Synthesis, structural analysis, and supramolecular assembly of a series of *in-situ* generated uranyl-peroxide complexes with functionalized 2,2'-bipyridine and varied carboxylic acid ligands

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Supporting Information

I. Table of N-Donor/O-Donor Reaction Attempts

N-Donor		Monocarboxylate O-Donor	Crystals?
2,2-bipyridine		**Acetate**	**Yes[1]**
		BA	**Yes[2]**
		2-FBA	No
		3-FBA	**Yes***
		4-FBA	No
		2-ClBA	No
		3-ClBA	**Yes***
		4-ClBA	No
		2-BrBA	No
		3-BrBA	No
		4-BrBA	No
		2-IBA	No
		3-IBA	**Yes***
		4-IBA	No
		3,5-ClBA	No
		2,3,5-ClBA	No
		2,3,4,5-ClBA	No
		4-Amino-BA	No
		4-Cyano-BA	No
		4-Mercapto-BA	No
		4-Nitro-BA	No
		Phosphonoacetic	No
		4-methyl-BA	**Yes***
		2-Thiophene	**Yes***
X, X'- methyl-2,2'-bipyridine	4,4'-Methyl-	Acetate	No
		BA	No
		4-methyl-BA	No
		4-BrBA	No
	5,5'-Methyl-	**Acetate**	**Yes[1]**
		BA	No
		4-methyl-BA	No
4,4'-bromo-2,2'-bipyridine		**Acetate**	**Yes***
		BA	**Yes***
		4-BrBA	No
		4-BrMeBA	**Yes***

Table S1 N-donor (Left Column) and O-donor (Middle Column) reaction pairing attempts and diffraction quality single crystals success (Right column). "**Yes[#]**" signifies a complex that has been previous synthesized and reported (1: S. G. Thangavelu and C. L. Cahill, *Inorg Chem*, 2015, 54, 4208-4221 and 2: Sokolova, M. N., Bessonov, A. A., Fedoseev, A. M., *Radiokhimiya*, 2012, 54, 313) and "**Yes***" shows a complex that is presented within this manuscript.

II. Powder X-ray Diffraction Data

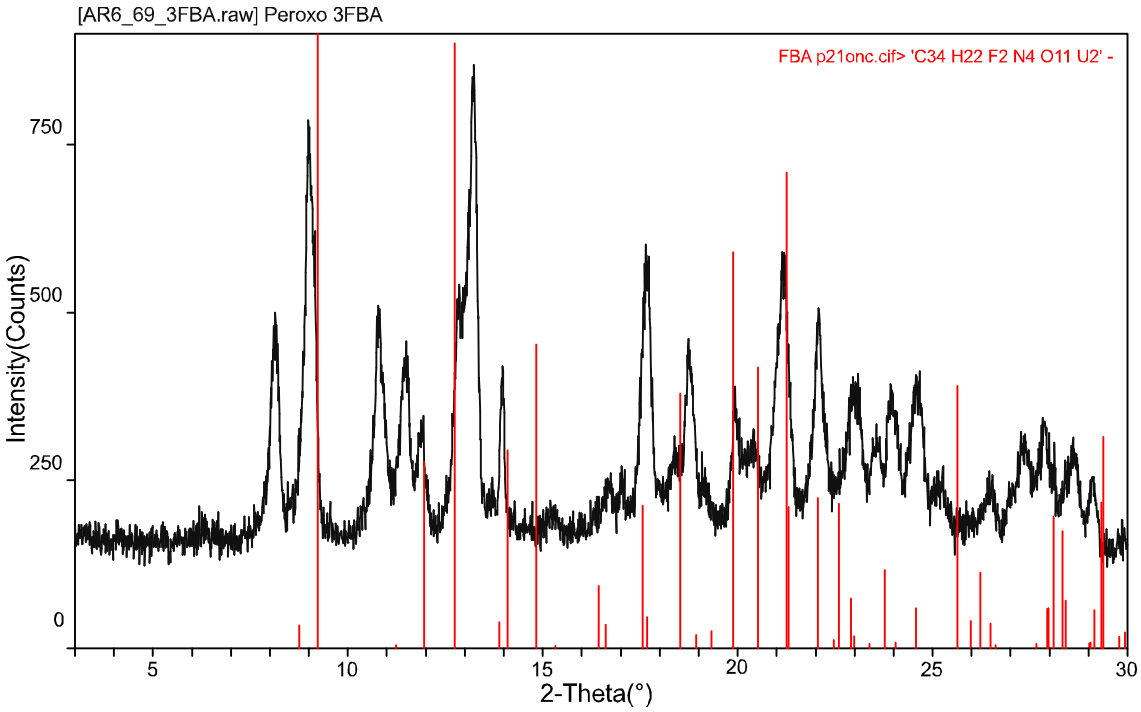


Figure S1: Powder X-ray fraction pattern of complex **1**, with the calculated pattern overlaid in red.

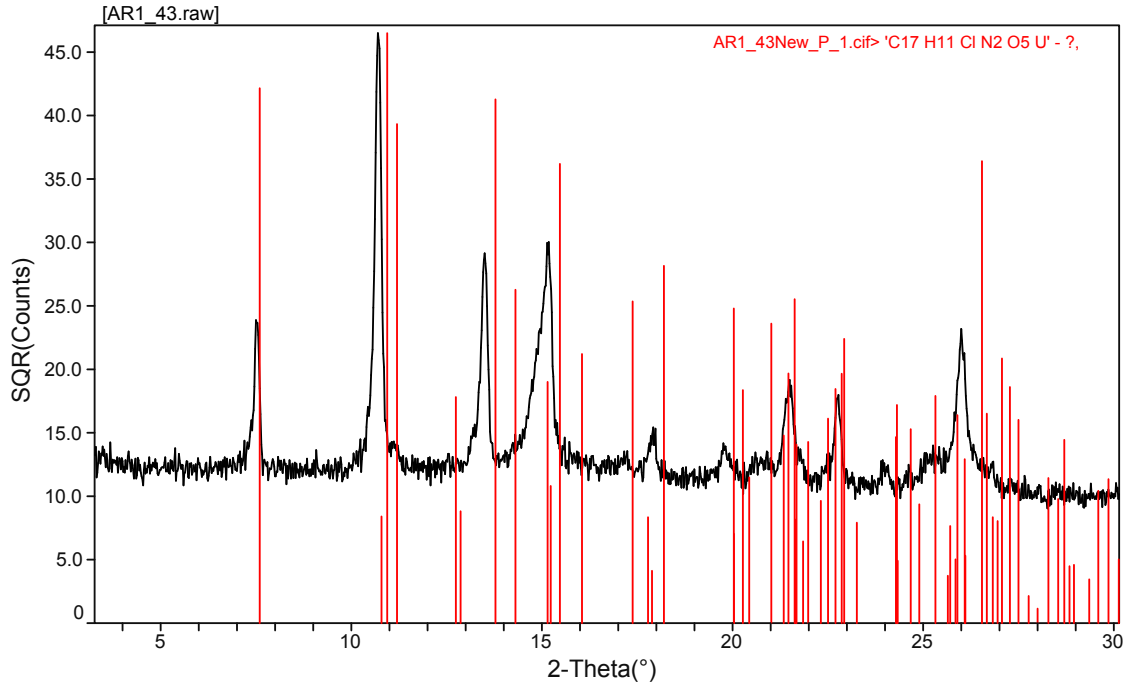


Figure S2: Powder X-ray fraction pattern of complex **2**, with the calculated pattern overlaid in red.

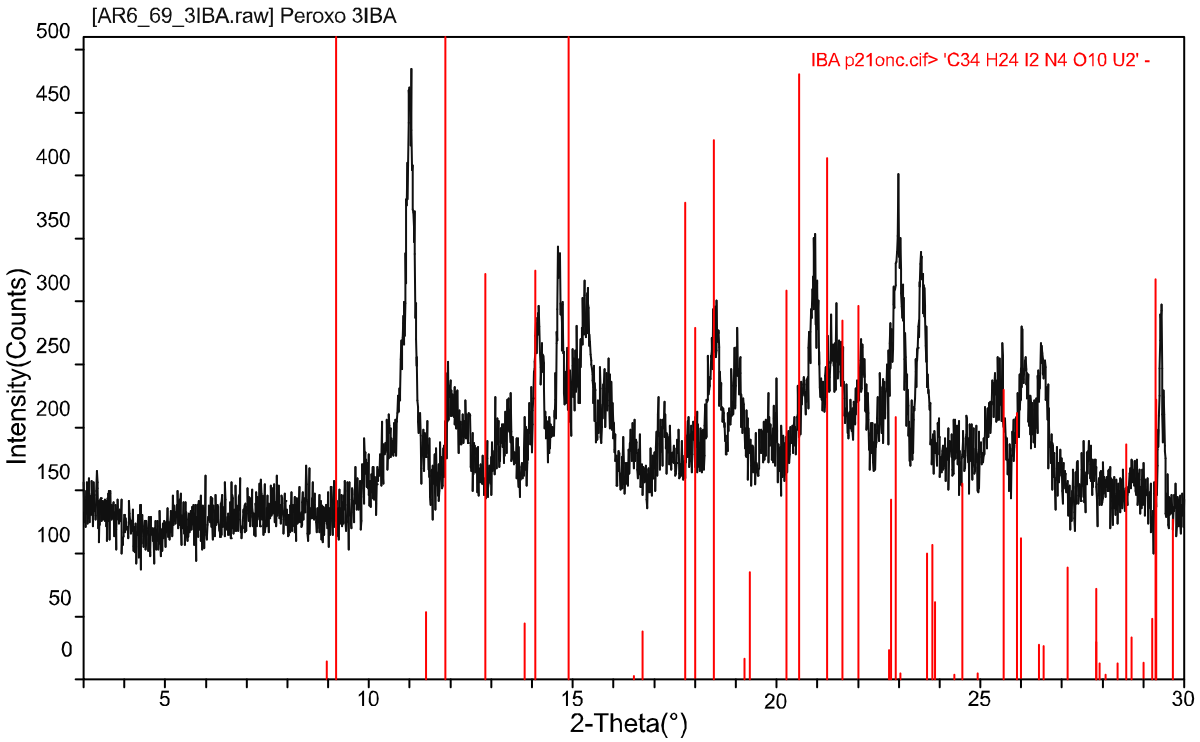


Figure S3: Powder X-ray fraction pattern of complex **3**, with the calculated pattern overlaid in red.

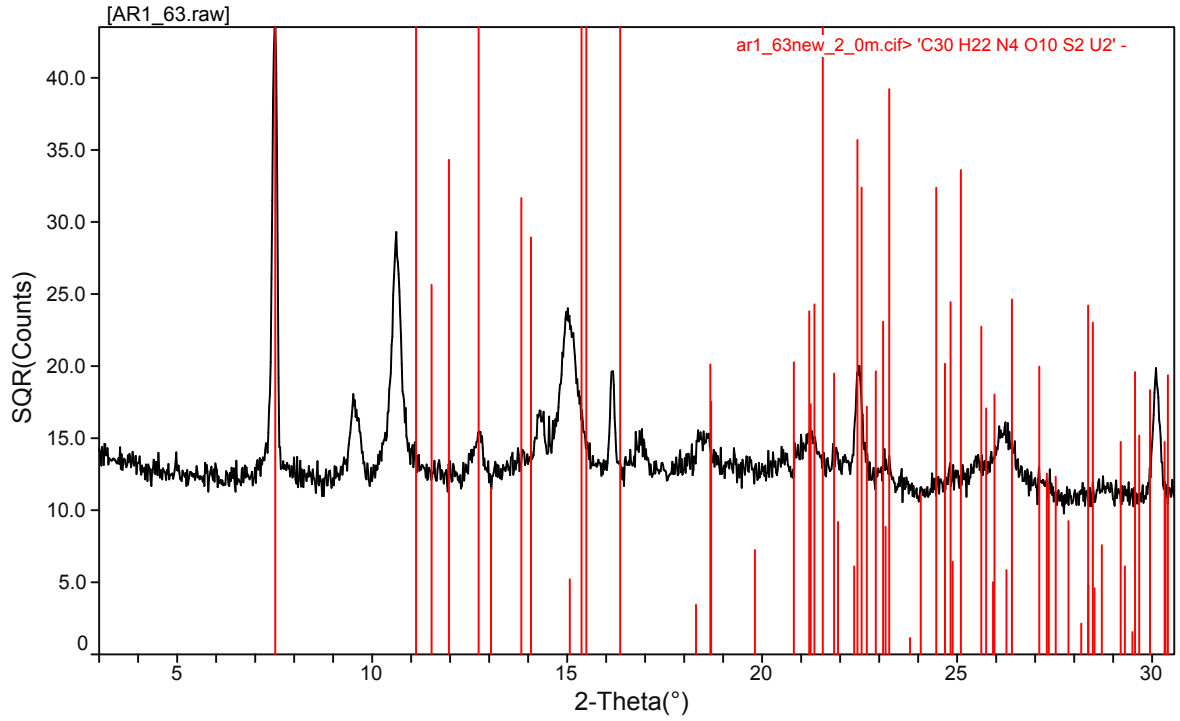


Figure S4: Powder X-ray fraction pattern of complex **4**, with the calculated pattern overlaid in red.

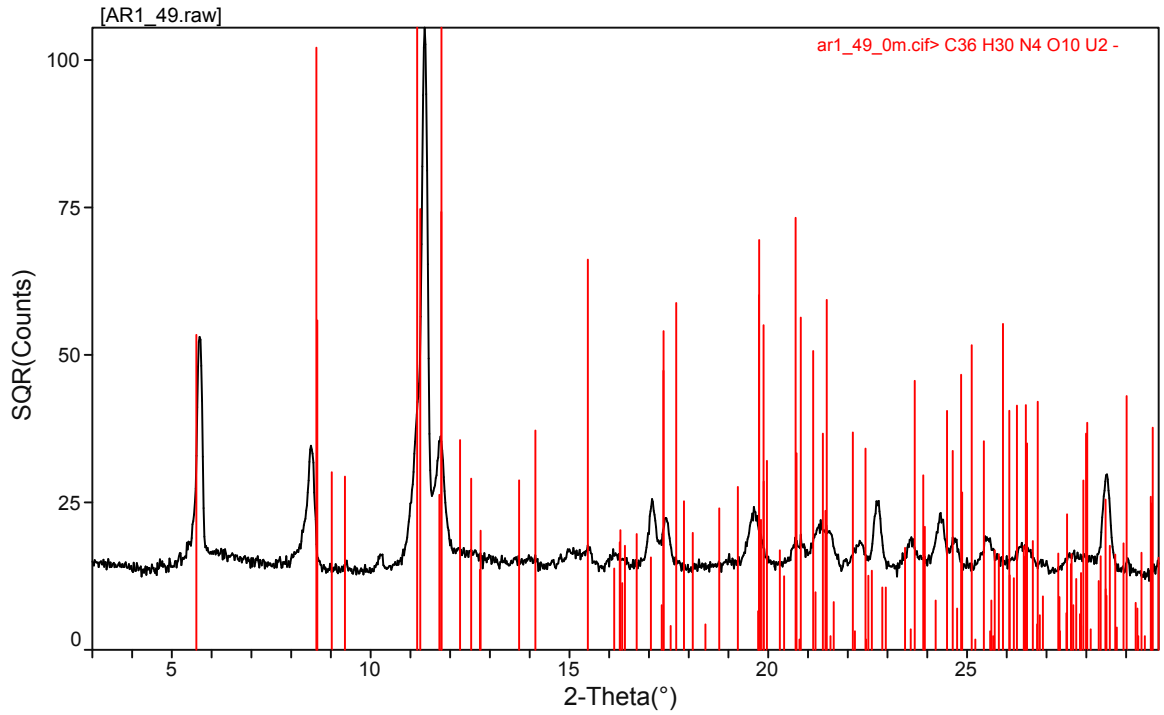


Figure S5: Powder X-ray fraction pattern of complex **5**, with the calculated pattern overlaid in red.

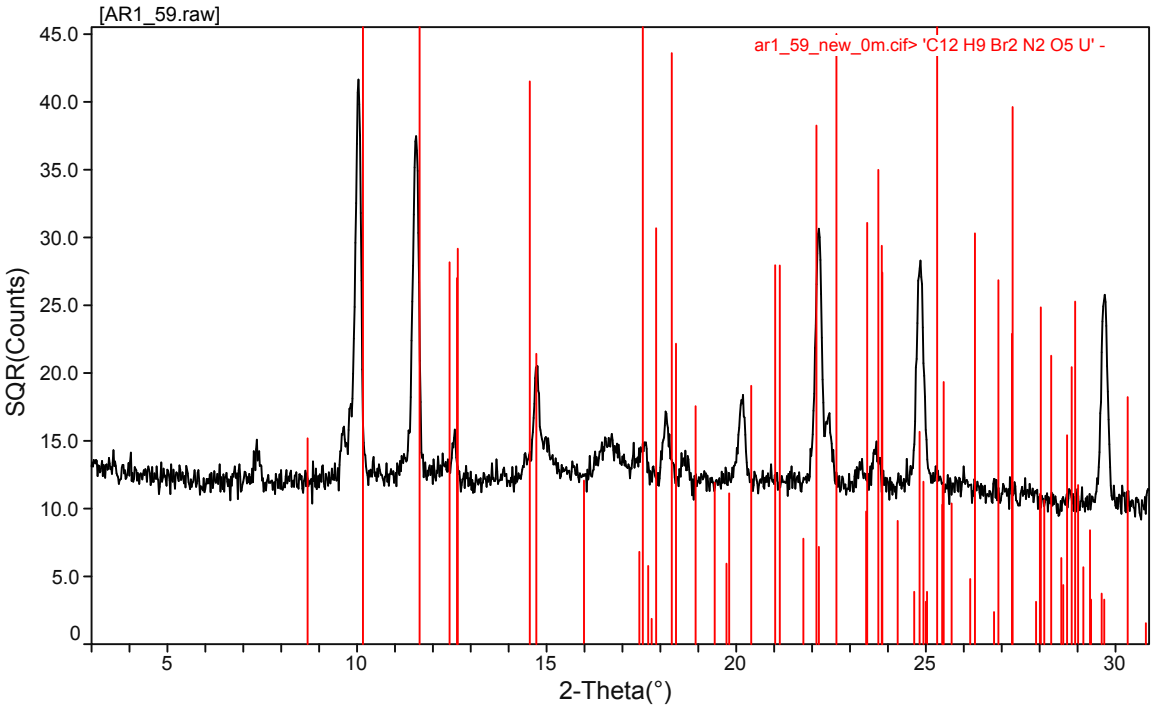


Figure S6: Powder X-ray fraction pattern of complex **6**, with the calculated pattern overlaid in red.

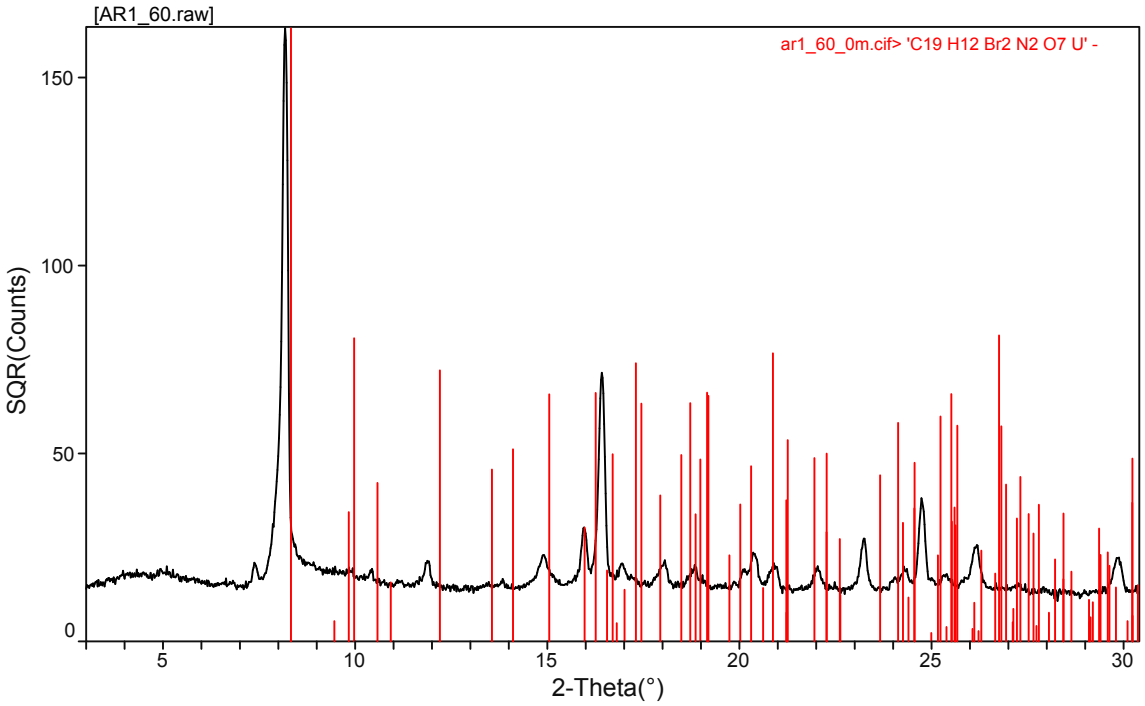


Figure S7: Powder X-ray fraction pattern of complex **7**, with the calculated pattern overlaid in red.

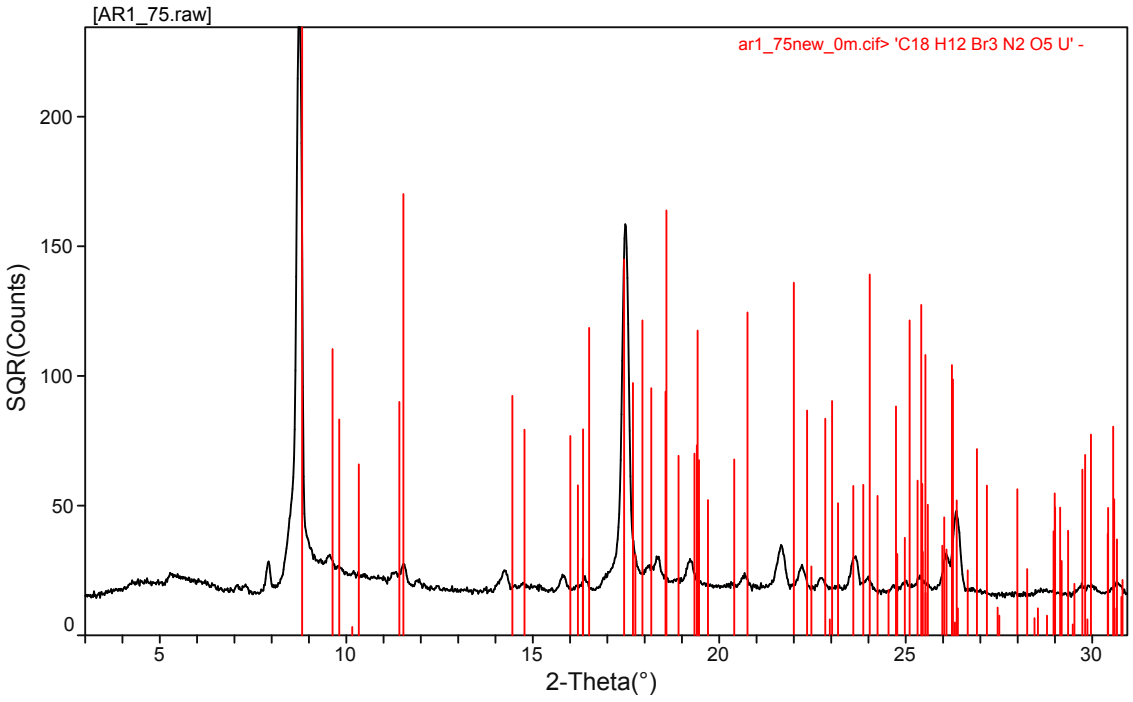


Figure S8: Powder X-ray fraction pattern of complex **8**, with the calculated pattern overlaid in red.

III. Thermal Ellipsoid Plots

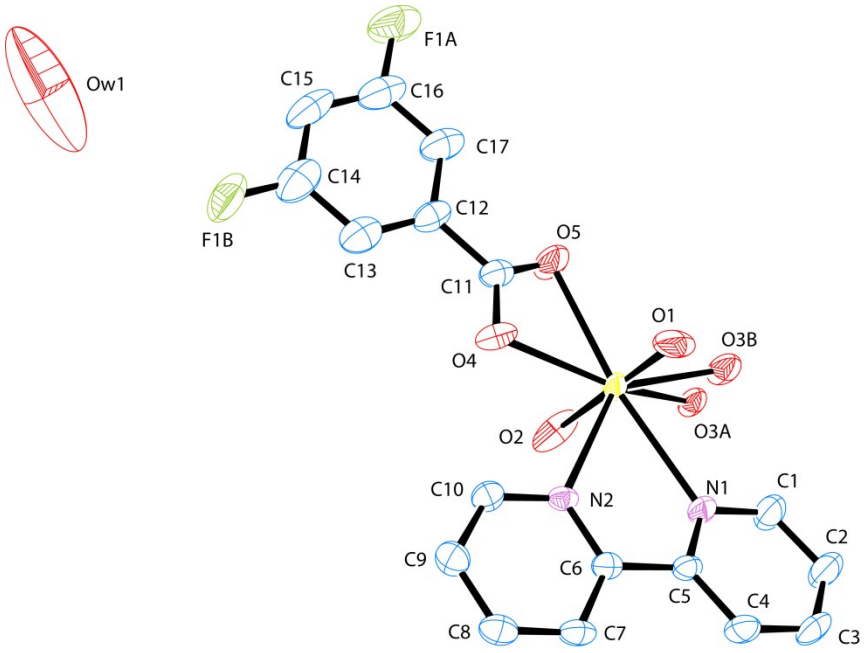


Figure S9: ORTEP illustration of complex **1**. Ellipsoids are shown at 50% probability level.

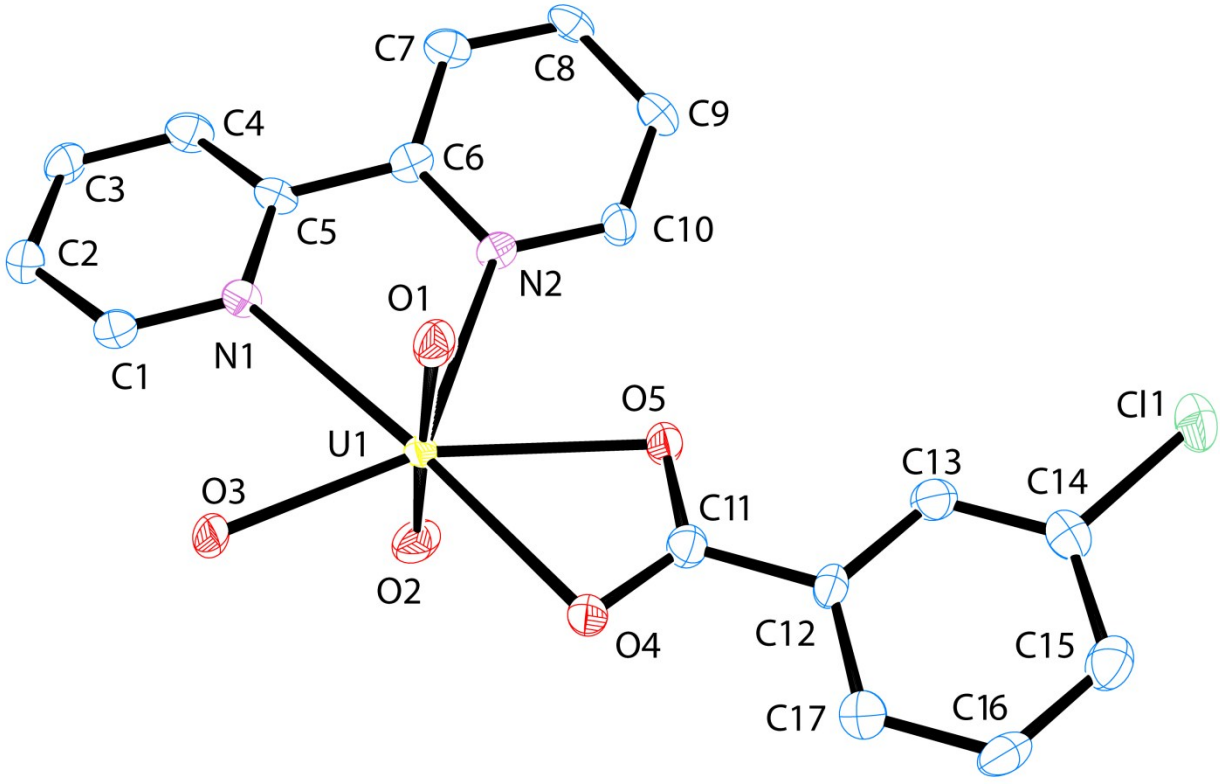


Figure S10: ORTEP illustration of complex **2**. Ellipsoids are shown at 50% probability level.

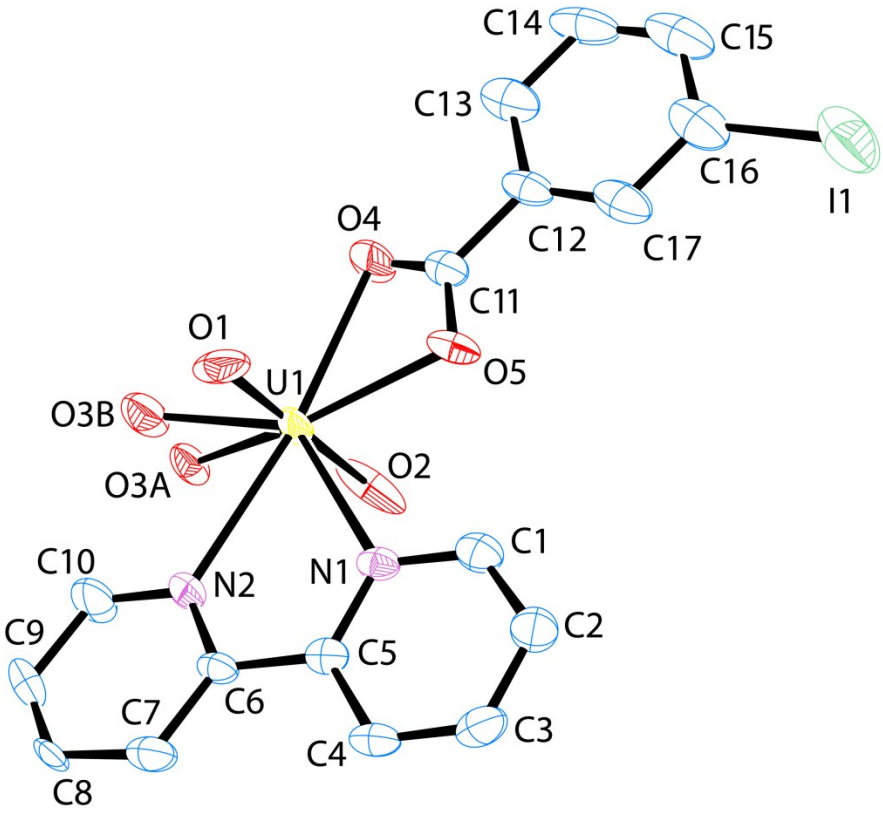


Figure S11: ORTEP illustration of complex **3**. Ellipsoids are shown at 50% probability level.

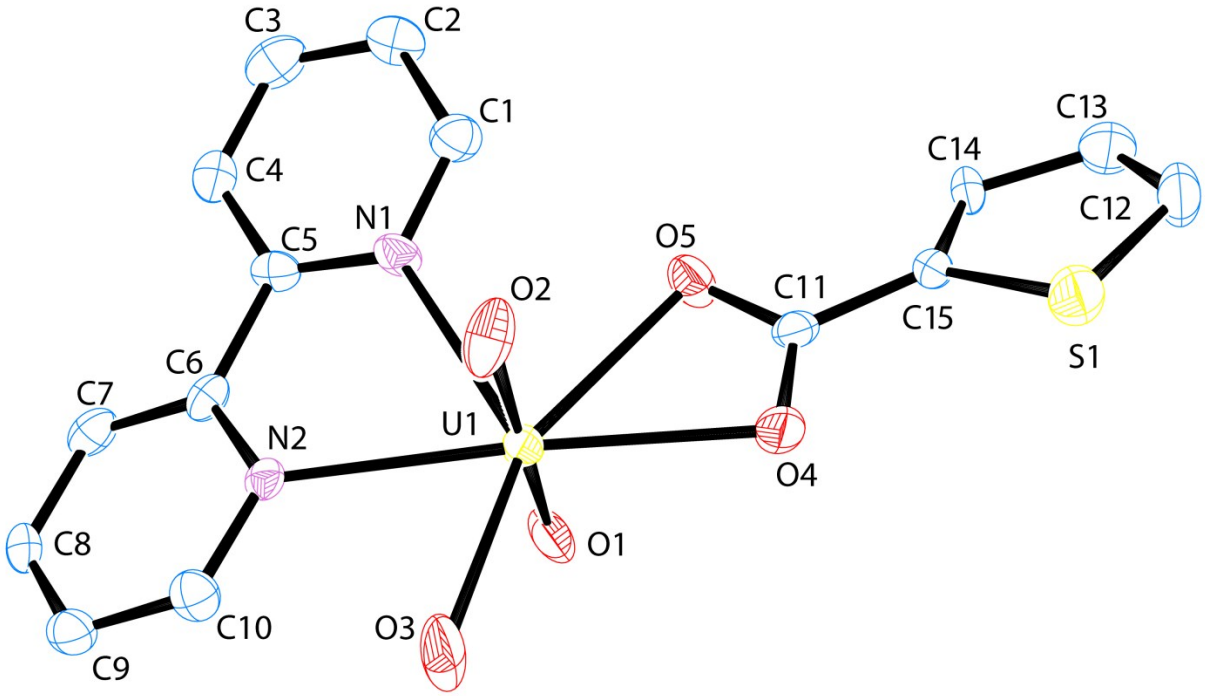


Figure S12: ORTEP illustration of complex **4**. Ellipsoids are shown at 50% probability level.

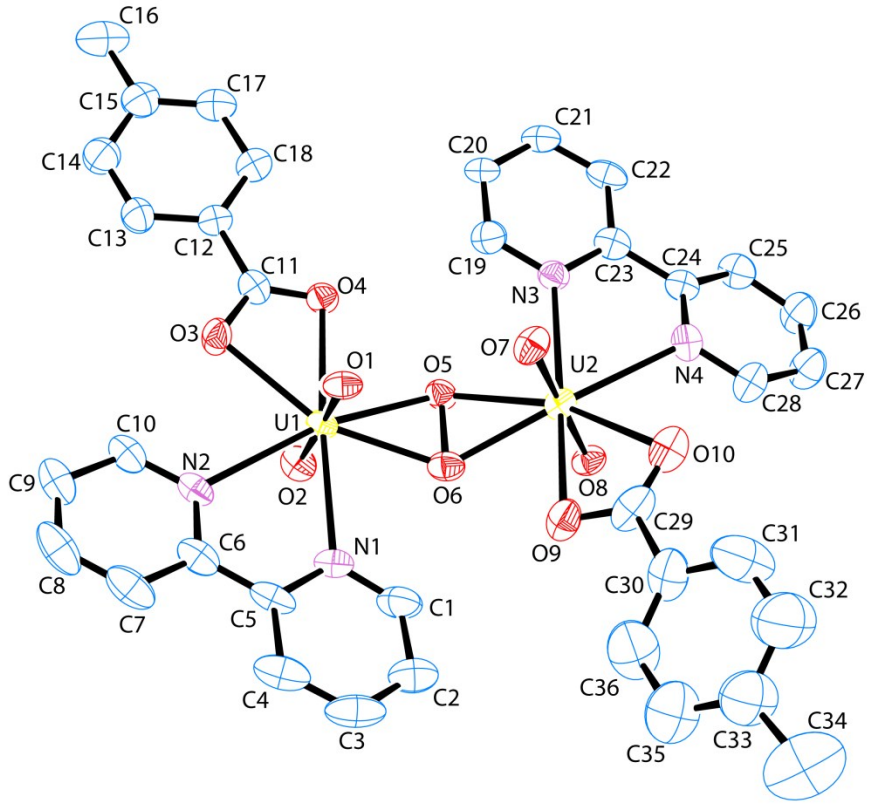


Figure S13: ORTEP illustration of complex **5**. Ellipsoids are shown at 50% probability level.

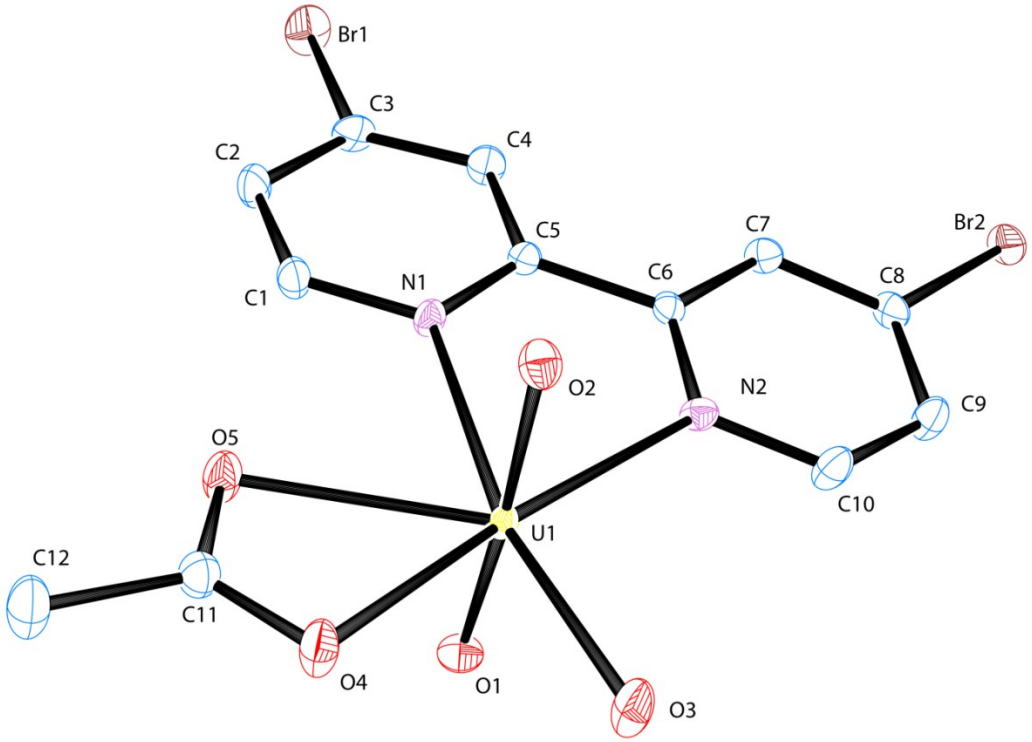


Figure S14: ORTEP illustration of complex **6**. Ellipsoids are shown at 50% probability level.

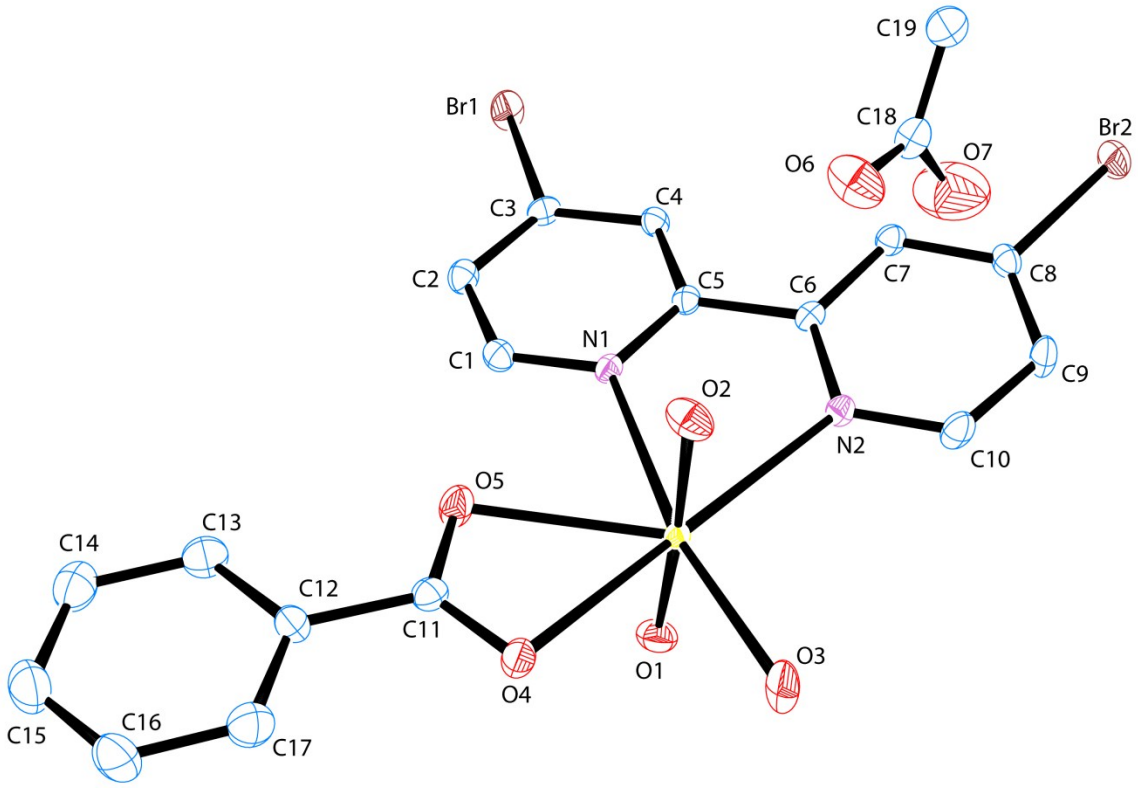


Figure S15: ORTEP illustration of complex **7**. Ellipsoids are shown at 50% probability level.

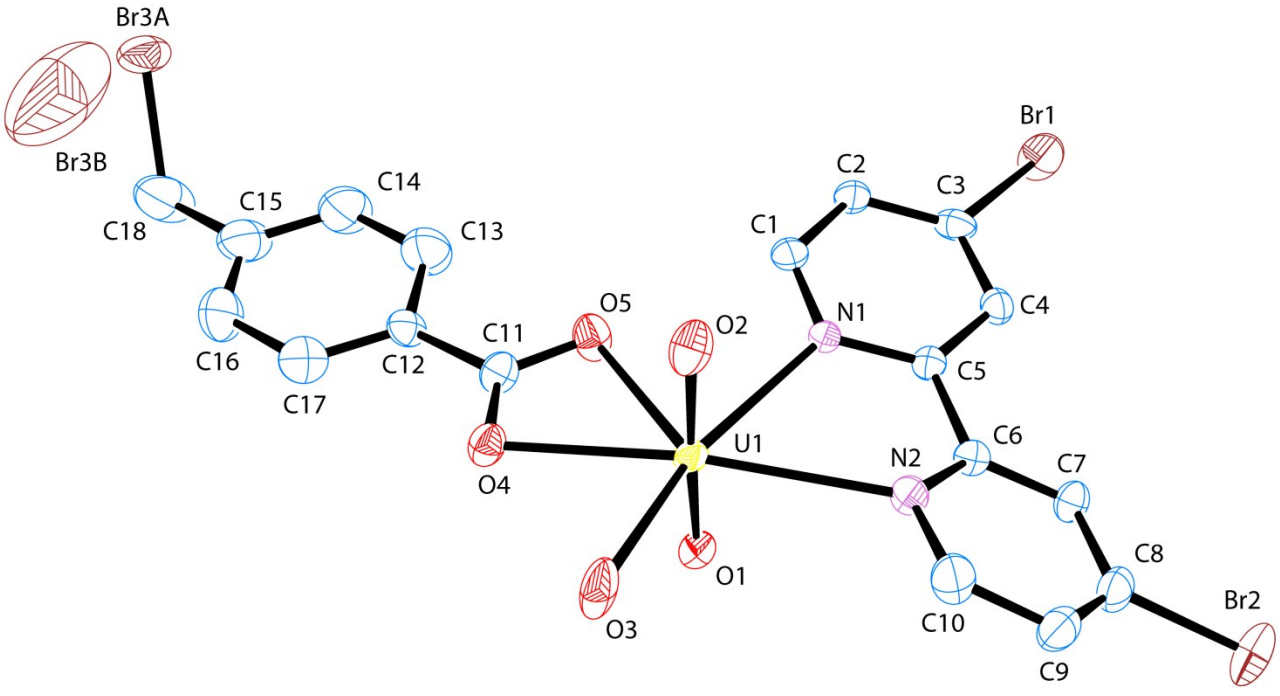


Figure S16: ORTEP illustration of complex **8**. Ellipsoids are shown at 50% probability level.

IV. Tables of Selected Bond Distances

Table S2 Metal to ligand (4,4'-dibromo 2,2'-bipyridine, 2,2'-bipyridine, assorted carboxylic acid, peroxide) bond lengths (U-N and U-O) for the uranyl-peroxide complexes **1-4** and **6-8**.

Complex #	d_{U1-N1} [Å]	d_{U1-N2} [Å]	d_{U1-O1} [Å] 'yl' oxygen	d_{U1-O2} [Å] 'yl' oxygen	d_{U1-O3} [Å]	$d_{U1-O3'}$ [Å]	d_{U1-O4} [Å]	d_{U1-O5} [Å]
1	2.610(5)	2.639(5)	1.757(7)	1.756(6)	See Table S3		2.483(5)	2.463(5)
2	2.632(4)	2.674(4)	1.773(4)	1.755(4)	2.329(4)	2.325(4)	2.490(4)	2.467(4)
3	2.636(6)	2.616(6)	1.750(9)	1.744(7)	See Table S3		2.481(6)	2.479(6)
4	2.631(7)	2.593(6)	1.753(7)	1.747(6)	2.317(7)	2.304(7)	2.476(6)	2.499(5)
6	2.664(3)	2.659(3)	1.790(2)	1.783(2)	2.336(2)	2.337(2)	2.458(2)	2.504(2)
7	2.673(3)	2.650(3)	1.779(3)	1.778(3)	2.320(3)	2.334(3)	2.522(3)	2.432(3)
8	2.644(6)	2.659(6)	1.765(5)	1.766(6)	2.316(5)	2.310(5)	2.487(5)	2.434(5)

Table S3 Metal to ligand (2,2'-bipyridine, 4-methyl-benzoic acid, peroxide) bond lengths (U-N and U-O) for the uranyl-peroxide complex **5**.

Complex 5	d_{U1-N1} [Å]	d_{U1-N2} [Å]	d_{U1-O1} [Å] 'yl' oxygen	d_{U1-O2} [Å] 'yl' oxygen	d_{U1-O3} [Å]	d_{U1-O4} [Å]	d_{U1-O5} [Å]	d_{U1-O6} [Å]
U1	2.640(6)	2.671(6)	1.776(5)	1.766(5)	2.435(5)	2.499(5)	2.363(5)	2.324(5)
	d_{U2-N3} [Å]	d_{U2-N4} [Å]	d_{U2-O5} [Å]	d_{U2-O6} [Å]	d_{U2-O7} [Å] 'yl' oxygen	d_{U2-O8} [Å] 'yl' oxygen	d_{U2-O9} [Å]	d_{U2-O10} [Å]
U2	2.623(6)	2.674(6)	2.346(5)	2.320(5)	1.777(5)	1.797(5)	2.467(5)	2.478(6)

Table S4 U-Peroxo bond distances in complexes **1** and **3** where a PART command was used to model disorder of the peroxo ligand.

Complex #	d_{U1-O3A} [Å]	$d_{U1-O3B'}$ [Å]	$d_{U1-O3A'}$ [Å]	d_{U1-O3B} [Å]
1	2.497(10)	2.444(10)	2.289(9)	2.243(9)
3	2.445(13)	2.404(13)	2.311(12)	2.261(13)

Table S5 Bond lengths between the two oxygens present in the peroxide ligands within complexes **1-8**.

Complex #	Peroxo Bond Distance (O-O) [Å]
1	O3A-O3B': **1.461(15)**
2	O3-O3': **1.467(7)**
3	O3-O3': **1.460(20)**
4	O3-O3': **1.474(13)**
5	O5-O6: **1.464(7)**
6	O3-O3': **1.482(4)**
7	O3-O3': **1.482(5)**
8	O3-O3': **1.458(11)**

V. Tables of Supramolecular Interaction Distances

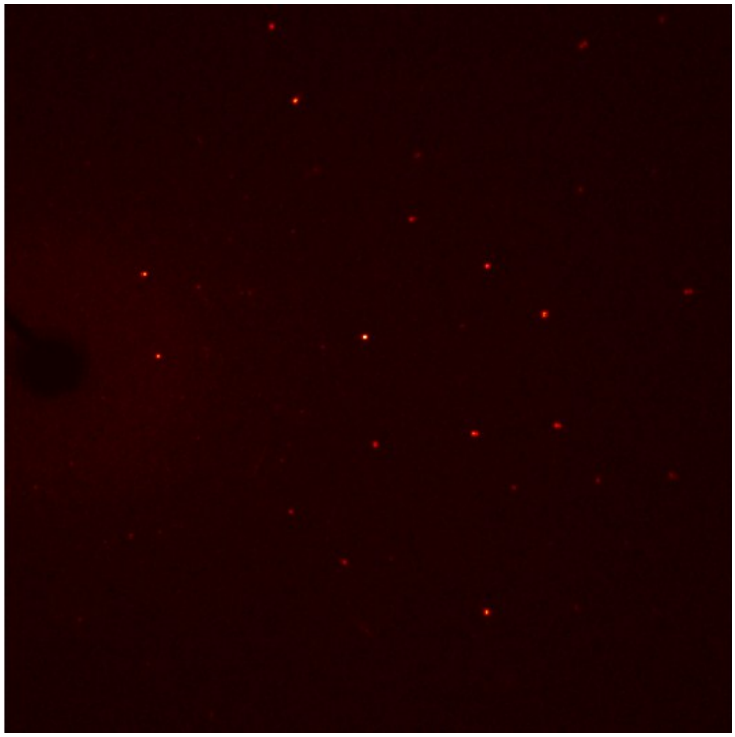
Table S6 Offset π-stacking interactions observed in the complexes **1-8**. The bold number corresponds to the distance between the two centroids of the interacting rings. The second number is the distance between the centroid and the perpendicular plane of the interacting ring. The beta angle is the corresponding angle formed by this created right triangle.

Complex #	Offset π-stacking Interactions Cg1-Cg2 [Å]	Offset π-stacking Interactions Cg1-Cg3 [Å]	Offset π-stacking Interactions Cg2-Cg3 [Å]	Offset π-stacking Interactions Cg1-Cg4 [Å]
1	-	-	**3.657(4)**, 3.326(4), β = 24.57°	-
2	-	**3.669(4)**, 3.367(4), β = 23.41°	**3.679(4)**, 3.600(4), β = 11.90°	-
3			**3.737(5)**, 3.543(5) β = 18.54°	
4	-	-	**3.776(5)**, 3.671(5), β = 13.54°	-
5	-	-	**3.582(5)**, 3.514(4), β = 11.18°	**3.736(6)**, 3.621(4), β = 14.25°
6	**3.576(3)**, 3.517(2), β = 10.42°	-	-	-
7	**3.705(3)**, 3.634(2), β = 11.23°	**3.564(3)**, 3.467(2), β = 13.40°	-	-
8	**3.773(5)**, 3.723(3), β = 9.34°	**3.737(5)**, 3.701 (3), β = 7.96°		

Table S7 Halogen based interaction distances for complexes **6-8**. The bold number is the interaction distance. An "*" represents an interaction where a part command was used to model positional disorder. An "#" shows a potential interaction that is not mentioned in the manuscript.

Complex #	Halogen-Oxo Interaction Br1-O1 [Å]	Halogen-π Interaction Localized: Br3A-C7 [Å]	Halogen-Halogen Interaction Br1-Br3B [Å]	Halogen-Halogen Interaction Br2-Br3A [Å]
6	**3.251(3)**, 96.47% VdW	-	-	-
7	-	-	-	-
8	-	**3.385(8)***, 95.35% VdW	**3.402(9)*#**, 91.95% VdW	**3.626(3)***, 98.00% VdW

VI. XRD Data Confirming Stability



Unit cell determined by SCXRD on April 28, 2015 from 9503 reflections.

a = 8.172(5)

b = 20.318(13)

c = 10.369(7)

β = 111.780(9)

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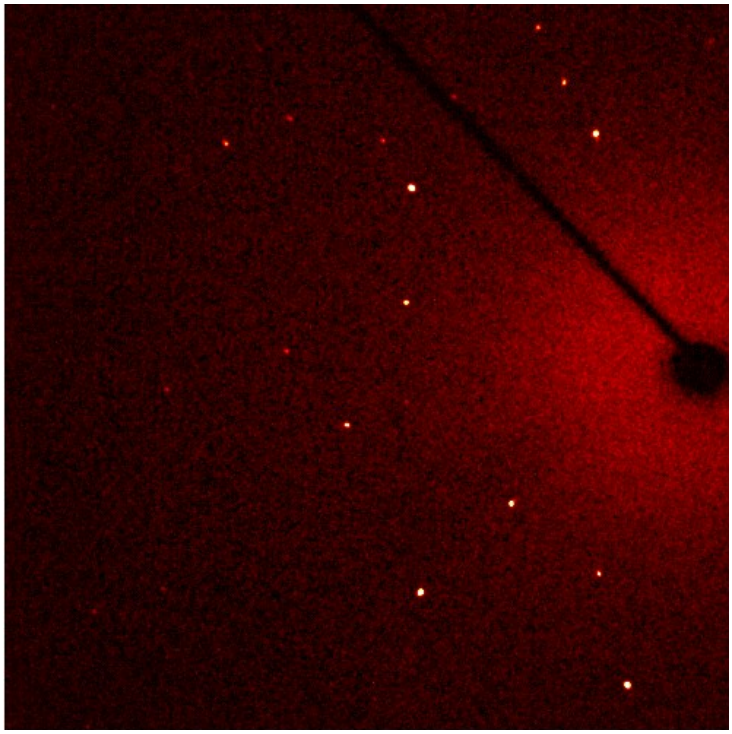
Figure S17: A single frame from the SCXRD data collection of complex **6** taken April 28, 2015



341 Reflections used to determine the unit cell of complex **6** as:

a = 8.165(4)

b = 20.309(11)

c = 10.392(5)

β = 111.912(9)

Vol: 1599(2)

Figure S18: A single frame from the SCXRD data collection of complex **6** taken December 7, 2017. Note that this was not the original crystal as in Figure S15, but was from the same sample preparation.