RE-*p*-halobenzoic acid-terpyridine complexes, Part III: structural and supramolecular trends in a series of *p*-iodobenzoic acid rare-earth materials

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Supporting Information Section

I. Powder X-ray diffraction data

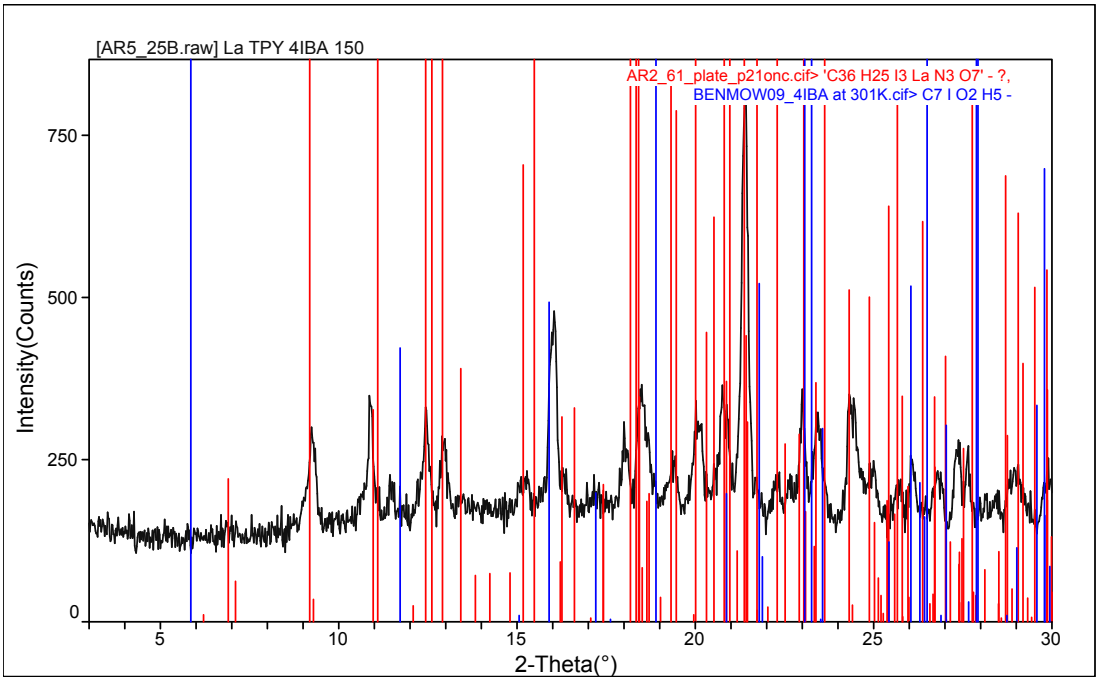

Figure S1: The PXRD pattern of complex **1** (structure type I) with the calculated pattern overlaid in red. The calculated pattern of *p*-iodobenzoic acid is also included in blue.

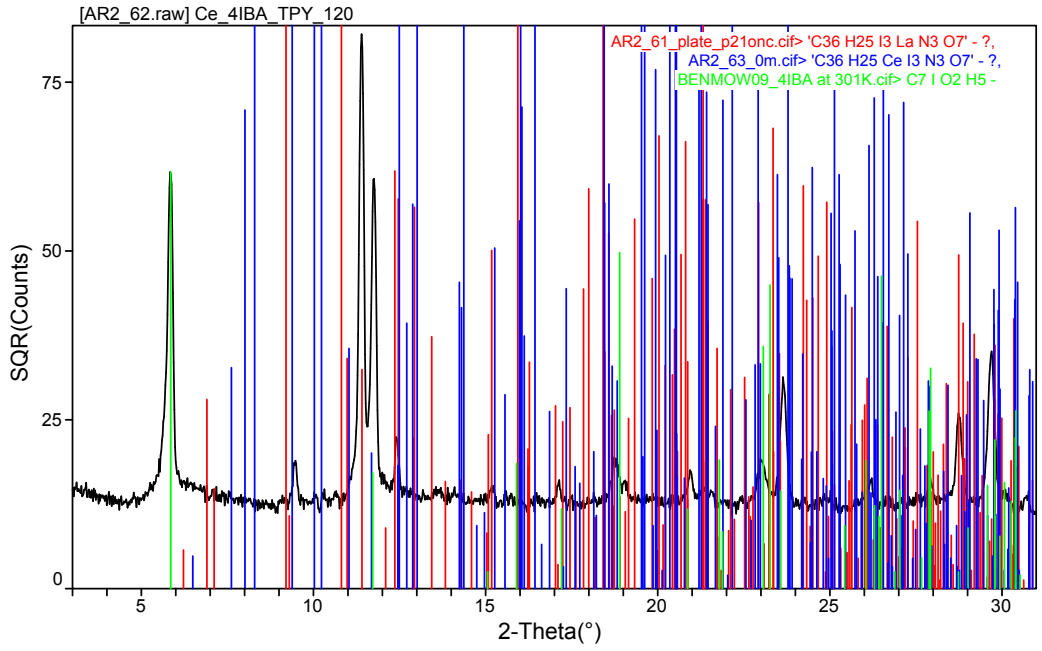

Figure S2: The PXRD pattern of complex **2** (structure type I) with the calculated pattern overlaid in red. The pattern of complex **2'** structure type IV) is also included in blue. The calculated pattern of *p*-iodobenzoic acid is also included in green.

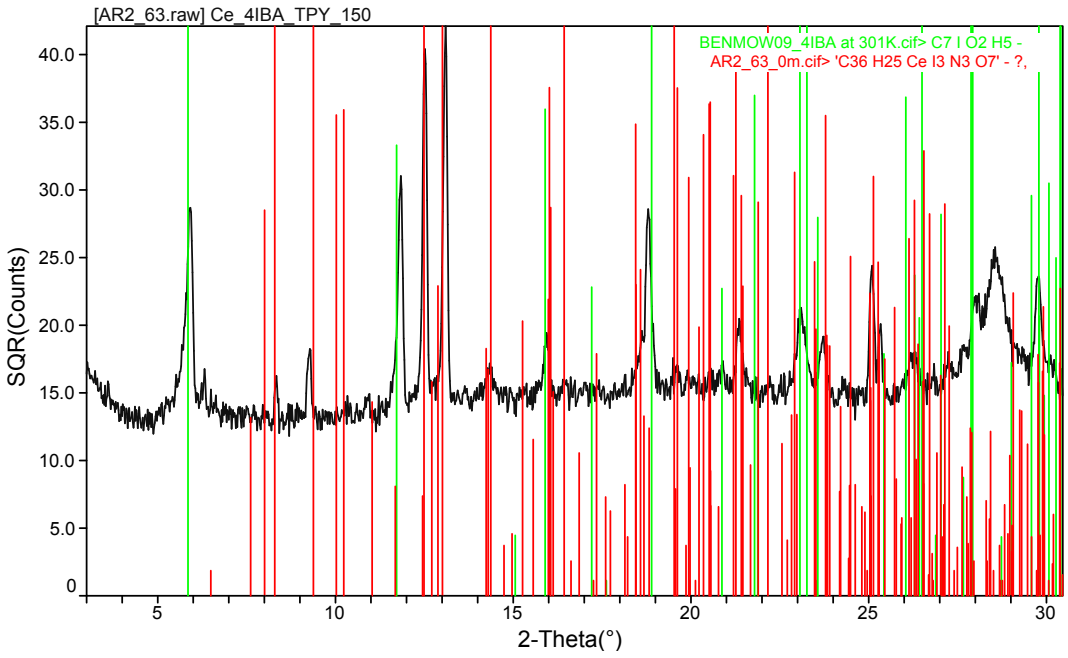

Figure S3: The PXRD pattern of complex **2'** (structure type IV) with the calculated pattern overlaid in red. The calculated pattern of *p*-iodobenzoic acid is also included in green.

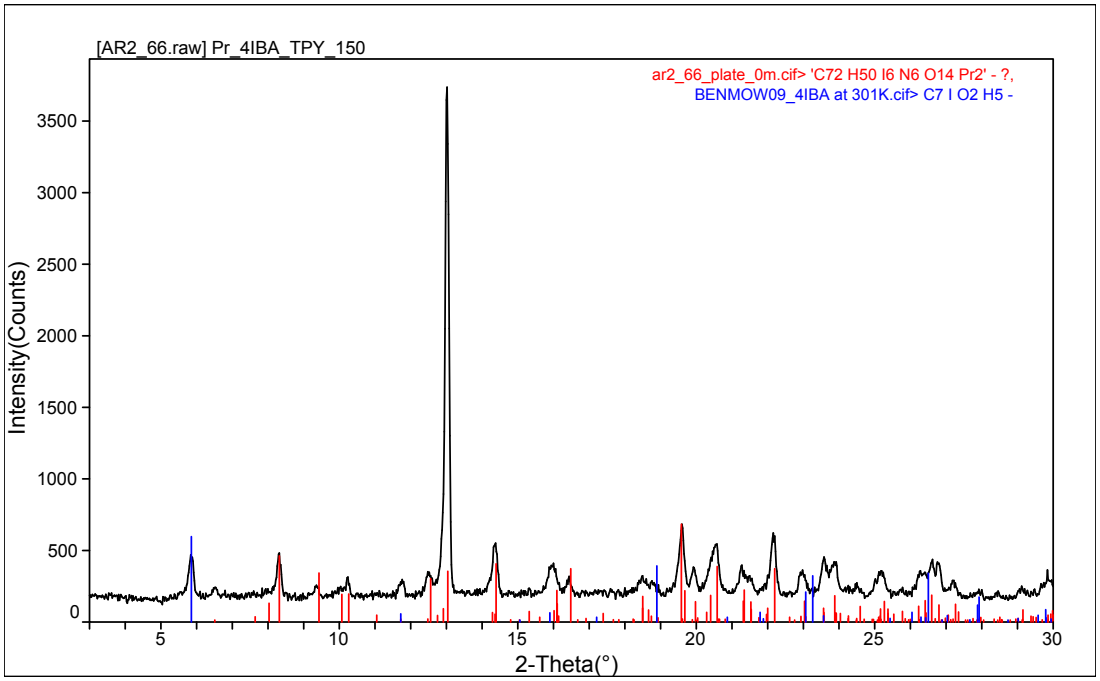

Figure S4: The PXRD pattern of complex **3** (structure type II) with the calculated pattern overlaid in red. The calculated pattern of *p*-iodobenzoic acid is also included in blue.

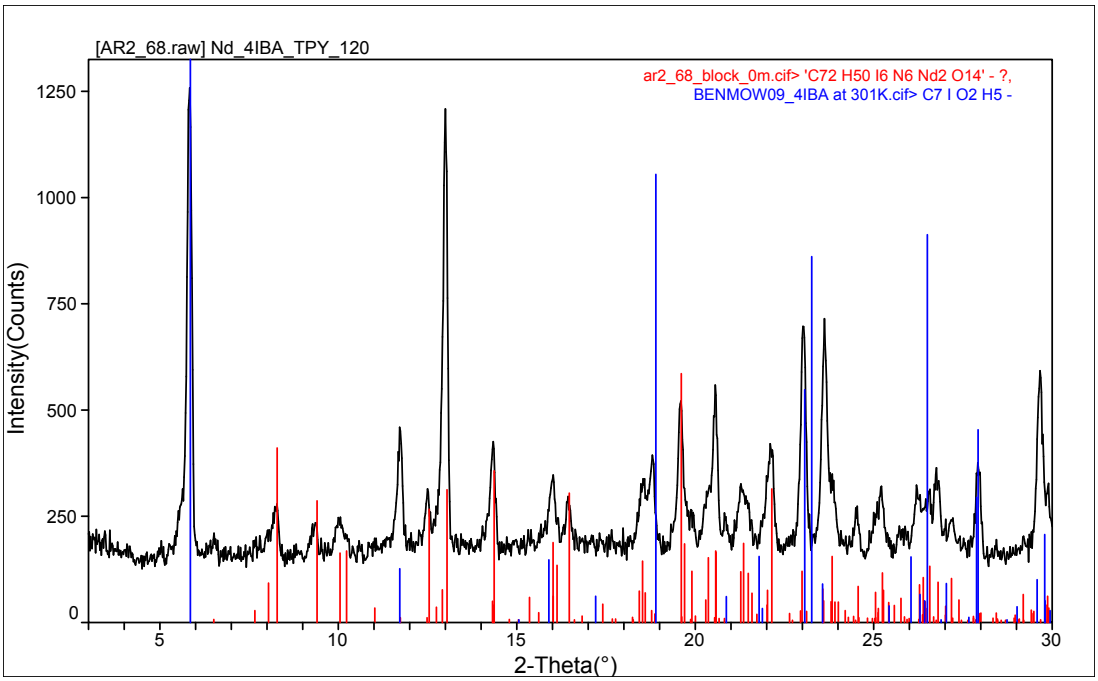

Figure S5: The PXRD pattern of complex **4** (structure type IV) with the calculated pattern overlaid in red. The calculated pattern of *p*-iodobenzoic acid is also included in blue.

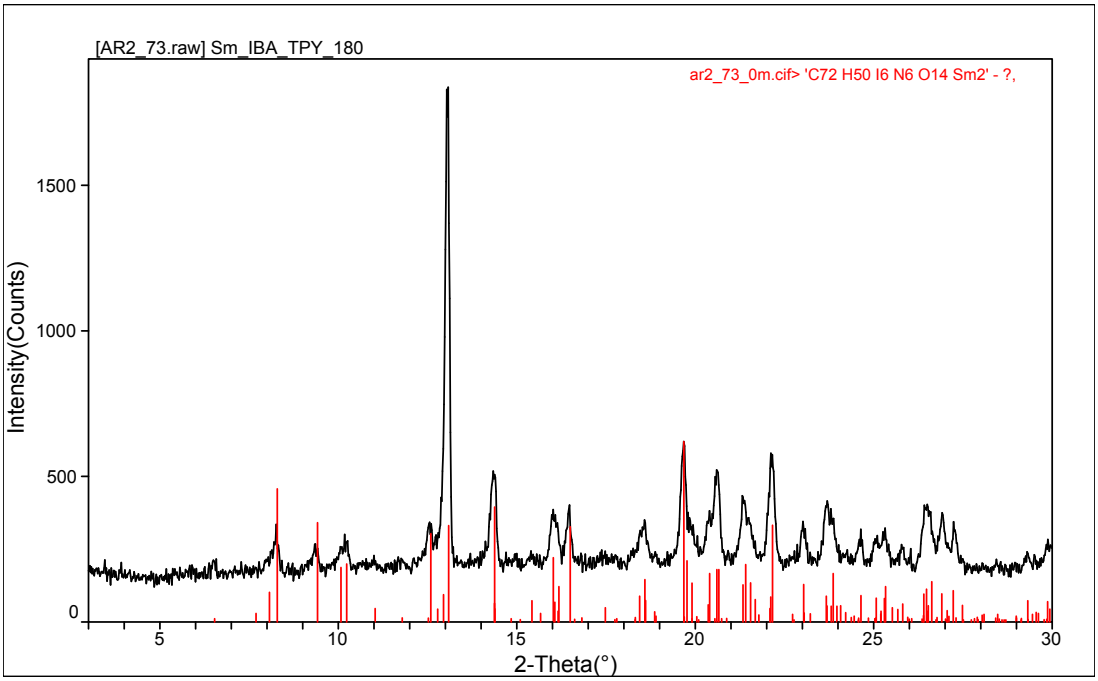

Figure S6: The PXRD pattern of complex **5** (structure type IV) with the calculated pattern overlaid in red.

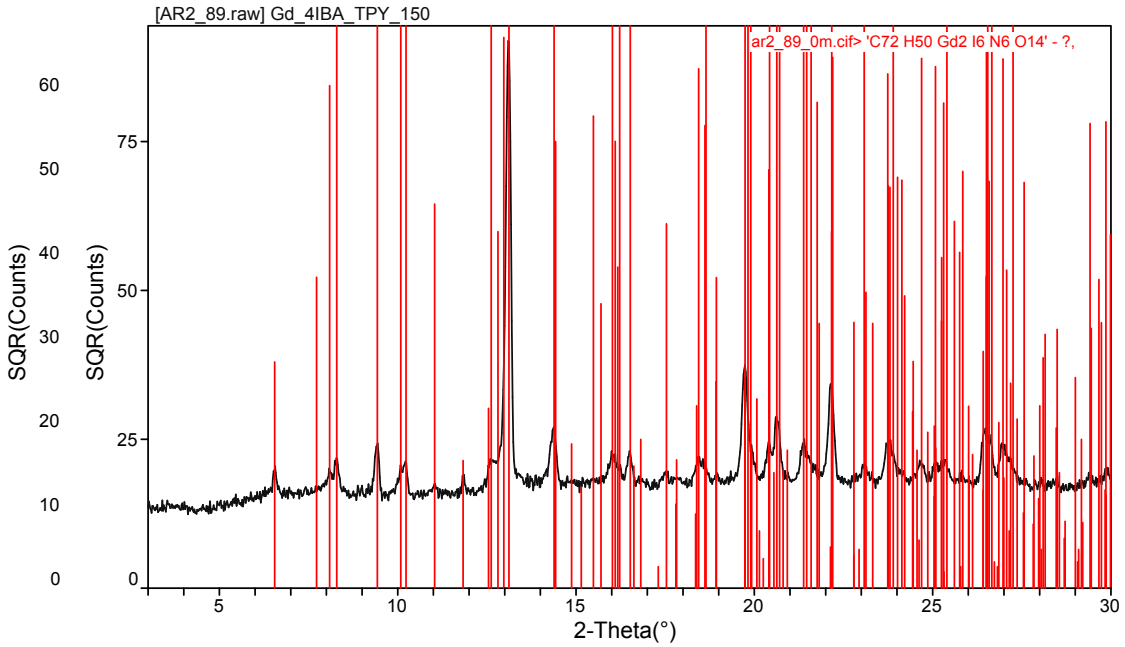

Figure S7: The PXRD pattern of complex **6** (structure type IV) with the calculated pattern overlaid in red.

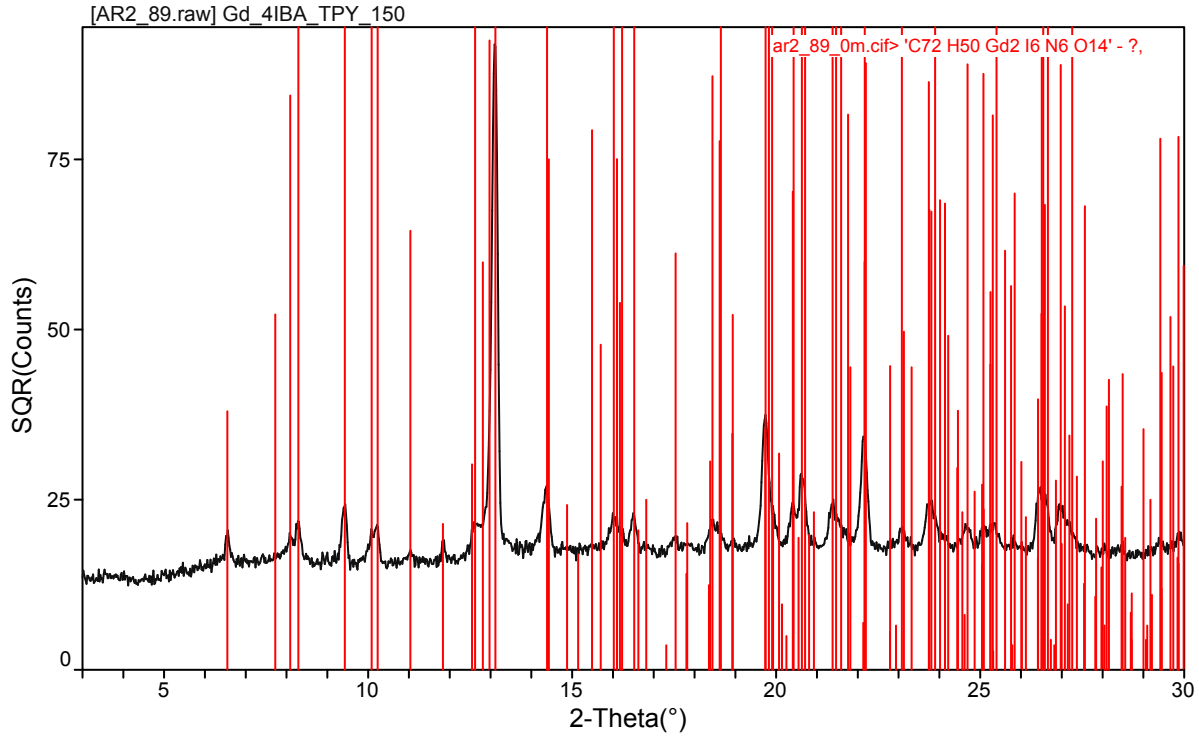

Figure S8: The PXRD pattern of complex **7** (structure type IV) with the calculated pattern overlaid in red.

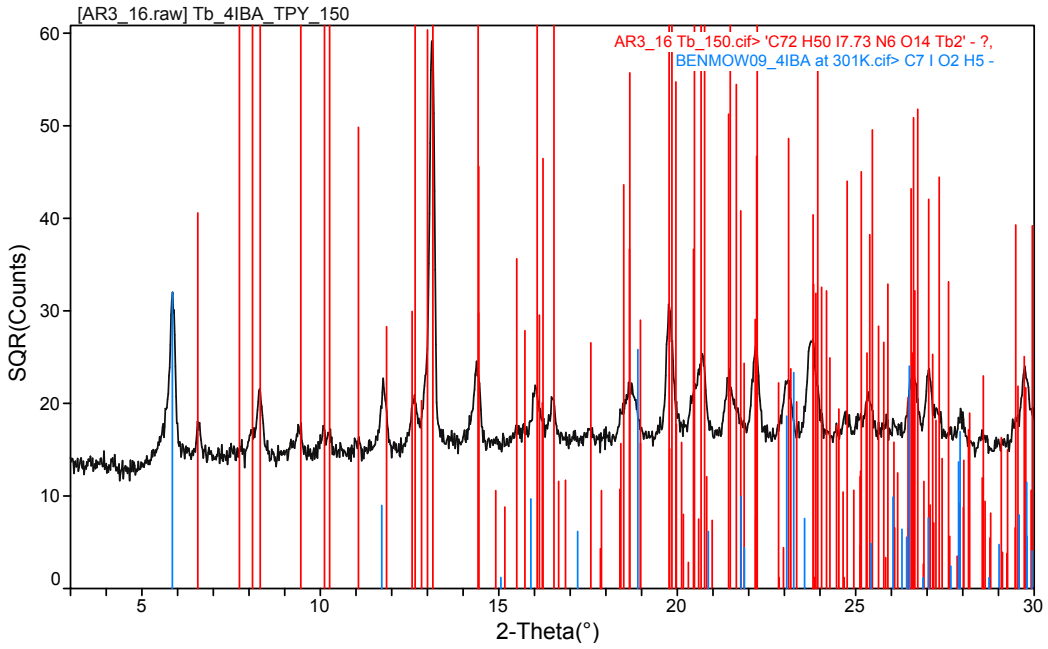

Figure S9: The PXRD pattern of complex **8** (structure type IV) with the calculated pattern overlaid in red. The calculated pattern of *p*-iodobenzoic acid is also included in blue.

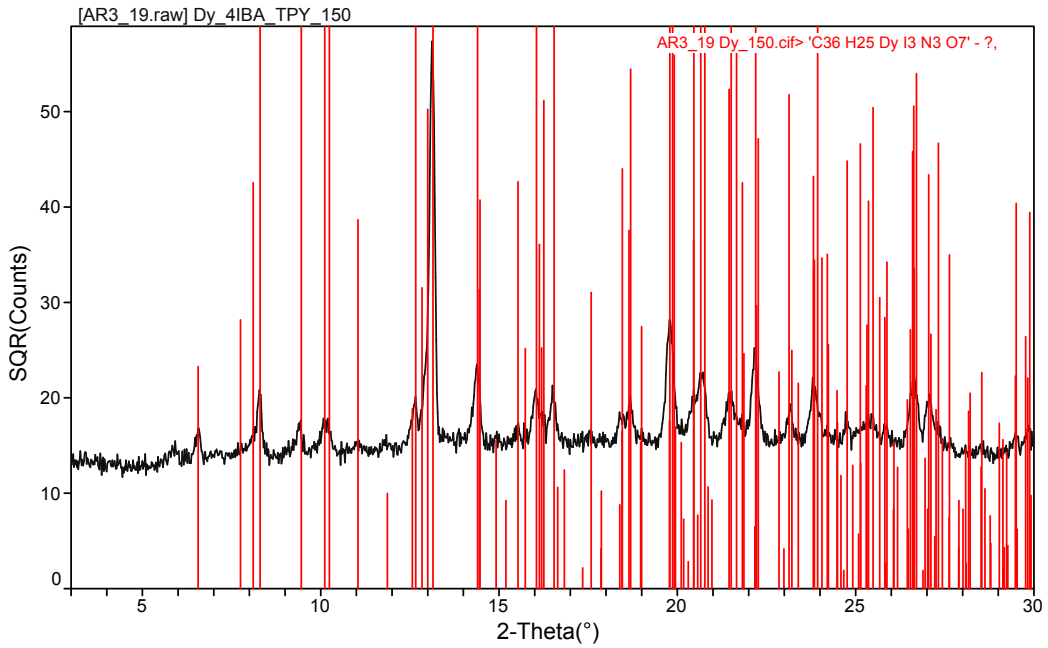

Figure S10: The PXRD pattern of complex **9** (structure type IV) with the calculated pattern overlaid in red.

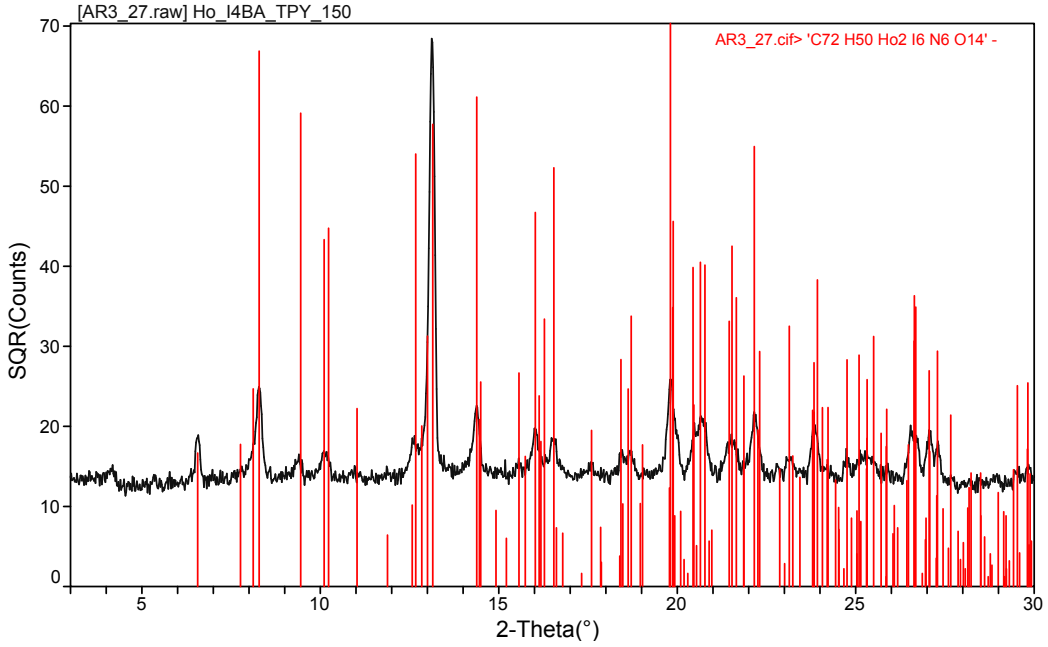

Figure S11: The PXRD pattern of complex **10** (structure type IV) with the calculated pattern overlaid in red.

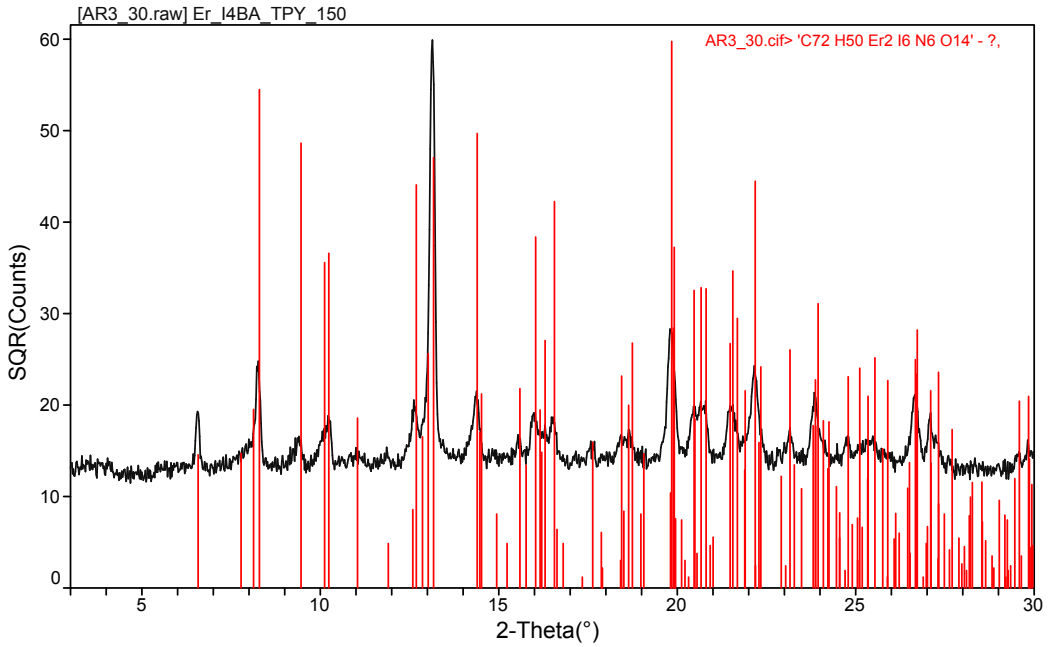

Figure S12: The PXRD pattern of complex **11** (structure type IV) with the calculated pattern overlaid in red.

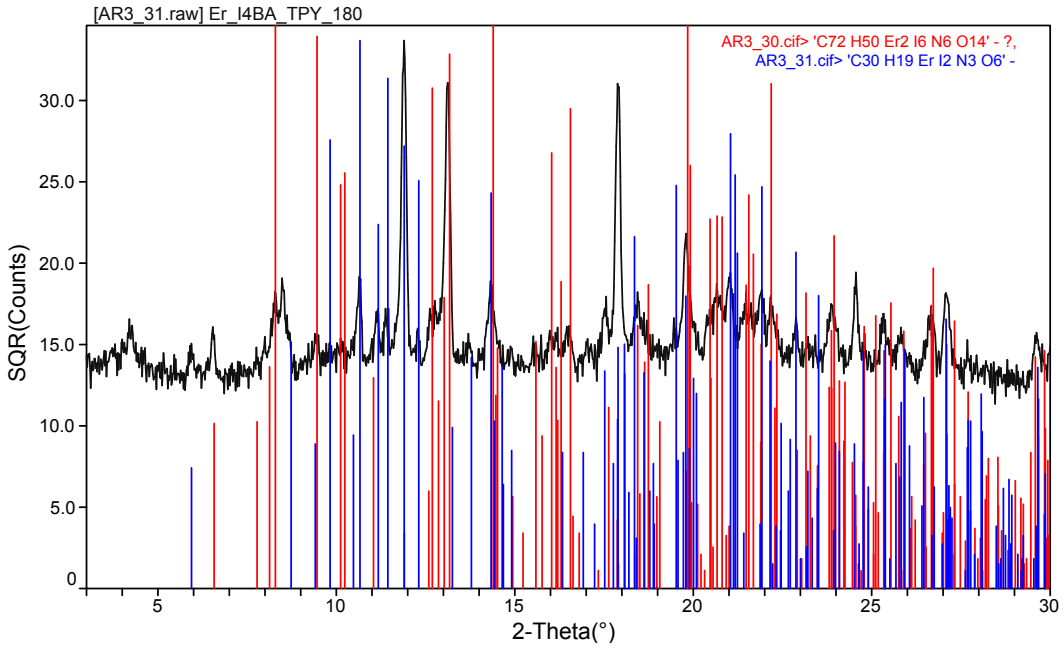

Figure S13: The PXRD pattern of complex **11'** (structure type VI) with the calculated pattern overlaid in blue. The pattern of complex **11** (structure type IV) is also included in red. We acknowledge that this sample contains small impurities.

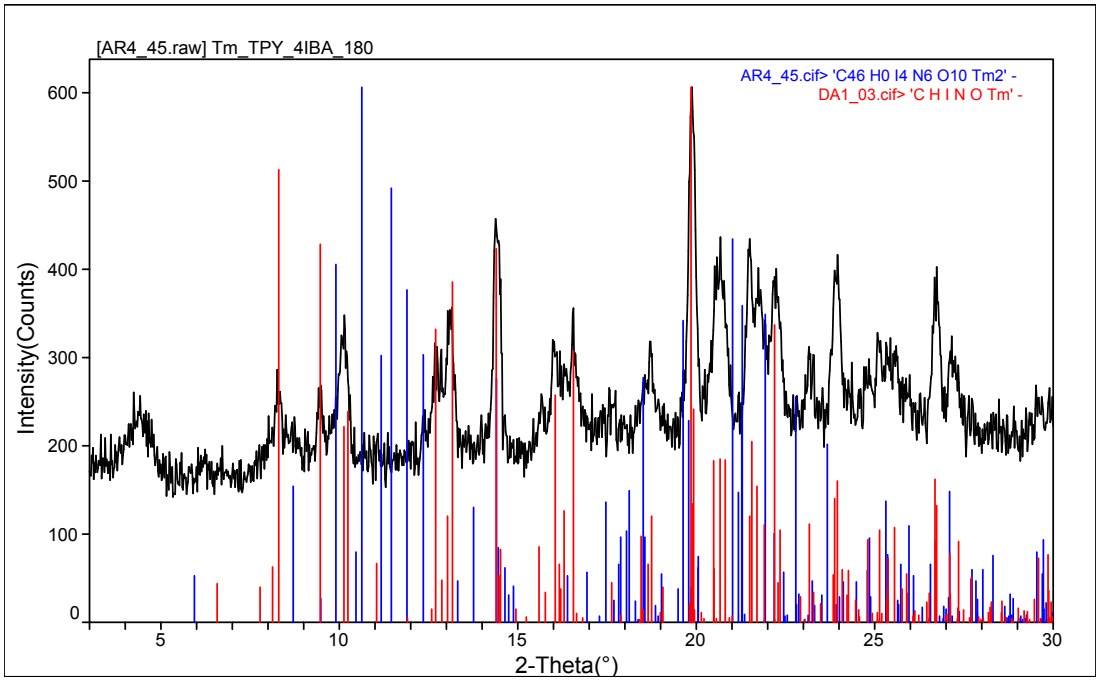

Figure S14: The PXRD pattern of complex **12** (structure type VI) with the calculated pattern overlaid in red. The pattern of complex **12'** (structure type IV) is also included in blue. We acknowledge that this sample contains small impurities.

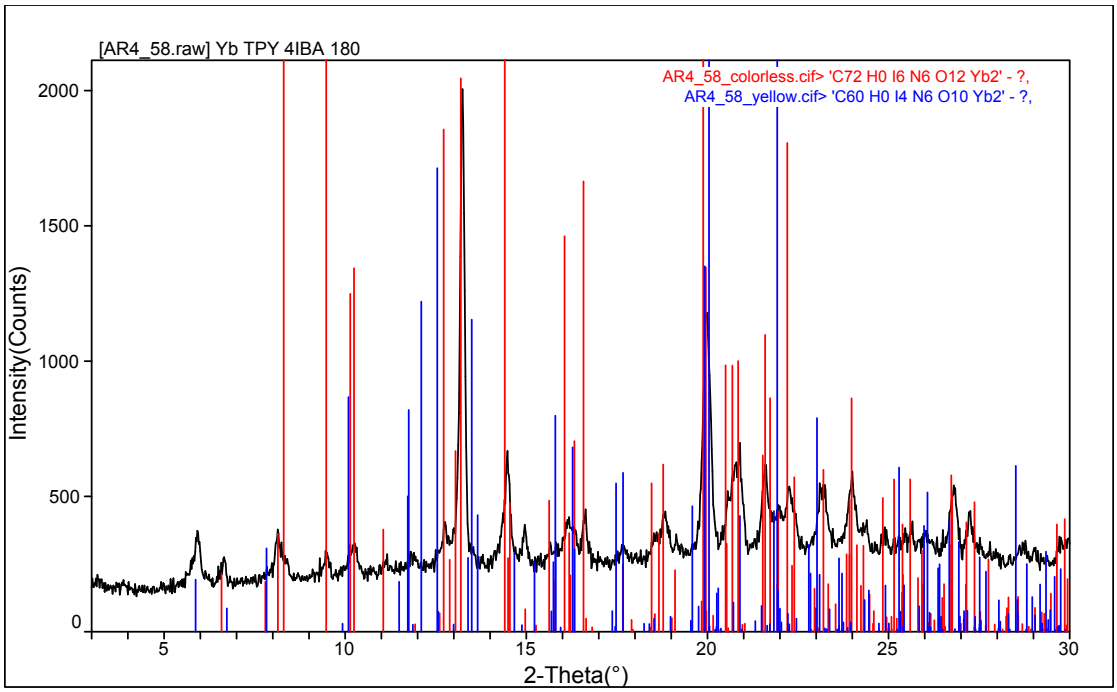

Figure S15: The PXRD pattern of complex **13** (structure type IV) with the calculated pattern overlaid in red. The pattern of complex **13'** (structure type III) is also included in blue.

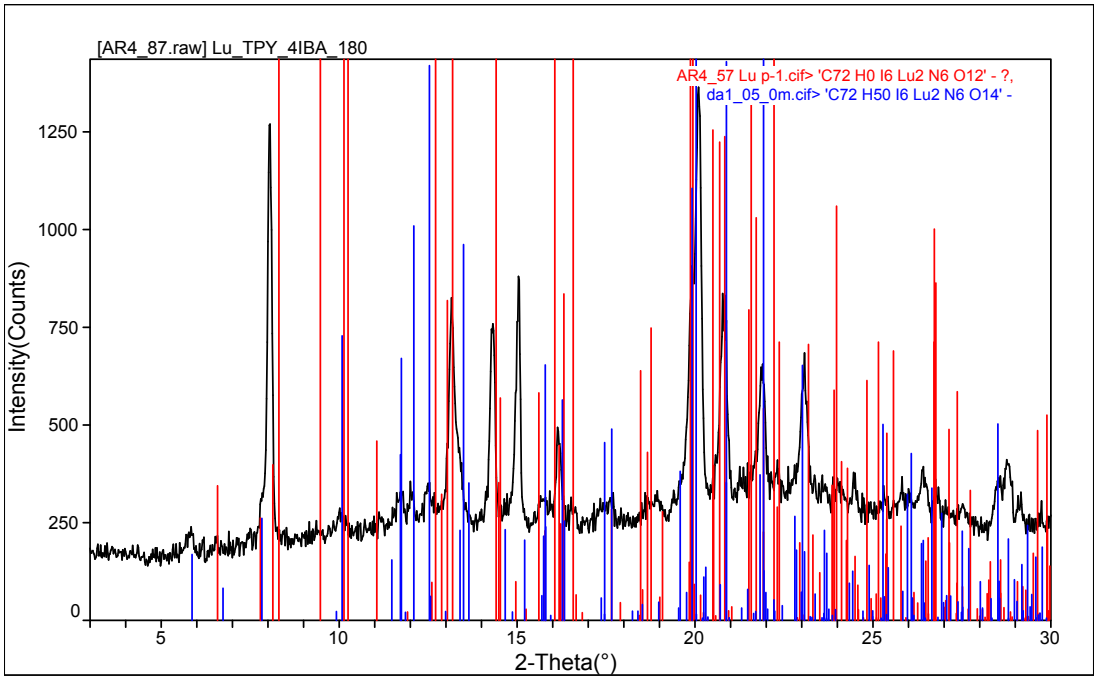

Figure S16: The PXRD pattern of complex **14** (structure type IV) with the calculated pattern overlaid in red. The pattern of complex **14'** (structure type III) is also included in blue.

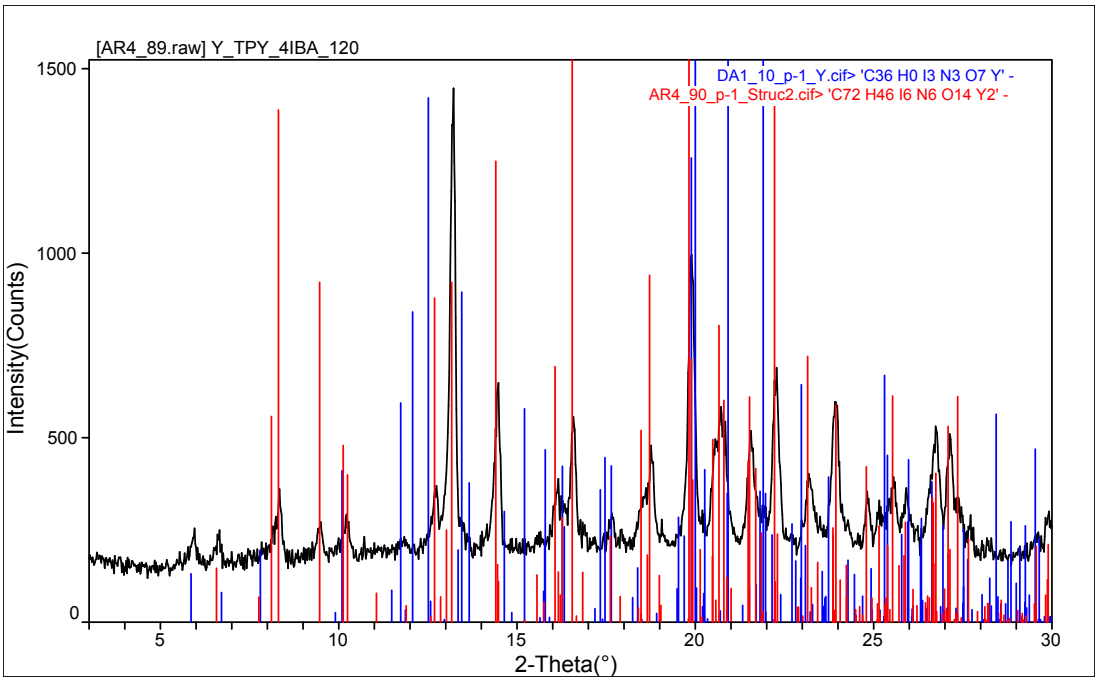

Figure S17: The PXRD pattern of complex **15** (structure type IV) with the calculated pattern overlaid in red. The pattern of complex **15'** (structure type III) is also included in blue.

II. Thermal Ellipsoid Plots

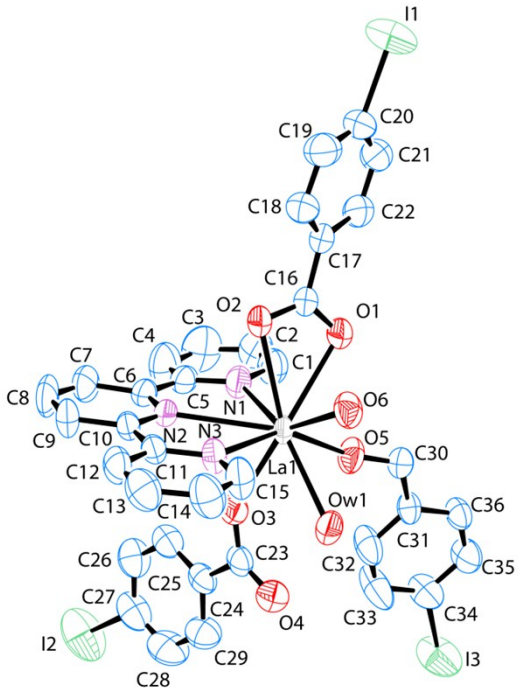

Figure S18: ORTEP illustration of structure **1**. Ellipsoids are shown at 50% probability level.

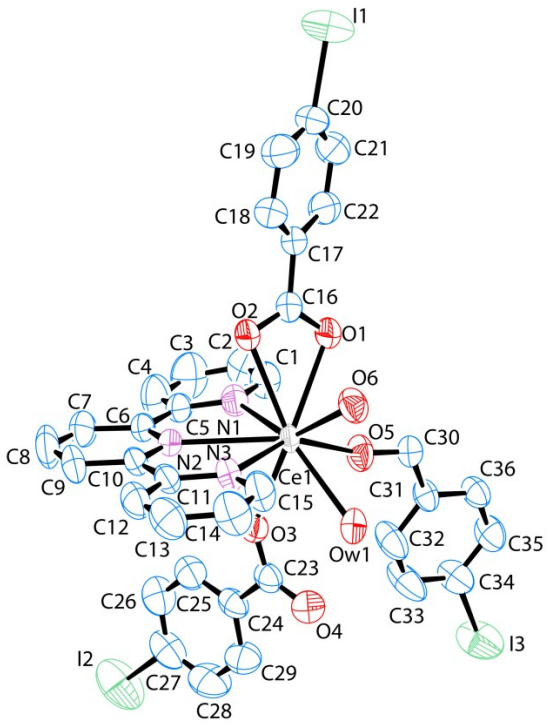

Figure S19: ORTEP illustration of structure **2**. Ellipsoids are shown at 50% probability level.

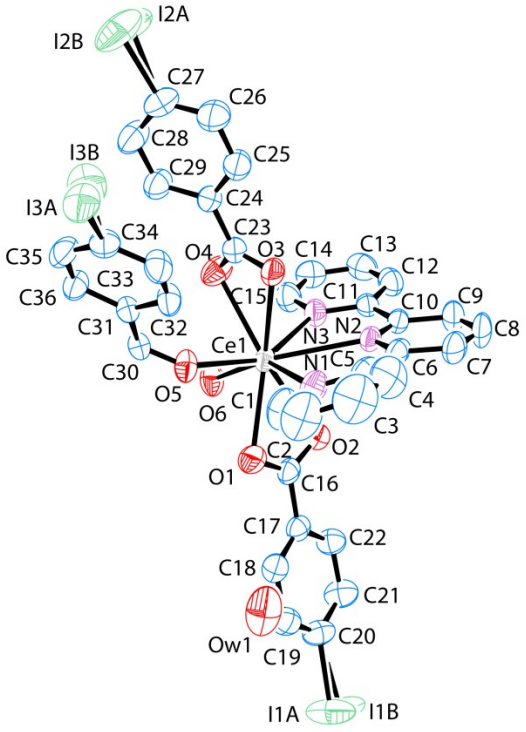

Figure S20: ORTEP illustration of structure **2'**. Ellipsoids are shown at 50% probability level.

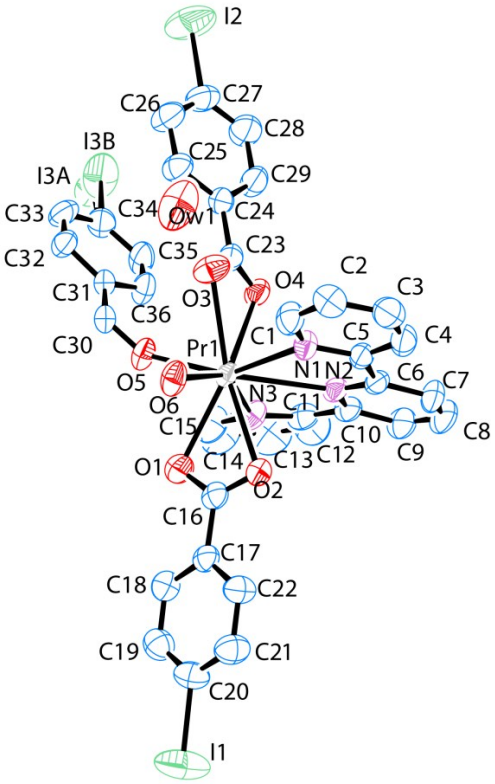

Figure S21: ORTEP illustration of structure **3**. Ellipsoids are shown at 50% probability level.

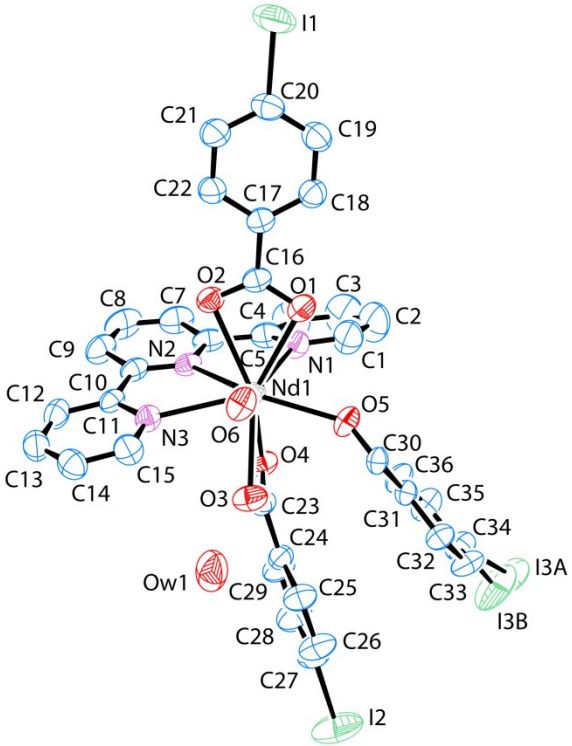

Figure S22: ORTEP illustration of structure **4**. Ellipsoids are shown at 50% probability level.

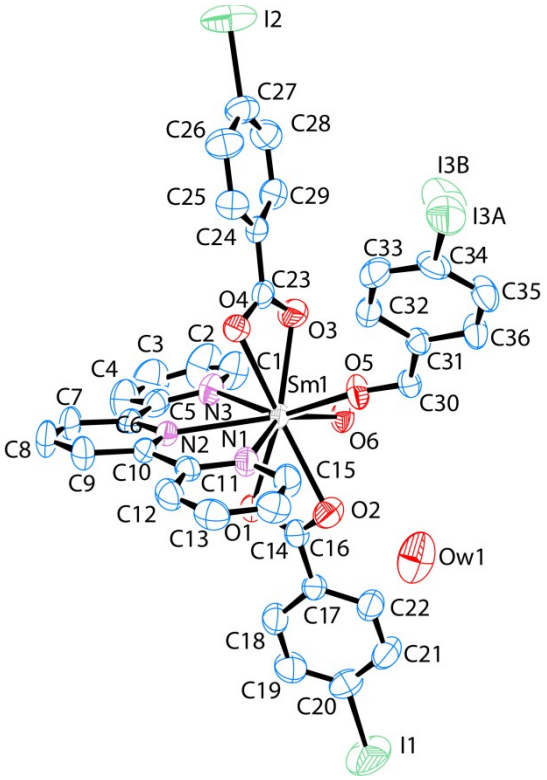

Figure S23: ORTEP illustration of structure **5**. Ellipsoids are shown at 50% probability level.

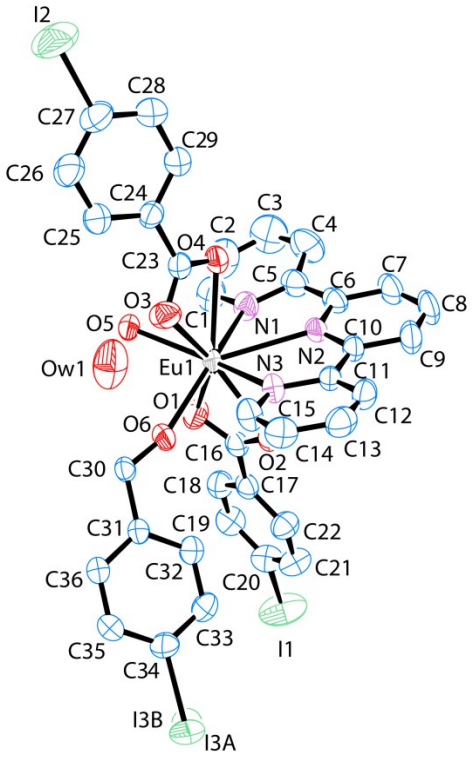

Figure S24: ORTEP illustration of structure **6**. Ellipsoids are shown at 50% probability level.

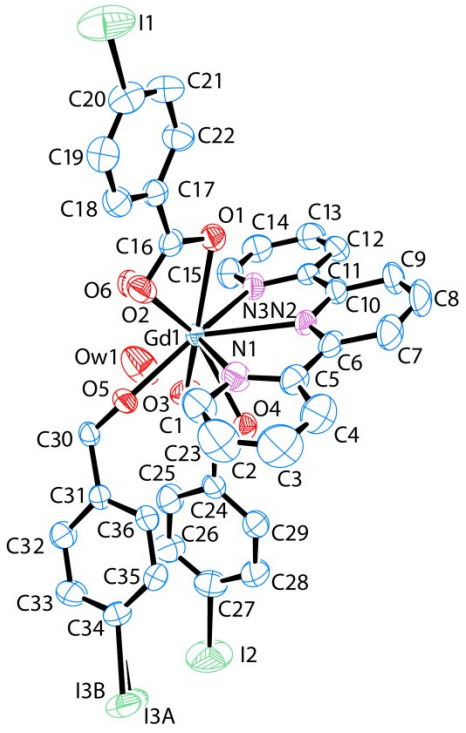

Figure S25: ORTEP illustration of structure **7**. Ellipsoids are shown at 50% probability level.

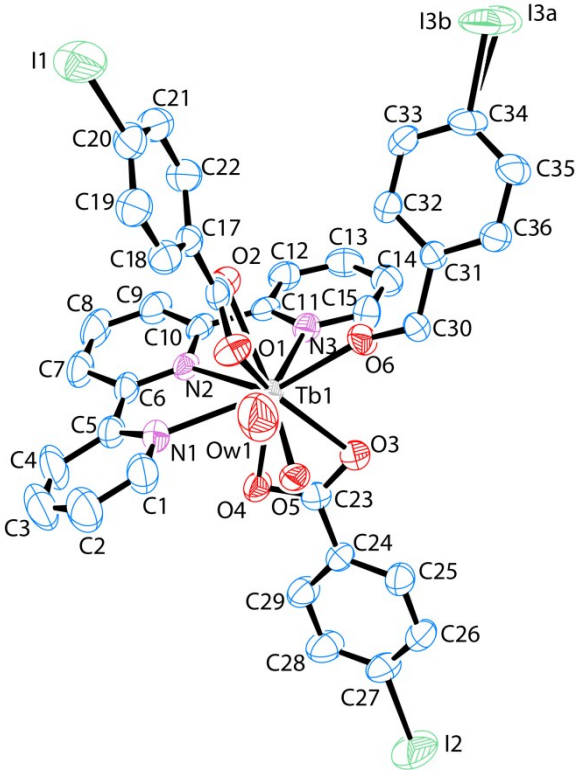

Figure S26: ORTEP illustration of structure **8**. Ellipsoids are shown at 50% probability level.

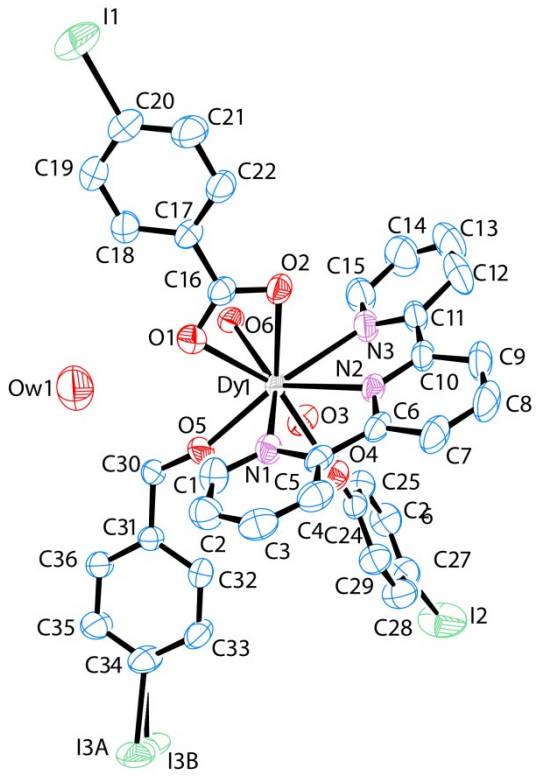

Figure S27: ORTEP illustration of structure **9**. Ellipsoids are shown at 50% probability level.

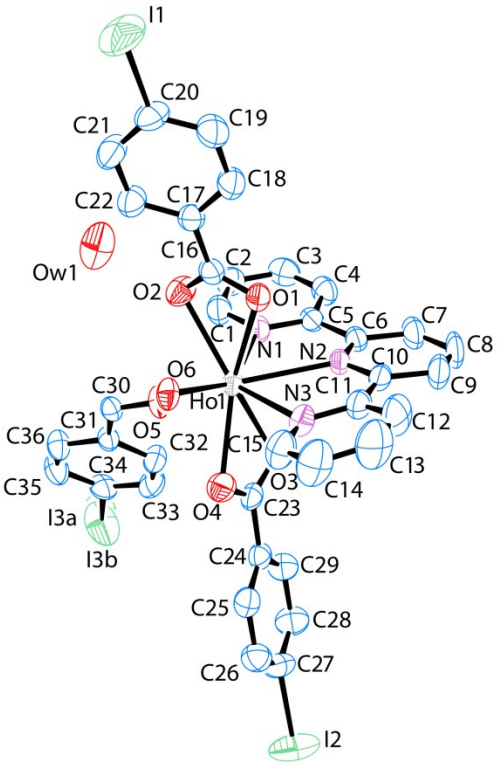

Figure S28: ORTEP illustration of structure **10**. Ellipsoids are shown at 50% probability level.

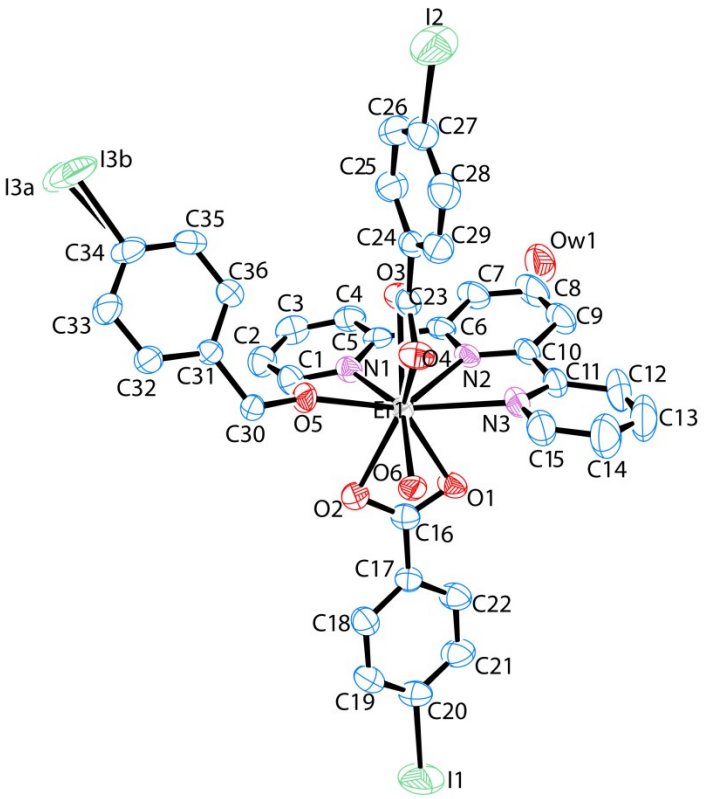

Figure S29: ORTEP illustration of structure **11**. Ellipsoids are shown at 50% probability level.

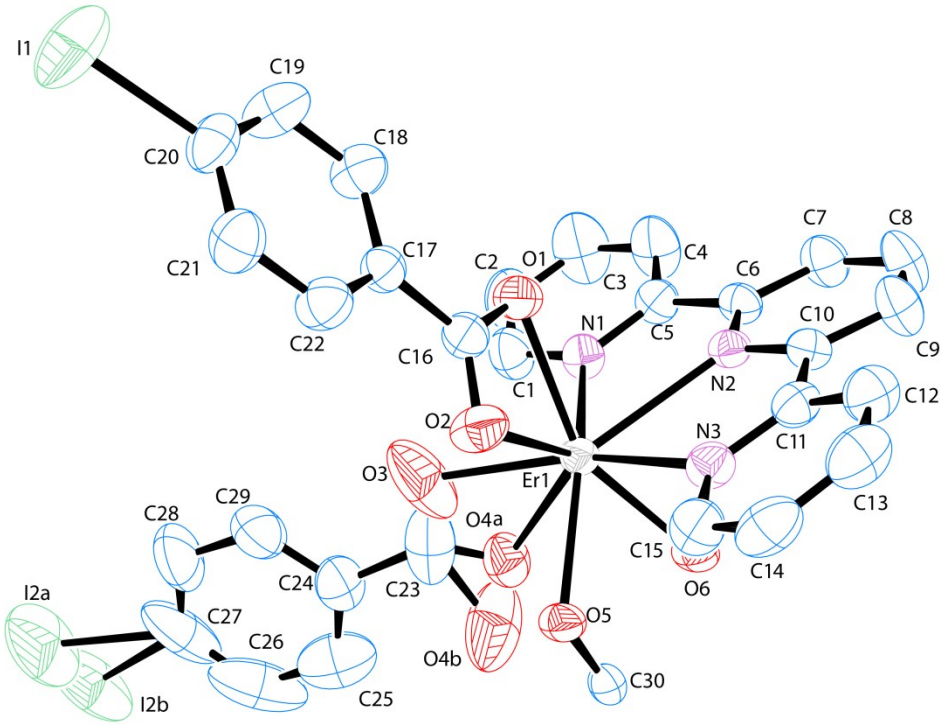

Figure S30: ORTEP illustration of structure **11'**. Ellipsoids are shown at 50% probability level.

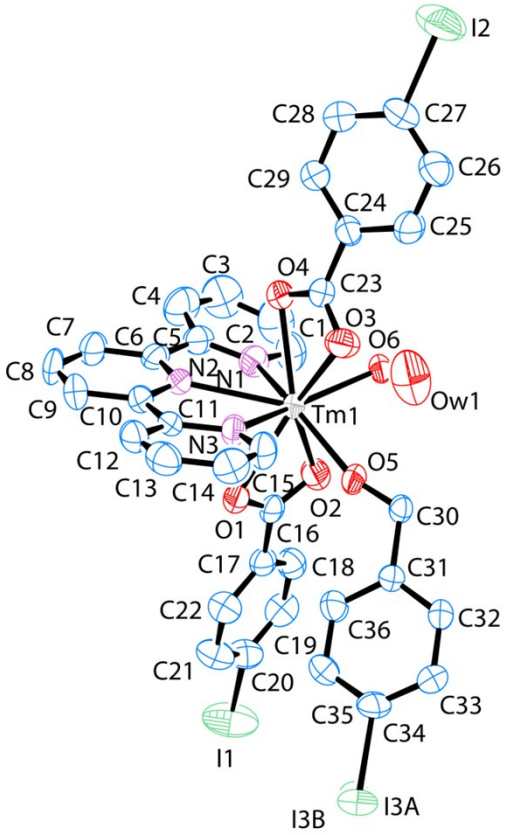

Figure S31: ORTEP illustration of structure **12**. Ellipsoids are shown at 50% probability level.

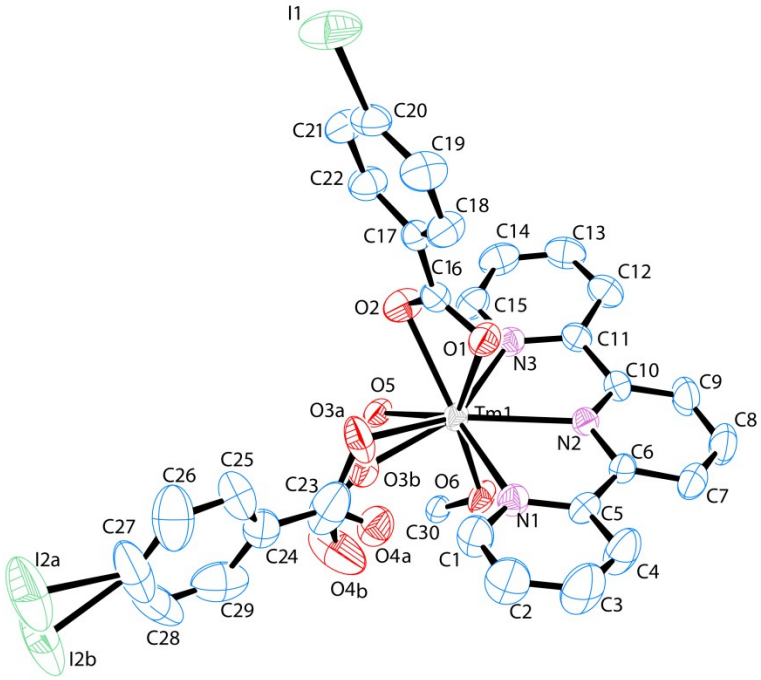

Figure S32: ORTEP illustration of structure **12'**. Ellipsoids are shown at 50% probability level.

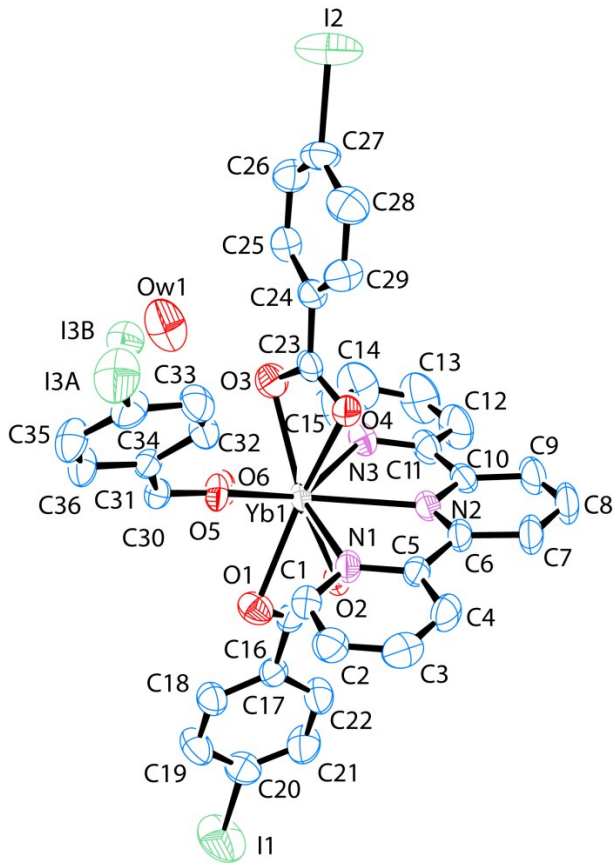

Figure S33: ORTEP illustration of structure **13**. Ellipsoids are shown at 50% probability level.

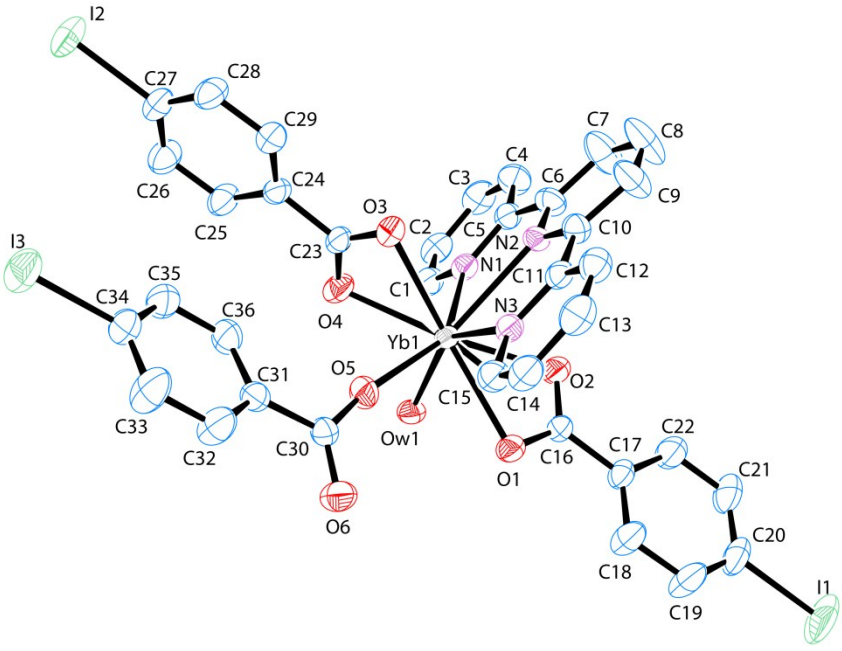

Figure S34: ORTEP illustration of structure **13'**. Ellipsoids are shown at 50% probability level.

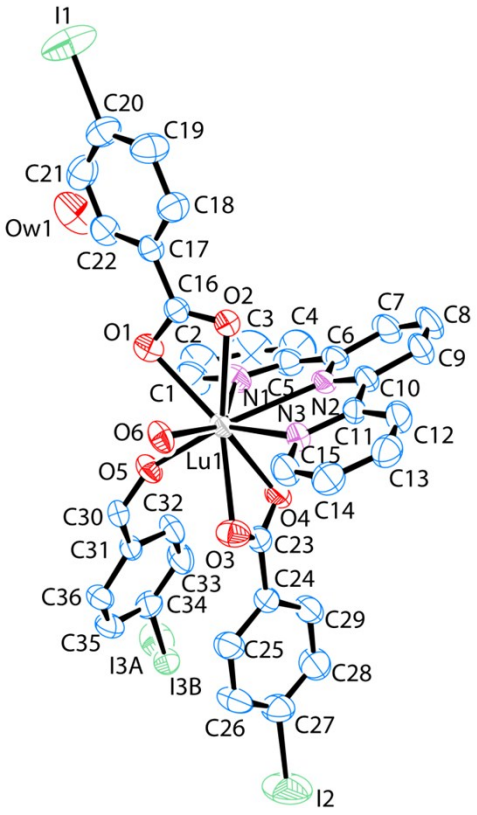

Figure S35: ORTEP illustration of structure **14**. Ellipsoids are shown at 50% probability level.

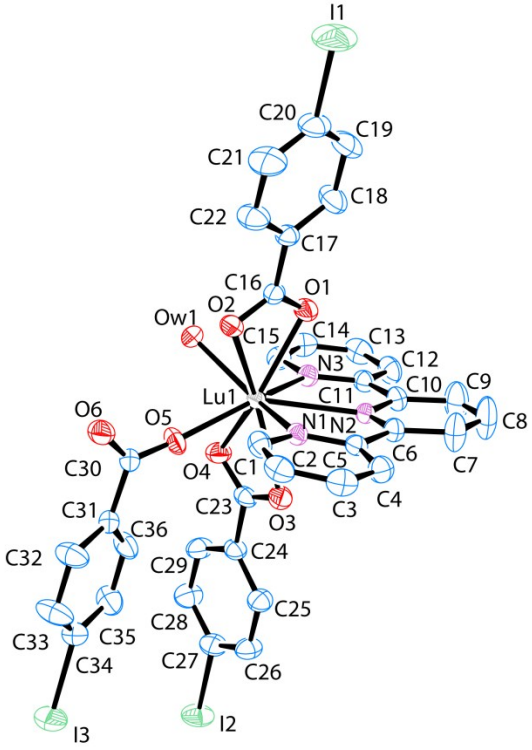

Figure S36: ORTEP illustration of structure **14'**. Ellipsoids are shown at 50% probability level.

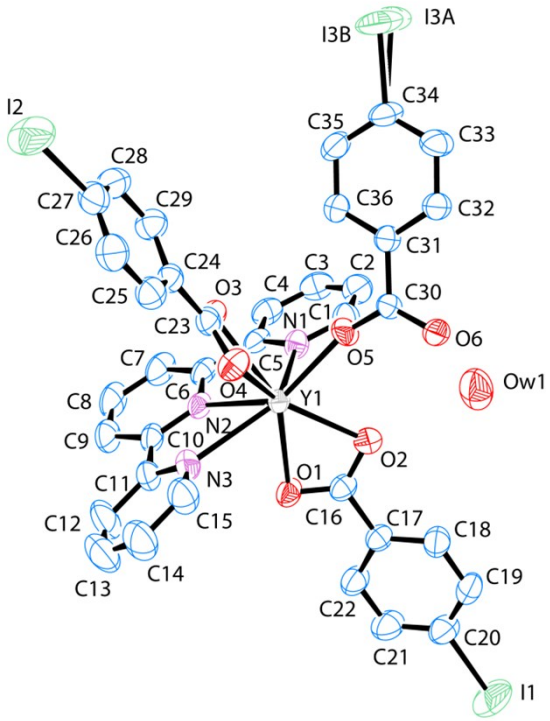

Figure S37: ORTEP illustration of structure **15**. Ellipsoids are shown at 50% probability level.

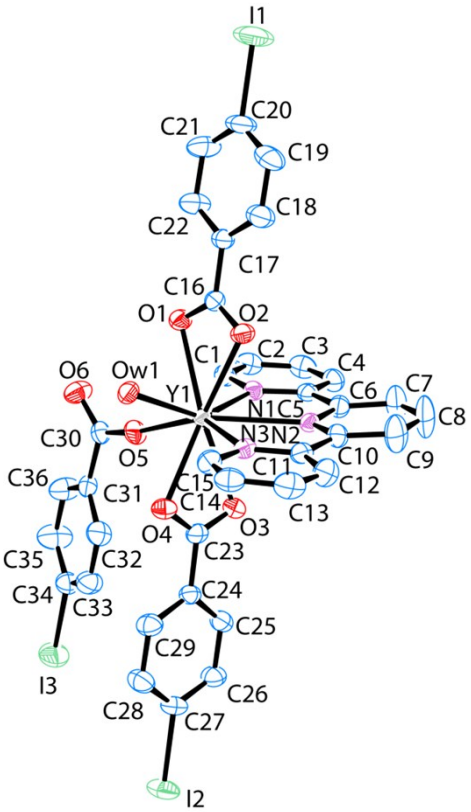

Figure S38: ORTEP illustration of structure **15'**. Ellipsoids are shown at 50% probability level.

III. Table of Bond Distances

Table S1: Bond Lengths RE-N in Rare Earth Complexes **1-15** with *p*-iodobenzoic acid and 2,2'-6',2"-terpyridine.

RE(III) Complexes	d_{Ln-N1} [Å]	d_{Ln-N2} [Å]	d_{Ln-N3} [Å]
1 (La)	2.681(5)	2.743(4)	2.699(4)
2 (Ce)	2.659(5)	2.714(4)	2.671(4)
2' (Ce)	2.665(2)	2.704(2)	2.649(2)
3 (Pr)	2.631(4)	2.689(3)	2.645(4)
4 (Nd)	2.630(3)	2.669(2)	2.615(3)
5 (Sm)	2.585(4)	2.635(3)	2.602(4)
6 (Eu)	2.595(3)	2.616(3)	2.575(4)
7 (Gd)	2.580(3)	2.605(3)	2.563(3)
8 (Tb)	2.570(4)	2.590(3)	2.548(4)
9 (Dy)	2.533(3)	2.576(3)	2.556(3)
10 (Ho)	2.529(3)	2.567(3)	2.556(3)
11 (Er)	2.517(3)	2.552(3)	2.542(3)
11' (Er)	2.539(3)	2.524(3)	2.520(3)
12 (Tm)	2.533(4)	2.543(4)	2.505(4)
12' (Tm)	2.531(3)	2.509(3)	2.508(3)
13 (Yb)	2.498(4)	2.534(4)	2.521(5)
13' (Yb)	2.514(3)	2.543(3)	2.495(3)
14 (Lu)	2.534(4)	2.542(3)	2.504(4)
14' (Lu)	2.510(3)	2.532(3)	2.486(3)
15 (Y)	2.528(4)	2.573(3)	2.556(4)
15' (Y)	2.547(2)	2.581(2)	2.523(2)

Table S2: Bond Lengths RE-O in Rare Earth Complexes **1-15** with *p*-iodobenzoic acid and 2,2'-6',2''-terpyridine. The O4 bond distance in the disordered complex **11'** is given as O4A and the O3 and O4 bond distances in the disordered complex **12'** are given as O3A and O4B, respectively.

RE(III) Complexes	d_{Ln-O1} [Å]	d_{Ln-O2} [Å]	d_{Ln-O3} [Å]	d_{Ln-O4} [Å]	d_{Ln-O5} [Å]	d_{Ln-O6} [Å]	d_{Ln-Ow1} [Å]
1 (La)	2.469(4)		2.645(4)	2.614(4)	2.421(4)	2.451(4)	2.592(4)
2 (Ce)	2.444(4)		2.627(4)	2.585(4)	2.403(4)	2.427(4)	2.567(4)
2' (Ce)	2.538(2)	2.593(2)	2.595(2)	2.559(2)	2.401(2)	2.390(2)	
3 (Pr)	2.522(3)	2.569(3)	2.545(3)	2.577(3)	2.386(3)	2.374(3)	
4 (Nd)	2.506(2)	2.556(2)	2.530(2)	2.564(2)	2.370(2)	2.361(2)	
5 (Sm)	2.532(3)	2.503(3)	2.479(3)	2.528(3)	2.326(3)	2.338(3)	
6 (Eu)	2.471(3)	2.514(3)	2.491(3)	2.520(3)	2.327(3)	2.320(3)	
7 (Gd)	2.505(3)	2.466(3)	2.487(3)	2.511(3)	2.313(3)	2.304(3)	
8 (Tb)	2.448(3)	2.489(3)	2.466(3)	2.493(3)	2.302(3)	2.291(3)	
9 (Dy)	2.462(4)	2.486(3)	2.444(3)	2.479(3)	2.279(3)	2.291(3)	
10 (Ho)	2.475(4)	2.453(3)	2.476(3)	2.428(3)	2.271(3)	2.277(3)	
11 (Er)	2.461(3)	2.450(3)	2.463(3)	2.420(3)	2.257(3)	2.265(2)	
11' (Er)	2.372(3)	2.413(3)	2.292(4)	O4B:2.572(10)	2.334(3)	2.305(3)	
12 (Tm)	2.450(4)	2.414(4)	2.439(4)	2.450(4)	2.250(3)	2.258(3)	
12' (Tm)	2.352(3)	2.409(3)	O3A:2.220(10)	O4B:2.629(12)	2.325(2)	2.281(2)	
13 (Yb)	2.434(4)	2.438(4)	2.405(4)	2.440(4)	2.238(3)	2.245(3)	
13' (Yb)	2.429(2)	2.413(3)	2.387(3)	2.471(3)	2.239(2)		2.305(3)
14 (Lu)	2.413(3)	2.451(3)	2.437(3)	2.452(3)	2.255(3)	2.245(3)	
14' (Lu)	2.379(2)	2.471(2)	2.415(3)	2.421(3)	2.230(2)		2.297(3)
15 (Y)	2.475(3)	2.450(3)	2.471(3)	2.428(3)	2.266(3)	2.269(3)	
15' (Y)	2.488(2)	2.423(2)	2.449(2)	2.450(2)	2.262(2)		2.337(2)

IV. Table of Supramolecular Interaction Distances

Table S3: Intermolecular Non-Covalent Interaction Distances in Structure Type I Complexes (**1**, **2)**

Compound	d(I3-π) localized [Å]/%VdW	d(Offset π) [Å]
1 (La)	3.5764(2)/[97.18%]	3.6260(2)
2 (Ce)	3.5922(3)/[97.61%]	3.6238(3)

Table S4: Intermolecular Non-Covalent Interaction Distances in Structure Type V Complexes (**2'**, **3-15)**. The **2'** (Ce^{3+}) complex has two distances for the for the I1-π interaction, due to two part atomic disorder of the iodine atom (The first value is the I1A-C6 distance and the second is the I1B-Cg6 distance).

Compound	d(I1-π) delocalized [Å]	d(I3A- π (C12)) localized [Å]	d(I3B- π (C13)) localized [Å]	d(Offset π) [Å]
2' (Ce)	3.4968(16)/3.6198(16)	3.8261(17)/[103.97%]	3.6346(16)/[98.77%]	3.8012(17)
3 (Pr)	3.5210(1)	3.8108(1)/[103.55%]	3.6334(1)/[98.73%]	3.7917(1)
4 (Nd)	3.5391(1)	3.8133(1)/[103.62%]	3.6475(1)/[99.12%]	3.8189(1)
5 (Sm)	3.5439(1)	3.7940(2)/[103.10%]	3.6565(2)/[99.36%]	3.8380(2)
6 (Eu)	3.5307(2)	3.7970(2)/[103.18%]	3.6520(2)/[99.24%]	3.8344(2)
7 (Gd)	3.5456(1)	3.7903(2)/[103.00%]	3.6321(2)/[98.70%]	3.8478(2)
8 (Tb)	3.5421(2)	3.7908(2)/[103.01%]	3.6384(2)/[98.87%]	3.8461(2)
9 (Dy)	3.5264(1)	3.7808(2)/[102.74%]	3.6205(2)/[98.38%]	3.8493(2)
10 (Ho)	3.5522(2)	3.7763(2)/[102.62%]	3.6705(2)/[98.74%]	3.8689(2)
11 (Er)	3.5471(1)	3.7784(1)/[102.67%]	3.6261(1)/[98.54%]	3.8715(1)
12 (Tm)	3.5495(11)	3.7893(12)/[102.97%]	3.6502(11)/[99.19%]	3.8766(12)
13 (Yb)	3.5494(2)	3.7920(2)/[103.04%]	3.6561(2)/[99.35%]	3.8773(2)
14 (Lu)	3.5406(3)	3.7739(3)/[102.55%]	3.6216(3)/[98.41%]	3.8701(3)
15 (Y)	3.5368(2)	3.7812(2)/[102.75%]	3.6334(2)/[98.73%]	3.8544(2)

Table S5: Delocalized Halogen-π Non-Covalent Interaction Distances in Structure Type V Complexes (**2'**, **3-15)**. These two interactions are from both parts of the disordered iodine to the centroid of Cg3 on the TPY ring.

Compound	d(I3A-π) delocalized [Å]	d(I3B-π) delocalized [Å]
2' (Ce)	3.7935(17)	3.6964(17)
3 (Pr)	3.7876(1)	3.7002(1)
4 (Nd)	3.7890(1)	3.6972(1)
5 (Sm)	3.7800(2)	3.6937(2)
6 (Eu)	3.7861(1)	3.6916(1)
7 (Gd)	3.7878(2)	3.6757(2)
8 (Tb)	3.7887(1)	3.6839(1)
9 (Dy)	3.7846(2)	3.6801(2)
10 (Ho)	3.7827(2)	3.7009(2)
11 (Er)	3.7872(1)	3.6798(1)
12 (Tm)	3.7972(12)	3.6916(12)
13 (Yb)	3.8008(2)	3.6874(2)
14 (Lu)	3.7927(3)	3.6765(3)
15 (Y)	3.7856(2)	3.6829(2)

Table S6: Intermolecular Non-Covalent Interaction Distances in Structure Type III Complexes (**13'**, **14'**, **15')**

Compound	d(I1-π (C12)) localized [Å]/%VdW	d(I2-π (C2)) localized [Å]/%VdW	d(Offset- π) [Å]
13' (Yb)	3.4428(2)/[93.55%]	3.5006(2)/[95.13%]	3.5419(2)
14' (Lu)	3.4545(5)/[93.87%]	3.5035(5)/[95.20%]	3.5416(5)
15' (Y)	3.4366(2)/[93.39%]	3.5071(2)/[95.30%]	3.5412(17)

Table S7: Intermolecular Non-Covalent Interaction Distances in Structure Type VI Complexes (**11'**, **12')**

Compound	d(I1A-π(C22)) localized [Å]/%VdW	d(I1B-π (C22)) localized [Å]/%VdW
11' (Er)	3.5050(1)/[98.73%]	3.6520(1)/[102.87%]
12' (Tm)	3.6583(1)/[103.51%]	3.4565(1)/[97.34%]

V. Table of PART Commands for Structure Type V Complexes

Table S8: Disordered Atoms and the Free Variables associated with PART commands of Complexes **2'-15**

Compound	Disordered Atoms	FVAR
2' (Ce)	I1A/I1B, I2A/I2B, I3A/I3B	0.60529, 0.65160, 0.51228
3 (Pr)	I3A/I3B	0.52206
4 (Nd)	I3A/I3B	0.52069
5 (Sm)	I3A/I3B	0.54630
6 (Eu)	I3A/I3B	0.55635
7 (Gd)	I3A/I3B	0..60910
8 (Tb)	I3A/I3B	0.60247
9 (Dy)	I3A/I3B	0.64991
10 (Ho)	I3A/I3B	0.57963
11 (Er)	I3A/I3B	0.64989
12 (Tm)	I3A/I3B	0.58911
13 (Yb)	I3A/I3B	0.58051
14 (Lu)	I3A/I3B	0.66956
15 (Y)	I3A/I3B	0.64409

VI. Tables of Halogen-π Interaction Angles

Table S9: Halogen-π Interaction Angles associated with the angle across from the halogen atom to aromatic ring perpendicular for all *p*-bromobenzoic acid complexes exhibiting structure type I, III, or V

Structure Type	Complex #	I1	I2	I3
I	1			65.07°
I	2			64.72°
I	3			64.59°
I	4			65.19°
V	5	80.54°		76.85°
V	6	80.03°		76.49°
V	7	79.65°		76.51°
V	8	79.25°		76.27°
III	7’	64.91°	74.37°	
III	8’	64.74°	74.45°	
III	9	64.84°	74.55°	
III	10	64.78°	74.90°	
III	11	64.98°	74.86°	
III	12	65.18°	75.10°	
III	13	65.32°	75.31°	
III	14	65.04°	75.07°	
III	15	64.66°	74.63°	

Table S10: Halogen-π Interaction Angles associated with the angle across from the halogen atom to aromatic ring perpendicular for all *p*-iodobenzoic acid complexes exhibiting structure type I, III, or V. Two values show an interaction where a PART command was used and the first value is for the A part and the second is for the B part.

Structure Type	Complex #	I1	I2	I3
I	1			65.74°
I	2			65.50°
V	2’	82.82°/82.03°		81.04°/75.51°
V	3	81.87°		80.66°/75.30°
V	4	81.97°		80.65°/75.76°
V	5	81.29°		80.32°/76.13°
V	6	81.16°		79.96°/75.98°
V	7	80.83°		79.92°/75.73°
V	8	80.62°		79.71°/75.84°
V	9	80.13°		79.27°/75.45°
V	10	80.32°		79.36°/76.16°
V	11	79.93°		79.11°/75.36°
V	12	79.73°		78.98°/75.79°
V	13	79.45°		79.02°/76.09°
V	14	79.56°		78.80°/75.20°
V	15	80.10°		79.28°/75.64°
III	13’	67.96°	72.98°	
III	14’	68.30°	72.94°	
III	15’	68.29°	72.83°	

VII. Additional Redundant Polyhedral Representations of Complex 1 and 13'

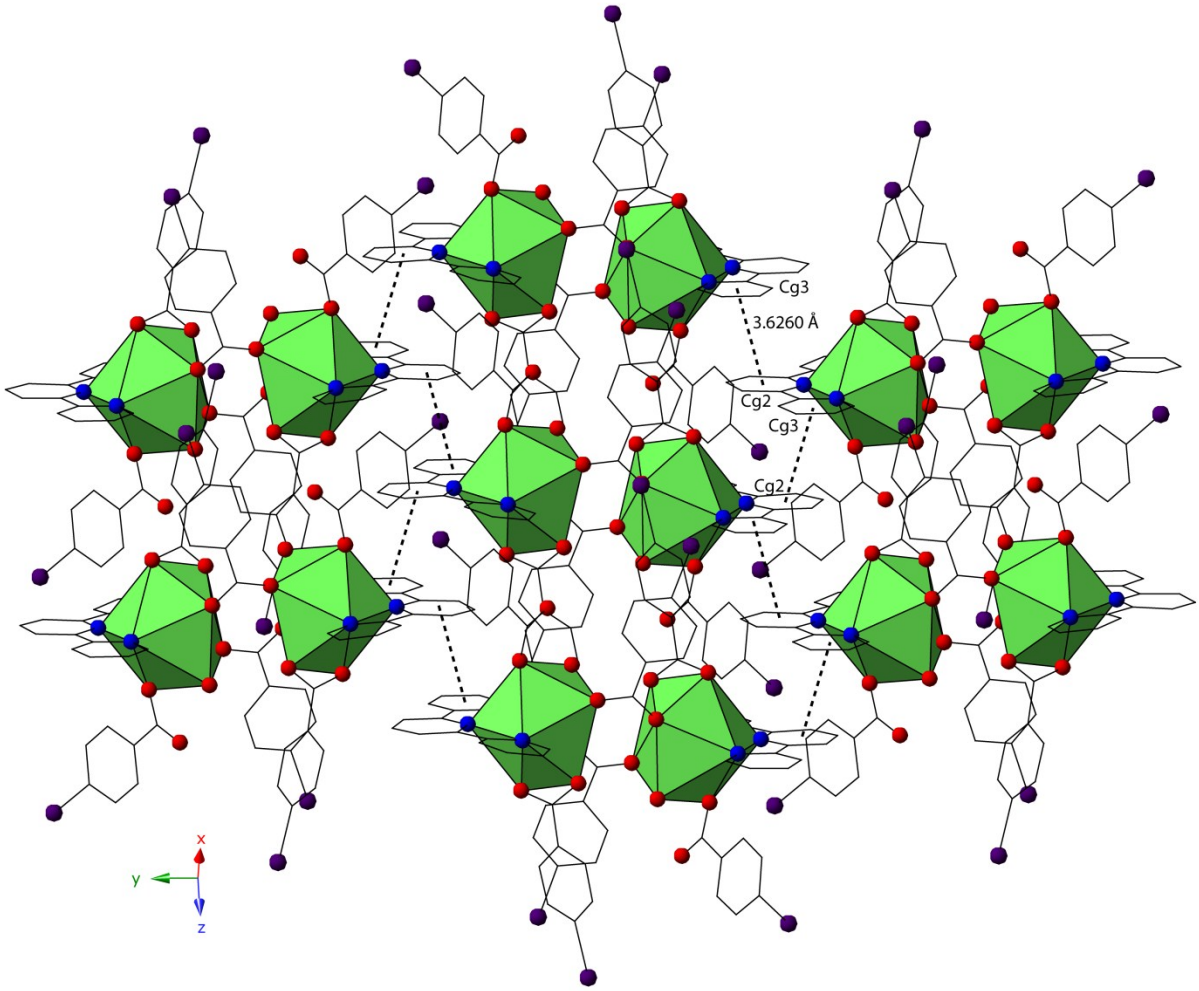

Figure S39: Polyhedral representation of complex **1** (La^{3+}) [structure type I] shown in the (011) plane. Offset π-stacking interactions assemble the tectons of **1** into 2D sheets are shown.

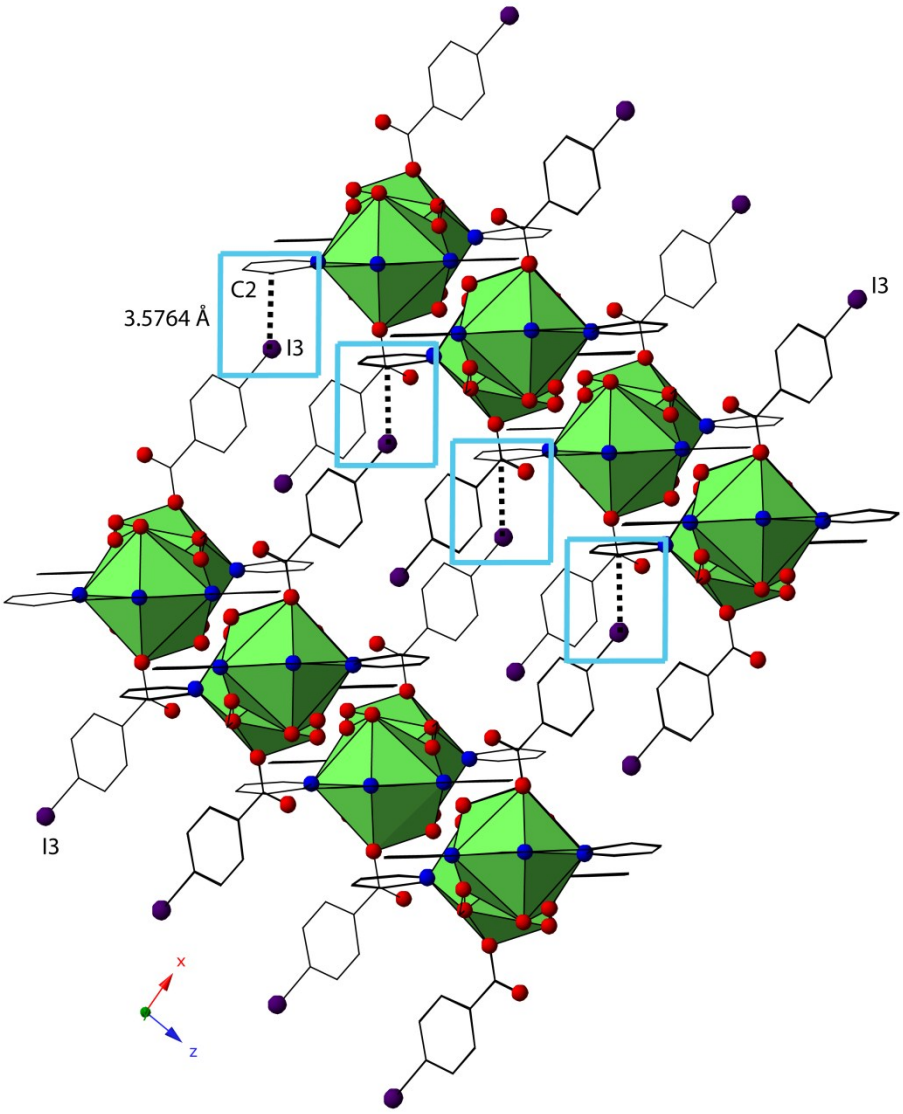

Figure S40: Polyhedral representation of complex **1** (La^{3+}) [structure type I] showing halogen-π interactions (light blue boxes) that assemble 2D sheets (show in Figure S39 in the (011) plane) into a third dimension shown along the [100].

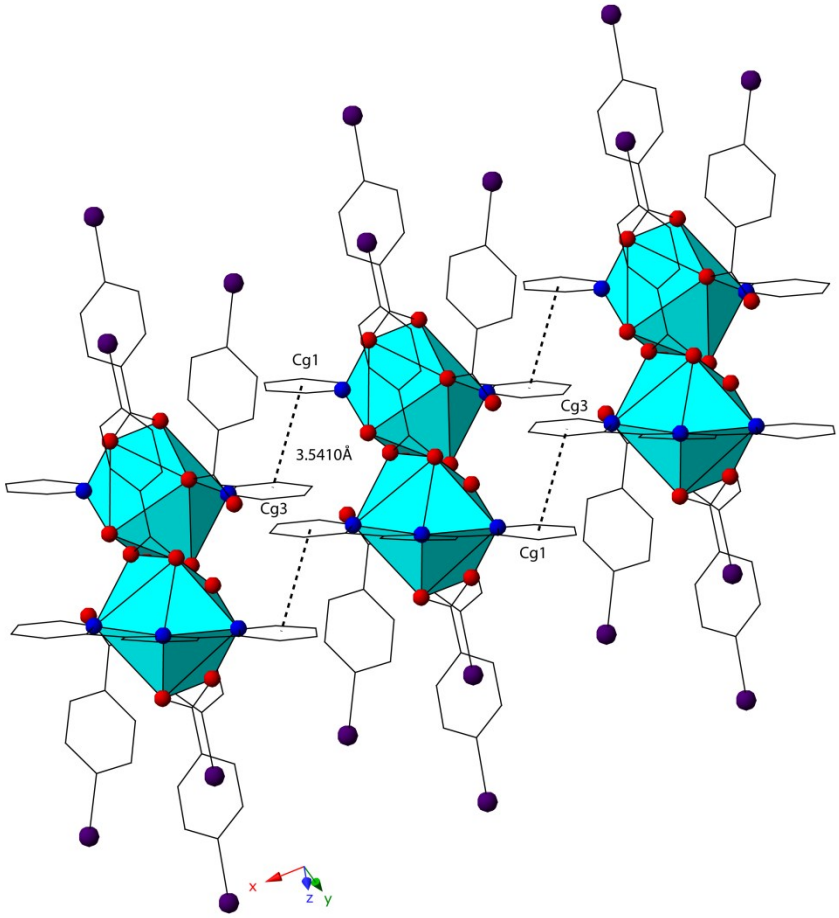

Figure S41: Polyhedral representation of complex **13'** (Yb^{3+}) [structure type III] showing offset π-stacking interactions that assemble tectons into 1D chains. Hydrogen interactions (not shown) assemble these 1D chains into a double-wide chain.

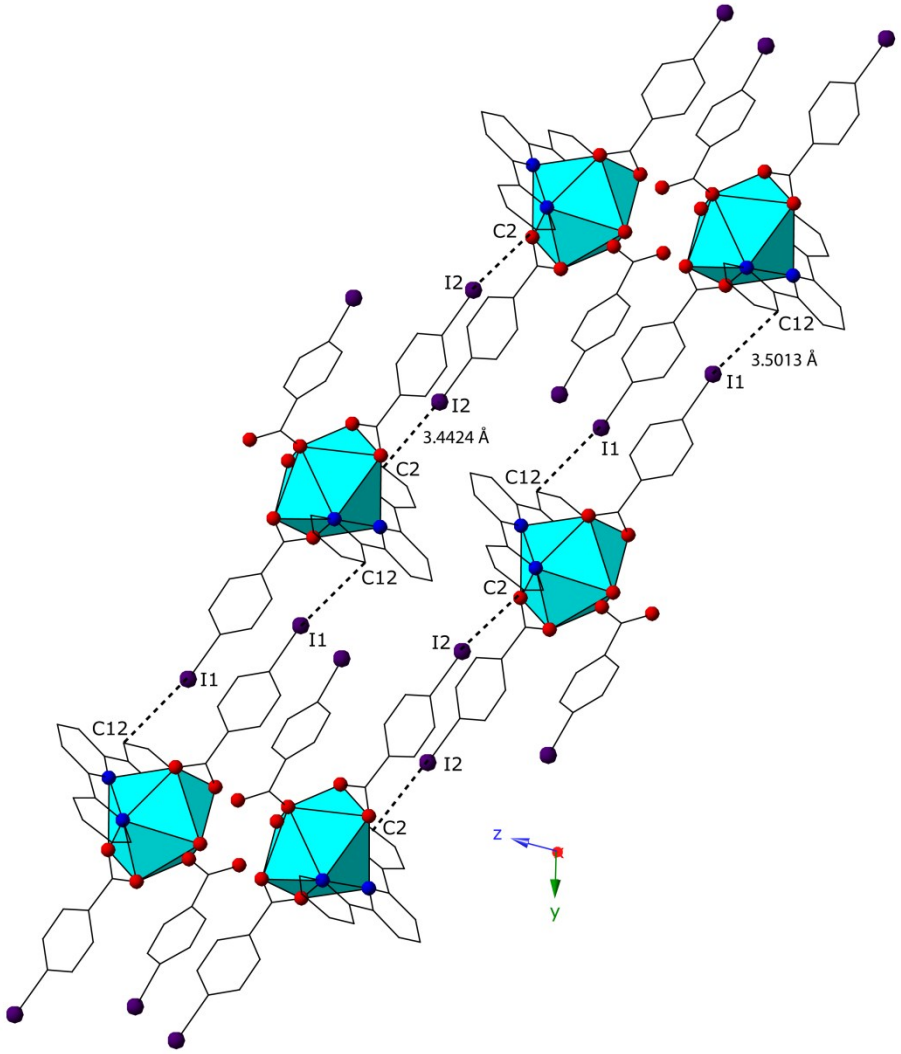

Figure S42: Polyhedral representation of complex **13'** (Yb^{3+}) [structure type III] showing halogen-π interactions that assemble tectons into 2D sheets.