Electronic Supplementary Information (ESI)

Systematic investigation of the lanthanide coordination polymers with γ-pyrone-2,6-dicarboxylic acid

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Supplementary Experiments:

$[Cu(CDO)(H_2O)_5]\cdot H_2O$ was synthesized from the mixture of H_2CDO (0.5 mmol, 0.0920 g), $Cu(NO_3)_3\cdot 6H_2O$ (0.25 mmol, 0.076 g), LiOH (0.5 mmol, 0.0210 g), and H_2O (15 mL) under reflux for 2 h. After filtering, the filtrate was kept at room temperature and after about one week, blue crystals were obtained by slow evaporation of the filtrate. Yields: 50%.

$[Mn(CDO)(H_2O)_4]\cdot 2H_2O$ was synthesized from the mixture of H_2CDO (0.5 mmol, 0.0920 g), $MnCl_2\cdot 4H_2O$ (0.25 mmol, 0.047 g), LiOH (0.5 mmol, 0.0210 g), and H_2O (15 mL) under reflux for 2 h. After filtering, the filtrate was kept at room temperature and after about one month, colorless crystals were obtained by slow evaporation of the filtrate. Yields: 40%.

$\{Ba(CDO)(H_2O)\}_n$ (Ba-10) was synthesized from the mixture of H_2CDO (0.5 mmol, 0.0920 g), $BaCl_2$ (0.25 mmol, 0.061 g), LiOH (0.5 mmol, 0.0210 g), and H_2O (15 mL) under reflux for 2 h. After filtering, the filtrate was kept at room temperature and after about one month, colorless crystals were obtained by slow evaporation of the filtrate. Element analysis (%) found (calcd.) for **Ba-10**, C 24.70 (24.92), H 1.22 (1.19); Yields: 21%. IR (KBr, cm^{-1}): 3229vs, br, 1635vs, 1128w, 969w, 898w, 809w, 722m, 475w.

$\{[Ho(H_2O)_{3.5}(CDO)_{1.5}]\cdot 2.5H_2O\}_n$ (Ho-6) was synthesized from the mixture of H_2CDO (0.5 mmol, 0.0920 g), $Ho(NO_3)_3\cdot 6H_2O$ (0.25 mmol, 0.1150 g), LiOH (0.5 mmol, 0.0210 g), and H_2O (15 mL) under 80 □ for two days. The reaction solution was cooled to room temperature for four days and tine crystals emerged. After about one month, prism crystals were harvested.

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[Ho(H_2O)$_4$(OX)$_{0.5}$(CDO)] (**Ho-11)** was synthesized from the mixture of H_2CDO (0.5 mmol, 0.0920 g), $Ho(NO_3)_3{\cdot}6H_2O$ (0.25 mmol, 0.1150 g), LiOH (0.5 mmol, 0.0210 g), and H_2O (15 mL) under 80 □ for two days. The reaction solution was cooled to room temperature for four days, and prism crystals were harvested. Element analysis (%) found (calcd.) for **Ho-11**, C 20.11 (19.97), H 2.48 (2.51); Yields: 44%. IR (KBr, cm^{-1}): 3406vs, br, 1631vs, 1406w, 1351s, 974w, 934w, 916w, 796m, 739m, 526w.

[Ho(H_2O)$_4$(OX)$_{0.5}$(CDO)] was synthesized from the mixture of H_2CDO (0.5 mmol, 0.0920 g), $Ho(NO_3)_3{\cdot}6H_2O$ (0.25 mmol, 0.1150 g), LiOH (0.5 mmol, 0.0210 g), and H_2O (15 mL) under 100 ℃ for two days. The reaction solution was cooled to room temperature for four days, and block crystals were harvested.

{[Ho$_2$(OX)$_3$(H_2O)$_6$]·4H_2O}$_n$ was synthesized from the mixture of H_2CDO (0.5 mmol, 0.0920 g), $Ho(NO_3)_3{\cdot}6H_2O$ (0.25 mmol, 0.1150 g), LiOH (0.5 mmol, 0.0210 g), and H_2O (15 mL) under 140 ℃ for two days. The reaction solution was cooled to room temperature for four days, and prism crystals were harvested.

Table S1. Selected Bond Lengths (Å) for the Nine Compounds.

Nd-1			
Nd(1)-O(18)	2.533(4)	Nd(1)-O(22)	2.519(4)
Nd(1)-O(9)#1	2.442(4)	Nd(1)-O(23)	2.600(5)
Nd(1)-O(2)	2.442(4)	Nd(2)-O(8)#2	2.447(4)
Nd(1)-O(19)	2.484(4)	Nd(2)-O(24)	2.483(5)
Nd(1)-O(4)#1	2.486(4)	Nd(2)-O(10)	2.485(4)
Nd(1)-O(20)	2.493(4)	Nd(2)-O(26)	2.486(4)
Nd(1)-O(21)	2.506(5)	Nd(2)-O(25)	2.486(5)
Nd(2)-O(28)	2.486(4)	Nd(2)-O(29)	2.498(4)
Nd(2)-O(3)	2.516(4)	Nd(2)-O(27)	2.553(5)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1 #2 -x+2,-y+1,-z+1			
Eu-2			
Eu(1)-O(20)	2.564(18)	Eu(1)-O(7)	2.290(19)
Eu(1)-O(1)	2.306(6)	Eu(1)-O(4)#1	2.335(6)
Eu(1)-O(13)	2.378(7)	Eu(1)-O(14)	2.383(6)
Eu(1)-O(6)#2	2.383(6)	Eu(1)-O(5)#3	2.393(7)
Eu(1)-O(15)	2.432(6)		
Gd-3			
Gd(1)-O(1)	2.303(2)	Gd(1)-O(14)	2.395(2)
Gd(1)-O(4)#1	2.350(2)	Gd(1)-O(5)#3	2.405(2)
Gd(1)-O(7)	2.370(19)	Gd(1)-O(15)	2.422(2)
Gd(1)-O(6)#2	2.382(2)	Gd(1)-O(20)	2.53(2)
Gd(1)-O(13)	2.392(2)		
Tb-4			
Tb(1)-O(7)	2.27(2)	Tb(1)-O(1)	2.288(4)
Tb(1)-O(4)#1	2.344(5)	Tb(1)-O(6)#2	2.362(5)
Tb(1)-O(14)	2.375(5)	Tb(1)-O(13)	2.385(5)
Tb(1)-O(5)#3	2.394(5)	Tb(1)-O(15)	2.404(5)

Tb(1)-O(20)	2.526(13)		

Dy-5

Dy(1)-O(1)	2.280(4)	Dy(1)-O(5)#4	2.376(5)
Dy(1)-O(7)	2.297(14)	Dy(1)-O(14)	2.378(5)
Dy(1)-O(4)#2	2.326(5)	Dy(1)-O(15)	2.407(5)
Dy(1)-O(13)	2.356(5)	Dy(1)-O(20)	2.545(14)
Dy(1)-O(6)#3	2.361(5)		

Ho-6

Ho(1)-O(1)	2.276(7)	Ho(1)-O(6)#2	2.356(7)
Ho(1)-O(4)#1	2.297(8)	Ho(1)-O(5)#3	2.359(8)
Ho(1)-O(13)	2.348(9)	Ho(1)-O(15)	2.390(8)
Ho(1)-O(7)	2.35(3)	Ho(1)-O(20)	2.48(3)
Ho(1)-O(14)	2.353(8)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1, #2 -x+1,-y,-z+1, #3 x+1,y,z-1

Er-7

Er(1)-O(6)	2.351(3)	Er(1)-O(8)	2.424(3)
Er(1)-O(9)	2.359(4)	Er(1)-O(12)	2.439(6)
Er(1)-O(4)	2.356(3)	Er(1)-O(7)	2.473(4)
Er(1)-O(10)	2.384(3)	Er(1)-O(2)	2.694(3)
Er(1)-O(11)	2.416(3)		

Tm-8

Tm(1)-O(5)	2.304(2)	Tm(1)-O(12)	2.377(2)
Tm(1)-O(9)	2.307(3)	Tm(1)-O(11)	2.396(2)
Tm(1)-O(2)	2.308(2)	Tm(1)-O(10)	2.424(2)
Tm(1)-O(8)#1	2.337(2)	Tm(1)-O(1)	2.651(2)
Tm(1)-O(7)	2.375(2)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Yb-9

Yb(2)-O(11)	2.275(5)	Yb(1)-O(25)	2.281(5)

Yb(2)-O(5)#1	2.286(5)	Yb(1)-O(26)	2.299(5)
Yb(2)-O(10)	2.297(5)	Yb(1)-O(27)	2.318(5)
Yb(2)-O(2)	2.308(5)	Yb(1)-O(22)	2.320(5)
Yb(2)-O(9)	2.311(5)	Yb(1)-O(23)	2.321(5)
Yb(2)-O(6)#2	2.419(5)	Yb(1)-O(21)#4	2.336(5)
Yb(2)-O(8)	2.506(5)	Yb(1)-O(20)	2.343(5)
Yb(1)-O(24)	2.389(5)		

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z; #2 -x+1,-y,-z; #4 -x+1,-y+1,-z+1

Ba-10

Ba(1)-O(3)#1	2.689(6)	Ba(1)-O(2)	2.842(4)
Ba(1)-O(2)#2	2.720(4)	Ba(1)-O(1)#4	2.921(5)
Ba(1)-O(2)#3	2.720(4)	Ba(1)-O(1)	2.921(5)
Ba(1)-O(4)	2.767(6)	Ba(1)-O(4)#2	2.942(7)
Ba(1)-O(2)#4	2.842(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 x,y,z+1 #3 x,-y+1/2,z+1

#4 x,-y+1/2,z #5 x,-y+3/2,z #6 x,y,z-1

Ho-11

Ho(1)-O(6)	2.333(2)	Ho(1)-O(7)	2.398(3)
Ho(1)-O(4)	2.337(2)	Ho(1)-O(12)	2.406(3)
Ho(1)-O(8)	2.356(3)	Ho(1)-O(10)	2.437(2)
Ho(1)-O(9)	2.373(3)	Ho(1)-O(2)	2.638(2)
Ho(1)-O(11)	2.376(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

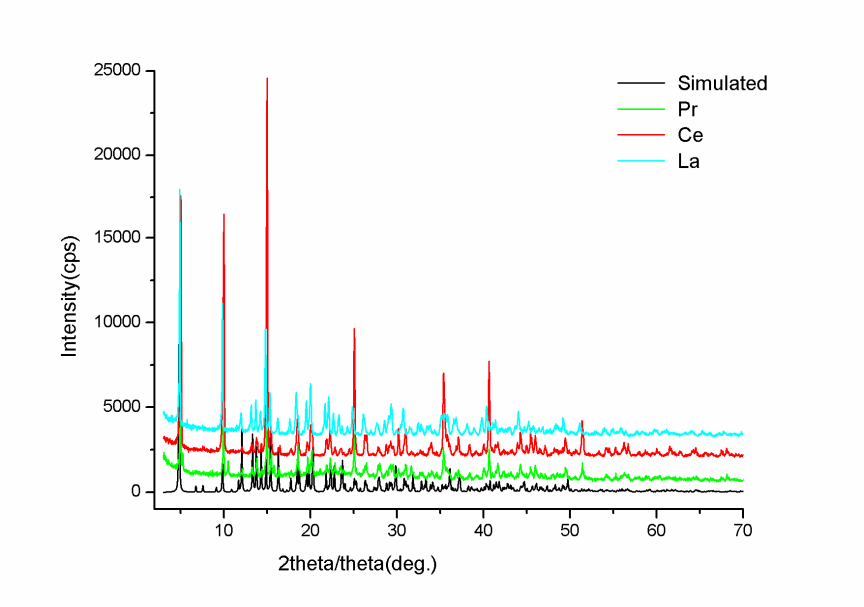

Figure S2. The simulated, experimental patterns of complexes La^{3+}, Ce^{3+}, Pr^{3+}. The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation of the powder sample during the collection of the experimental PXRD data

Table S2. Details on crystal data collection and structure refinement of **Ba-10** and **Ho-11**

Complex	**Ba-10**	**Ho-11**
Formula	$C_7H_4O_7Ba_1$	$C_{16}H_{24}O_{26}Ho_2$
Fw	337.43	962.22
Cryst size, mm	0.10 x 0.05 x 0.05	0.20 x 0.10 x 0.10
Temp, K	113(2)	113(2)
Cryst syst	Orthorhombic	Triclinic
Space group	Pnma	P-1
a, Å	19.441(2)	6.1814(4)
b, Å	10.0363(12)	10.0963(7)
c, Å	4.3190(5)	10.8666(7)
α, deg	90	97.249(6)
β, deg	90	95.999(5)
γ, deg	90	103.840(6)
V, Å^3	842.70(16)	646.81(7)
Z	8	2
D_c, g/cm^3	2.660	2.470
μ, mm^{-1}	4.728	6.191
no. of data/params	6384 / 74	2644 / 199
obs reflns	778	4424
θ range, deg	4.06-24.96	2.61-26.37
GOOF	1.179	1.072
F(000)	632	462
R_{int}	0.0326	0.0159
R1 [$I > 2\acute{o}(I)$]	0.0184	0.0193
wR2 (all data)	0.0406	0.0485
max/min, e Å^{-3}	0.206 / -0.412	0.879 / -0.924

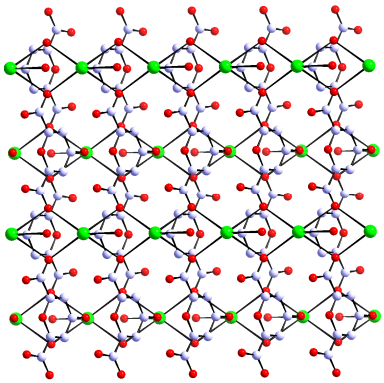

Figure S3. The 2D layer of $\{Ba(CDO)(H_2O)\}_n$.

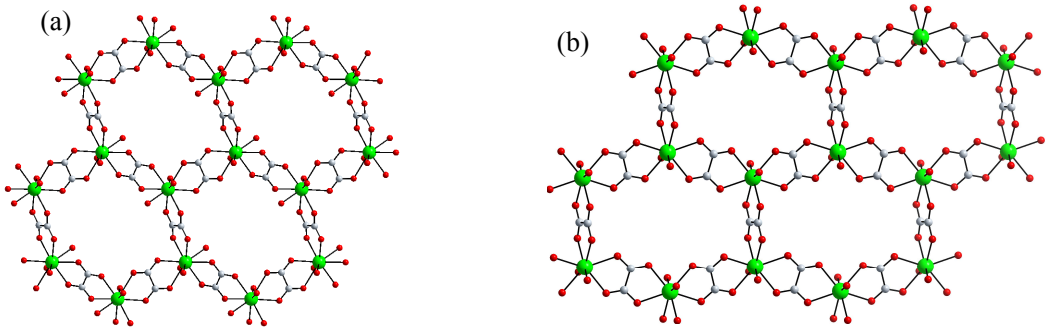

Figure S4. (a) $\{[Ho_2(OX)_3(H_2O)_6]\cdot 4H_2O\}_n$, the hydrothermal product of Ho^{3+} ions and H_2CDO at 80 □. Ho(III) atoms are nine-coordinated. (b) $\{[Ho_2(OX)_3(H_2O)_4]\cdot 2H_2O\}_n$, the hydrothermal product at 140 □. Ho(III) atoms are eight-coordinated..