Supplementary materials

Synthesis, Structure and Photoluminescence Properties of Cd and Cd-Ln Pentafluorobenzoates with 2,2′:6′,2′-terpyridine Derivatives

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I. Supplementary PXRD data

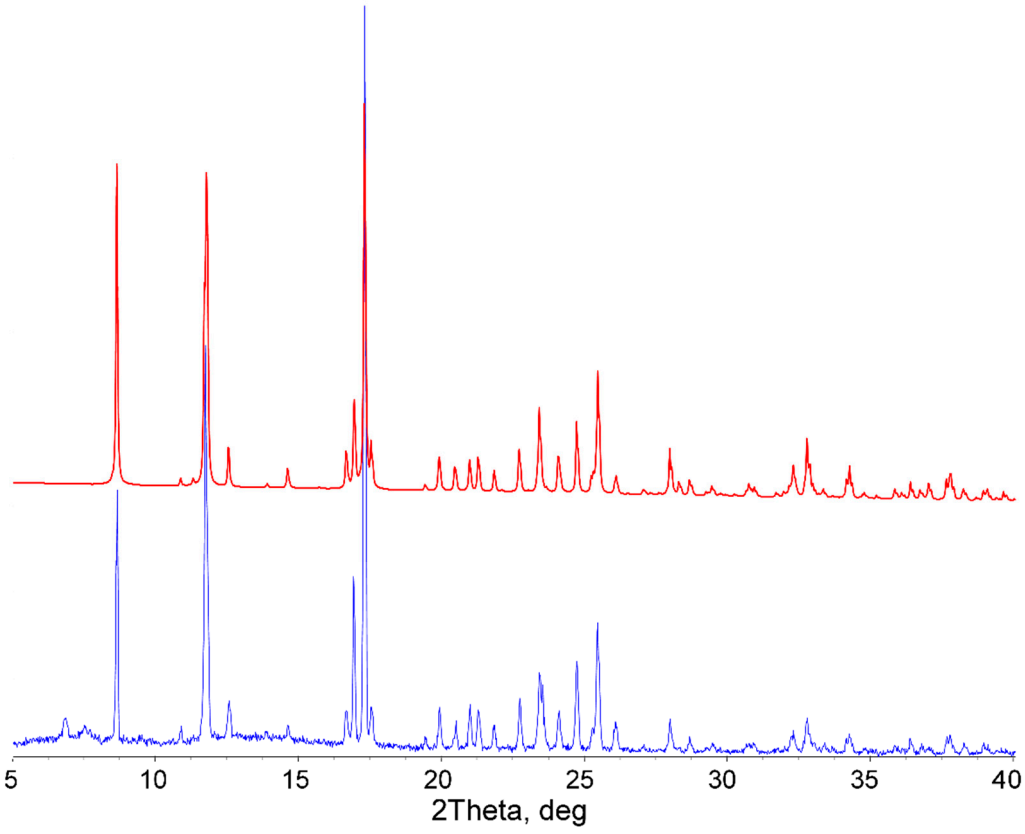


Figure S1 – XRD patterns comparison for calculated (red) and experimental polycrystalline sample of 1 (blue).

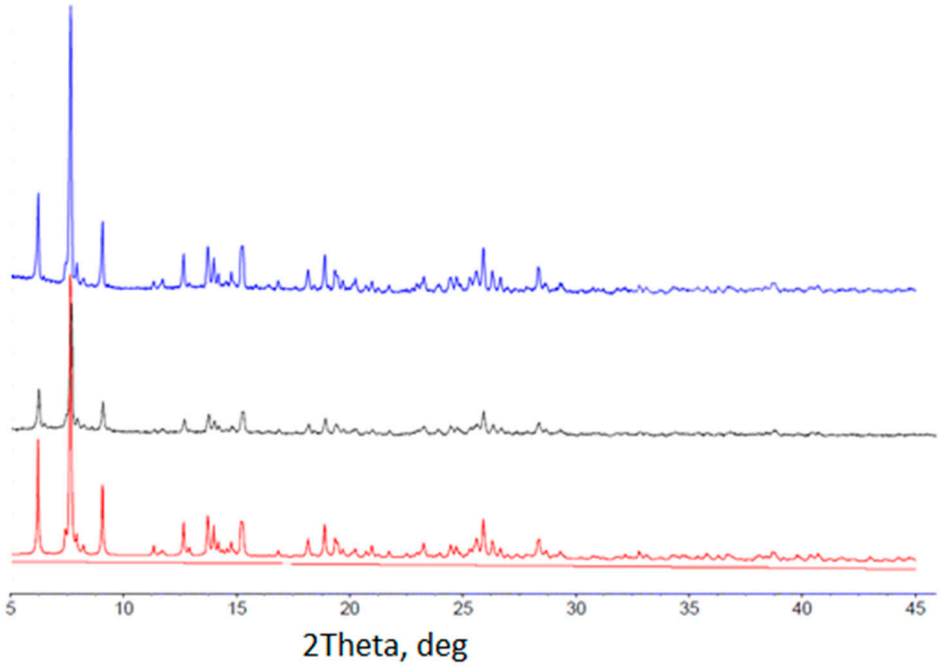


Figure S2 – XRD patterns comparison for calculated (red) and experimental polycrystalline samples of 2_{Eu} (blue) and 2_{Tb} (black).

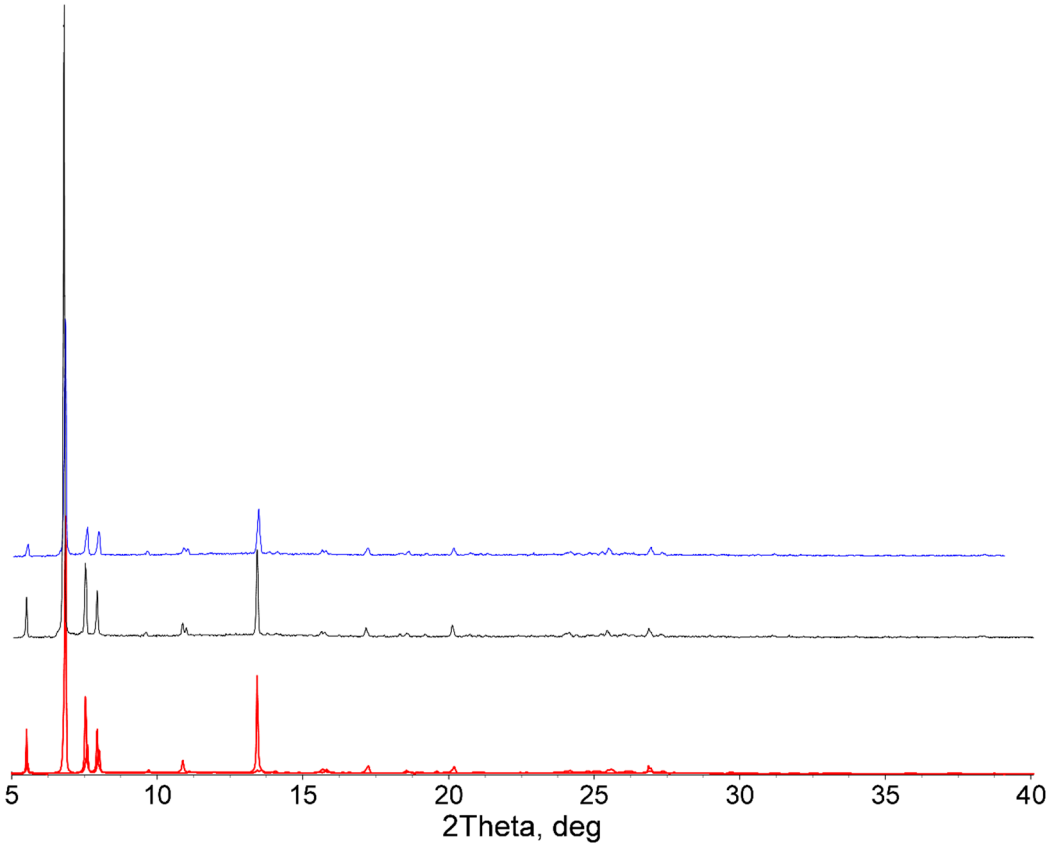
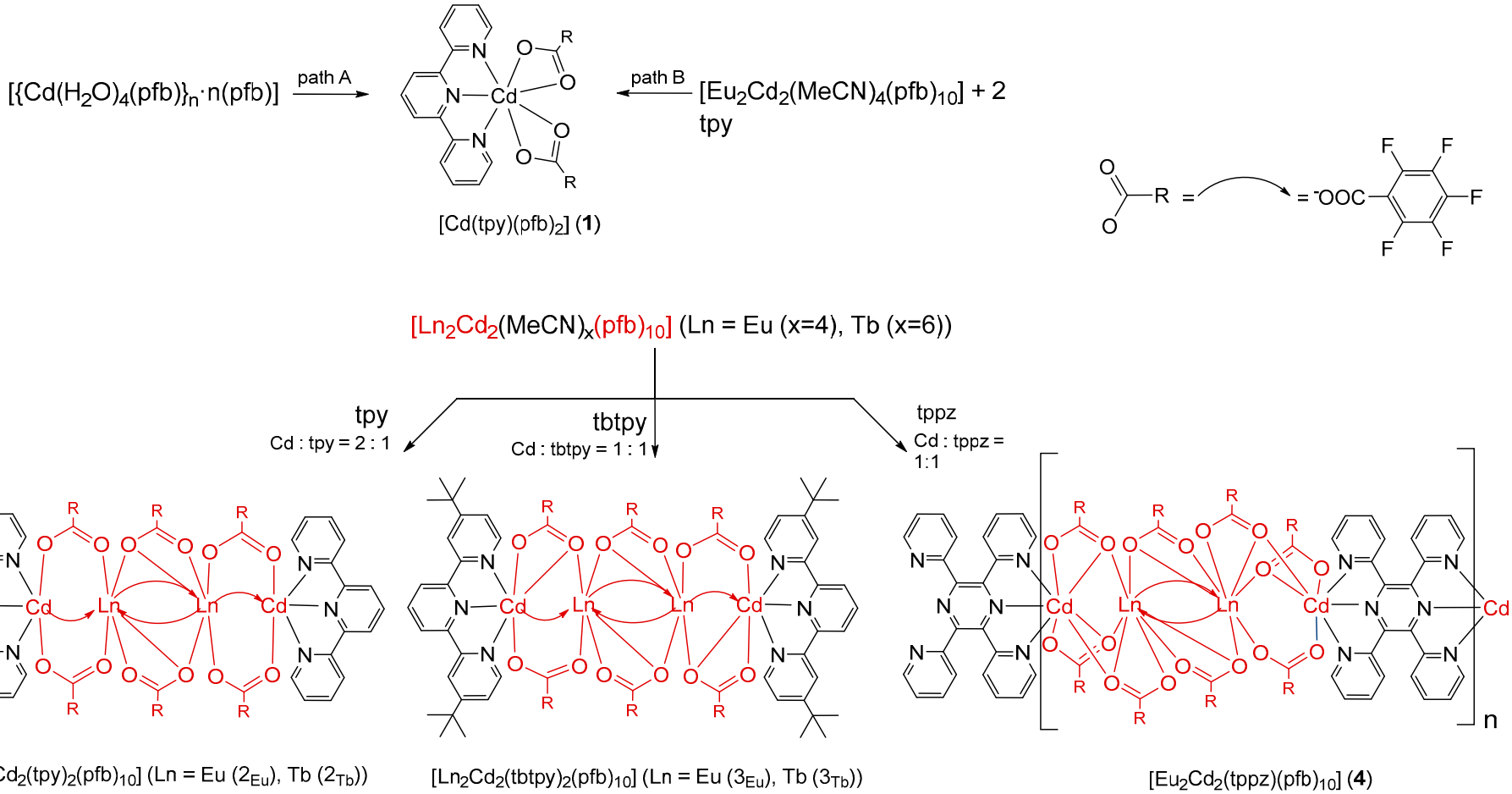


Figure S3 – XRD patterns comparison for calculated (red) and experimental polycrystalline samples of 3_{Eu} (blue) and 3_{Tb} (black).

II. Supplementary synthetic data



Scheme S1. Synthesis of complexes 1-4.

III. Supplementary structural data

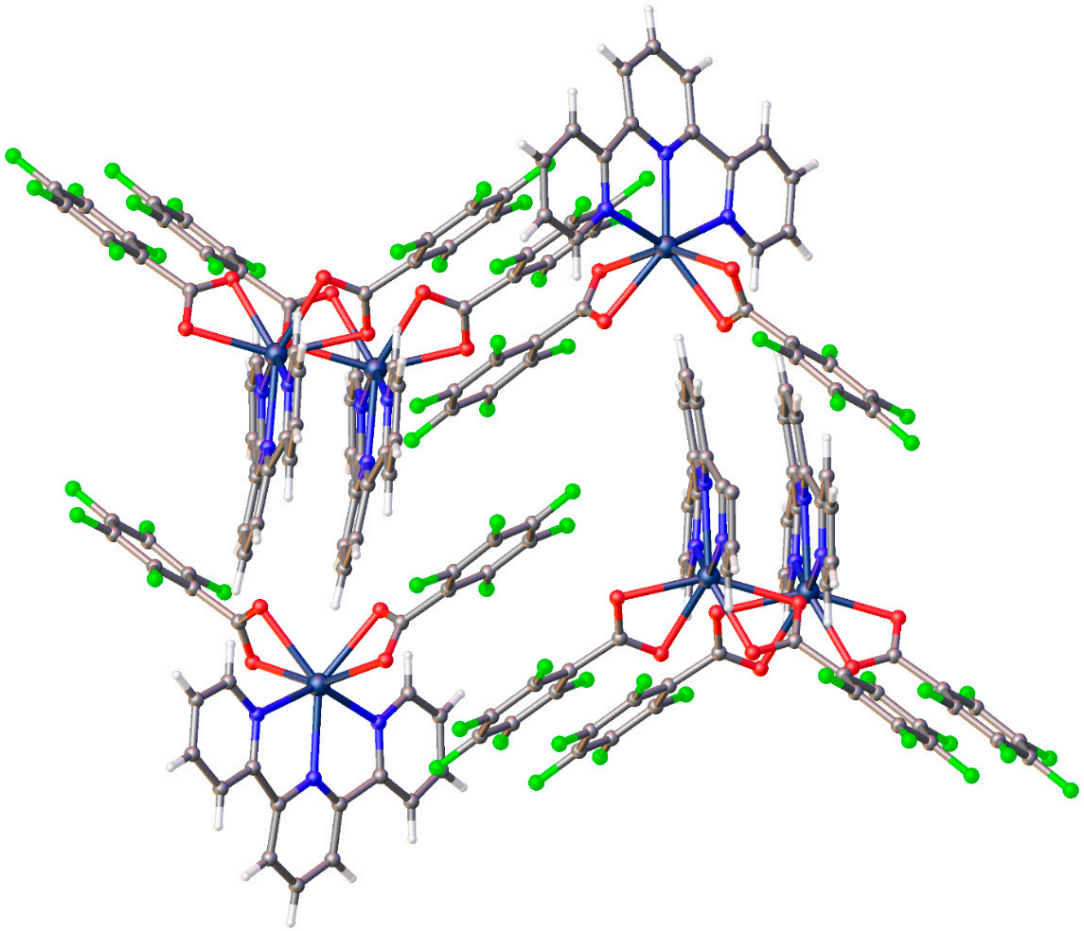
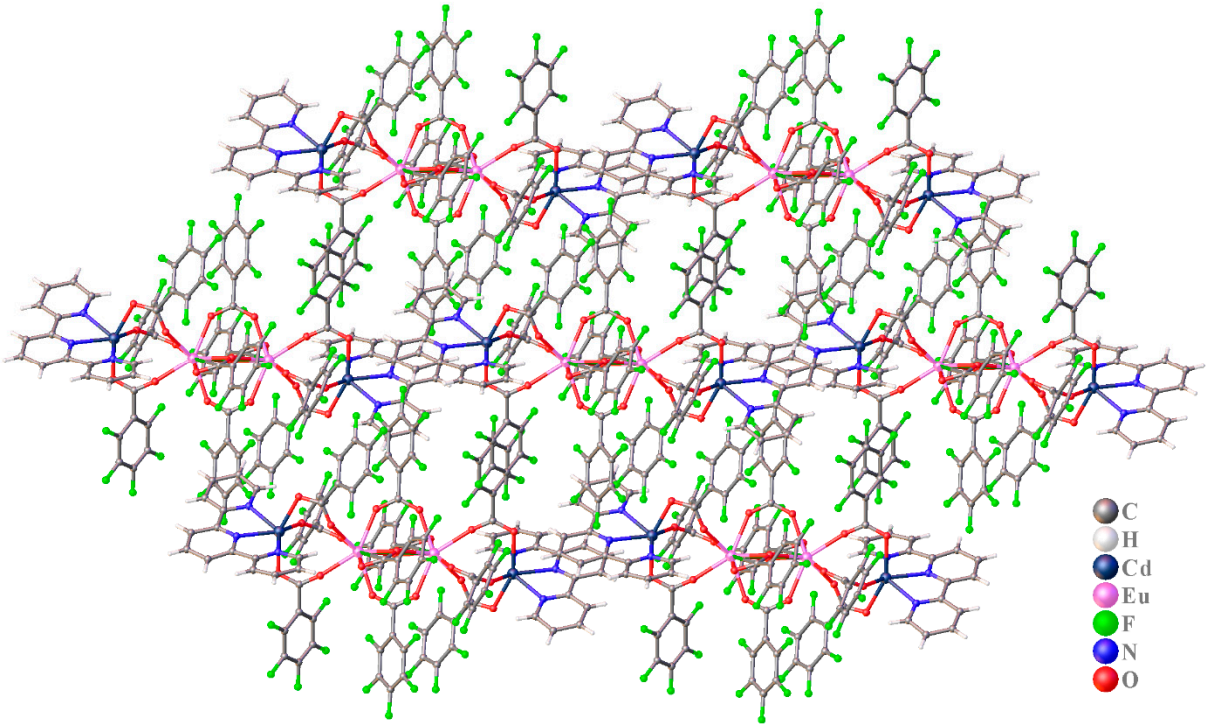
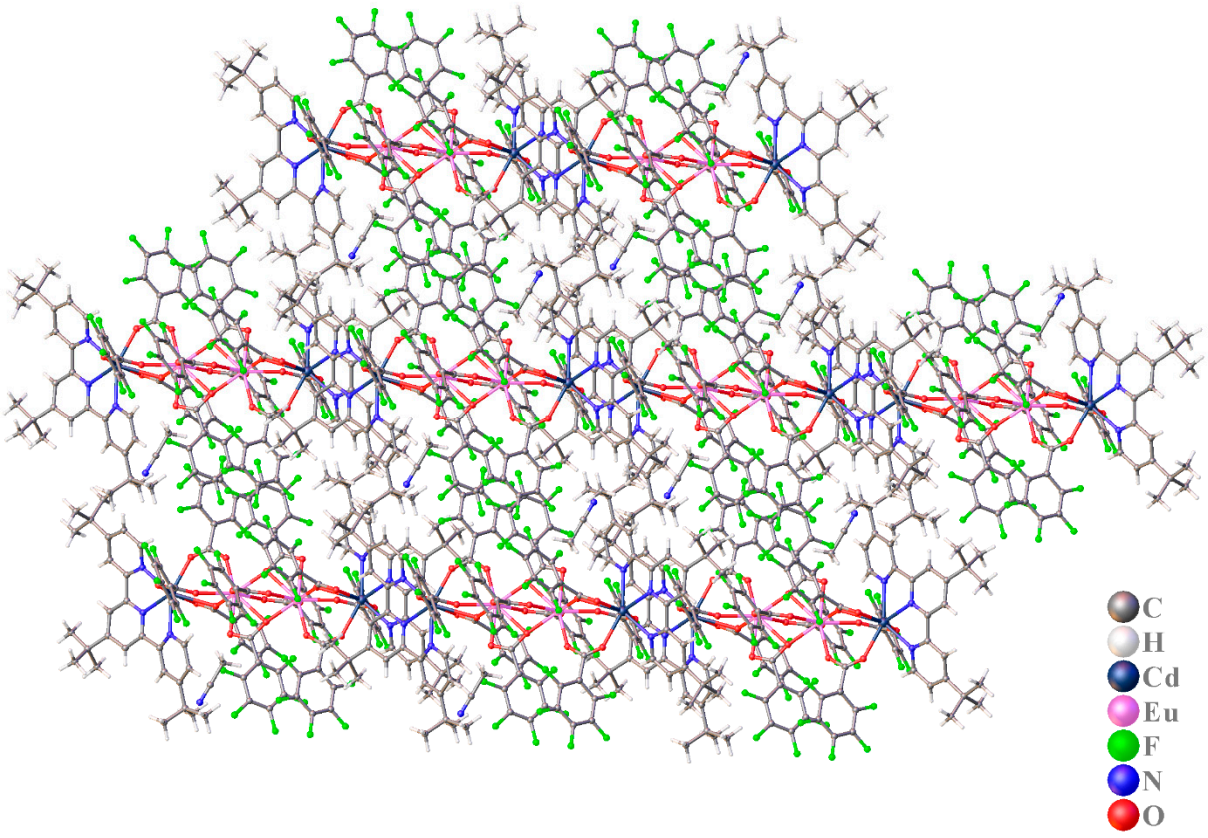


Figure S4. Fragment of the crystal packing of 1.



a)



b)

Figure S5. Fragments of the crystal packing of 2_{Eu} (a) и 3_{Eu} (b). Projections along plane a are shown.

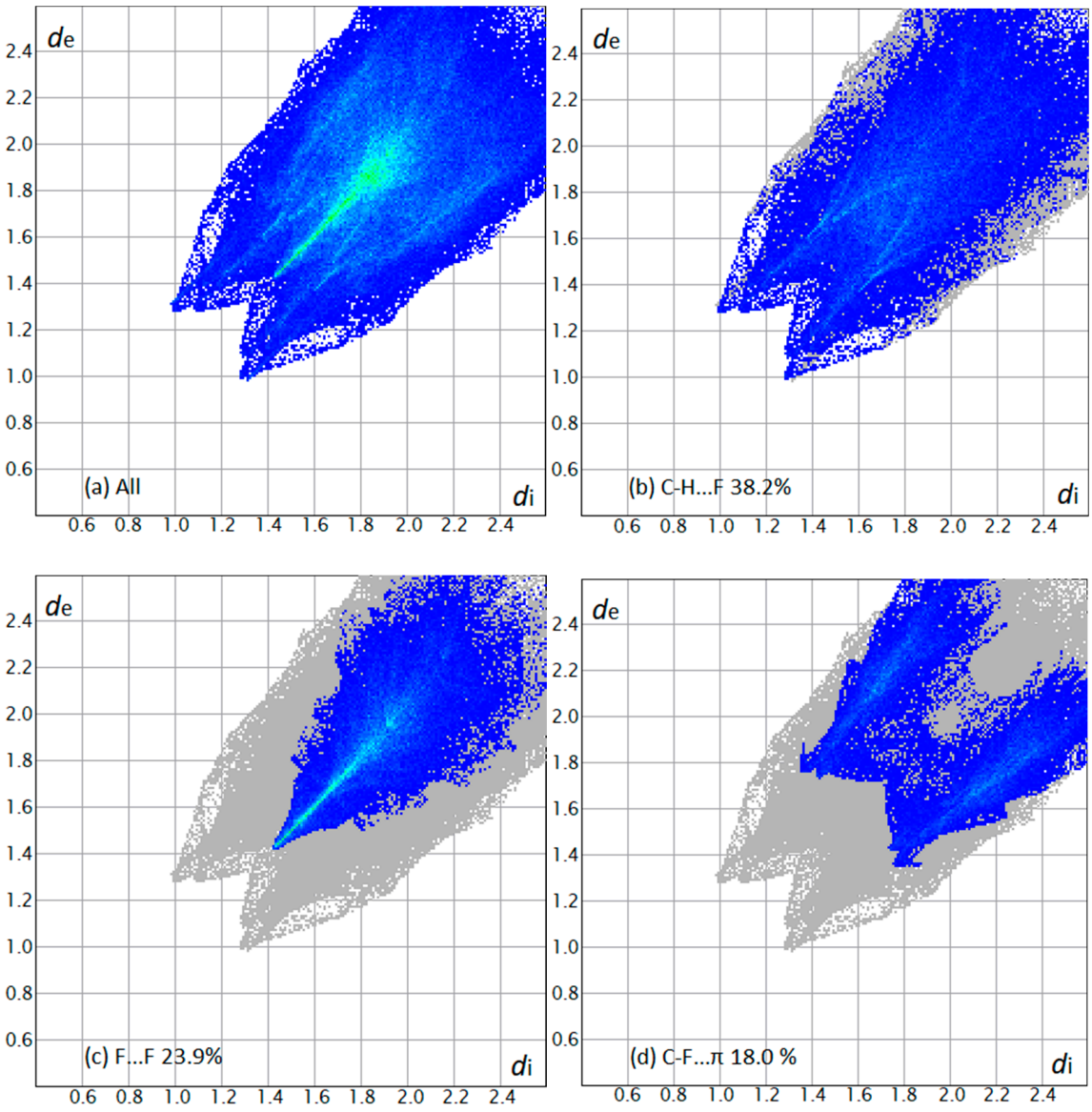


Figure S6. 2D fingerprint plots (a) and sections of the graph, which correspond to C-H…F(b), F…F(c) и C-H… π(d) interactions in the structure 2_{Eu}

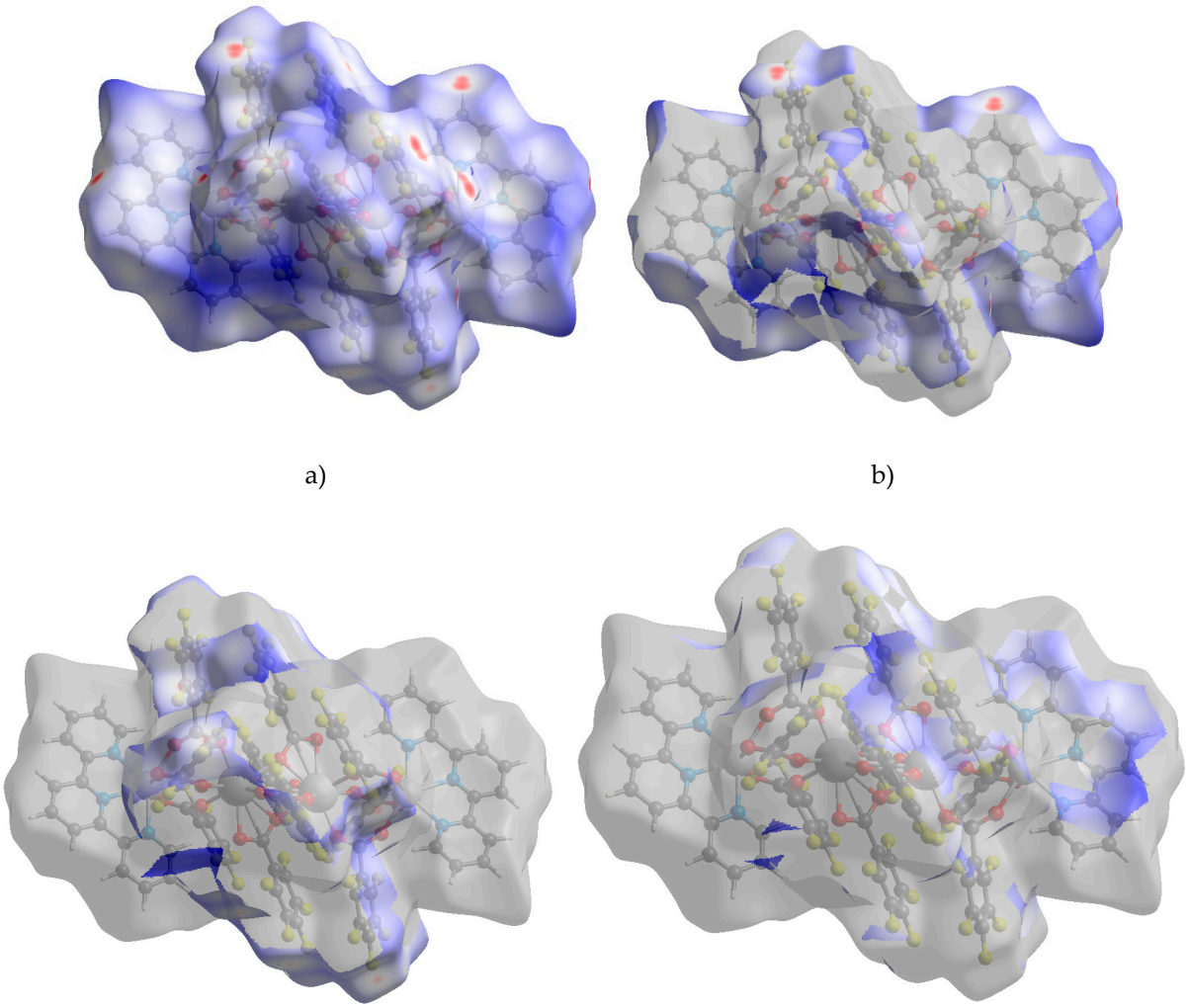


Figure S7. Hirshfeld surface (a) and contribution of C-H…F(b), F…F(c) and C-H… π(d) interactions in structure 2_{Eu}.

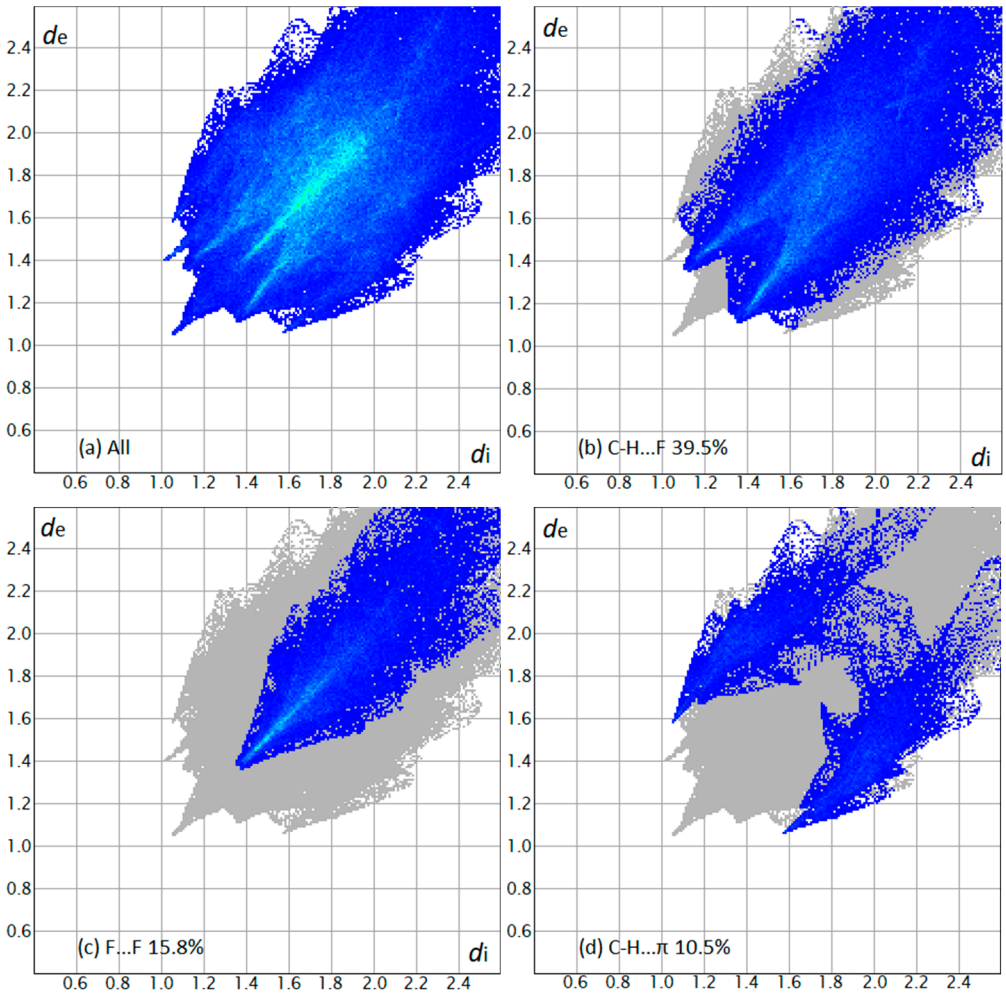


Figure S8. 2D fingerprint plots (a) and sections of the graph, which correspond to C-H…F(b), F…F(c) и C-H… π(d) interactions in the structure 3_{Eu}.

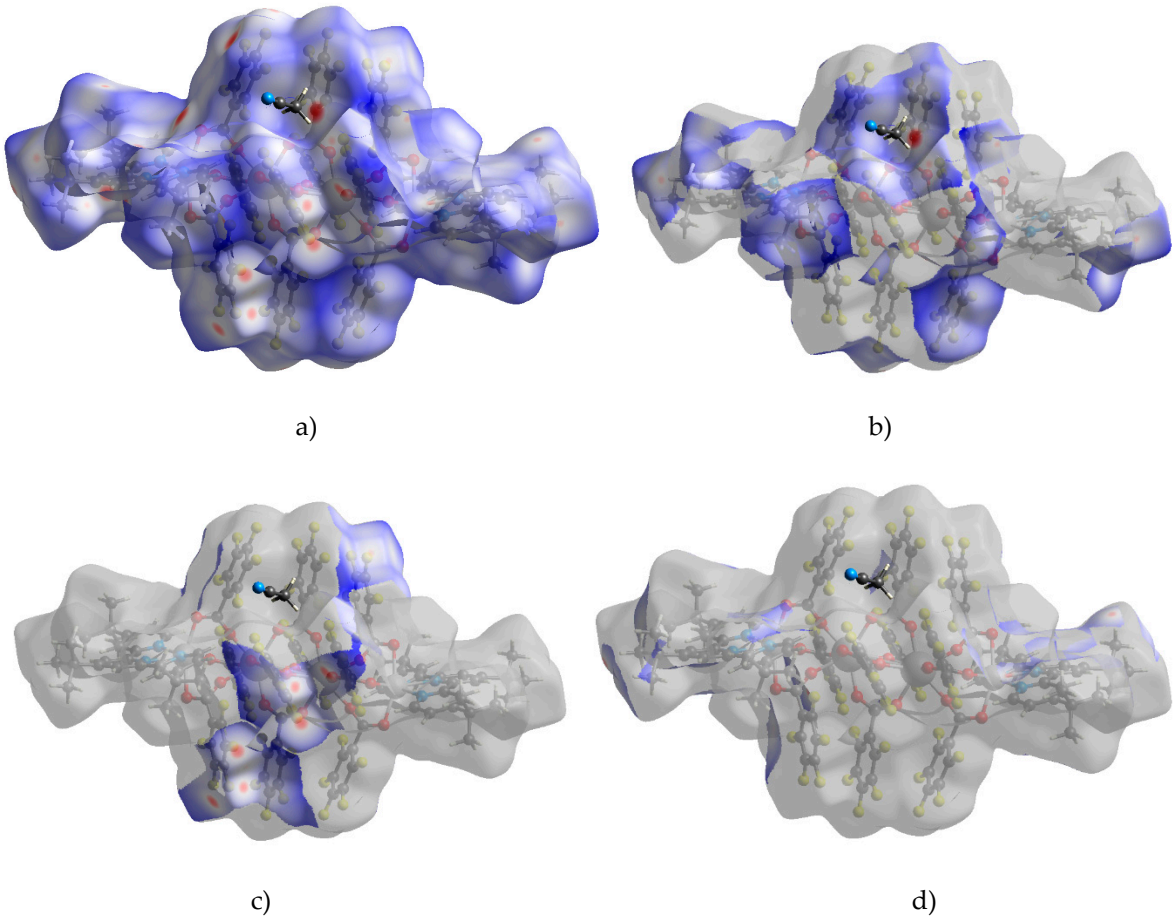


Figure S9. Hirshfeld surface (a) and contribution of C-H…F(b), F…F(c) and C-H… π(d) interactions in structure 3_{Eu}.

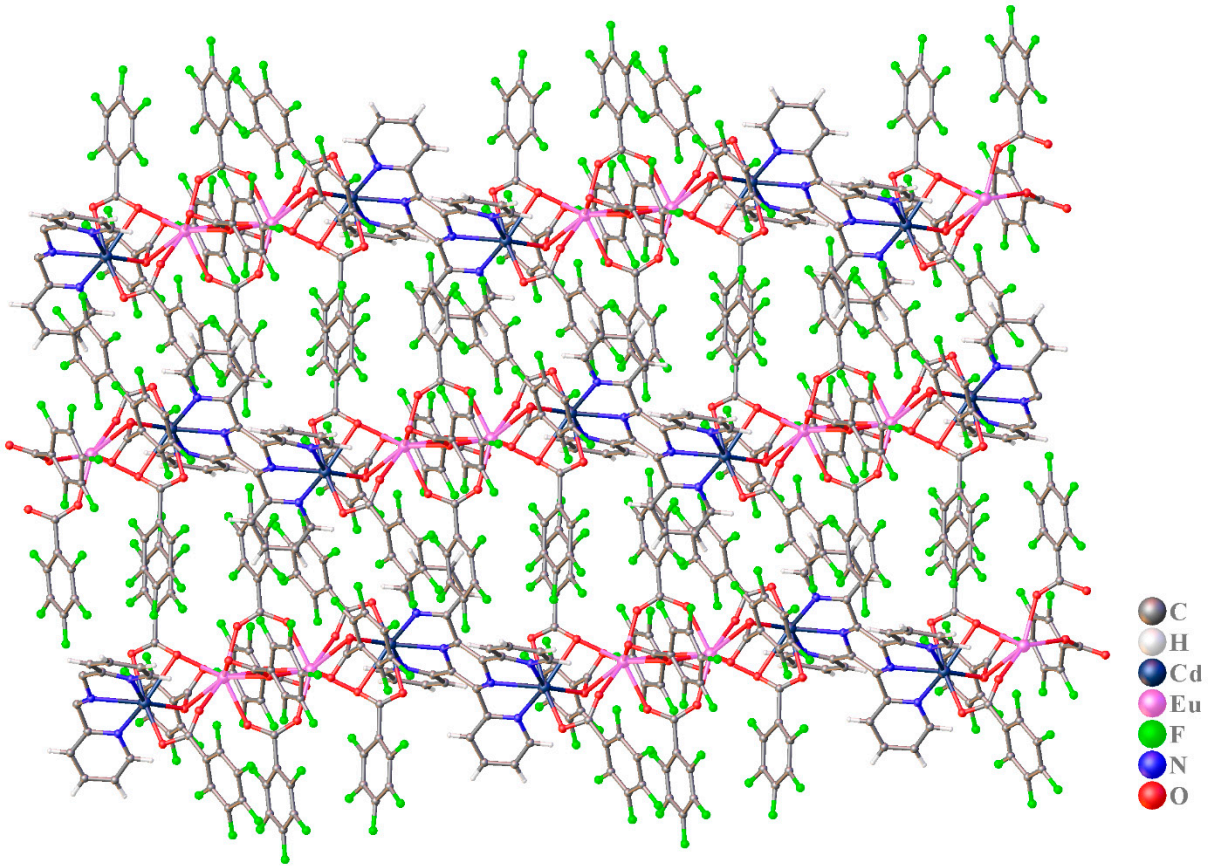


Figure S10. Fragment of the crystal packing of 4. Projections along plane a are shown.

Table S1.The main crystallography data and refinement details for structures 1, 2_{Eu}, 3_{Eu} and 4.

Parameter	1	2_{Eu}	3_{Eu}	4
Formula weight (g·mol^{-1})	767.81	3105.95	3524.68	3027.85
T, K	120	296	100	296
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	*Pnna*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	16.1677(7)	14.3318(5)	14.219(2)	14.1316(16)
b, Å	20.2820(9)	14.4293(5)	15.455(3)	14.5434(18)
c, Å	8.4259(4)	15.8527(7)	16.941(3)	14.9932(18)
α, °	90	81.9780(10)	76.287(6)	74.804(4)
β, °	90	66.3180(10)	72.339(5)	66.842(4)
γ, °	90	65.5510(10)	71.076(5)	64.748(3)
V, Å^3	2763.0(2)	2731.62(18)	3315.8(10)	2545.9(5)
Z	4	1	1	1
d_{calc}, g·cm^{-3}	1.846	1.888	1.765	1.975
μ, cm^{-1}	0.901	1.672	1.389	1.791
θ_{max} (deg)	29.999	25.997	26.000	26.000
T_{min}/T_{max}	0.693/ 0.900	0.653/ 0.746	0.551/0.746	0.631/0.746
Reflections measured	34631	27362	17522	23029
Independent reflections	4034	10707	12505	9957
Reflections with $I > 2s(I)$	2851	7977	8409	4470
R_{int}	0.0605	0.0947	0.0490	0.1275
GOOF	1.044	1.021	1.039	0.966
R_1 ($I > 2\sigma(I)$)	0.0330	0.0553	0.0784	0.0781
wR_2 ($I > 2\sigma(I)$)	0.0737	0.1415	0.2229	0.1897
Residual electron density, e·Å^{-3}(d_{min}/d_{max})	–0.401/0.438	-1.538/2.039	-2.547/2.754	–1.264/0.850

Table S2. Continuous Shape Measures (CShM) values for the potential coordination polyhedron of Eu and Cd atoms in 1, 2_{Eu}, 3_{Eu} and 4.

	Cd	Eu
1	Pentagonal bipyramid, D5h (5.828) Capped trigonal prism, C2v, (6.094) Capped octahedron, C3v (7.539)	-
2_{Eu}	Trigonal prism, D3h (3.330) Octahedron, Oh (11.257) Pentagonal pyramid, C5v (13.341)	Square antiprism, D4d (1.418) Triangular dodecahedron, D2d (1.802) Biaugmented trigonal prism, C2v, (2.408)
3_{Eu}	Capped trigonal prism, C2v (4.434) Pentagonal bipyramid, D5h (4.671) Capped octahedron, C3v (4.986)	Triangular dodecahedron, D2d (1.417) Square antiprism, D4d (1.917) Biaugmented trigonal prism, C2v (2.188)
4	Snub disphenoid, D2d (4.884) Square antiprism, D2d (5.294) Biaugmented trigonal prism, C2v (5.796)	Capped square antiprism, C4v (2.011) Capped square antiprism J10, C4v (2.716) Tricapped trigonal prism, D3d (3.046)

Table S3 Table of C-F… π interactions in the crystal packing of 1, 2_{Eu}, 3_{Eu} and 4.

Interaction	F..Cg, Å	F-Perp, Å	Gamma, °	C-F- Cg, °	C..Cg, Å
1					
C5-F5… Cg2	3.458(5)	3.223	21.20	53.05	4.762(5)
C6-F6… Cg1	3.179(3)	3.161	6.12	47.22	4.323(4)
2_{Eu}					
C4-F4…Cg6	3.516(12)	3.168	25.70	0.71	4.184(18)
C19-F19…Cg2	2.841(8)	2.829	2.69	58.06	4.024(11)
C20-F20…Cg10	3.383(8)	3.120	22.74	9.39	3.467(12)
C26-F26…Cg9	3.328(10)	3.254	12.09	0.65	3.734(16)
3_{Eu}					
C4-F4…Cg1	3.776(9)	3.282	29.62	144.0(7)	4.929(14)
C6-F6…Cg7	3.384(10)	3.325	10.61	83.8(7)	3.499(13)
C14-F14…Cg1	3.492(8)	3.057	28.94	121.6(6)	4.332(13)
C28-F28…Cg4	3.459(8)	3.442	5.64	83.7(5)	3.563(11)
4					
C6-F6…Cg3	3.322(12)	-3.270	10.17	49.98	4.480(15)
C18-F18…Cg8	3.523(17)	-3.504	6.08	6.08	3.84(2)
C26-F26…Cg7	3.585(16)	-3.441	16.29	1.13	3.79(3)
C32-F32…Cg1	3.618(15)	-3.306	23.95	27.01	4.76(2)

Table S4 Parameters of hydrogen bonds in the crystal packing of 1, 2_{Eu} and 3_{Eu}.

Hydrogen bond	Symmetry code	D – H, Å	H...A, Å	D...A, Å	D – H– A, °
1					
C8-H8A… O2		0.95	2.50	3.108(3)	122
C9-H9A… O1	x,y,-1+z	0.95	2.58	3.405(4)	146
C11-H11A… O2	-1/2+x,y,-z	0.95	2.48	3.424(4)	176
C14`-H14B… O2	-1/2+z,y,-z	0.95	2.27	3.178(6)	159
2_{Eu}					
C36-H36…O6		0.93	2.39	3.126(12)	135
C38-H38…F13	1+x,y,z	0.93	2.46	2.993(19)	116
C43-H43…F14	-x,2-y,2-z	0.93	2.43	3.233(16)	145
C44-H44…O1	-x,2-y,2-z	0.93	2.46	3.342(14)	159
C50-H50…O3		0.93	2.40	2.933(11)	116
3_{Eu}					
C36-H36…O2		0.95	2.50	3.281(13)	139
C3S-H3SA…F35		0.98	2.34	3.01(3)	124
C36-H36…O10	1-x,1-y,1-z	0.95	2.32	3.009(12)	129
C50-H50…O5		0.95	2.47	3.010(12)	116
C58-H58…F10	1-x,-y,2-z	0.98	2.55	3.257(15)	129

Table S5. The main geometric characteristics of 1, 2_{Eu}, 3_{Eu} and 4.

Bond	Values			
	1	2_{Eu}	3_{Eu}	4
Cd–N (L)	2.342(3), 2.385(2)	2.338(6)-2.419(7)	2.366(8)-2.408(7)	2.367(11)-2.421(9)
Cd–O ($C_6F_5COO^-$)	2.375(2), 2.436(2)	2.302(6)–2.328(6)	2.299(6)-2.677(7)	2.252(9)–2.760(9)
Ln–O ($C_6F_5COO^-$)	-	2.292(4)–2.555(4)	2.291(6)-2.613(6)	2.355(9)–2.643(9)
Cd…Cd	9.116(1)	7.890(1)	8.511(2)	7.175(3)
Cd…Eu	-	4.239(1)	4.209(1)	3.751(1)
Eu…Eu	-	3.895(1)	3.999(1)	3.902(1)
Angle	ω, deg			
Cd-Eu-Eu	-	165.7(1)	172.7(2)	166.5(1)

Table S6 Table of F… F interactions in the crystal packing of complexes 2_{Eu}, 3_{Eu} and 4.

Interaction	F..F, Å	Symmetry code	% of sum of Van der Waals radii
2_{Eu}			
F3…F28	2.868(9)		97.5
F10…F35	2.751(10)	1-x,1-y,1-z	93.5
F12…F21	2.872(12)	-x,2-y,1-z	97.6
F14…F5	2.900(13)	-x,1-y,2-z	98.6
F18…F25	2.892(12)	1+x,y,z	98.3
3_{Eu}			
F5…F27	2.908(11)	1-x,1-y,1-z	98.9
F12…F19	2.745(10)	1+x,y,z	93.3
F13…F32	2.786(14)	1+x,y,z	94.7
F21…F24	2.750(10)		93.5
F28…F31	2.927(10)	1-x,1-y,1-z	99.5
4			
F4…F25	2.830(20)	-1+x,y,z	96.2
F6…F12	2.917(17)	2-x,-y,1-z	99.2
F13…F19	2.849(19)	1-x,1-y,2-z	96.9
F28…F35	2.911(16)		99.0

IV. Supplementary Photoluminescence data

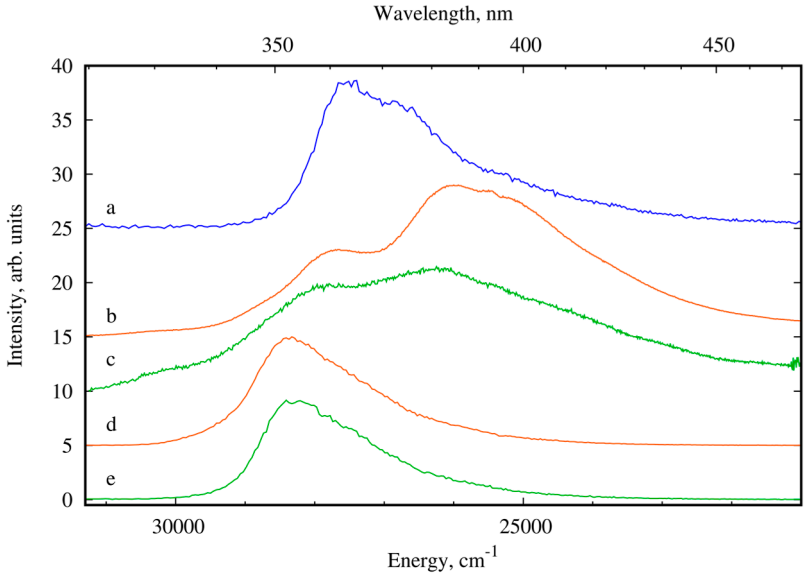


Figure S11. Luminescence spectra of complexes **1** (a), **2**$_{Eu}$ (b), **2**$_{Tb}$ (c), **3**$_{Eu}$ (d) and **3**$_{Tb}$ (e) at λ_{exc} = 280 nm and T = 300 K. The luminescence bands of the *d*-block are shown on the spectra.