Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Highly chemical and thermally stable lanthanide coordination polymers for luminescent probe and white light emitting diodes

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Table S1 The Selected bond distances and angles of compounds **1-3**.

Compound **1**			
Tb1—O5	2.3060 (19)	Tb1—O1^{i}	2.4616 (19)
Tb1—O5^{i}	2.3061 (19)	Tb1—O1	2.4617 (19)
Tb1—O4^{ii}	2.317 (2)	Tb1—O2^{i}	2.467 (2)
Tb1—O4^{iii}	2.317 (2)	Tb1—O2	2.467 (2)
O5—Tb1—O5^{i}	84.33 (10)	O4^{ii}—Tb1—O1^{i}	86.55 (7)
O5—Tb1—O4^{ii}	93.26 (8)	O4^{iii}—Tb1—O1^{i}	73.76 (7)
O5^{i}—Tb1—O4^{ii}	157.34 (7)	O5—Tb1—O1	77.20 (7)
O5—Tb1—O4^{iii}	157.34 (7)	O5^{i}—Tb1—O1	127.07 (7)
O5^{i}—Tb1—O4^{iii}	93.26 (8)	O4^{ii}—Tb1—O1	73.75 (7)
O4^{ii}—Tb1—O4^{iii}	97.28 (12)	O4^{iii}—Tb1—O1	86.55 (7)
O5—Tb1—O1^{i}	127.07 (7)	O1^{i}—Tb1—O1	150.20 (10)
O5^{i}—Tb1—O1^{i}	77.20 (7)	O5—Tb1—O2^{i}	74.69 (7)
O4^{ii}—Tb1—O2^{i}	80.20 (8)	O5^{i}—Tb1—O2^{i}	77.44 (7)
O4^{iii}—Tb1—O2^{i}	126.84 (7)	O4^{ii}—Tb1—O2	126.84 (7)
O1^{i}—Tb1—O2^{i}	53.10 (6)	O4^{iii}—Tb1—O2	80.20 (8)
O1—Tb1—O2^{i}	140.13 (7)	O1^{i}—Tb1—O2	140.13 (7)
O5—Tb1—O2	77.43 (7)	O1—Tb1—O2	53.10 (6)
O5^{i}—Tb1—O2	74.69 (7)	O2^{i}—Tb1—O2	142.09 (10)

Symmetry codes: (i) −*x*, *y*, −*z*+1/2; (ii) −*x*, −*y*+1, −*z*; (iii) *x*, −*y*+1, *z*+1/2.

Compound **2**			
Eu1—O1	2.3323 (19)	Eu1—O8^{ii}	2.4893 (19)
Eu1—O1^{i}	2.3323 (19)	Eu1—O8^{iii}	2.4893 (19)
Eu1—O6^{i}	2.344 (2)	Eu1—O7^{iii}	2.4903 (19)
Eu1—O6	2.344 (2)	Eu1—O7^{ii}	2.4903 (19)
O1—Eu1—O1^{i}	84.75 (10)	O1—Eu1—O7^{iii}	74.72 (7)
O1—Eu1—O6^{i}	93.06 (8)	O1^{i}—Eu1—O7^{iii}	77.49 (7)
O1^{i}—Eu1—O6^{i}	157.33 (7)	O6^{i}—Eu1—O7^{iii}	80.16 (7)
O1—Eu1—O6	157.33 (7)	O6—Eu1—O7^{iii}	126.89 (7)
O1^{i}—Eu1—O6	93.06 (8)	O8^{ii}—Eu1—O7^{iii}	140.52 (7)
O6^{i}—Eu1—O6	97.31 (12)	O8^{iii}—Eu1—O7^{iii}	52.58 (6)
O1—Eu1—O8^{ii}	77.08 (7)	O1—Eu1—O7^{ii}	77.49 (7)
O1^{i}—Eu1—O8^{ii}	126.63 (6)	O1^{i}—Eu1—O7^{ii}	74.72 (7)
O6^{i}—Eu1—O8^{ii}	74.32 (6)	O6^{i}—Eu1—O7^{ii}	126.89 (7)
O6—Eu1—O8^{ii}	86.37 (7)	O6—Eu1—O7^{ii}	80.16 (7)
O1—Eu1—O8^{iii}	126.63 (6)	O8^{ii}—Eu1—O7^{ii}	52.58 (6)
O1^{i}—Eu1—O8^{iii}	77.08 (7)	O8^{iii}—Eu1—O7^{ii}	140.52 (7)
O6^{i}—Eu1—O8^{iii}	86.37 (7)	O7^{iii}—Eu1—O7^{ii}	142.07 (10)
O6—Eu1—O8^{iii}	74.32 (6)	O8^{ii}—Eu1—O8^{iii}	150.75 (9)

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) *x*, −*y*, *z*−1/2; (iii) −*x*+1, −*y*, −*z*+1.

Compound **3**

Gd1—O6^{i}	2.3188 (18)	Gd1—O2	2.478 (2)
Gd1—O6	2.3188 (18)	Gd1—O2^{i}	2.478 (2)
Gd1—O3^{ii}	2.3308 (19)	Gd1—O1	2.4813 (19)
Gd1—O3^{iii}	2.3308 (19)	Gd1—O1^{i}	2.4813 (19)
O6^{i}—Gd1—O6	84.43 (9)	O6^{i}—Gd1—O1	74.75 (7)
O6^{i}—Gd1—O3^{ii}	93.29 (7)	O6—Gd1—O1	77.39 (7)
O6—Gd1—O3^{ii}	157.29 (7)	O3^{ii}—Gd1—O1	80.20 (7)
O6^{i}—Gd1—O3^{iii}	157.29 (7)	O3^{iii}—Gd1—O1	126.88 (7)
O6—Gd1—O3^{iii}	93.29 (7)	O2—Gd1—O1	52.74 (6)
O3^{ii}—Gd1—O3^{iii}	97.17 (11)	O2^{i}—Gd1—O1	140.44 (6)
O6^{i}—Gd1—O2	126.80 (6)	O6^{i}—Gd1—O1^{i}	77.39 (7)
O6—Gd1—O2	77.19 (7)	O6—Gd1—O1^{i}	74.75 (7)
O3^{ii}—Gd1—O2	86.34 (7)	O3^{ii}—Gd1—O1^{i}	126.87 (7)
O3^{iii}—Gd1—O2	74.14 (6)	O3^{iii}—Gd1—O1^{i}	80.20 (7)
O6^{i}—Gd1—O2^{i}	77.19 (7)	O2—Gd1—O1^{i}	140.45 (6)
O6—Gd1—O2^{i}	126.80 (6)	O2^{i}—Gd1—O1^{i}	52.74 (6)
O3^{ii}—Gd1—O2^{i}	74.14 (6)	O1—Gd1—O1^{i}	142.08 (10)
O3^{iii}—Gd1—O2^{i}	86.34 (7)	O2—Gd1—O2^{i}	150.48 (9)

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) *x*, −*y*, *z*+1/2; (iii) −*x*+1, −*y*, −*z*.

Table S2 Bond lengths (Å) and angles (º) of hydrogen bonds for compound **1**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1-H1A···O6^{ii}	0.88	1.86	2.731	172
N2-H2A···O3^{iii}	0.88	1.79	2.666	177
C6-H6B···O2^{ii}	0.98	2.60	3.514	155
C6-H6B···O5^{iv}	0.98	2.51	3.269	134
C13-H13B···O1^{i}	0.98	2.40	3.232	143
C13-H13C···O7^{v}	0.98	2.59	3.416	142

Symmetry codes: (i) -x, 1-y, -z; (ii) -1/2-x, 1/2-y, -z; (iii) -x, y, -1/2-z, (v) 1/2-x, 1/2-y, -z; (iv) -1/2+x, 1/2-y, -1/2+z.

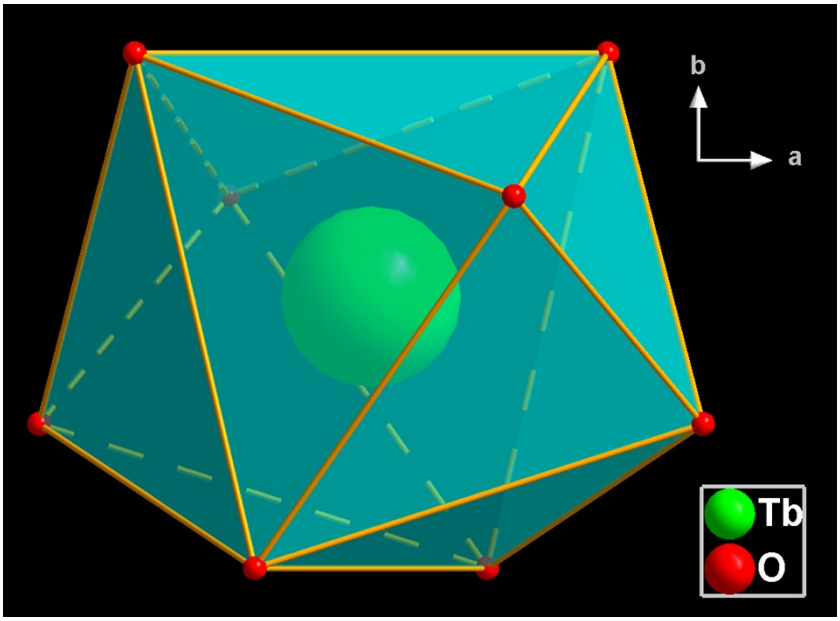

Figure S1 The geometric configuration of Tb(III) ions in the compound **1**.

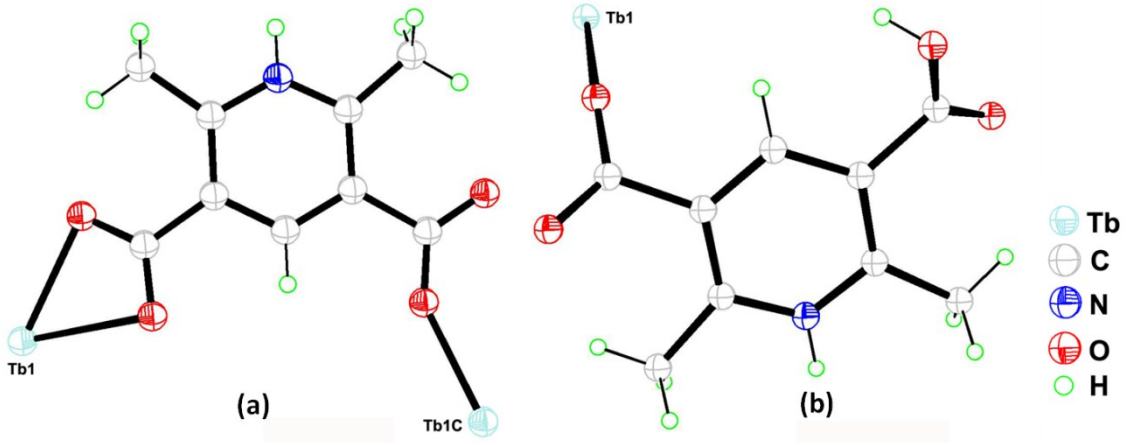

Figure S2 (a) The coordination type of $Hmpda^-$ ligand in compound **1**. (b) The coordination type of H_2mpda ligand in compound **1**.

Table S3 Continuous Shape Measurement calculations for Ln(III) ions in compounds **1**-**3**.

	1 {Tb}	**2 {Eu}**	**3 {Gd}**
Ln(III)	TbO8	EuO8	GdO8
OP-8	30.41087	30.24795	30.36976
HPY-8	24.76389	24.74078	24.77900
HBPY-8	11.76136	11.71511	11.75861
CU-8	10.47197	10.52796	10.52220
SAPR-8	5.16736	5.26532	5.21338
TDD-8	**3.36275**	**3.41398**	**3.39727**
JGBF-8	9.44946	9.45735	9.44126
JETBPY-8	25.32052	25.29241	25.31634
JBTPR-8	4.22377	4.29835	4.25342

OP-8	1 D8h	Octagon
HPY-8	2 C7v	Heptagonal pyramid
HBPY-8	3 D6h	Hexagonal bipyramid
CU-8	4 Oh	Cube
SAPR-8	5 D4d	Square antiprism
TDD-8	6 D2d	Triangular dodecahedron
JGBF-8	7 D2d	Johnson gyrobifastigium J26
JETBPY-8	8 D3h	Johnson elongated triangular bipyramid J14
JBTPR-8	9 C2v	Biaugmented trigonal prism J50

Table S4 Bond valence sum calculations for the Ln ions in compounds **1**-**3**.

	Compound **1**	Compound **2**	Compound **3**
Atom	Tb	Eu	Gd
BVS	3.12	3.26	3.29
Dmax	2.4670	2.4900	2.4810
Nsum	8	8	8

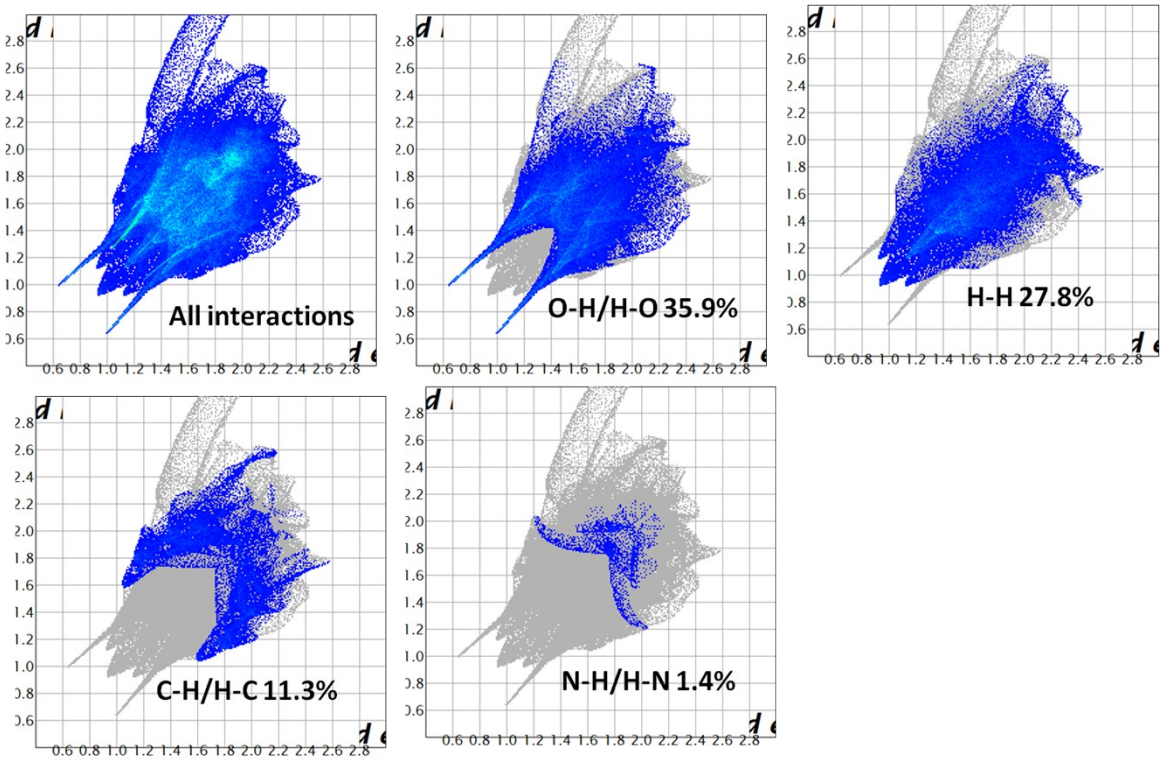

Figure S3 Hirshfeld surface mapped with the fingerprint plots of compound **1**.

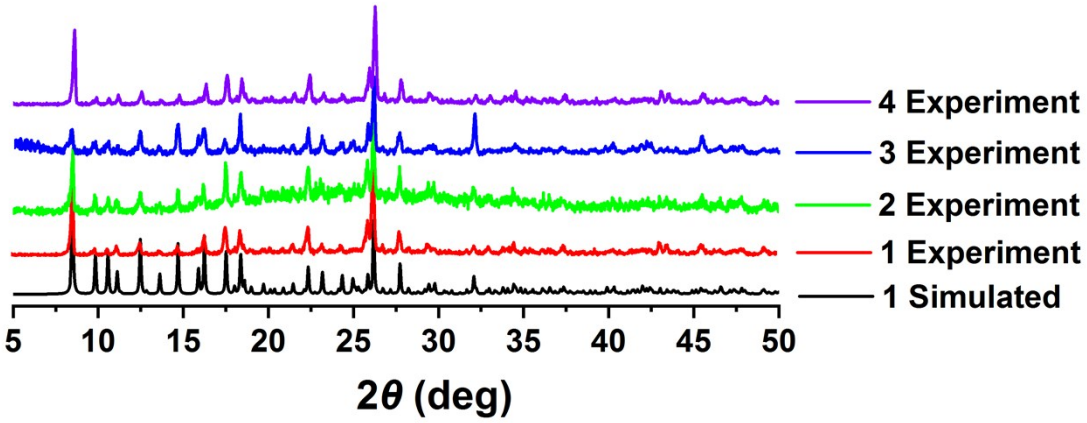

Figure S4 Experimental and simulated powder X-ray diffraction patterns for compounds **1**-**4**.

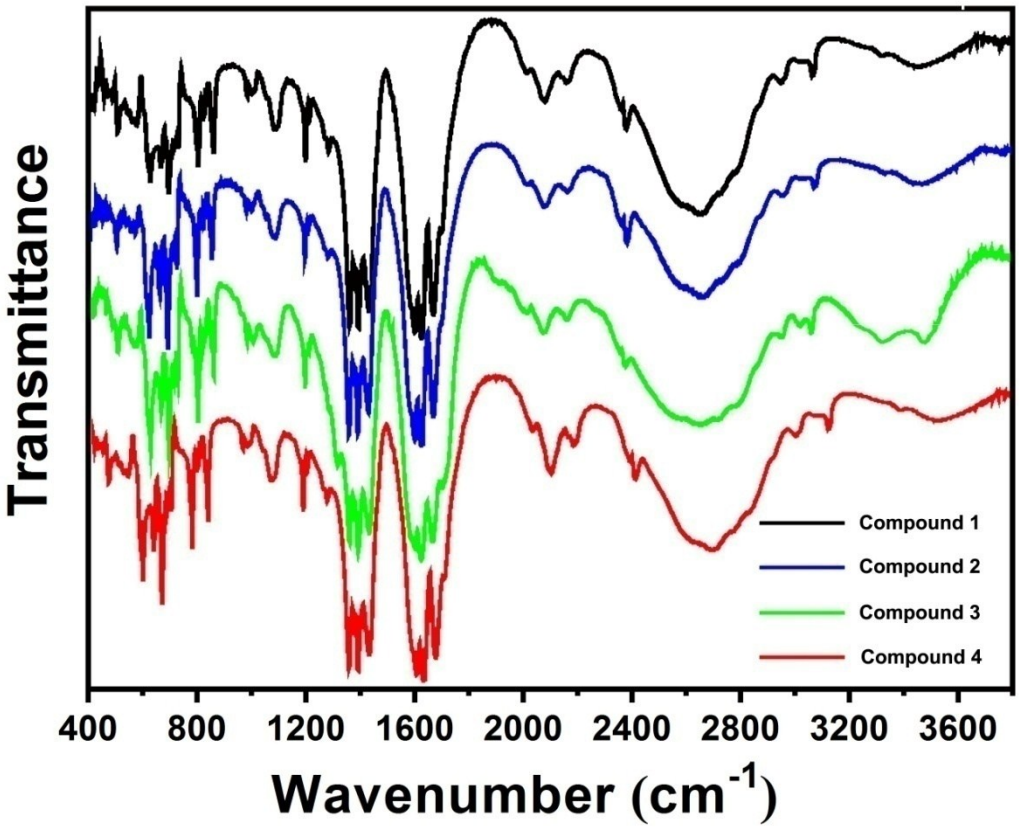

Figure S5 The IR spectra of compounds **1**-**4**.

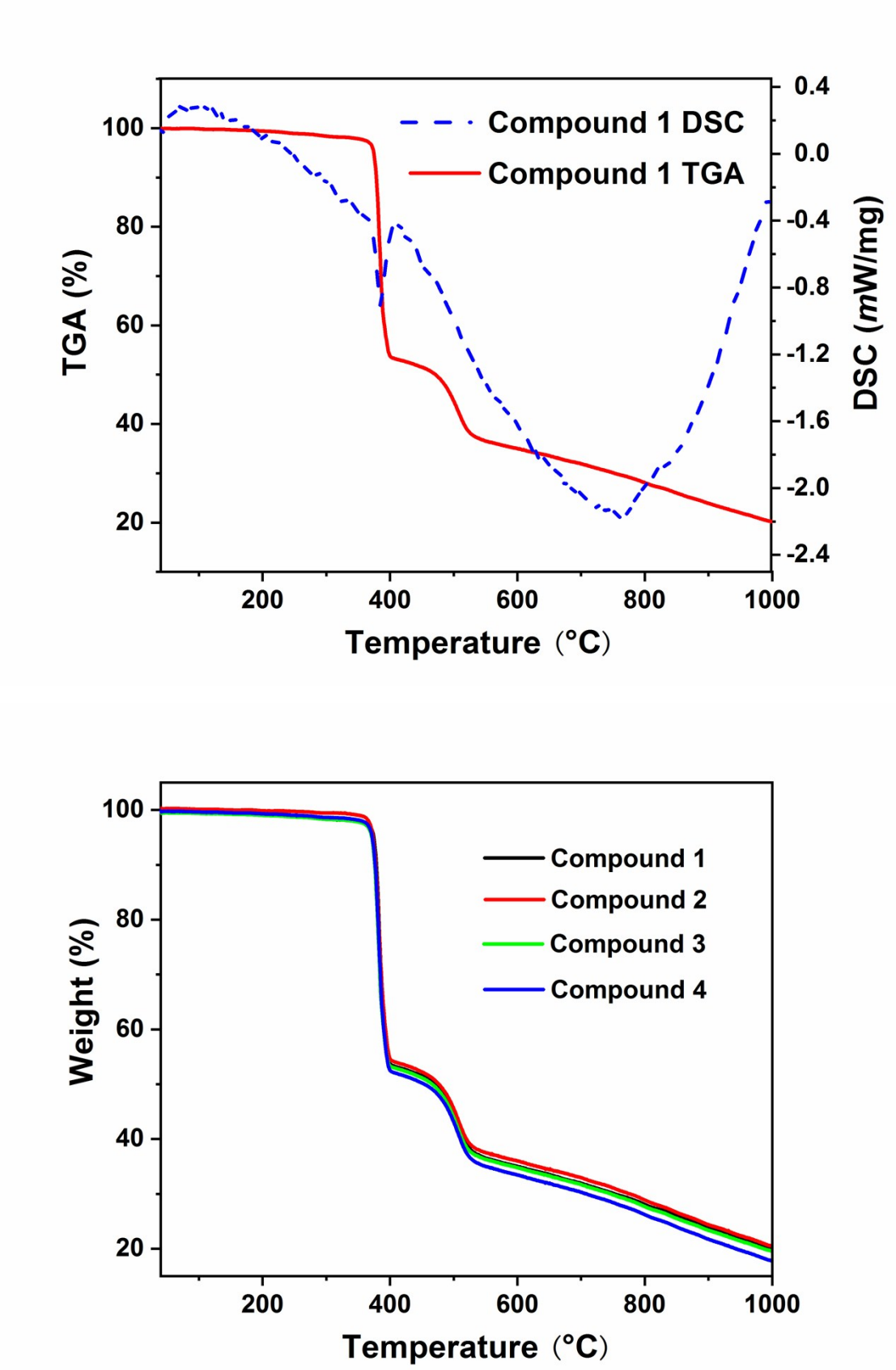

Figure S6 The TGA and DSC curves of compound **1** (up) and the TGA curves of compounds **1-4** (down).

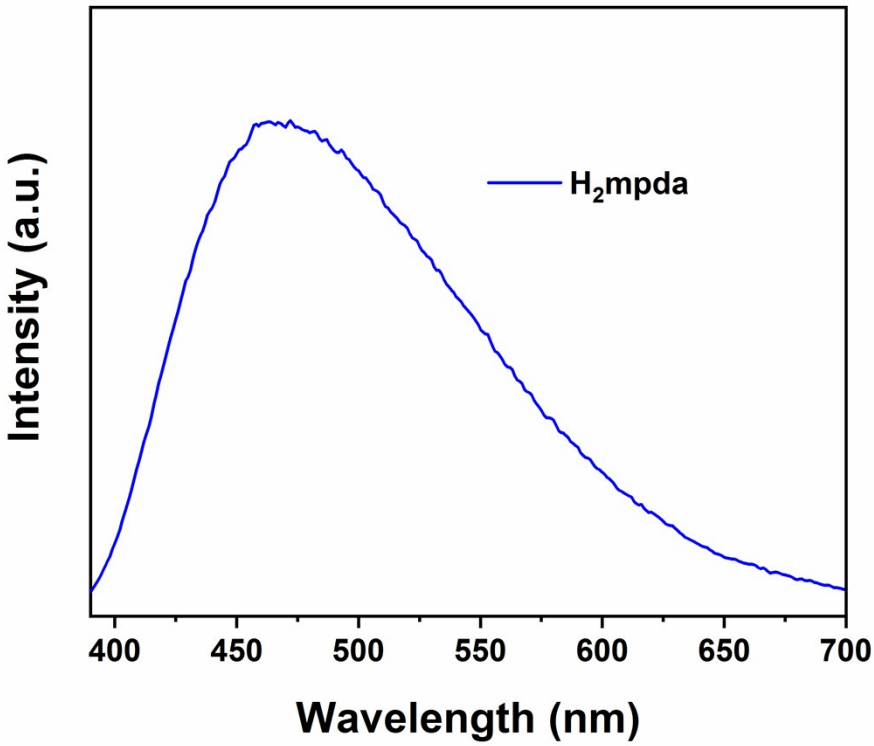

Figure S7 The solid-state emission spectra of the free H_2mpda ligand.

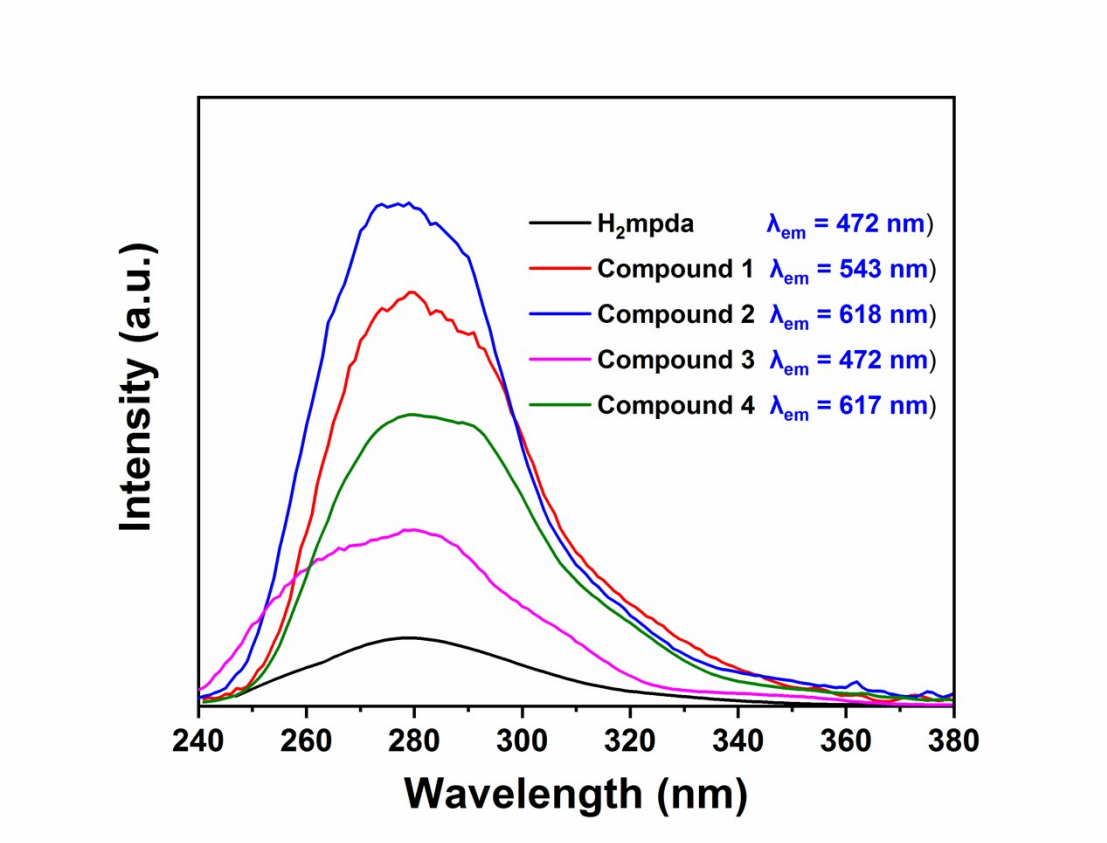

Figure S8 Solid-state excitation spectra of the free H_2mpda ligand and compounds **1**-**4**.

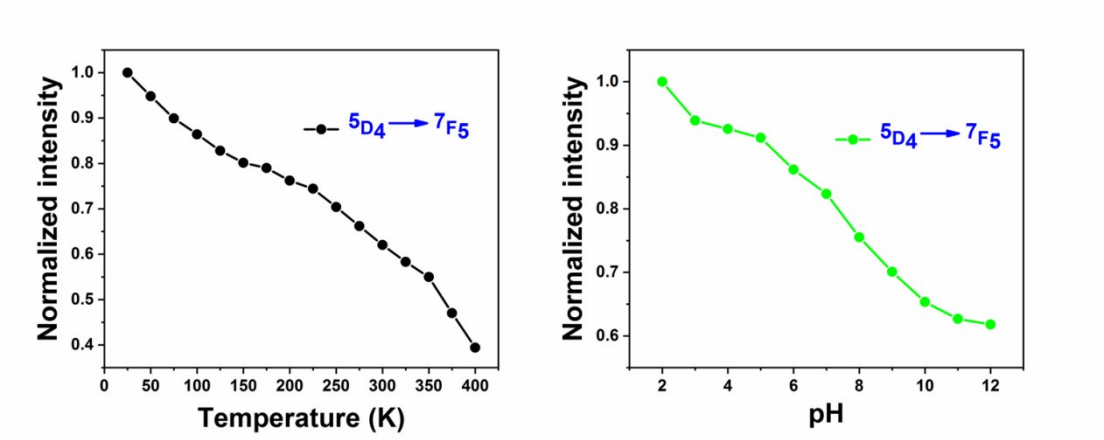

Figure S9 The normalized intensity at different temperatures (25-400 K) (**left**) and the normalized intensity of different pH (2-12) (**right**).

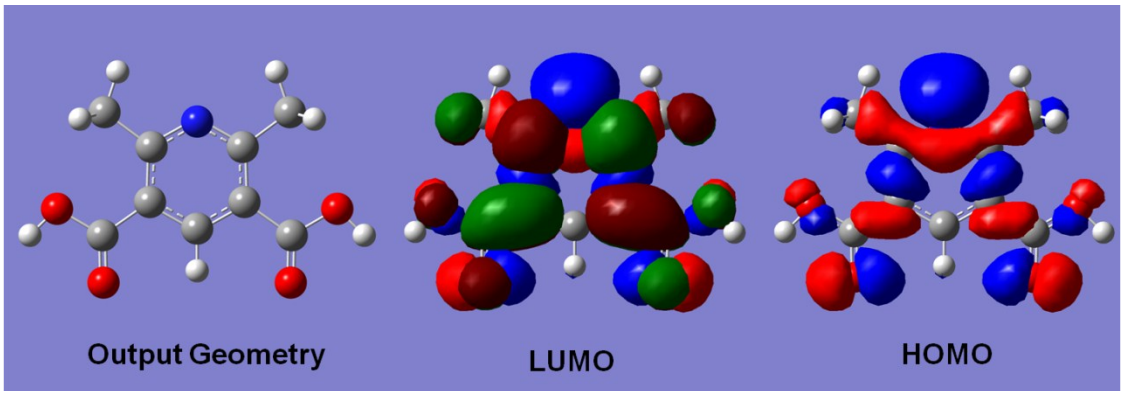

Figure S10 Calculated output geometry obtained from static B3LYP/6-311G (d, p) geometry optimization and corresponding molecular orbital diagrams for H_2mpda ligand.

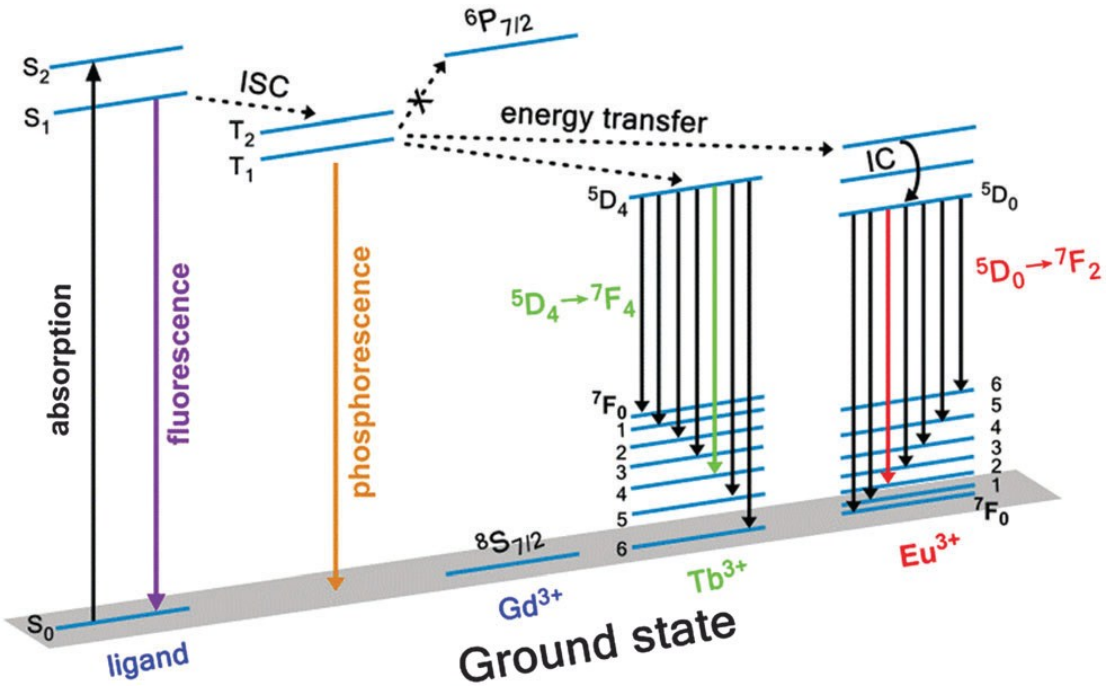

Figure S11 Schematic representation of the energy adsorption, migration and emission processes of the Ln-CPs. S = singlet states, T = triplet states; IC = internal conversion, and ISC = intersystem crossing[S1].

Table S5 The intermetallic distances of Ln-Ln and their relatively optical properties.

Compound	Ln-Ln distances (Å)	Quantum Yield (%)	Ref.
$[Eu(BTB)(DMSO)_2]\cdot H_2O$	4.1853	19.89	S2
$[H_2NMe_2]_3[Eu(2,6\text{-}dpa)_3]$	Mononuclear and 0D	71	S3
$[Eu_4(m\text{-}BDC)_6(H_2O)_4(DMF)]\cdot(H_2O)_2\cdot(DMF)]$	4.5137-5.4842	22.73	S4
$[Eu_2(PIP)_2(HPIP)(HCO_2)(H_2O)_2]\cdot H_2O]$	4.4596 and 4.3478	5.49	S5
$[Eu_2(PIP)_3(H_2O)_4]\cdot 2DMF\cdot 3H_2O]$	4.1351	17.82	S6
$[Eu_2(m\text{-}BDC)_3(phen)_2]\cdot(DMF)]$	4.0149 and 4.2736	75	S7
$[(H_3O)_n[Eu(L)(H_2O)]_n\cdot nH_2O$	5.3787	19.10	S8
$[HNMe_2][Eu_2(m\text{-}BDC)_3(phen)_2]$	4.0577	86.87	S9
$Eu_2(m\text{-}BDC)_4(MV)$	5.9059 and 5.8570	5.70	S10
$[Eu_2(1,3\text{-}BDC)_2(phen)_2(ox)(H_2O)]$	5.5416 and 6.2335	63.21	S11
[Eu(MBDC)(STP)]	4.0989	41	S12
$[NMe_4][Eu(m\text{-}BDC)_2]$	3.9661	78.1	S13
$[Eu_2PDC_3(H_2O)_3]H2O$	3.8527 and 5.2986	16	S14
$[Eu(Hmpda)_3(H_2mpda)]$	**8.2723** **Mononuclear and 1D**	**32.21**	**This work**

Table S6 The CRI and CCT of the LED devices in compounds **1**, **2** and **4**.

Compound	Current (mA)	CRI	CCT (K)
1	60	70.4	2929
	120	72.2	3020
	180	72.1	3061
	240	72.4	3096
	300	71.1	3095
2	60	79.7	1717
	120	80.3	1657
	180	80.3	1644
	240	80.5	1645
	300	81.0	1652
4	60	85.9	2826
	120	87.9	2956
	180	89.0	3066
	240	89.7	3144
	300	90.4	3198

Reference

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