

The influence of synthesis and crystallization conditions on the structure and photoluminescent properties of {ZnLn} (Ln = Eu, Tb) complexes with benzoate anions

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I. Synthetic data

Synthesis of all obtained compounds was carried out in air using EtOH (96%), acetonitrile (99%), benzene (reagent grade), methanol (reagent grade). The following reagents were used to obtain new compounds: $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%, « Lankhit »), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, « Lankhit»), 1,10-phenanthroline monohydrate ($\text{phen} \cdot \text{H}_2\text{O}$, 99%, “Aldrich-Chemie”). $[\text{Zn}(\text{H}_2\text{O})_2(\text{bz})_2] \cdot \text{Hbz}$ and $[\text{Ln}(\text{bz})_3(\text{H}_2\text{O})_4]$ $\text{Ln} = \text{Eu}, \text{Tb}$ was synthesized using a known procedure^{S1, S2}.

Infrared spectra of the complexes were recorded in the frequency range 4000–400 cm^{-1} on a Perkin-Elmer Spectrum 65 Fourier transform infrared spectrometer equipped with Quest ATR Accessory (Specac). Elemental CHNS analysis of the synthesized compounds was carried out on a EuroEA 3000 CHNS analyzer (EuroVector, S.p.A.).

The powder diffraction patterns were obtained using the Bruker D8 Advance diffractometer with a LynxEye detector in Bragg-Brentano geometry. The sample was finely dispersed on a silicon holder with a zero background, $\lambda(\text{CuK}\alpha) = 1.54060 \text{ \AA}$. The acquired data were refined using the Topas 4 software^{S3}.

Photoluminescence excitation, emission spectra, and luminescence decays were recorded at room temperature with a Horiba-Jobin-Yvon Fluorolog-QM spectrofluorimeter equipped with a 75 W ArcTune xenon lamp and a Hamamatsu R-FL-QM-R13456 photomultiplier sensitive in the 200–980 nm emission range. The luminescence quantum yield (Φ) values were measured by absolute method, employing the same setup equipped with a G8 Spectralon[®]-covered sphere (GMP SA, Switzerland) and Hamamatsu R13456 photomultiplier. A diffusing screen was mounted inside the sphere to avoid direct irradiation of the detector. The measurements were carried out at ambient temperature. The samples in quartz cells were placed near the center of the sphere. A NIST-traceable 45 W quartz tungsten-halogen bulb emission standard (Oriel) was employed to measure the instrument response function. All QY measurements were repeated at least three times to achieve an experimental error below 15%.

Synthesis of [Zn₂Eu₂(EtOH)₂(phen)₂(bz)₈(NO₃)₂] (1)

KOH (0.032 g, 0.595 mmol) and Hbz (0.069 g, 0.595 mmol) were dissolved in 20 mL of EtOH at 50°C and stirred for 20 min. Zn(NO₃)₂·6H₂O (0.035 g, 0.119 mmol) and Eu(NO₃)₃·6H₂O (0.053 g, 0.119 mmol) were then added to the resulting colorless solution, and the reaction mixture was stirred for an additional 10 min, during which the formation of a KNO₃ precipitate was observed. The precipitate was filtered off, and phen (0.024 g, 0.119 mmol) was added to the mother liquor, followed by stirring at 50°C for 30 min. The resulting solution was left to evaporate slowly in air at room temperature. After two days, colorless crystals of compound **1** suitable for single-crystal X-ray diffraction were obtained. The crystals were separated from the mother liquor by decantation and washed with cold EtOH (*T* = ~5°C). The yield of **1** was 0.050 g (43%) based on Zn(NO₃)₂·6H₂O). Found, %: C, 51.2; H, 3.4; N, 4.0. For Eu₂Zn₂C₈₄H₆₈O₂₄N₆ calculated, %: C, 50.9; H, 3.5; N, 4.3.

IR(ATR), v/cm⁻¹: 3064 w, 2360 w, 2337 w, 1714 w, 1639 w, 1601 m, 1560 m, 1518 m, 1493 m, 1446 m, 1396 s, 1346 m, 1304 m, 1227 w, 1174 w, 1144 w, 1105 w, 1070 w, 1024 w, 939 w, 849 m, 820 w, 775 w, 715 s, 679 m, 646 m, 621 w, 561 m.

Synthesis of [Zn₂Eu(phen)₂(bz)₇]-1.5C₆H₆·0.5H₂O (2)

A solution of [Eu(bz)₃(H₂O)₄] (0.019 g, 0.033 mmol) and [Zn(H₂O)₂(bz)₂]-Hbz (0.016 g, 0.033 mmol) in 15 mL of MeOH with the addition of 10 mL C₆H₆ was stirred at 50°C for 20 min. Phen (0.007 g, 0.033 mmol) was then added to the resulting colorless solution, and the reaction mixture was stirred for an additional 10 min. The resulting solution was left to evaporate slowly in air at room temperature. After 10 days, colorless crystals of compound **2** suitable for single-crystal X-ray diffraction were obtained. The crystals were separated from the mother liquor by decantation and washed with MeCN (*T* = ~5°C). The yield of **2** was 0.011 g (41%) based on [Zn(H₂O)₂(bz)₂]-Hbz). Found, %: C, 60.8; H, 3.8; N, 3.3. For EuZn₂C₈₂H₆₁O_{14.5}N₄ calculated, %: 60.9; H, 3.8; N, 3.5.

IR(ATR), v/cm⁻¹: 3070 w, 3034 w, 1602 m, 1561 m, 1536 m, 1517 w, 1493 w, 1479 w, 1415 w, 1425 m, 1411 m, 1396 s, 1346 w, 1305 w, 1224 w, 1175 w, 1143 w, 1104 w, 1070 w, 1024 m, 939 w, 849 m, 776 m, 713 s, 673 s, 642 w, 562 w.

Synthesis of [Zn₂Tb(phen)₂(bz)₇]-4MeCN (3)

A solution of [Tb(bz)₃(H₂O)₄]-H₂O (0.020 g, 0.033 mmol) and [Zn(H₂O)₂(bz)₂]-Hbz (0.016 g, 0.033 mmol) in 15 mL of MeOH and 10 mL of MeCN was stirred at 50°C for 20 min. Phen (0.007 g, 0.033 mmol) was then added to the resulting colorless solution, and the reaction mixture was stirred for an additional 10 min. The resulting solution was left to evaporate slowly in air at room temperature. After 5 days, colorless crystals of compound **3** suitable for single-crystal X-ray diffraction were obtained. The crystals were separated from the mother liquor by decantation and washed with MeCN (*T* = ~5°C). The yield of **3** was 0.015 g (55%) based on [Zn(H₂O)₂(bz)₂]-Hbz). Found, %: C, 58.6; H, 4.0; N, 6.6. For TbZn₂C₈₁H₆₃O₁₄N₈ calculated, %: C, 58.5; H, 3.8; N, 6.7.

IR(ATR), v/cm⁻¹: 3063 w, 2986 w, 2903 w, 1602 m, 1558 m, 1398 s, 1310 m, 1223 w, 1173 w, 1140 w, 1101 w, 1068 w, 1024 w, 938 w, 848 m, 769 w, 714 s, 679 s, 645 w, 562 w, 419 m.

Supplementary PXRD data

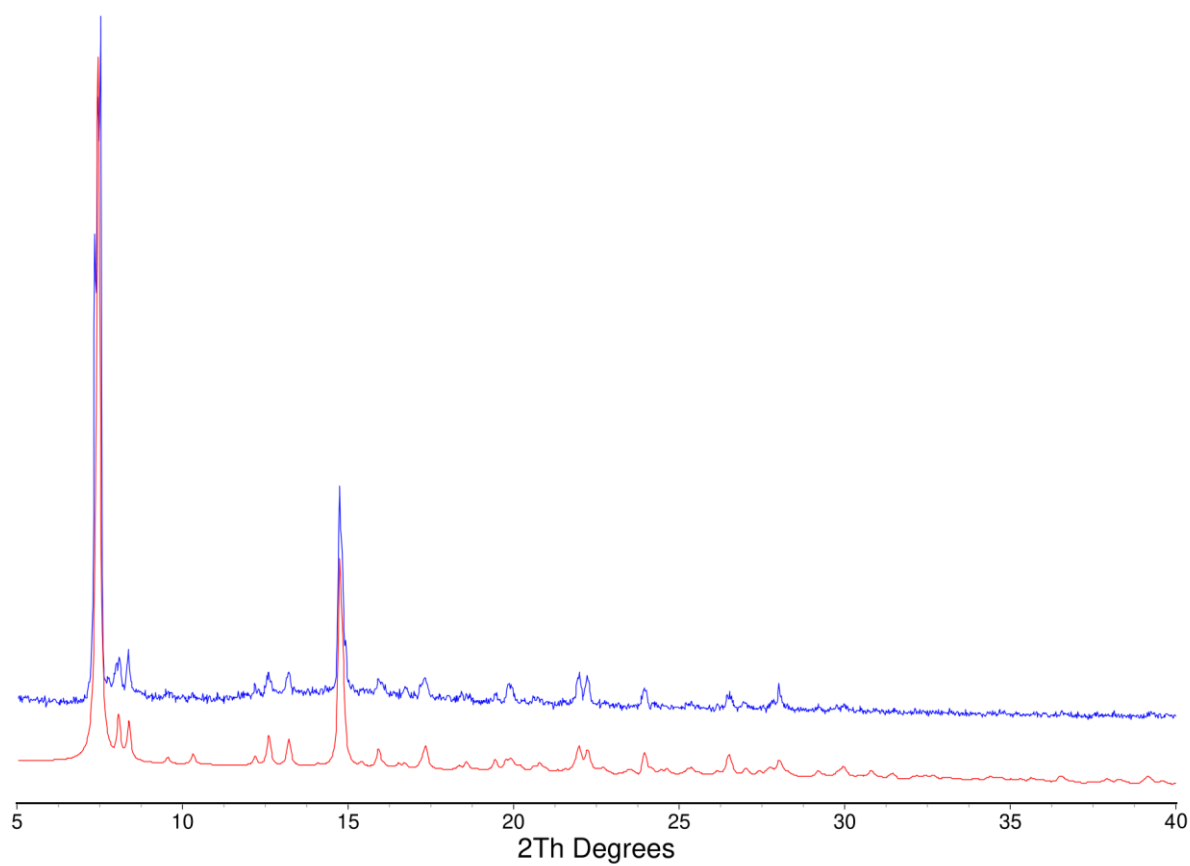


Figure S1. Theoretical (red line) and experimental (blue line) powder patterns of compound **2**.

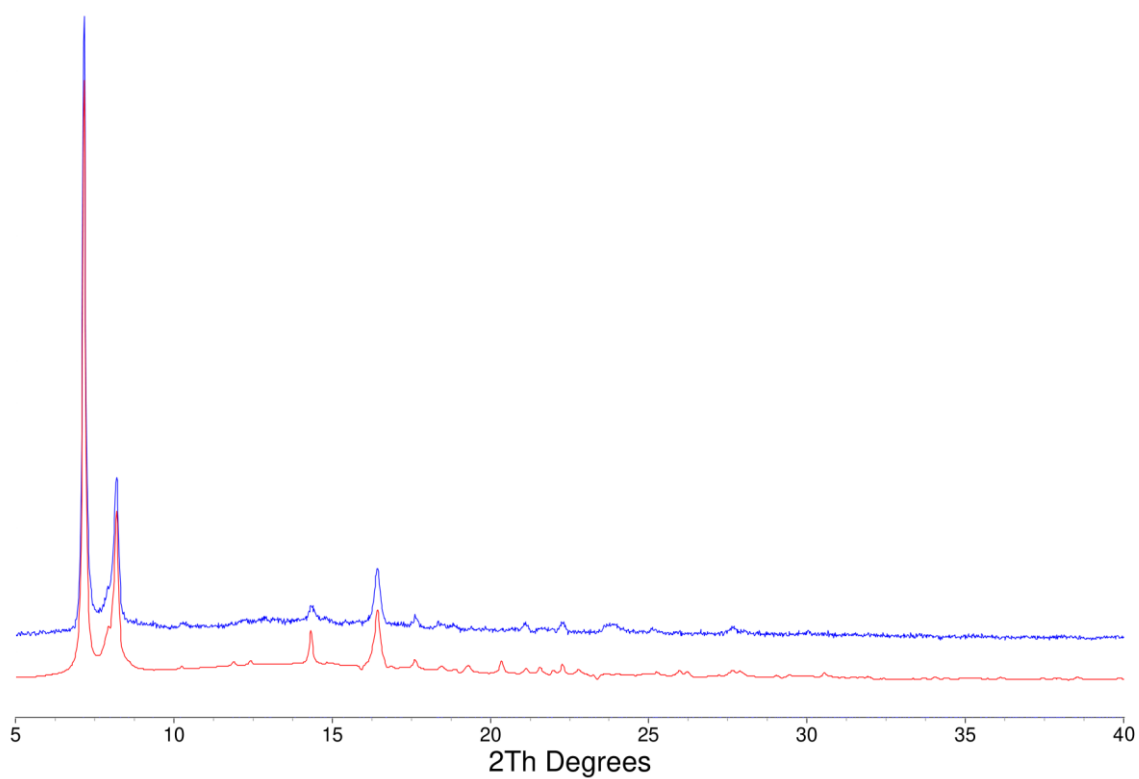
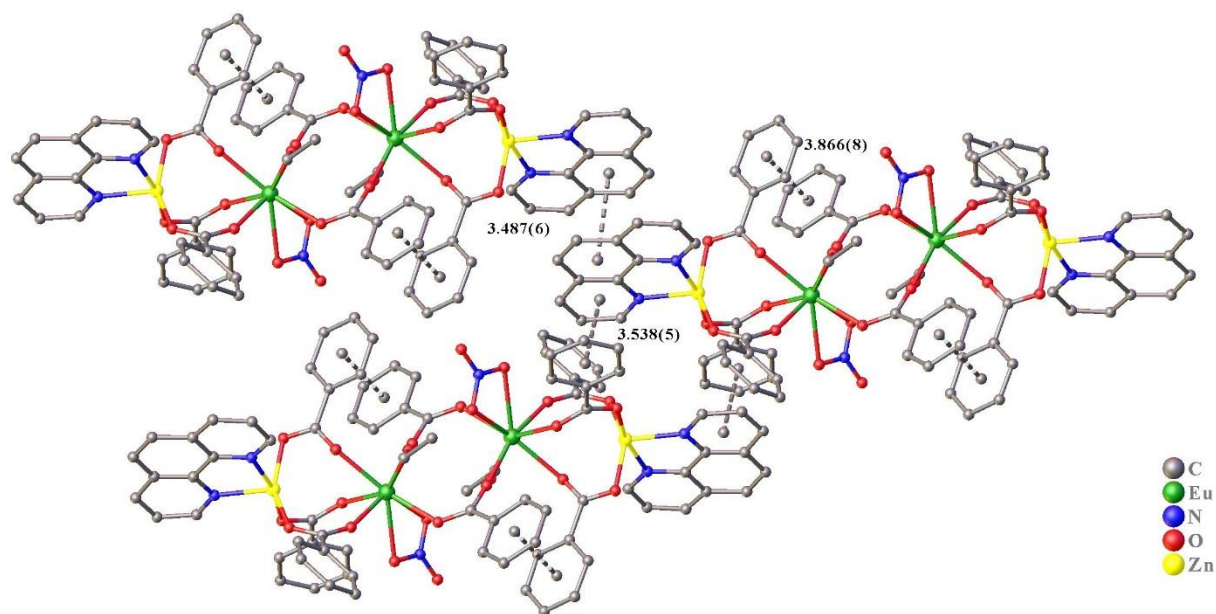
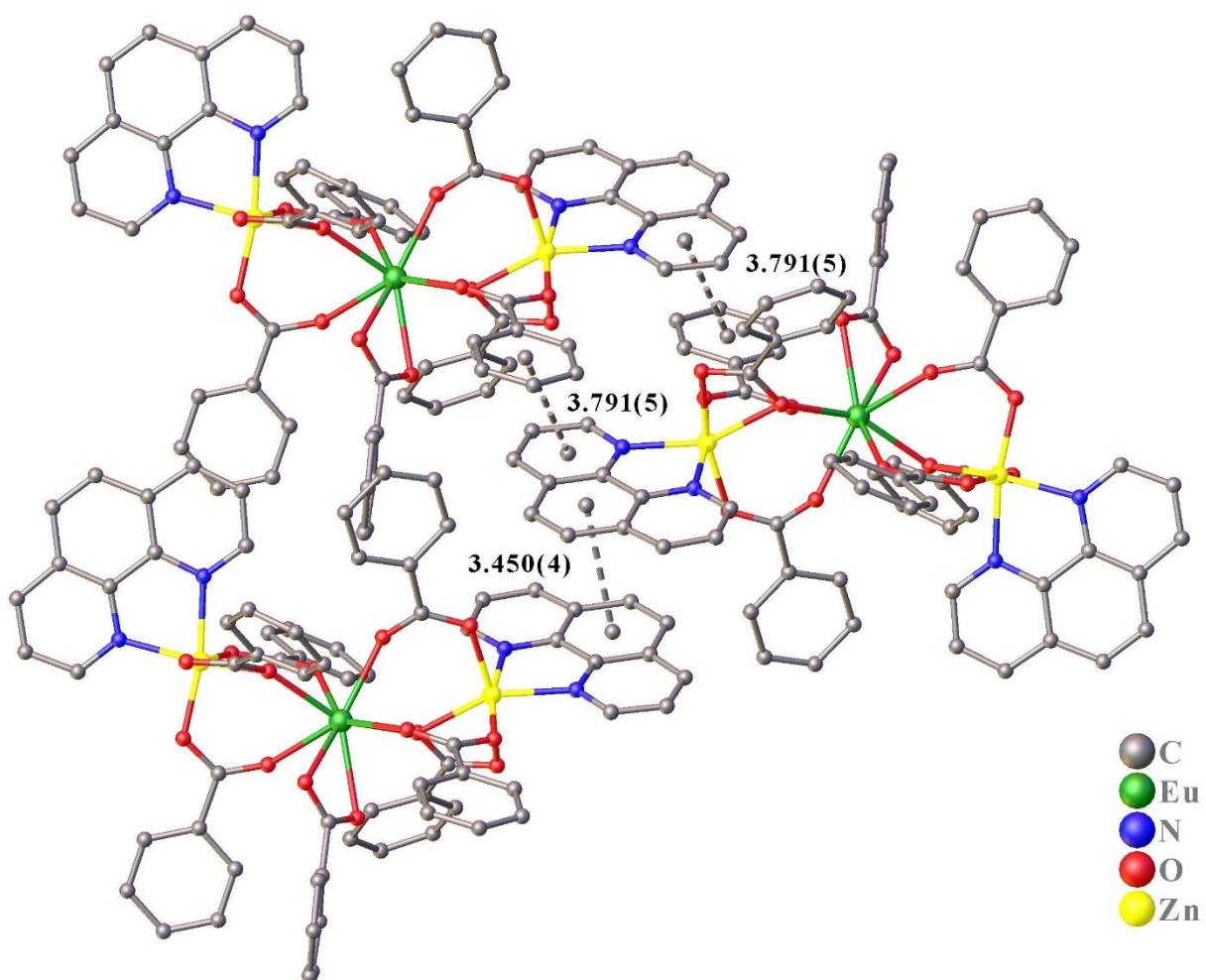


Figure S2. Theoretical (red line) and experimental (blue line) powder patterns of compound **3**.

Supplementary structural data



a)



b)

Figure S3. Fragment of the crystal packing of complexes **1** (a) and **2** (b). The dotted lines show the $\pi \cdots \pi$ interactions.

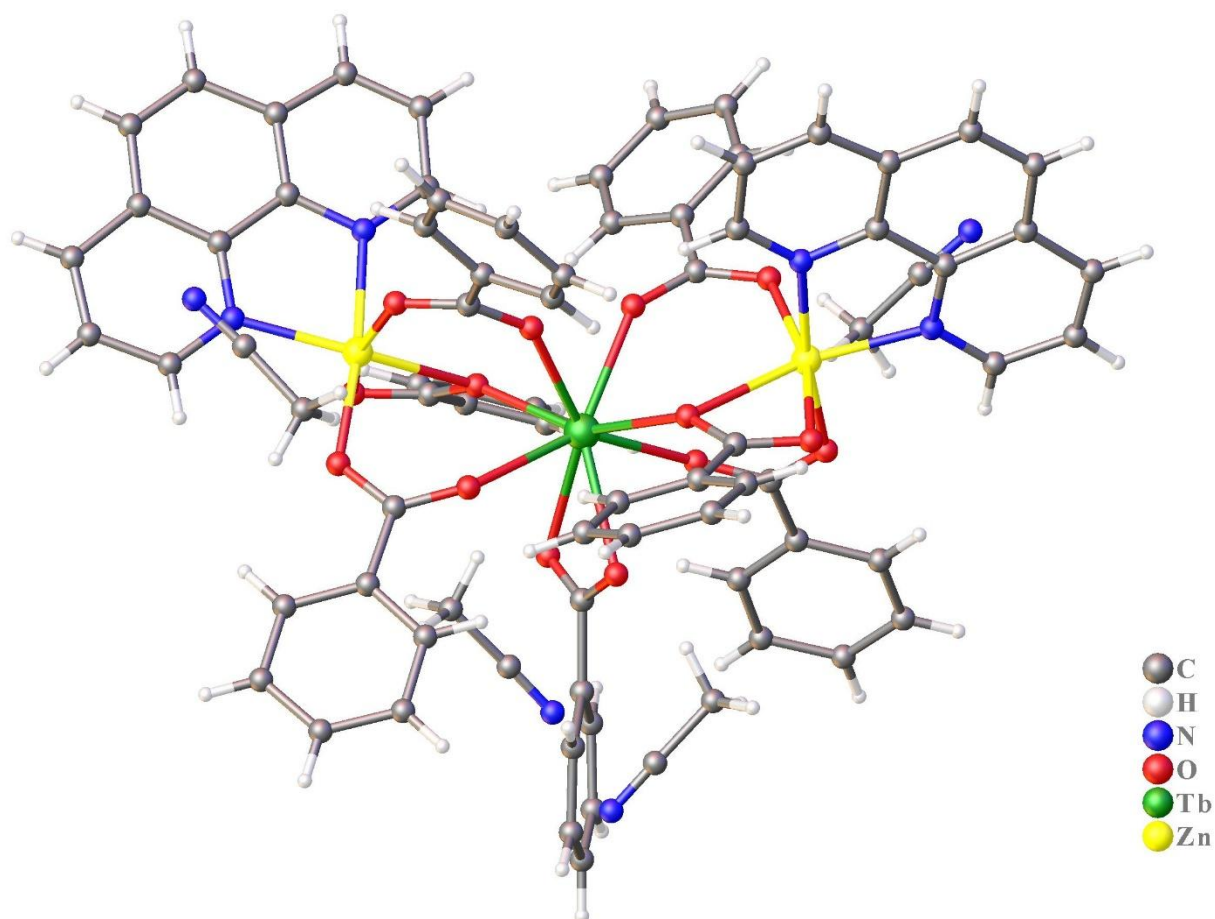


Figure S4. Structure of complex **3**.

Table S1. Basic geometric parameters of complexes **1–3** and $[\text{Zn}_2\text{Eu}_2(\text{phen})_2(\text{bz})_{10}]$ (**4**).

Bond	Distance, Å			
	1	2	3	4
Zn–N (phen)	2.110(6), 2.207(9)	2.121(4), 2.154(5)	2.106(8), 2.157(9)	2.107(6), 2.177(6)
Zn–O (bz)	2.015(6)- 2.060(5)	1.992(4)- 2.296(4)	1.993(7)- 2.372(8)	2.025(5)- 2.313(6)
Ln–O (bz)	2.259(6)- 2.431(6)	2.351(4)- 2.471(4)	2.337(7)- 2.458(7)	2.314(5)- 2.637(5)
Ln–O (NO ₃)	2.471(6), 2.573(6)	-	-	-
Ln–O (EtOH)	2.500(6)	-	-	-
Ln···Ln	4.876(1)	-	-	4.145(1)
Zn···Ln	4.030(1)	3.861(1)	3.873(1)	3.801(1)
Angle, °				
Zn···Ln···Ln	154.84(3)	-	-	146.86(2)
Zn···Ln···Zn	-	144.1(1)	142.5(1)	-

Table S2. Continuous Shape Measures (CShM) values for the potential coordination polyhedron of Eu atoms in complexes **1–4**.

	Zn	Ln
1	Trigonal bipyramid, D3h (1.686)	Biaugmented trigonal prism, C2v (2.066) Biaugmented trigonal prism J50, C2v (2.397) Triangular dodecahedron, D2d (2.726)
2	Octahedron, Oh (3.105)	Square antiprism, D4d (1.456) Biaugmented trigonal prism, C2v (2.031) Triangular dodecahedron, D2d (2.108)
3	Octahedron, Oh (3.032)	Square antiprism, D4d (1.506) Triangular dodecahedron, D2d (2.393) Biaugmented trigonal prism, C2v (2.705)
4	Octahedron, Oh (2.774)	Square antiprism, D4d (1.108) Biaugmented trigonal prism, C2v (1.887) Triangular dodecahedron, D2d (2.423)

Table S3. Hydrogen bonds in the crystal packing of complexes **1–3**.

Interaction	Distance, Å				Symmetry code
	D–H	D – H⋯A, °	H⋯A	D⋯A	
Complex 1					
O(12)–H(12)⋯O(10)	0.88(6)	147(9)	1.96(5)	2.740(9)	1-x,1-y,1-z
C(31)–H(31)⋯O(5)	0.95	117	2.53	3.080(11)	
Complex 2					
C(32)–H(32)⋯O(1SA)	0.95	159	2.44	3.34(3)	1-x,-y,1-z
Complex 3					
C(28)–H(28)⋯O(7)	0.93	137	2.58	3.318(13)	1-x,1-y,1-z

Table S4. Table of $\pi\cdots\pi$ interactions in crystal packing of complexes **1–3**.

Interactions	Cg···Cg, Å	Cg···Perp, Å	Symmetry code	α , deg
Complex 1				
phen···bz	3.538(5)	1-x,-y,2-z	3.338(4)	5.3(4)
bz···bz	3.866(8)		3.611(5)	8.3(7)
phen···phen	3.487(6)	-x,-y,2-z	3.442(4)	0.0(5)
Complex 2				
phen···phen	3.450(4)	1-x,-y,1-z	3.322(3)	0.0(3)
phen···bz	3.791(5)	1-x,1-y,1-z	3.531(3)	9.3(3)
Complex 3				
phen···phen	3.486(7)	1-x,-y,1-z	3.359(5)	0.0(6)
phen···bz	3.690(6)	1-x,1-y,1-z	3.589(5)	13.9(5)

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

Supplementary photoluminescent data

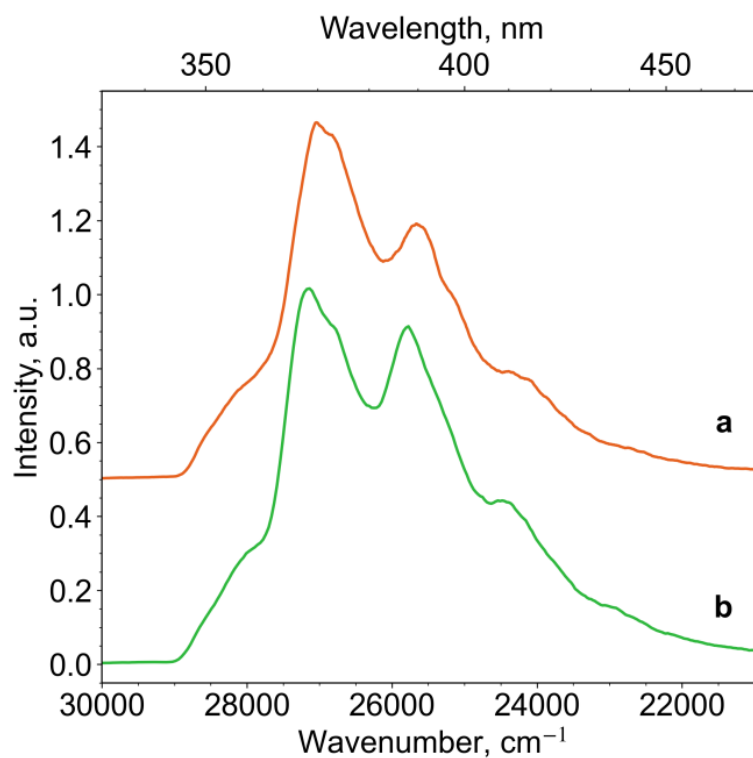


Figure S5. Luminescence spectra of complexes **2** (a) and **3** (b) in the solid state at $\lambda_{\text{ex}} = 300$ nm and $T = 77$ K.

II. References

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- S3 N. V. Y. Scarlett and I. C. Madsen, *Powder Diffr.*, 2006, **21**, 278; <https://doi.org/10.1154/1.2362855>.