Controlling dimensionality via crystal engineering in Ln-2,5-thiophene dicarboxylic acid-terpyridine coordination polymers

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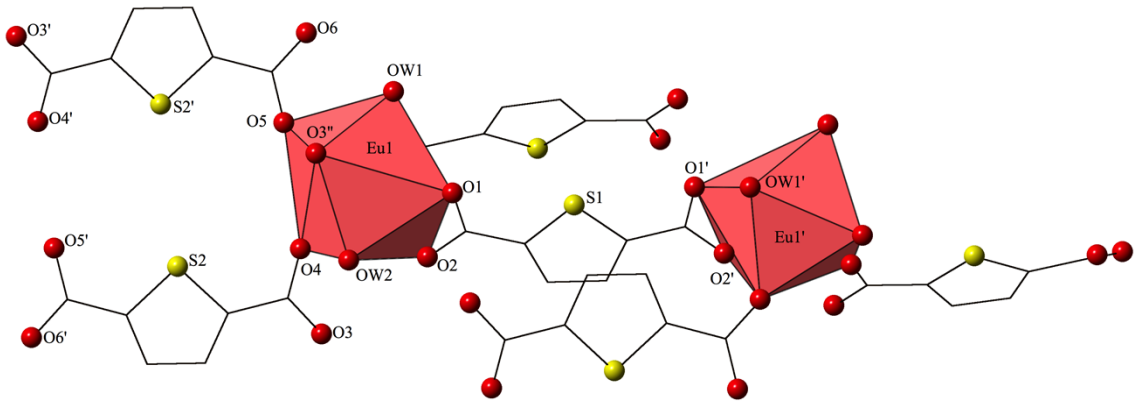
I. Additional Single Crystal XRD Data

Table S1 Crystallographic data for Ln-25TDC-TPY impurity, an Ln-25TDC MOF. Representative example here with Eu^{3+}. Analogous materials also co-form with complexes **4-8**.

	Impurity-3
chem formula	$C_{18}H_{14}S_3O_{16}Eu_2$
formula weight	886.39
cryst system	monoclinic
space group	C2/c
a (Å)	25.3425(8)
b (Å)	5.8193(2)
c (Å)	18.9762(6)
α (deg)	90
β (deg)	124.123(5)
γ (deg)	90
V (Å^3)	2316.72(17)
Z	4
T (K)	293
λ (Mo Kα)	0.71073
D_{calc} (g cm^{-3})	2.541
μ (mm^{-1})	5.720
R_{int}	0.0213
R1 [I>2σ(I)]	0.0149
wR2 [I>2σ(I)]	0.0346



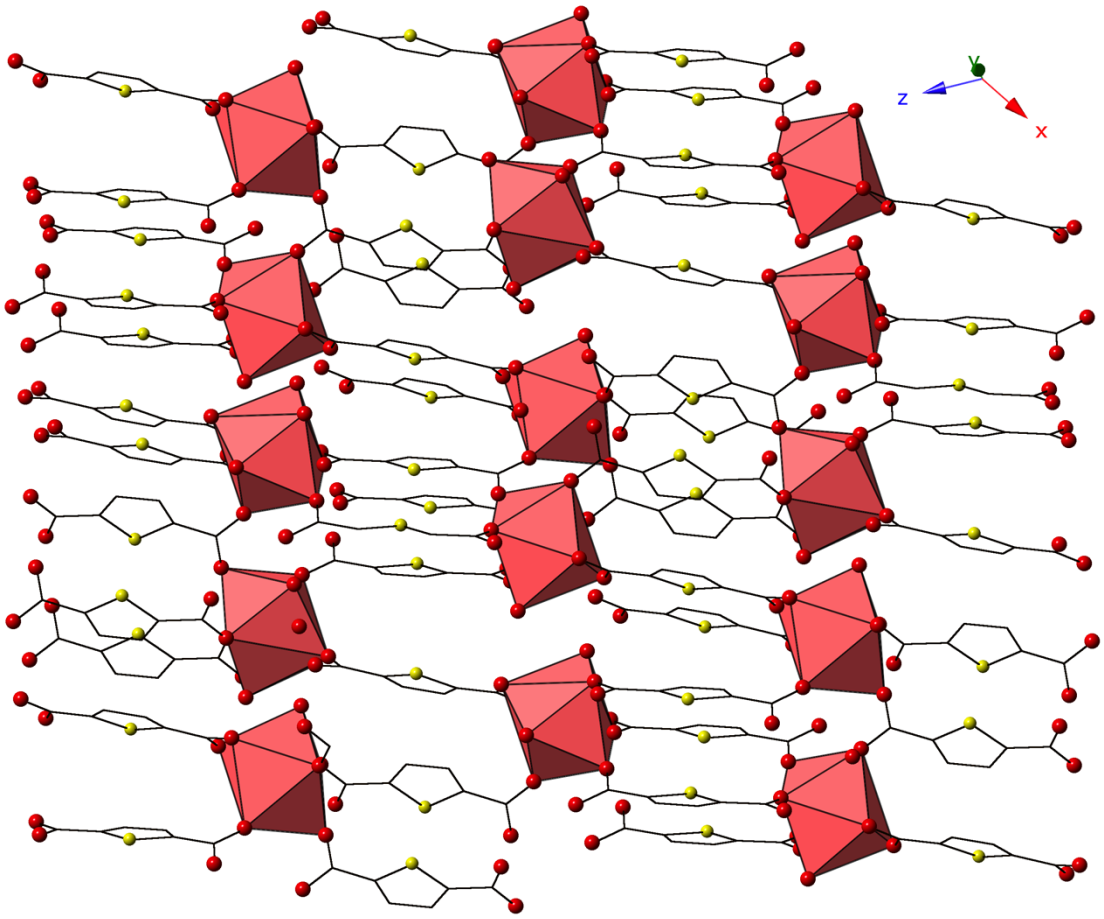


Figure S1 (Top) Polyhedral representation of local structure Eu-impurity $[Eu_2(2,5\text{-}TDC)_3(H_2O)_4]_n$. Red polyhedra represent europium metal centers, whereas spheres represent nitrogen (blue), oxygen (red), and sulfur (yellow). All H atoms have been omitted for clarity. **(Bottom)** 3D framework of Eu-impurity viewed in approximately the (101) plane.

II. Powder X-ray diffraction data

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

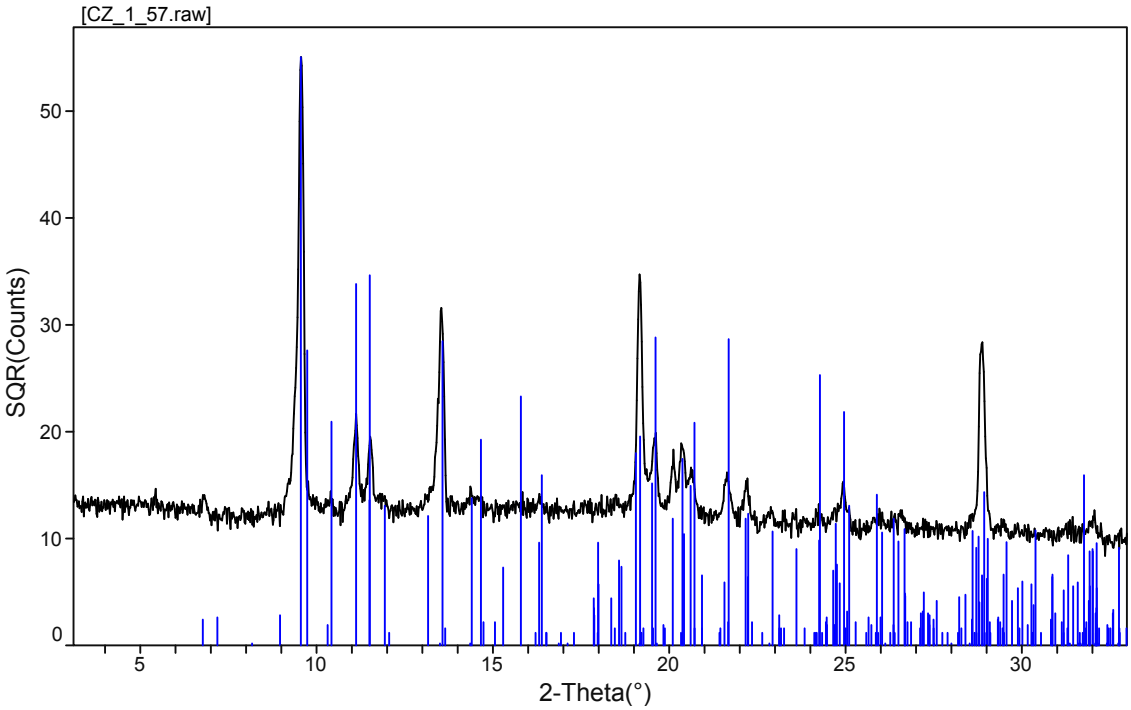


Figure S2 The observed PXRD pattern of complex **1** with calculated pattern overlaid in blue.

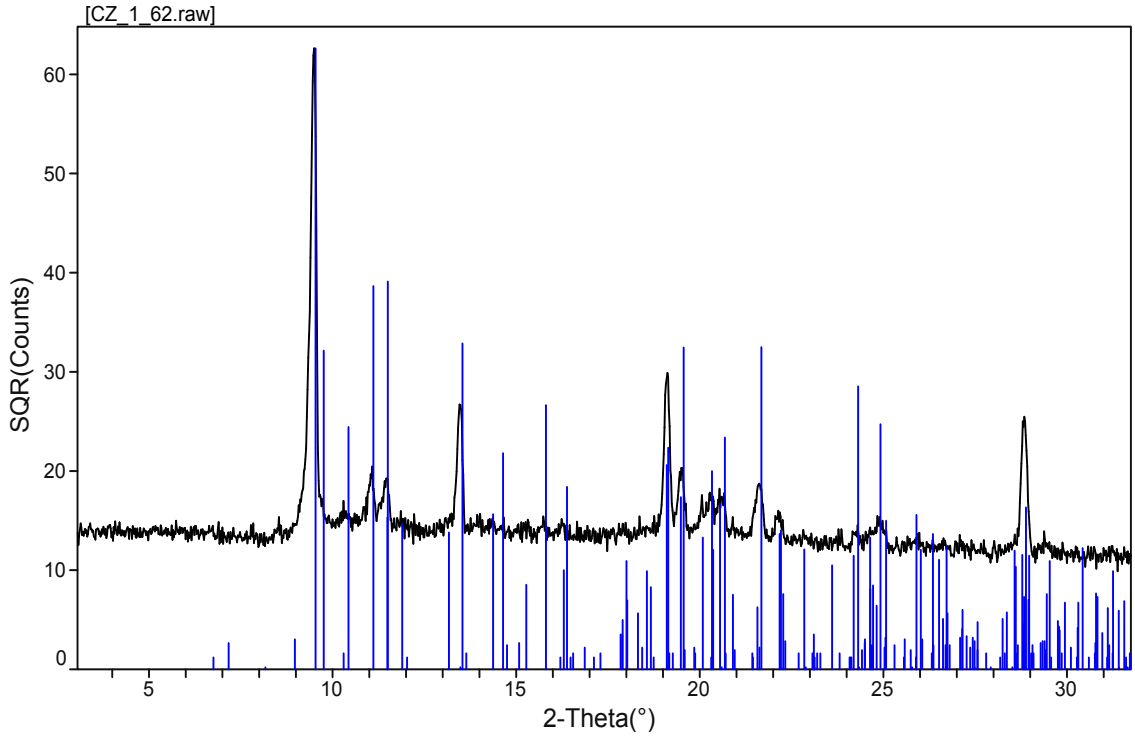


Figure S3 The observed PXRD pattern of complex **2** with calculated pattern overlaid in blue.

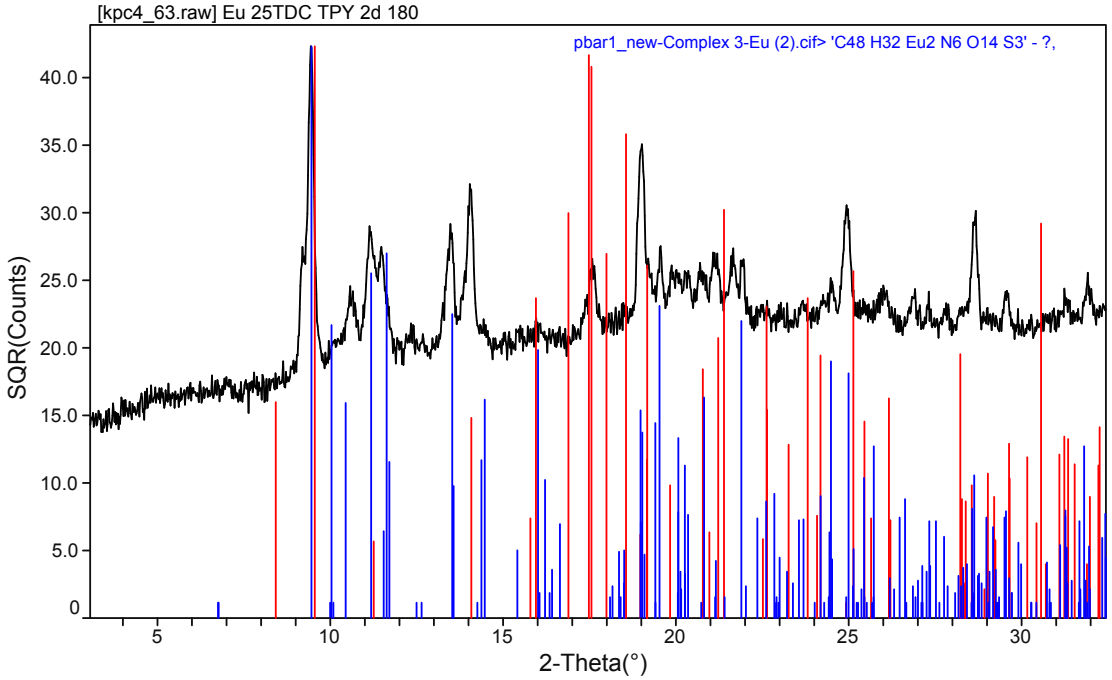


Figure S4 The observed PXRD pattern of complex **3** with calculated pattern overlaid in blue. Impurities in **3** have been identified as $[Eu_2(2,5\text{-}TDC)_3(H_2O)_4]_n$ (calculated CIF overlaid in red).

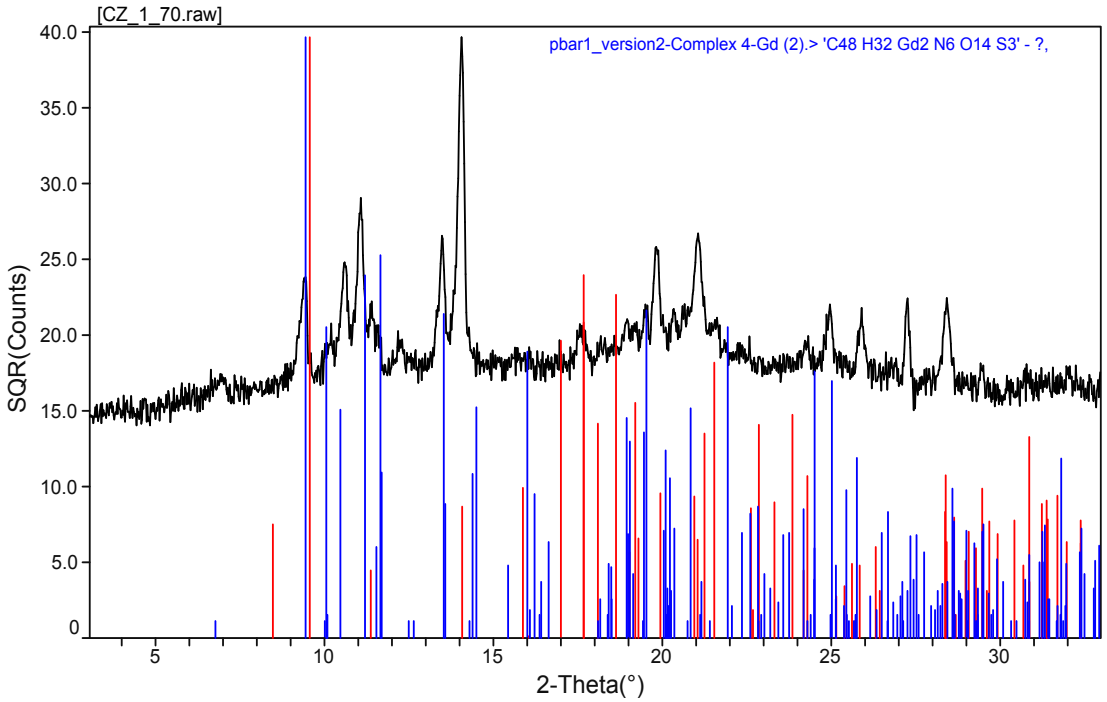


Figure S5 The observed PXRD pattern of complex **4** with calculated pattern overlaid in blue. Impurities in **4** have been identified as $[Gd_2(2,5\text{-}TDC)_3(H_2O)_4]_n$ (calculated CIF from CSD overlaid in red).[1]

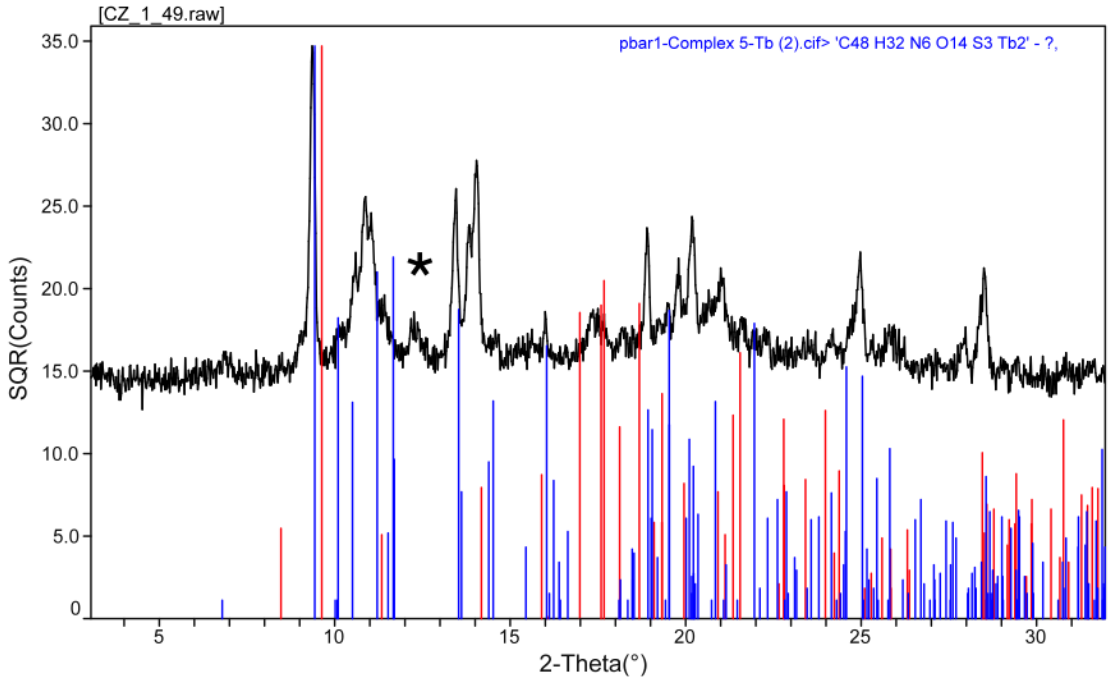


Figure S6 The observed PXRD pattern of structure **5** with calculated pattern overlaid in blue. Most impurities in **5** have been identified as $[Tb_2(2,5\text{-}TDC)_3(H_2O)_4]_n$ (calculated

CIF from CSD overlaid in red).[2] We acknowledge one additional minor impurity as denoted with an asterisk.

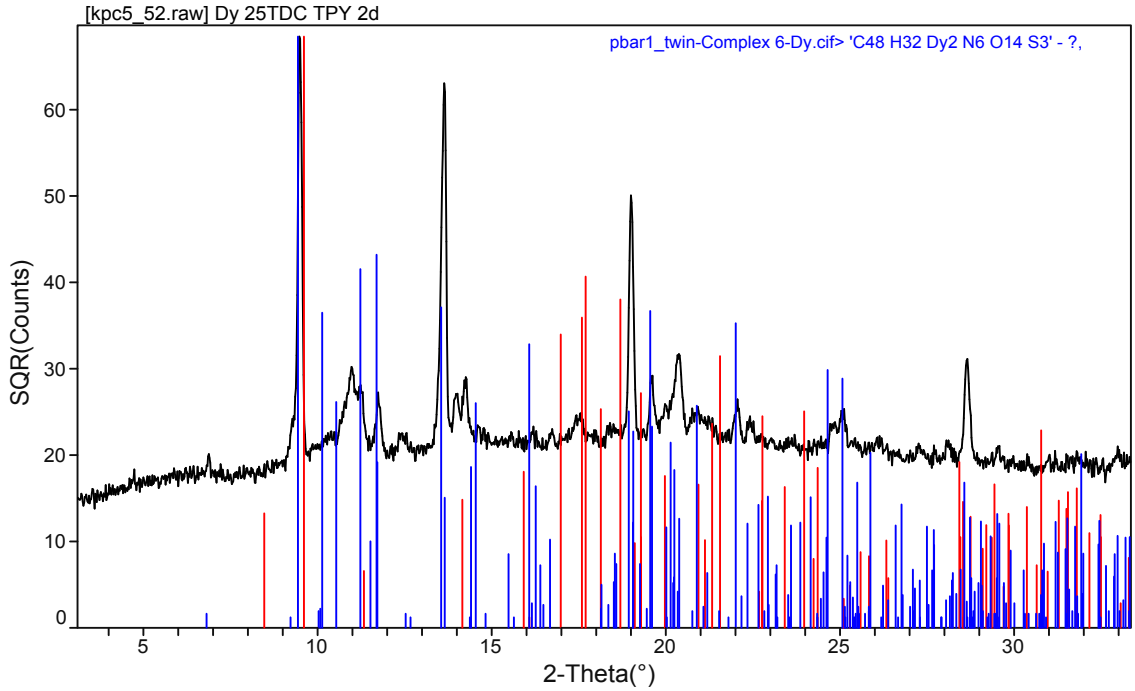


Figure S7 The observed PXRD pattern of complex **6** with calculated pattern overlaid in blue. Impurities in **6** have been identified as $[Dy_2(2,5\text{-}TDC)_3(H_2O)_4]_n$ (calculated CIF from CSD overlaid in red).[1, 3]

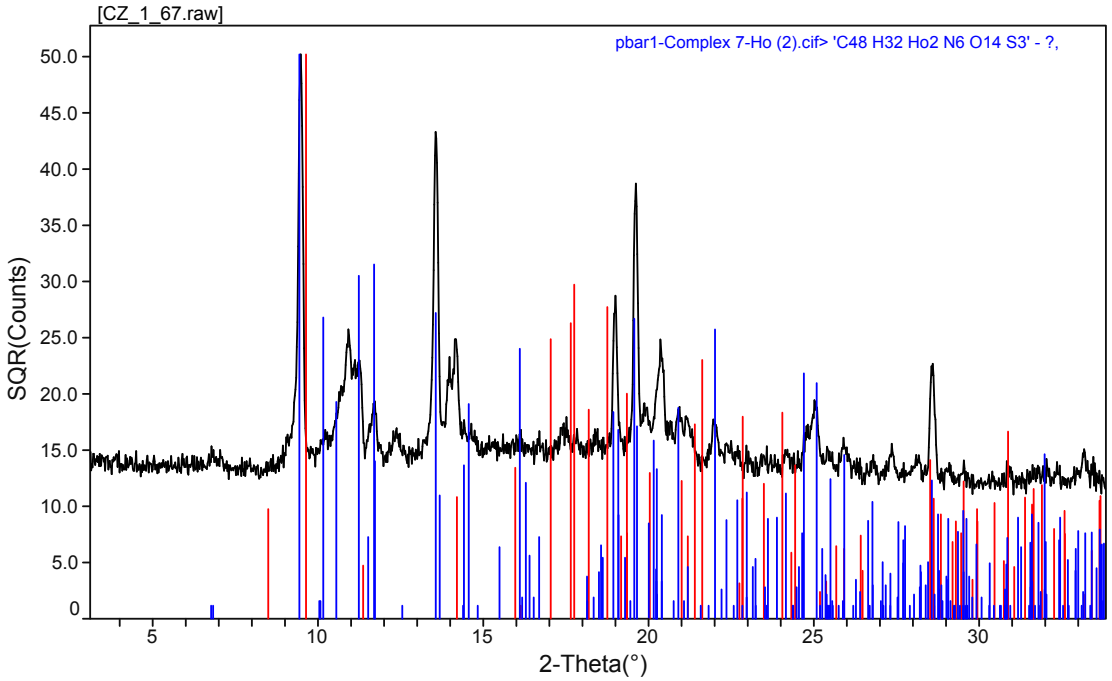


Figure S8 The observed PXRD pattern of complex **7** with calculated pattern overlaid in blue. Impurities in **7** have been identified as $[Ho_2(2,5\text{-}TDC)_3(H_2O)_4]_n$ (calculated CIF from CSD overlaid in red).[3]

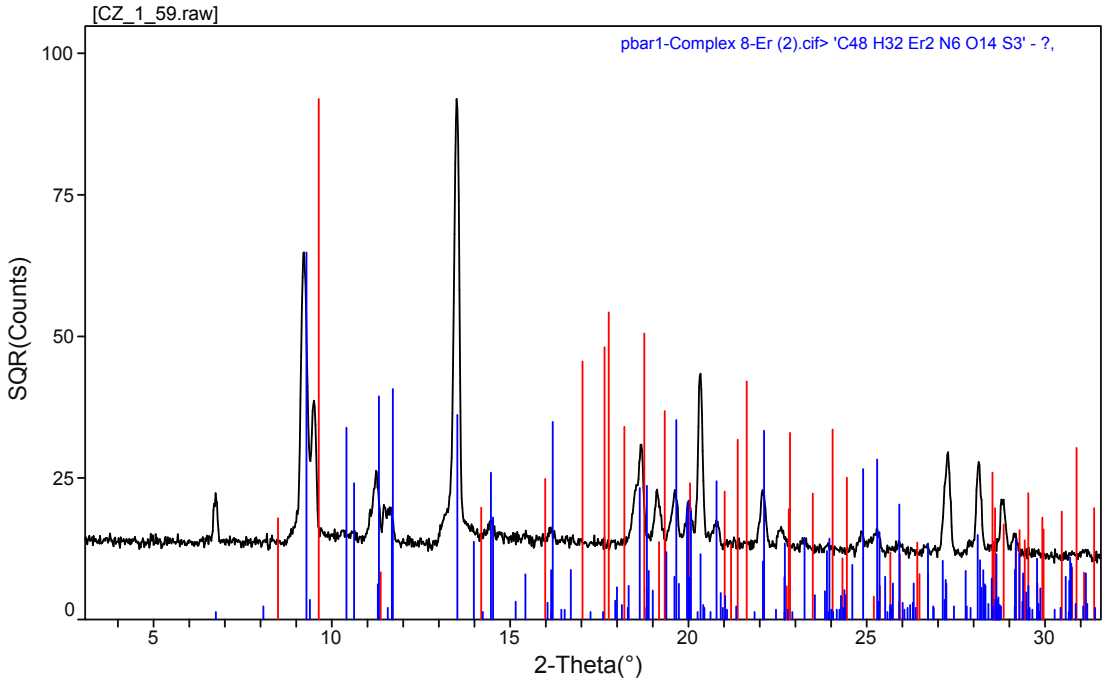


Figure S9 The observed PXRD pattern of complex **8** with calculated pattern overlaid in blue. Impurities in **8** have been identified as $[Er_2(2,5\text{-}TDC)_3(H_2O)_4]_n$ (calculated CIF from CSD overlaid in red).[3]

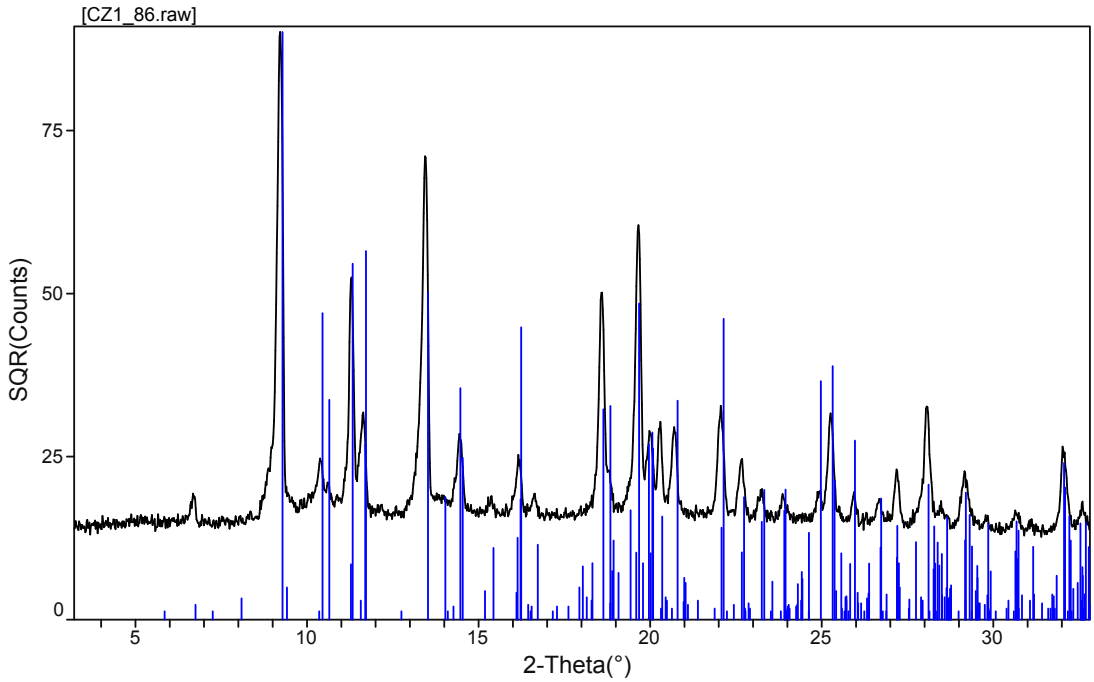


Figure S10 The observed PXRD pattern of complex **9** with calculated pattern overlaid in blue.

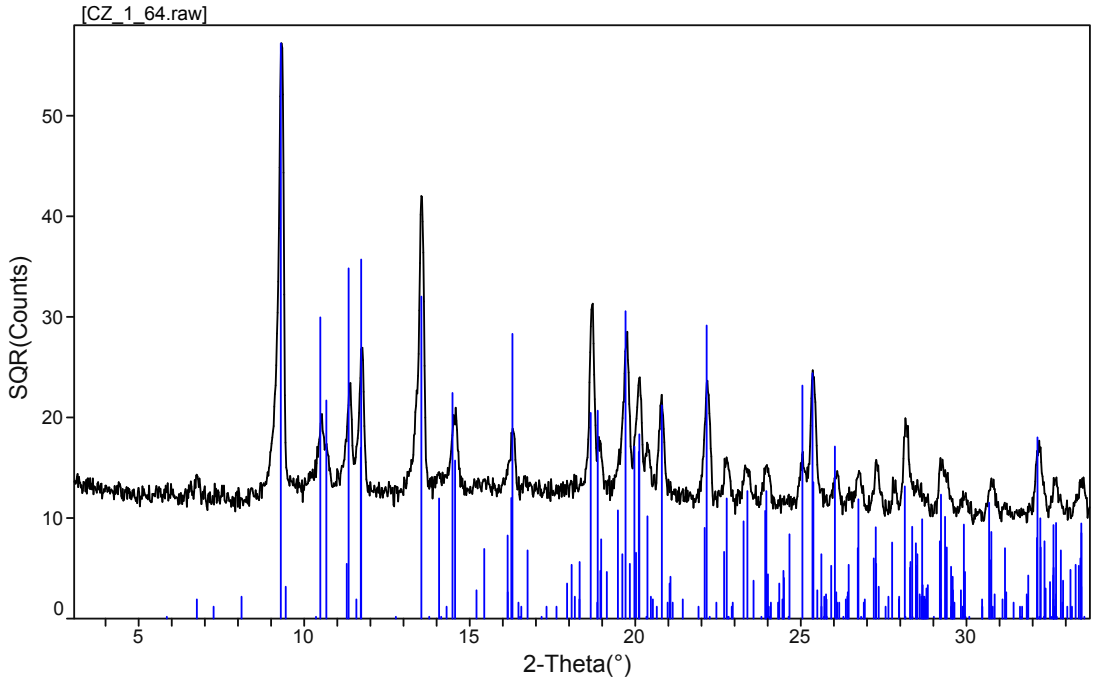


Figure S11 The observed PXRD pattern of complex **10** with calculated pattern overlaid in blue.

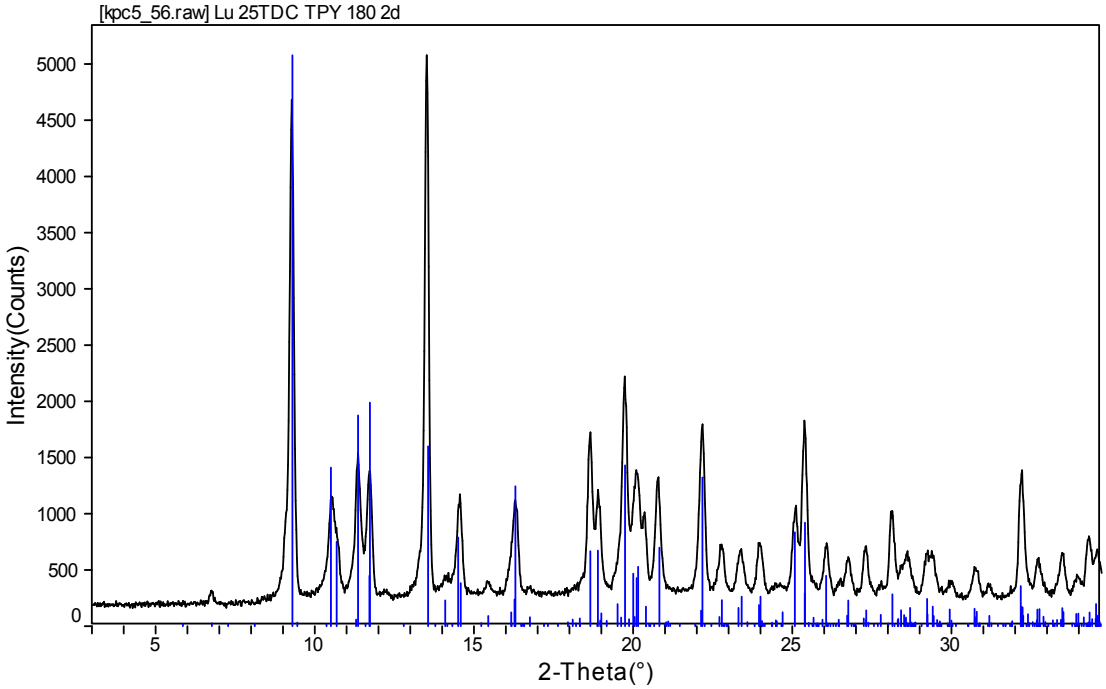


Figure S12 The observed PXRD pattern of complex **11** with calculated pattern overlaid in blue.

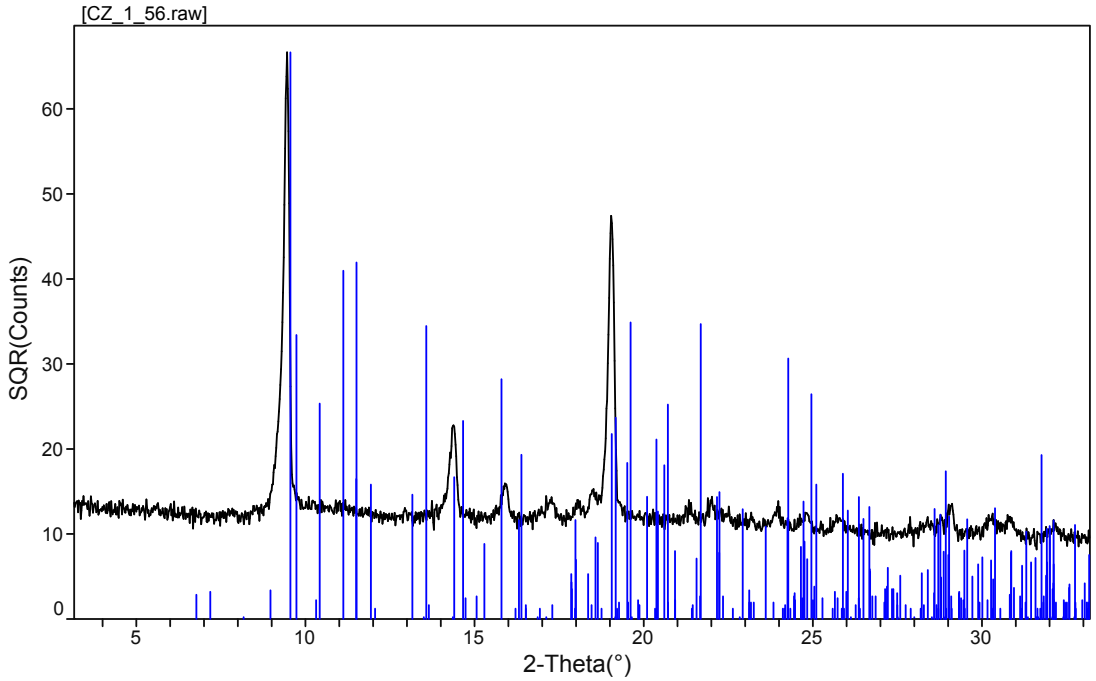


Figure S13 The observed PXRD pattern of complex **12** (Ce^{3+}) with calculated pattern of **1** overlaid in blue.

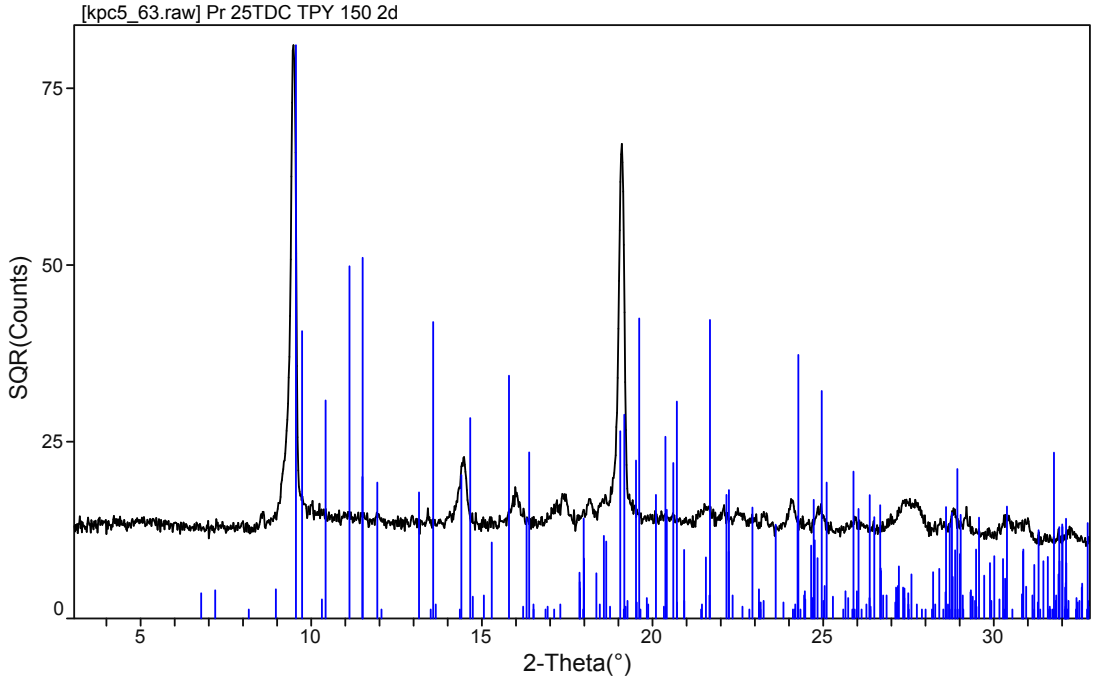


Figure S14 The observed PXRD pattern of complex **13** (Pr^{3+}) with calculated pattern of **1** overlaid in blue.

III. Thermal Ellipsoid Plots

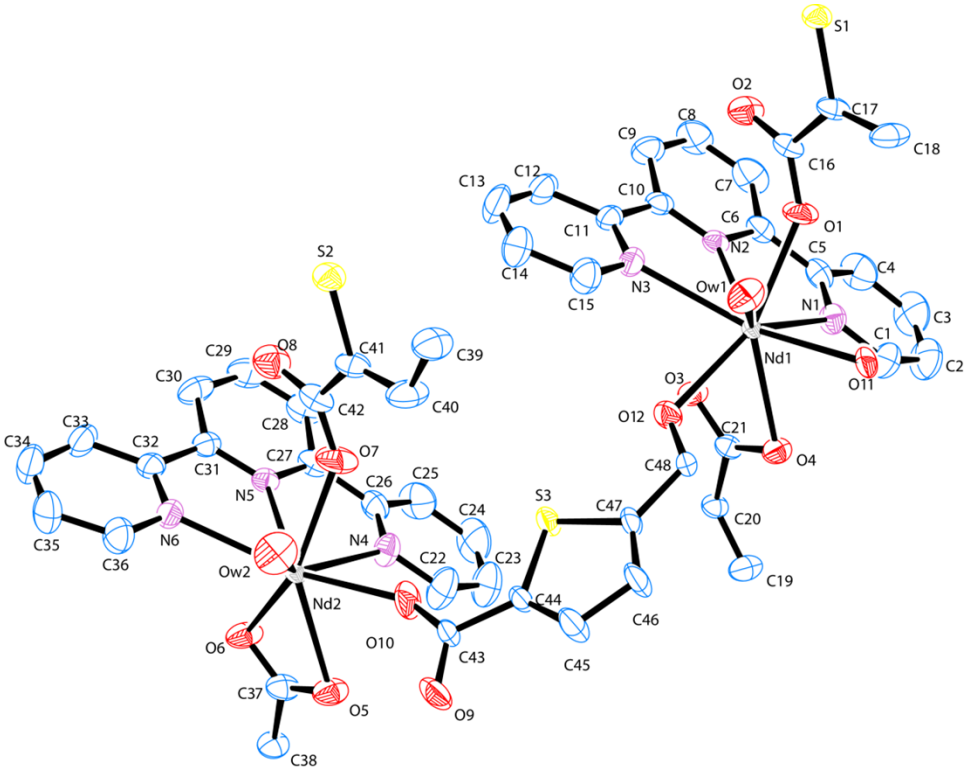


Figure S15 ORTEP illustration of structure **1**. Ellipsoids are shown at 50% probability level.

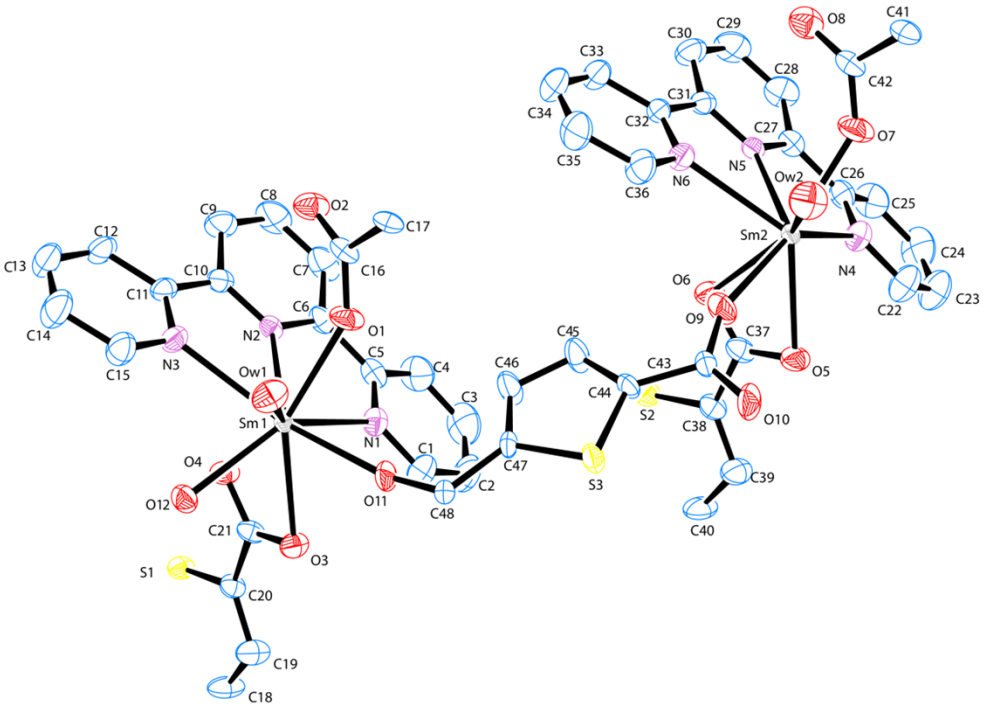


Figure S16 ORTEP illustration of structure **2**. Ellipsoids are shown at 50% probability level.

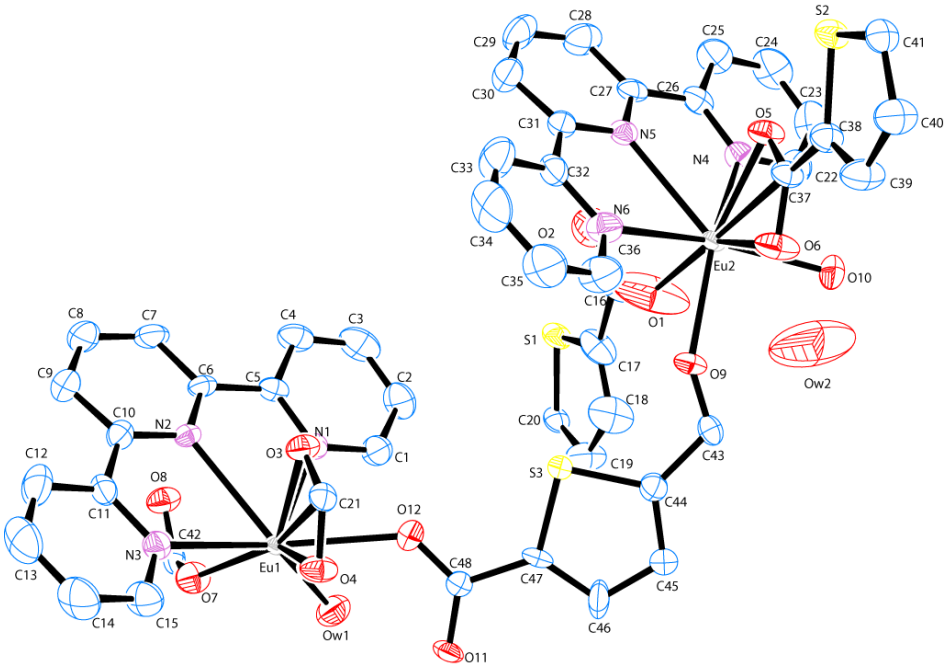


Figure S17 ORTEP illustration of structure **3**. Ellipsoids are shown at 50% probability level.

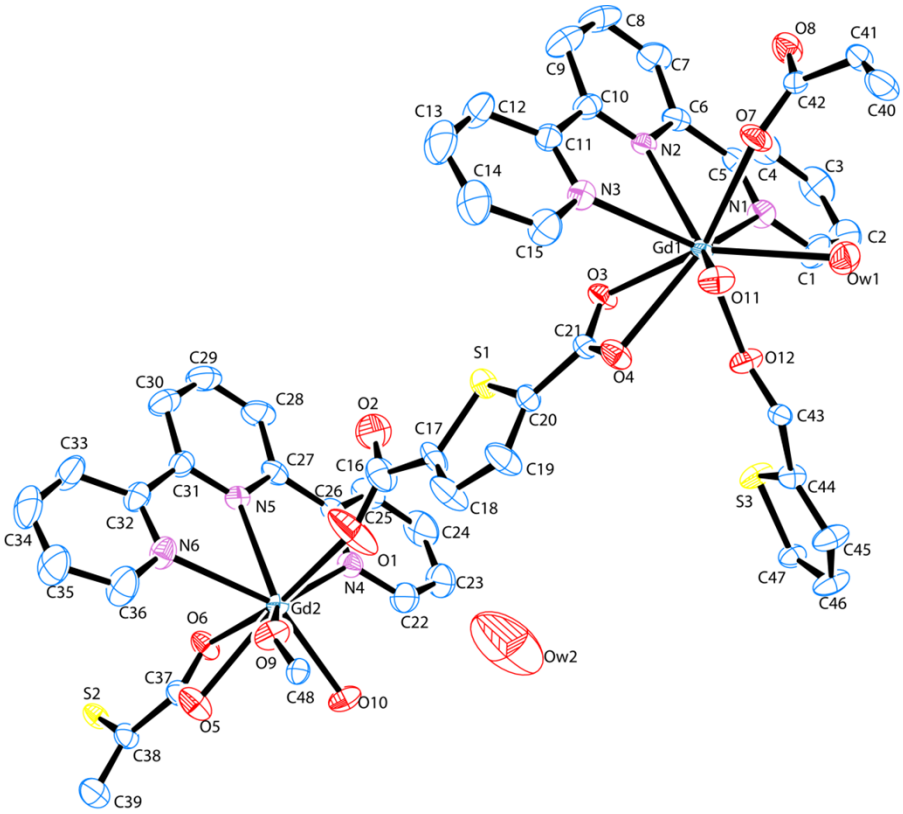


Figure S18 ORTEP illustration of structure **4**. Ellipsoids are shown at 50% probability level.

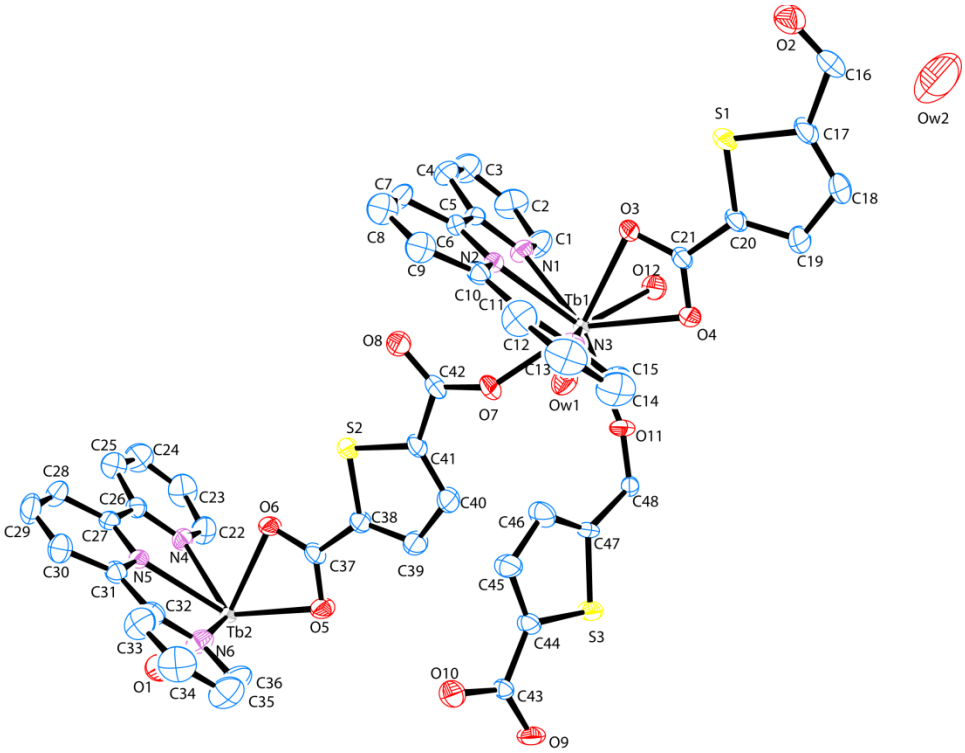


Figure S19 ORTEP illustration of structure **5**. Ellipsoids are shown at 50% probability level.

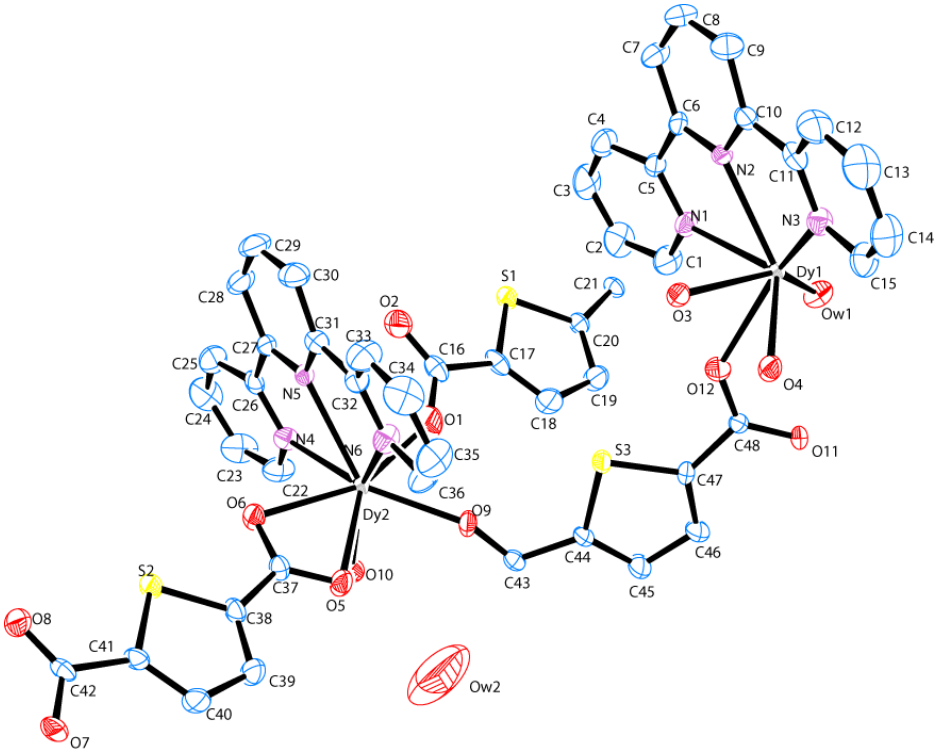


Figure S20 ORTEP illustration of structure **6**. Ellipsoids are shown at 50% probability level.

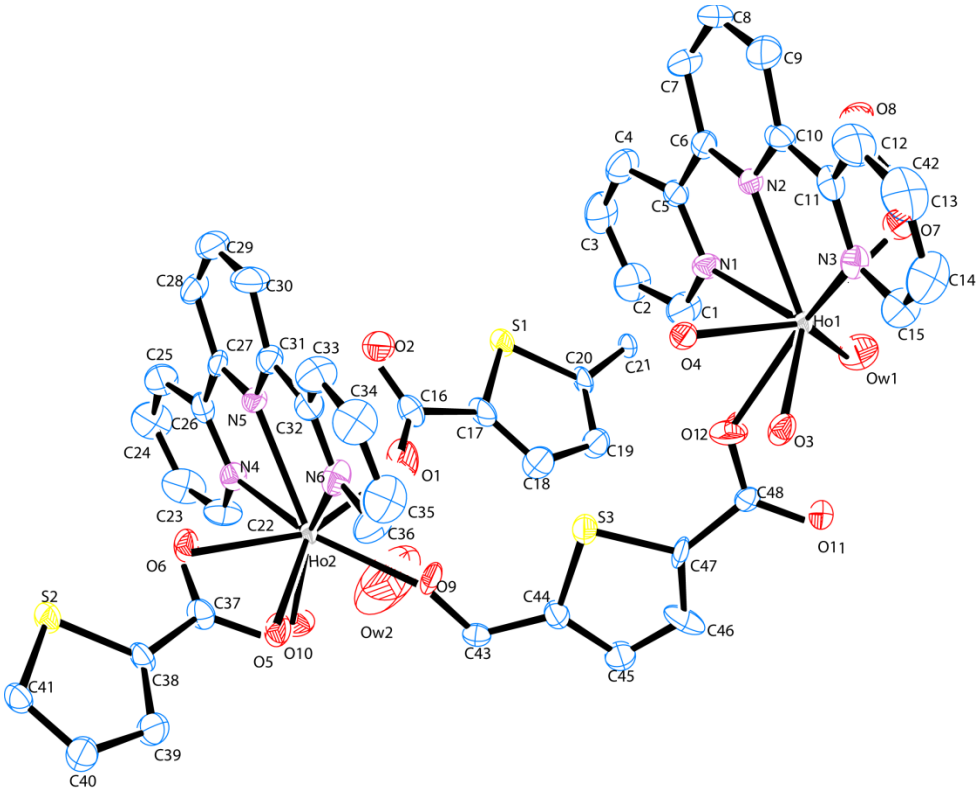


Figure S21 ORTEP illustration of structure **7**. Ellipsoids are shown at 50% probability level.

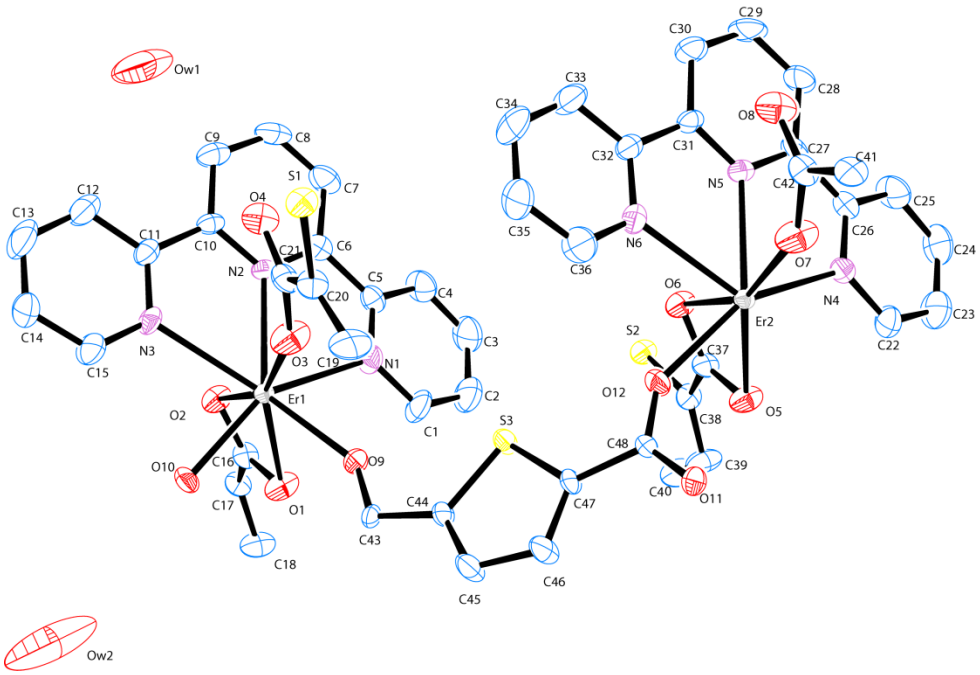


Figure S22 ORTEP illustration of structure **8**. Ellipsoids are shown at 50% probability level.

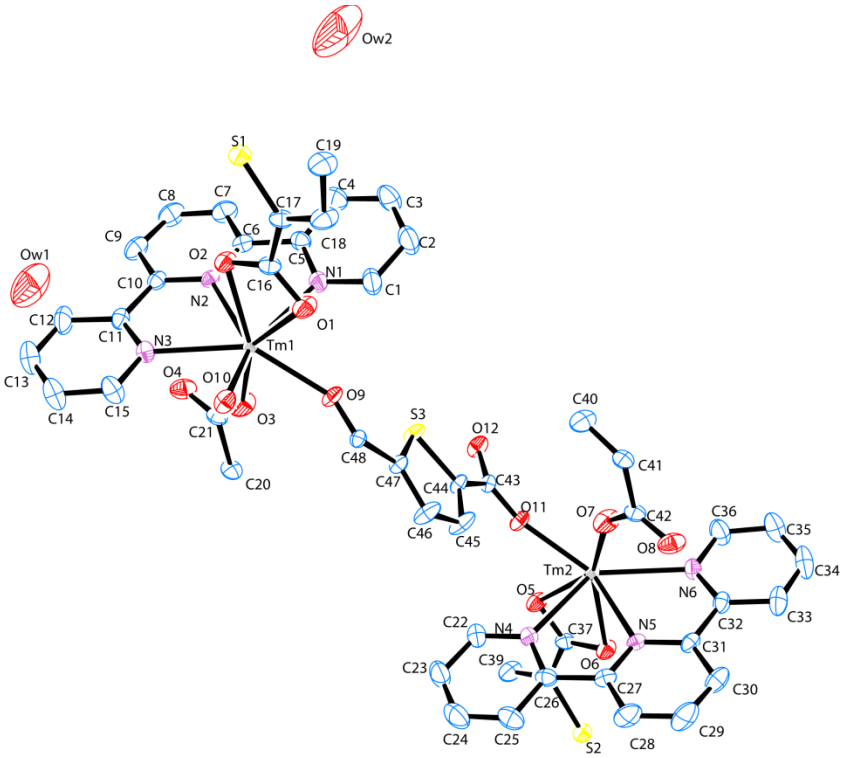


Figure S23 ORTEP illustration of structure **9**. Ellipsoids are shown at 50% probability level.

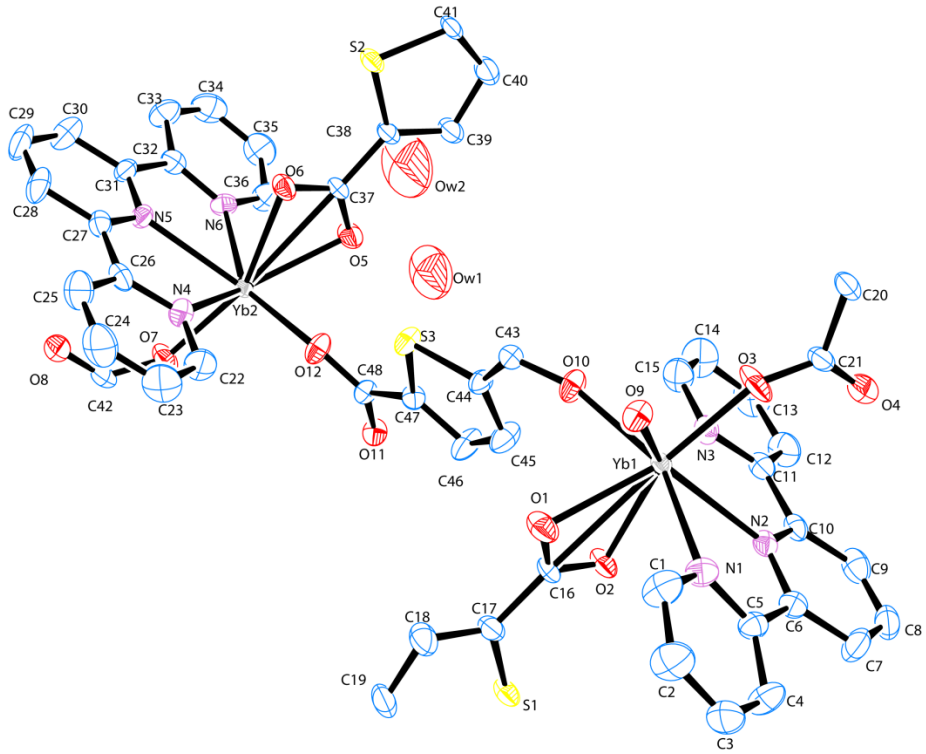


Figure S24 ORTEP illustration of structure **10**. Ellipsoids are shown at 50% probability level.

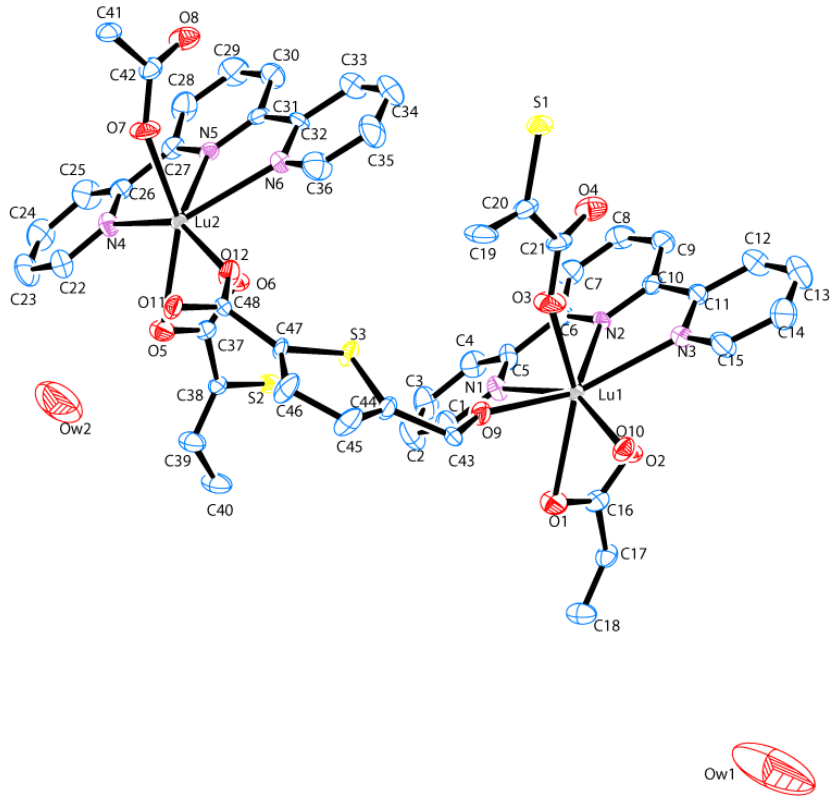


Figure S25 ORTEP illustration of structure **11**. Ellipsoids are shown at 50% probability level.

IV. Tables of Bond Distances

Table S2 Ln-O Bond Lengths in structure type I Ln^{3+} complexes (**1** and **2**) with thiophene-2,5-dicarboxylic acid and 2,2':6',2''-terpyridine.

Complex (Ln^{3+})	d_{Ln1-O1} [Å]	d_{Ln1-O3} [Å]	d_{Ln1-O4} [Å]	$d_{Ln1-O11}$ [Å]	$d_{Ln1-O12}$ [Å]	$d_{Ln1-OW1}$ [Å]	d_{Ln2-O5} [Å]	d_{Ln2-O6} [Å]	d_{Ln2-O7} [Å]	d_{Ln2-O9} [Å]	$d_{Ln2-O10}$ [Å]	$d_{Ln2-OW2}$ [Å]
1	2.395 (2)	2.541 (2)	2.533 (2)	2.385 (3)	2.466 (2)	2.619 (3)	2.567 (3)	2.535 (3)	2.377 (3)	2.377 (2)	2.366 (3)	2.650 (3)
2	2.374 (2)	2.520 (2)	2.515 (2)	2.364 (2)	2.451 (2)	2.603 (2)	2.556 (2)	2.514 (2)	2.361 (2)	2.358 (2)	2.350 (2)	2.646 (3)

Table S3 Ln-O Bond Lengths in structure type II Ln^{3+} complexes (**3-7**) with thiophene-2,5-dicarboxylic acid and 2,2':6',2''-terpyridine.

Complex (Ln^{3+})	d_{Ln1-O3} [Å]	d_{Ln1-O4} [Å]	d_{Ln1-O7} [Å]	$d_{Ln1-O11}$ [Å]	$d_{Ln1-O12}$ [Å]	$d_{Ln1-OW1}$ [Å]	d_{Ln2-O1} [Å]	d_{Ln2-O5} [Å]	d_{Ln2-O6} [Å]	d_{Ln2-O9} [Å]	$d_{Ln2-O10}$ [Å]
3	2.500 (3)	2.503 (3)	2.358 (3)	2.356 (3)	2.432 (3)	2.613 (4)	2.265 (5)	2.491 (3)	2.487 (4)	2.350 (3)	2.291 (3)
4	2.488 (2)	2.500 (3)	2.354 (3)	2.346 (3)	2.418 (2)	2.587 (3)	2.260 (3)	2.480 (3)	2.479 (3)	2.341 (3)	2.277 (3)
5	2.466 (2)	2.490 (2)	2.337 (2)	2.329 (2)	2.411 (2)	2.590 (3)	2.247 (3)	2.462 (3)	2.459 (2)	2.327 (3)	2.260 (3)
6	2.453 (3)	2.483 (3)	2.326 (3)	2.322 (3)	2.394 (3)	2.578 (3)	2.239 (3)	2.453 (3)	2.443 (3)	2.313 (3)	2.244 (3)
7	2.445 (4)	2.476 (4)	2.314 (4)	2.310 (4)	2.381 (4)	2.587 (5)	2.237 (5)	2.446 (4)	2,435 (4)	2.300 (4)	2.224 (4)

Table S4 Ln-O Bond Lengths in structure type III Ln^{3+} complexes (**8-11**) with thiophene-2,5-dicarboxylic acid and 2,2':6',2''-terpyridine.

Complex (Ln^{3+})	d_{Ln1-O1} [Å]	d_{Ln1-O2} [Å]	d_{Ln1-O3} [Å]	d_{Ln1-O9} [Å]	$d_{Ln1-O10}$ [Å]	d_{Ln2-O5} [Å]	d_{Ln2-O6} [Å]	d_{Ln2-O7} [Å]	$d_{Ln2-O11}$ [Å]	$d_{Ln2-O12}$ [Å]
8	2.440 (4)	2.414 (4)	2.228 (4)	2.305 (4)	2.231 (4)	2.430 (4)	2.409 (4)	2.240 (4)	2.281 (4)	2.264 (4)
9	2.4351 (14)	2.4046 (13)	2.2146 (14)	2.2894 (13)	2.2260 (13)	2.4145 (13)	2.4006 (13)	2.2305 (14)	2.2692 (13)	2.2488 (13)
10	2.427 (5)	2.385 (5)	2.201 (5)	2.280 (4)	2.211 (5)	2.406 (5)	2.388 (5)	2.218 (5)	2.256 (4)	2.234 (5)
11	2.431 (3)	2.388 (3)	2.197 (3)	2.270 (3)	2.202 (3)	2.400 (3)	2.380 (3)	2.212 (3)	2.247 (3)	2.223 (3)

Table S5 Ln-N Bond Lengths in Ln^{3+} complexes (**1-11**) with thiophene-2,5-dicarboxylic acid and 2,2':6',2''-terpyridine.

Complex (Ln^{3+})	d_{Ln1-N1} [Å]	d_{Ln1-N2} [Å]	d_{Ln1-N3} [Å]	d_{Ln2-N4} [Å]	d_{Ln2-N5} [Å]	d_{Ln2-N6} [Å]
1 (Nd)	2.618(3)	2.640(3)	2.600(3)	2.602(3)	2.633(3)	2.599(3)
2 (Sm)	2.596(3)	2.614(2)	2.580(3)	2.585(3)	2.609(3)	2.582(3)
3 (Eu)	2.566(4)	2.586(4)	2.573(4)	2.575(4)	2.600(4)	2.565(4)
4 (Gd)	2.562(3)	2.577(3)	2.565(3)	2.569(3)	2.587(3)	2.541(3)
5 (Tb)	2.550(3)	2.561(3)	2.558(3)	2.559(3)	2.563(3)	2.527(3)
6 (Dy)	2.536(3)	2.550(3)	2.545(3)	2.553(3)	2.551(3)	2.519(3)
7 (Ho)	2.522(5)	2.538(5)	2.524(5)	2.538(5)	2.536(5)	2.506(5)
8 (Er)	2.492(5)	2.517(4)	2.545(5)	2.488(5)	2.504(5)	2.531(5)
9 (Tm)	2.4814(16)	2.5099(15)	2.5289(16)	2.4801(16)	2.4941(15)	2.5260(16)

10 (Yb)	2.468(6)	2.501(5)	2.521(6)	2.460(6)	2.483(5)	2.516(6)
11 (Lu)	2.457(4)	2.492(4)	2.513(4)	2.454(4)	2.468(4)	2.507(4)

V. Tables of Supramolecular Interaction Distances

Table S6 π-π Interactions in Ln^{3+} complexes (**1**-**11**) with thiophene-2,5-dicarboxylic acid and 2,2':6',2''-terpyridine.

Complex (Ln^{3+})	Cg•••Cg (1) (Å)	Cg•••Cg (2) (Å)	Cg⊥•••Cg⊥ (1) (Å)	Cg⊥•••Cg⊥ (2) (Å)	β (1) (deg)	β (2) (deg)
1 (Nd)	3.670(3)	3.790(3)	3.3144(17)	3.6680(19)	25.44	14.60
2 (Sm)	3.694(2)	3.805(2)	3.3063(16)	3.6669(17)	26.47	15.46
3 (Eu)	3.684(4)	3.771(4)	3.308(2)	3.601(2)	26.13	17.29
4 (Gd)	3.680(3)	3.777(3)	3.2997(18)	3.6015(18)	26.28	17.55
5 (Tb)	3.693(2)	3.774(3)	3.3058(18)	3.5841(18)	26.48	18.26
6 (Dy)	3.690(3)	3.779(3)	3.2920(18)	3.5788(19)	26.85	18.74
7 (Ho)	3.700(4)	3.781(4)	3.289(3)	3.565(3)	27.26	19.47
8 (Er)	3.707(4)	3.798(4)	3.366(3)	3.542(3)	22.23	28.18
9 (Tm)	3.7042(14)	3.8047(14)	3.3596(8)	3.5250(10)	22.94	28.90
10 (Yb)	3.709(5)	3.819(5)	3.362(3)	3.527(4)	23.45	29.14
11 (Lu)	3.712(3)	3.830(3)	3.359(2)	3.525(2)	23.80	29.54

Table S7 Hydrogen Bonding Interaction Distances in structure type II Ln^{3+} complexes (**3**-**7**) with thiophene-2,5-dicarboxylic acid and 2,2':6',2''-terpyridine.

Complex (Ln^{3+})	O-H•••OW2 Interaction (Å)	C-H•••OW2 Interaction (Å)
3	2.798(10)	3.427(12)
4	2.789(8)	3.405(9)
5	2.780(8)	3.383(10)
6	2.793(9)	3.341(10)
7	2.762(15)	3.333(17)

Table S8 Hydrogen Bonding Interaction Distances in structure type III Ln^{3+} complexes (**8-11**) with thiophene-2,5-dicarboxylic acid and 2,2':6',2''-terpyridine.

Complex (Ln^{3+})	O-H•••OW1 Interaction (Å)	C-H•••OW1 Interaction (Å)	O-H•••OW2 Interaction (Å)	C-H•••OW2 Interaction (Å)
8	2.869(17)	3.256(18)	2.767(11)	3.333(14)
9	2.857(5)	3.254(5)	2.765(3)	3.339(4)
10	2.872(17)	3.268(18)	2.759(12)	3.346(15)
11	2.870(10)	3.256(11)	2.753(7)	3.349(9)

VI. References

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