Electronic Supplementary Information

Luminescence, magnetocaloric effect of Ln_4 clusters (Ln = Eu, Gd, Tb, Er) bridged by CO_3^{2-} deriving from spontaneous fixation of carbon dioxide in atmosphere

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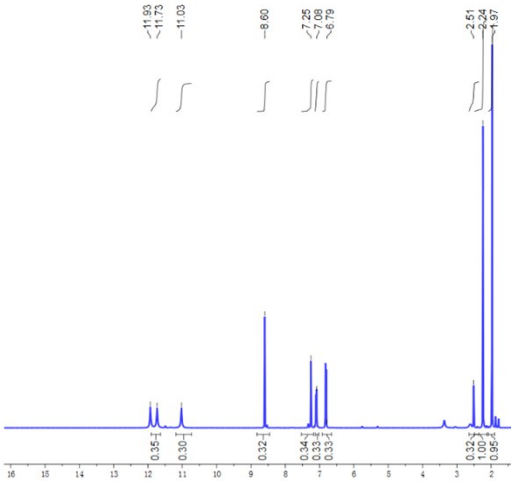

Fig. S1 The ^{1}H NMR spectrum of 2-(hydroxyimino)-2-[(2-hydroxy-5-methylphenyl)methylene]hydrazide

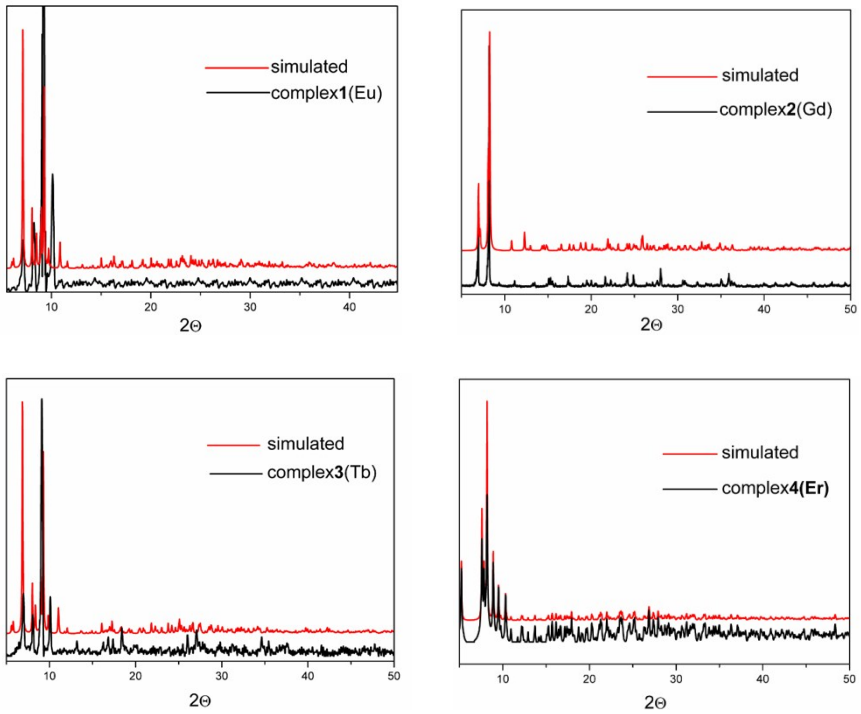

Fig. S2 The experimental and simulated PXRD patterns of complexes **1** − **4**.

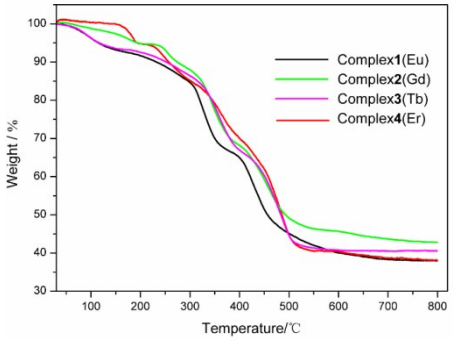

Fig. S3 TG curves of complexes **1** − **4**.

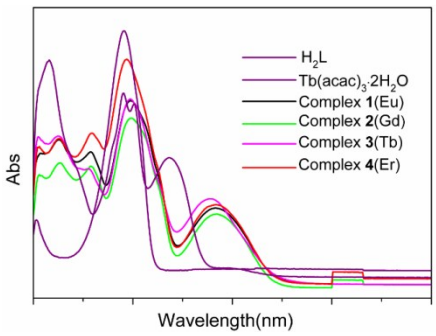

Fig. S4 UV-vis absorption spectra of complexes **1** − **4**, H_2L and $[Tb(acac)_3(H_2O)_2]$ in CH_3OH solution.

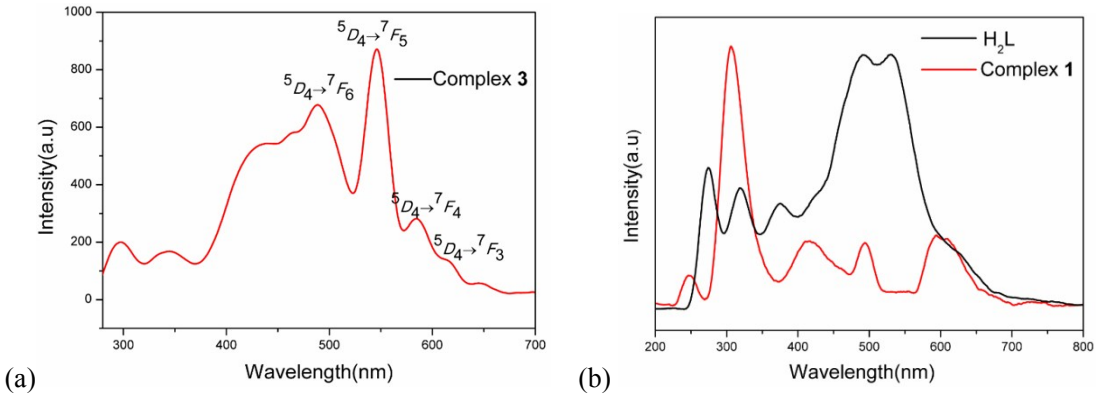

Fig. S5 (a) The luminescence spectra of complex **3** (λ_{ex} = 292 nm); (b) The luminescence spectra of complex **1** (λ_{ex} = 245 nm) and H_2L (λ_{ex} = 270 nm) in methanol solution.

Section S2

Table S1 Crystal Data and Structure Refinements for complexes **1** – **4**.

Complex	**1**	**2**	**3**	**4**
Formula	$C_{59}H_{88}Eu_4N_{12}O_{30}$	$C_{62}H_{84}Cl_2Gd_4N_{12}O_{25}$	$C_{58}H_{80}Tb_4N_{12}O_{27}$	$C_{60}H_{79}Er_4N_{13}O_{25}$
M_r (g mol^{-1})	2053.25	2097.31	2013.02	2051.40
Cryst. Syst.	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/C$	$C222_1$	$P2_1/C$	$C2/c$
a (Å)	16.194(1)	14.800(3)	16.219(2)	29.452(2)
b (Å)	22.288(2)	24.707(3)	22.058(3)	32.301(2)
c (Å)	21.540(2)	21.429(2)	21.639(3)	19.940(2)
β (°)	103.346(2)	90	102.577(3)	127.720(1)
V (Å^3)	7565.1(11)	7835.8(18)	7555.5(19)	15005.5(19)
Z	4	4	4	8
D_c (g cm^{-3})	1.803	1.778	1.770	1.816
μ (mm^{-1})	3.360	3.490	3.782	4.511
F (000)	4072.0	4120.0	3952.0	8016.0
Crystal size (mm^3)	0.22 × 0.14× 0.12	0.20 × 0.18× 0.12	0.18× 0.16× 0.14	0.22 × 0.18× 0.12
θ / °	3.013 to 27.506	3.21 to 25.02	3.006 to 27.525	3.013 to 27.686
Limiting indices	-15≤ h ≤21 -28≤ k ≤28 -27≤ l ≤27	-17≤ h ≤17 -25≤ k ≤29 -25≤ l ≤25	-21≤ h ≤17 -28≤ k ≤28 -28≤ l ≤25	-38≤ h ≤33 -39≤ k ≤42 -25≤ l ≤25
Reflections collected	75835	33987	73781	76320
Independent reflection	17191	6912	17195	17204
R_{int}	0.0350	0.0585	0.0525	0.0455
Data / restraints / parameters	17191/7/985	6912/26/501	17195/6/938	17204/21/948
GOF on F^2	1.016	1.030	1.040	1.029
Final R indices [$I > 2\sigma(I)$]	R_1 [a] = 0.0244, wR_2 [b] = 0.0575	R_1 [a] = 0.0229, wR_2 [b] = 0.0555	R_1 [a] = 0.0330, wR_2 [b] = 0.0855	R_1 [a] = 0.0261, wR_2 [b] = 0.0609
R indices (all data)	R_1 = 0.0338, wR_2 = 0.0606	R_1 = 0.0240, wR_2 = 0.0557	R_1 = 0.0410, wR_2 = 0.0884	R_1 = 0.0328, wR_2 = 0.0638

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 The range of important bond lengths (Å) and angles (°) of complexes **1**-**4**.

Complexes	The range of Ln-O bond lengths / Å	The range of Ln-N bond lengths / Å	The range of O-Ln-O bond angles / º	The distance of Ln···Ln / Å	The bond angles of Ln-Ln-Ln / º
1	2.259(2)-2.594(2)	2.515(3)-2.724(3)	66.40(7)-156.19(7)	3.9461(4), 3.9472(3), 3.9668(4), 3.9108(3).	79.392(5), 99.898(6), 78.708(5), 100.168(5).
2	2.259(3)-2.581(3)	2.513(4)-2.586(4)	66.70(10)-149.06(11)	3.9166(5), 3.9603(7).	76.348(9), 101.143(9).
3	2.236(3)-2.582(3)	2.488(3)-2.685(3)	66.38(8)-155.83(9)	3.8827(6), 3.9051(5), 3.9205(6), 3.9380(6).	78.963(7), 79.446(7), 99.857(8), 99.941(7).
4	2.202(2)-2.631(2)	2.435(3)-2.627	65.77(8)-153.82(8)	3.8339(3), 3.8764(3), 3.8458(3), 3.8905(3).	99.949(6), 78.376(6), 99.988(6), 78.063(6).

Table S3 The hydrogen bonds for complexes **2.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O6	H6	O1	0.84	2.01	2.690(5)	136.8
O11	H11	O7	0.95	2.03	2.829(5)	141.1
O12	H12	O13	0.95	1.92	2.671(6)	133.8
O13	H13A	O10	0.95	1.92	2.671(6)	133.8

.

Table S4 The hydrogen bonds for complexes **1.**

D	H	A	*d*(D-H)/Å	*d*(H-A)/Å	*d*(D-A)/Å	D-H-A/°
O3	H3	O26	0.84	1.82	2.649(4)	169.4
O6	H6	O1	0.84	1.99	2.657(3)	136.2
O9	H9	$O28^{1}$	0.84	1.82	2.649(4)	166.4
O12	H12	O7	0.84	1.98	2.661(3)	137
O20	H20A	O31	0.91	1.96	2.765(4)	147.2
O20	H20B	O27	0.91	1.79	2.680(4)	165.7
O21	H21A	O29	0.91	2.04	2.801(4)	140.2
O21	H21B	O24	0.91	1.66	2.565(4)	172.5
O22	H22	O13	0.867(9)	1.970(11)	2.803(3)	160.5(18)
O23	H23	O16	0.869(9)	2.011(11)	2.854(3)	163.2(19)
C40	H40	$O31^{2}$	0.95	2.6	3.500(5)	159.1
C44	H44B	$O27^{2}$	0.98	2.59	3.564(5)	172.2
C50	H50B	O30	0.98	2.51	3.335(5)	142.1
O24	H24A	O19	0.84	1.86	2.673(3)	163.7
C59	H59C	$O12^{3}$	0.98	2.56	3.451(5)	151.8
O26	H26A	O21	0.87	1.95	2.816(3)	174.7
O26	H26B	O14	0.87	1.98	2.776(3)	151.5
O27	H27A	$N5^{3}$	0.87	2.33	3.195(4)	174.4
O27	H27B	O19	0.87	1.84	2.701(4)	168.5
O28	H28A	$O20^{4}$	0.87	2.01	2.869(4)	169.3
O28	H28B	$O15^{4}$	0.87	2.04	2.771(4)	140.6

Table S5 The hydrogen bonds for complexes **4.**

D	H	A	*d*(D-H)/Å	*d*(H-A)/Å	*d*(D-A)/Å	D-H-A/°
O3	H3	O10	0.84	1.95	2.622(4)	136.4
O6	H6	O16	0.84	2.3	2.905(4)	129.6
O9	H9	O4	0.84	1.95	2.622(4)	135.9
O12	H12	O27	0.84	1.84	2.684(4)	176.9
O21	H21	O14	0.879(9)	1.980(13)	2.820(3)	159(2)
O22	H22B	O24	0.88	1.84	2.711(4)	171.6
O23	H23B	O15	0.89	2.02	2.878(3)	163
C11	H11C	O12[1]	0.98	2.59	3.527(5)	159.3
C57	H57A	O6	0.98	2.59	3.182(7)	119.3
C58	H58C	O12[1]	0.98	2.62	3.503(5)	150.1
O24	H24A	O19	0.84	1.87	2.702(4)	172.7
O27	H27B	O13	0.87	1.98	2.753(4)	147.7

Table S6 The hydrogen bonds for complexes **3.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O3	H3	O26	0.84	1.78	2.617(5)	171.4
O6	H6	O1	0.84	1.99	2.650(4)	134.4
O9	H9	O28[1]	0.84	1.81	2.642(5)	170.4
O12	H12	O7	0.84	1.98	2.655(4)	136.6
O20	H20B	O27	0.89	2.01	2.865(5)	159.7
O21	H21B	O24	0.9	1.66	2.558(5)	173.7
O22	H22	O13	0.863(9)	1.977(12)	2.805(4)	160(2)
O23	H23	O16	0.873(9)	1.998(12)	2.837(4)	160.7(19)
C22	H22B	O9[2]	0.98	2.66	3.542(6)	150.7
O24	H24A	O19	0.84	1.92	2.708(4)	156
C59	H59C	O12[3]	0.98	2.54	3.479(6)	160.3
O26	H26A	O21	0.87	1.94	2.789(5)	164.8
O26	H26B	O14	0.87	1.95	2.782(4)	159.2
O27	H27B	O19	0.87	1.85	2.670(5)	155.7
O28	H28A	O20[4]	0.87	1.99	2.853(5)	172.6
O28	H28B	O15[4]	0.87	1.95	2.779(5)	157.5