Exploring supramolecular assembly and luminescent behavior in a series of RE-*p*-chlorobenzoic acid-1,10-phenanthroline complexes

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Supporting Info Section

I. Powder X-ray diffraction data

For complexes **1-11**, calculated and observed patterns were both collected a room temperature (298K).

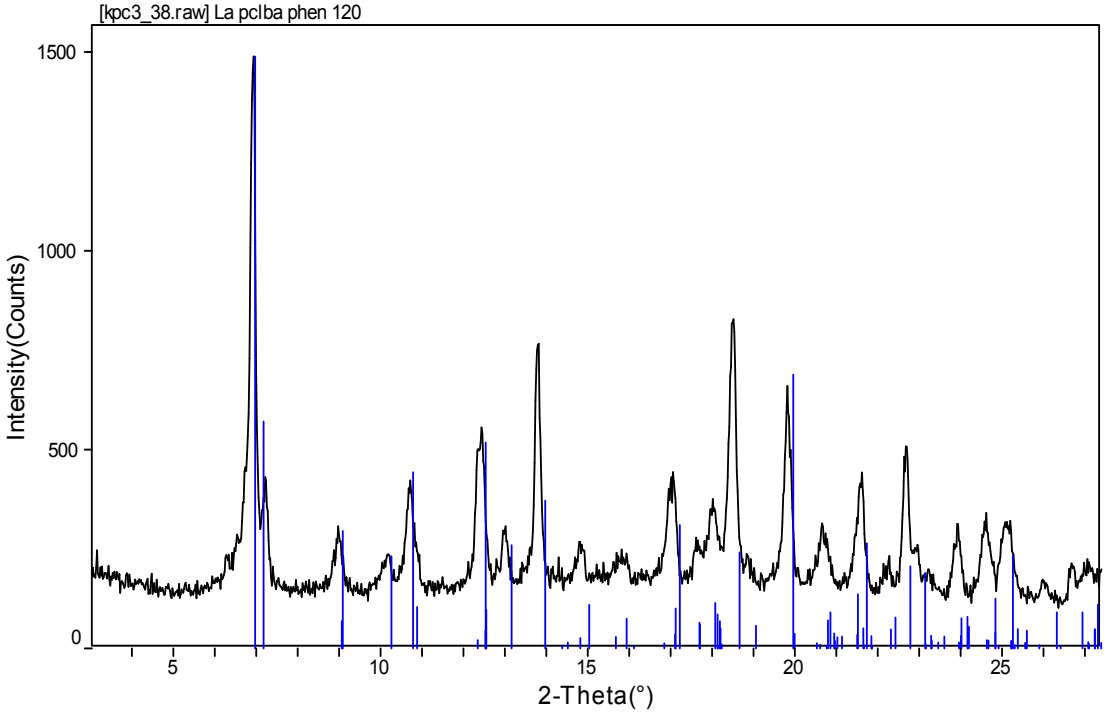

Figure S1: The observed PXRD pattern of structure **1** with calculated pattern overlaid in blue.

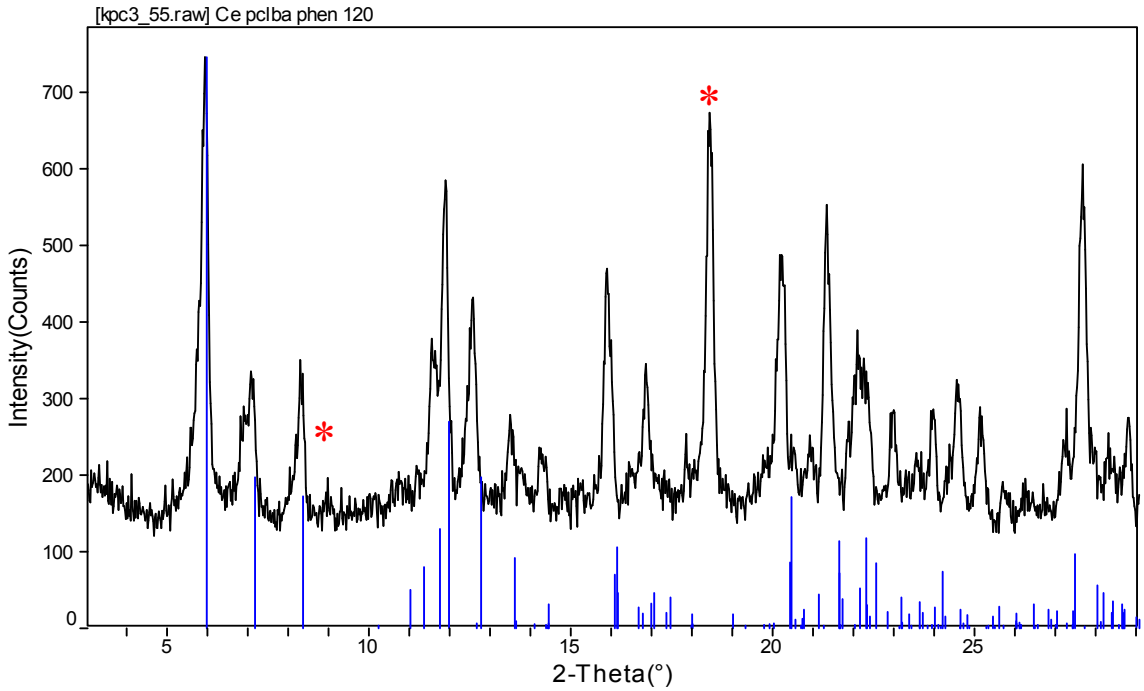

Figure S2: The observed PXRD pattern of structure **2** with calculated pattern overlaid in blue. We acknowledge two minor impurities as indicated with asterisks. The intensity of the impurity peak at approximately 19 ° 2θ is due to preferred orientation. Both impurity peaks have been identified as excess *p*-chlorobenzoic acid via the search match function in JADE.[1]

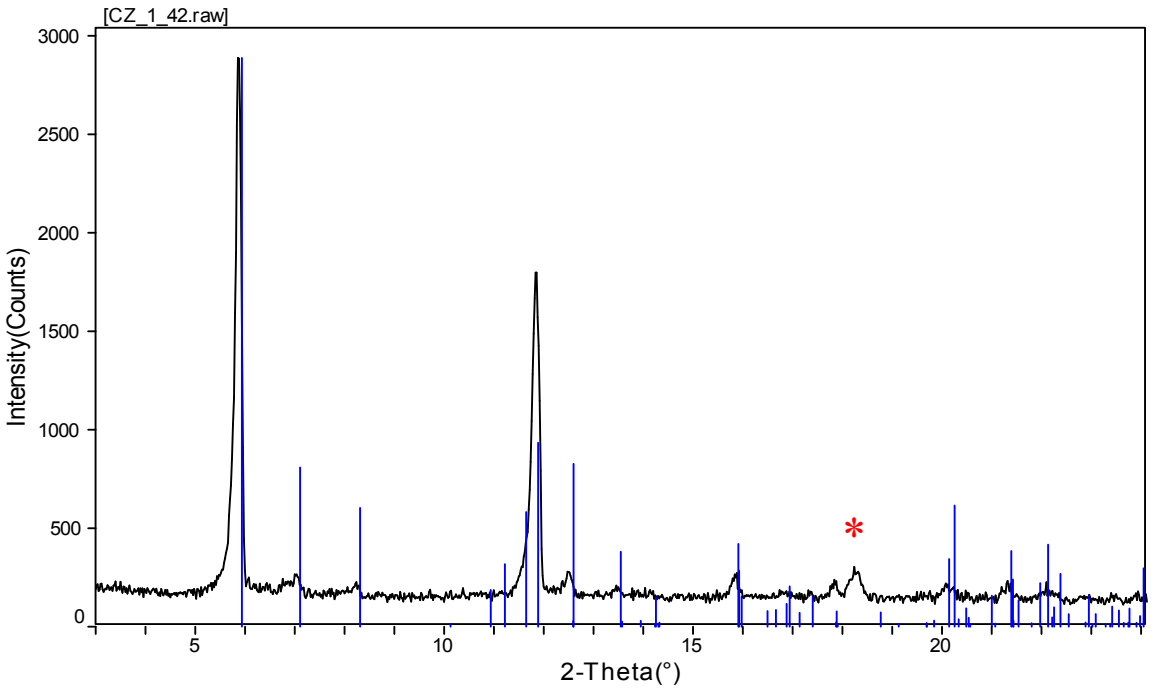

Figure S3: The observed PXRD pattern of structure **3** with calculated pattern overlaid in blue. We acknowledge a minor impurity as indicated with an asterisk. The impurity peak has been identified as excess *p*-chlorobenzoic acid via the search match function in JADE.

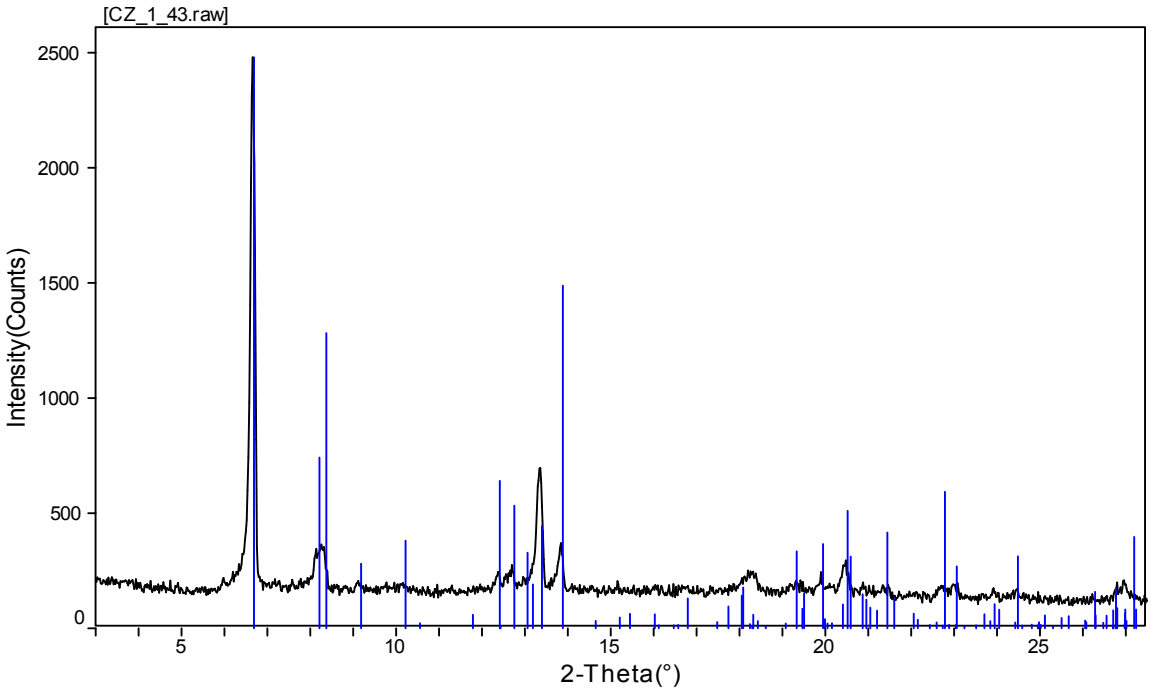

Figure S4: The observed PXRD pattern of structure **4** with calculated pattern overlaid in blue.

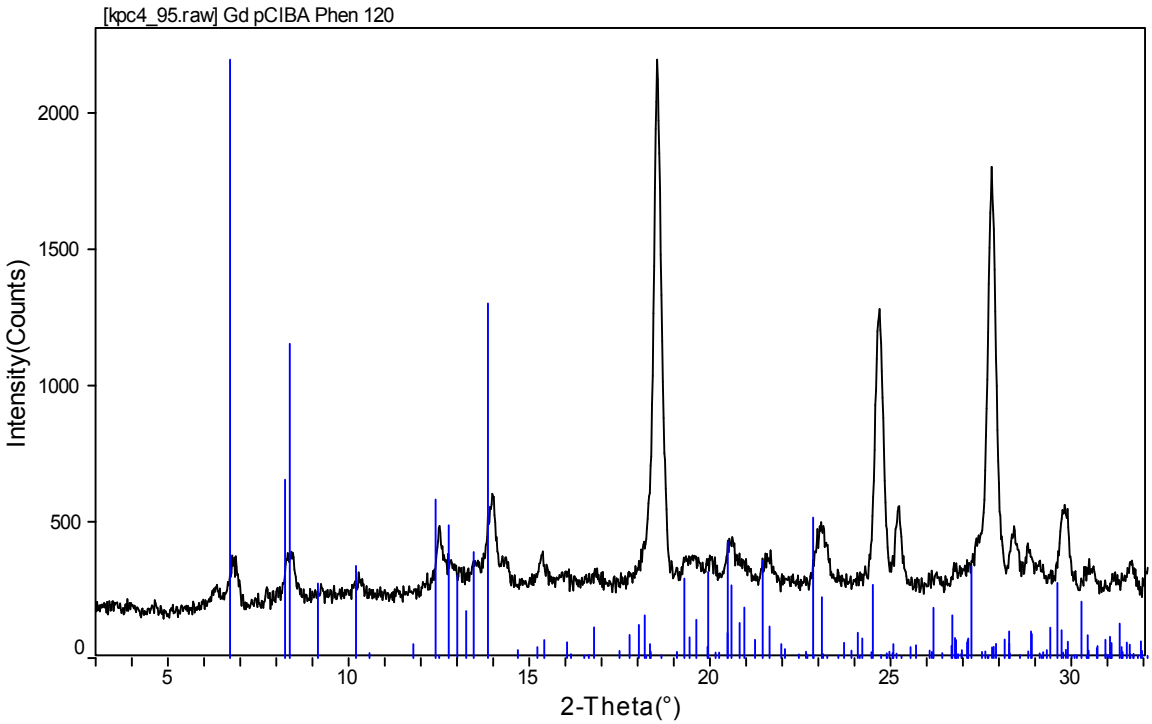

Figure S5: The observed PXRD pattern of structure **5** with calculated pattern overlaid in blue.

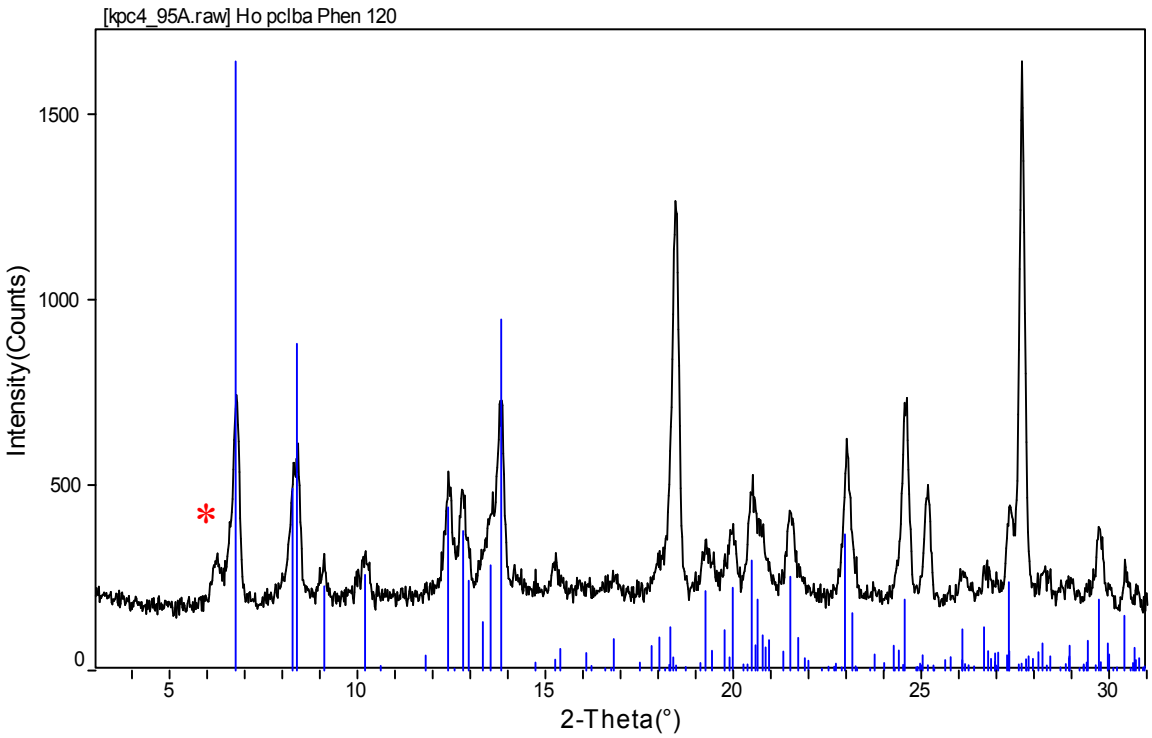

Figure S6: The observed PXRD pattern of structure **6** with calculated pattern overlaid in blue. We acknowledge a minor impurity as indicated with an asterisk.

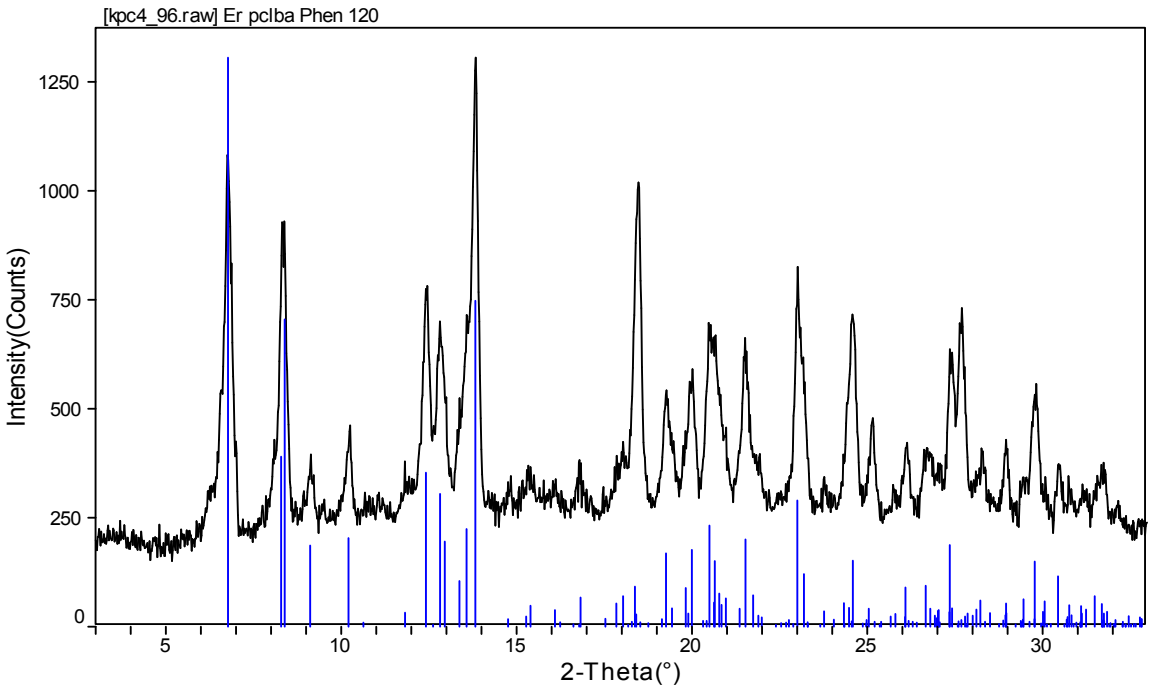

Figure S7: The observed PXRD pattern of structure **7** with calculated pattern overlaid in blue.

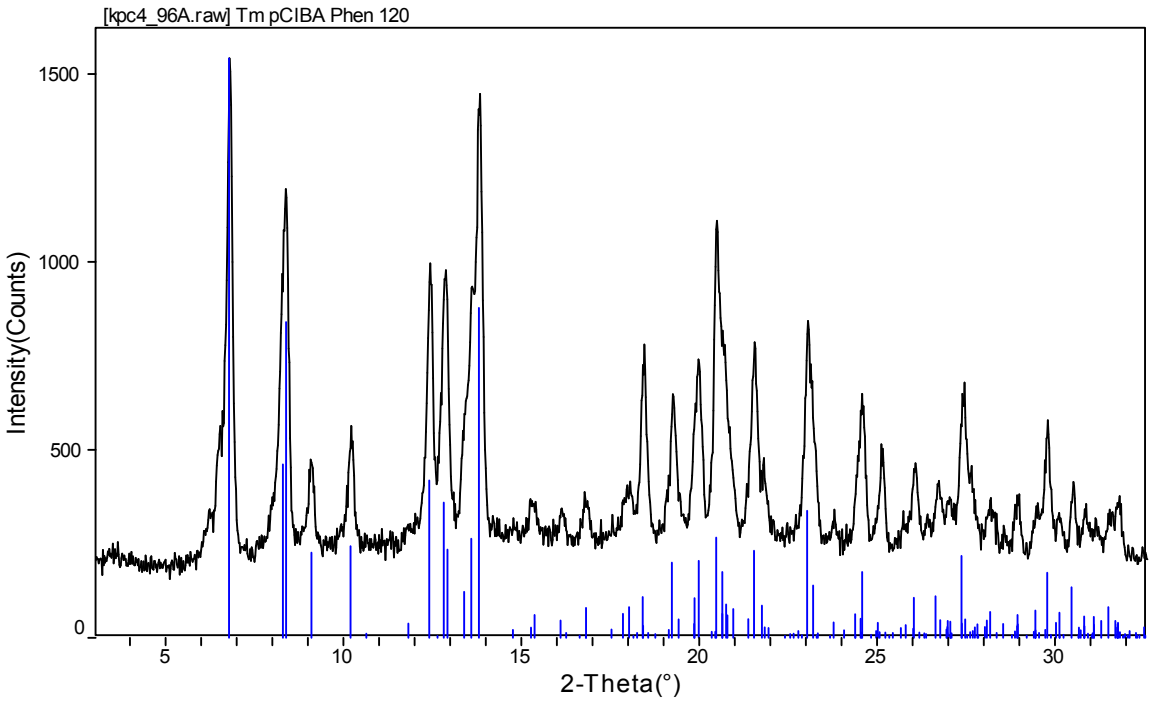

Figure S8: The observed PXRD pattern of structure **8** with calculated pattern overlaid in blue.

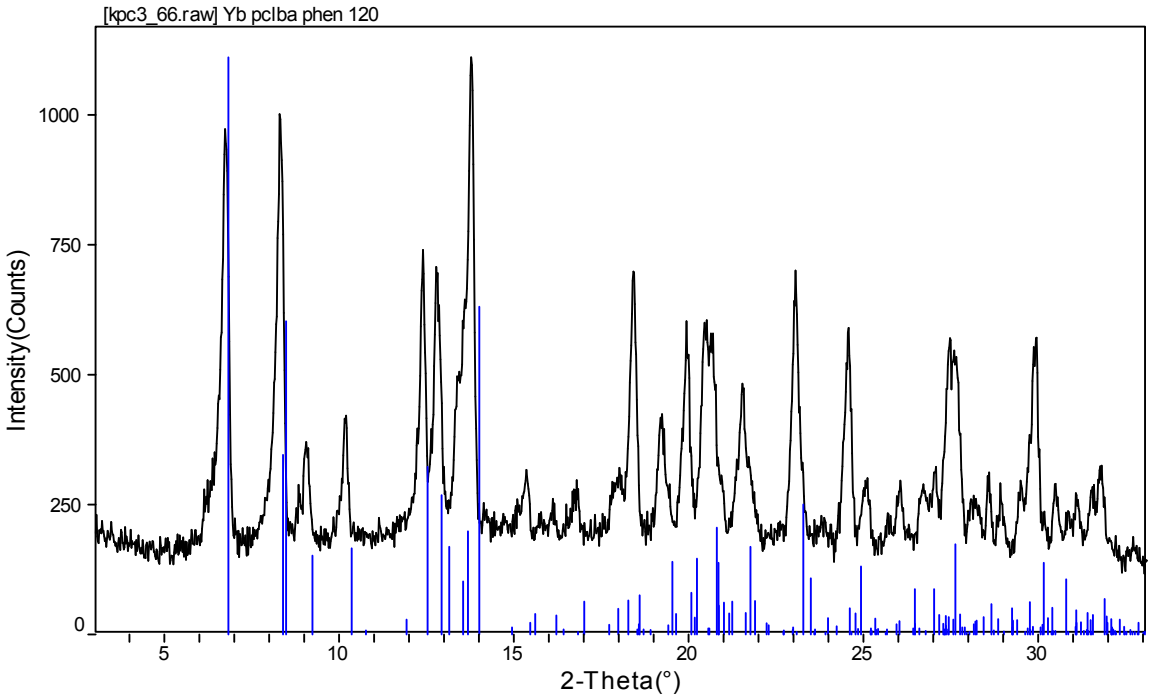

Figure S9: The observed PXRD pattern of structure **9** with calculated pattern overlaid in blue.

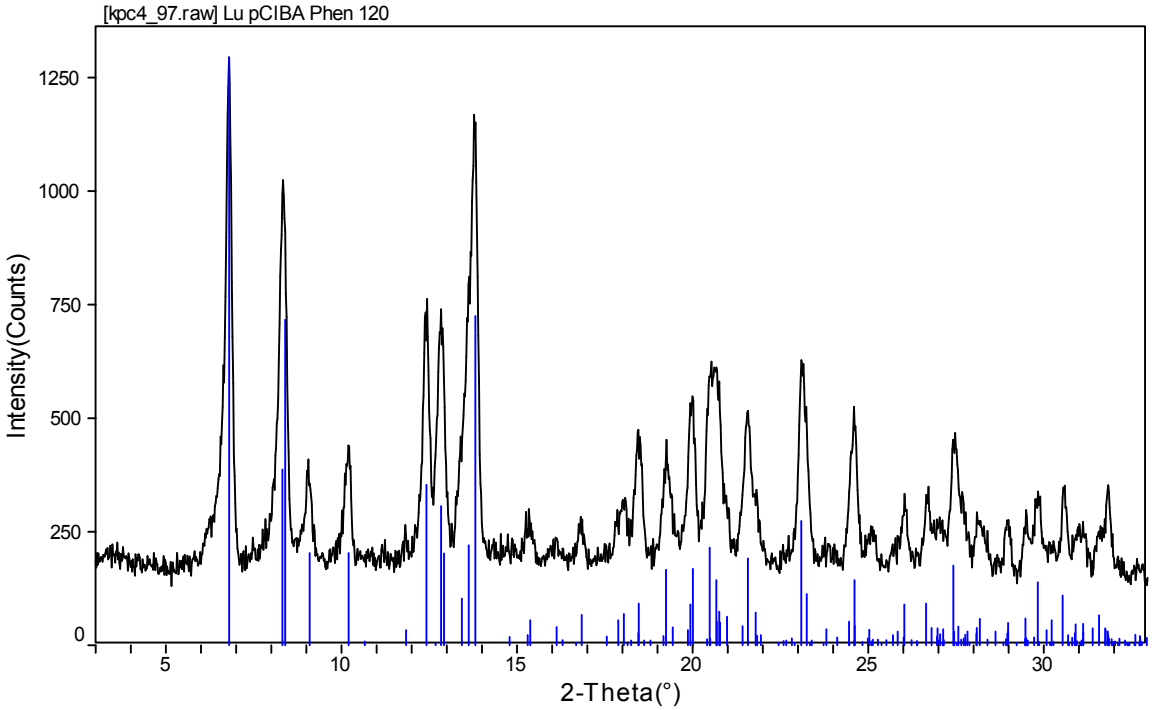

Figure S10: The observed PXRD pattern of structure **10** with calculated pattern overlaid in blue.

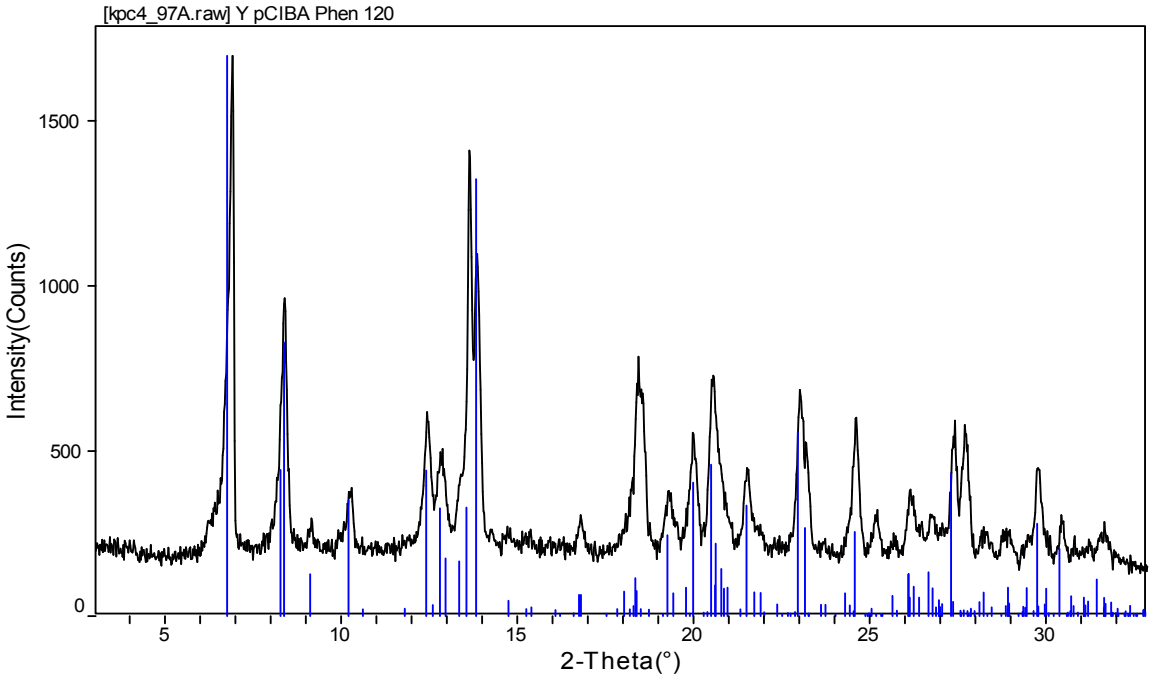

Figure S11: The observed PXRD pattern of structure **11** with calculated pattern overlaid in blue.

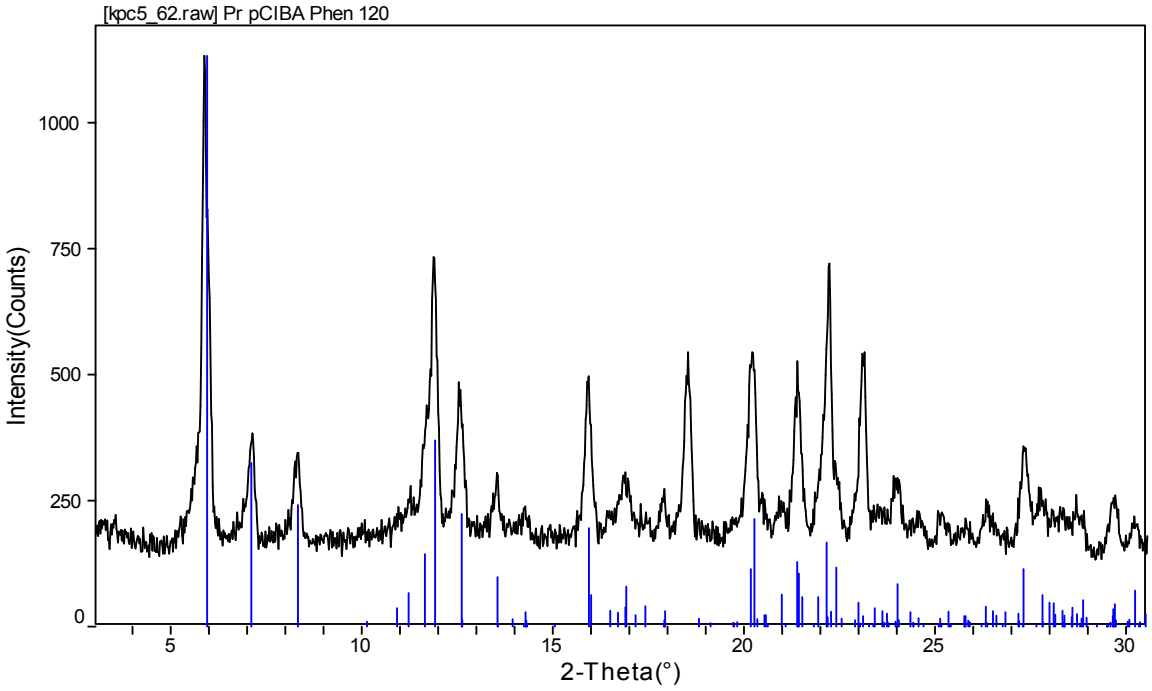

Figure S12: The observed PXRD pattern of the known Pr isomorph[2] ($[Pr(C_{12}H_8N_2)(C_7H_4ClO_2)_3(H_2O)]_2$) with calculated pattern of published CIF overlaid in blue.

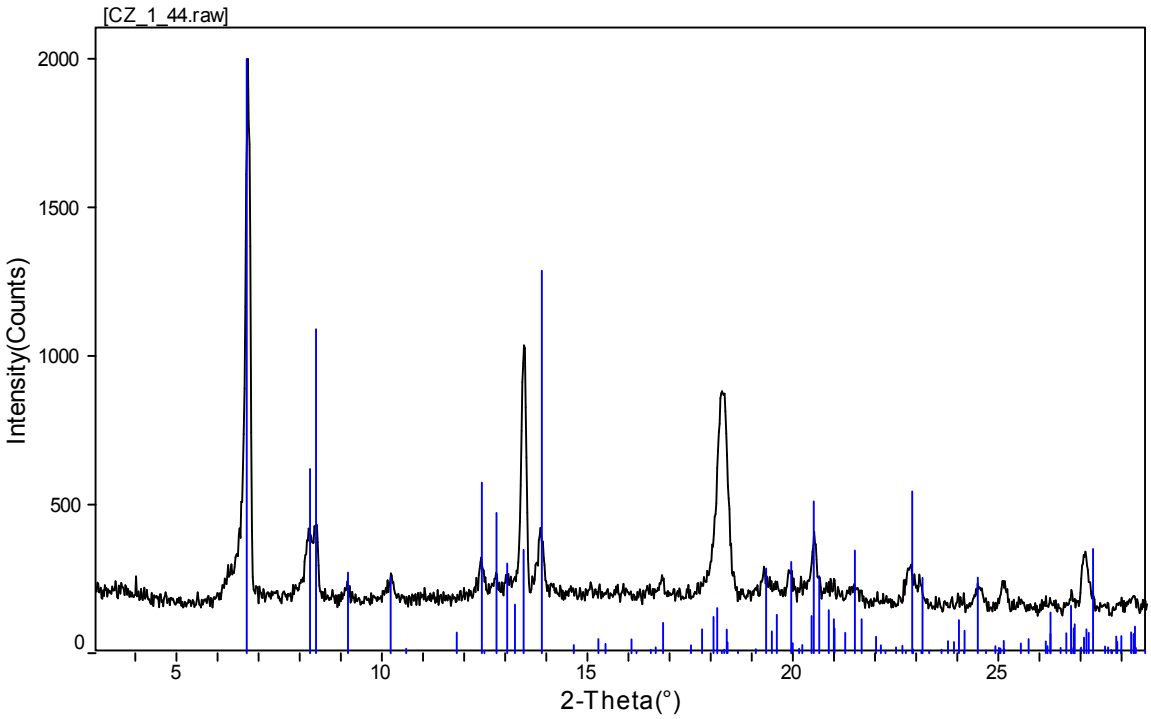

Figure S13: The observed PXRD pattern of the known Eu isomorph[3] ($[Eu(C_{12}H_8N_2)(C_7H_4ClO_2)_3]_2$) with calculated pattern of published CIF overlaid in blue.

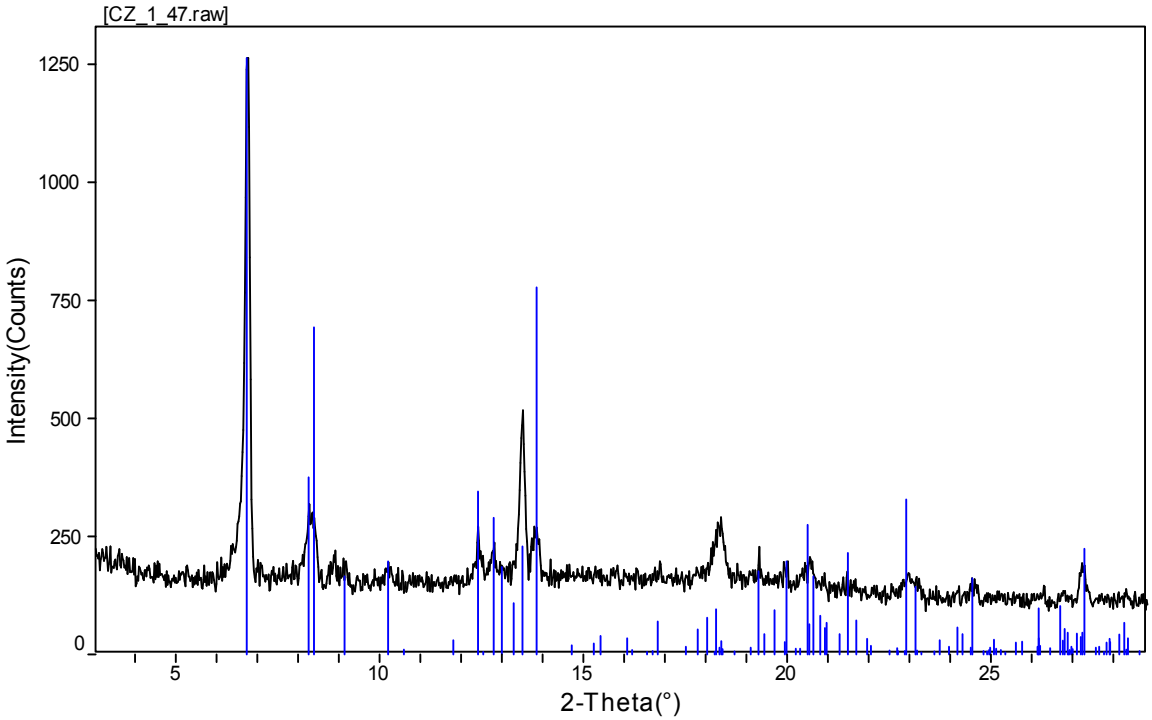

Figure S14: The observed PXRD pattern of the known Tb isomorph[4] ($[Tb(C_{12}H_8N_2)(C_7H_4ClO_2)_3]_2$) with calculated pattern of published CIF overlaid in blue.

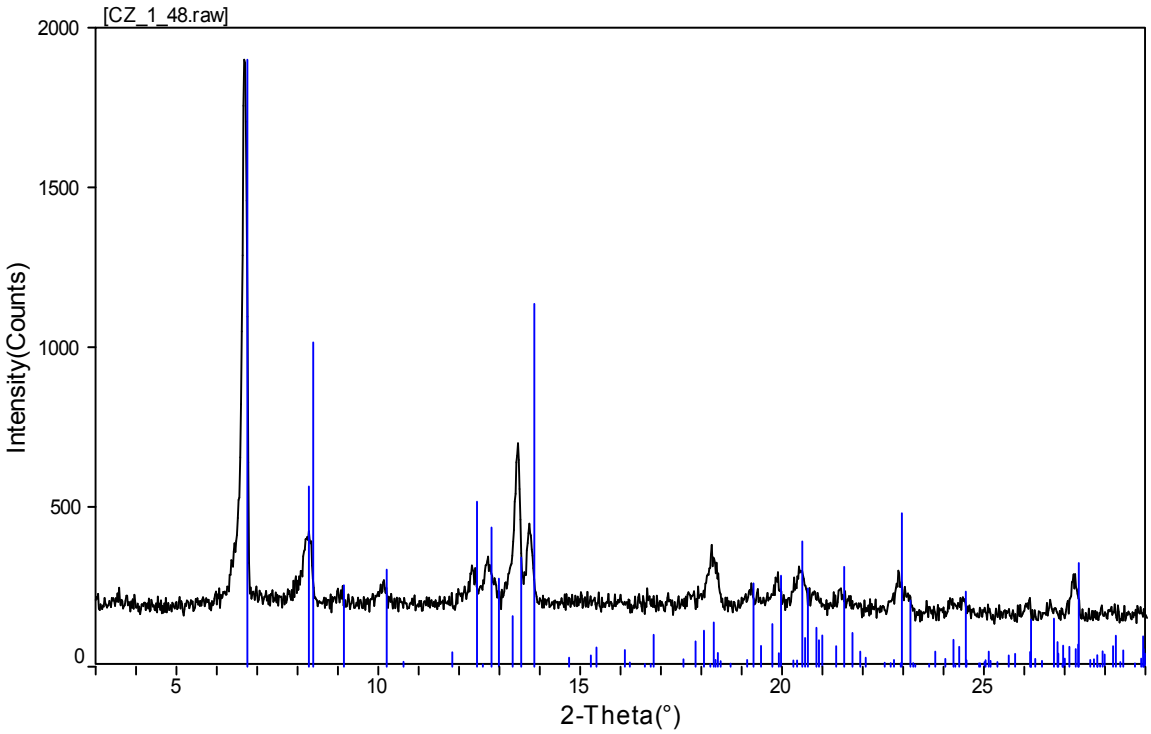

Figure S15: The observed PXRD pattern of the known Dy isomorph[5] ($[Dy(C_{12}H_8N_2)(C_7H_4ClO_2)_3]_2$) with calculated pattern of published CIF overlaid in blue.

II. Thermal Ellipsoid Plots

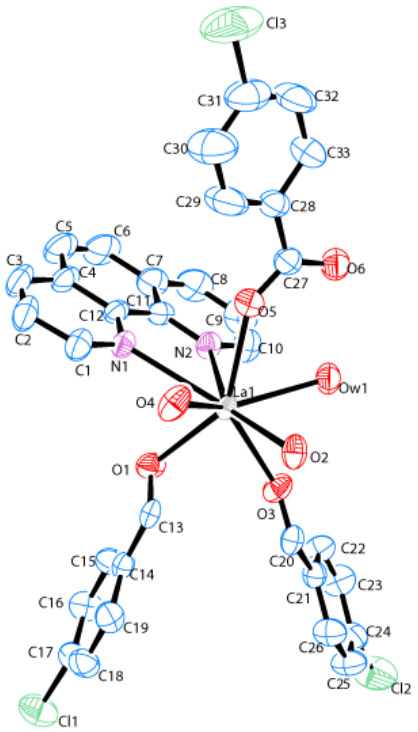

Figure S16: ORTEP illustration of structure **1**. Ellipsoids are shown at 50% probability level.

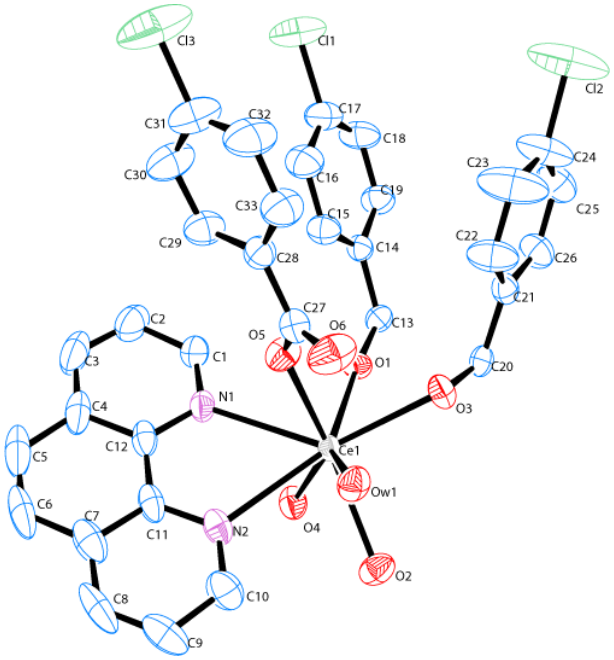

Figure S17: ORTEP illustration of structure **2**. Ellipsoids are shown at 50% probability level.

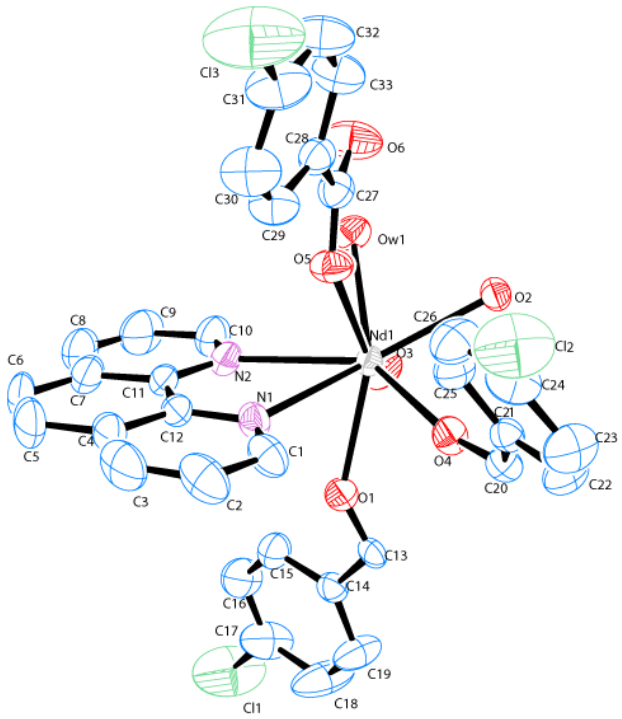

Figure S18: ORTEP illustration of structure **3**. Ellipsoids are shown at 50% probability level.

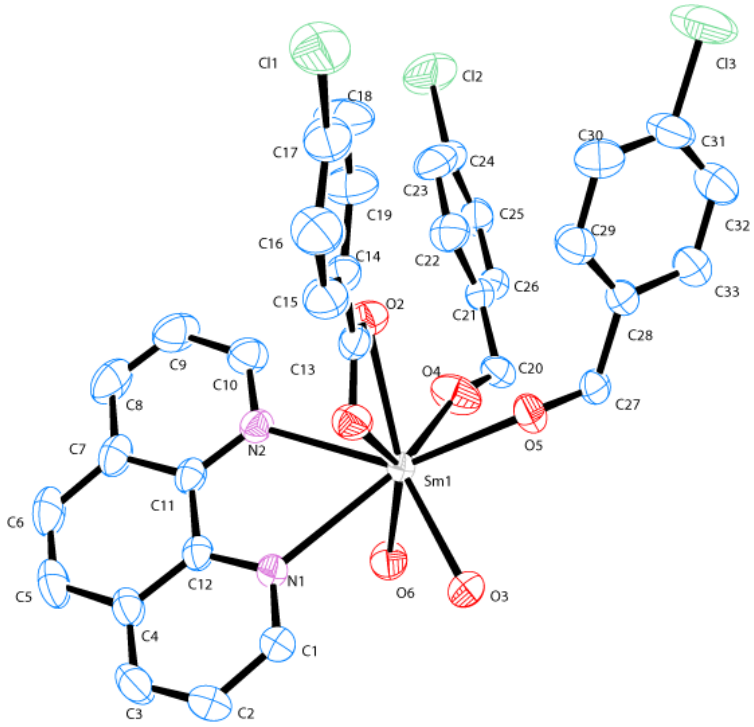

Figure S19: ORTEP illustration of structure **4**. Ellipsoids are shown at 50% probability level.

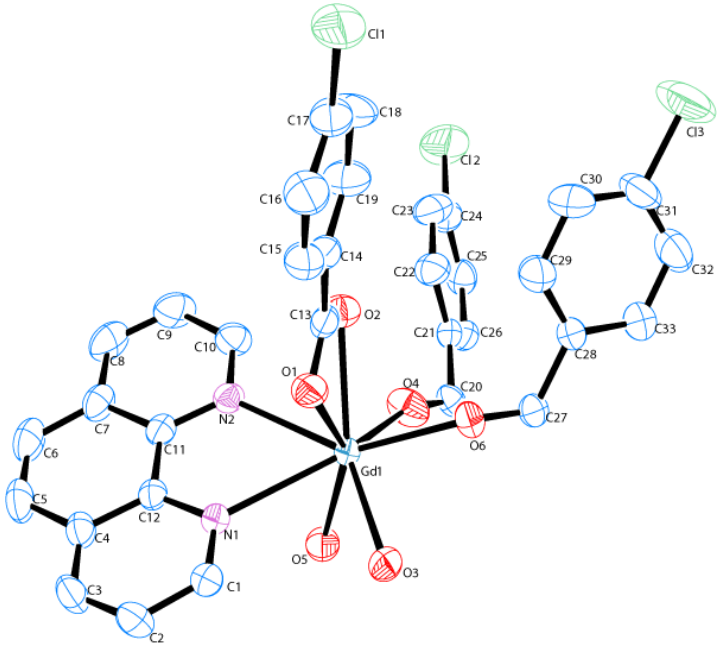

Figure S20: ORTEP illustration of structure **5**. Ellipsoids are shown at 50% probability level.

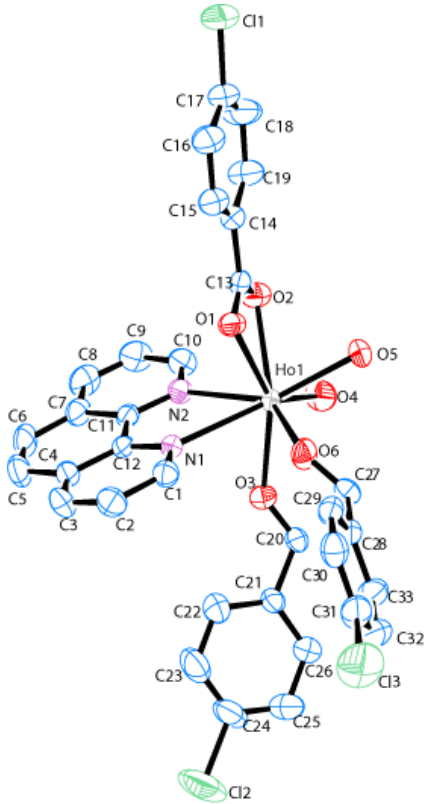

Figure S21: ORTEP illustration of structure **6**. Ellipsoids are shown at 50% probability level.

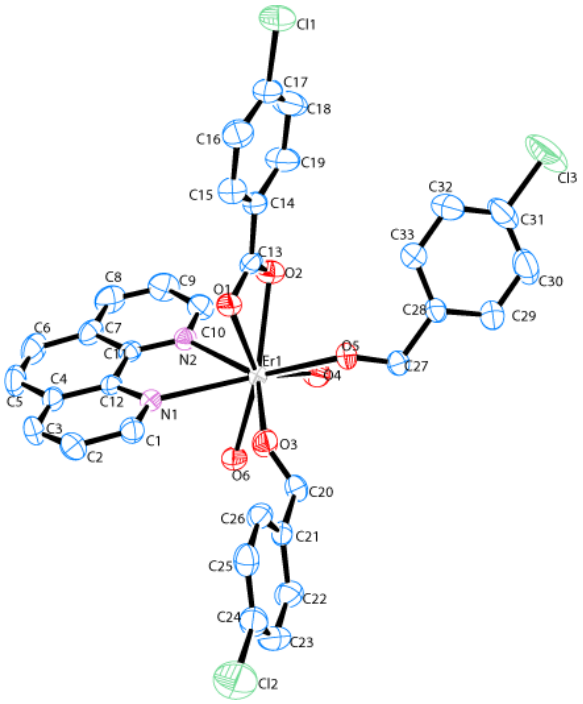

Figure S22: ORTEP illustration of structure **7**. Ellipsoids are shown at 50% probability level.

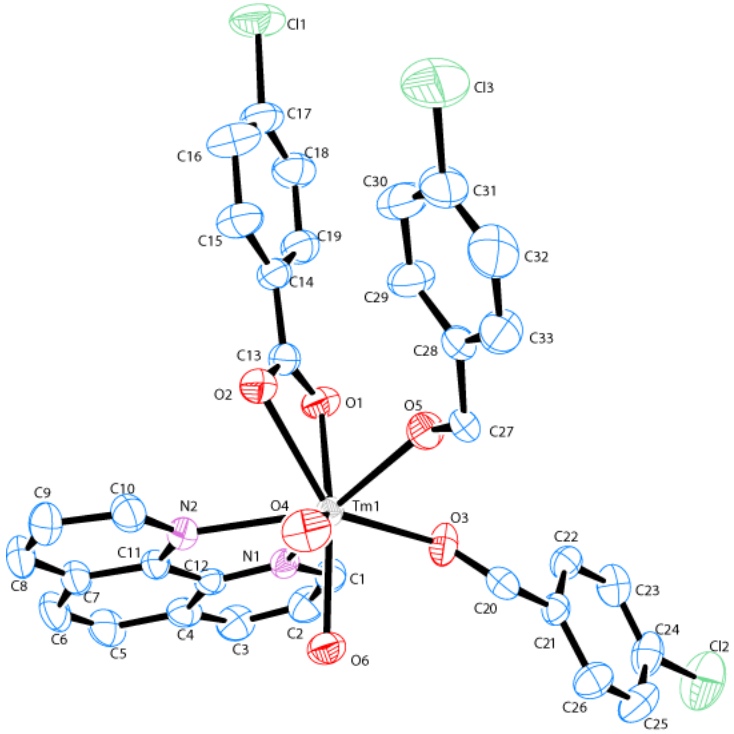

Figure S23: ORTEP illustration of structure **8**. Ellipsoids are shown at 50% probability level.

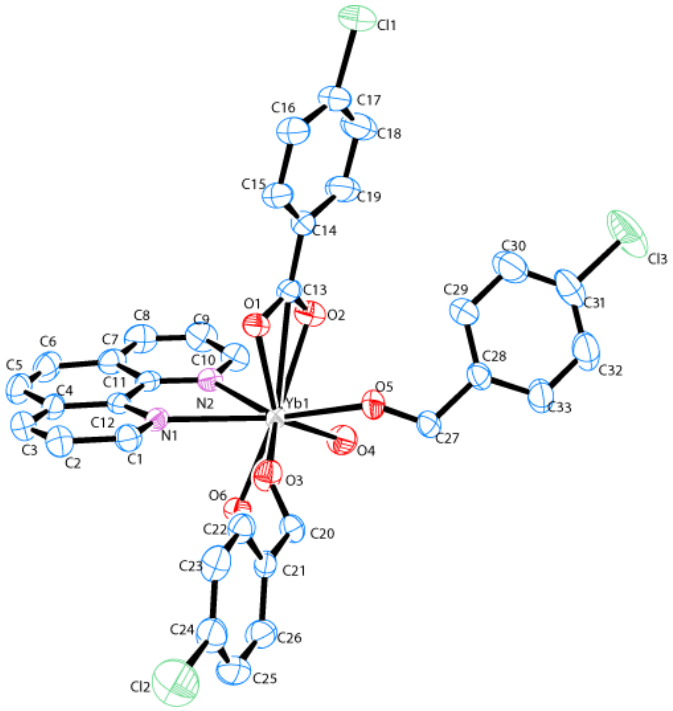

Figure S24: ORTEP illustration of structure **9**. Ellipsoids are shown at 50% probability level.

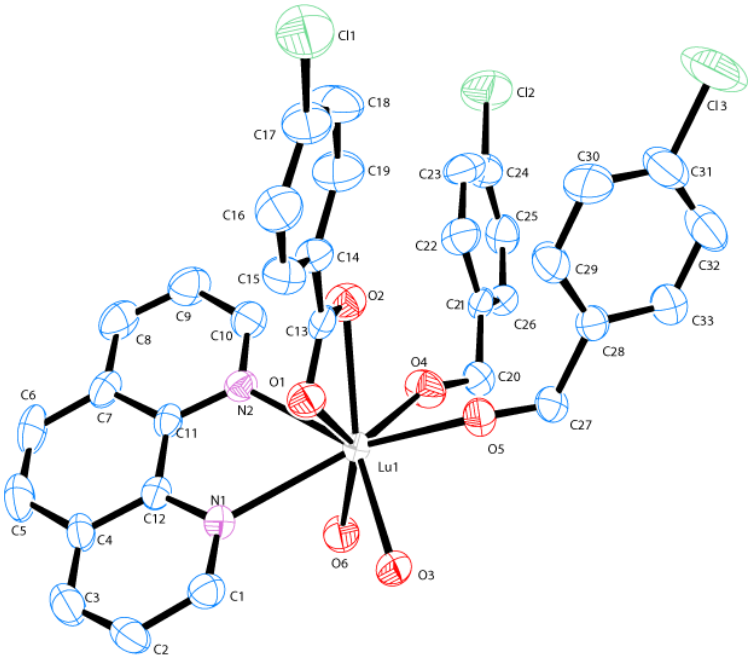

Figure S25: ORTEP illustration of structure **10**. Ellipsoids are shown at 50% probability level.

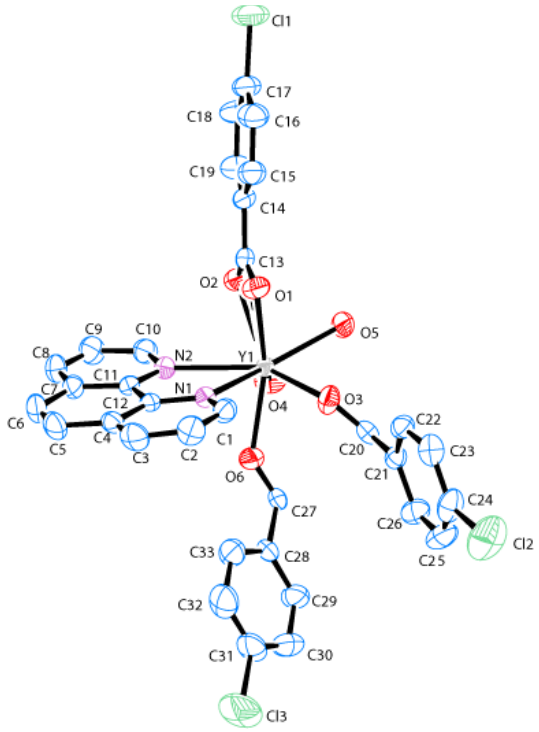

Figure S26: ORTEP illustration of structure **11**. Ellipsoids are shown at 50% probability level.

III. Table of Bond Distances

Table S1: Ln-O Bond Lengths in Ln^{3+} complexes (**1-11**) with *p*-chlorobenzoic acid and 1,10-phenanthroline. Where complexes had been previously synthesized (Pr, Eu, Tb and Dy) bond length data comes from corresponding CIF.

f electrons (Ln^{3+})	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]
0 (La)	2.542(2)	2.517(2)	2.5172(16)	2.437(2)	2.466(2)		2.551(2)
1 (Ce)	2.448(2)	2.497(2)	2.472(2)	2.461(2)	2.446(2)		2.511(3)
2 (Pr)[1]	2.435(2)	2.450(2)	2.471(2)	2.424(2)	2.428(2)		2.497(2)
3 (Nd)	2.419(2)	2.4391(19)	2.456(2)	2.3995(19)	2.408(2)		2.488(2)
4 (Pm)							
5 (Sm)	2.4086(14)	2.5270(14)	2.3840(14)	2.3307(15)	2.3783(14)	2.3743(14)	
6 (Eu)[2]	2.397(7)	2.526(5)	2.360(5)	2.323(6)	2.390(6)	2.355(8)	
7 (Gd)	2.3883(15)	2.5063(16)	2.3567(16)	2.3069(16)	2.3526(16)	2.3516(16)	
8 (Tb)[3]	2.379(5)	2.487(5)	2.341(5)	2.280(6)	2.330(5)	2.322(6)	
9 (Dy)[4]	2.357(4)	2.476(4)	2.320(4)	2.276(4)	2.321(4)	2.316(4)	
10 (Ho)	2.3484(17)	2.4761(17)	2.3115(17)	2.2705(17)	2.3141(17)	2.3125(16)	
11 (Er)	2.3354(17)	2.4671(17)	2.3030(16)	2.2588(17)	2.3024(17)	2.2994(17)	
12 (Tm)	2.324(2)	2.459(2)	2.291(2)	2.249(2)	2.294(2)	2.2841(19)	
13 (Yb)	2.314(2)	2.453(2)	2.281(2)	2.242(2)	2.285(2)	2.272(2)	
14 (Lu)	2.309(3)	2.449(3)	2.267(3)	2.230(3)	2.269(3)	2.263(3)	
0* (Y)	2.3436(19)	2.470(2)	2.3131(19)	2.268(2)	2.3075(19)	2.306(2)	

Naming convention from literature examples were different than those used as part of this work so transformations are noted here.

1. From Li et. al. Chin. J. Inorg. Chem.[2] O5→O1, O7→O2, O4→O3, O3→O4, O1→O5, O6→OW1
2. From Jin. et. al. J. Rare Earths.[3] O4→O1, O3→O2, O6→O3, O5→O4, O2→O5, O1→O6
3. From Wang et. al. Chin. J. Inorg. Chem.[4] O5→O3, O6→O4, O4→O5, O3→O6
4. From Zhange Acta E.[5] O4→O1, O3→O2, O6→O3, O5→O4, O1→O5, O2→O6

IV. Tables of Supramolecular Interaction Distances

Table S2: Cl-π interaction distances and angles in Ln^{3+} complexes (**4-11**) with *p*-chlorobenzoic acid and 1,10-phenanthroline.

Complex	Cl-π distance [Å]
4 (Sm)	3.286(3)
5 (Gd)	3.288(4)
6 (Ho)	3.276(4)
7 (Er)	3.275(4)
8 (Tm)	3.273(4)
9 (Yb)	3.268(5)
10 (Lu)	3.265(7)
11 (Y)	3.280(4)

Table S3: π-π interaction distances and angles in Ln^{3+} complexes (**1-11**) with *p*-chlorobenzoic acid and 1,10-phenanthroline.

Complex	Cg•••Cg [Å]	Cg⊥•••Cg⊥ [Å]	Beta [deg]
1 (La)	3.667(2)	3.3947(14)	22.23
2 (Ce)	3.717(3)	3.4270(19)	25.21
3 (Nd)	3.739(2)	3.3722(15)	23.41
4 (Sm)	3.5465(13)	3.3783(9)	17.72
5 (Gd)	3.5473(15)	3.3704(10)	18.17
6 (Ho)	3.5447(16)	3.3542(11)	18.87
7 (Er)	3.5446(15)	3.3494(11)	19.11
8 (Tm)	3.5490(19)	3.3507(13)	19.24
9 (Yb)	3.546(2)	3.3495(15)	19.17
10 (Lu)	3.543(3)	3.333(2)	19.88
11 (Y)	3.5447(19)	3.3532(13)	18.92

V. Low Temperature XRD Data

Table S4: Representative low temperature (100K) single crystal XRD data for structure types I-III.

	Structure Type I-La (complex 1)	**Structure Type II-Ce (complex 2)**	**Structure Type III-Yb (complex 9)**
chem formula	$C_{66}H_{44}Cl_6N_4O_{14}La_2$	$C_{66}H_{44}Cl_6N_4O_{14}Ce_2$	$C_{66}H_{40}Cl_6N_4O_{12}Yb_2$
formula weight	1607.57	1609.99	1639.80
cryst system	triclinic	triclinic	triclinic
space group	P-1	P-1	P-1
a (Å)	9.9879(15)	8.354(3)	9.957(3)
b (Å)	12.5775(19)	12.787(4)	11.686(4)
c (Å)	13.1024(19)	15.315(5)	14.147(5)
α (deg)	99.015(2)	99.319(7)	111.258(5)
β (deg)	100.668(2)	100.245(6)	96.102(4)
γ (deg)	95.998(3)	100.713(6)	101.549(5)
V (Å^3)	1582.3(4)	1549.5(9)	1474.0(9)
Z	1	1	1
T (K)	100	100	100
λ (Mo Kα)	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	1.687	1.725	1.847
μ (mm^{-1})	1.655	1.780	3.495
R_{int}	0.0524	0.0994	0.0752
R1 [$I>2\sigma(I)$]	0.0312	0.0540	0.0416
wR2 [$I>2\sigma(I)$]	0.0720	0.1263	0.0888

VI. References

1. *JADE*, Materials Data Inc., Livermore, California, USA, 2003.
2. Y. Li, R. Wang, S.-Y. Niu, J. Jin and Z.-L. Wang, *Chinese Journal of Inorganic Chemistry*, 2008, 24, 1753-1760.
3. L. Jin, R.-F. Wang, L. Li and S.-Z. Lu, *Journal of Rare Earths*, 1996, 14, 161-166.
4. S.-P. Wang, R.-F. Wang and J. J. Zhang, *Chinese Journal of Inorganic Chemistry*, 2007, 23, 862-866.
5. B.-S. Zhang, *Acta Crystallographica Section E*, 2006, 62, m2645-m2647.