Online supplementary materials for

The effect of terminal N-donor aromatic ligands on sensitization and emission of lanthanide ions in Zn_2Ln (Ln = Eu, Tb) complexes with 4-biphenylcarboxylate anions

Stanislav N. Melnikov,[a] Igor S. Evstifeev,[a] Stanislav A. Nikolaveskii,[a*] Ivan V. Ananyev,[b] Evgenia A. Varaksina,[b,c] Ilya V. Taydakov,[b,c] Alexander S. Goloveshkin,[b] Aleksey A. Sidorov,[a] Mikhail A. Kiskin[a] and Igor L. Eremenko[a]

[a]*Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russian Federation*

[b]*Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilova St. 28, 119334, Moscow, Russian Federation*

[c]*Lebedev Institute of Physics of the Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russian Federation*

e-mail: sanikol@igic.ras.ru

Table of Contents

X-Ray powder diffraction patterns

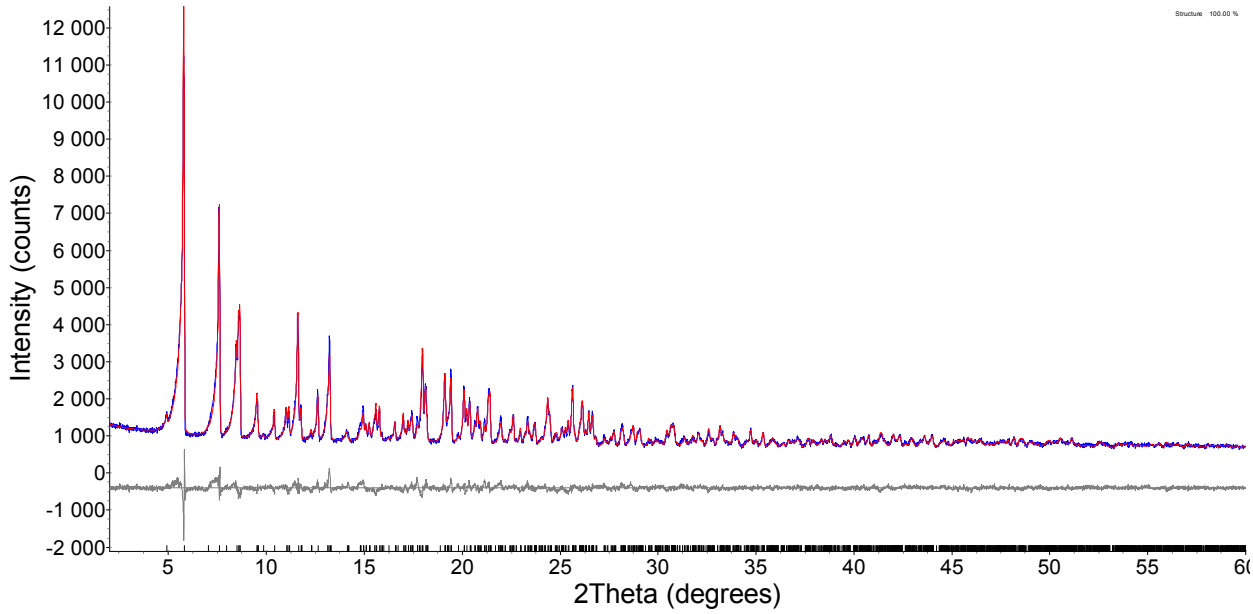

Fig. S1. Theoretical (red line) and experimental (blue line) patterns of **$Zn_2Eu\_py^{II}$** and their difference (grey line).

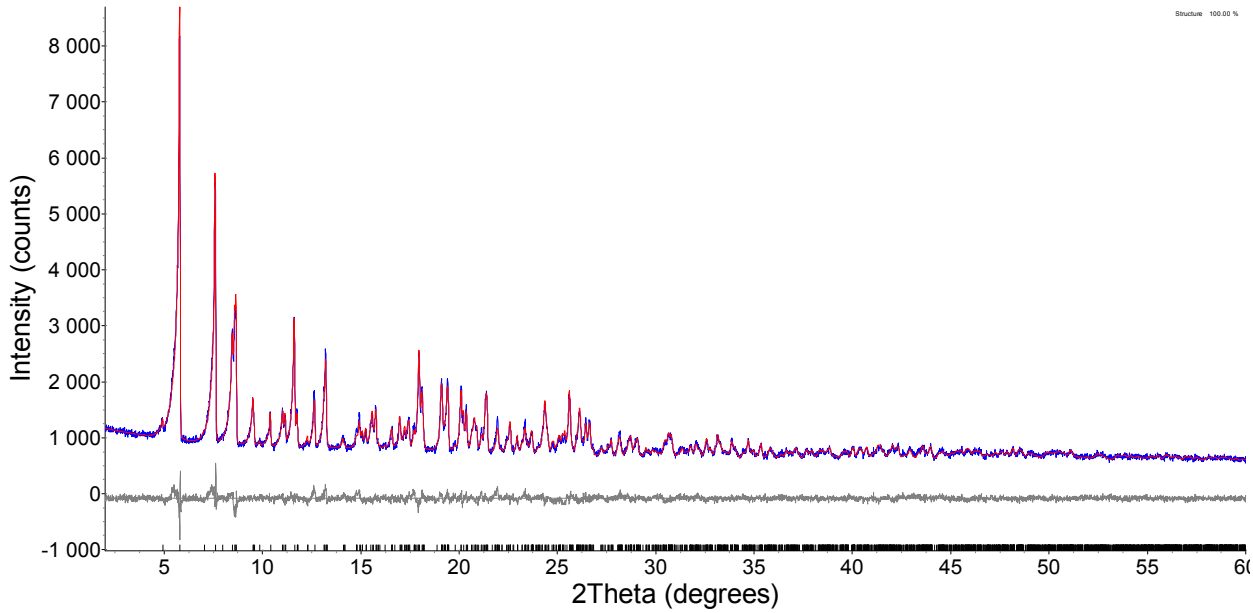

Fig. S2. Theoretical (red line) and experimental (blue line) patterns of **Zn_2Gd_py** and their difference (grey line).

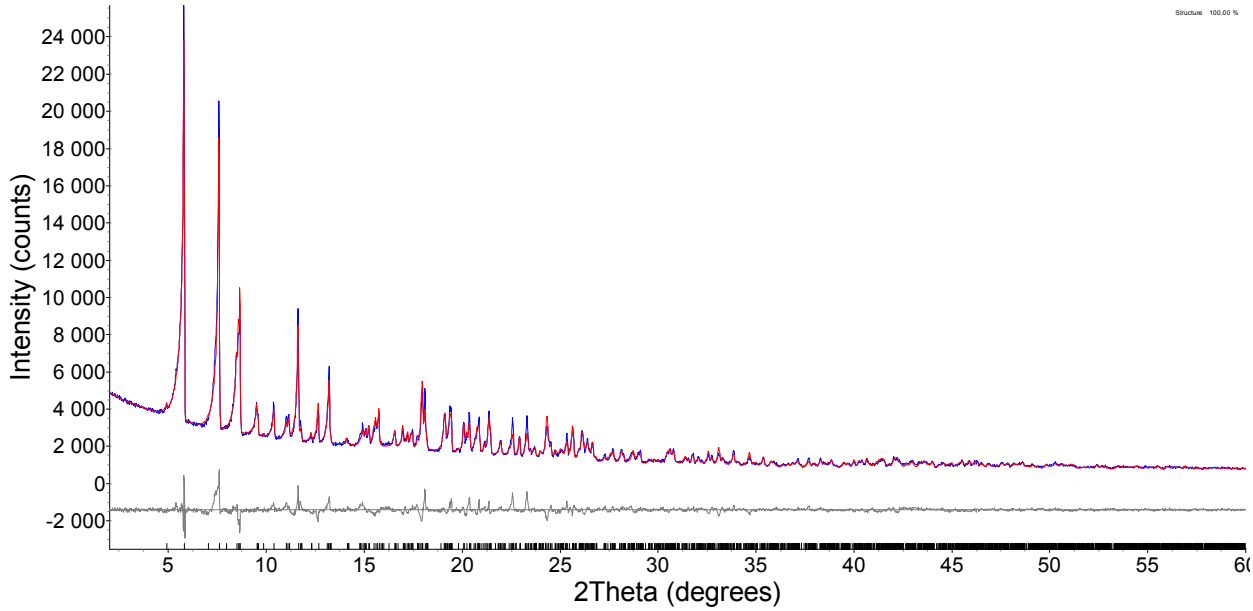

Fig. S3. Theoretical (red line) and experimental (blue line) patterns of **Zn_2Tb_py** and their difference (grey line).

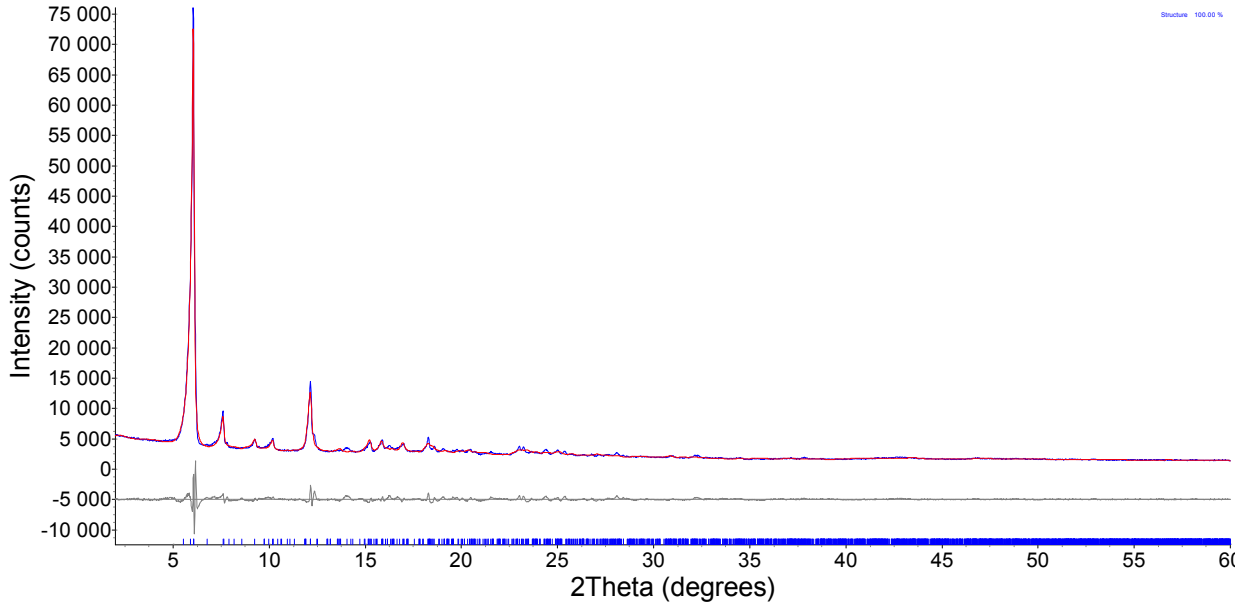

Fig. S4. Theoretical (red line) and experimental (blue line) patterns of **Zn_2Eu_lut** and their difference (grey line).

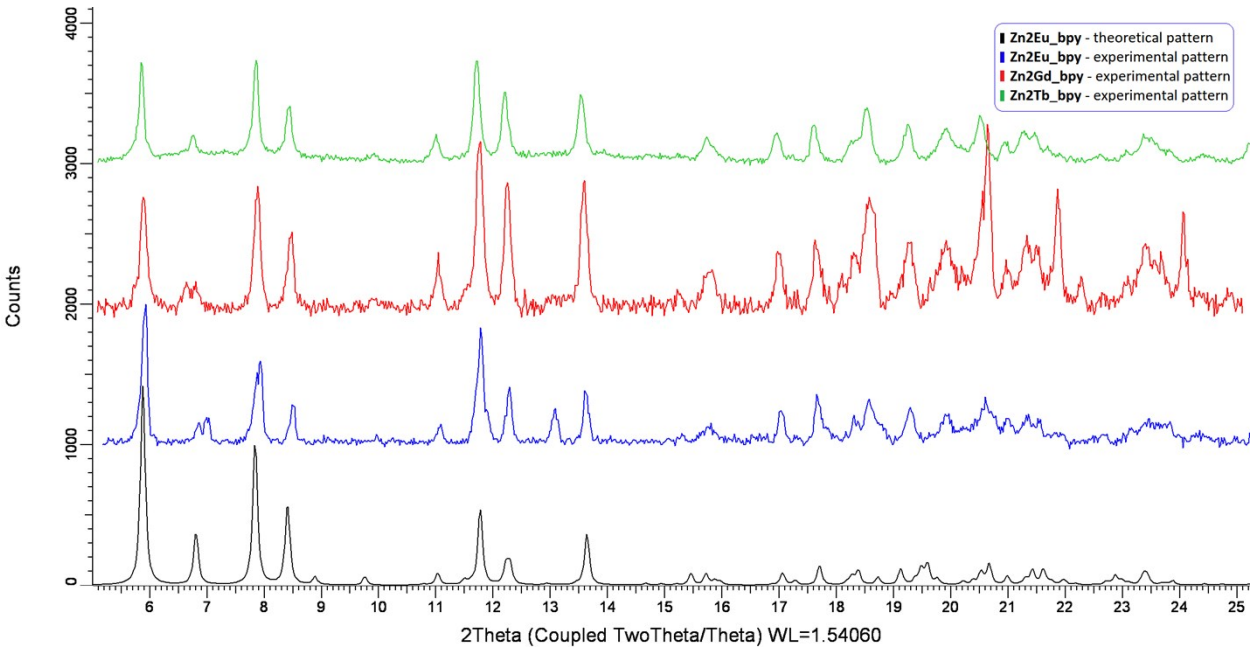

Fig. S5. Theoretical (black line) and experimental patterns of **Zn_2Eu_bpy** (blue line), **Zn_2Gd_bpy** (red line) and **Zn_2Tb_bpy** (green line).

Single Crystal X-ray Diffraction Studies

Table S1. Crystallography parameters and structure refinement details.

Sample	**Zn_2Eu_py**	**Zn_2Eu_py^{II}**	**Zn_2Tb_py**	**Zn_2Eu_lut**	**Zn_2Eu_bpy**
Formula	$C_{90}H_{67}EuN_4O_{15}Zn_2$	$C_{91}H_{68.50}EuN_{4.50}O_{15}Zn_2$	$C_{91}H_{68.50}N_{4.50}O_{15}TbZn_2$	$C_{98.50}H_{81.75}EuN_{6.25}O_{15}Zn_2$	$C_{102}H_{76}EuN_7O_{15}Zn_2$
M, g mol^{-1}	1727.17	1754.66	1754.66	1875.65	1922.39
T, K	120(2)	296.15	296.15	296.15	153(2)
Radiation source	MoKα, 0.71073 Å				
Crystal system, group	Triclinic, P-1	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, Å	16.666(5)	11.7393(5)	11.7358(14)	17.717(2)	30.502(2)
b, Å	16.983(5)	22.1195(10)	22.044(3)	28.415(4)	14.3818(11)
c, Å	17.358(5)	30.8117(13)	30.788(4)	18.868(3)	20.1905(16)
α, deg.	67.158(5)	90	90	90	90
β, deg.	75.572(5)	100.6610(10)	100.651(3)	102.100(2)	100.1210(10)
γ, deg.	88.289(5)	90	90	90	90
V, Å^3	4373(2)	7862.7(6)	7827.9(16)	9288(2)	8719.2(11)
Z	2	4	4	4	4
D_{calc}, g cm^{-3}	1.312	1.482	1.489	1.341	1.464
μ, mm^{-1}	1.316	1.566	1.573	1.245	1.329
Reflections collected	35418	66532	101766	66712	24100
Independent reflections collected	15308	19345	23359	18997	9764
Reflections with $I > 2\sigma(I)$	5971	16234	14986	9445	7558
R_{int}	0.1304	0.0352	0.1145	0.1267	0.0488
R_1 (all data)	0.2358	0.0465	0.1032	0.1739	0.0707
R_1 ($I > 2\sigma(I)$)	0.1237 Caused by bad quality of a crystal	0.0346	0.0505	0.0867	0.0507
wR_2 (all data)	0.3815	0.0849	0.1045	0.2405	0.1311
wR_2 ($I >$	0.3014	0.0798	0.0873	0.2006	0.1204

$2\sigma(I)$)					
GooF	1.014	1.036	1.010	1.032	1.032
$\theta_{min,}$ deg.	1.265	2.204	1.35	1.32	2.250
$\theta_{max,}$ deg.	25.346	28.239	30.42	26.37	27.553

Interactions analysis and contacts

Table S2. Stacking interactions in Zn_2Eu_py.

Plane A with Plane B	Angle	Centroids dist	Min Dist
C78C79C80C81C82C83 with N2C84C85C86C87C88	23.94	3.883	3.210 (N2/C82)
C34C35C36C37C38C39 with C2C3C4C5C6C7	3.44	3.830	3.301 (C2/C36)
C28C29C30C31C32C33 with C8C9C10C11C12C13	5.35	3.760	3.410 (C12/C28)

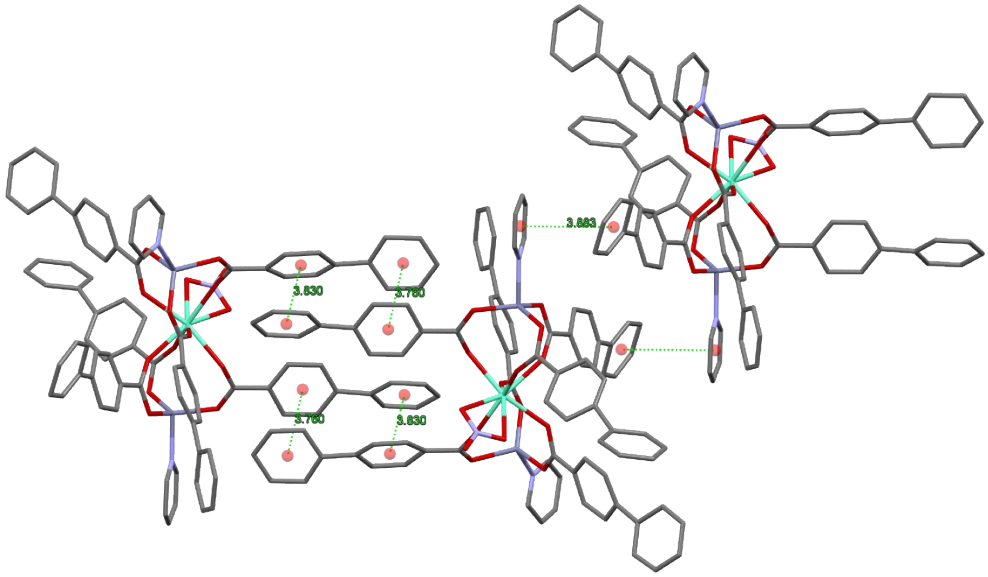

Fig. S6. Stacking interactions in **Zn_2Eu_py**.

Our analysis of the **$Zn_2Eu\_py^{II}$** and **Zn_2Tb_py** modifications did not reveal stacking interactions. The main contribution to intermolecular interactions in the packing of these crystalline modifications are caused by π-CH and O-CH-contacts. The π-π contacts between solvate MeCN molecules and phenyl-rings are also observed.

Table S3. Stacking interactions in Zn_2Eu_lut.

Plane A with Plane B	Angle	Centroids dist	Min Dist
C2C3C4C5C6C7 with C21C22C23C24C25C26	8.11	4.073	3.501 (C2/C23)
C8C9C10C11C12C13 with C15C16C17C18C19C20	8.44	3.883	3.517 (C12/C15)
C47C48C49C50C51C52 with C54C55C56C57C58C59	11.71	4.313	3.517 (C51/C59)

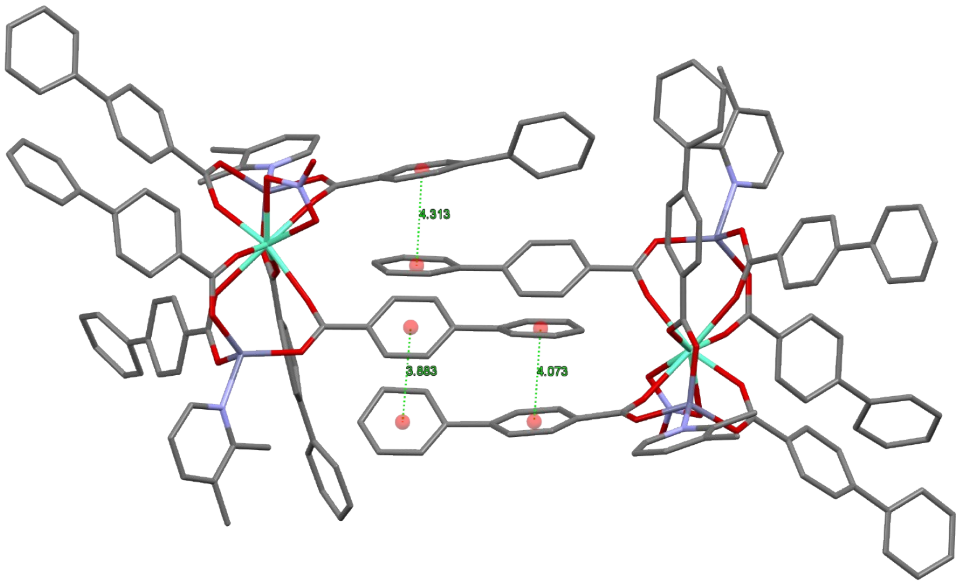

Fig. S7. Stacking interactions in **Zn_2Eu_lut**.

Table S4. Stacking interactions in Zn2Eu_bpy.

Plane A with Plane B	Angle	Centroids dist	Min Dist
N1C40C41C42C43C44 with N1C40C41C42C43C44	0	3.750	3.521 (C40/C42)
C28C29C30C31C38C39 with C32C33C34C35C36C37	35.94	4.000	3.317 (C34/C39)

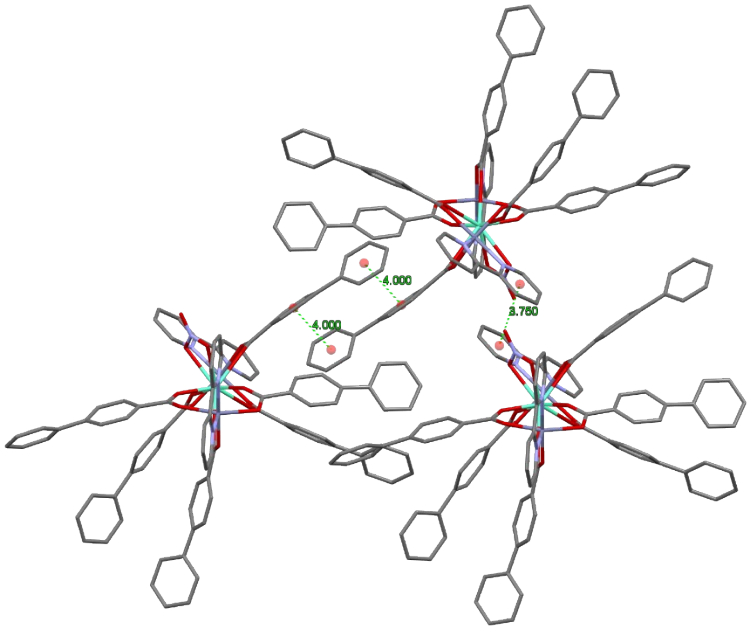

Fig. S8. Stacking interactions in **Zn_2Eu_bpy**.

Table S5. Intermolecular interactions in Zn_2Eu_py.

Number	Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length-VdW
1	C50	C18	x,y,z	x,y,-1+z	3.299	-0.101
2	C83	H23A	x,y,z	x,y,-1+z	2.743	-0.157
3	O1	H67A	x,y,z	-x,-y,3-z	2.662	-0.058
4	O6	H66A	x,y,z	-x,-y,3-z	2.638	-0.082
5	O13	H67A	x,y,z	-x,-y,3-z	2.456	-0.264
6	O15	H68A	x,y,z	-x,-y,3-z	2.718	-0.002
7	O3	H36A	x,y,z	-x,1-y,2-z	2.708	-0.012
8	C2	C36	x,y,z	-x,1-y,2-z	3.301	-0.099
9	C37	C40	x,y,z	-x,1-y,2-z	3.359	-0.041
10	H37A	C40	x,y,z	-x,1-y,2-z	2.645	-0.255
11	H37A	C41	x,y,z	-x,1-y,2-z	2.763	-0.137
12	N2	C82	x,y,z	1-x,-y,2-z	3.210	-0.040
13	C82	C84	x,y,z	1-x,-y,2-z	3.375	-0.025
14	C14	H62A	x,y,z	1-x,-y,3-z	2.800	-0.100
15	C15	H62A	x,y,z	1-x,-y,3-z	2.827	-0.073
16	C18	H61A	x,y,z	1-x,-y,3-z	2.894	-0.006
17	H24A	C71	x,y,z	1-x,-y,3-z	2.735	-0.165
18	C25	C59	x,y,z	1-x,-y,3-z	3.336	-0.064
19	C26	C59	x,y,z	1-x,-y,3-z	3.352	-0.048
20	O8	H88A	x,y,z	1-x,1-y,2-z	2.568	-0.152
21	O9	H87A	x,y,z	1-x,1-y,2-z	2.625	-0.095
22	O14	H87A	x,y,z	1-x,1-y,2-z	2.348	-0.372

Table S6. Intermolecular interactions in Zn_2Eu_py^{II}.

Number	Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length-VdW
1	H17A	C8	x,y,z	-1+x,y,z	2.889	-0.011
2	C22	H6A	x,y,z	-1+x,y,z	2.800	-0.100

3	H25A	C44	x,y,z	-1+x,y,z	2.893	-0.007
4	H63A	C46	x,y,z	-1.5-x,-1/2+y,1.5-z	2.818	-0.082
5	O14	C87	x,y,z	-1/2-x,-1/2+y,1.5-z	3.088	-0.132
6	O14	H87A	x,y,z	-1/2-x,-1/2+y,1.5-z	2.384	-0.336
7	C32	H45A	x,y,z	-1/2-x,-1/2+y,1.5-z	2.841	-0.059
8	H81A	O15	x,y,z	-1/2-x,-1/2+y,1.5-z	2.547	-0.173
9	H82A	O13	x,y,z	-1/2-x,-1/2+y,1.5-z	2.583	-0.137
10	H37A	C57	x,y,z	-1-x,2-y,1-z	2.885	-0.015
11	H37A	C60	x,y,z	-1-x,2-y,1-z	2.652	-0.248
12	H37A	C65	x,y,z	-1-x,2-y,1-z	2.740	-0.160
13	C35	C36	x,y,z	-x,2-y,1-z	3.395	-0.005
14	C35	H36A	x,y,z	-x,2-y,1-z	2.798	-0.102
15	C36	C36	x,y,z	-x,2-y,1-z	3.350	-0.050
16	C6	H13A	x,y,z	-x,2-y,2-z	2.865	-0.035
17	C30	H51A	x,y,z	-1/2+x,2.5-y,-1/2+z	2.879	-0.021
18	C53	H50A	x,y,z	-1/2+x,2.5-y,-1/2+z	2.833	-0.067
19	C44	C76	x,y,z	-1/2+x,2.5-y,1/2+z	3.378	-0.022
20	H9A	N1S	x,y,z	1/2+x,2.5-y,1/2+z	2.655	-0.095
21	C34	C4S	x,y,z	x,y,z	3.001	-0.399
22	C35	C4S	x,y,z	x,y,z	2.666	-0.734
23	C36	C4S	x,y,z	x,y,z	2.620	-0.780
24	C37	C4S	x,y,z	x,y,z	2.913	-0.487
25	C38	C4S	x,y,z	x,y,z	3.200	-0.200
26	C39	C4S	x,y,z	x,y,z	3.237	-0.163
27	H33A	N2S	x,y,z	-1-x,2-y,1-z	2.529	-0.221

Table S7. Intermolecular interactions in Zn_2Tb_py.

Number	Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length-VdW
1	H17	C34	x,y,z	-1+x,y,z	2.879	-0.021
2	C22	H32	x,y,z	-1+x,y,z	2.797	-0.103
3	H25	C57	x,y,z	-1+x,y,z	2.858	-0.042
4	H76	C59	x,y,z	-1/2-x,-1/2+y,1.5-z	2.819	-0.081
5	O13	C87	x,y,z	1/2-x,-1/2+y,1.5-z	3.077	-0.143
6	O13	H87	x,y,z	1/2-x,-1/2+y,1.5-z	2.364	-0.356
7	H81	O14	x,y,z	1/2-x,-1/2+y,1.5-z	2.529	-0.191
8	H82	O15	x,y,z	1/2-x,-1/2+y,1.5-z	2.576	-0.144
9	C4	H58	x,y,z	1/2-x,-1/2+y,1.5-z	2.852	-0.048
10	C70	H11	x,y,z	-x,1-y,1-z	2.857	-0.043
11	C78	H11	x,y,z	-x,1-y,1-z	2.860	-0.040
12	C73	H11	x,y,z	-x,1-y,1-z	2.763	-0.137
13	H49	C12	x,y,z	1-x,1-y,1-z	2.844	-0.056
14	H49	C11	x,y,z	1-x,1-y,1-z	2.895	-0.005
15	C13	C12	x,y,z	1-x,1-y,1-z	3.262	-0.138
16	C13	H12	x,y,z	1-x,1-y,1-z	2.548	-0.352
17	H13	C12	x,y,z	1-x,1-y,1-z	2.790	-0.110
18	C12	C12	x,y,z	1-x,1-y,1-z	3.261	-0.139
19	C12	H12	x,y,z	1-x,1-y,1-z	2.788	-0.112

20	C32	H39	x,y,z	1-x,1-y,2-z	2.841	-0.059
21	C66	H63	x,y,z	-1/2+x,1.5-y,-1/2+z	2.826	-0.074
22	C6	H64	x,y,z	-1/2+x,1.5-y,-1/2+z	2.889	-0.011
23	C57	C50	x,y,z	-1/2+x,1.5-y,1/2+z	3.350	-0.050
24	H35	N1S	x,y,z	1+x,y,z	2.619	-0.131
25	C51	C4S	x,y,z	x,y,z	3.264	-0.136
26	C51	H4SA	x,y,z	x,y,z	2.595	-0.305
27	C13	H4SB	x,y,z	x,y,z	2.831	-0.069
28	C12	H4SB	x,y,z	x,y,z	2.688	-0.212
29	C3	N2S	x,y,z	-x,1-y,1-z	3.232	-0.018
30	H3	N2S	x,y,z	-x,1-y,1-z	2.388	-0.362

Table S8. Intermolecular interactions in Zn_2Eu_lut.

Number	Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length-VdW
1	O13	H36	x,y,z	1/2-x,-1/2+y,1/2-z	2.619	-0.101
2	O15	H35	x,y,z	1/2-x,-1/2+y,1/2-z	2.656	-0.064
3	O15	H74	x,y,z	1/2-x,-1/2+y,1/2-z	2.687	-0.033
4	C18	H37	x,y,z	1/2-x,-1/2+y,1/2-z	2.864	-0.036
5	H32	C85	x,y,z	-x,1-y,-z	2.697	-0.203
6	O15	H88	x,y,z	-1/2+x,1/2-y,-1/2+z	2.536	-0.184
7	H81	O15	x,y,z	-1/2+x,1/2-y,-1/2+z	2.712	-0.008
8	H82	C41	x,y,z	-1/2+x,1/2-y,-1/2+z	2.864	-0.036
9	H23	O6	x,y,z	-1/2+x,1/2-y,1/2+z	2.705	-0.015
10	H24	C27	x,y,z	-1/2+x,1/2-y,1/2+z	2.701	-0.199
11	H65	C42	x,y,z	-1/2+x,1/2-y,1/2+z	2.872	-0.028
12	H65	C43	x,y,z	-1/2+x,1/2-y,1/2+z	2.794	-0.106
13	C66	H50	x,y,z	-1/2+x,1/2-y,1/2+z	2.898	-0.002
14	C32	H4SC	x,y,z	x,y,z	2.899	-0.001
15	C33	H4SC	x,y,z	x,y,z	2.816	-0.084
16	C61	H4SB	x,y,z	1/2-x,-1/2+y,1/2-z	2.624	-0.276
17	C62	C4S	x,y,z	1/2-x,-1/2+y,1/2-z	3.310	-0.090
18	C62	H4SB	x,y,z	1/2-x,-1/2+y,1/2-z	2.677	-0.223
19	H62	C4S	x,y,z	1/2-x,-1/2+y,1/2-z	2.654	-0.246
20	H77	N3S	x,y,z	-1/2+x,1/2-y,1/2+z	2.741	-0.009
21	C84	C8S	x,y,z	-x,1-y,-z	3.318	-0.082
22	C84	H8SA	x,y,z	-x,1-y,-z	2.420	-0.480
23	H84C	C8S	x,y,z	-x,1-y,-z	2.392	-0.508
24	N1S	H2SC	x,y,z	1-x,1-y,1-z	2.570	-0.180
25	H2SC	C1S	x,y,z	1-x,1-y,1-z	2.756	-0.144
26	C6S	N95	x,y,z	1/2-x,-1/2+y,1/2-z	3.076	-0.174
27	H6SC	C94	x,y,z	1/2-x,-1/2+y,1/2-z	2.804	-0.096
28	H6SC	N95	x,y,z	1/2-x,-1/2+y,1/2-z	2.119	-0.631
29	C8S	H8SB	x,y,z	-x,1-y,-z	2.810	-0.090
30	H93B	N95	x,y,z	-x,1-y,1-z	2.666	-0.084

Table S9. Intermolecular interactions in Zn_2Eu_bpy.

Number	Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length-VdW
1	H9	C32	x,y,z	x,-1+y,z	2.875	-0.025
2	H9	C37	x,y,z	x,-1+y,z	2.725	-0.175
3	C3	H47	x,y,z	x,-y,-1/2+z	2.889	-0.011
4	O4	H13	-x,y,1/2-z	x,-y,-1/2+z	2.701	-0.019
5	O8	H43	x,y,z	x,1-y,-1/2+z	2.557	-0.163
6	O6	H42	-x,y,1/2-z	x,1-y,-1/2+z	2.627	-0.093
7	C27	H42	-x,y,1/2-z	x,1-y,-1/2+z	2.618	-0.282
8	C28	H42	-x,y,1/2-z	x,1-y,-1/2+z	2.838	-0.062
9	C23	H30	x,y,z	-1/2+x,-1/2+y,z	2.893	-0.007
10	C24	H30	x,y,z	-1/2+x,-1/2+y,z	2.815	-0.085
11	H25	C33	x,y,z	-1/2+x,-1/2+y,z	2.667	-0.233
12	H25	C34	x,y,z	-1/2+x,-1/2+y,z	2.801	-0.099
13	C2	H36	-x,y,1/2-z	-1/2+x,1/2-y,-1/2+z	2.810	-0.090
14	C3	H36	-x,y,1/2-z	-1/2+x,1/2-y,-1/2+z	2.876	-0.024
15	C33	C38	-x,y,1/2-z	-1/2+x,1/2-y,-1/2+z	3.399	-0.001
16	C34	C39	-x,y,1/2-z	-1/2+x,1/2-y,-1/2+z	3.317	-0.083
17	C34	H39	-x,y,1/2-z	-1/2+x,1/2-y,-1/2+z	2.837	-0.063
18	C35	C39	-x,y,1/2-z	-1/2+x,1/2-y,-1/2+z	3.326	-0.074

Photophysical properties

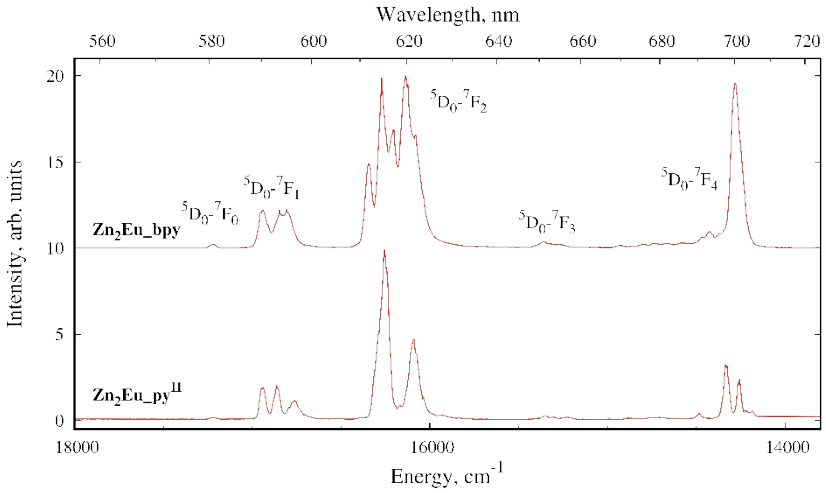

Fig. S9. Luminescence spectra of **Zn_2Eu_bpy** (a) and **Zn_2Eu_py^{II}** (b) recorded at λ_{ex} = 340 nm and T = 77 K.

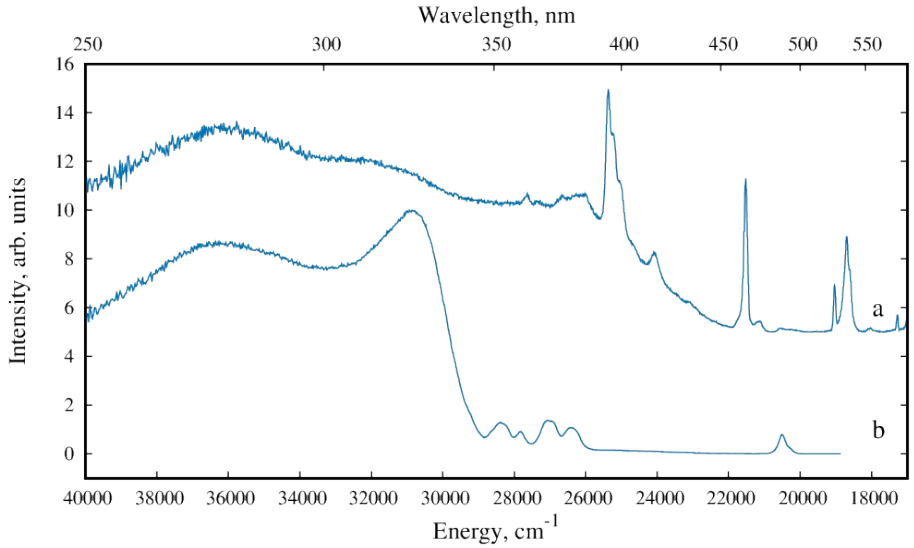

Fig. S10. Excitation spectra of $[Eu(phbz)_3]_n$ (a, λem = 615 nm) and $[Tb(phbz)_3]_n$ (b, λem = 545 nm) recorded at T = 300 K.

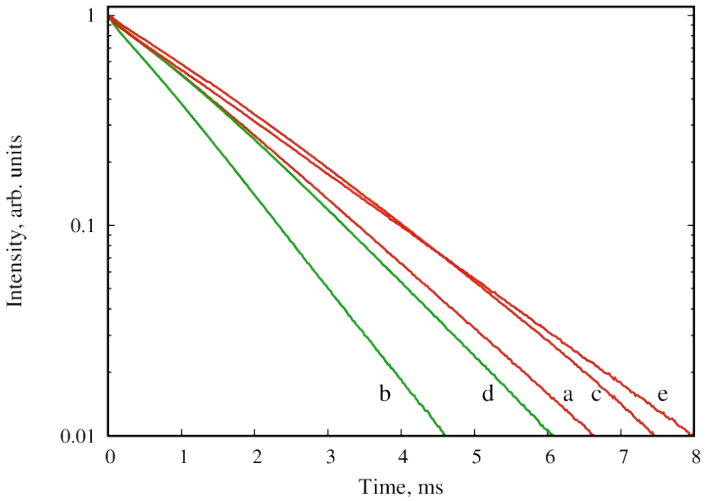

Fig. S11. Luminescence decays for **Zn_2Eu_bpy** (a), **Zn_2Tb_bpy** (b), **$Zn_2Eu\_py^{II}$** (c), **Zn_2Tb_py** (d) and **Zn_2Eu_lut** (e) at T = 300 K.