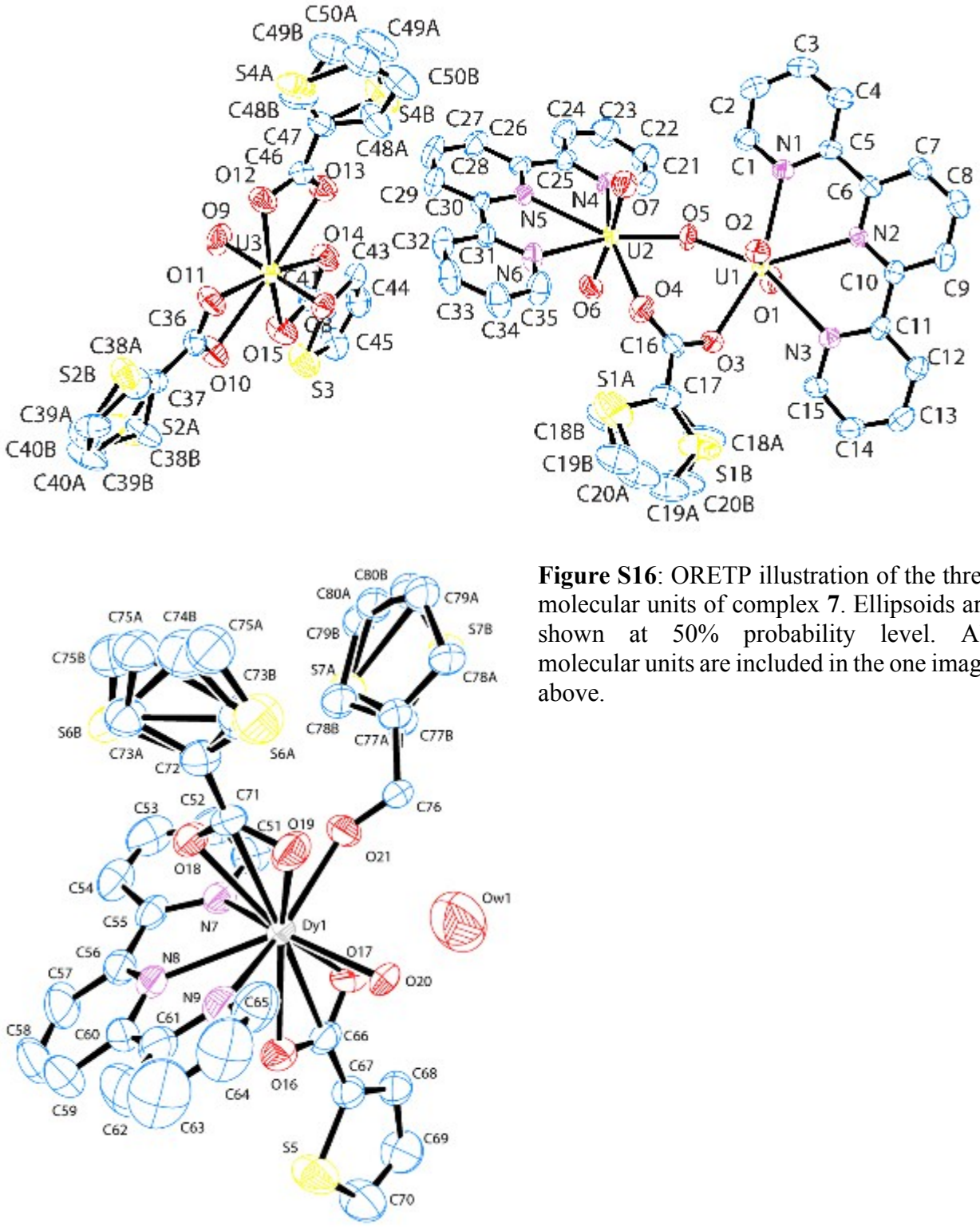


Figure S16: ORETP illustration of the three molecular units of complex **7**. Ellipsoids are shown at 50% probability level. All molecular units are included in the one image above.

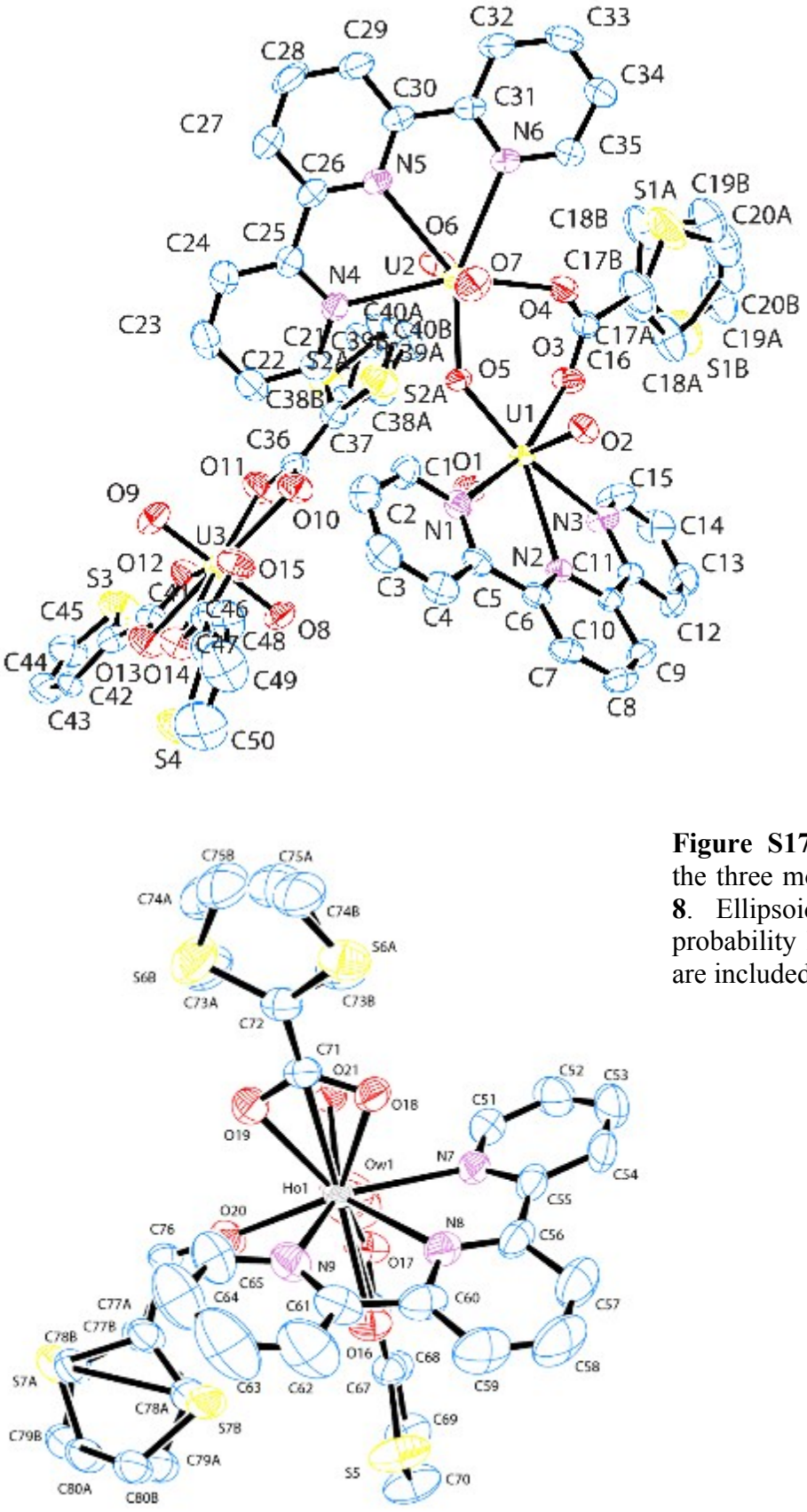


Figure S17: ORETP illustration of the three molecular units of complex **8**. Ellipsoids are shown at 50% probability level. All molecular units are included in the one image above.

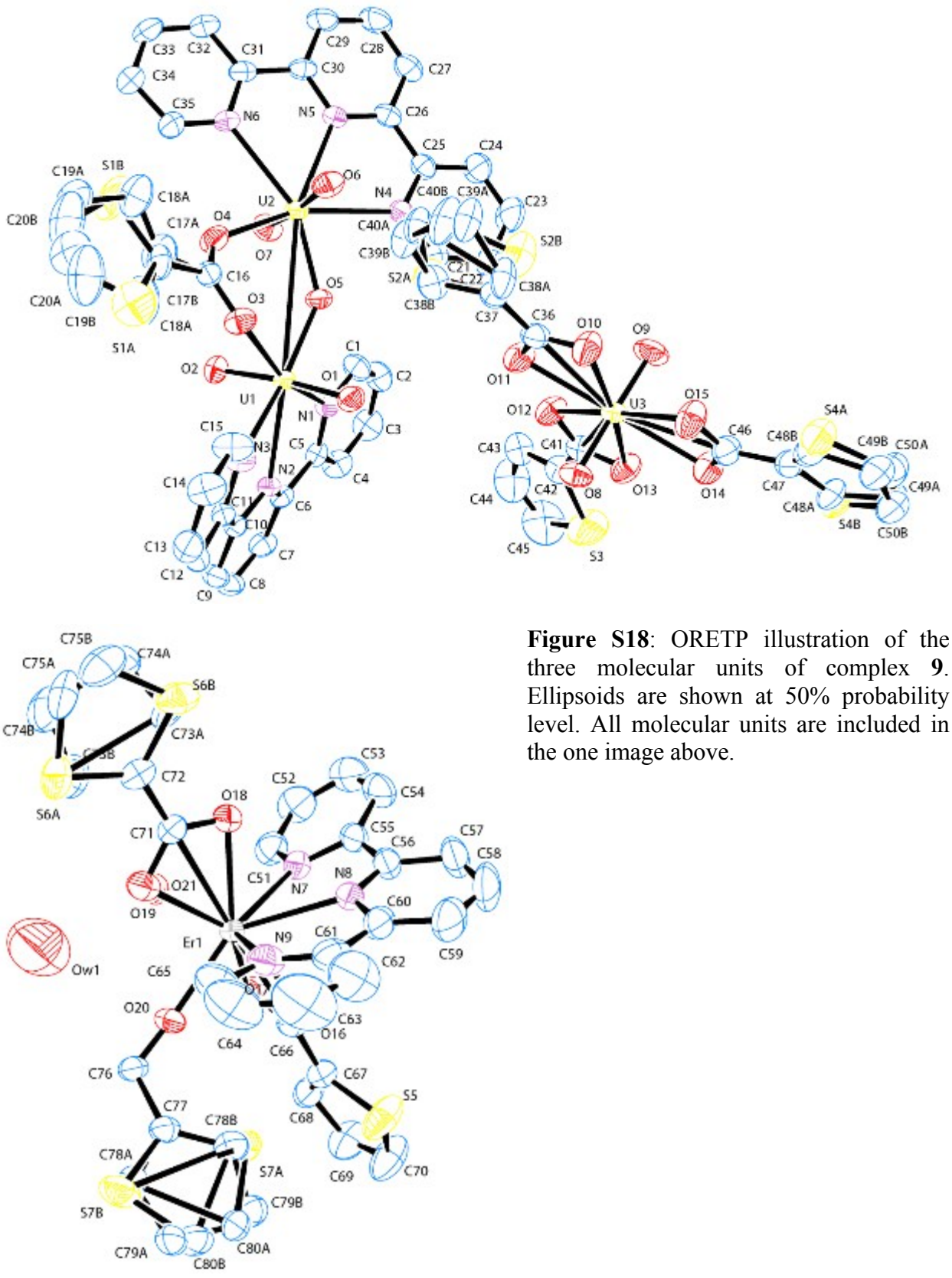


Figure S18: ORETP illustration of the three molecular units of complex **9**. Ellipsoids are shown at 50% probability level. All molecular units are included in the one image above.

III. Table of Free Variables

A table of free variables is provided for all heterometallic complexes, as all complexes exhibit significant thiophene ring disorder.

	Free Variables for a given Thiophene Ring (TRX), where X corresponds to sulfur atom				
Complex #	TR1	TR2	TR4	TR6	TR7
1	0.83291	0.77854	0.73204	0.36485	0.65651
2	0.84874	0.78618	0.24424	0.36960	0.65921
3	0.83166	0.78747	0.78460	0.65017	0.37800
4	0.83898	0.81137	0.78390	0.69134	0.60951
5	0.83505	0.79624	0.86018	0.29872	0.54258
6	0.83169	0.79044	0.15891	0.70150	0.57960
7	0.83893	0.78912	0.05473	0.28535	0.57521
8	0.84573	0.78828	-	0.71974	0.54705
9	0.84544	0.79527	0.88251	0.71680	0.45032

Table S1: Table of Free Variable values for all heterometallic complexes. "TR" stands for "Thiophene Ring" and the "X" represented a number corresponding to the nomenclature of the sulfur atom present in that thiophene ring.

IV. Tables of Selected Bond Distances

Compound #	U1-O1	U1-O2	U1-O3	U1-O5	U1-N1	U1-N2	U1-N3
1 (Pr)	1.775(3)	1.788(3)	2.396(3)	2.092(3)	2.578(3)	2.628(3)	2.598(3)
2 (Nd)	1.805(3)	1.822(3)	2.437(4)	2.130(3)	2.617(4)	2.666(4)	2.636(4)
3 (Sm)	1.775(3)	1.787(3)	2.396(3)	2.095(3)	2.603(4)	2.631(3)	2.578(3)
4 (Eu)	1.770(3)	1.784(2)	2.406(3)	2.095(2)	2.597(3)	2.634(3)	2.581(3)
5 (Gd)	1.776(3)	1.790(3)	2.402(3)	2.095(3)	2.581(3)	2.626(3)	2.596(3)
6 (Tb)	1.775(3)	1.790(3)	2.399(3)	2.096(3)	2.579(3)	2.631(3)	2.592(3)
7 (Dy)	1.774(3)	1.793(3)	2.399(3)	2.096(3)	2.574(4)	2.627(3)	2.593(4)
8 (Ho)	1.772(3)	1.792(3)	2.404(3)	2.100(3)	2.588(3)	2.631(3)	2.602(4)
9 (Er)	1.777(2)	1.791(2)	2.401(2)	2.094(2)	2.583(2)	2.631(2)	2.594(3)

Table S2: Table of bond distances for the uranium atom U1, present in the uranyl dimer unit.

Compound #	U2-O4	U2-O5	U2-O6	U2-O7	U2-N4	U2-N5	U2-N6
1 (Pr)	2.425(3)	2.119(3)	1.772(3)	1.766(3)	2.566(3)	2.607(3)	2.615(3)
2 (Nd)	2.461(4)	2.153(3)	1.799(4)	1.793(4)	2.607(4)	2.647(4)	2.654(4)
3 (Sm)	2.425(3)	2.120(3)	1.772(3)	1.766(3)	2.612(4)	2.606(3)	2.567(4)
4 (Eu)	2.424(3)	2.121(2)	1.777(3)	1.774(3)	2.613(3)	2.605(3)	2.571(3)
5 (Gd)	2.422(3)	2.118(2)	1.770(3)	1.770(3)	2.572(3)	2.604(3)	2.609(3)
6 (Tb)	2.421(3)	2.120(3)	1.779(3)	1.773(3)	2.568(3)	2.603(3)	2.613(3)
7 (Dy)	2.421(3)	2.115(3)	1.770(3)	1.767(3)	2.575(4)	2.600(3)	2.608(4)
8 (Ho)	2.424(3)	2.121(3)	1.776(3)	1.772(3)	2.576(4)	2.600(3)	2.613(4)
9 (Er)	2.426(2)	2.122(2)	1.778(2)	1.772(2)	2.571(3)	2.602(2)	2.615(3)

Table S3: Table of bond distances for the uranium atom U2, present in the uranyl dimer unit.

Compound #	U3-O8	U3-O9	U3-O10	U3-O11	U3-O12	U3-O13	U3-O14	U3-O15
1 (Pr)	1.765(3)	1.753(3)	2.446(3)	2.480(3)	2.478(3)	2.485(3)	2.461(3)	2.452(3)
2 (Nd)	1.795(4)	1.787(4)	2.483(4)	2.518(4)	2.514(4)	2.527(4)	2.496(4)	2.488(4)
3 (Sm)	1.766(3)	1.754(3)	2.446(3)	2.481(3)	2.480(3)	2.485(3)	2.460(3)	2.452(3)
4 (Eu)	1.754(3)	1.765(3)	2.450(3)	2.460(3)	2.486(3)	2.480(3)	2.480(3)	2.450(3)
5 (Gd)	1.764(3)	1.757(3)	2.448(3)	2.479(3)	2.478(3)	2.483(3)	2.459(3)	2.446(3)
6 (Tb)	1.772(3)	1.761(3)	2.447(3)	2.477(3)	2.482(3)	2.482(3)	2.459(3)	2.447(3)
7 (Dy)	1.766(3)	1.759(3)	2.445(3)	2.474(3)	2.478(3)	2.480(3)	2.454(3)	2.452(4)
8 (Ho)	1.764(3)	1.751(3)	2.481(3)	2.450(3)	2.453(3)	2.458(3)	2.487(3)	2.482(3)
9 (Er)	2.767(2)	1.757(2)	2.449(2)	2.480(2)	2.481(2)	2.485(2)	2.461(2)	2.452(2)

Table S4: Table of bond distances for the uranium atom U3, present in the uranyl monomer unit.

Compound #	Ln1-O16	Ln1-O17	Ln1-O18	Ln1-O19	Ln1-O20	Ln1-O21	Ln1-N7	Ln1-N8	Ln1-N9
1 (Pr)	2.547(3)	2.521(4)	2.551(3)	2.543(4)	2.373(3)	2.415(3)	2.672(4)	2.695(4)	2.635(5)
2 (Nd)	2.575(4)	2.555(5)	2.578(4)	2.575(4)	2.394(4)	2.437(4)	2.697(5)	2.714(5)	2.650(5)
3 (Sm)	2.492(4)	2.493(3)	2.511(3)	2.508(4)	2.330(3)	2.376(3)	2.633(4)	2.645(4)	2.590(4)
4 (Eu)	2.492(3)	2.494(3)	2.498(3)	2.496(3)	2.361(3)	2.321(3)	2.580(4)	2.628(3)	2.617(4)
5 (Gd)	2.441(3)	2.474(3)	2.459(3)	2.454(3)	2.274(3)	2.319(3)	2.586(4)	2.590(4)	2.547(4)
6 (Tb)	2.464(3)	2.478(3)	2.472(3)	2.470(3)	2.286(3)	2.335(3)	2.597(4)	2.603(4)	2.556(4)
7 (Dy)	2.453(3)	2.468(4)	2.458(3)	2.459(4)	2.277(3)	2.318(3)	2.587(4)	2.590(4)	2.547(5)
8 (Ho)	2.440(3)	2.468(4)	2.452(3)	2.451(4)	2.259(3)	2.315(3)	2.576(4)	2.587(4)	2.541(4)
9 (Er)	2.423(2)	2.467(3)	2.439(2)	2.444(3)	2.253(2)	2.298(2)	2.561(3)	2.568(3)	2.527(3)

Table S5: Table of bond distances for the lanthanide atom Ln1, present in the lanthanide dimer unit.

V. Raman Spectra

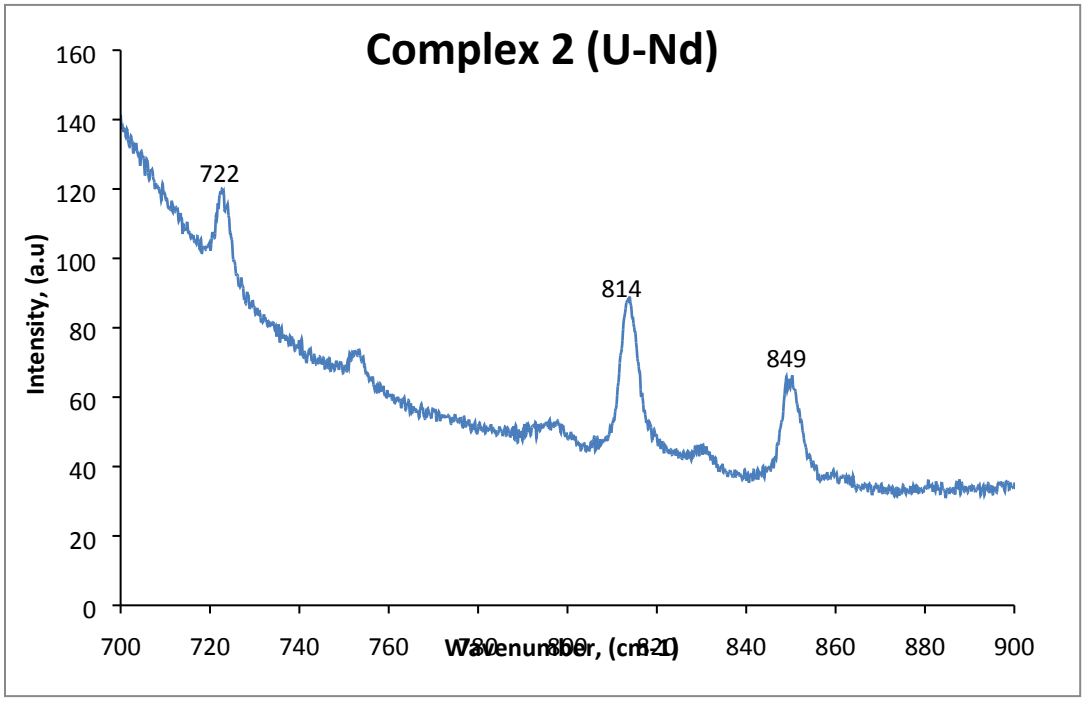


Figure S19: Raman spectra of collected on a single crystal of complex **2**.

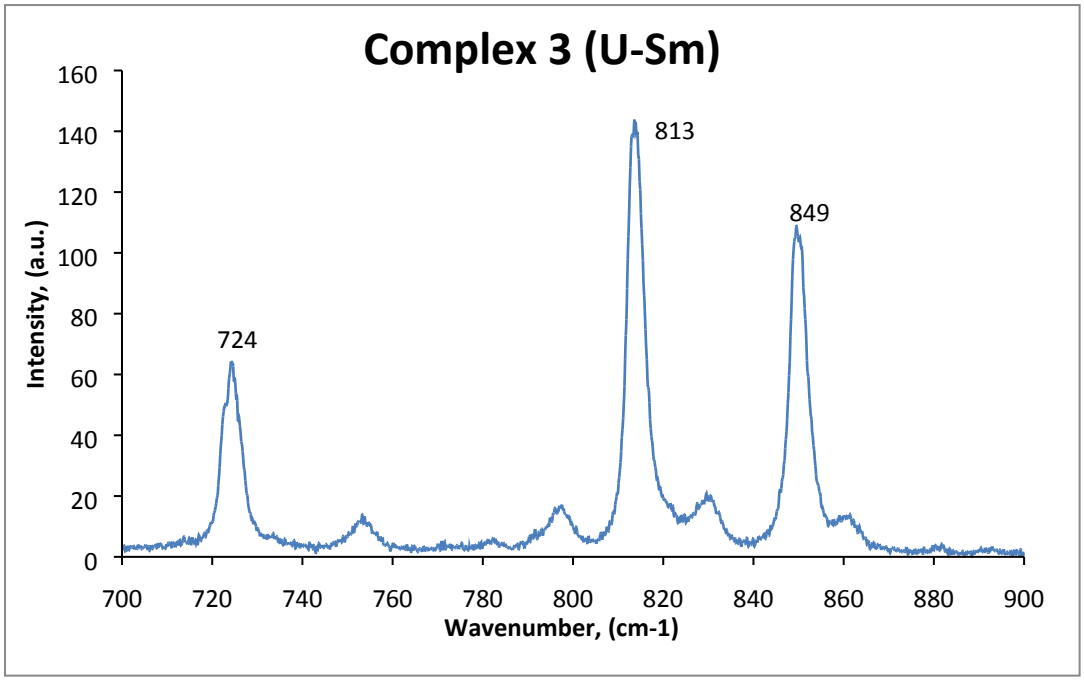


Figure S20: Raman spectra of collected on a single crystal of complex **3**.

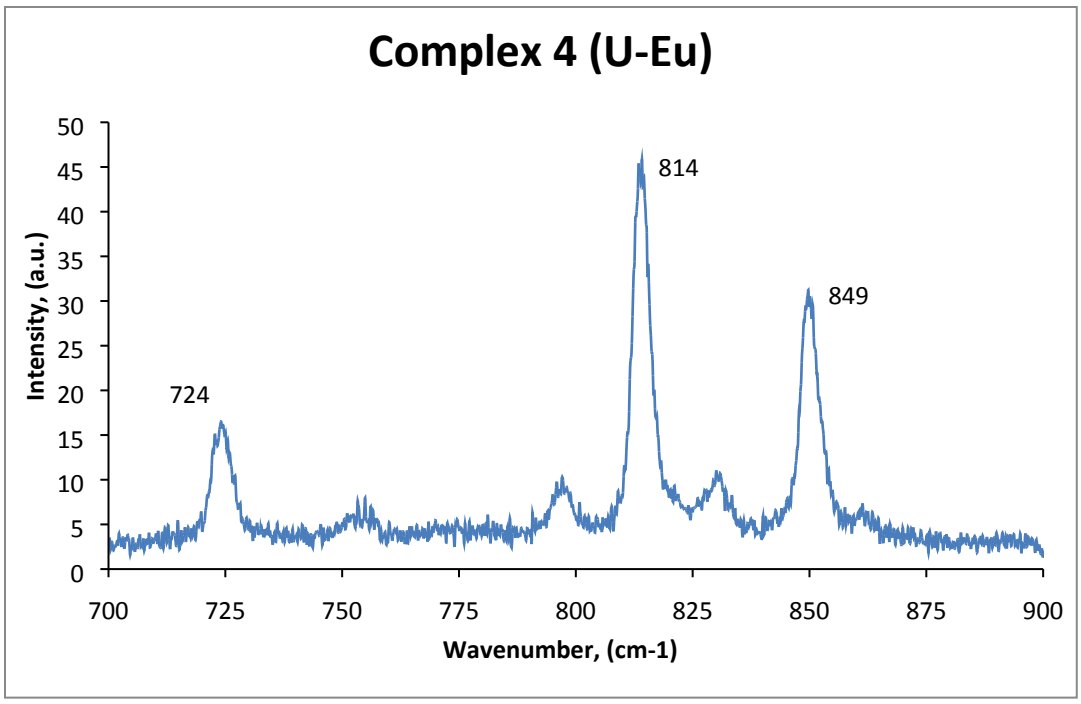


Figure S21: Raman spectra of collected on a single crystal of complex **4**.

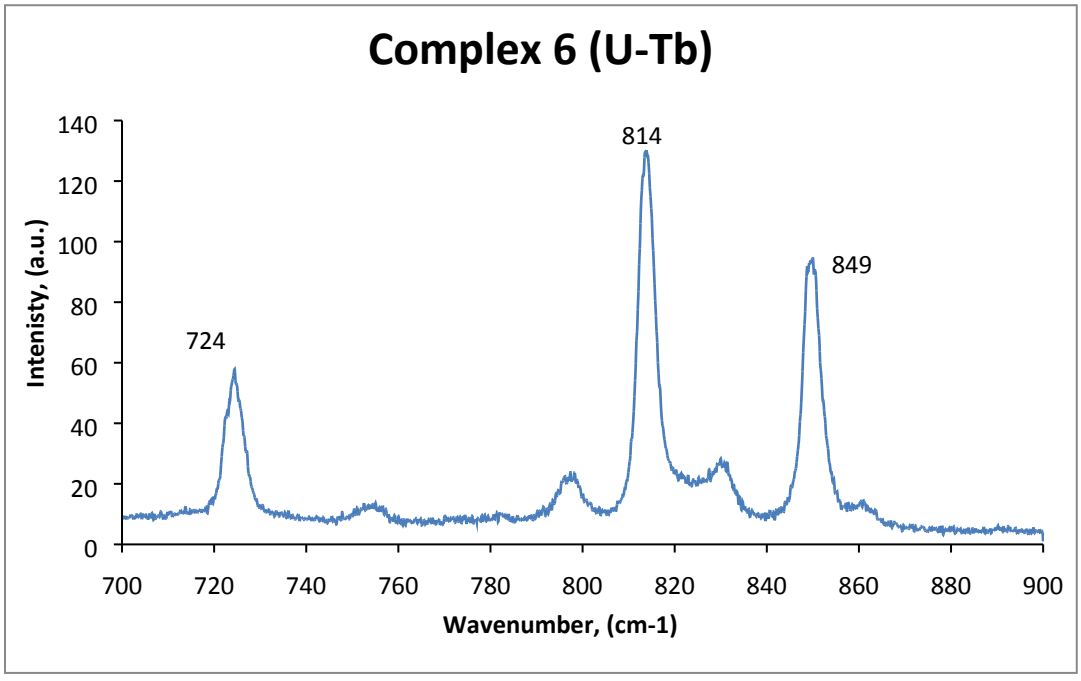


Figure S22: Raman spectra of collected on a single crystal of complex **6**.

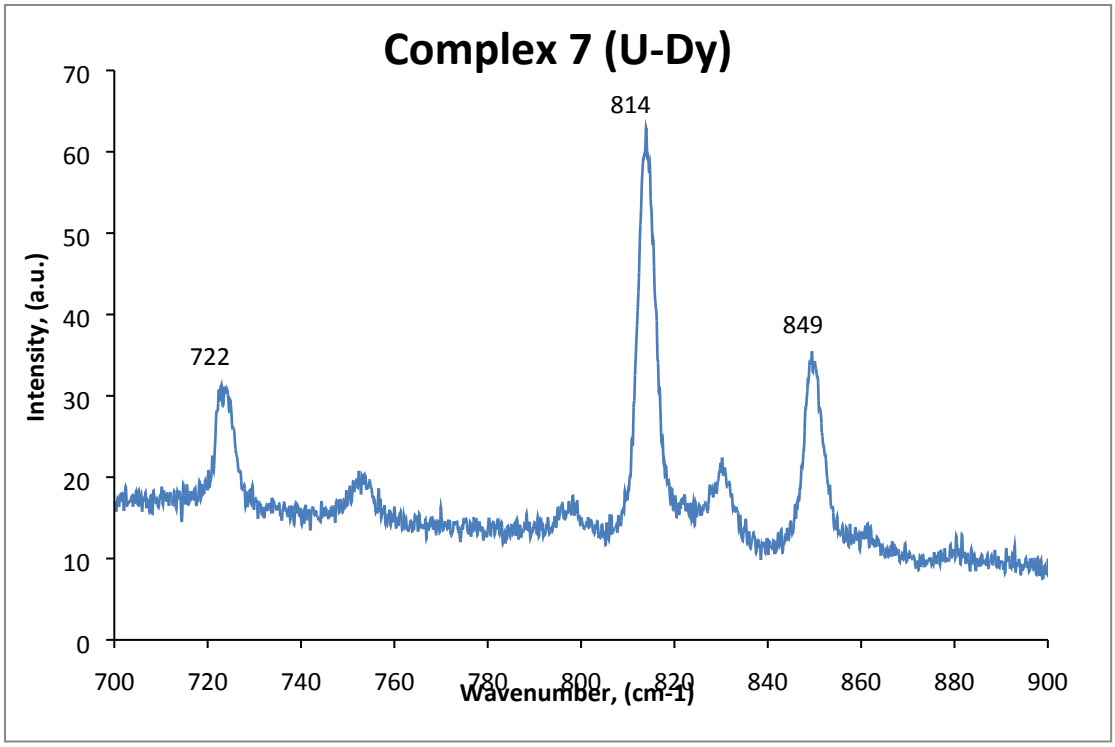


Figure S23: Raman spectra collected on a single crystal of complex **7.**

VI. Complex 10: Supramolecular Interactions, Free Variables, PXRD, and Raman

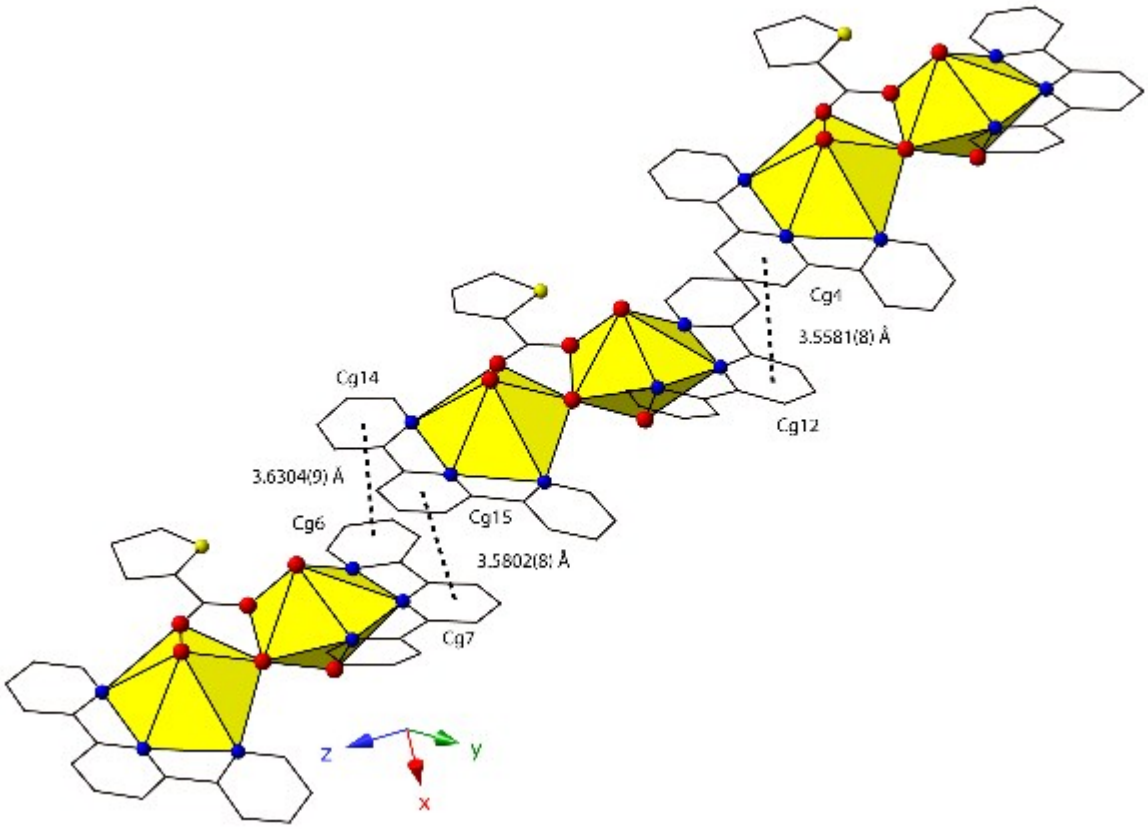


Figure S24: Polyhedral representation of complex **10** showing offset pi-stacking interactions assembling both unique uranyl dimers into a 1D chain. Hydrogen atoms have been removed for clarity.

	Free Variables for a given Thiophene Ring (TRX), where X corresponds to sulfur atom					
Complex #	TR1	TR2	TR3	TR4	TR5	OW3
10	0.65159	0.75098	0.81650	0.88758	0.46864	0.46530

Table S6: Table of Free Variable values for the uranyl only complex. "TR" stands for "Thiophene Ring" and the "X" represented a number corresponding to the nomenclature of the sulfur atom present in that thiophene ring. A disordered water molecule (OW3) is also included.

Compound **10**	U1-O1	U1-O2	U1-O3	U1-O5	U1-N1	U1-N2	U1-N3
	1.7895(4)	1.779(4)	2.3904(5)	2.1522(5)	2.5589(5)	2.621(6)	2.5704(6)
	U2-O4	U2-O5	U2-O6	U2-O7	U2-N4	U2-N5	U2-N6
	2.4019(5)	2.0022(4)	1.8009(4)	1.8046(4)	2.6109(6)	2.6008(6)	2.5507(5)
U3-O8	U3-O9	U3-O10	U3-O11	U3-O12	U3-O13	U3-O14	U3-O15
1.8165(4)	1.753(4)	2.4599(5)	2.4812(5)	2.4958(5)	2.4517(5)	2.4499(5)	2.4703(5)
	U4-O16	U4-O17	U4-O18	U4-O20	U4-N7	U4-N8	U4-N9
	1.7874(4)	1.7999(4)	2.3973(5)	2.1356(5)	2.5781(6)	2.6218(6)	2.6127(6)
	U5-O19	U5-O20	U5-O21	U5-O22	U5-N10	U4-N11	U5-N12
	2.403(5)	2.0717(4)	1.8068(4)	1.7908(4)	2.5901(6)	2.6430(6)	2.5489(5)

Table S7: Table of selected bond distances for the uranium only phase complex **10**.

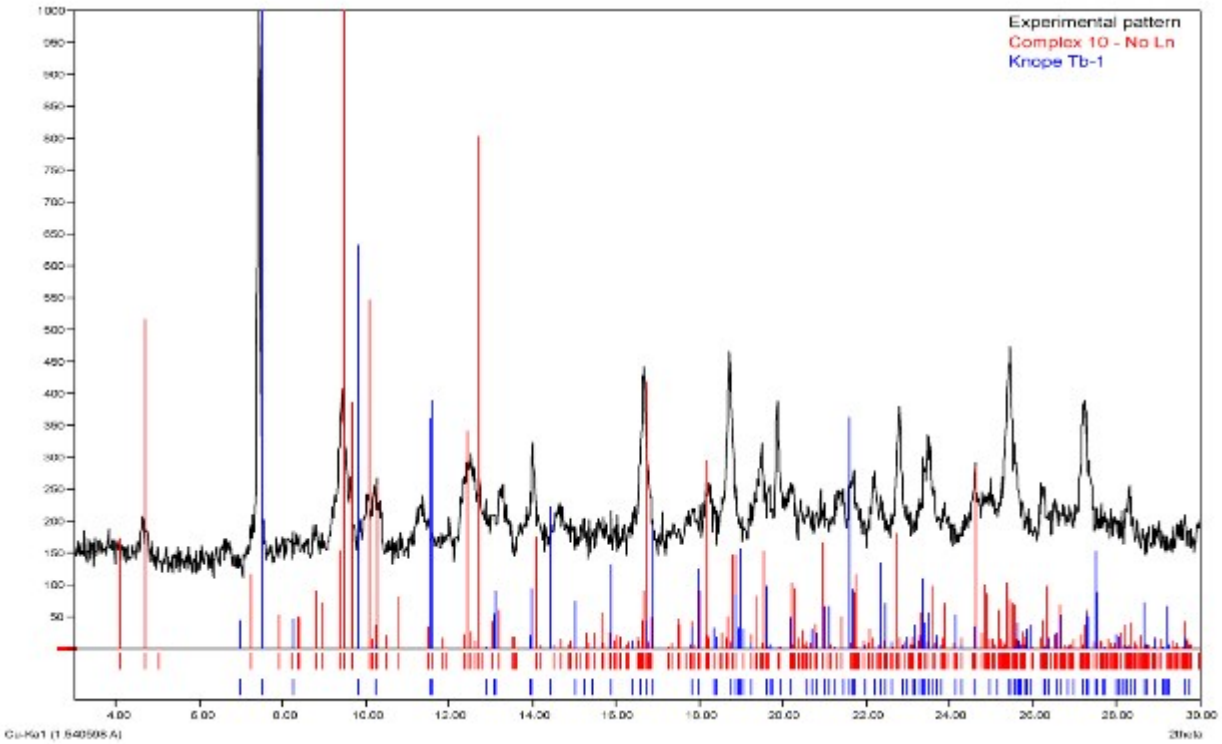


Figure S25: The PXRD pattern of the bulk product of complex **10** with the calculated pattern overlaid in red. The calculated pattern of the Tb^{3+} only phase from Knope *et al.* is given in blue.

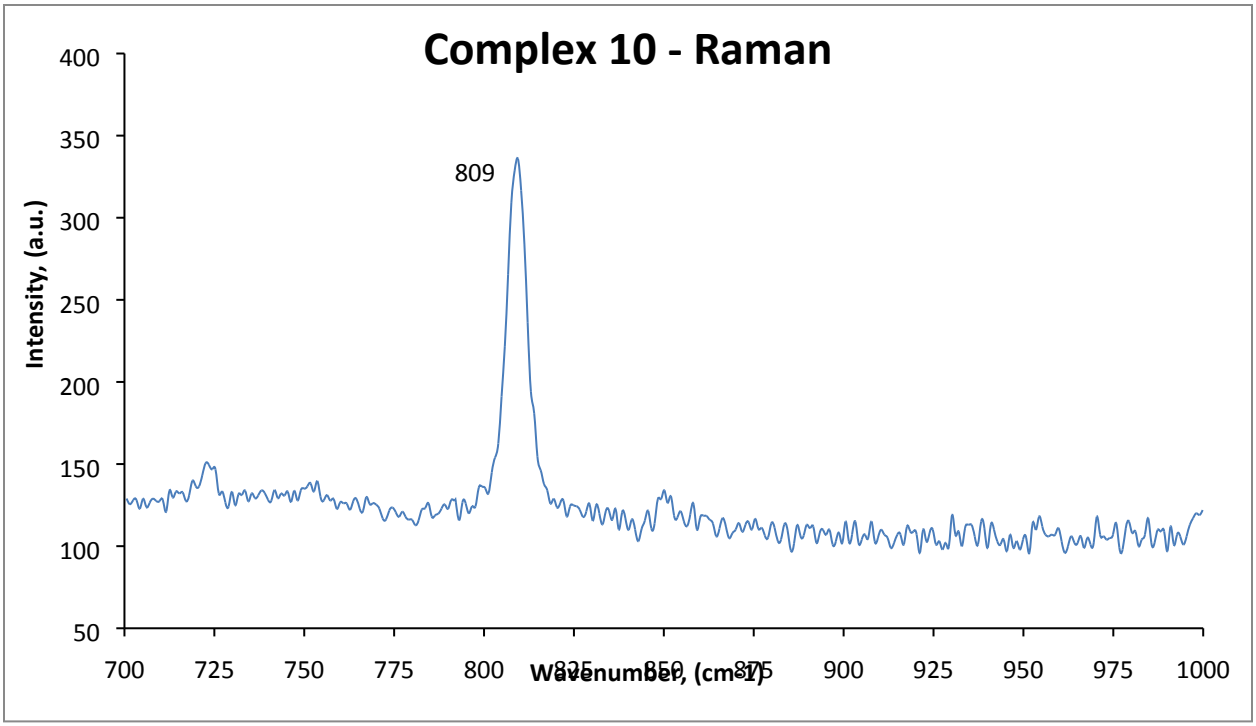


Figure S26: Raman spectra collected on a single crystal of complex **10**.

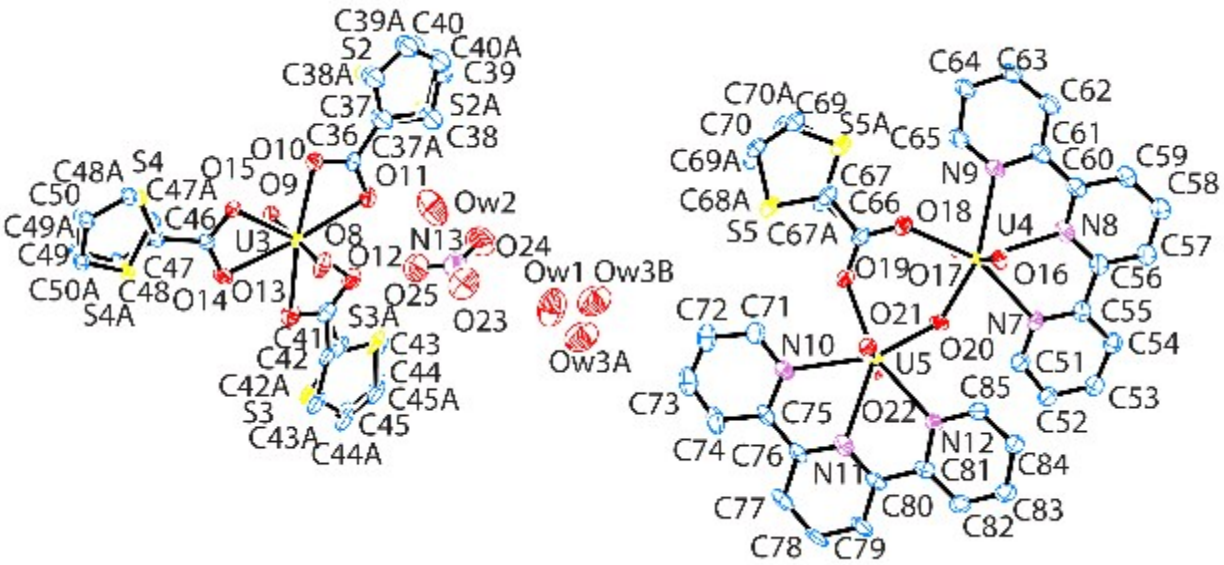


Figure S27: One portion of the ORETP illustration of complex **10** showing one of the dimeric units. Ellipsoids are shown at 50% probability level.

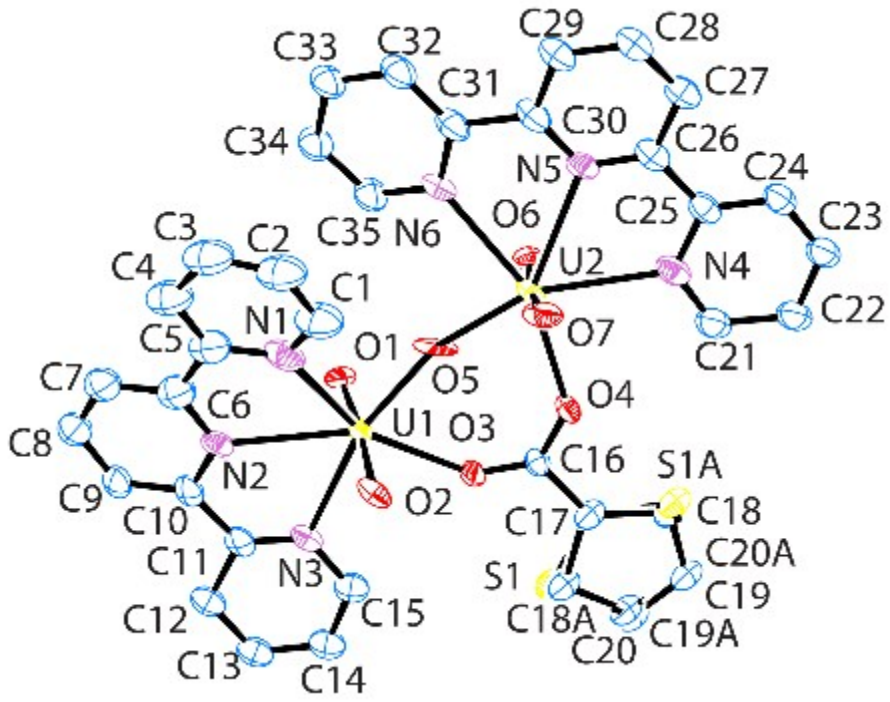


Figure S28: One portion of the ORETP illustration of complex **10** showing one of the dimeric units. Ellipsoids are shown at 50% probability level.

VII. Lifetimes for Complexes 4 and 10

Lifetime measurements were done with a Horiba JobinYvon Fluorolog-3 spectrometer adapted for time-correlated single photon counting (TCSPC) and multichannel scaling (MCS) measurements using a Xenon flash lamp as a light source. Lifetime profiles below were obtained using the Jobin Yvon FluoroHub single photon counting module and the data were fit using DAS6 software.

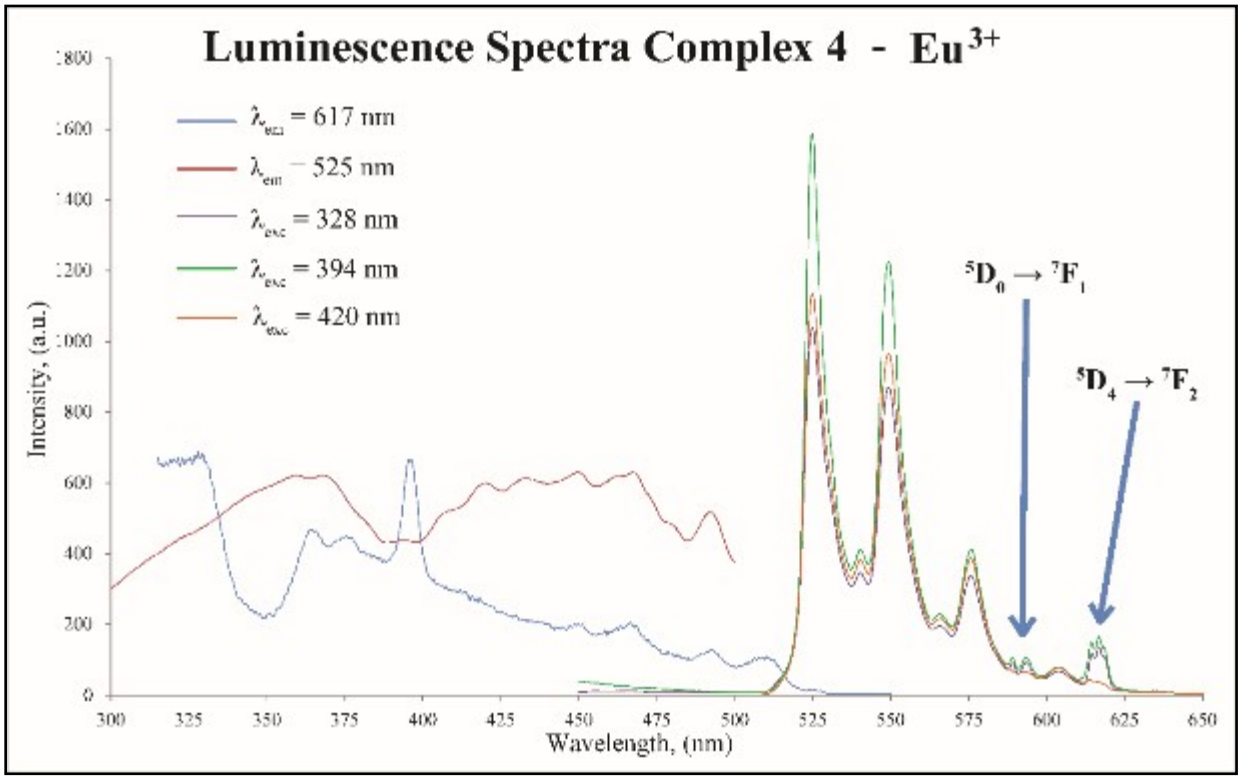


Figure S29: Luminescence spectra for complex **4** for reference to Table S8 containing luminescent lifetimes.

Exc. λ (nm)	Em. λ (nm)	τ [Rel. Ampl.] (sec, %)	Std. Dev. (sec)	χ^2 (%)
328	525 (UO_2^{2+})	1.815003E-6 [23.98] 1.405049E-5 [76.02]	4.186105E-8 1.201044E-7	1.262073
328	535 (UO_2^{2+})	1.40775E-6 [31.58] 1.15445E-5 [68.42]	3.810928E-8 2.638351E-7	1.267584
328	617 (Eu^{3+})	6.032983E-4 [100.00]	5.527187E-6	1.164164

Table S8: Tabulated lifetime data for complex **4**.

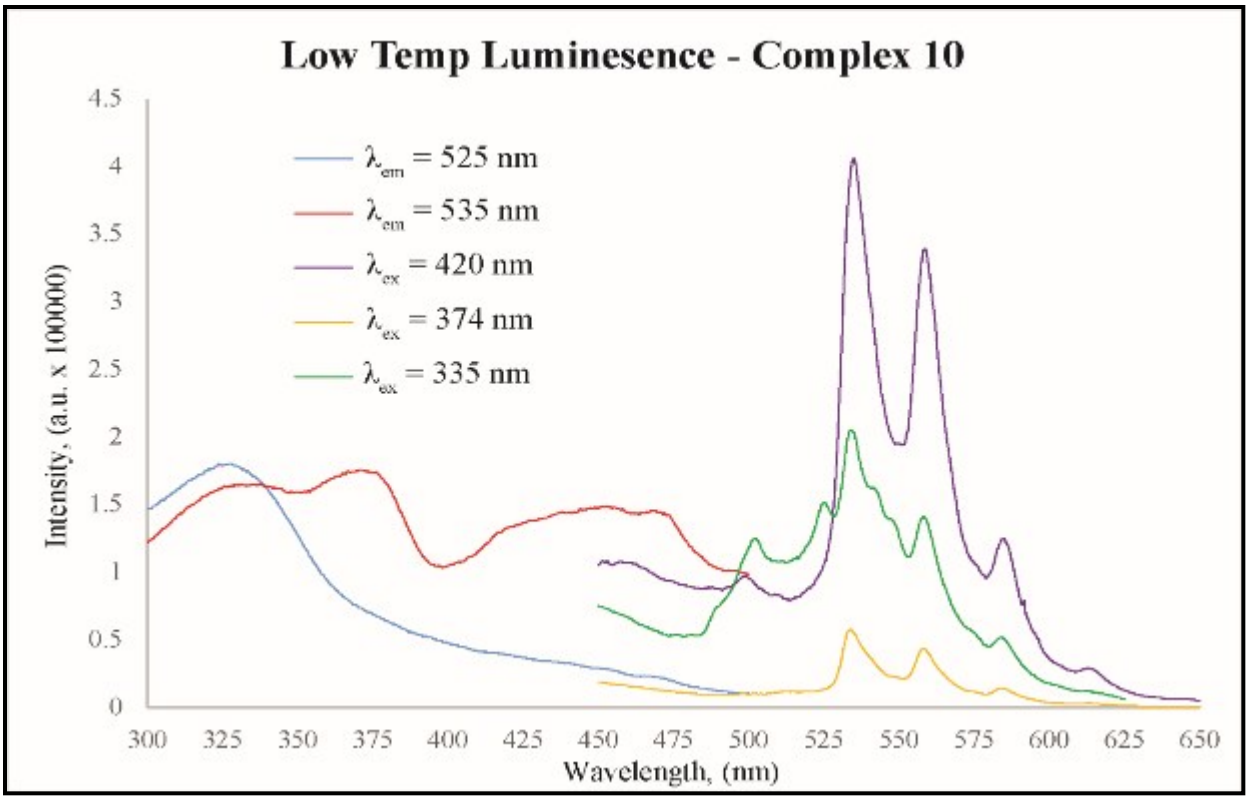


Figure S30: Luminescence spectra for complex **10** for reference to Table S9 containing luminescent lifetimes.

Exc. λ (nm)	Em. λ (nm)	τ [Rel. Ampl.] (sec, %)	Std. Dev. (sec)	χ^2 (%)
335	525 (UO_2^{2+})	1.685149E-5 [23.38] 1.048551E-4 [76.62]	2.848216E-7 8.651544E-7	1.115812
335	535 (UO_2^{2+})	2.623367E-5 [26.49] 1.189298E-4 [73.51]	4.236711E-7 8.602612E-7	1.052305
420	525 (UO_2^{2+})	1.465152E-5 [13.99] 8.793233E-5 [86.01]	3.217546E-7 4.424322E-7	1.036737
420	535 (UO_2^{2+})	7.490564E-5 [47.13] 1.19636E-4 [52.87]	3.751099E-6 1.330866E-6	1.024075

Table S9: Tabulated lifetime data for complex **10**.

VIII. Bond Valence for all Compounds

Compound #	U1-O1	U1-O2	U1-O3	U1-O5	U1-N1	U1-N2	U1-N3	Bond Valence Sum
1 (Pr)	1.69870	1.64080	0.50752	**0.91518**	0.35809	0.32520	0.34455	5.79004
2 (Nd)	1.58792	1.53675	0.46987	**0.84893**	0.33217	0.30224	0.32023	5.39811
3 (Sm)	1.68242	1.64080	0.50849	**0.90641**	0.34125	0.32333	0.35809	5.76078
4 (Eu)	1.69870	1.65349	0.49879	**0.90816**	0.34522	0.32146	0.35602	5.78185
5 (Gd)	1.67918	1.63449	0.50265	**0.90816**	0.35602	0.32646	0.34588	5.75283
6 (Tb)	1.68242	1.63449	0.50556	**0.90641**	0.35740	0.32333	0.34856	5.75816
7 (Dy)	1.68566	1.62507	0.50556	**0.90641**	0.36086	0.32583	0.34789	5.75727
8 (Ho)	1.69217	1.62820	0.50072	**0.89945**	0.35126	0.32333	0.34191	5.73702
9 (Er)	1.67595	1.63134	0.50362	**0.90991**	0.35466	0.32333	0.34722	5.74601

Table S10: Bond valence tables for the U1 atom in the uranyl dimer. The oxide is in bold.

Compound #	U2-O4	U2-O5	U2-O6	U2-O7	U2-N4	U2-N5	U2-N6	Bond Valence Sum
1 (Pr)	0.48552	**0.86378**	1.68891	1.70526	0.36646	0.33863	0.33345	5.78201
2 (Nd)	0.44864	**0.81213**	1.60639	1.62507	0.33863	0.31351	0.30931	5.45367
3 (Sm)	0.48086	**0.86712**	1.69217	1.71185	0.33474	0.33994	0.36295	5.78962
4 (Eu)	0.48179	**0.86378**	1.67595	1.68566	0.33538	0.33863	0.36225	5.74344
5 (Gd)	0.48365	**0.86879**	1.69870	1.69870	0.36225	0.34059	0.33733	5.79001
6 (Tb)	0.48458	**0.86545**	1.66950	1.68891	0.36506	0.34125	0.33474	5.74948
7 (Dy)	0.48458	**0.87383**	1.69870	1.70855	0.36016	0.34323	0.33798	5.80703
8 (Ho)	0.48179	**0.86378**	1.67918	1.69217	0.35947	0.34323	0.33474	5.75435
9 (Er)	0.47994	**0.86212**	1.67272	1.69217	0.36295	0.34191	0.33345	5.74525

Table S11: Bond valence tables for the U2 atom in the uranyl dimer. The oxide is in bold.

Compound **10**	U1-O1	U1-O2	U1-O3	U1-O5	U1-N1	U1-N2	U1-N3	Bond Valence Sum
	1.63606	1.66950	0.51401	**0.81338**	0.37151	0.32962	0.36337	5.69746
	U2-O4	U2-O5	U2-O6	U2-O7	U2-N4	U2-N5	U2-N6	
	0.50275	**1.08596**	1.60052	1.58915	0.33609	0.34270	0.37743	5.83460
U3-O8	U3-O9	U3-O10	U3-O11	U3-O12	U3-O13	U3-O14	U3-O15	
1.5531261	1.75527	0.44959	0.43151	0.41954	0.45675	0.45834	0.44067	5.96479
	U4-O16	U4-O17	U4-O18	U4-O20	U4-N7	U4-N8	U4-N9	
	1.64270	1.60361	0.50722	**0.83982**	0.35802	0.32911	0.33493	5.61540
	U5-O19	U5-O20	U5-O21	U5-O22	U5-N10	U4-N11	U5-N12	
	0.50168	**0.94986**	1.58243	1.63197	0.34984	0.31594	0.37874	5.71045

Table S12: Bond valence tables for the all U atoms in the complex **10**. The oxides are in bold.

IX. Masses of Reactants in Synthesis

Compound #	**$UO_2(CH_3OO)_2$**	**$(C_{15}H_{11}N_3)$ L[1]**	**$(C_5H_3O_2S)$ L[2]**	**$Ln(NO_3)_3$**
1 (Pr)	0.0456 g	0.0235 g	0.0375 g	0.0192 g
2 (Nd)	0.0455 g	0.0226 g	0.0370 g	0.0187 g
3 (Sm)	0.0440 g	0.0239 g	0.0371 g	0.0187 g
4 (Eu)	0.0416 g	0.0233 g	0.0360 g	0.0187 g
5 (Gd)	0.0430 g	0.0240 g	0.0355 g	0.0186 g
6 (Tb)	0.0450 g	0.0232 g	0.0375 g	0.0188 g
7 (Dy)	0.0479 g	0.0240 g	0.0360 g	0.0177 g
8 (Ho)	0.0465 g	0.0235 g	0.0353 g	0.0167 g
9 (Er)	0.0411 g	0.0223 g	0.0365 g	0.0187 g
10* (Tb)	0.0480 g	0.0232 g	0.0360 g	0.0171 g

Table S13: Masses of reactants used in the synthesis of complexes **1**-**10**. * In complex **10**, a uranyl nitrate salt ($UO_2(NO_3)_2 \cdot 6H_2O$) was substituted for the uranyl acetate starting material. Additionally, despite the use of a $Tb(NO_3)_3$ salt in the synthesis of complex **10**, not Tb^{3+} incorporated into the structure.