Electronic Supplementary Information

3D Oxalato-Bridged Lanthanide(III) MOFs with Magnetocaloric, Magnetic and Photoluminescent Properties

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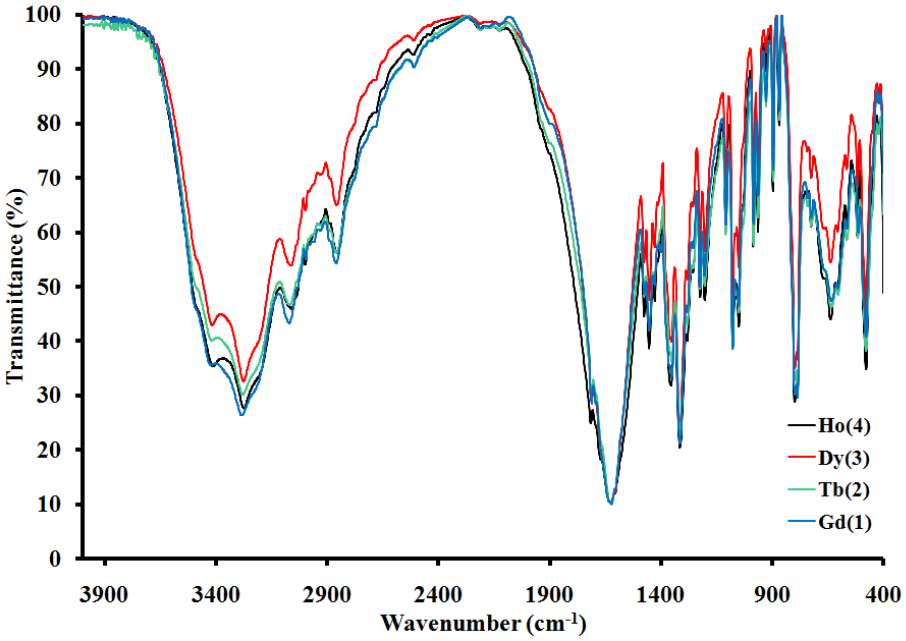
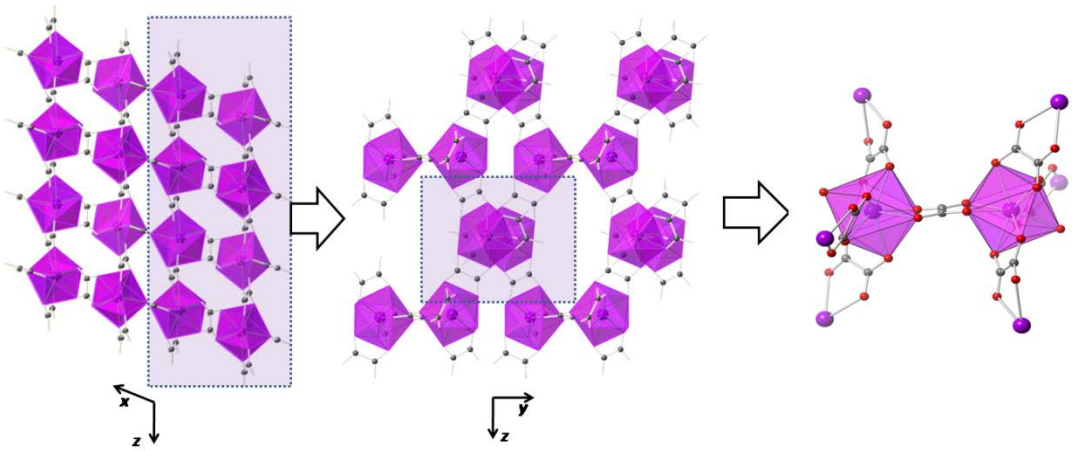


Fig. S1: FTIR spectra of **1-4**.



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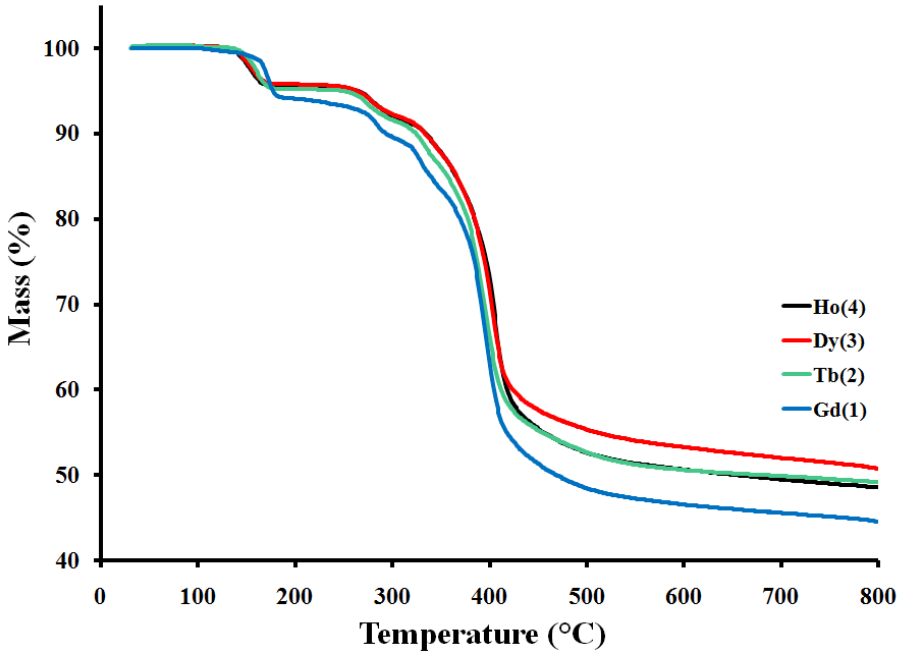


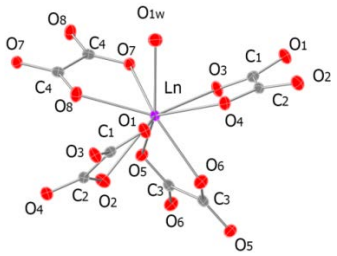
Fig. S3: TGA curves of **1-4**

Table S1.Crystal data and structure refinement for **1-4**.

	1	**2**	**3**	**4**
Empirical formula	$C_9H_{15}GdNO_{11}$	C_9H_{15} $TbNO_{11}$	$C_9H_{15}DyNO_{11}$	$C_9H_{15}HoNO_{11}$
Formula Weight	470.47	472.14	475.72	478.15
Temperature/K	153(2)	120(2)	137(2)	120(2)
Crystal system	Monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a /Å	10.3203(7)	10.314(2)	10.2355(4)	10.2074(4)
b /Å	11.7949(8)	11.767(2)	11.7090(4)	11.6791(4)
c /Å	11.5472(7)	11.499(2)	11.4476(4)	11.4238(4)
β /°	105.129(2)	104.17(3)	104.393(1)	104.246(1)
V /Å^3	1356.89(15)	1353.2(5)	1328.90(8)	1319.99(9)
Z	4	4	4	4
D_{calcd} /mg/mm^3	2.303	2.342	2.378	2.406
μ/mm^{-1}	4.949	5.345	5.686	6.058
Crystal size/mm^3	0.16 × 0.14 × 0.12	0.15 × 0.13 × 0.12	0.11 × 0.05 × 0.04	0.09 × 0.05 × 0.04
$2\theta_{max}$ to$2\theta_{min}$(°)	55.0 to 7.1	50.1 to 5.1	50.05 to 5.9	55.1 to 5.1
F(000)	912	1305	920	924
Reflections collected	10499	10003	16829	15157
Independent reflections	3071 [R_{int} = 0.0353]	2357 [R_{int} = 0.0214]	2337[R_{int} = 0.0156]	3033 [R_{int} = 0.0320]
restraints/parameters	0/202	0/202	0/202	0/206
GOF (S) on F^2	1.044	1.112	1.102	1.080

R_1	0.0353	0.0185	0.0156	0.0210
wR_2 [I>2σ(I)](all data)	0.0824	0.0451	0.0398	0.433
largest diff. peak/hole/eÅ^{-3}	2.95/ -1.62	2.09/-82	1.93/-0.73	2.47/-0.83

Table S2. Ball-and-Stick model of the environment around Ln and selected bond distances and angles for **1**-**4**.



distances	Gd	Tb	Dy	Ho
Ln_1-O_1	2.409(3)	2.389(2)	2.378(2)	2.367(2)
Ln_1-O_2^{i}	2.428(3)	2.402(2)	2.385(2)	2.378(2)
Ln_1-O_3	2.528(3)	2.520(2)	2.517(2)	2.509(2)
Ln_1-O_4^{i}	2.472(3)	2.458(2)	2.452(2)	2.448(2)
Ln_1-O_5	2.436(3)	2.415(2)	2.402(2)	2.390(2)
Ln_1-O_6^{iii}	2.454(3)	2.446(2)	2.438(2)	2.433(2)
Ln_1-O_7	2.418(3)	2.405(2)	2.389(2)	2.379(2)
Ln_1-O_8^{ii}	2.435(3)	2.419(2)	2.406(2)	2.394(2)
Ln_1-O_{1W}	2.444(3)	2.421(2)	2.410(2)	2.397(2)
Ln_1^{iii}-O_6	2.454(3)	2.445(2)	2.438(2)	2.433(2)
Ln_1^{ii}-O_8	2.435(3)	2.419(2)	2.410(2)	2.397(2)
Ln_1^{iv}-O_2	2.428(3)	2.402(2)	2.385(2)	2.378(2)
Ln_1^{iv}-O_4	2.472(3)	2.458(2)	2.452(2)	2.448(2)
O_1-C_1	1.257(5)	1.260(4)	1.263(4)	1.263(3)
O_2-C_1	1.248(6)	1.247(4)	1.250(4)	1.249(3)
O_3-C_2	1.254(6)	1.250(4)	1.252(4)	1.247(3)
O_4-C_2	1.256(5)	1.263(4)	1.264(4)	1.254(4)
O_5-C_3	1.245(5)	1.246(4)	1.247(4)	1.247(4)
O_9-C_7	1.429(6)	1.426(4)	1.426(3)	1.426(4)
O_{10}-C_9	1.459(7)	1.457(5)	1.448(4)	1.451(5)
O_6-C_3	1.256(5)	1.259(3)	1.255(3)	1.254(4)
O_7-C_4	1.256(6)	1.252(4)	1.249(3)	1.251(4)

O_8-C_4	1.259(6)	1.259(4)	1.257(3)	1.254(4)
O_9-C_8	1.492(9)	1.496(5)	1.508(4)	1.503(5)
C_1-C_2	1.557(6)	1.549(4)	1.546(3)	1.536(4)
C_3-C_3^{iii}	1.557(8)	1.550(6)	1.546(5)	1.539(7)
C_4-C_4^{ii}	1.547(9)	1.550(6)	1.552(4)	1.549(6)
C_5-C_5^{v}	1.513(10)	1.522(7)	1.524(5)	1.529(7)
C_6-C_7	1.514(7)	1.516(5)	1.512(4)	1.510(5)
Ln…Ln^{i}	6.224(5)	6.207(1)	6.174(4)	6.162(4)
Ln…Ln^{vi}	6.253(4)	6.235(1)	6.199(4)	6.179(4)
Ln…Ln^{vi}	6.324(4)	6.312(1)	6.274(4)	6.258(4)
O_1-Ln_1-O_2^{i}	134.26(11)	134.44(7)	134.39(7)	134.32(8)
O_2^{i}-Ln_1-O_3	145.81(11)	145.64(8)	145.87(7)	145.69(8)
O_4^{i}-Ln_1-O_3	121.98(11)	122.03(8)	122.81(8)	121.87(7)
O_5-Ln_1-O_6^{iii}	66.27(11)	66.35(8)	66.50(7)	66.72(8)
O_7-Ln_1-O_8^{ii}	67.22(10)	67.55(8)	67.75(6)	67.96(7)

^{i}+x,1/2-y,1/2+z; ^{ii}1-x,1-y,2-z; ^{iii}2-x,1-y,2-z; ^{iv}+x,1/2-y,-1/2+z; ^{v}1-x,1-y,1-z, ^{vi}-x,-y,-z

Table S3. MCE data of some Gadolinium structures.

	J $kg^{-1}K^{-1}$	Debye Temperature (K)		Reference
$Gd_7(OH)_6$	23	?	MOF	[1]
$[Gd_2(N\text{-}BDC)_3(dmf)_4$	29	45.4	MOF	[2]
(choline)[Gd(ox)$(H_2O)_3$Cl]Cl.H_2O	32.9	279		[3]
Gd(HCOO)$(C_8H_4O_4)$	33.3	?	MOF	[4]
1	35.9	342.5	MOF	This article
$Gd_3Ga_5O_{12}$ (GGG)*	38.3	~500		[5]
$[Gd(HCOO)(OAc)_2(H_2O)_2$	45.9 (9T)	80.4	MOF	[2]
$Gd_2(ox)_3(H_2O)_6{\cdot}0.6H_2O$	46.6	?	MOF	[6]
[Gd(ox)$(H_2O)_3$Cl]	48	282	2D network	[7]
$[Gd(HCOO)_3]_n$	55.9	168	MOF	[8]
$Gd_2O(OH)_4(H_2O)_2$	59.1	?	3D	[9]
$Gd(OH)_3$	62	?	3D	[9]
$[Gd(OH)CO_3]_n$	66.4	313	1D	[10]
$[Gd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}H_2O)]^{8+}$	51.5		Cluster	[11]
$[Gd_{10}(\mu_3\text{-}OH)_8]^{22+}$	31.2		Cluster	[12]
$[Gd(cit)(H_2O)]_\infty$	41.5		3D	[13]
$[Gd(nta)(H_2O)2]_\infty$	42.0		3D	[13]
$Gd_2(fum)_3(H_2O)_4{\cdot}3H_2O$	20.7 (5T)			[14]

$[Gd(OAc)_3(H2O)_{0.5}]_n$	47.7	?	MOF	[15]
$[\{Gd(OAc)_3(H_2O)_2\}_2].4H_2O$	40	61.6		[16]
$[Gd_4(OAc)_4(acac)_8(H_2O)_4]$	37.7	?		[15]

* This compound is commercially available as good MCE

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