Supplementary Materials

I. Supplementary PXRD data

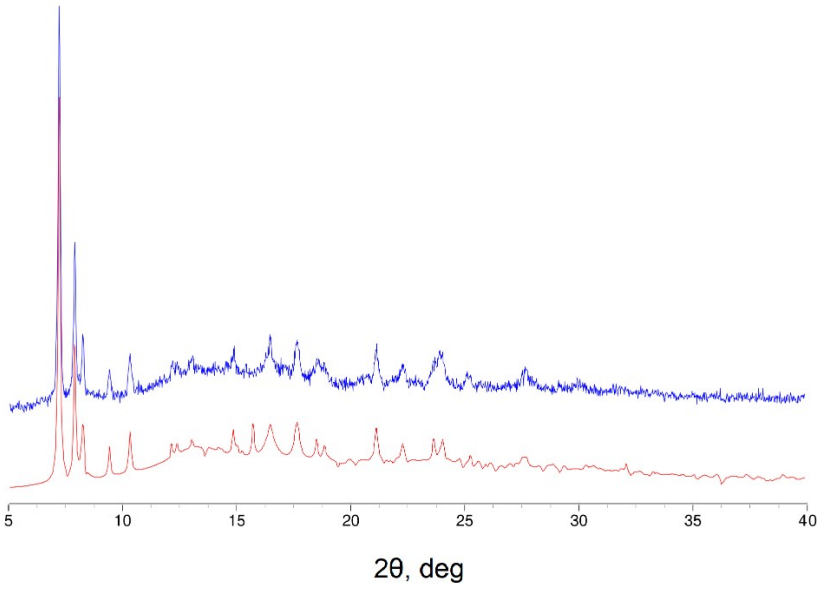


Fig. S1. Theoretical (red line) and experimental (blue line) powder patterns of the compound $\mathbf{1}_{\mathbf{Eu}}$

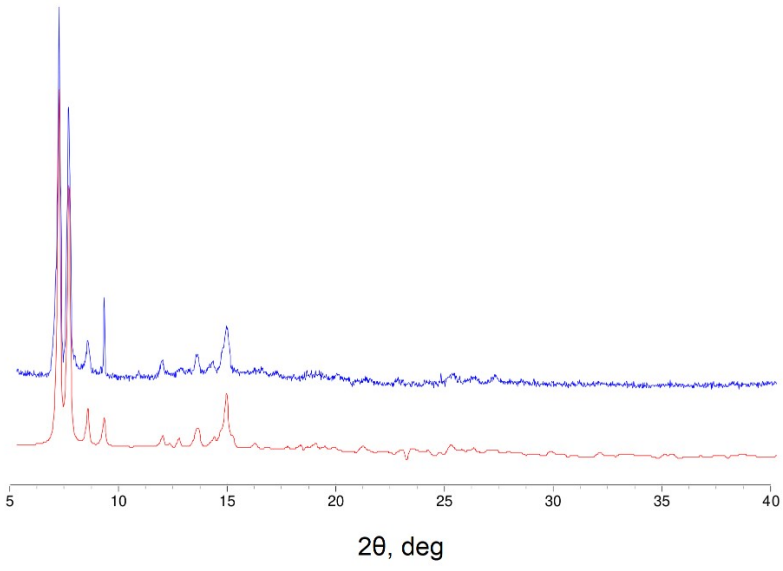


Fig. S2. Theoretical (red line) and experimental (blue line) powder patterns of the compound $\mathbf{1}_{\mathbf{Tb}}$.

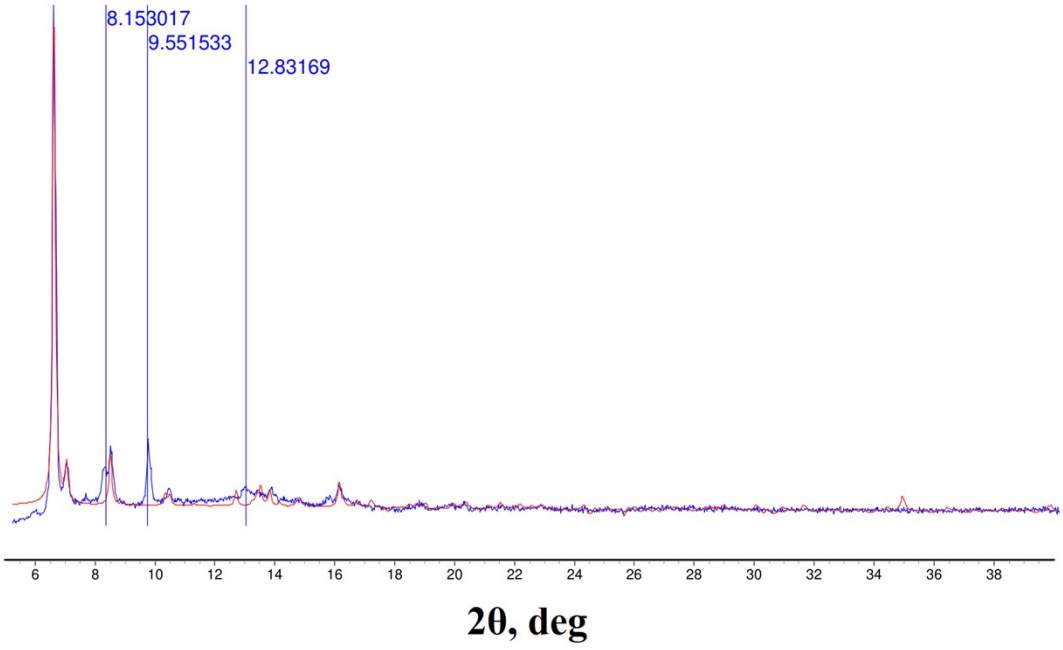


Fig. S3. Theoretical (red line) and experimental (blue line) powder patterns of the compound $\mathbf{2}_{\mathbf{Eu}}$. The vertical lines show the impurity phase.

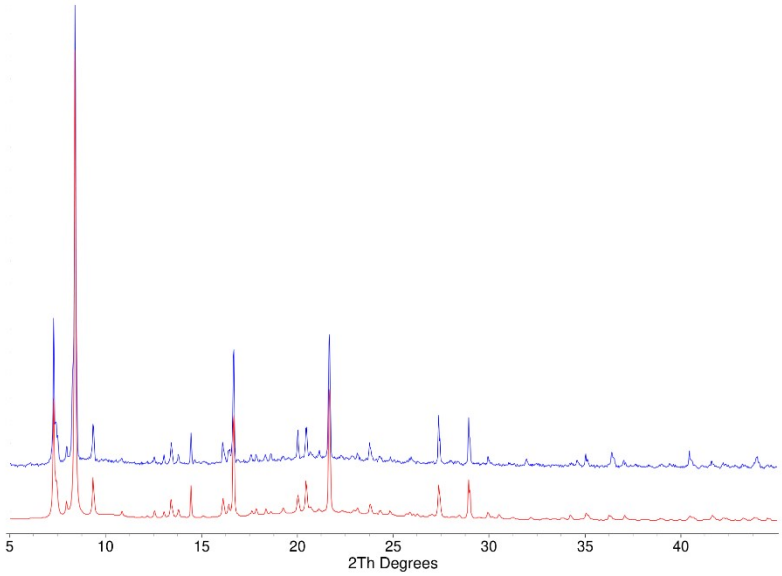


Fig. S4. Theoretical (red line) and experimental (blue line) powder patterns of the compound $\mathbf{3}_{\mathbf{Eu}}$.

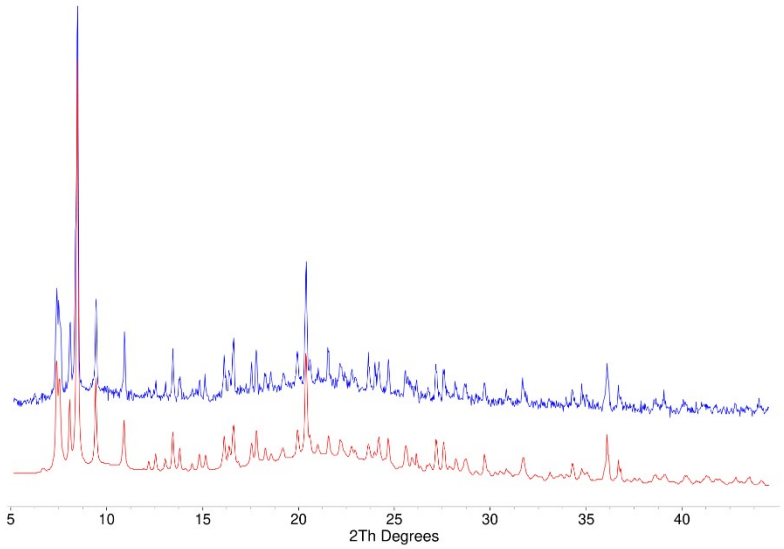


Fig. S5. Theoretical (red line) and experimental (blue line) powder patterns of the compound $\mathbf{3}_{\mathbf{Tb}}$.

II. Supplementary IR spectroscopy data

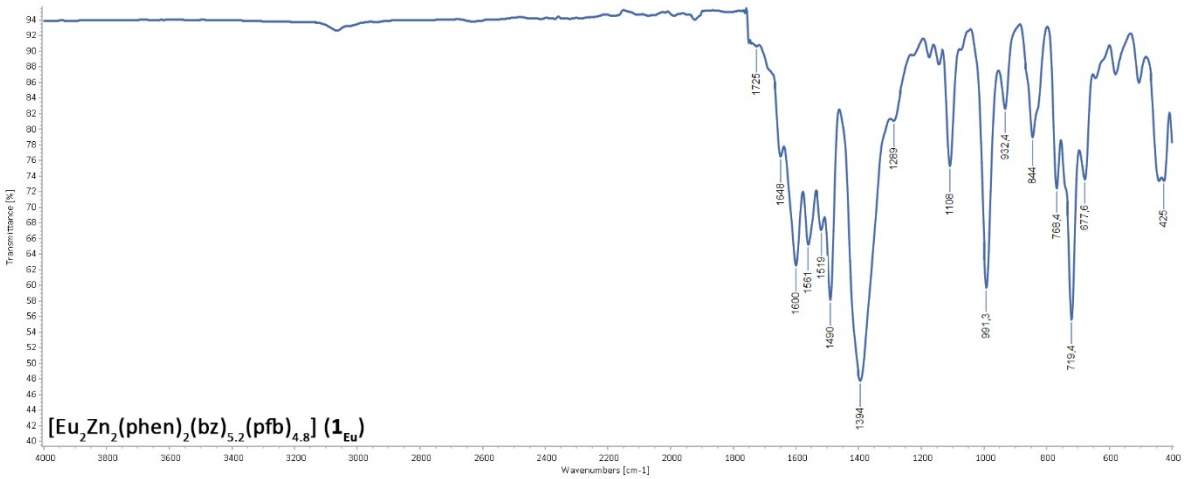


Figure S6. Full width FT-IR spectra of **[$Eu_2Zn_2(phen)_2(bz)_{5.2}(pfb)_{4.8}$] ($1_{Eu}$)**

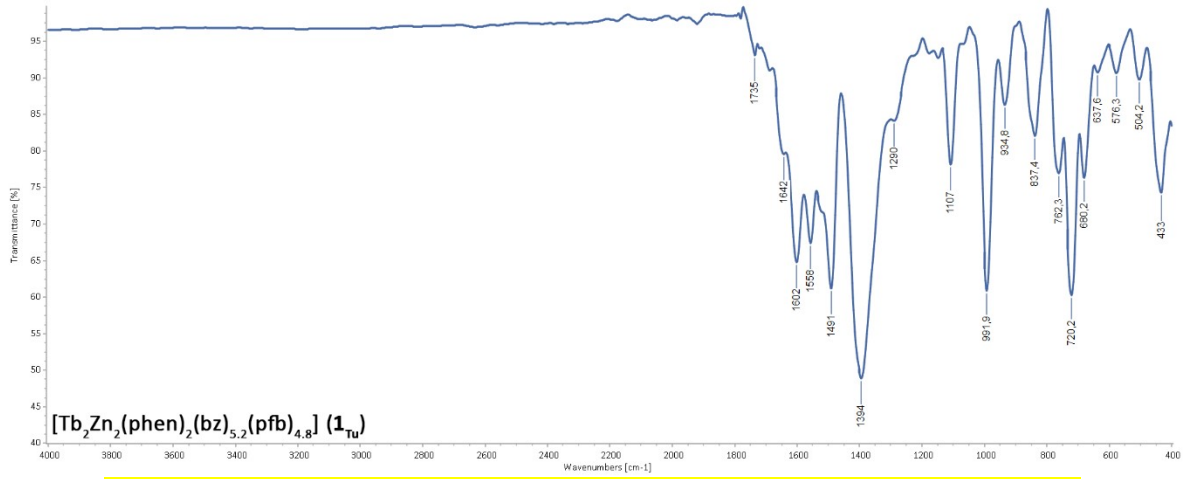


Figure S7. Full width FT-IR spectra of **[$Tb_2Zn_2(phen)_2(bz)_{5.2}(pfb)_{4.8}$] ($1_{Tb}$)**

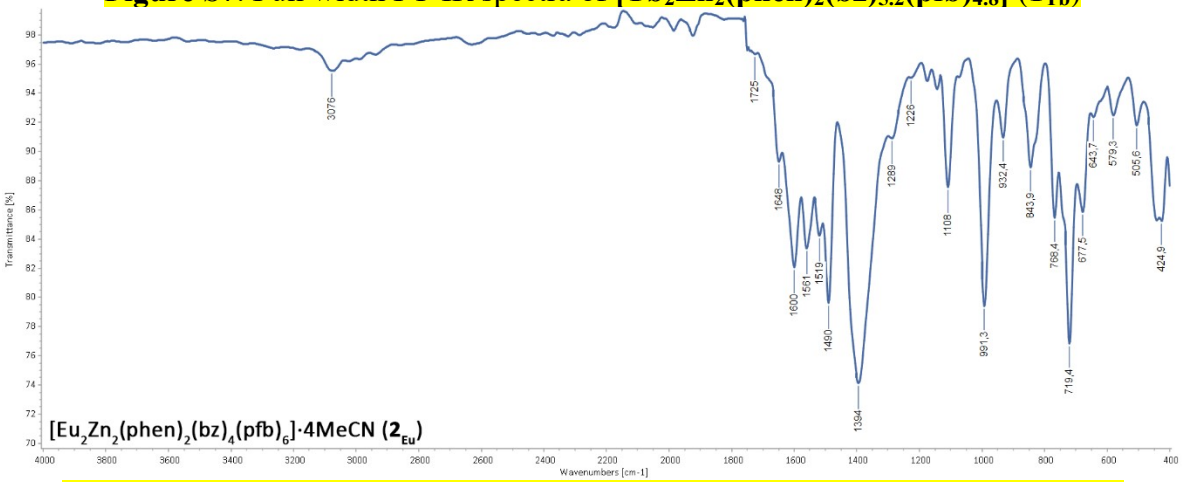


Figure S8. Full width FT-IR spectra of **[$Eu_2Zn_2(phen)_2(bz)_4(pfb)_6$]·4MeCN ($2_{Eu}$)**

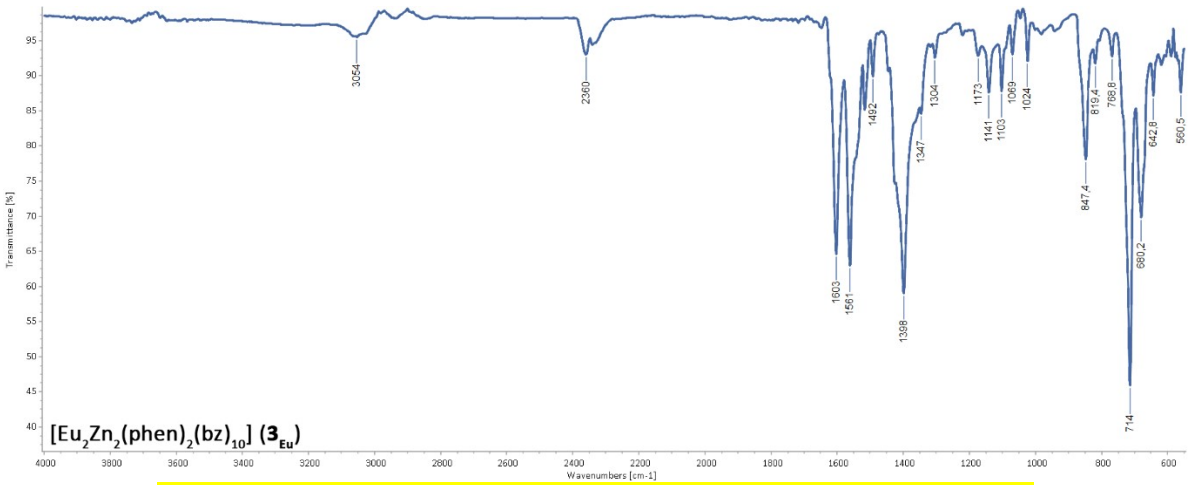


Figure S9. Full width FT-IR spectra of **[$Eu_2Zn_2(phen)_2(bz)_{10}$] ($3_{Eu}$)**

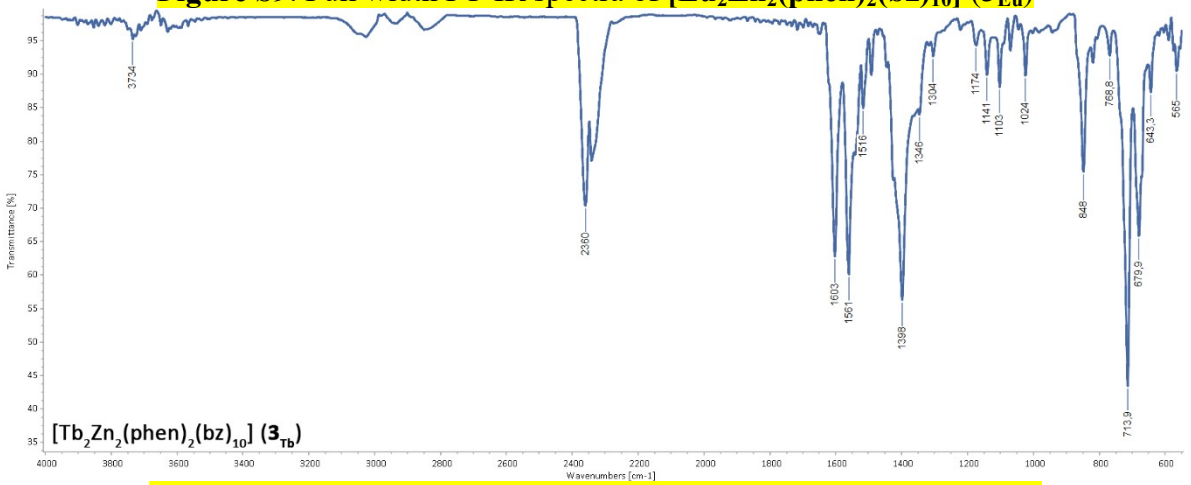


Figure S10. Full width FT-IR spectra of **[$Tb_2Zn_2(phen)_2(bz)_{10}$] ($3_{Tb}$)**

III. Supplementary structural data

Single crystal X-ray diffraction analysis of compounds was performed on a Bruker D8 Venture diffractometer equipped with a CCD detector (MoKα, λ = 0.71073 Å; CuKα, λ = 1.54178 Å, graphite monochromator). A semi-empirical absorption correction using the SADABS program was applied to all compounds. Using Olex2(1), the structure was solved with a ShelXS structure solution program using Direct Methods and refined using a ShelXL(2) refinement package with the Least Squares minimization in anisotropic approximation for nonhydrogen atoms. The H-atoms were added in the calculated positions and refined using the riding model in isotropic approximation. The occupancies of the disordered pfb/bz anions were determined using free variables and then fixed to one decimal place. The geometry of the metal polyhedra was determined using the program SHAPE 2.1(3).The CShM coefficient indicates the deviation of atom coordinates in the coordination sphere of the metal ion from the vertices of ideal polyhedra. Full correspondence of the polyhedron geometry with ideal polyhedra is achieved when the CShM value is equal to 0. The crystallographic parameters and details of the structural refinement are given in Table S1, the main distances and angles in Table 1, the key distances and angles of intra- and intermolecular interactions in Tables 2, S2, S3, and the CShM coefficients in Table S4.

CCDC 2343086 ($\mathbf{1}_{\mathbf{Eu}}$) and 2343087 ($\mathbf{1}_{\mathbf{Tb}}$), 2343088 ($\mathbf{2}_{\mathbf{Eu}}$), 2390847 ($\mathbf{3}_{\mathbf{Eu}}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

Table S1. The main crystallography data and refinement details for structures of $\mathbf{1_{Eu}}$, $\mathbf{1_{Tb}}$, $\mathbf{2_{Eu}}$ **and** $\mathbf{3_{Eu}}$.

	$\mathbf{1_{Eu}}$	$\mathbf{1_{Tb}}$	$\mathbf{2_{Eu}}$	$\mathbf{3_{Eu}}$
Formula	$C_{94}H_{42}Eu_2F_{24}N_4O_{20}Zn_2$	$C_{94}H_{42}F_{24}N_4O_{20}Tb_2Zn_2$	$C_{100}H_{45}F_{30}N_7O_{20}Eu_2Zn_2$	$C_{94}H_{66}Eu_2N_4O_{20}Zn_2$
Mass	2437.97	2451.89	2669.09	2006.16
T, K	100	100	150	100
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
Z (Z')	1	1	1	2
a, Å	14.2568(15)	14.2636(10)	13.496(3)	11.9014(13)
b, Å	14.7337(15)	14.6822(9)	14.461(3)	13.4139(15)
c, Å	14.9365(18)	14.8804(10)	14.786(3)	14.6057(15)
α, °	63.284(3)	63.435(2)	63.754(4)	107.083(5)
β, °	83.911(4)	84.216(2)	86.131(6)	111.257(5)
γ, °	63.764(3)	63.913(2)	78.080(5)	98.010(7)
V, Å^3	2497.0(5)	2485.4(3)	2531.4(8)	1996.5(4)
d_{calc}, g·cm^{-3}	1.638	1.621	1.751	1.669
μ, cm^{-1}	1.826	1.826	1.818	12.414
F(000)	1200	1196	1310	1004
$2q_{max}$, °	52	52	49.4	136.5
Reflections measured	16385	18052	15962	17827
Independent reflections	9582	9729	8505	7058
Reflections with $I > 2s(I)$	6959	8115	6233	6239
R_{int}	0.0450	0.0357	0.0598	0.0942
R_1	0.0501	0.0385	0.0569	0.0782
wR_2	0.1210	0.0944	0.1644	0.2067
GOOF	1.042	1.053	1.025	1.038
Residual electron density (d_{min}/d_{max})	-1.422/0.853	-1.315/1.015	-1.532/2.146	-1.864/2.343

Table S2. C-F···π and C-N···π interactions in the crystal packing of complexes $\mathbf{1}_{Eu}$, $\mathbf{1}_{Tb}$ and $\mathbf{2}_{Eu}$.

Interaction	F···Cg, Å	Symmetry code	F···Perp, Å	C-F···Cg,°
Complex $\mathbf{1}_{Eu}$				
C(20A)–F(20A)···Cg	3.296(18)		3.023	79.9(13)
C(21A)–F(21A)···Cg	3.633(12)	1-x,1-y,2-z	3.246	67.9(9)
Complex $\mathbf{1}_{Tb}$				
C(15A)–F(15A)···Cg	3.603(8)		3.208	66.8(6)
C(16A)–F(16A)···Cg	3.297(11)	1-x,1-y,2-z	3.083	79.4(8)
Complex $\mathbf{2}_{Eu}$				
C(12A)-F(12A)···Cg	3.288(8)	-x,1-y,-z	2.920	134.6(13)
C(18)-F(18)···Cg	3.055(8)	1-x,1-y,1-z	2.920	151.3(7)
C(19)-F(19)···Cg	2.989(9)	1-x,1-y,1-z	2.945	133.7(6)
C(21)-F(21)···Cg	3.273(7)		3.028	130.5(5)
C(4S)-N(4S)···Cg	3.50(3)		3.340	121(2)

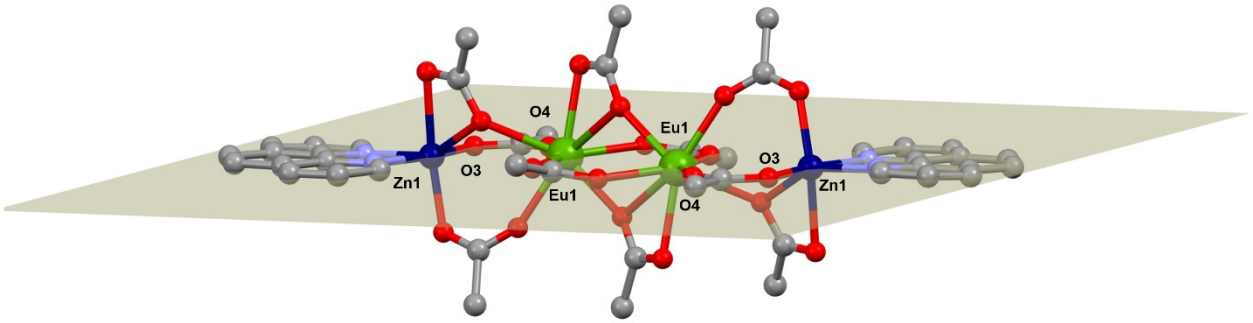
Note. Cg is the centroid of aromatic rings, Perp is perpendicular to the plane of the ring, α is the angle between the planes of aromatic fragments.

Table S3. Hydrogen bonds in the crystal packing of complexes $\mathbf{1}_{Eu}$, $\mathbf{1}_{Tb}$, $\mathbf{2}_{Tb}$, $\mathbf{2}_{Eu}$ and $\mathbf{3}_{Eu}$.

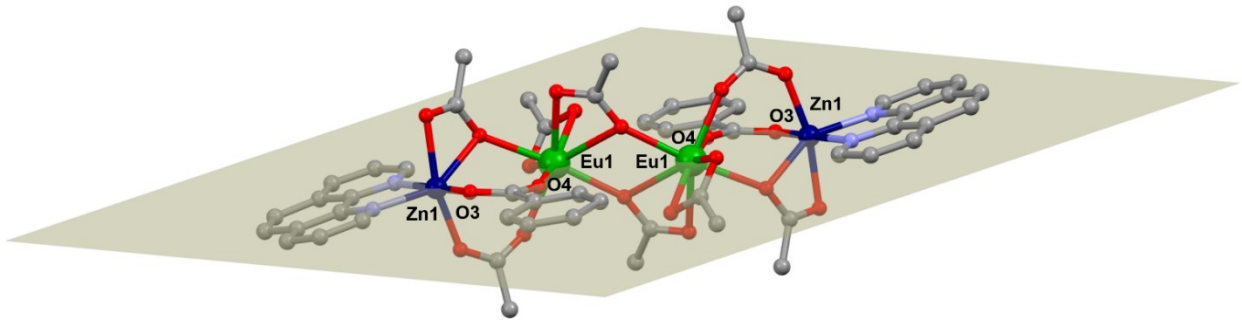
Interaction	Distance, Å				D – H···A, °
	D–H	Symmetry code	H···A	D···A	
Complex $\mathbf{1}_{Eu}$					
C(4)–H(4)···F(20A)	0.95	x,-1+y,z	2.51	3.257(13)	136
C(14)–H(14)···O(10)	0.95	1-x,1-y,1-z	2.39	3.319(10)	165
C(43)–H(43)···F(17A)	0.95	1-x,-y,2-z	2.55	3.142(10)	121
C(45)–H(45)···F(38)	0.95	1-x,-y,2-z	2.50	3.259(8)	137
C(52)–H(52)···F(42)	0.95	1-x,1-y,1-z	2.50	3.243(9)	135
Complex $\mathbf{1}_{Tb}$					
C(1)–H(1)···F(43)	0.95	1-x,1-y,1-z	2.51	3.254(7)	135
C(10)–H(10)···F(47)	0.95	1-x,-y,2-z	2.51	3.261(5)	137
C(12)–H(12)···O(5)	0.95		2.50	3.091(5)	116
C(26)–H(26)···O(10)	0.95	1-x,1-y,1-z	2.37	3.302(8)	167
C(32)–H(32)···F(16B)	0.95	x,-1+y,z	2.50	3.229(9)	134
Complex $\mathbf{2}_{Eu}$					
C(3S)–H(3SB)···F(17)	0.98		2.41	3.111(19)	128
C(3S)–H(3SC)···F(14A)	0.98	1-x,-y,1-z	2.52	3.482(18)	169
C(6S)–H(6SB)···F(31A)	0.98	-1+x,y,z	2.06	2.99(5)	156
C(36)–H(36)···F(14A)	0.95	1-x,-y,1-z	2.54	3.129(11)	120
C(38)–H(38)···F(28)	0.95	x,-1+y,1+z	2.37	3.267(11)	157
C(40)–H(40)···F(28)	0.95	-x,1-y,1-z	2.48	3.196(12)	132
Complex $\mathbf{3}_{Eu}$					
C(35)–H(35)···O(7)	0.95	1-x,1-y,1-z	2.44	3.361(11)	164
C(36)–H(36)···O(5)	0.95	1-x,-y,2-z	2.54	3.321(11)	140
C(43)–H(43)···O(1)	0.95		2.54	3.400(11)	151
C(45)–H(45)···O(6)	0.95	1-x,1-y,1-z	2.52	3.043(11)	115

Table S4. Continuous Shape Measures (CShM) values for the potential coordination polyhedron of Ln and Zn atoms in $\mathbf{1}_{Eu}$, $\mathbf{2}_{Eu}$, $\mathbf{3}_{Eu}$ and $\mathbf{1}_{Tb}$.

	Zn	Ln
$\mathbf{1}_{Eu}$	Octahedron, Oh (2.792)	Square antiprism, D4d (1.131) Biaugmented trigonal prism, C2v (1.902) Triangular dodecahedron, D2d (2.772)
$\mathbf{2}_{Eu}$	Octahedron, Oh (2.577)	Square antiprism, D4d (1.223) Biaugmented trigonal prism, C2v (1.787) Triangular dodecahedron, D2d (2.601)
$\mathbf{3}_{Eu}$	Octahedron, Oh (2.990)	Biaugmented trigonal prism, C2v (3.515) Square antiprism, D4d (4.225) Triangular dodecahedron, D2d (4.273)
$\mathbf{4}_{Eu}$	Octahedron, Oh (3.190)	Biaugmented trigonal prism, C2v (1.576) Triangular dodecahedron, D2d (1.991) Square antiprism, D4d (3.115)
$\mathbf{1}_{Tb}$	Octahedron, Oh (2.774)	Square antiprism, D4d (1.108) Biaugmented trigonal prism, C2v (1.887) Triangular dodecahedron, D2d (2.423)
$\mathbf{4}_{Tb}$	Octahedron, Oh (3.110)	Biaugmented trigonal prism, C2v (1.620) Triangular dodecahedron, D2d (1.911) Square antiprism, D4d (3.561)

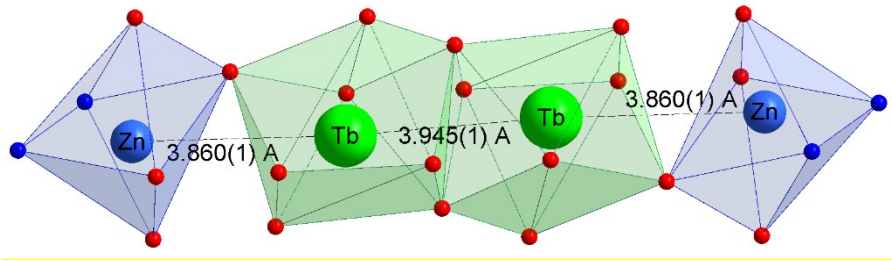


a)

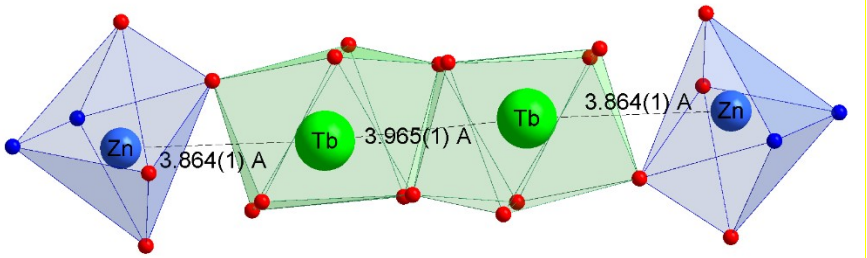


b)

Fig. S11. The main plane (Zn1-O3-O4-Eu1) in the molecules of investigated compounds on the example of compound $\mathbf{1}_{\mathbf{Eu}}$ (a) and $\mathbf{3}_{\mathbf{Eu}}$ (b). The maximum deviation from the plane was found for the O4 atom (0.054(4) Å for $\mathbf{1}_{\mathbf{Eu}}$ and 0.111(6) Å) for $\mathbf{3}_{\mathbf{Eu}}$). The maximum deviations from the plane in the molecules of the remaining compounds are within the margin of error.



a)



b)

Fig. S12. Coordination polyhedral ions of metals Zn and Eu and metal-metal distances in complexes $\mathbf{1}_{\mathbf{Tb}}$ (a) and $\mathbf{4}_{\mathbf{Tb}}$ (b).

IV. Supplementary photoluminescent data

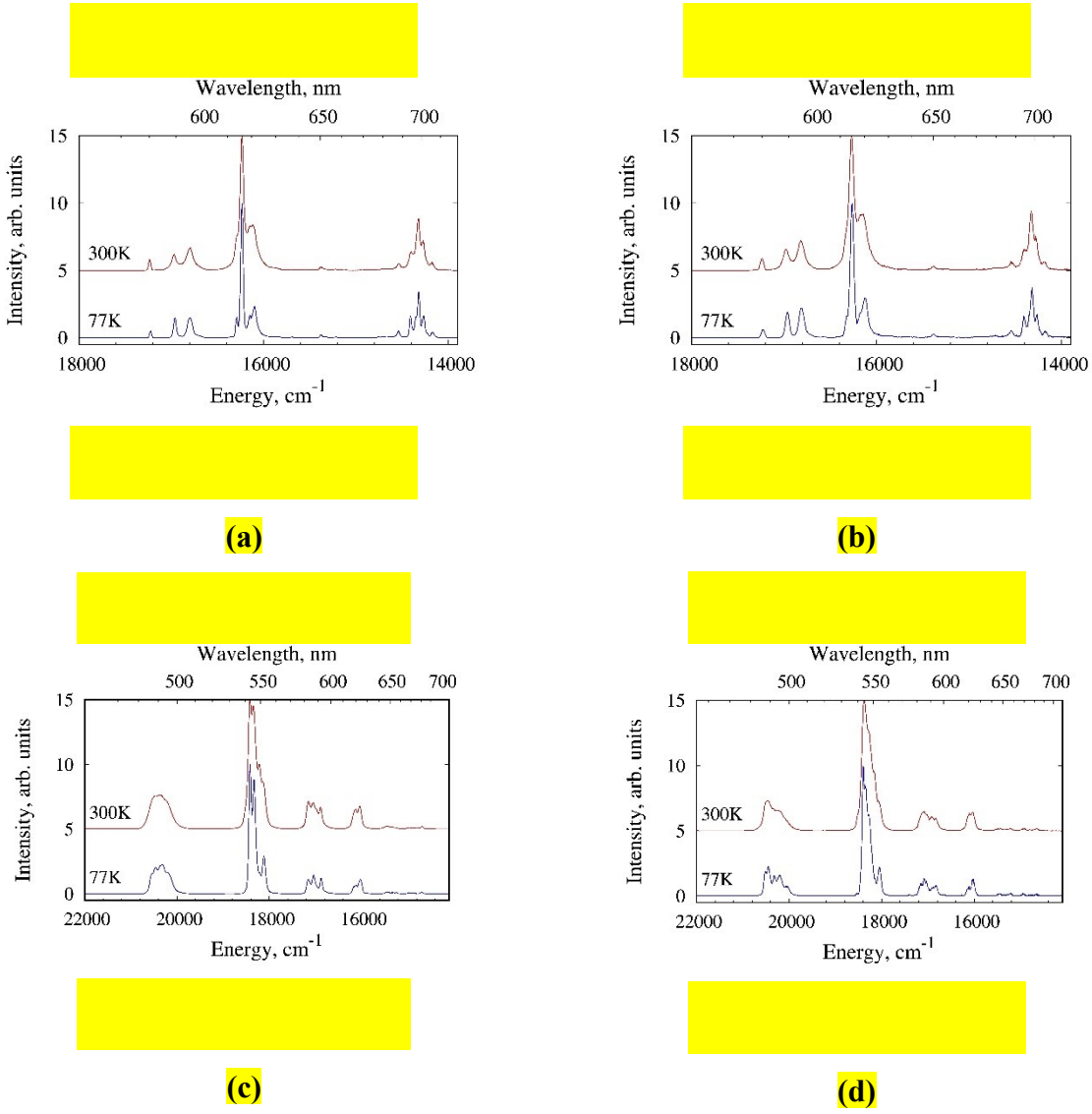
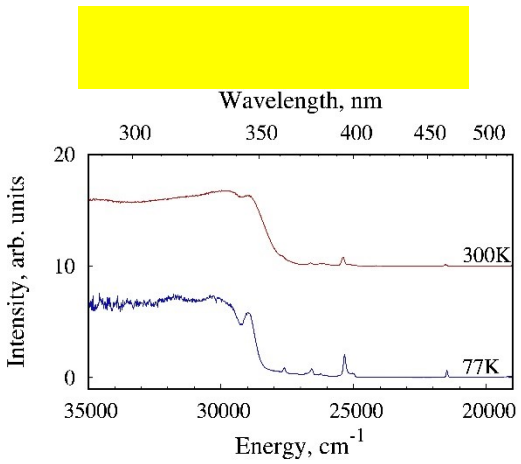
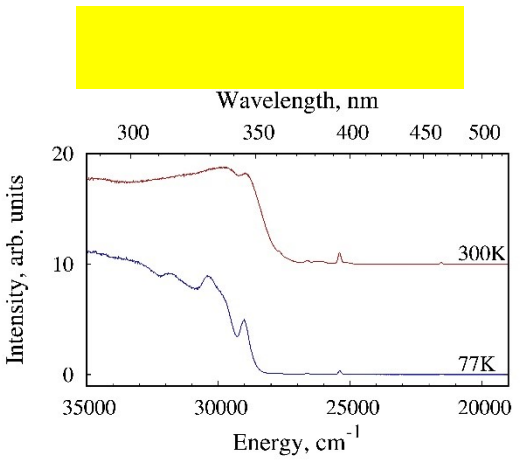


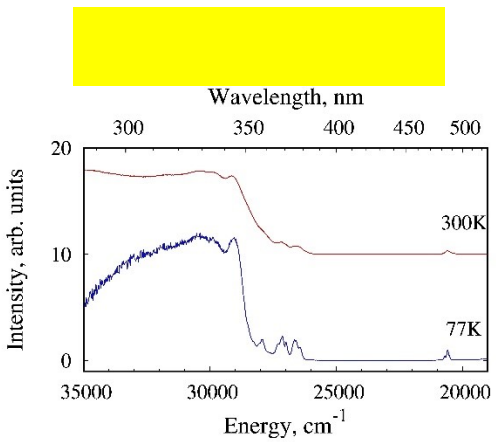
Figure S13. Emission spectra of $\mathbf{1}_{Eu}$ (a), $\mathbf{3}_{Eu}$ (b), $\mathbf{1}_{Tb}$ (c) and $\mathbf{3}_{Tb}$ (d) at 300K and 77K, λ_{ex}=280 nm.



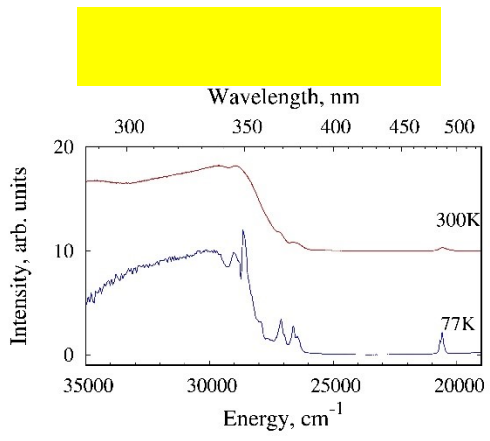
(a)



(b)



(c)



(d)

Figure S14. Excitation spectra of $\mathbf{1_{Eu}}$ (a), $\mathbf{3_{Eu}}$ (b), $\mathbf{1_{Tb}}$ (c) and $\mathbf{3_{Tb}}$ (d) at 300K and 77K, λ_{ex}=280 nm.

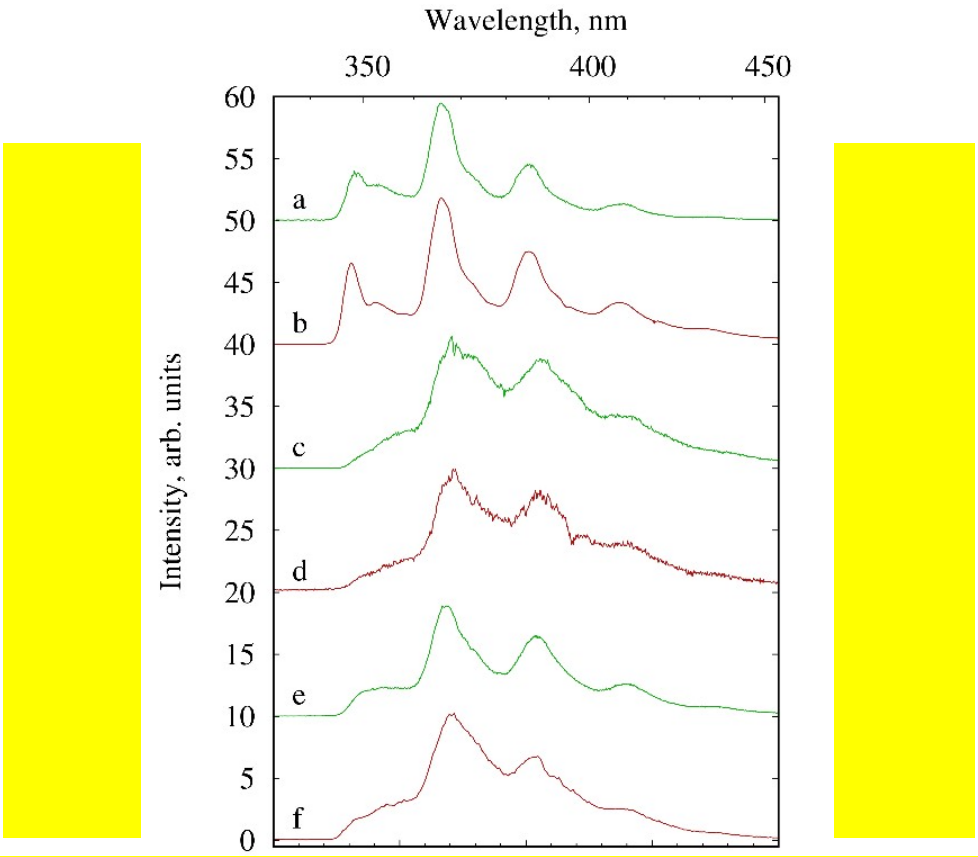


Figure S15. Emission spectra of $\mathbf{4}_{\mathbf{Tb}}$ (a), $\mathbf{4}_{\mathbf{Eu}}$ (b)(4), $\mathbf{1}_{\mathbf{Tb}}$ (c), $\mathbf{1}_{\mathbf{Eu}}$ (d), $\mathbf{3}_{\mathbf{Tb}}$ (e) and $\mathbf{3}_{\mathbf{Eu}}$ (f) at

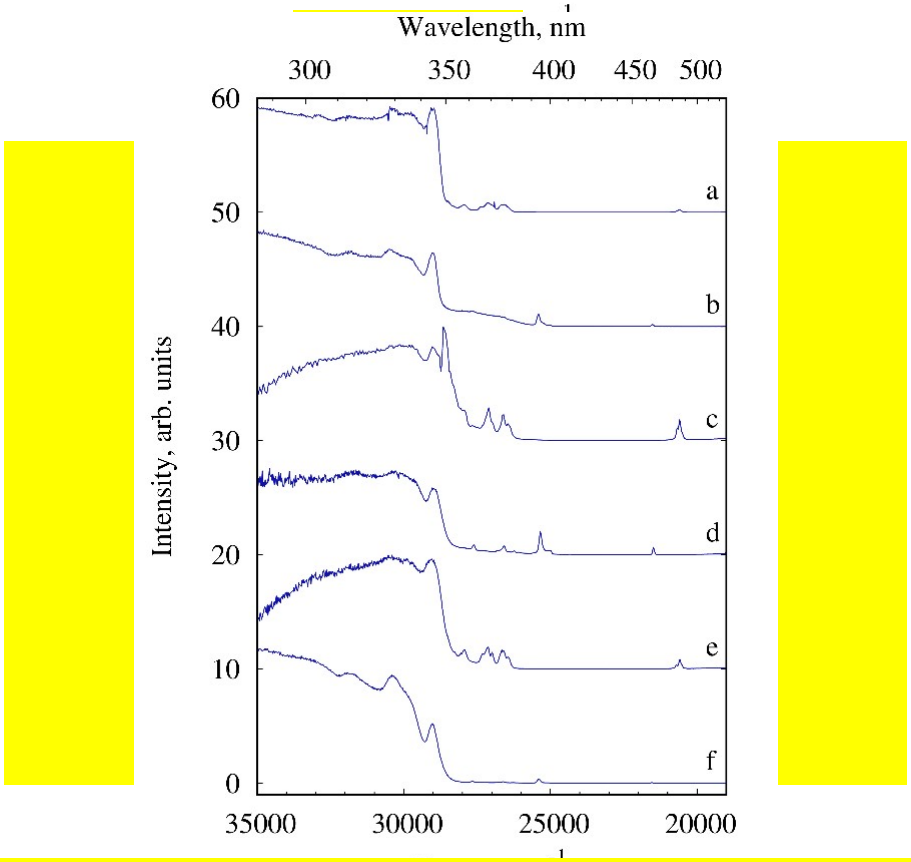


Figure S16. Excitation spectra of $\mathbf{4}_{\mathbf{Tb}}$ (a), $\mathbf{4}_{\mathbf{Eu}}$ (b)(4), $\mathbf{1}_{\mathbf{Tb}}$ (c), $\mathbf{1}_{\mathbf{Eu}}$ (d), $\mathbf{3}_{\mathbf{Tb}}$ (e) and $\mathbf{3}_{\mathbf{Eu}}$ (f) at 77K.

V. References

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