Electronic Supplementary Material (ESI) for CrystEngComm

An exploration of homo- and heterometallic UO_2^{2+} hybrid materials containing chelidamic acid: synthesis, structure, and luminescence studies

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Supporting Information Section

SI Table 1 – Synthetic conditions for compounds 1-8.

	(1) $[UO_2(C_7H_2NO_5)•Et_3NH]$	**(2)** $[(UO_2)_2(C_7H_2NO_5)_2]•4H_2O$	**(3)** $[(UO_2)_2(C_7H_2NO_5)(OH)_2(H_2O)_2]•H_2O$	**(4)** $[(UO_2)_2(C_7H_2NO_5)_2(H_2O)]$	**(5)** $[(UO_2)_2(SmO)_7(C_7H_2NO_5)_2(C_7H_4NO_5)_2(OH)_4(NO_3)(H_2O)_3]•2H_2O$	**(6)** $[(UO_2)_2(C_7H_2NO_4Cl)_2(H_2O)_3]•H_2O$	**(7)** $[(UO_2)(C_7H_2NO_4Cl)_2(H_2O)]•H_2O$	**(8)** $Na_2[(UO_2)_3(C_7H_2NO_4Cl)_4]$
$(UO_2)(NO_3)_2•6H_2O$ (molar ratio)	1	1	1	1	1	1	1	1
chelidamic acid (molar ratio)	0.95	0.98	1.01	0.46	0.52			
4-chloro-2,6-pydc (molar ratio)						1.02	0.44	0.49
metal (molar ratio)					$Sm(NO_3)_3•6H_2O$ 3.79		$CaCO_3$ 0.70	
water (molar ratio)	308	433	413		150	153	152	213
nitric acid (molar ratio)						1.56		
ammonium hydroxide (molar ratio)	0.57	4.4	2.78		10.8			
2M sodium hydroxide$_{(aq)}$ (molar ratio)								6.8
$NaHCO_{3(aq)}$				6.58				
triethylamine (molar ratio)	0.19							
T (°C)	120	120	120	180	180	120	180	120
time (days)	3	3	3	1	3	3	1	3
pH_i/pH_f	3.62/1.73	4.77/3.81	5.42/3.82	7.21/5.80	7.17/5.51	4.46/3.78	6.12/4.89	5.10/5.70
yield (%, based on uranium)	10	10	15	10	45	40	20	30
crystal color and habit	yellow cubes	yellow rods	yellow plates	yellow plates	dark yellow plates	yellow plates	yellow rods	yellow plates

II. Bond valence summations

SI Table 2 – Bond valence summations for oxygen atoms in compound 3

O9		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U2	2.4936(6)	0.4469
O10		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U2	2.4765(9)	0.4725
O11		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U1	2.3419(6)	0.6001
U2	2.3295(5)	0.6165
		1.2166

Bond valence summations for select oxygen atoms in compound **3**. The values indicate that both O9 and O10 are water molecules while O11 is an hydroxyl group.[1, 2]

SI Table 3 – Bond valence summations for oxygen atoms in compound 4

O5		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U1	2.4437(7)	0.4644

The bond valence summation for oxygen atom O5 in compound **4**. The value indicates that O5 is a water molecule.[1,2]

SI Table 4 – Bond valence summations for oxygen atoms in compound 5

O4		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C6	1.2413(1)	1.4678
O6		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C7	1.2441(5)	1.4833
O13		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
Sm1	2.4236(4)	0.3573
Sm2	2.3895(4)	0.3998
Sm3	2.5208(5)	0.2830
		1.040
O14		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
Sm1	2.3871(4)	0.4075
Sm3	2.4253(4)	0.3675

Sm4	2.4837(4)	0.3139
		1.089
O15		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
Sm1	2.3693(4)	0.4276
Sm2	2.3602(4)	0.4382
Sm4	2.4870(4)	0.3111
		1.177
O17		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
Sm2	2.3942(4)	0.3998
Sm3	2.5220(4)	0.2830
Sm4	2.4049(4)	0.3884
		1.071
O16		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
Sm4	2.4573(6)	0.3371
O19		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
Sm3	2.4947(5)	0.3047
O30		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
Sm1	2.4958(6)	0.3038
O3		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C6	1.2846(7)	1.3295
U1	2.4151(5)	0.3778
		1.707
O5		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C3	1.329(8)	0.2163
Sm1	2.621(5)	0.3692
Sm4	2.423(5)	1.179
		1.764
O7		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C7	1.281(9)	1.344
U1	2.487(9)	0.4519
Sm1	2.466(1)	0.3289
		2.120
O10		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**

C10	1.284(7)	1.330
Sm4	2.256(4)	0.5796
		1.909
O11		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C14	1.246(7)	1.508
Sm4	2.405(4)	0.3381
		1.896
O12		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U1	2.188(4)	0.8040
U1’	2.232(4)	0.7388
Sm1	2.522(4)	0.2830
		1.825
O18		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C14	1.268(7)	1.389
Sm2	2.405(4)	0.3875
Sm3	2.585(4)	0.2385
		2.015
O20		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C13	1.274(7)	1.365
Sm3	2.522(4)	0.2824
Sm3’	2.530(4)	0.2767
		1.942
O40		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
C13	1.237(8)	1.508
Sm4	2.405(9)	0.3881
		1.896

The bond valence summation for oxygen atoms in compound **5**. The values indicate that oxygen atoms O4, O6, O13, O14, O15, and O17 are hydroxyl groups. The bond valence summations for oxygen atoms O16, O19, and O30 indicate the presence of a water molecule. For oxygen atoms O3, O5, O7, O10, O11, O12, O18, O20, and O40 the values indicate oxides.[1,2]

SI Table 5 – Bond valence summations for oxygen atoms in compound 6

O3		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U1	2.4075(9)	0.4978
O9		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U2	2.4285(5)	0.4780

The bond valence summations for select oxygen atoms in compound **6**. The values indicate that O3and O9 are both water molecules.[1,2]

SI Table 6 – Bond valence summations for oxygen atoms in compound 7

O10		
Bonded Atom	**Distance (Å)**	**Bond valence summation (vu)**
U2	2.3876(4)	0.5173

The bond valence summation for oxygen atom O10 in compound **7**. The value indicates that O10 is a water molecule.[1,2]

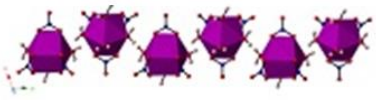
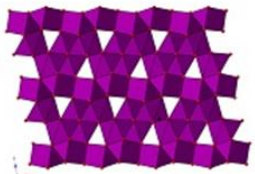
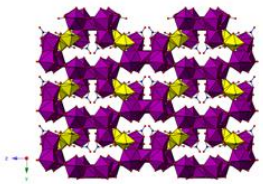
III. Bond Distances

SI Table 7 – Na-O bond distances of compound 8

Na-O bond	**Bond Distance (Å)**
Na1-O2	2.4511(9)
Na1-O3	2.3707(6)
Na1-O5	2.3225(4)
Na1-O10	2.4214(9)
Na1-O11	2.8294(1)
Na1-OW1	2.7701(1)
Na1-OW1	2.5050(2)

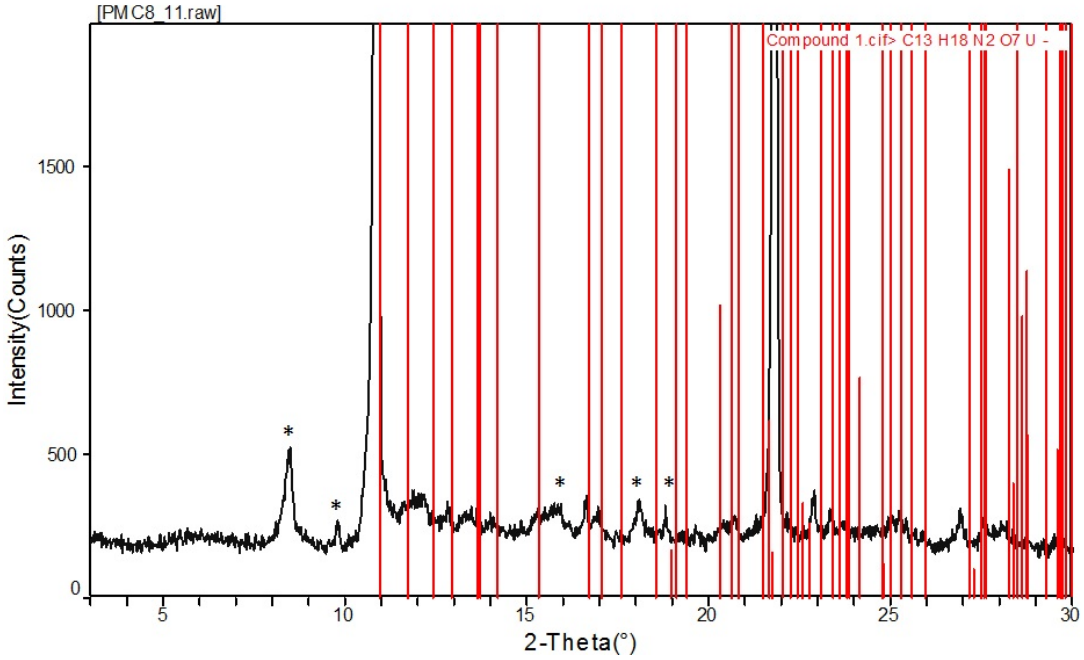
IV. Comparison of samarium structures

SI Table 8 – Topology, Sm-Sm bond distances, and corresponding emission results of the following complexes: $Sm(NO_3)_2\ 6H_2O$,[3] Sm_2O_3,[4] and compound 5

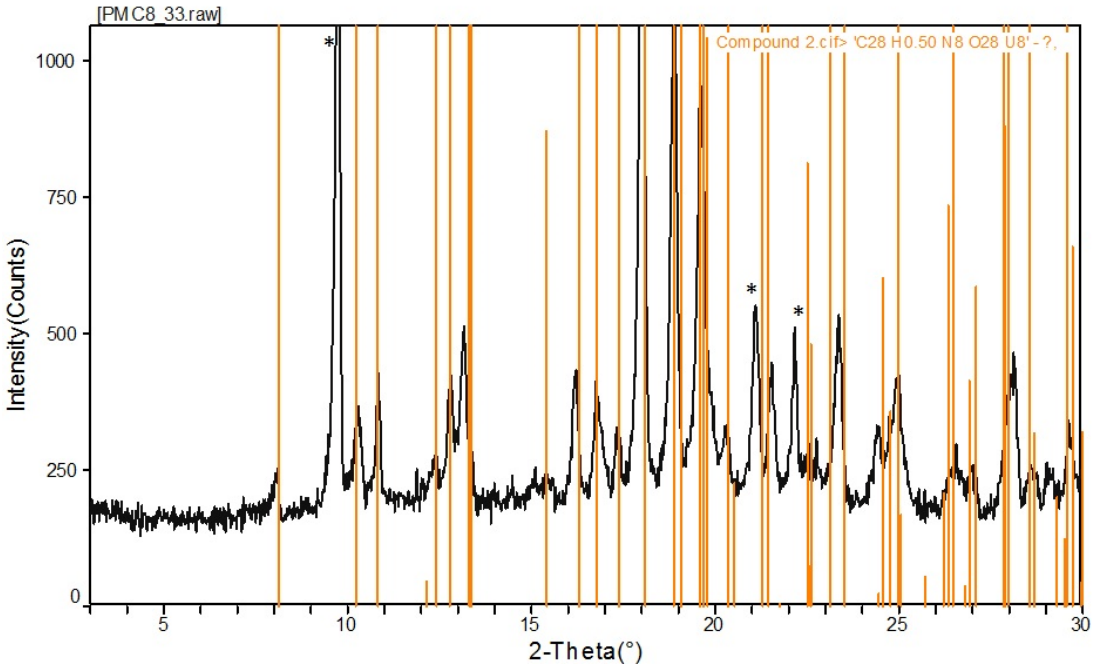
Compound	**Topology**	**Sm-Sm bond distance(s) (Å)**	**Exhibits Sm emission? (λ_{ex} = 420 nm)**
(a) $Sm(NO_3)_2 \cdot 6H_2O$	 monomeric units	Sm1-Sm1 7.570	yes
(b) Sm_2O_3	 edge-sharing 2D sheet	Sm1-Sm2 3.342 Sm3-Sm3 3.618 Sm1-Sm1 3.633 Sm2-Sm2 3.743 Sm1-Sm3 3.854	no
(c) $[(UO_2)_2(Sm)_7(C_7H_2N_1O_5)_2(C_7H_4O_5N_1)_2(O)_7(OH)_4(NO_3)(H_2O)_3] \cdot 2H_2O$	 3D framework	Sm1-Sm4 3.6812(8) Sm2-Sm3 3.7087(7) Sm2-Sm4 3.8488(6) Sm3-Sm4 3.9062(6) Sm3-Sm1 4.0787(8)	no

V. Powder X-ray diffraction data

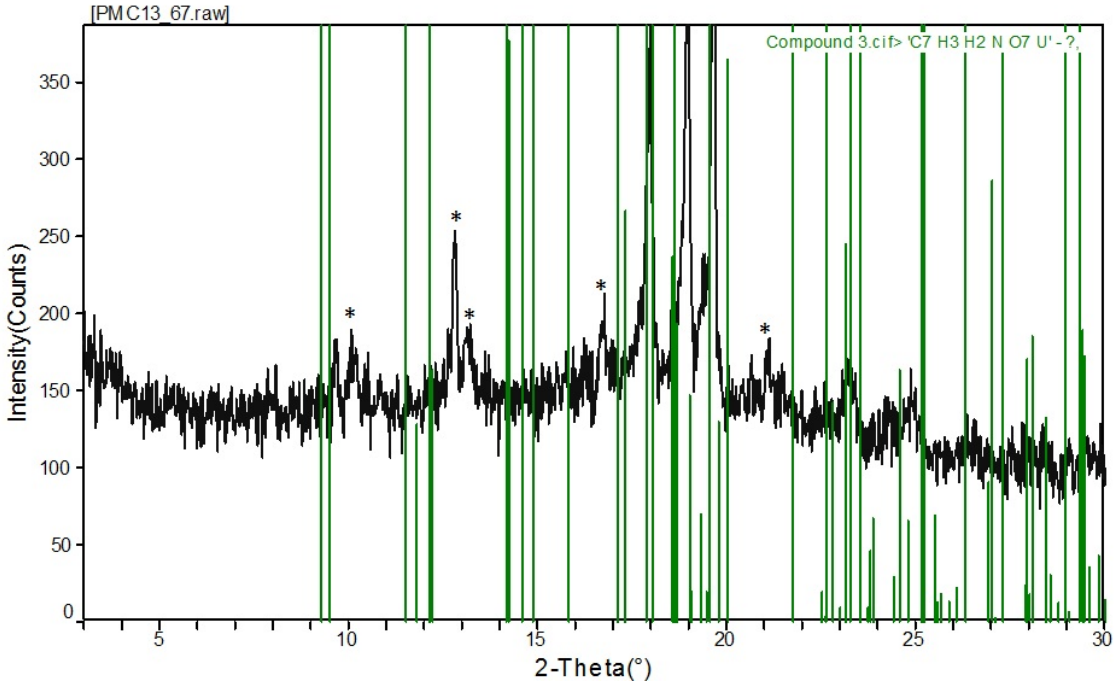
For the following PXRD data it is important to note that calculated patterns were collected at low temperature (100 K) while observed patterns were collected at room temperature (298 K). This may account for signal shifts and data resolution.



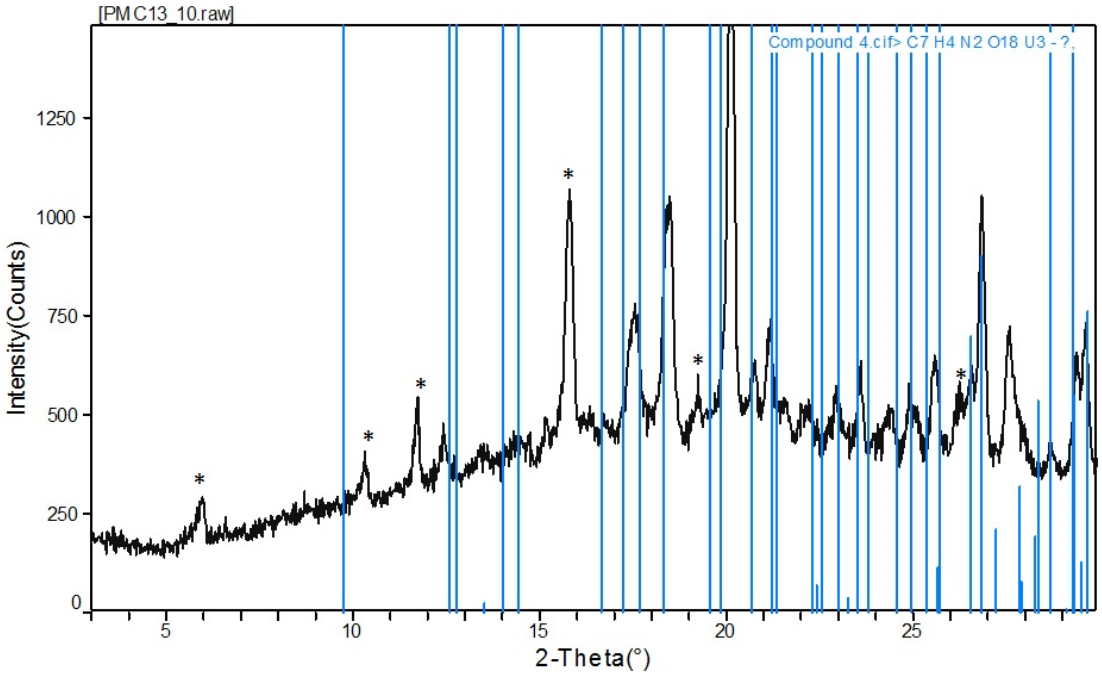
SI Figure 1 – The PXRD pattern of **1** overlaid with the calculated pattern (red lines). The asterisks indicate unidentified end products.



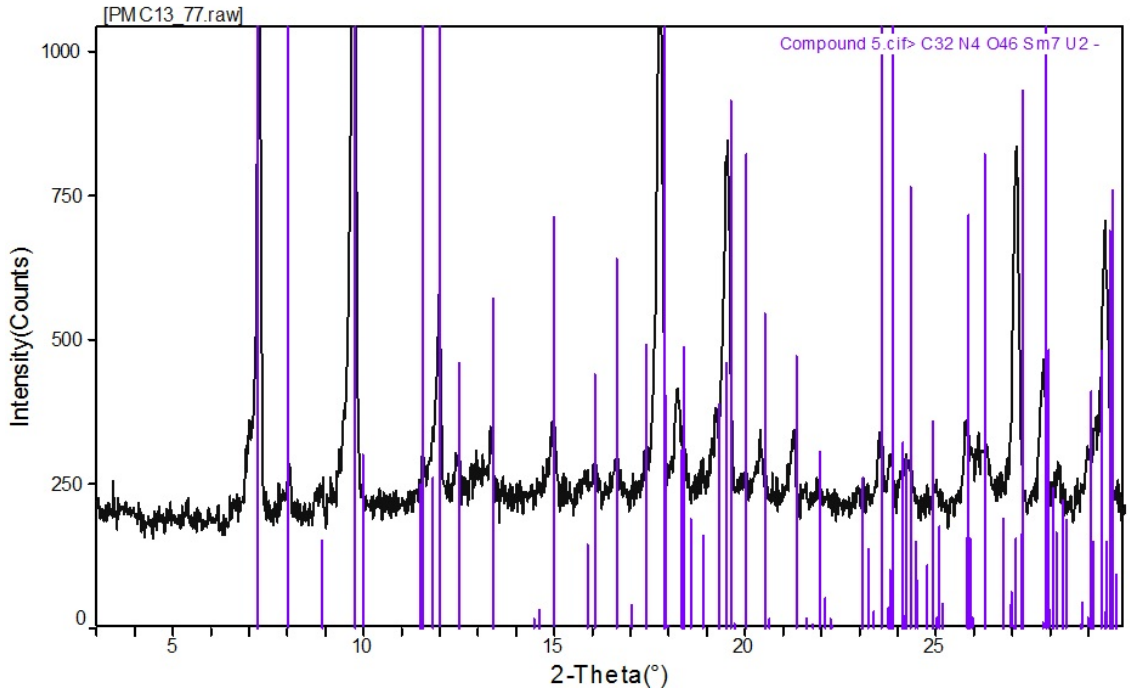
SI Figure 2 – The PXRD pattern of **2** overlaid with the calculated pattern (orange lines). The asterisks indicate unidentified end products.



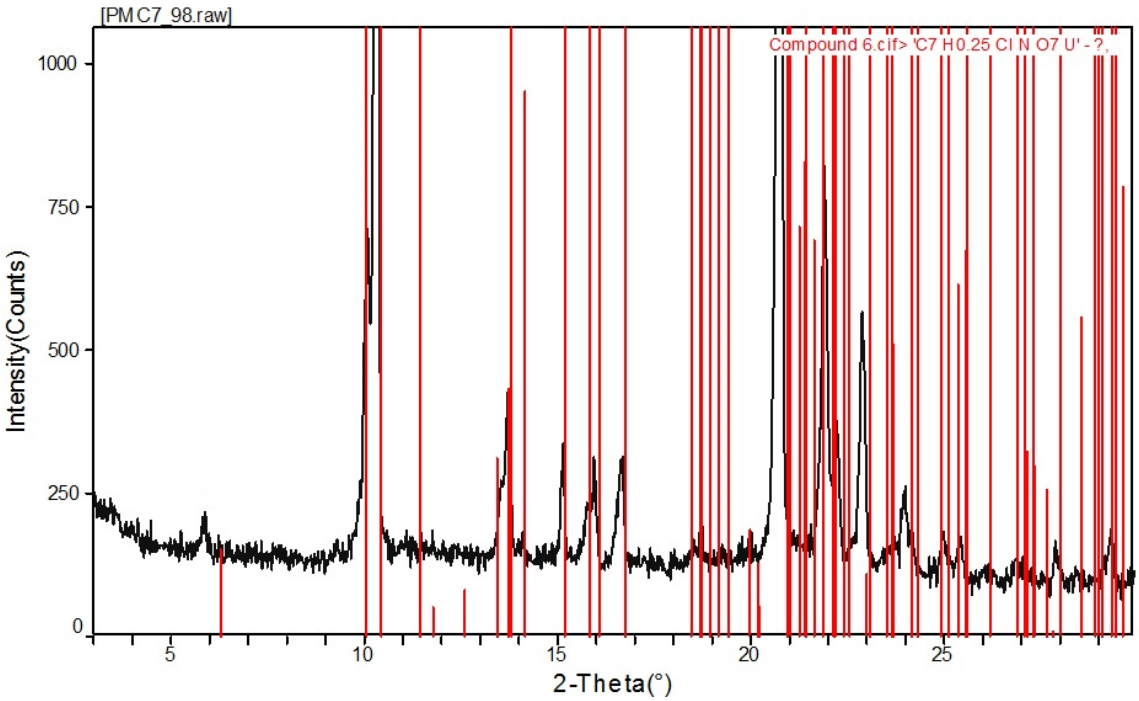
SI Figure 3 – The PXRD pattern of 3 overlaid with the calculated pattern (green lines). The asterisks indicate unidentified end products.



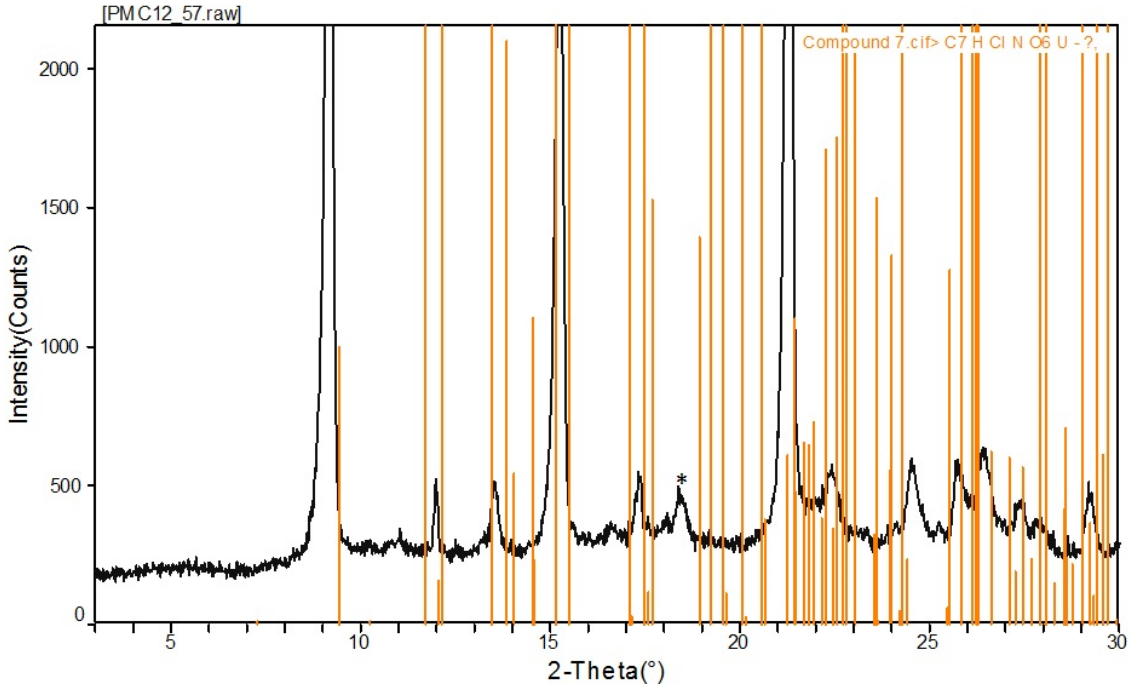
SI Figure 4 – The PXRD pattern of **4** overlaid with the calculated pattern (blue lines). The asterisks indicate unidentified end products.



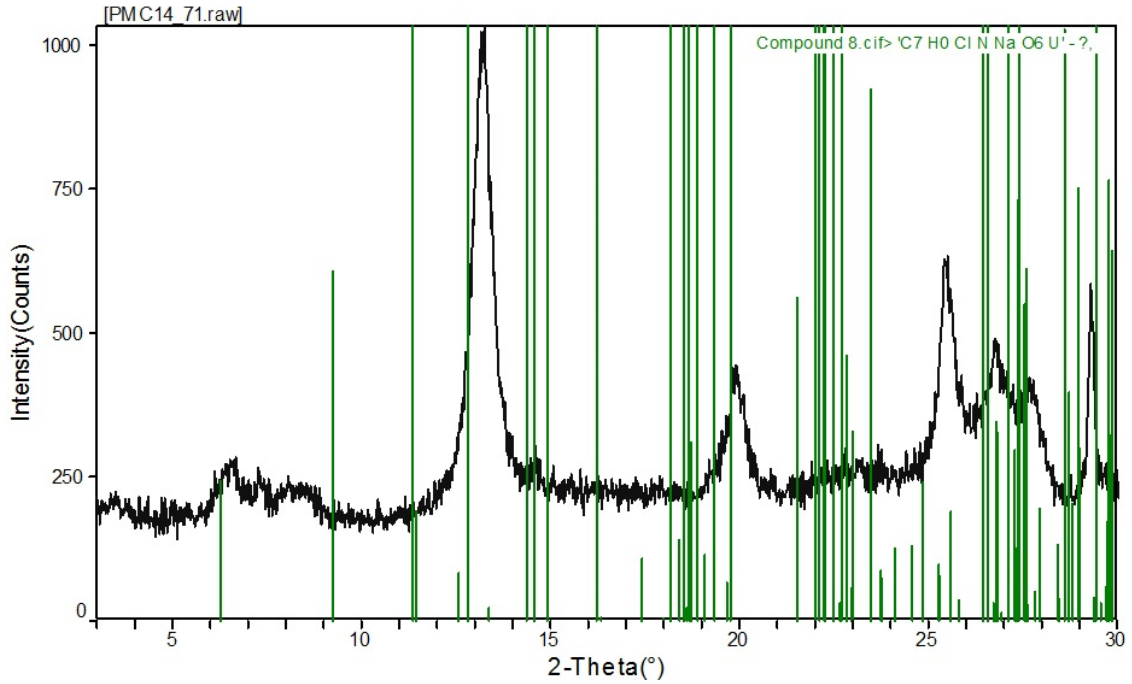
SI Figure 5 – The PXRD pattern of **5** overlaid with the calculated pattern (purple lines).



SI Figure 6 – The PXRD pattern of **6** overlaid with the calculated pattern (red lines).

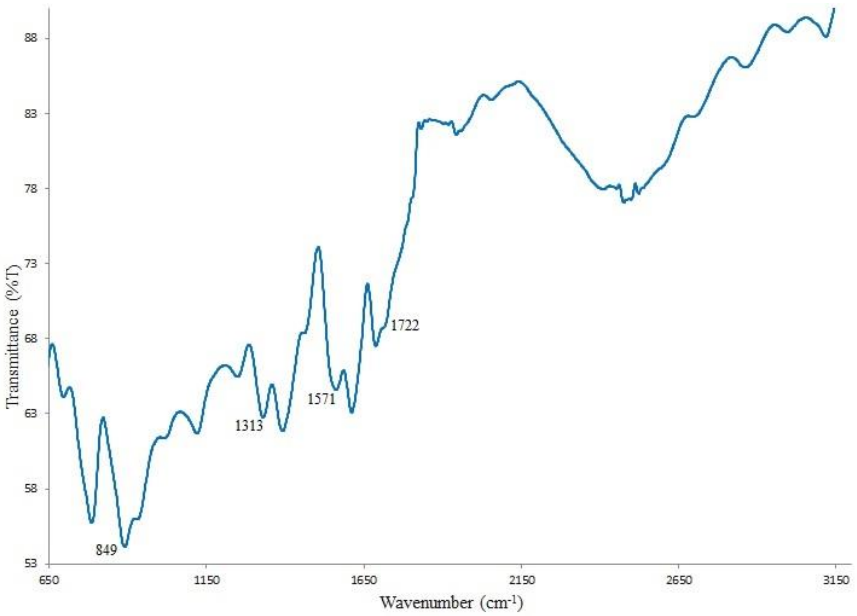


SI Figure 7 – The PXRD pattern of **7** overlaid with the calculated pattern (orange lines). The asterisk indicates an unidentified end product.



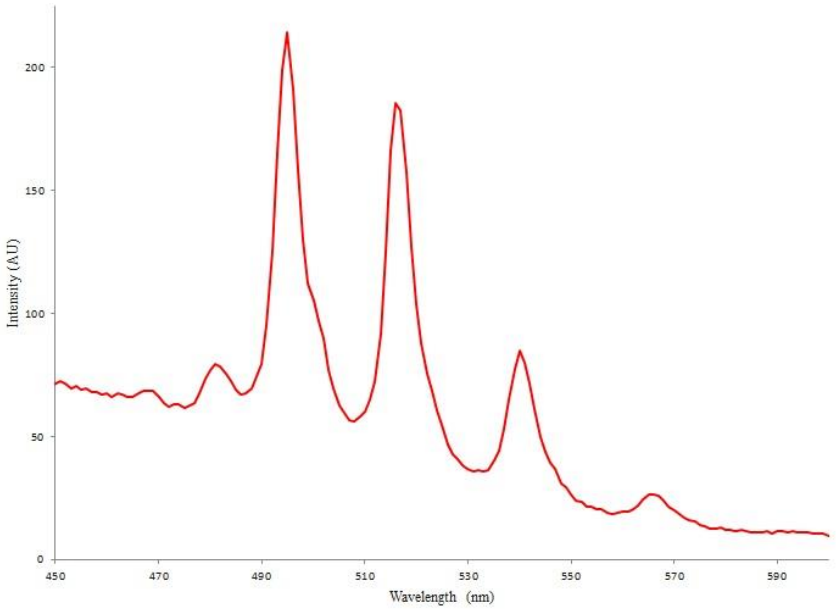
SI Figure 8 – The PXRD pattern of **8** overlaid with the calculated pattern (green lines).

VI. IR spectra

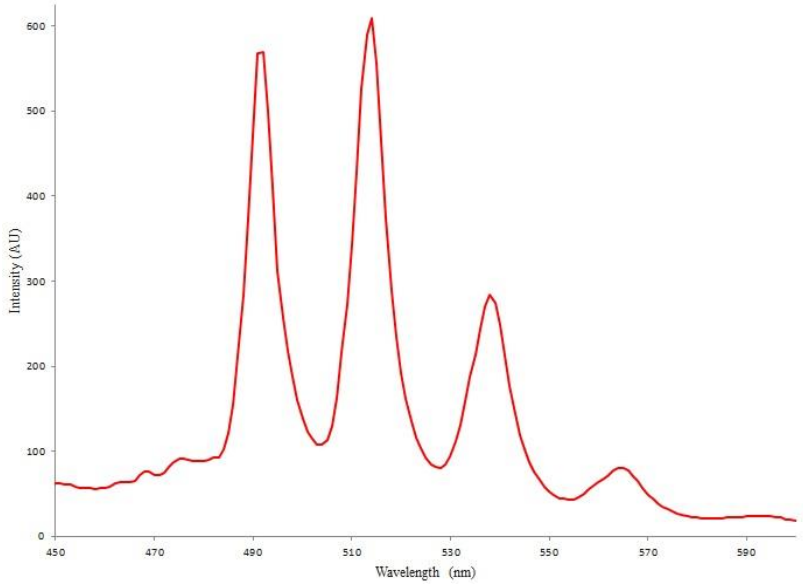


SI Figure 9 – The IR spectra of 4-chloro-2,6-pyridine dicarboxylic acid (blue line). The strongest vibrations (1722 cm^{-1}, 1571 $cm^{-1,}$ 1313 cm^{-1}, and 849 cm^{-1}) are in agreement with literature values.[5]

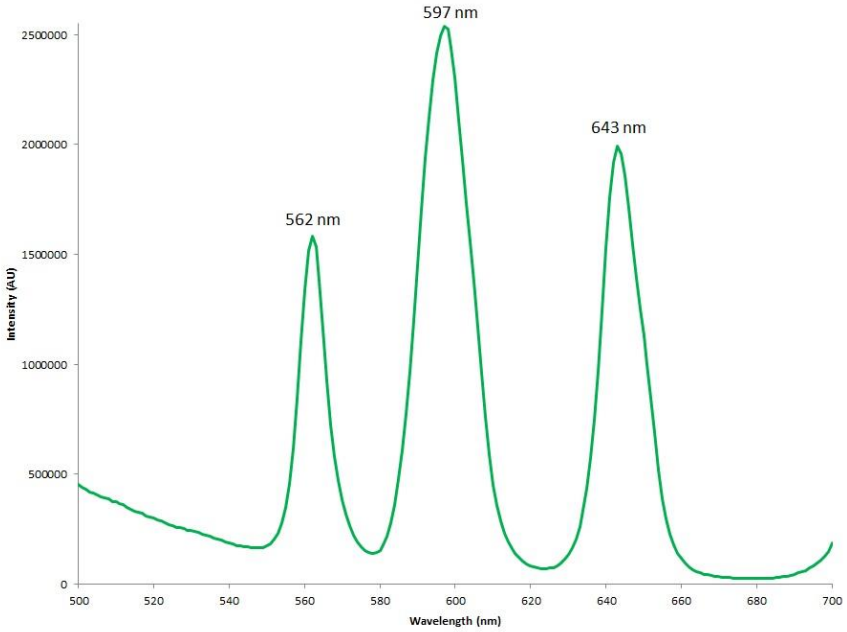
VII. Luminescence Studies



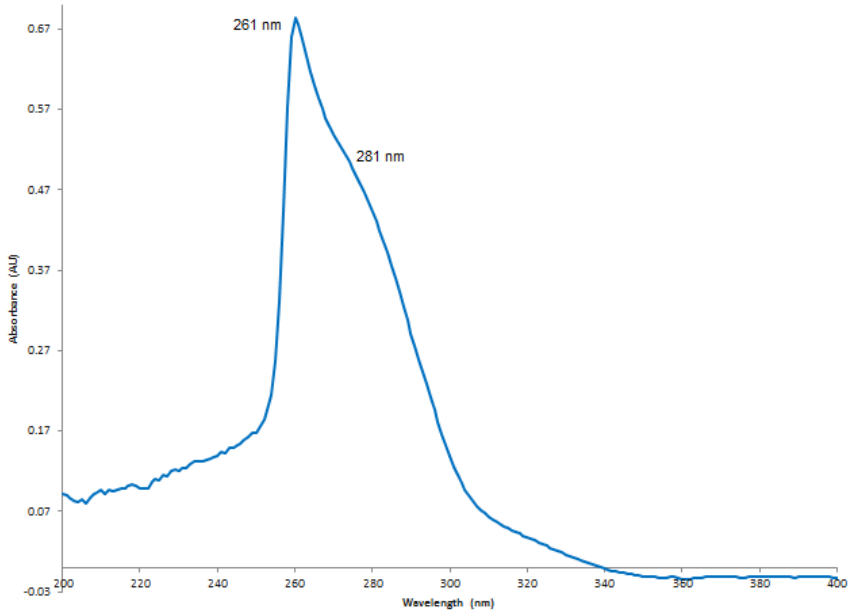
SI Figure 10 - Emission spectrum for **1** (red line, λ_{ex} = 365nm). This data is included for completeness, yet due to the impurity in the PXRD data (SI Fig. 1) we hesitate to attribute definitively the uranyl emission solely to compound **1**.



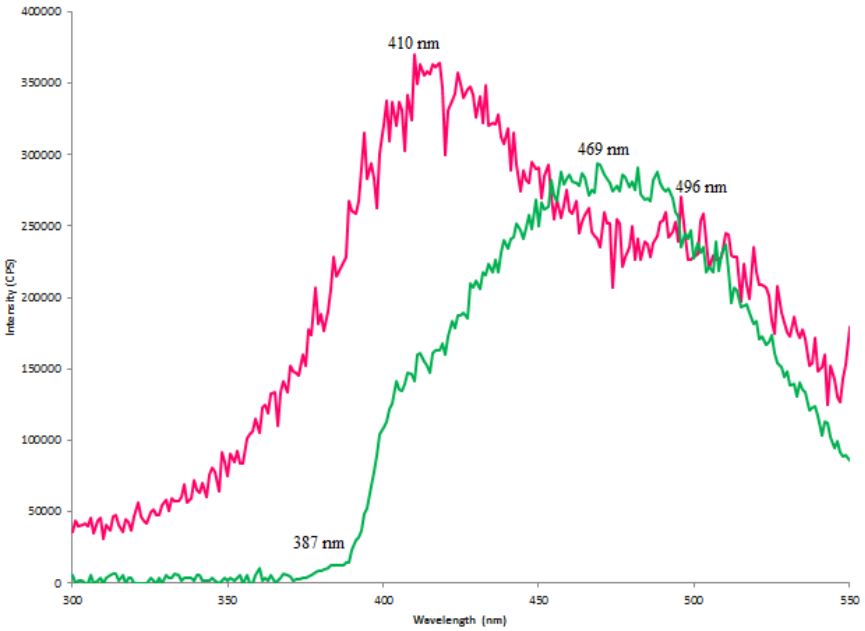
SI Figure 11 – Emission spectrum for **6** (red line, λ_{ex} = 365nm).



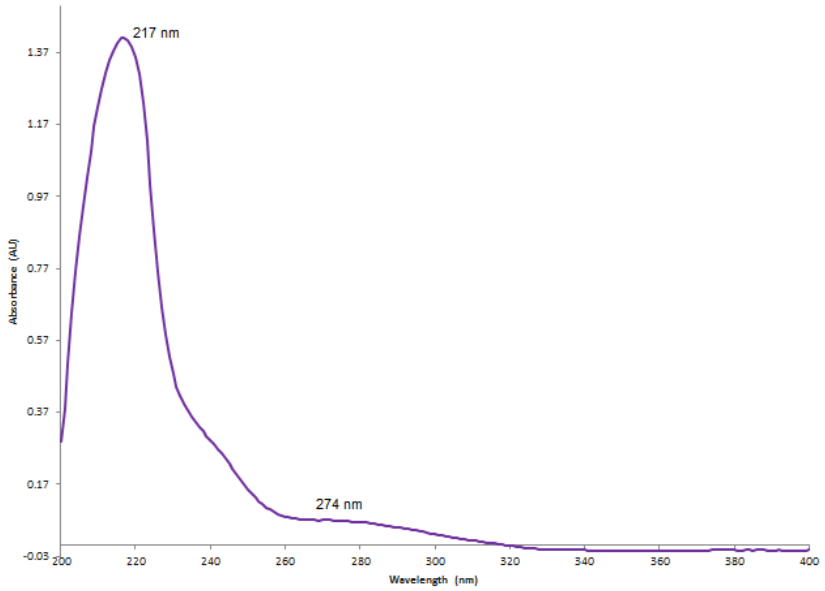
SI Figure 12 – A segment of the emission spectrum of $Sm(NO_3)_3 \cdot 6H_2O$. Bands in the visible region are located at 562 nm, 597 nm, and 643 nm.



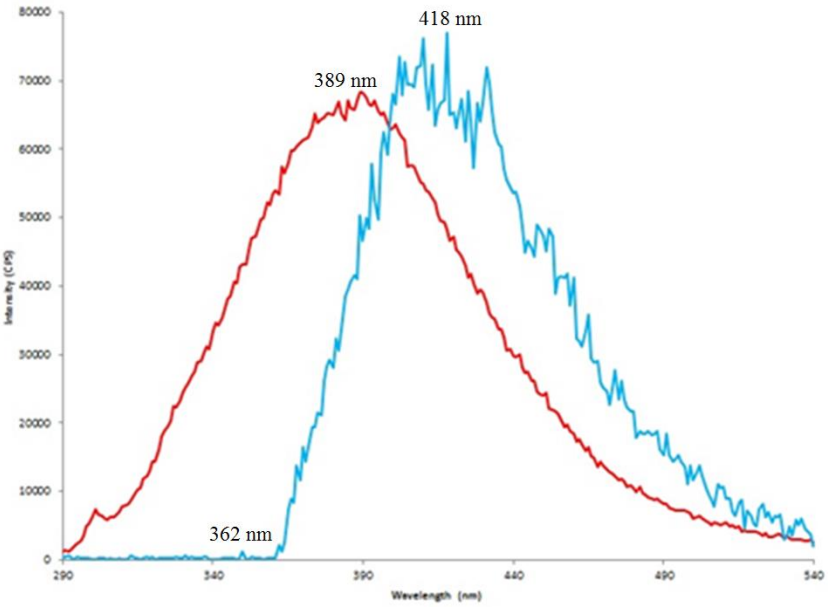
SI Figure 13 – The solution state UV-vis absorbance spectra of chelidamic acid dissolved in isopropanol (0.0001 M) with two peak maxima: 261 nm and 281 nm. Solid state fluorescence of chelidamic acid was collected with excitation wavelengths of 261 and 281 nm, yet only 281 nm produced a fluorescence spectrum of the free ligand.



SI Figure 14 – These two spectra represent the room temperature solution state fluorescence spectra of chelidamic acid (pink) excited at 281 nm and the low temperature solution state phosphorescence spectra of chelidamic acid (green) using the same excitation wavelength. The triplet state on-set is observed at 387 nm.

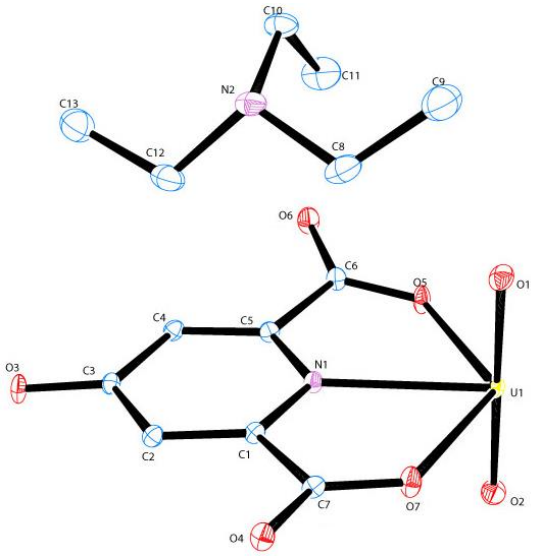


SI Figure 15 - The solution state UV vis absorbance spectra of 4-chloro-2,6-pydc dissolved in isopropanol (0.0001 M). Although there are two maxima (261 and 274 nm) as indicated by the absorbance spectra, an excitation wavelength of 274 nm was the only wavelength to generate fluorescence spectra of the free ligand.

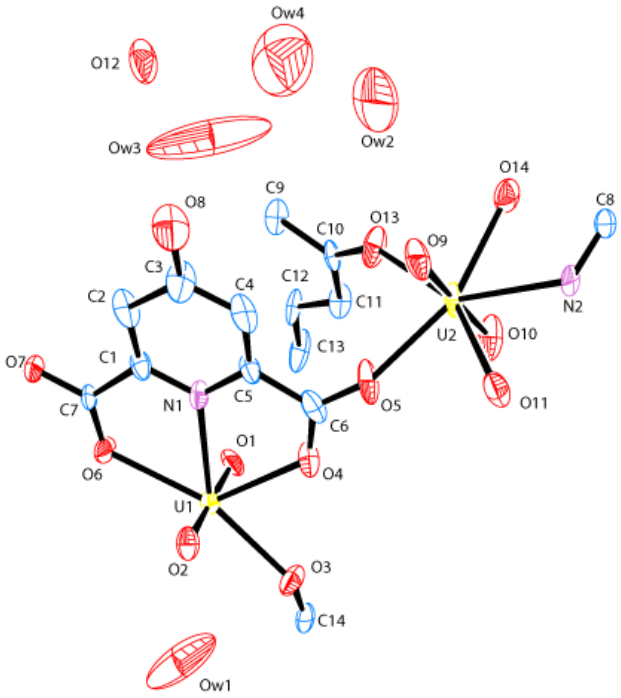


SI Figure 16 – These two spectra represent the room temperature solution state fluorescence spectra of 4-chloro-2,6-pydc (red) excited at 274 nm and the low temperature solution state phosphorescence spectra of the same ligand (blue) also at 274 nm. The triplet state on-set is observed at 362 nm.

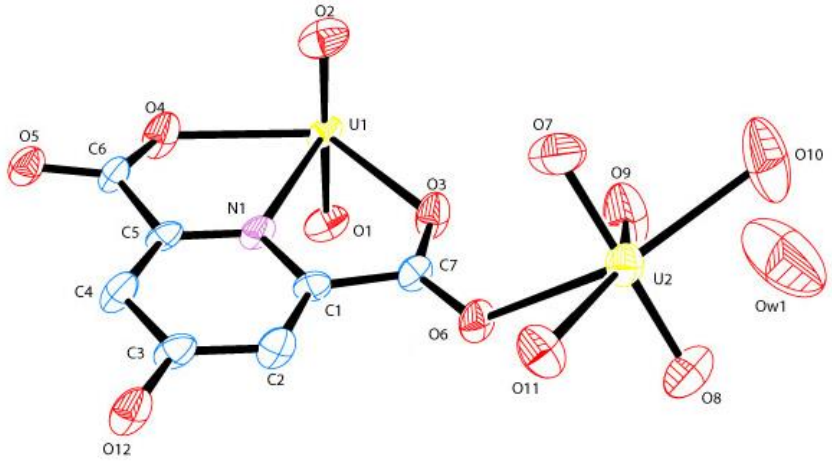
VIII. Thermal Ellipsoid Plots



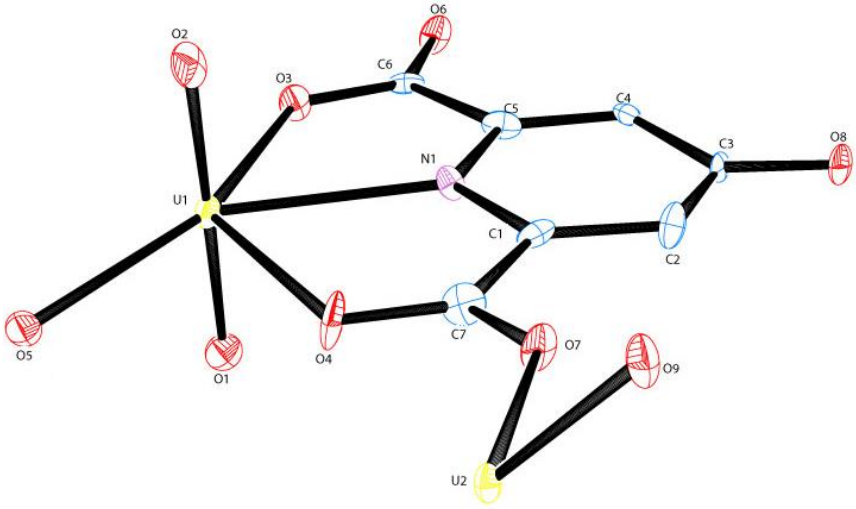
SI Figure 17 – ORTEP of the asymmetric unit of **1** shown with ellipsoids at 50% probability.



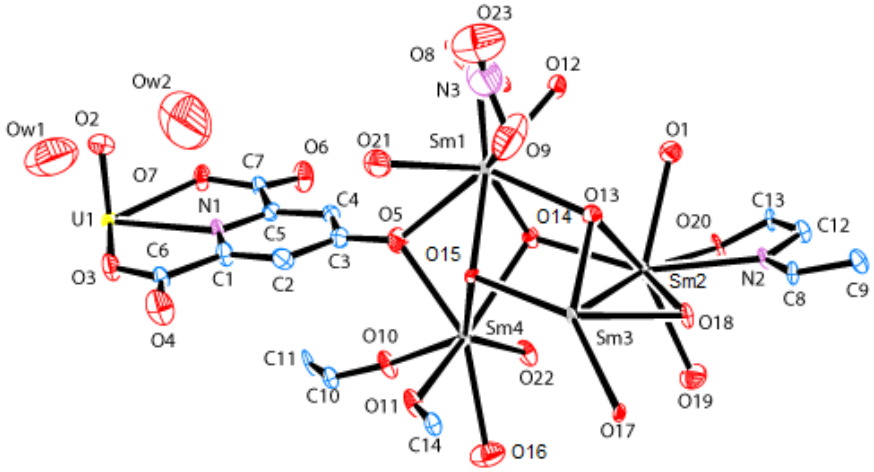
SI Figure 18 – ORTEP of the asymmetric unit of **2** shown with ellipsoids at 50% probability.



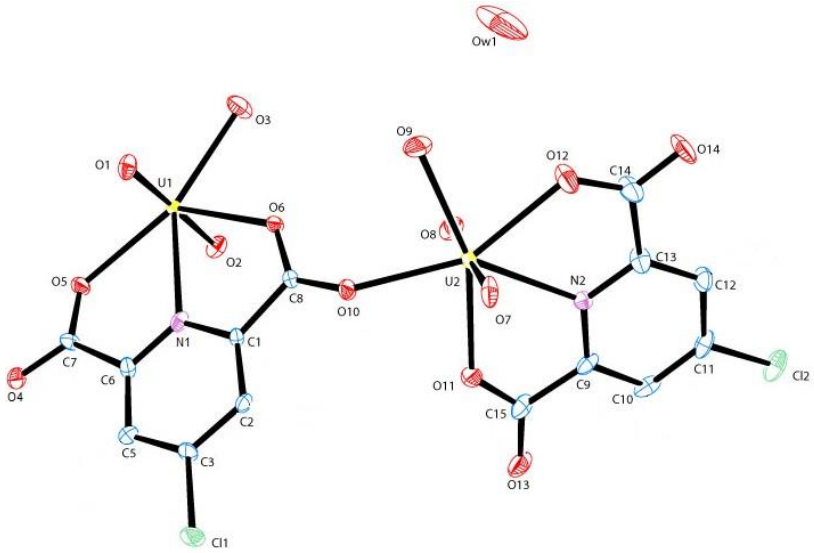
SI Figure 19 – ORTEP of the asymmetric unit of **3** shown with ellipsoids at 50% probability.



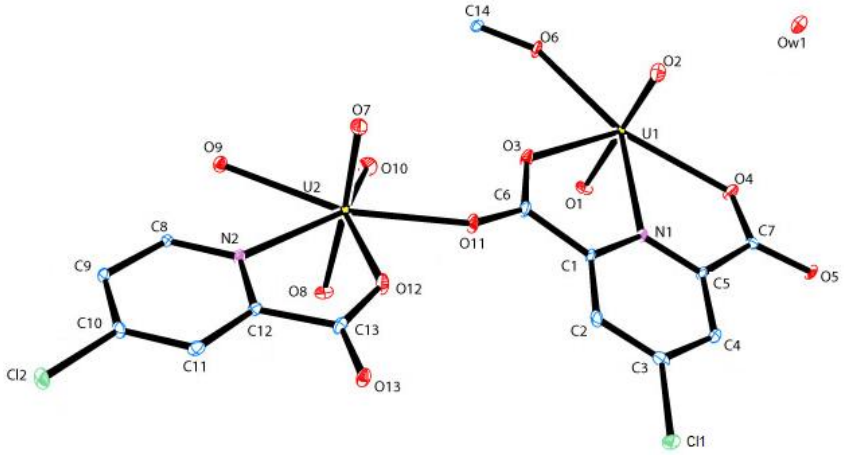
SI Figure 20 – ORTEP of the asymmetric unit of **4** shown with ellipsoids at 50% probability.



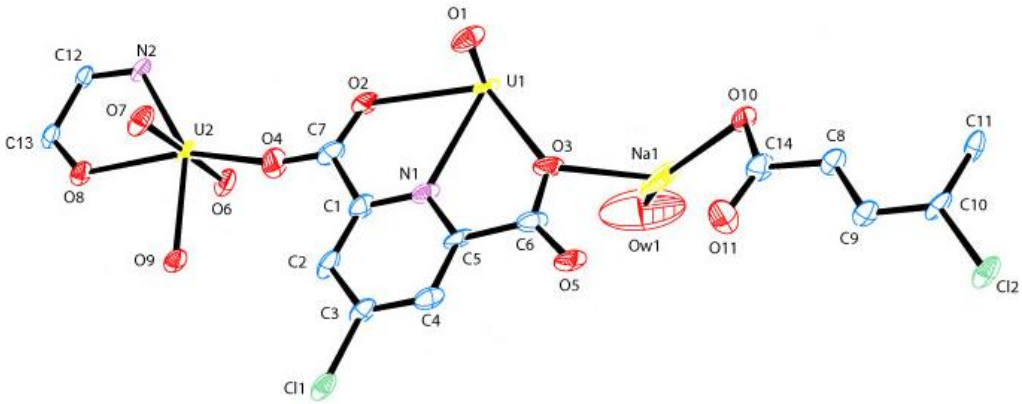
SI Figure 21 – ORTEP of the asymmetric unit of **5** shown with ellipsoids at 50% probability.



SI Figure 22 – ORTEP of the asymmetric unit of **6** shown with ellipsoids at 50% probability.



SI Figure 23 – ORTEP of the asymmetric unit of **7** shown with ellipsoids at 50% probability.



SI Figure 24 – ORTEP of the asymmetric unit of **8** shown with ellipsoids at 50% probability.

IX. References

1. I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B: Struct. Sci.*, 1985, **41**, 244-247.
2. P. A. Giesting and P. C. Burns, *Crystallogr. Rev.*, 2006, **12**, 205-255.
3. R. S. Kawashima, Michio; Satoh, Shoichi; Isoda, Hiroshi; Kino, Yukihiro; Shiozaki, Yoichi, *J. Phys. Soc. Jpn.*, 2000, **69**, 3297-3303.
4. D. T. Cromer, *J. Phys. Chem.*, 1957, **61**, 753-755.
5. M. R. George, C. A. Golden, M. C. Grossel and R. J. Curry, *Inorg. Chem.*, 2006, **45**, 1739-1744.