Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Heteronuclear Eu_2Pt_2 Luminescent Arrays: Composition−Thermometric Properties Correlations.

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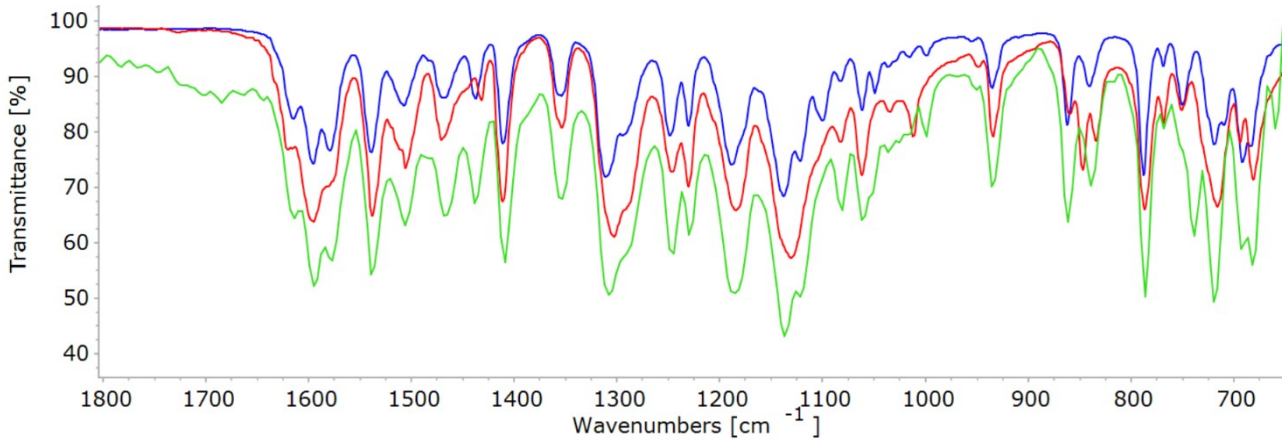

Figure S1: IR spectra of **1** (blue), **3** (green) and $[Eu(tta)_3(pyrzMO)]_2$ (red).

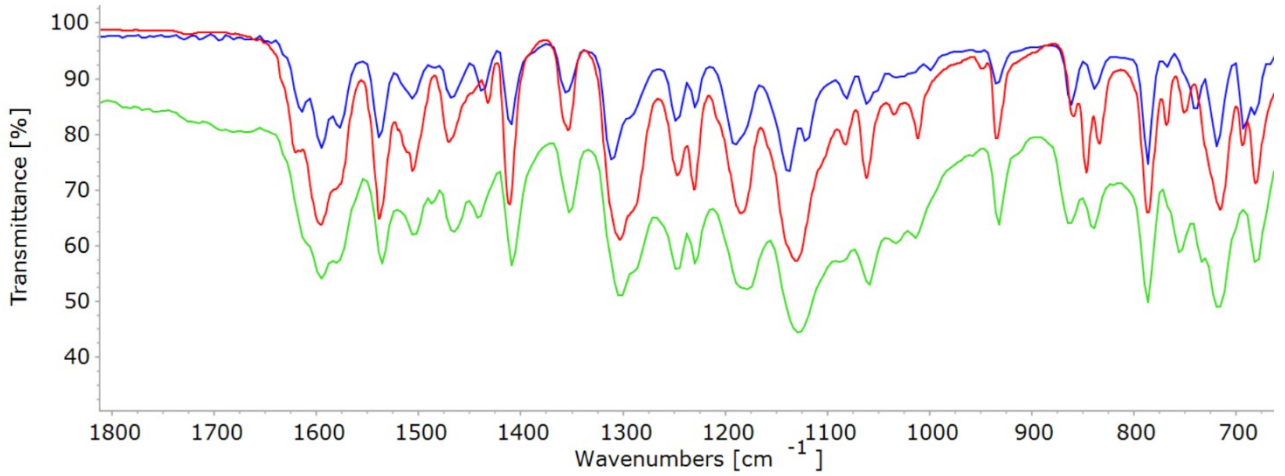

Figure S2: IR spectra of **2** (blue), **4** (green) and $[Gd(tta)_3(pyrzMO)]_2$ (red).

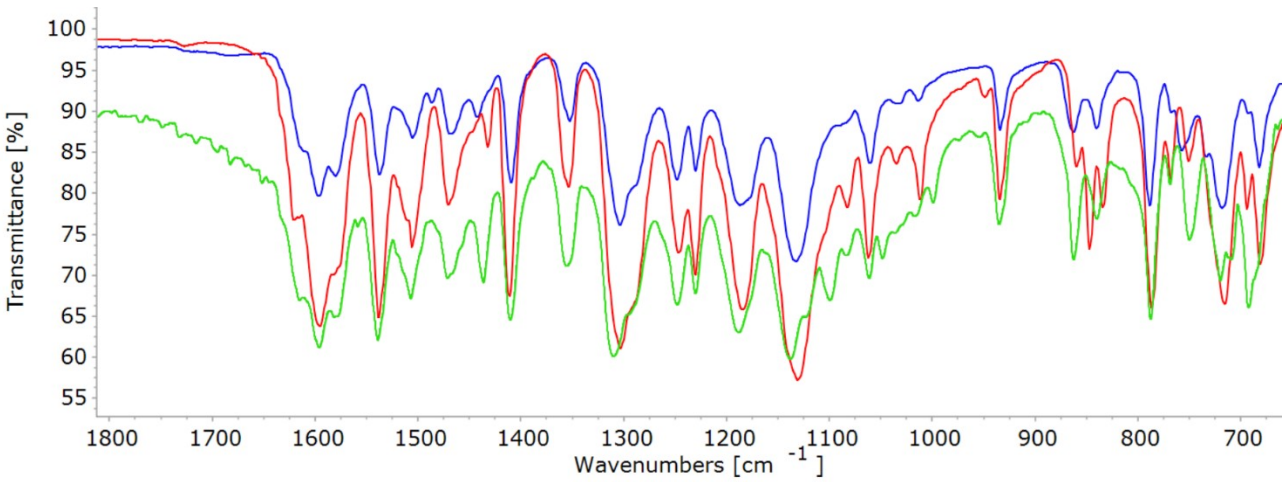

Figure S3: IR spectra of **6** (blue), **7** (green) and $[Eu(tta)_3(pyrzMO)]_2$ (red).

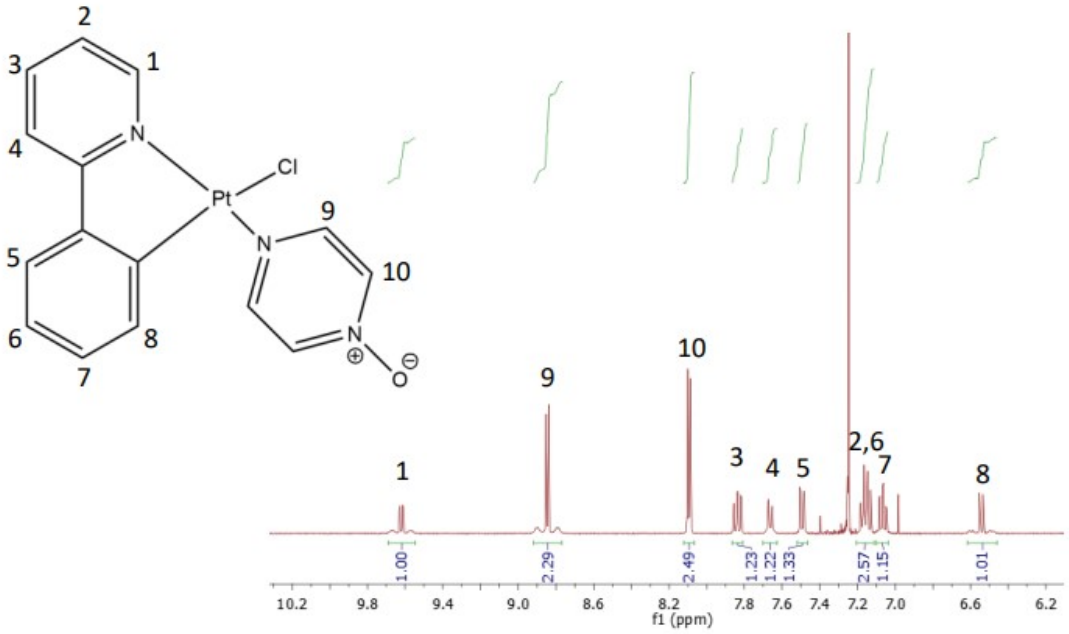

Figure S4: ^{1}H NMR spectra of **5**.

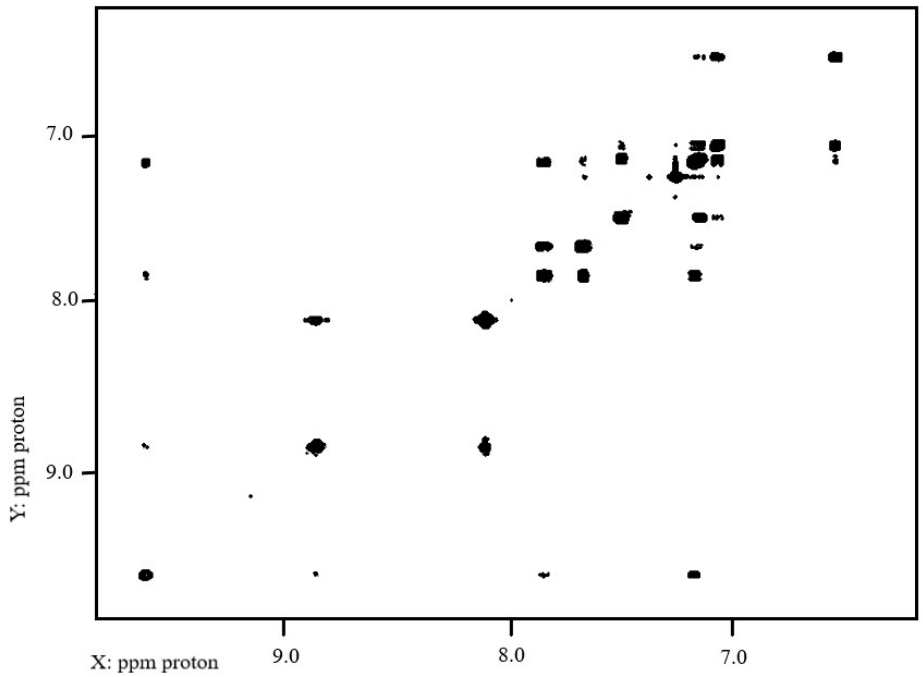

Figure S5. ^{1}H-^{1}H COSY NMR of **5**.

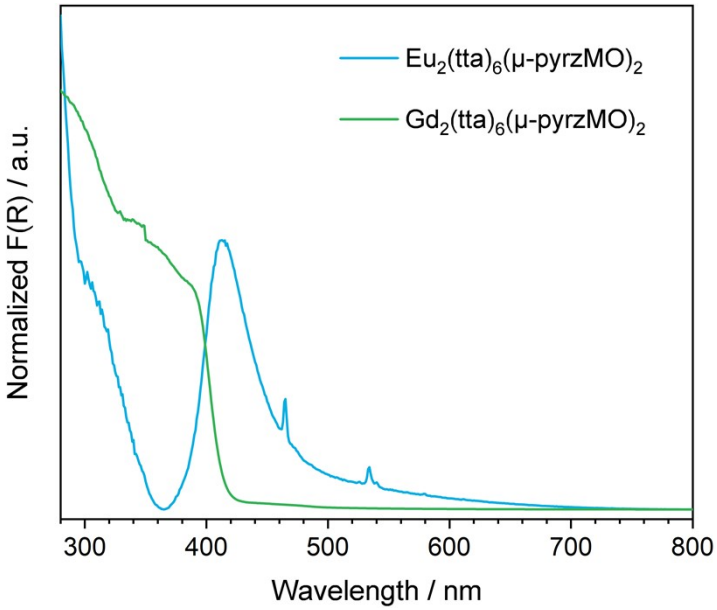

Figure S6. Comparison of diffuse reflectance spectra of $Gd_2(tta)_6(\mu\text{-pyrzMO})_2$ and $Eu_2(tta)_6(\mu\text{-pyrzMO})_2$complexes.

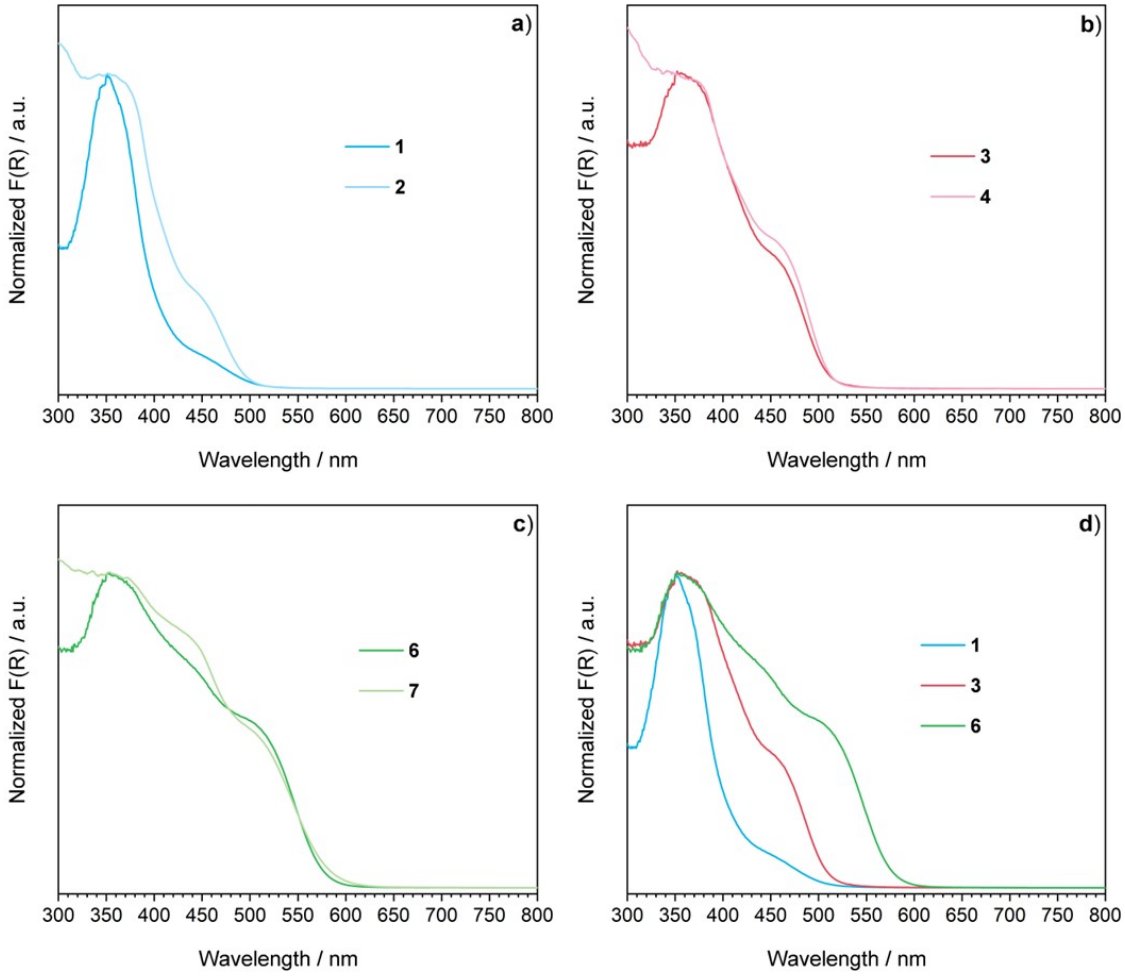

Figure S7. Comparison of diffuse reflectance spectra of Eu_2Pt_2 and Gd_2Pt_2 complexes.

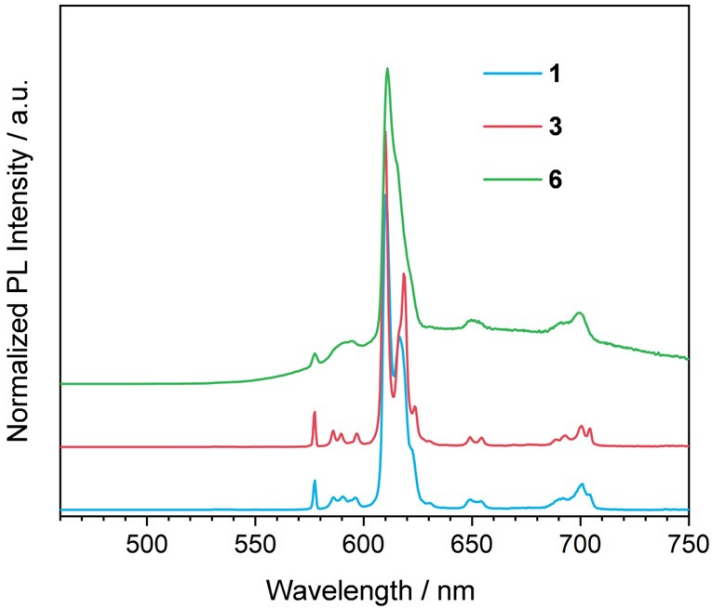

Figure S8. Extended range PL spectra of **1**, **3** and **6**. λ_{exc} = 375 nm.

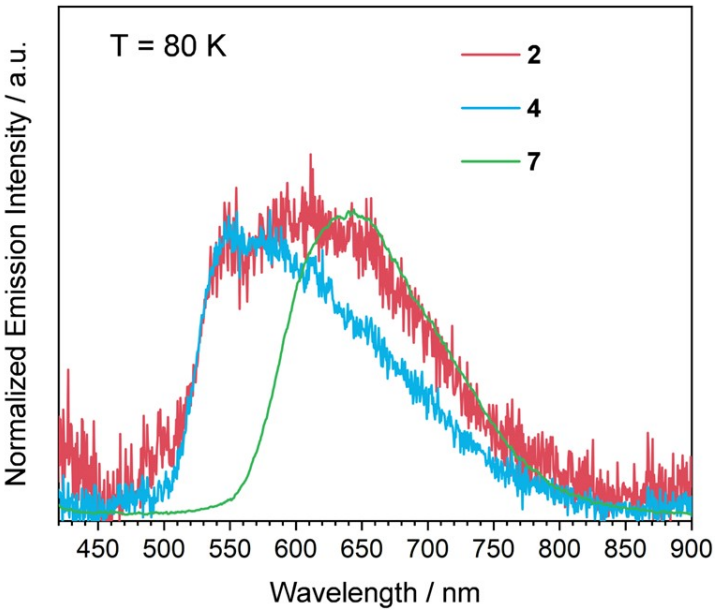

Figure S9. PL spectra of **2**, **4** and **7**, collected at 80 K. l_{exc} = 375 nm.

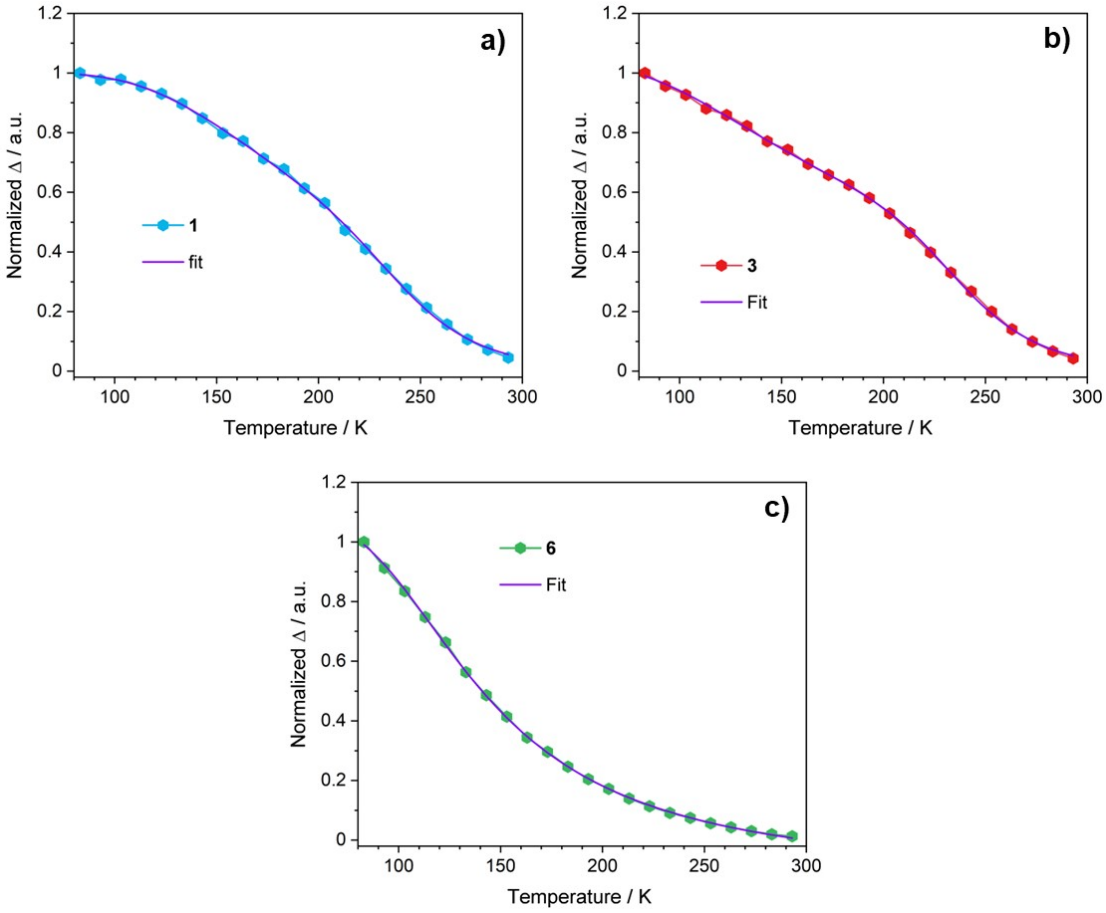

Figure S10. Experimental thermometric parameter Δ and fitted curves for **1** a), **3** b) and **6** c) and fitted curves.

Refinement details for compound 1

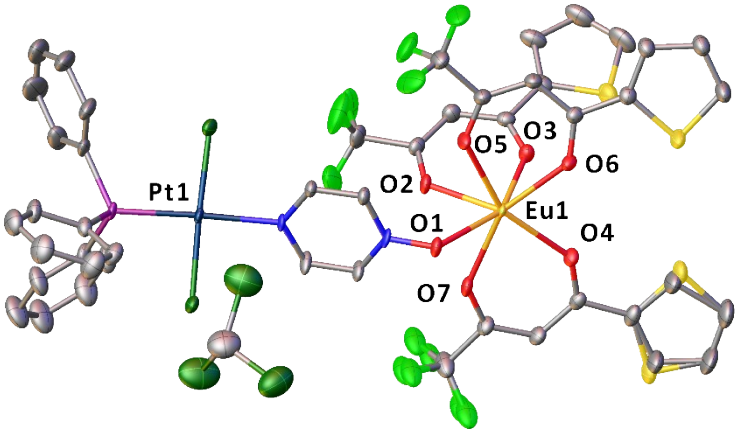

Figure S11. The asymmetric unit for compound **1**, thermal ellipsoids drawn at 50% probability level. Color code: C, grey; O, red; N, blue; F, light green; Cl, dark green; P, violet; Pt, dark blue; Eu, orange. H atoms omitted for clarity.

The compound crystallizes in the $P2_1/n$ space group. The asymmetric unit is constituted by half molecule. A CF_3 and thienyl group have been split into two parts the occupancies of which were constrained to sum to 1.0. RIGU, SADI and FLAT restraints to selected atoms as detailed reported in the CIF file. Reflections with |error/esd| > 5 were omitted. The final Fourier map revealed the presence of non-negligible residual peaks located in a large array of voids. A solvent mask (OLEX2[1] routine based on BYPASS[2]) was calculated (probe radius 1.2 Å), and 236 electrons were found in a volume of 838 $Å^3$ per unit cell. This is consistent with the presence of four $CHCl_3$ per unit cell which account for 232 electrons.

Solvent masking output:

use_set_completion: True
solvent_radius: 1.20
shrink_truncation_radius: 1.20
van der Waals radii:

C	Cl	Eu	F	H	N	O	P	Pt	S
1.70	1.75	2.00	1.47	1.09	1.55	1.52	1.80	1.72	1.80

Total solvent accessible volume / cell = 838.0 Ang^3 [14.0%]
Total electron count / cell = 245.6

gridding: (64,180,72)

Void	#Grid points	Vol/A^3	Vol/%	Centre of mass (frac)	Eigenvectors (frac)
1	27339	197.4	3.3	(0.133, 0.325, 0.059)	1 (0.665, 0.136, 0.735)
					2 (0.733, 0.075,-0.677)

				3 (-0.147, 0.988,-0.050)		
2	1680	12.1	0.2	(-0.089, 0.479, 0.638)	1	(0.848,-0.011, 0.530)
				2 (-0.530,-0.009, 0.848)		
				3 (0.005, 1.000, 0.013)		
3	1680	12.1	0.2	(0.089, 0.521, 0.362)	1	(0.848,-0.011, 0.530)
				2 (-0.530,-0.009, 0.848)		
				3 (0.005, 1.000, 0.013)		
4	27339	197.4	3.3	(-0.133, 0.675,-0.059)	1	(0.665, 0.136, 0.735)
				2 (0.733, 0.075,-0.677)		
				3 (-0.147, 0.988,-0.050)		
5	27339	197.4	3.3	(0.367, 0.825, 0.441)	1	(0.665,-0.136, 0.735)
				2 (0.733,-0.075,-0.677)		
				3 (0.147, 0.988, 0.050)		
6	1680	12.1	0.2	(0.411, 0.021, 0.138)	1	(0.848, 0.011, 0.530)
				2 (-0.530, 0.009, 0.848)		
				3 (-0.005, 1.000,-0.013)		
7	27339	197.4	3.3	(0.633, 0.175, 0.559)	1	(0.665,-0.136, 0.735)
				2 (0.733,-0.075,-0.677)		
				3 (0.147, 0.988, 0.050)		
8	1680	12.1	0.2	(0.589, 0.979, 0.862)	1	(0.848, 0.011, 0.530)
				2 (-0.530, 0.009, 0.848)		
				3 (-0.005, 1.000,-0.013)		

Void	Vol/Ang^3	#Electrons
1	197.4	59.0
2	12.1	0.0
3	12.1	0.0
4	197.4	63.9
5	197.4	60.4
6	12.1	0.0
7	197.4	62.3
8	12.1	0.0

Refinement details for compound 2

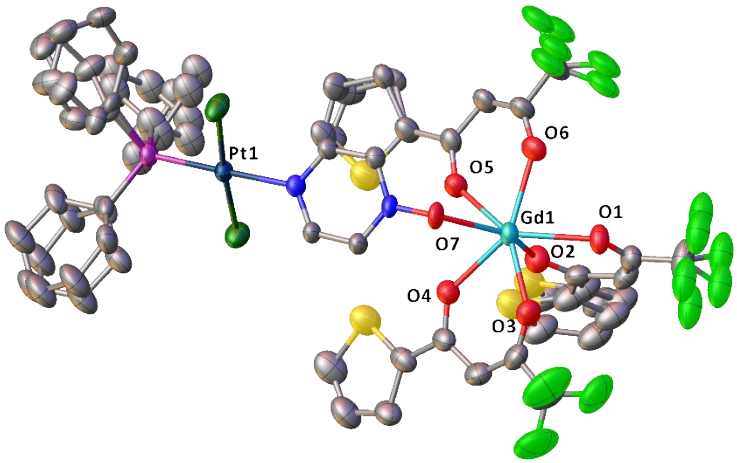

Figure S12. The asymmetric unit for compound **2**, thermal ellipsoids drawn at 30% probability level. Color code: C, grey; O, red; N, blue; F, light green; Cl, dark green; P, violet; Pt, dark blue; Gd, azure. H atoms omitted for clarity.

The compound crystallizes in the *C*2/*c* space group. The asymmetric unit is constituted by half molecule. Two CF_3, two thienyl and three phenyl groups have been split into two parts the occupancies of which were constrained to sum to 1.0. RIGU, SADI and FLAT restraints and EADP constraints were applied to selected atoms as detailed reported in the CIF file. Reflections with |error/esd| > 10 were omitted.

Refinement details for compound 3

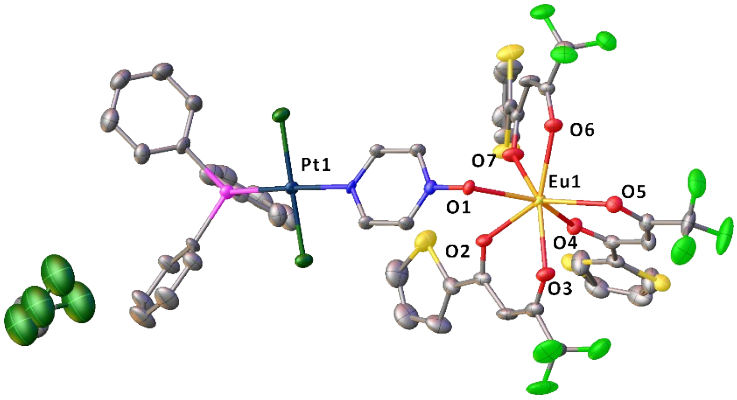

Figure S13. The asymmetric unit for compound **3**, thermal ellipsoids drawn at 50% probability level. Color code: C, grey; O, red; N, blue; F, light green; Cl, dark green; As, pink; Pt, dark blue; Eu, orange. H atoms omitted for clarity.

The compound crystallizes in the *P*-1 space group. The asymmetric unit is constituted by half molecule. One thienyl group and the CH_2Cl_2 have been split into two parts, the occupancies of which were constrained to sum to 1.0. RIGU, SADI and FLAT restraints and EADP constraints were applied to selected atoms. Reflections with |error/esd| > 10 were omitted.

Refinement details for compound 5

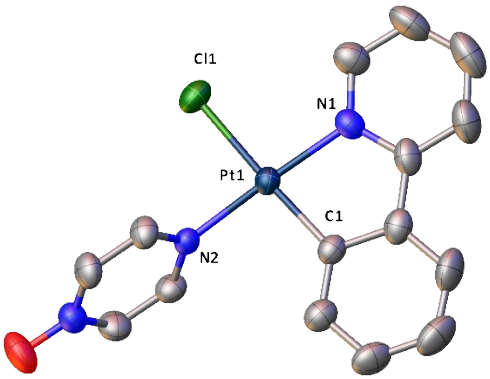

Figure S14. The asymmetric unit for compound **5**, thermal ellipsoids drawn at 50% probability level. Color code: C, grey; O, red; N, blue; Cl, dark green; Pt, dark blue. H atoms omitted for clarity.

The refinement has been carried out as described above in the general description.

Refinement details for compound 6

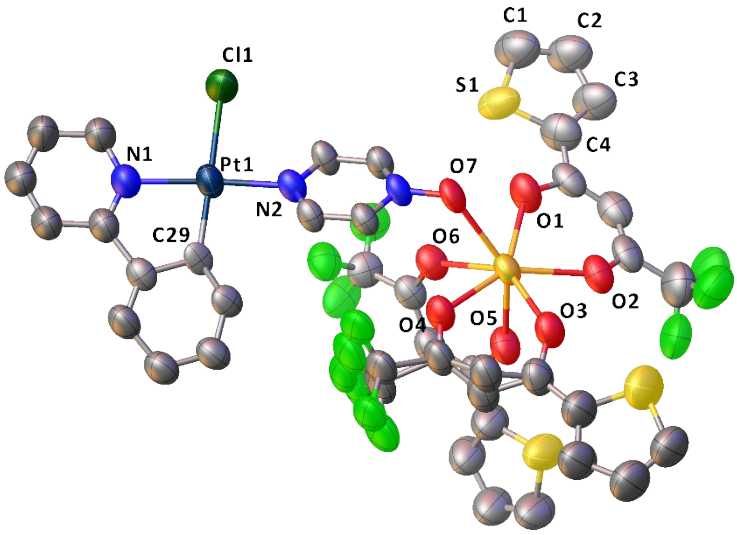

Figure S15. The asymmetric unit for compound **6**, thermal ellipsoids drawn at 30% probability level. Color code: C, grey; O, red; N, blue; F, light green; Cl, dark green; Pt, dark blue; Eu, orange. H atoms omitted for clarity.

The compound crystallizes in the $P2_1/n$ space group. The asymmetric unit is constituted by half molecule. In one β-diketonate ligand, a CF_3 group and the α-carbon have been split into two parts the occupancies of which were constrained to sum to 1.0. The thienyl groups were modelled with a combination of restraints as exemplified by the ring composed of atoms S1-C1-C2-C3-C4:

RIGU 0.002 0.002
DFIX 1.71 S1 C4 S1 C1
DANG 2.31 C4 C2 C3 C1
DFIX 1.36 C4 C3 C2 C1
DFIX 1.42 C3 C2
FLAT S1 C4 C3 C2 C1
DANG 2.54 S1 C3 S1 C2
SIMU S1 C4 C3 C2 C1

Reflections with |error/esd| > 10 were omitted. The final Fourier map revealed the presence of non-negligible residual peaks located in a large array of voids. A solvent mask (OLEX2[1] routine based on BYPASS[2]) was calculated (probe radius 1.2 Å), and 162 electrons were found in a volume of 700 $Å^3$ in four voids per unit cell. This is consistent with the presence of four CH_2Cl_2 per unit cell which account for 168 electrons.

Solvent masking output:

use_set_completion: True

solvent_radius: 1.20

shrink_truncation_radius: 1.20

van der Waals radii:

C	Cl	Eu	F	H	N	O	Pt	S
1.70	1.75	2.00	1.47	1.09	1.55	1.52	1.72	1.80

Total solvent accessible volume / cell = 700.9 Ang^3 [14.5%]

Total electron count / cell = 162.0

gridding: (72,80,100)

Void	#Grid points	Vol/A^3	Vol/%	Centre of mass (frac)	Eigenvectors (frac)
1	20827	175.2	3.6	(0.147, 0.284, 0.756)	1 (-0.545, 0.713,-0.441)
					2 (0.832, 0.524,-0.183)
					3 (-0.101, 0.467, 0.879)
2	20827	175.2	3.6	(-0.147, 0.716, 0.244)	1 (-0.545, 0.713,-0.441)
					2 (0.832, 0.524,-0.183)
					3 (-0.101, 0.467, 0.879)
3	20827	175.2	3.6	(0.353, 0.784, 0.744)	1 (0.545, 0.713, 0.441)
					2 (0.832,-0.524,-0.183)
					3 (-0.101,-0.467, 0.879)
4	20827	175.2	3.6	(0.647, 0.216, 0.256)	1 (0.545, 0.713, 0.441)
					2 (0.832,-0.524,-0.183)
					3 (-0.101,-0.467, 0.879)

Void	Vol/Ang^3	#Electrons
1	175.2	39.4
2	175.2	41.6
3	175.2	37.6
4	175.2	43.4

Table S1 Crystal data and structure refinement.

	1	2	3	5	6
Empirical formula	$C_{96}H_{66}Cl_{16}Eu_2F_{18}N_4O_{14}P_2Pt_2S_6$	$C_{46}H_{31}Cl_2F_9GdN_2O_7PPtS_3$	$C_{47}H_{33}AsCl_4EuF_9N_2O_7PtS_3$	$C_{15}H_{12}ClN_3OPt$	$C_{78}H_{46}Cl_2Eu_2F_{18}N_6O_{14}Pt_2S_6$
Formula weight/ g mol^{-1}	3357.12	1445.12	1568.70	480.82	2590.57
Temperature/K	150(3)	298.3(9)	149(2)	295.8(3)	296.1(4)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c	P-1	$P2_1/c$	$P2_1/n$
a/Å	12.5622(3)	34.8427(11)	11.7915(4)	5.8219(2)	14.6534(7)
b/Å	34.5447(7)	16.2795(6)	14.0299(6)	25.1197(9)	16.0682(8)
c/Å	13.9645(4)	19.8361(8)	18.5196(4)	10.1551(4)	21.6641(9)
α/°	90	90	103.579(3)	90	90
β/°	98.839(3)	97.689(3)	90.735(2)	105.406(4)	108.190(5)
γ/°	90	90	114.440(4)	90	90
Volume/Å^3	5988.0(2)	11150.3(7)	2690.25(18)	1431.77(10)	4846.0(4)
Z	2	8	2	4	2
ρ_{calc} / g cm^3	1.862	1.722	1.937	2.231	1.775
μ/mm^{-1}	16.927	3.999	17.379	9.987	16.938
F(000)	3248.0	5576.0	1512.0	904.0	2484.0
Crystal size/mm^3	0.27 × 0.16 × 0.05	0.22 × 0.2 × 0.1	0.28 × 0.18 × 0.11	0.12 × 0.08 × 0.01	0.13 × 0.11 × 0.05
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.898 to 137.402	6.88 to 58.84	7.174 to 137.136	7.26 to 58.45	8.404 to 121.64
Index ranges	-15 ≤ h ≤ 15, -41 ≤ k ≤ 40, -11 ≤ l ≤ 16	-45 ≤ h ≤ 47, -22 ≤ k ≤ 22, -26 ≤ l ≤ 25	-11 ≤ h ≤ 14, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22	-7 ≤ h ≤ 7, -33 ≤ k ≤ 34, -12 ≤ l ≤ 13	-16 ≤ h ≤ 16, -17 ≤ k ≤ 18, -24 ≤ l ≤ 22
Reflections collected	28202	61464	20631	16230	17783
Independent reflections	10788 [R_{int} = 0.0515, R_{sigma} = 0.0527]	13531 [R_{int} = 0.0678, R_{sigma} = 0.0484]	9635 [R_{int} = 0.0513, R_{sigma} = 0.0536]	3549 [R_{int} = 0.0465, R_{sigma} = 0.0370]	7220 [R_{int} = 0.0492, R_{sigma} = 0.0584]
Data/restraints/parameters	10788/126/732	13531/946/656	9635/649/670	3549/0/190	7220/764/618
Goodness-of-fit on F^2	1.064	1.038	1.028	1.082	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0462, wR_2 = 0.1227	R_1 = 0.0696, wR_2 = 0.1831	R_1 = 0.0624, wR_2 = 0.1646	R_1 = 0.0344, wR_2 = 0.0653	R_1 = 0.1326, wR_2 = 0.3486
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.1293	R_1 = 0.0998, wR_2 = 0.2107	R_1 = 0.0639, wR_2 = 0.1662	R_1 = 0.0433, wR_2 = 0.0687	R_1 = 0.1704, wR_2 = 0.3757
Largest diff. peak/hole / e Å^{-3}	1.80/-1.17	1.93/-1.13	3.31/-2.29	0.96/-1.03	2.46/-1.23
CCDC number	2395042	2395043	2395044	2395089	2395045

Table S2 Unit cell parameters for compounds **4** and **7**

	4	**7**
a/Å	11.781(5)	14.675(5)
b/Å	14.058(4)	16.124(7)
c/Å	18.624(4)	21.731(8)
α/°	103.89(5)	90
β/°	90.86(3)	108.22(4)
γ/°	114.52(4)	90

Continuous shape measures analysis

A continuous shape measures analysis of Ln ions coordination polyhedra has been performed with the SHAPE 2.1 software considering an eight-coordination. The closer the value is to zero, the better it fits to the ideal geometry (**Table S4**).

Table S3 Coordination geometries evaluated by SHAPE 2.1 considering an eight-coordination.

Abbreviation	Symmetry	Ideal geometry
OP-8	D_{8h}	Octagon
HPY-8	C_{7v}	Heptagonal pyramid
HBPY-8	D_{6h}	Hexagonal bipyramid
CU-8	O_h	Cube
SAPR-8	D_{4d}	Square antiprism
TDD-8	D_{2d}	Triangular dodecahedron
JGBF-8	D_{2d}	Johnson gyrobifastigium J26
JETBPY-8	D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR-8	C_{2v}	Biaugmented trigonal prism J50
BTPR-8	C_{2v}	Biaugmented trigonal prism
JSD-8	D_{2d}	Snub disphenoid
TT-8	T_d	Triakis tetrahedron
ETBPY-8	D_{3h}	Elongated trigonal bipyramid

Table S4 Output of the SHAPE 2.1 software.

Compound	Ln	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
1	Eu	31.258	24.093	13.705	6.414	1.452	**0.776**	15.837	29.111	3.282	2.609	4.323	7.305	23.577
2	Gd	31.441	22.689	15.175	10.348	**1.172**	1.902	14.226	27.673	1.961	1.265	4.356	11.119	23.642
3	Eu	32.397	24.244	15.719	8.455	2.341	**0.359**	14.886	29.810	3.143	2.466	3.194	9.199	24.071
6	Eu	31.016	22.991	16.344	10.616	**0.894**	1.485	14.527	28.790	2.484	1.835	3.911	11.311	24.163

References

1) O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, (2009), J. Appl. Cryst. 42, 339-341.

2) P. van der Sluis and A. L. Spek, Acta Cryst. (1990). A46, 194-201