Supporting information

Dinuclear Lanthanide-Lithium Complexes Based on Fluorinated β-Diketonate with Acetal Group: Magnetism and Effect of Crystal Packing on Mechanoluminescence

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S1. EXPERIMENTAL SECTION

LiL was synthesized according to the procedure described in our previous work [1]. Lanthanide salts $TbCl_3 \cdot 6H_2O$ (99.99%), $Dy(OAc)_3 \cdot 4H_2O$ (99.99%), $Dy(NO_3)_3 \cdot 5H_2O$ (99.9%) were obtained from Alfa Aesar, $EuCl_3 \cdot 6H_2O$ (99.99%) and $Eu(NO_3)_3 \cdot 5H_2O$ (99.9%) – from Merck and used without further purification.

^1H, ^{19}F and ^{13}C NMR spectra were recorded on AVANCE-500 spectrometer in methanol-d_4 using Me_4Si and C_6F_6 as internal standards. In ^1H NMR spectra the solvent residual signals observed at δ 3.32 (methanol) and 4.87 (water) ppm. IR diffuse-reflectance spectra were recorded with a Perkin-Elmer Spectrum One FTIR instrument in the range 400–4000 cm^{-1}. Fluorescence and phosphorescence spectra were recorded in the solid state on a Varian Cary Eclipse fluorescence spectrophotometer with mutually perpendicular beams. Triboluminescence was measured in "Bio/Chemiluminescence" mode. Elemental analysis was performed using a Perkin Elmer PE 2400 Series II analyzer.

X-ray diffraction studies of the single crystals of **1-6** were carried out on an Xcalibur 3 diffractometer (Oxford Diffraction, UK) with CCD detector according to standard procedure [monochromatized Mo Kα radiation; ω-scanning with a step 1° at 295(2) K]. A correction for absorption was applied empirically. The structures were solved by the direct statistical method and refined by full-matrix least-squares method (with F^2) in an anisotropic approximation for all non-hydrogen atoms except those for the disordered fragments. Hydrogen atoms were added in calculated positions and refined in an isotropic approximation in the "riding" model. All calculations were performed using Olex shell [2] and SHELX program package [3].

The main crystallographic data and experimental details are collected in Table S1. CCDC file numbers 1855391-1855396 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

The magnetic susceptibility of the polycrystalline samples was measured with a Quantum Design MPMS*XL* SQUID magnetometer in the temperature range 2-300 K in the magnetic field of 5 kOe. Diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$. Frequency dependent *ac* susceptibilities were measured under 1 kOe dc field at various temperatures.

Lithium (2Z)-1,1,1-trifluoro-5,5-dimethoxy-4-oxohex-2-en-2-olate (**LiL**). White solid, m.p. 270 °C (dec.). IR (ATR, cm^{-1}): 2999, 2947, 2841 (ν $C_{sp3}H$); 1645 s (ν_s C=O); 1515, 1481 (ν C=C);

1306, 1246 (δ C–H); 1184, 1136 s (ν_s C–F); 707 (δ CF_3). ^{1}H NMR (500 MHz) δ 1.37 s (3H, CH_3), 3.22 s (6H, OCH_3) , 5.97 s (1H, CH); ^{19}F NMR (470 MHz) δ 87.70 s (3F, CF_3); ^{13}C NMR (125 MHz) δ 12.36, 80.68, 87.72, 91.81, 111.02 (q, CF*3*, J_{CF} = 287 Hz), 163.97 (q, J = 30 Hz), 186.72.

Synthesis of Ln/Li complexes 1-6. *General procedure*. To a solution of LiL (200 mg, 0.85 mmol) in 15 mL of methanol (for **1-3**) or ethanol (for **4-6**), the Ln(III) salt (0.22 mmol) was added and the mixture was strirred at room temperature for a further 1 h. The resulting solution was slowly evaporated to afford colorless or slightly colored crystals suitable for single-crystal X-ray diffraction structure analysis.

Preparation of [(LnL_3)(LiL)(H_2O)] **4-6** *from [(LnL_3)(LiL)(MeOH)]* **1-3**. Complex **1-3** was dissolved in ethanol (5% water content) and heated under reflux until a clear solution was obtained. After cooling to room temperature, the resulting solution was slowly evaporated to afford crystalline complex **4-6**.

Preparation of [(LnL_3)(LiL)(MeOH)] **1-3** *from [(LnL_3)(LiL)(H_2O)]* **4-6**. Complex **4-6** was dissolved in methanol and heated under reflux until a clear solution was obtained. After cooling to room temperature, the resulting solution was slowly evaporated to afford crystalline complex **1-3**.

[(EuL_3)(LiL)(MeOH)] (**1**). Yield 222 mg (92%). IR (ATR, cm^{-1}): 3694, 3395 br (ν_s O–H); 2949, 2841 (ν C_{sp3}H); 1634 s (ν_s C=O); 1519, 1473, 1435 (ν C=C); 1314, 1246 (δ C–H); 1187, 1139 s (ν_s C–F); 704 (δ CF_3). Anal. Calcd for $C_{33}H_{44}F_{12}LiO_{17}Eu$: C, 36.05; H, 4.03. Found: C, 35.81; H, 3.88.

[(TbL_3)(LiL)(MeOH)] (**2**). Yield 231 mg (95%). IR (ATR, cm^{-1}): 3695, 3387 br (ν_s O–H); 2950, 2841 (ν C_{sp3}H); 1635 s (ν_s C=O); 1519, 1476 s, 1437 (ν C=C); 1315, 1247 (δ C–H); 1188, 1141 s (ν_s C–F); 705 (δ CF_3). Anal. Calcd for $C_{33}H_{44}F_{12}LiO_{17}Tb$: C, 35.82; H, 4.01. Found: C, 35.63; H, 3.79.

[(DyL_3)(LiL)(MeOH)] (**3**). Yield 215 mg (88%). IR (ATR, cm^{-1}): 3695, 3383 br (ν_s O–H); 2949, 2841 (ν C_{sp3}H); 1635 s (ν_s C=O); 1518, 1476 s, 1435 (ν C=C); 1315, 1246 (δ C–H); 1186, 1139 s (ν_s C–F); 704 (δ CF_3). Anal. Calcd for $C_{33}H_{44}F_{12}LiO_{17}Dy$: C, 35.70; H, 4.00. Found: C, 35.49; H, 3.84.

[(EuL_3)(LiL)(H_2O)] (**4**). Yield 169 mg (71%). IR (ATR, cm^{-1}): 3534, 3487 (ν_s O–H); 2998, 2958, 2841 (ν C_{sp3}H); 1633 s (ν_s C=O); 1517, 1463 s, 1435 (ν C=C); 1318, 1246 (δ C–H); 1197, 1142 s (ν_s C–F); 708 (δ CF_3). Anal. Calcd for $C_{32}H_{42}EuF_{12}LiO_{17}$: C, 35.41; H, 3.90. Found: C, 35.23; H, 3.82.

[(TbL$_3$)(LiL)(H$_2$O)] (**5**). Yield 180 mg (75%). IR (ATR, cm^{-1}): 3536, 3487 (ν_s O–H); 2998, 2951, 2841 (ν C_{sp3}H); 1634 s (ν_s C=O); 1517, 1467 s, 1436 (ν C=C); 1319, 1247 (δ C–H); 1197, 1141 s (ν_s C–F); 705 (δ CF_3). Anal. Calcd for $C_{32}H_{42}TbF_{12}LiO_{17}$: C, 35.18; H, 3.87. Found: C, 35.03; H, 3.79.

[(DyL$_3$)(LiL)(H$_2$O)] (**6**). Yield 164 mg (68%). IR (ATR, cm^{-1}): 3537, 3487 (ν_s O–H); 3002, 2969, 2841 (ν C_{sp3}H); 1634 s (ν_s C=O); 1517, 1466 s, 1436 (ν C=C); 1319, 1247 (δ C–H); 1198, 1143 s (ν_s C–F); 708 (δ CF_3). Anal. Calcd for $C_{32}H_{42}DyF_{12}LiO_{17}$: C, 35.06; H, 3.86. Found: C, 34.88; H, 3.72.

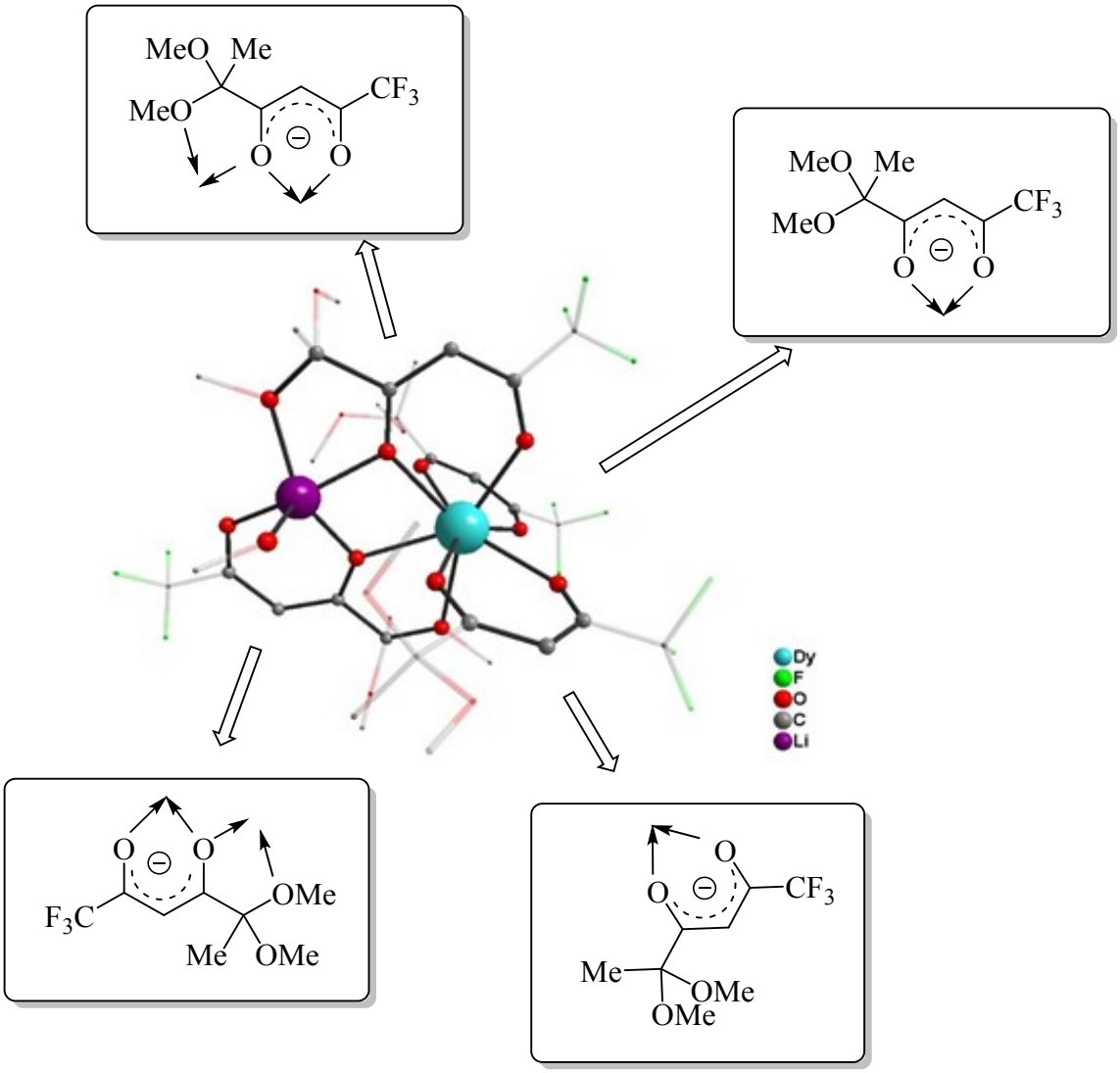
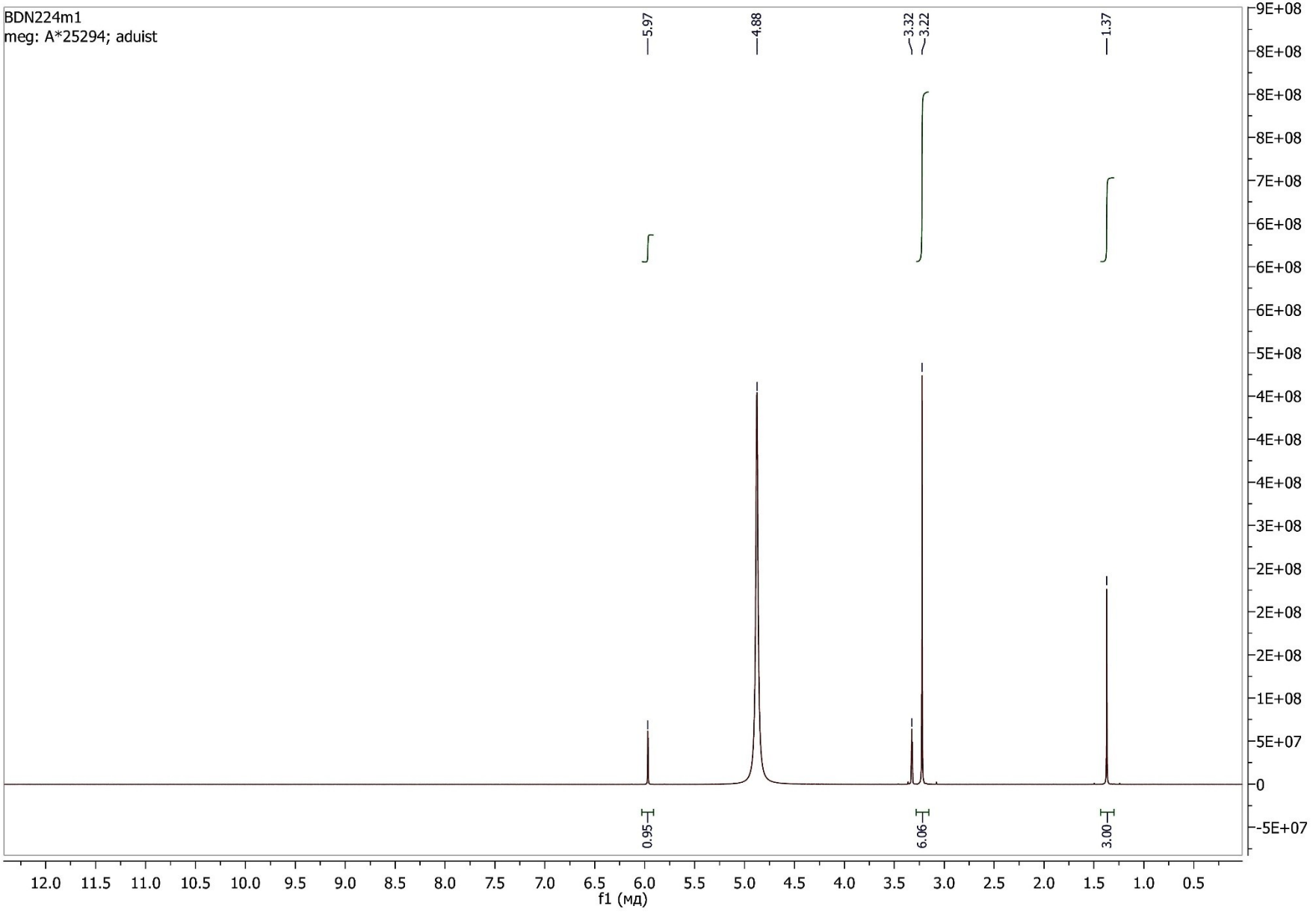
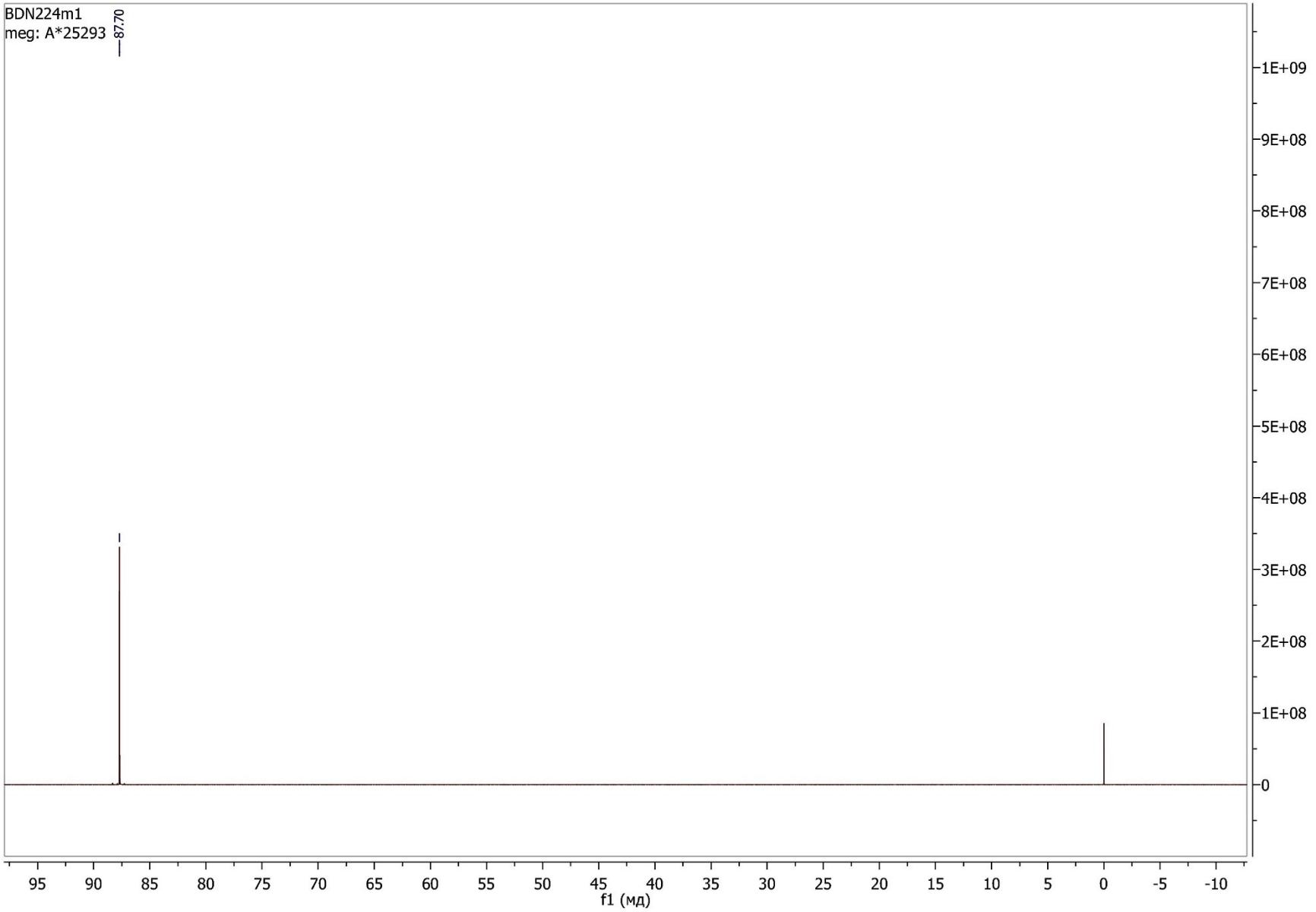


Figure S1. The core of bimetallic complex **3** and coordination mode of diketonate anion (L^-). Hydrogens are not shown for clarity

^{1}H NMR spectrum of LiL.



^{19}F NMR spectrum of LiL.



^{13}C NMR spectrum of LiL.

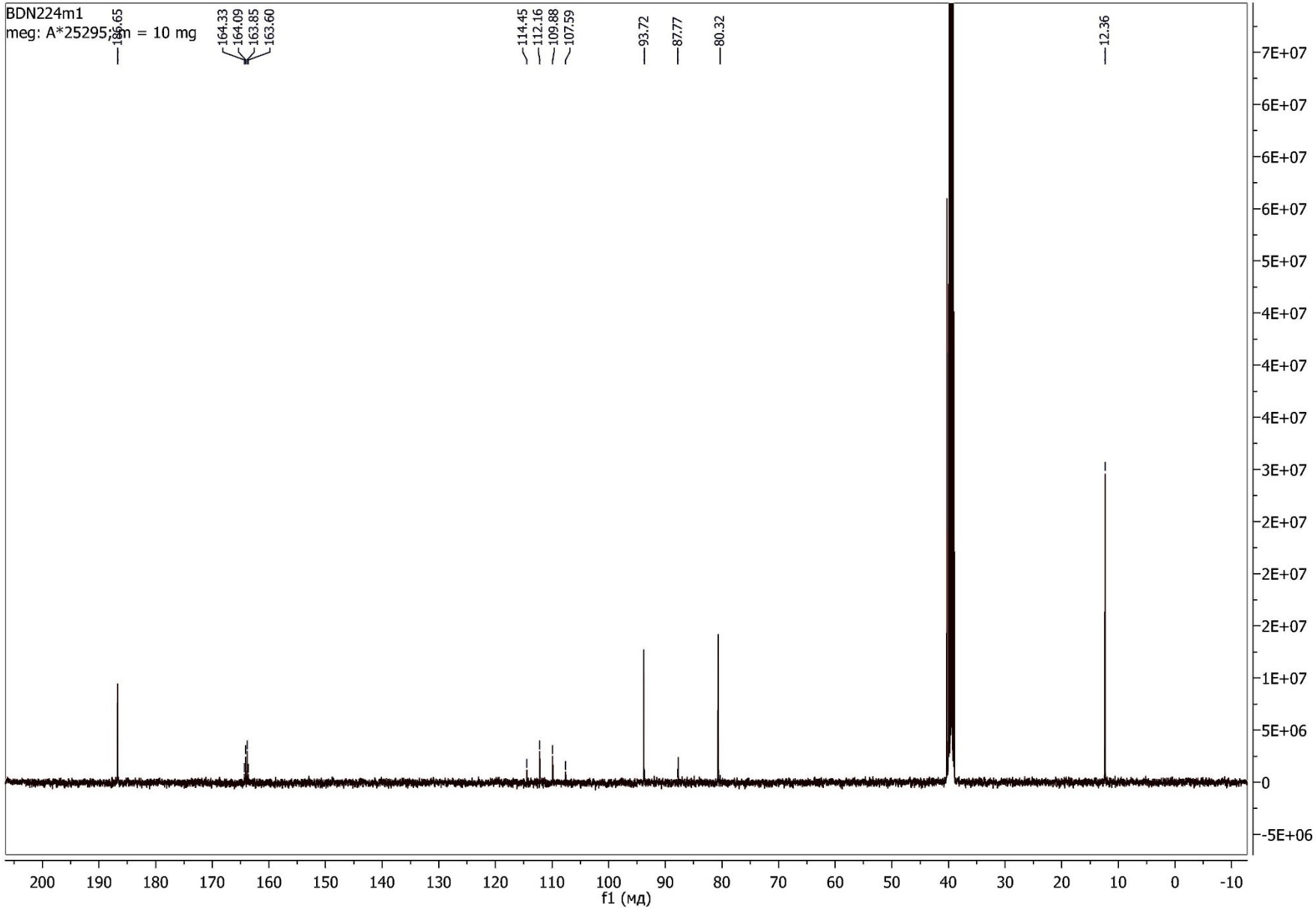


Table S1. Main Crystallographic Data and Experimental Details for **1-6**

	1 **[(EuL$_3$)LiL(MeOH]**	**2** **[(TbL$_3$)LiL(MeOH)]**	**3** **[(DyL$_3$)LiL(MeOH)]**	**4** **[(EuL$_3$)LiL(H$_2$O)]**	**5** **[(TbL$_3$)LiL(H$_2$O)]**	**6** **[(DyL$_3$)LiL(H$_2$O)]**
empirical formula	$C_{33}H_{44}EuF_{12}LiO_{17}$	$C_{33}H_{44}F_{12}LiO_{17}Tb$	$C_{33}H_{44}DyF_{12}LiO_{17}$	$C_{32}H_{42}EuF_{12}LiO_{17}$	$C_{32}H_{42}F_{12}LiO_{17}Tb$	$C_{32}H_{42}DyF_{12}LiO_{17}$
colour	colourless	colourless	colourless	light pink	colourless	colourless
crystal size, mm^3	0.26 × 0.22 × 0.17	0.25 × 0.20 × 0.15	0.34 × 0.27 × 0.18	0.25 × 0.20 × 0.15	0.25 × 0.20 × 0.15	0.25 × 0.20 × 0.15
fw	1099.58	1106.54	1110.12	1085.56	1092.52	1096.10
T, K	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	Pn	Pn	Pn	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	2	2	2	4	4	4
a, Å	12.1561(6)	12.1678(6)	12.3203(4)	17.0562(4)	17.0754(4)	17.0892(3)
b, Å	12.2251(4)	12.1989(3)	12.2197(4)	12.0115(4)	11.9683(4)	11.9719(2)
c, Å	15.8952(4)	15.8643(5)	15.8773(5)	22.3205(6)	22.2027(7)	22.2112(5)
α, deg	90	90	90	90	90	90
β, deg	94.761(3)	94.541(4)	94.512(3)	94.358(3)	94.196(3)	94.1377(19)
γ, deg	90	90	90	90	90	90
V, Å^3	2354.02(16)	2347.41(15)	2382.94(14)	4559.6(2)	4525.3(2)	4532.35(16)
d_{calc}, g·cm^{-3}	1.550	1.566	1.546	1.581	1.582	1.606
μ, mm^{-1}	1.443	1.617	1.677	1.488	1.675	1.762
F(000)	1102	1108	1108	2176	2148	2188
$2\theta_{max}$, deg	61.62	61.36	61.84	61.94	61.72	61.80
no. of rflns meased	13076	13147	11726	27583	27320	26513
no. of indep rflns (R_{int})	9182(0.032)	7815 (0.030)	8042 (0.030)	12583 (0.027)	12533 (0.033)	12473 (0.030)
no. of obsd rflns/restraints/params	7822/151/758	6641/134/707	6984/186/748	9490/122/697	8917/181/740	9424/252/747
R,[a] % ($I > 2\sigma(I)$)	0.037	0.034	0.037	0.034	0.051	0.034
R_w,[b] %	0.096	0.087	0.101	0.133	0.172	0.100
GOF[c]	1.009	1.002	1.012	1.006	1.012	1.008
residual electron density, e·Å^{-3} (d_{max}/d_{min})	0.69/-0.97	1.09/-0.693	1.01/-0.95	1.22/-0.63	4.29/-0.62	0.75/-0.62

[a] $R = \Sigma\|\|F_o| - |F_c\|\|/\sum|F_o|$. [b] $R_w = [\sum(w(Fo2 - Fc2)2)/\sum(w(\mathrm{Fo}2))]1/2$. [c] $\mathrm{GOF} = \left[\sum w(Fo2 - Fc2)2/(Nobs - Nparam)\right]1/2.$

S2. SHAPE measurements of the coordination sphere geometry for the Ln(III) and Li(I) centers in the complexes 1-6.

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*******************************************************************
 S H A P E   v2.1         Continuous Shape Measures calculation
 (c) 2013  Electronic Structure Group, Universitat de Barcelona
 Contact:  llunell@ub.edu
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Table S2. Geometry of LnO_8 polyhedron in the complexes **1-3**

Complex	S_Q(P) value†												
	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTP-8	BTRP-8	JSD-8	TT-8	ETBPY-8
[(EuL_3)(LiL)(MeOH)] (**1**)	32.224	23.882	15.732	11.619	2.161	**1.315**	12.784	29.730	2.524	1.983	3.754	12.253	24.265
[(TbL_3)(LiL)(MeOH)] (**2**)	31.873	24.097	15.933	11.669	2.036	**1.134**	12.973	29.921	2.422	1.902	3.550	12.499	24.566
[(DyL_3)(LiL)(MeOH)] (**3**)	31.531	24.083	15.916	11.640	1.908	**1.145**	13.035	30.084	2.385	1.862	3.593	12.406	24.381

OP-8	Octagon (D8h symmetry)	JETBPY-8	Johnson – Elongated triangular bipyramid J14 (D3h symmetry)
HPY-8	Heptagonal pyramid (C7v symmetry)	JBTP-8	Johnson – Biaugmented trigonal prism J50 (C2v symmetry)
HBPY-8	Hexagonal bipyramid (D6h symmetry)	BTRP-8	Johnson – Biaugmented trigonal prism J50 (C2v symmetry)
CU-8	Cube (Oh symmetry)	JSD-8	Snub disphenoid J84 (D2d symmetry)
SAPR-8	Square antiprism (D4d symmetry)	TT-8	Triakis tetrahedron (Td symmetry)
TDD-8	Triangular dodecahedron (D2d symmetry)	ETBPY-8	Elongated trigonal bipyramid (D3h symmetry)
JGBF-8	Johnson - Gyrobifastigium J26 (D2d symmetry)		

† S_Q(P) value measures the distortion of the LnO_8 coordination polyhedron from the ideal symmetry [4, 5]. S_Q(P) = 0 if the polyhedron corresponds to the ideal symmetry, while distortions of this object from the ideal symmetry will lead to higher values of the measure. Therefore, the smaller S_Q(P) value, the closer LnO_8 coordination geometry to the ideal polyhedron.

Table S3. Geometry of LiO_5 polyhedron in the complexes **1-3**

Complex	S_Q(P) value					Trigonality index τ_5*
	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5	
[(EuL_3)(LiL)(MeOH)] (**1**)	28.167	2.092	4.805	**0.689**	7.677	0.166
[(TbL_3)(LiL)(MeOH)] (**2**)	28.381	2.032	4.683	**0.668**	7.567	0.171
[(DyL_3)(LiL)(MeOH)] (**3**)	28.231	2.029	4.945	**0.679**	7.820	0.155

PP-5	Pentagon (D5h symmetry)
vOC-5	Vacant octahedron (Johnson square pyramid, J1) (C4v symmetry)
TBPY-5	Trigonal bipyramid (D3h symmetry)
SPY-5	Square pyramid (C4v symmetry)
JTBPY-5	Johnson trigonal bipyramid (J12) (D3h symmetry)

* Trigonality index τ_5 indicates the degree of LiO_5 coordination center distortion from ideal square pyramidal geometry ($\tau_5 = 0$) towards trigonal bipyramidal geometry ($\tau_5 = 1$) [6]. It is defined as $(\beta - \alpha) / 60$ where β and α are the two greatest angles of the coordinated atom.

Table S4. Geometry of LnO_8 polyhedron in the complexes **4-6**

Complex	S_Q(P) value												
	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTP-8	BTRP-8	JSD-8	TT-8	ETBPY-8
$[(EuL_3)(LiL)(H_2O)]$ (**4**)	32.600	21.611	13.153	10.167	3.777	**2.019**	11.382	26.588	3.052	2.161	4.379	10.758	22.410
$[(TbL_3)(LiL)(H_2O)]$ (**5**)	32.260	21.889	13.245	10.162	3.535	**1.867**	11.601	27.023	2.890	2.012	4.167	10.742	22.386
$[(DyL_3)(LiL)(H_2O)]$ (**6**)	32.206	21.911	13.251	10.096	3.490	**1.780**	11.746	27.098	2.854	1.991	4.058	10.663	22.396

OP-8	Octagon (D8h symmetry)	JETBPY-8	Johnson – Elongated triangular bipyramid J14 (D3h symmetry)
HPY-8	Heptagonal pyramid (C7v symmetry)	JBTP-8	Johnson – Biaugmented trigonal prism J50 (C2v symmetry)
HBPY-8	Hexagonal bipyramid (D6h symmetry)	BTRP-8	Johnson – Biaugmented trigonal prism J50 (C2v symmetry)
CU-8	Cube (Oh symmetry)	JSD-8	Snub disphenoid J84 (D2d symmetry)
SAPR-8	Square antiprism (D4d symmetry)	TT-8	Triakis tetrahedron (Td symmetry)
TDD-8	Triangular dodecahedron (D2d symmetry)	ETBPY-8	Elongated trigonal bipyramid (D3h symmetry)
JGBF-8	Johnson - Gyrobifastigium J26 (D2d symmetry)		

Table S5. Geometry of LiO_5 polyhedron in the complexes **4-6**

Complex	S_Q(P) value					Trigonality index τ_5*
	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5	
[(EuL_3)(LiL)(H_2O)] (**4**)	30.179	2.034	4.135	**0.950**	6.891	0.279
[(TbL_3)(LiL)(H_2O)] (**5**)	30.149	2.015	4.234	**0.986**	6.969	0.283
[(DyL_3)(LiL)(H_2O)] (**6**)	30.713	1.954	4.124	**0.931**	6.825	0.278

PP-5	Pentagon (D5h symmetry)
vOC-5	Vacant octahedron (Johnson square pyramid, J1) (C4v symmetry)
TBPY-5	Trigonal bipyramid (D3h symmetry)
SPY-5	Square pyramid (C4v symmetry)
JTBPY-5	Johnson trigonal bipyramid (J12) (D3h symmetry)

S3. Bond lengths (Å) of the metal coordination environments for complexes 1-6

Table S6. Selected bond lengths (Å) for **1-3**

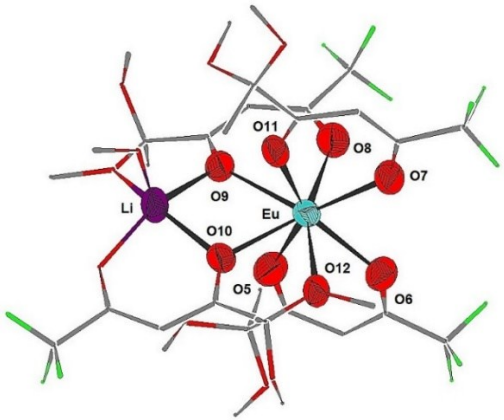
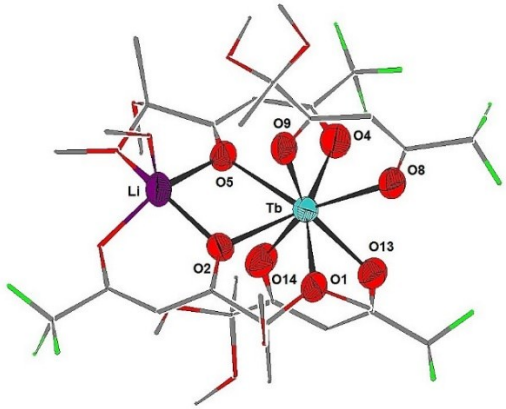
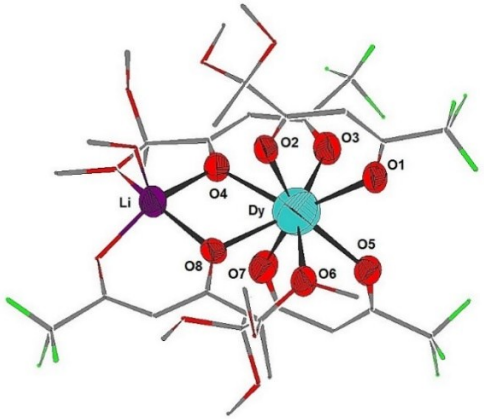
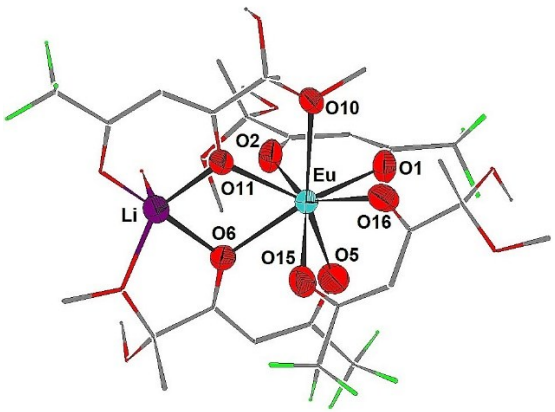
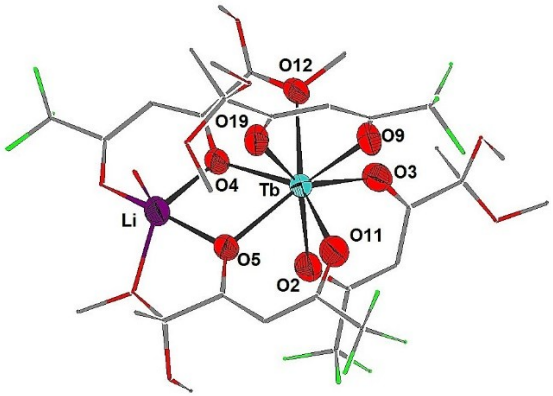
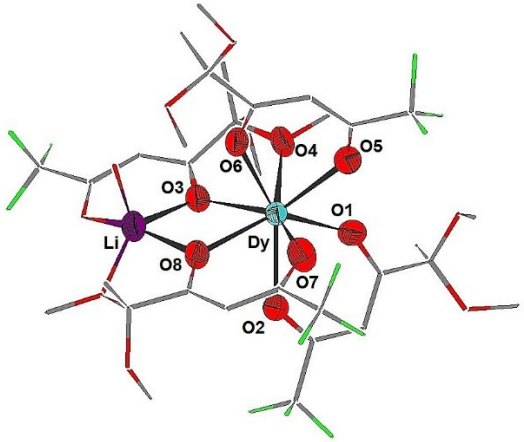
[(EuL_3)(LiL)(MeOH)] (**1**)		[(TbL_3)(LiL)(MeOH)] (**2**)		[(DyL_3)(LiL)(MeOH)] (**3**)	
					
Bond	Å	Bond	Å	Bond	Å
Eu-O7	2.349(4)	Tb-O8	2.334(4)	Dy-O1	2.323(5)
Eu-O11	2.366(4)	Tb-O9	2.340(4)	Dy-O2	2.336(5)
Eu-O8	2.334(5)	Tb-O4	2.306(5)	Dy-O3	2.298(5)
Eu-O9	2.426(3)	Tb-O5	2.404(4)	Dy-O4	2.395(4)
Eu-O6	2.358(4)	Tb-O13	2.337(4)	Dy-O5	2.323(5)
Eu-O5	2.398(4)	Tb-O14	2.371(5)	Dy-O7	2.357(5)
Eu-O10	2.362(4)	Tb-O2	2.350(4)	Dy-O8	2.340(4)
Eu-O12	2.533(4)	Tb-O1	2.505(4)	Dy-O6	2.504(4)
Eu ⋯ Eu	10.5273(5)	Tb ⋯ Tb	10.5516(5)	Dy ⋯ Dy	10.6150(5)
Eu ⋯Li	3.498(10)	Tb ⋯ Li	3.471(10)	Dy ⋯Li	3.452(13)

Table S7. Selected bond lengths (Å) for **4-6**

[(EuL_3)(LiL)(H_2O)] (**4**)		[(TbL_3)(LiL)(H_2O)] (**5**)		[(DyL_3)(LiL)(H_2O)] (**6**)	
					
Bond	Å	Bond	Å	Bond	Å
Eu-O15	2.369(3)	Tb-O2	2.348(2)	Dy-O2	2.342(2)
Eu-O16	2.346(2)	Tb-O3	2.320(3)	Dy-O1	2.311(2)
Eu-O5	2.361(3)	Tb-O11	2.328(3)	Dy-O7	2.319(2)
Eu-O6	2.412(2)	Tb-O5	2.389(2)	Dy-O8	2.383(2)
Eu-O1	2.346(3)	Tb-O9	2.321(2)	Dy-O5	2.316(2)
Eu-O2	2.403(2)	Tb-O19	2.375(2)	Dy-O6	2.363(2)
Eu-O11	2.361(2)	Tb-O4	2.330(2)	Dy-O3	2.321(2)
Eu-O10	2.523(2)	Tb-O12	2.503(2)	Dy-O4	2.496(2)
Eu ⋯ Eu	9.6133(3)	Tb ⋯ Tb	9.6232(3)	Dy ⋯ Dy	9.6333(3)
Eu ⋯Li	3.508(6)	Tb ⋯ Li	3.494(6)	Dy ⋯Li	3.482(5)

S4. H-bond parameters for complexes 4-6

Table S8. Hydrogen-bond geometry (distances in Å, angles in degrees) in complexes **4-6**

Complex	Bond type	*D*–H···A	D–H	H···*A*	*D*···*A*	∠*D*–H···A	Symmetry
4	intra[a]	O20–H20B···O2	0.862	2.235	3.023(4)	152	–
	intra	O20–H20B···O4	0.862	2.311	2.966(4)	133	–
	inter[b]	O20–H20A···O9′	0.862	2.307	2.862(7)	122	-x, y+1/2, -z+1/2
5	intra	O1–H1B···O17	0.896	2.284	2.944(4)	130	–
	intra	O1–H1B···O19	0.896	2.218	3.023(4)	149	–
	inter	O1–H1A···O15′	0.902	2.138	2.771(8)	127	-x, y-1/2, -z+1/2
6	intra	O9–H9B···O6	0.862	2.342	3.031(3)	137	–
	intra	O9–H9B···O17	0.862	2.213	2.950(4)	143	–
	inter	O9–H9A···O19′	0.862	2.425	2.769(7)	104	-x+1, y-1/2, -z+1/2

[a] Intramolecular H-bond.

[b] Intermolecular H-bond

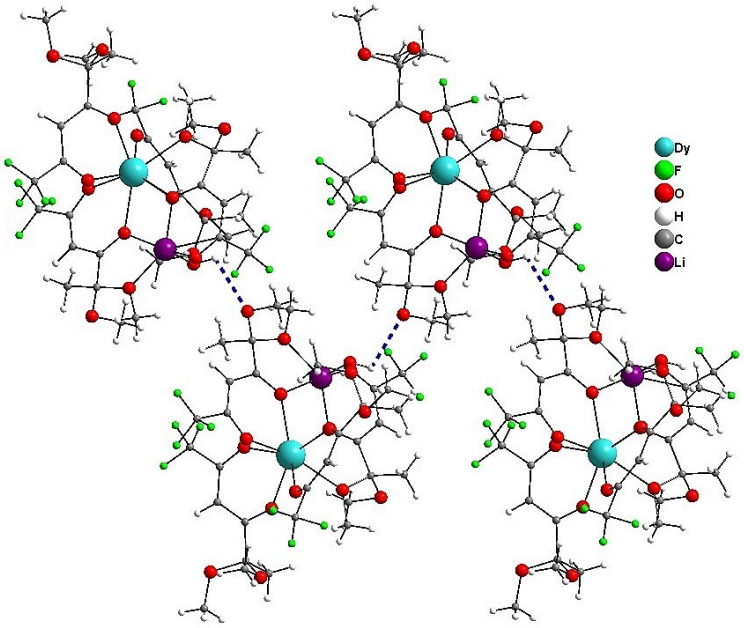


Figure S2. The 2D H-bonded framework in the crystal structure of **6**. Intermolecular hydrogen bonds are shown as blue dashed lines.

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S5. Luminescence of complexes 1-3

Table S9. Photophysical Data for complexes **1-6**

Complex	Transition	λ (nm)	% of total emission	Lifetimes (μs) of solids
$[(EuL_3)(LiL)(MeOH)]$ (**1**)	$^5D_0 \rightarrow {}^7F_0$ $^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_4$	580 592 612 652 702	0.8 5.9 87.9 2.3 3.1	732
$[(EuL_3)(LiL)(H_2O)]$ (**4**)		580 593 613 652 704	1.2 4.2 90.1 1.8 2.7	642
$[(TbL_3)(LiL)(MeOH)]$ (**2**)	$^5D_4 \rightarrow {}^7F_6$ $^5D_4 \rightarrow {}^7F_5$ $^5D_4 \rightarrow {}^7F_4$ $^5D_4 \rightarrow {}^7F_3$ $^5D_4 \rightarrow {}^7F_2$	490 546 582 621 650	23.0 66.3 6.0 3.6 1.1	648
$[(TbL_3)(LiL)(H_2O)]$ (**5**)		490 546 583 621 652	21.8 67.6 5.6 3.8 1.3	520
$[(DyL_3)(LiL)(MeOH)]$ (**3**)	$^4F_{9/2} \rightarrow {}^6H_{15/2}$ $^4F_{9/2} \rightarrow {}^6H_{13/2}$ $^4F_{9/2} \rightarrow {}^6H_{11/2}$ $^4F_{9/2} \rightarrow {}^6F_{11/2} + {}^6H_{9/2}$	481 576 664 752	21.3 74.2 3.4 1.1	14
$[(DyL_3)(LiL)(H_2O)]$ (**6**)		481 574 664 751	15.7 79.7 3.5 1.0	21

Triboluminescence of complexes 1-3

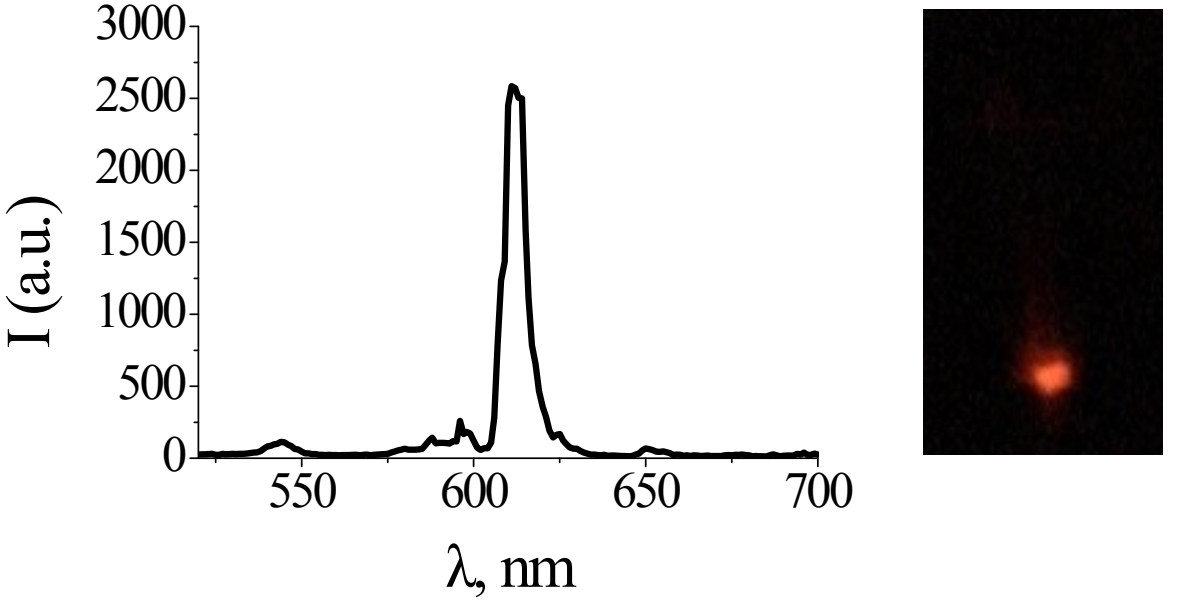


Figure S3. Triboluminescence spectrum of [(EuL_3)(LiL)(MeOH)] **1**

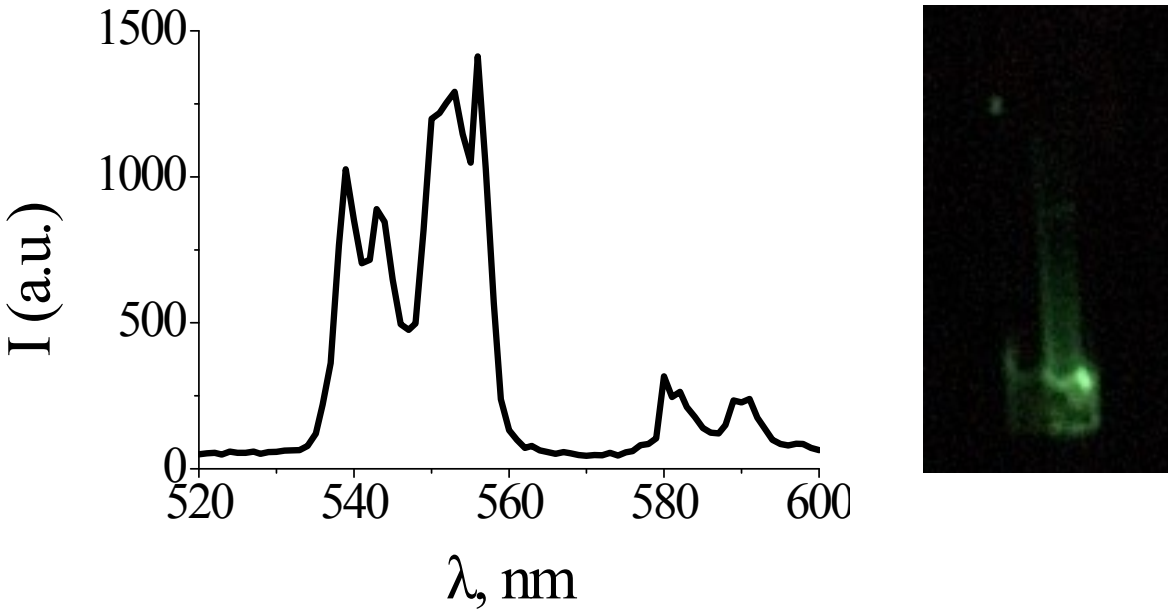


Figure S4. Triboluminescence spectrum of [(TbL_3)(LiL)(MeOH)] **2**

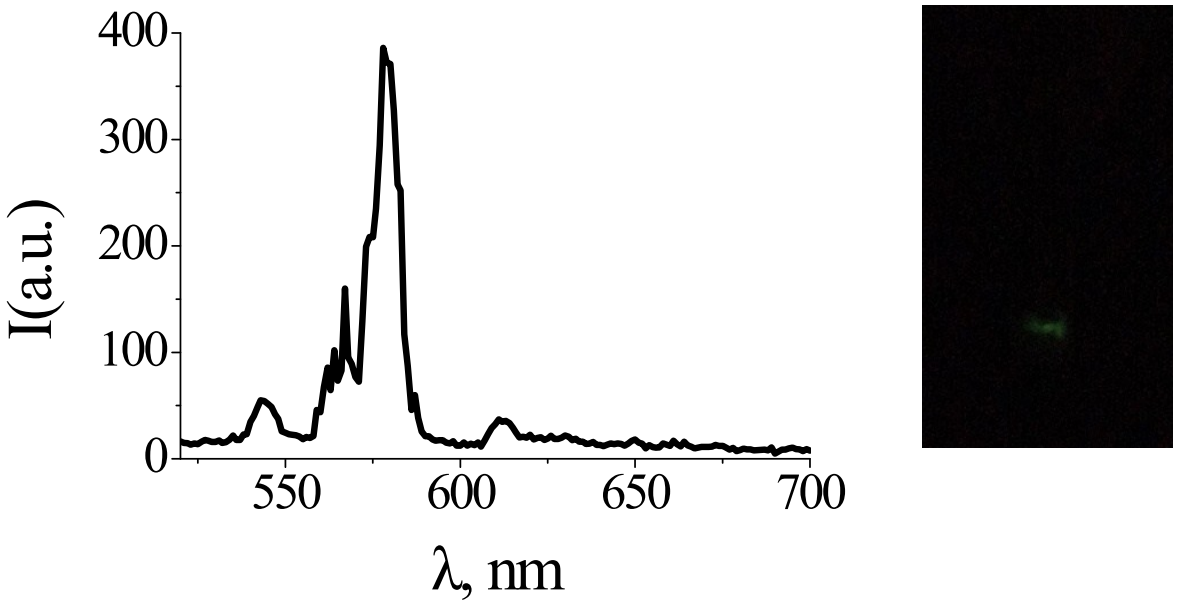
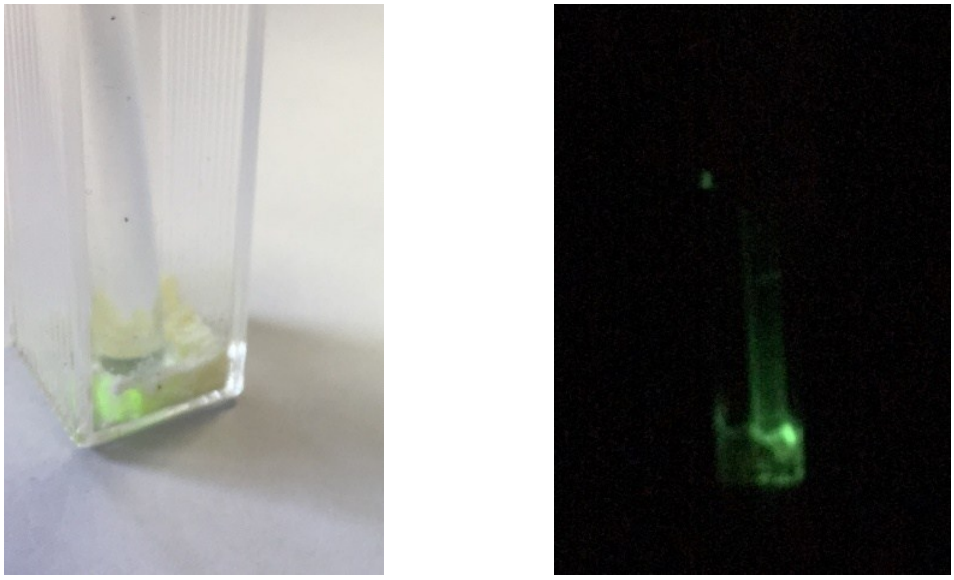


Figure S5. Triboluminescence spectrum of [(DyL_3)(LiL)(MeOH)] **3**



At daylight In the dark

Figure S6. Mechanoluminescence of [(TbL_3)(LiL)(MeOH)] **2**

Solid-state fluorescence of complexes 1-3

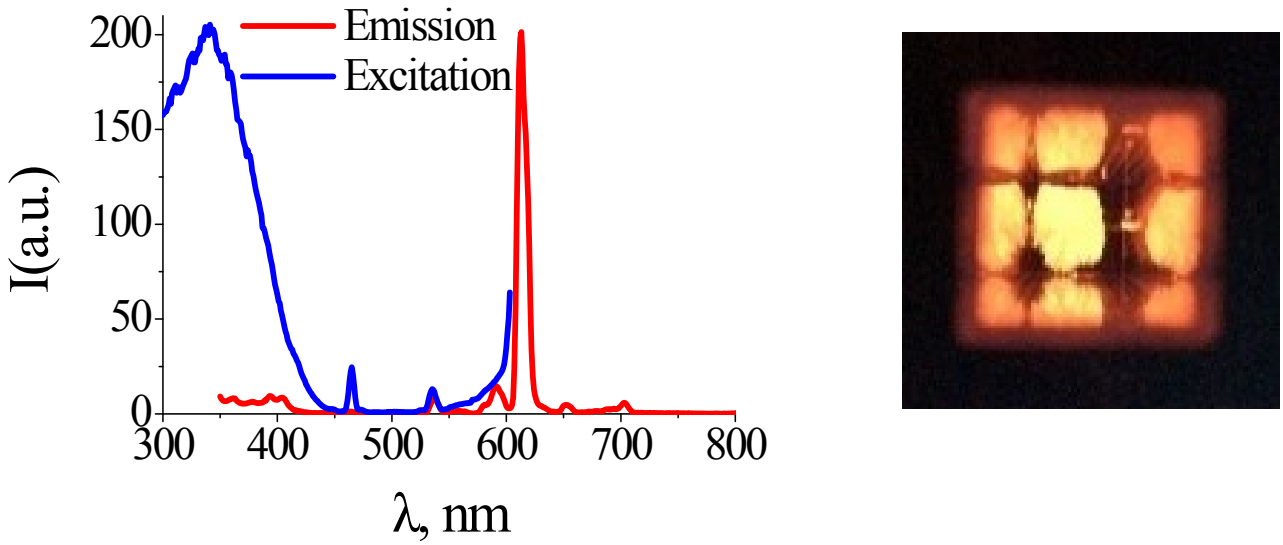


Figure S7. Solid-state fluorescence spectrum of [(EuL_3)(LiL)(MeOH)] **1**

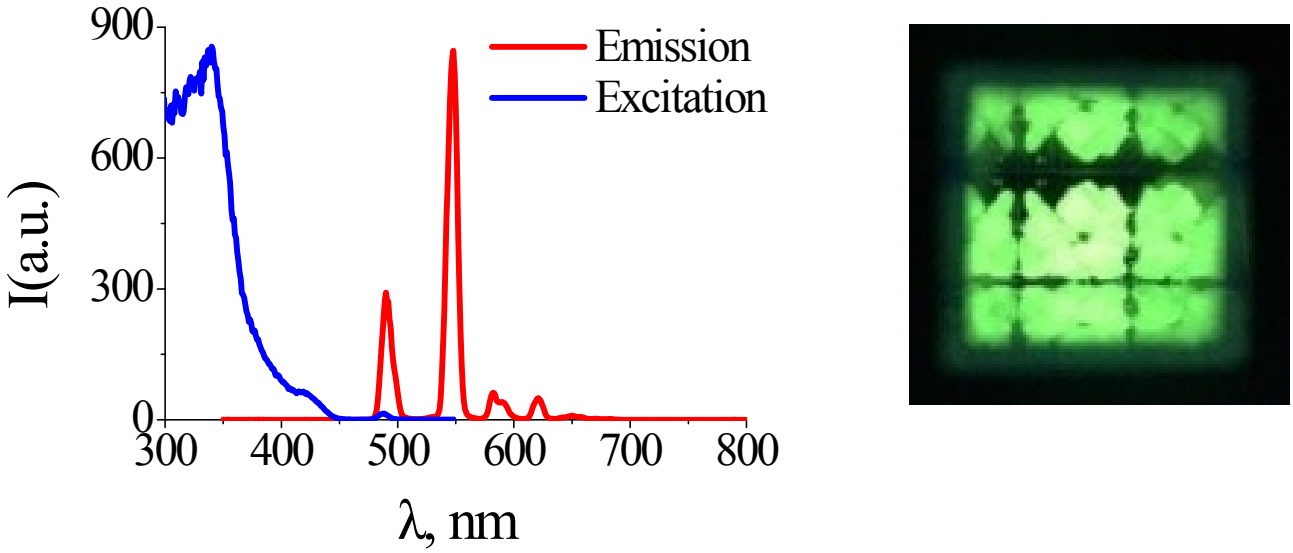


Figure S8. Solid-state fluorescence spectrum of [(TbL_3)(LiL)(MeOH)] **2**

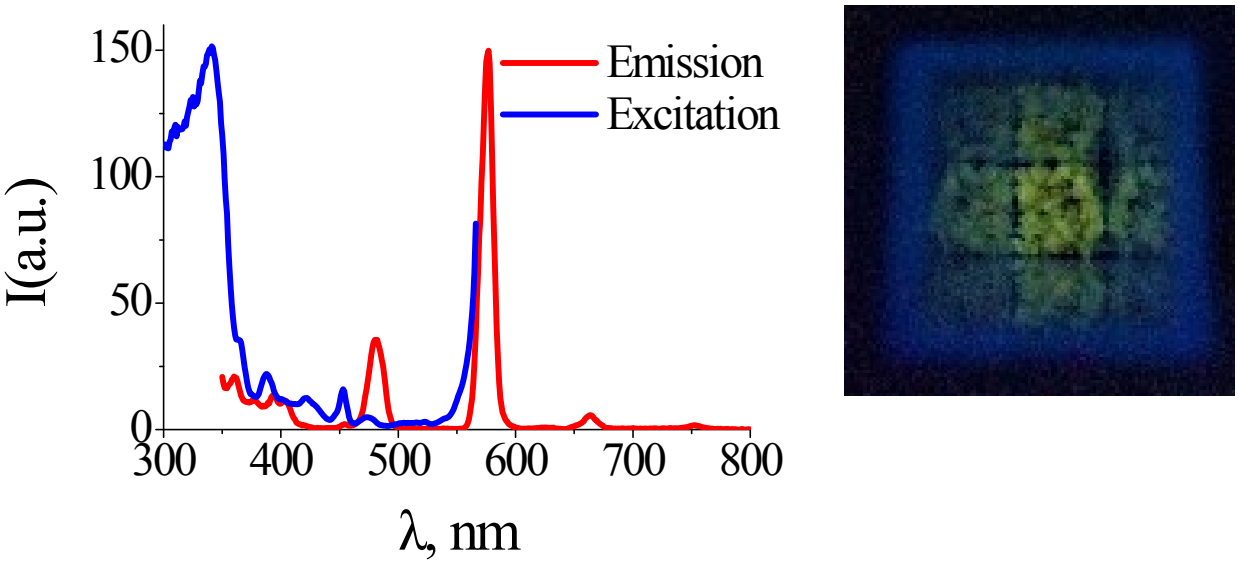
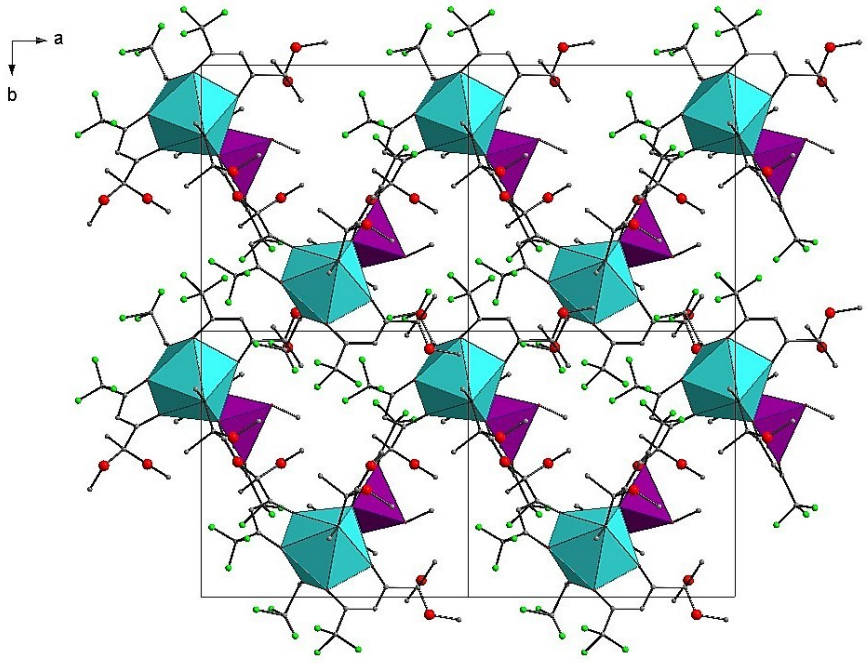
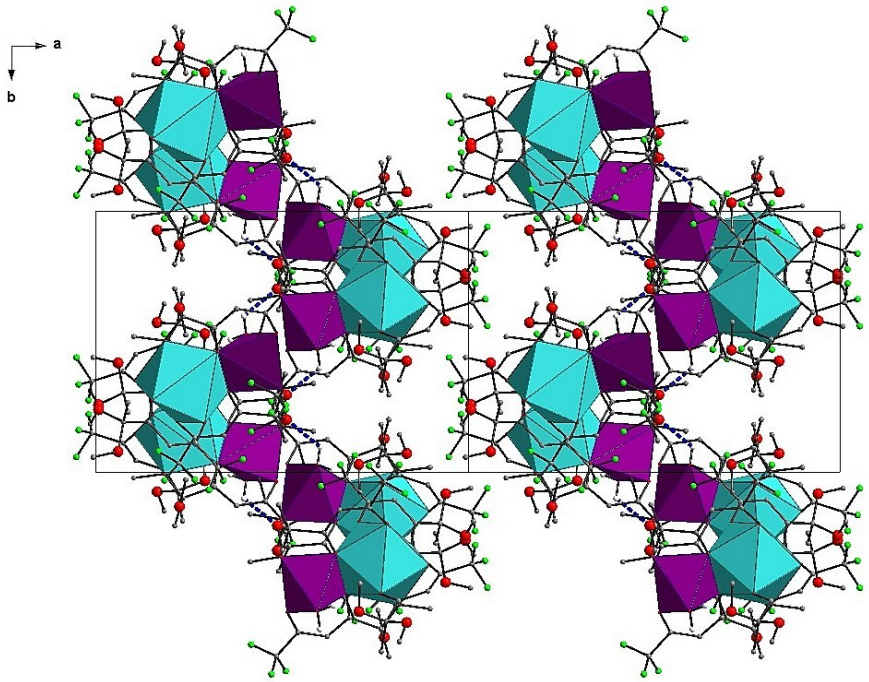


Figure S9. Solid-state fluorescence spectrum of [(DyL_3)(LiL)(MeOH)] **3**

S6. Crystal packings of Dy (III) complexes 3 and 6



a



b

Figure S10. Molecular structures of: (***a***) [(DyL_3)(LiL)MeOH] **3** (hydrogens are not shown for clarity); (***b***) [(DyL_3)(LiL)H_2O] **6** (only hydrogens of solvate water molecule are shown; intermolecular hydrogen bonds are represented as blue dashed lines). Color code: DyO_8 polyhedra in blue, LiO_5 polyhedra in violet.

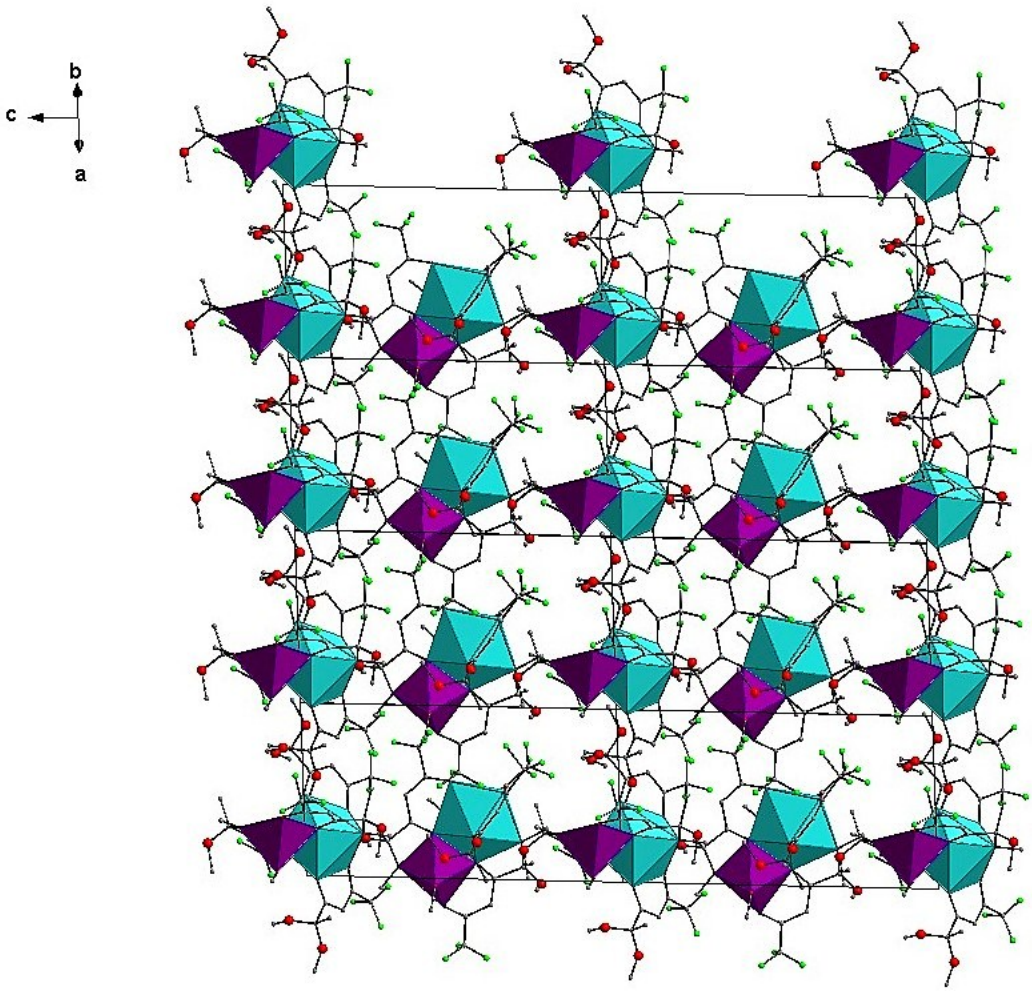


Figure S11. Crystal packing of triboluminescent complex [(DyL_3)(LiL)(MeOH)] **3**. Hydrogens are omitted for clarity.

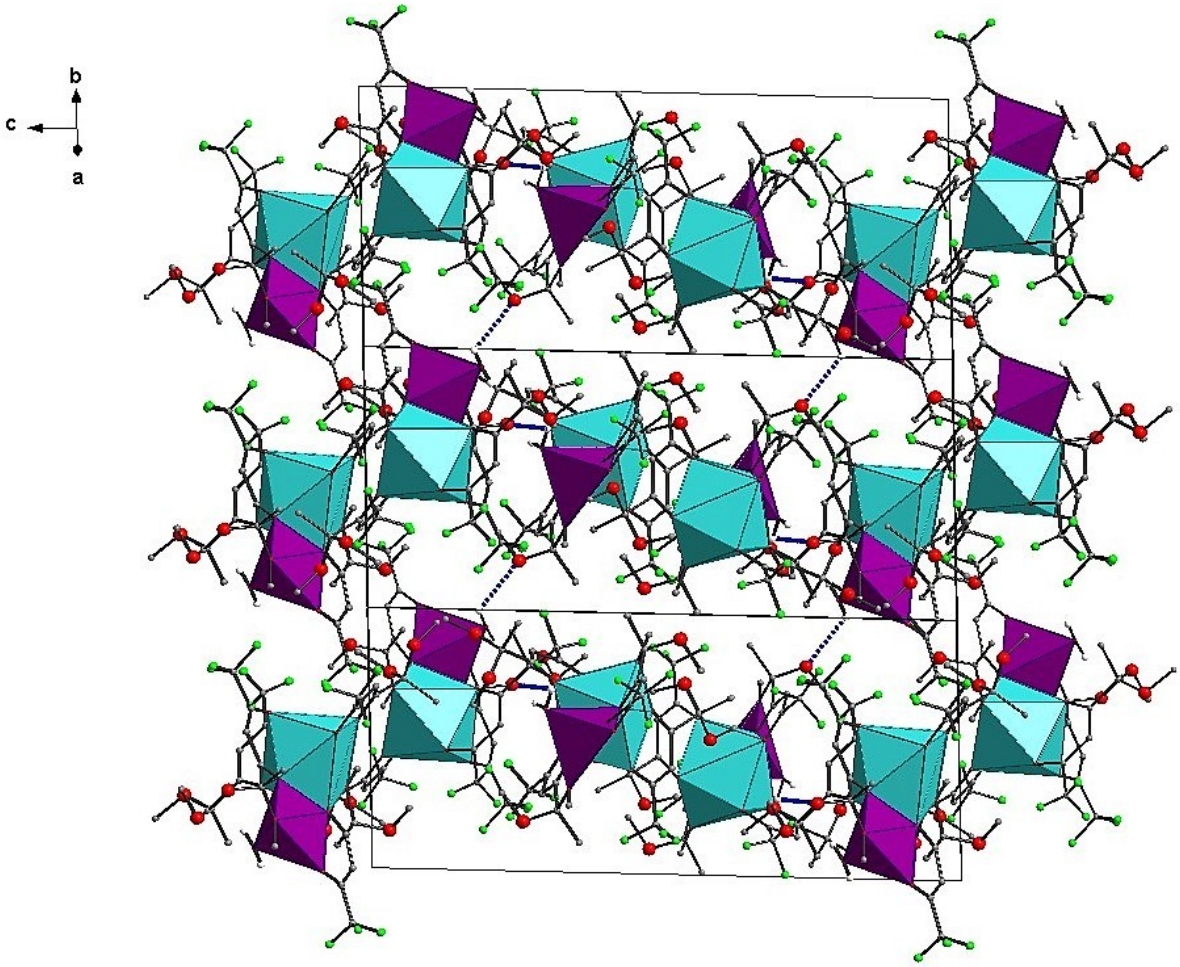
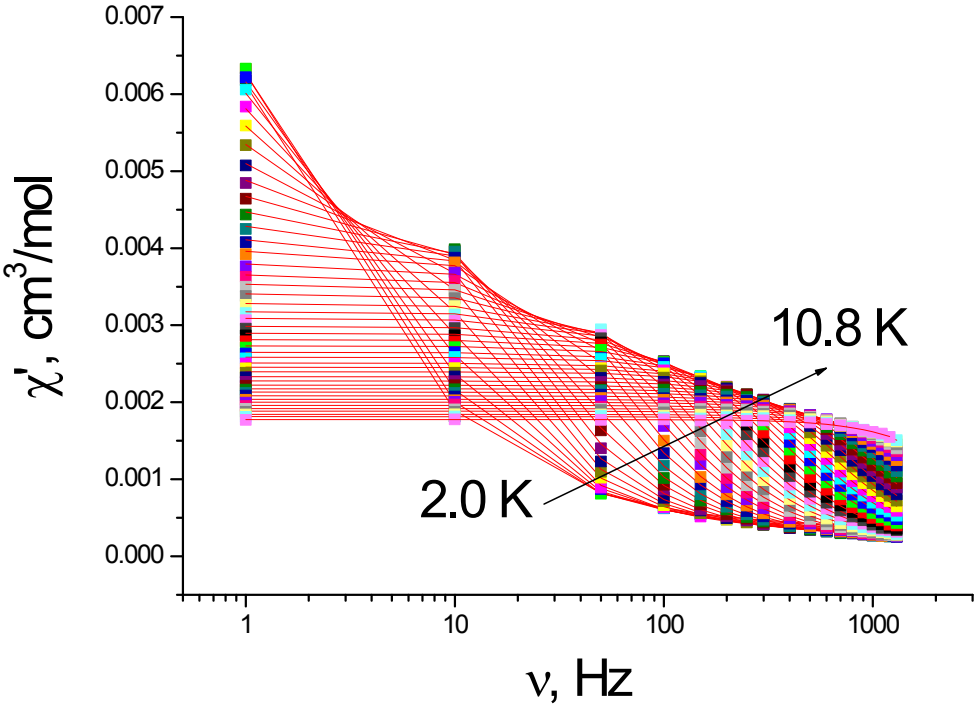
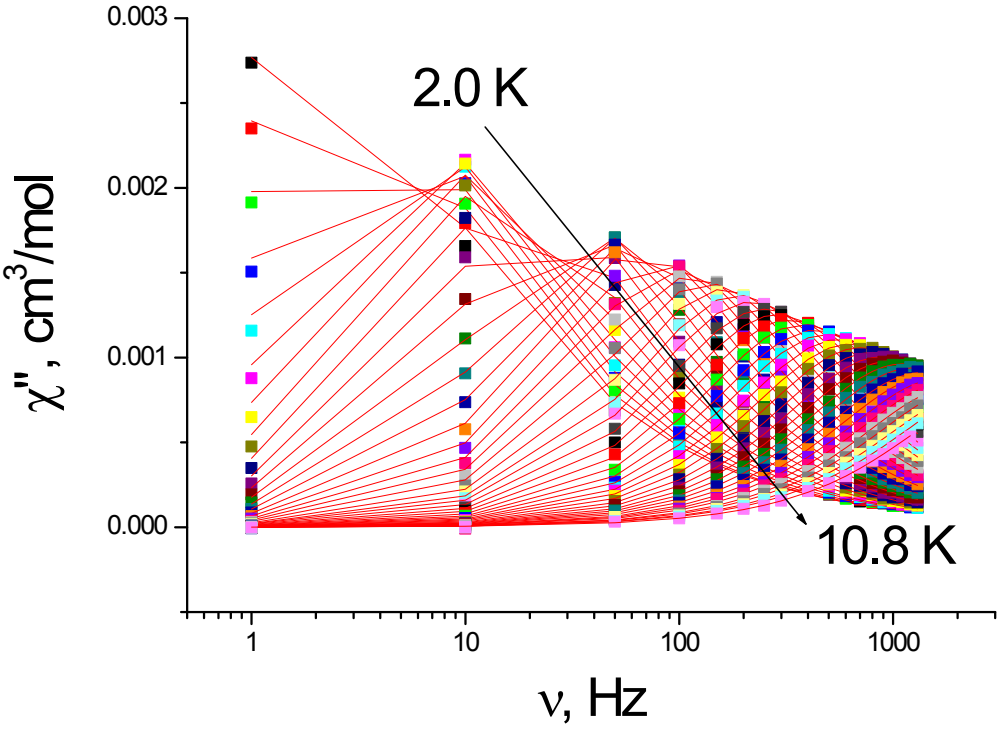


Figure S12. Crystal packing of non-triboluminescent complex [(DyL_3)(LiL)(H_2O)] **6**. Only hydrogens of solvate water molecule are shown. Intermolecular hydrogen bonds are represented as blue dashed lines.

S7. Magnetic measurements for [(DyL_3)(LiL)(MeOH)]



a



b

Figure S13. The frequency dependencies of the in-phase (χ') (***a***) and out-of-phase (χ'') (***b***) parts of magnetic susceptibility at different frequencies for **3** (solid line – a theoretical curve).

Table S10. The best fit values of χT, χS, τ and α

T, K	χT, cm^3/mol	χS, cm^3/mol	τ, s	α
2.0	3.319E-4	0.01004	0.6499	0.3243
2.2	3.303E-4	0.00897	0.4445	0.2942
2.4	3.138E-4	0.00809	0.3139	0.2705
2.6	3.033E-4	0.00738	0.2282	0.2498
2.8	2.892E-4	0.00683	0.1693	0.2316
3.0	2.787E-4	0.00633	0.1264	0.2069
3.2	2.673E-4	0.00594	0.0961	0.1951
3.4	2.565E-4	0.00557	0.0723	0.1766
3.6	2.531E-4	0.00524	0.0558	0.1591
3.8	2.397E-4	0.00497	0.0430	0.1457
4.0	2.325E-4	0.00474	0.0342	0.1366
4.2	2.291E-4	0.00451	0.02758	0.1230
4.4	2.163E-4	0.00431	0.02225	0.1147
4.6	2.087E-4	0.00413	0.01811	0.1094
4.8	2.099E-4	0.00397	0.01494	0.0929
5.0	2.029E-4	0.00381	0.01231	0.0889
5.2	1.943E-4	0.00366	0.01038	0.0841
5.4	1.857E-4	0.00354	0.00876	0.0803
5.6	1.798E-4	0.00341	0.00738	0.0742
5.8	1.861E-4	0.00328	0.00622	0.0630
6.0	1.835E-4	0.00318	0.00531	0.0576
6.2	1.737E-4	0.003091	0.00463	0.0597
6.4	1.667E-4	0.002987	0.00398	0.0588
6.6	1.626E-4	0.002896	0.00344	0.0544
6.8	1.668E-4	0.002814	0.003006	0.0487
7.0	1.748E-4	0.002732	0.002635	0.0420
7.2	1.644E-4	0.002649	0.002294	0.0418
7.4	1.689E-4	0.002586	0.002033	0.0389
7.6	1.63E-4	0.002510	0.001785	0.0365
7.8	1.682E-4	0.002454	0.001592	0.0365
8.0	1.718E-4	0.002397	0.001420	0.0317
8.2	1.806E-4	0.002332	0.001264	0.02759
8.4	1.814E-4	0.002277	0.001128	0.02656
8.6	1.972E-4	0.002222	0.001023	0.02002
8.8	1.787E-4	0.002175	9.066E-4	0.02321
9.0	1.775E-4	0.002132	8.112E-4	0.02562
9.2	1.847E-4	0.002084	7.292E-4	0.02579
9.4	2.234E-4	0.002038	6.75E-4	0.01460
9.6	1.972E-4	0.002001	5.997E-4	0.01932
9.8	1.849E-4	0.001960	5.361E-4	0.02256
10	2.688E-4	0.001917	5.182E-4	7.496E-4
10.2	1.793E-4	0.001885	4.384E-4	0.01848
10.4	2.345E-4	0.001842	4.118E-4	0.00906
10.6	8.975E-5	0.001813	3.341E-4	0.02982
10.8	2.342E-4	0.001775	3.395E-4	0.00044

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