Supporting Information

Ionothermal Syntheses, Crystal Structures and Properties of Three-Dimensional Rare Earth Metal Organic Frameworks with 1,4-naphthalenedicarboxylic acid

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Table S1. Selected bond lengths (Å) and angles (°) for compounds **1-6**[a].

	La-1	**Ce-2**	**Pr-3**	**Nd-4**	**Sm-5**	**Eu-6**
M(1)-O(7)#1	2.408(2)	2.378(2)	2.363(2)	2.352(2)	2.336(3)	2.319(2)
M(1)-O(1)	2.439(2)	2.409(2)	2.393(2)	2.375(2)	2.347(4)	2.332(3)
M(1)-O(5)#2	2.444(2)	2.413(2)	2.393(3)	2.376(2)	2.351(4)	2.335(3)
M(1)-O(6)#3	2.445(2)	2.418(3)	2.401(3)	2.385(2)	2.361(4)	2.338(2)
M(1)-O(3)	2.458(2)	2.435(2)	2.417(2)	2.404(2)	2.361(4)	2.353(3)
M(1)-O(2)#4	2.456(2)	2.436(2)	2.419(2)	2.406(2)	2.377(4)	2.364(3)
M(1)-Cl(1)	2.9358(8)	2.9091(8)	2.8889(8)	2.8717(9)	2.8428(13)	2.8323(9)
M(1)-M(1)#4	4.4298(2)	4.4429(2)	4.4342(2)	4.4185(2)	4.3974(3)	4.3875(3)
M(2)-O(11)#1	2.430(2)	2.402(2)	2.379(2)	2.354(2)	2.320(3)	2.296(3)
M(2)-O(4)	2.408(2)	2.387(2)	2.365(2)	2.354(2)	2.324(3)	2.314(2)
M(2)-O(10)#5	2.430(2)	2.406(2)	2.385(2)	2.372(2)	2.342(3)	2.332(2)
M(2)-O(8)#1	2.479(2)	2.455(2)	2.430(2)	2.421(2)	2.394(3)	2.372(2)
M(2)-O(9)	2.498(2)	2.480(2)	2.454(2)	2.442(2)	2.412(4)	2.403(2)
M(2)-O(12)#6	2.525(2)	2.502(3)	2.477(3)	2.459(2)	2.424(4)	2.408(3)
M(2)-Cl(1)	2.9087(8)	2.8867(8)	2.8639(8)	2.8470(8)	2.8185(12)	2.8067(9)
M(2)-O(11)#6	2.895(2)	2.899(3)	2.906(2)	2.926(3)	2.975(3)	3.009(3)
M(2)-M(2)#5	4.1836(2)	4.1650(2)	4.1543(2)	4.1467(2)	4.1453(3)	4.1503(3)
O(7)#1-M(1)-O(1)	80.79(8)	81.17(9)	81.14(9)	80.87(8)	80.28(13)	80.02(9)
O(7)#1-M(1)-O(5)#2	149.44(9)	149.13(10)	148.85(10)	148.23(10)	147.22(15)	146.68(11)
O(1)-M(1)-O(5)#2	77.36(9)	77.55(10)	77.93(10)	77.83(9)	77.96(15)	77.52(11)
O(7)#1-M(1)-O(6)#3	75.00(9)	75.88(10)	76.16(10)	76.60(9)	77.35(14)	77.39(10)
O(1)-M(1)-O(6)#3	82.52(9)	81.68(11)	81.21(10)	81.09(10)	80.80(16)	80.86(11)
O(5)#2-M(1)-O(6)#3	122.30(9)	122.10(10)	122.40(10)	122.31(9)	122.33(14)	122.26(10)
O(7)#1-M(1)-O(3)	82.68(9)	82.30(10)	82.34(9)	82.37(9)	82.24(14)	82.25(10)
O(1)-M(1)-O(3)	96.79(9)	96.57(11)	96.55(10)	97.30(10)	97.98(16)	97.98(11)
O(5)#2-M(1)-O(3)	79.00(8)	78.24(9)	77.45(9)	77.31(9)	76.88(14)	76.88(10)
O(6)#3-M(1)-O(3)	157.51(9)	158.13(10)	158.48(10)	158.91(9)	159.47(14)	159.50(10)
O(7)#1-M(1)-O(2)#4	138.69(9)	138.63(10)	138.74(10)	139.07(9)	140.15(15)	140.36(10)

O(1)-M(1)-O(2)#4	125.82(8)	124.91(8)	124.69(8)	124.78(9)	124.75(14)	124.72(9)
O(5)#2-M(1)-O(2)#4	71.88(9)	72.23(10)	72.39(10)	72.68(9)	72.60(15)	72.95(11)
O(6)#3-M(1)-O(2)#4	77.99(9)	77.20(10)	77.13(10)	77.05(9)	77.26(15)	77.18(10)
O(3)-M(1)-O(2)#4	118.92(9)	120.04(11)	120.18(10)	119.50(9)	118.64(16)	118.66(11)
O(7)#1-M(1)-Cl(1)	75.45(6)	75.82(6)	75.91(6)	76.31(6)	76.73(9)	76.88(7)
O(1)-M(1)-Cl(1)	155.94(6)	156.71(7)	156.79(7)	156.91(6)	156.68(10)	156.55(7)
O(5)#2-M(1)-Cl(1)	126.05(7)	124.96(8)	124.41(8)	124.36(7)	124.46(12)	125.04(8)
O(6)#3-M(1)-Cl(1)	87.68(7)	89.27(8)	89.92(7)	90.20(7)	90.32(11)	90.12(8)
O(3)-M(1)-Cl(1)	84.03(6)	83.92(7)	83.88(7)	83.21(7)	82.87(11)	82.98(7)
O(2)#4-M(1)-Cl(1)	72.76(6)	73.02(6)	73.20(6)	73.04(6)	73.22(10)	73.29(7)
O(4)-M(2)-O(10)#5	153.10(8)	153.17(9)	153.33(9)	153.50(9)	154.42(14)	154.64(9)
O(4)-M(2)-O(11)#1	103.93(8)	102.40(9)	101.47(9)	100.64(8)	99.17(14)	98.33(10)
O(10)#5-M(2)-O(11)#1	77.67(9)	78.32(10)	78.59(10)	79.01(9)	79.59(15)	80.21(10)
O(4)-M(2)-O(8)#1	75.89(8)	75.71(9)	75.72(8)	75.92(8)	76.42(13)	76.68(9)
O(10)#5-M(2)-O(8)#1	77.96(8)	77.96(9)	77.99(9)	77.88(8)	78.19(13)	78.11(9)
O(11)#1-M(2)-O(8)#1	80.56(7)	81.15(8)	81.03(8)	81.07(8)	80.58(13)	80.67(9)
O(4)-M(2)-O(9)	73.28(8)	73.27(8)	73.29(8)	73.44(8)	73.68(13)	73.86(9)
O(10)#5-M(2)-O(9)	131.34(8)	131.08(8)	130.76(8)	130.40(8)	129.20(13)	128.86(9)
O(11)#1-M(2)-O(9)	74.36(8)	74.35(9)	74.45(9)	74.47(8)	74.70(13)	74.76(9)
O(8)#1-M(2)-O(9)	133.64(8)	134.73(10)	135.22(9)	135.98(8)	137.12(14)	137.98(9)
O(4)-M(2)-O(12)#6	110.46(9)	111.63(10)	112.49(10)	113.45(9)	114.84(15)	115.92(10)
O(10)#5-M(2)-O(12)#6	89.91(9)	89.26(11)	88.57(10)	87.74(9)	86.01(15)	84.83(10)
O(11)#1-M(2)-O(12)#6	122.24(8)	122.31(8)	122.60(8)	122.50(8)	122.82(13)	122.92(9)
O(8)#1-M(2)-O(12)#6	151.54(8)	150.69(9)	150.16(9)	149.70(9)	148.98(14)	148.07(10)
O(9)-M(2)-O(12)#6	73.11(9)	72.90(10)	73.07(10)	73.01(9)	72.95(15)	73.16(10)
O(4)-M(2)-Cl(1)	83.09(6)	83.53(7)	83.53(6)	83.41(6)	83.28(10)	83.30(7)
O(10)#5-M(2)-Cl(1)	88.05(6)	88.44(7)	88.98(7)	89.44(6)	90.43(10)	90.57(7)
O(11)#1-M(2)-Cl(1)	160.80(6)	161.32(7)	161.50(6)	161.72(6)	161.83(10)	161.82(7)
O(8)#1-M(2)-Cl(1)	83.97(5)	83.26(6)	83.03(6)	82.69(6)	82.54(9)	82.11(6)
O(9)-M(2)-Cl(1)	124.82(7)	124.26(7)	123.89(7)	123.54(6)	122.91(10)	122.68(7)
O(12)#6-M(2)-Cl(1)	69.82(6)	69.98(6)	70.06(6)	70.50(6)	70.94(9)	71.18(7)

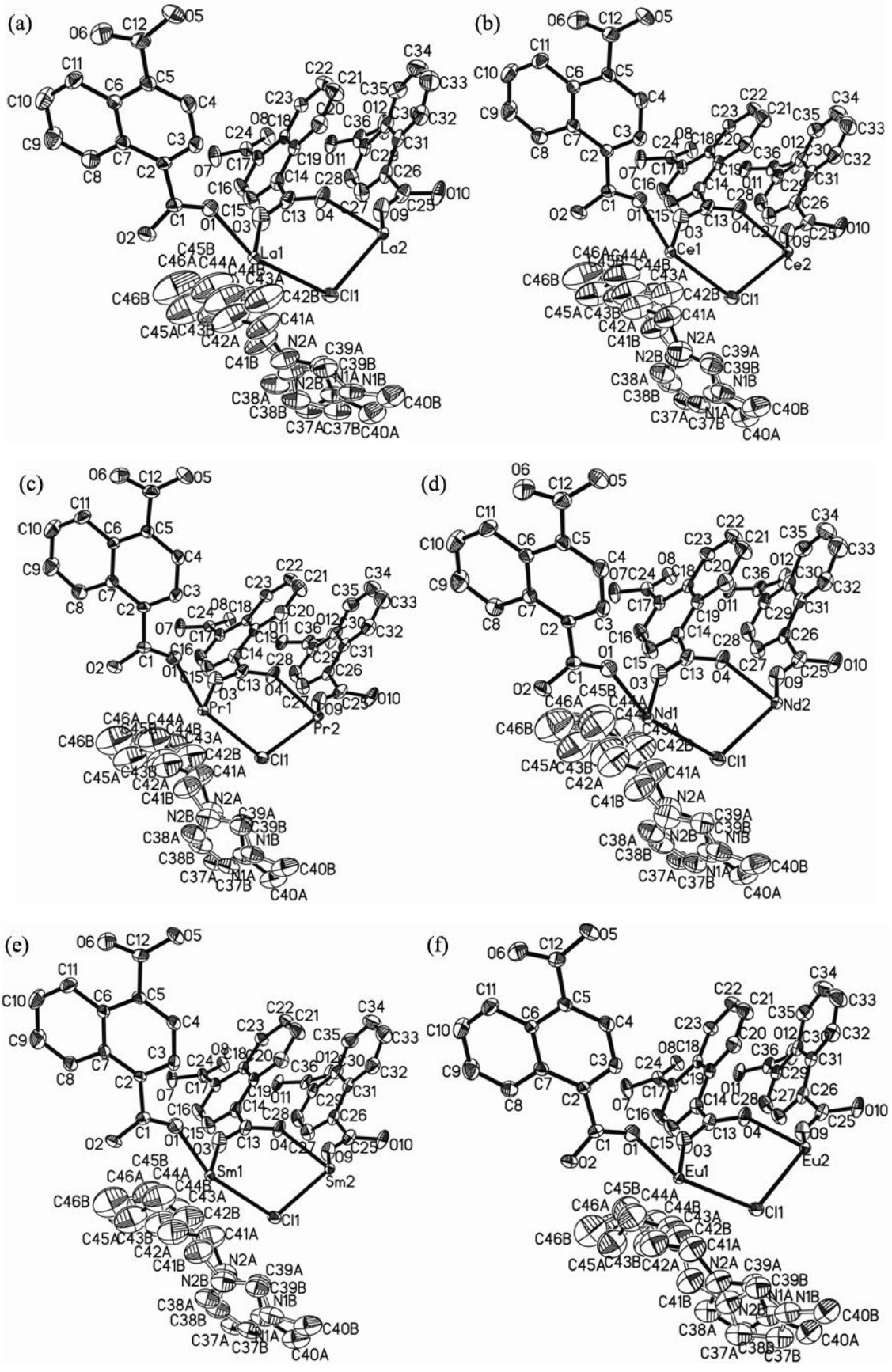
[a]Symmetry transformations used to generate equivalent atoms: #1 *x*,-*y*+1/2,*z*-1/2; #2 *x*, -*y*+1/2,*z*+1/2; #3 -*x*+1,*y*-1/2, -*z*-1/2; #4 -*x*+1,-*y*,-*z*; #5 -*x*,-*y*,-*z*; #6 -*x*,*y*-1/2,-*z*+1/2.

Table S2. Selected bond lengths (Å) and angles (°) for compounds **7-12**[a].

	Gd-7	**Tb-8**	**Dy-9**	**Ho-10**	**Er-11**	**Y-12**
M(1)-O(7)#1	2.309(2)	2.294(3)	2.284(2)	2.277(4)	2.267(3)	2.269(3)
M(1)-O(1)	2.315(3)	2.305(3)	2.293(3)	2.275(4)	2.264(3)	2.279(3)
M(1)-O(5)#2	2.328(2)	2.305(3)	2.295(3)	2.278(4)	2.277(3)	2.277(3)
M(1)-O(6)#3	2.331(3)	2.320(3)	2.302(3)	2.282(5)	2.281(3)	2.285(3)
M(1)-O(3)	2.336(3)	2.320(3)	2.305(3)	2.292(5)	2.284(3)	2.292(3)
M(1)-O(2)#4	2.351(3)	2.338(3)	2.321(2)	2.310(5)	2.303(3)	2.307(3)
M(1)-Cl(1)	2.8211(9)	2.8125(12)	2.8000(9)	2.7885(16)	2.7872(10)	2.8009(11)
M(1)-M(1)#4	4.3687(2)	4.3575(3)	4.3484(2)	4.3327(4)	4.3340(3)	4.3472(5)
M(2)-O(11)#1	2.286(2)	2.263(3)	2.254(2)	2.243(4)	2.226(3)	2.236(3)
M(2)-O(4)	2.299(2)	2.283(3)	2.274(2)	2.257(4)	2.251(3)	2.259(3)
M(2)-O(10)#5	2.318(2)	2.305(3)	2.291(2)	2.285(4)	2.266(3)	2.276(3)
M(2)-O(8)#1	2.365(2)	2.346(3)	2.329(2)	2.312(4)	2.311(2)	2.316(3)

M(2)-O(9)	2.386(2)	2.371(3)	2.364(2)	2.343(4)	2.337(3)	2.340(3)
M(2)-O(12)#6	2.394(3)	2.384(3)	2.365(2)	2.360(4)	2.343(3)	2.353(3)
M(2)-Cl(1)	2.7914(9)	2.7718(12)	2.7603(9)	2.7499(15)	2.7407(10)	2.7602(11)
M(2)-O(11)#6	3.034(3)	3.091(4)	3.120(3)	3.139(5)	3.172(3)	3.173(3)
M(2)-M(2)#5	4.1496(2)	4.1615(3)	4.1689(2)	4.1645(4)	4.1796(3)	4.1836(5)
O(7)#1-M(1)-O(1)	79.82(9)	79.29(12)	79.24(9)	79.01(16)	79.10(10)	78.98(11)
O(7)#1-M(1)-O(5)#2	146.01(11)	145.42(14)	144.91(11)	144.28(19)	144.39(12)	143.98(13)
O(1)-M(1)-O(5)#2	77.33(11)	77.33(14)	77.14(11)	77.00(19)	77.06(12)	76.88(13)
O(7)#1-M(1)-O(6)#3	77.52(10)	77.68(13)	78.09(10)	78.29(18)	78.49(11)	78.67(12)
O(1)-M(1)-O(6)#3	81.05(11)	80.79(15)	80.85(11)	81.14(19)	80.83(12)	80.73(13)
O(5)#2-M(1)-O(6)#3	122.64(10)	122.60(13)	122.61(10)	122.98(17)	122.65(11)	122.62(11)
O(7)#1-M(1)-O(3)	82.24(10)	82.42(13)	82.40(10)	82.24(18)	82.23(11)	82.22(12)
O(1)-M(1)-O(3)	98.61(12)	99.01(15)	99.30(11)	99.47(19)	100.08(12)	100.02(13)
O(5)#2-M(1)-O(3)	76.73(10)	76.53(13)	76.29(10)	76.10(17)	76.38(11)	76.16(11)
O(6)#3-M(1)-O(3)	159.51(10)	159.79(13)	160.12(10)	160.04(17)	160.17(11)	160.37(11)
O(7)#1-M(1)-O(2)#4	140.84(10)	141.21(13)	141.60(10)	141.78(18)	142.14(11)	142.22(12)
O(1)-M(1)-O(2)#4	124.86(10)	124.95(13)	124.61(10)	124.90(16)	124.71(11)	124.77(10)
O(5)#2-M(1)-O(2)#4	73.12(11)	73.35(14)	73.48(10)	73.92(19)	73.44(11)	73.77(13)
O(6)#3-M(1)-O(2)#4	77.45(11)	77.48(14)	77.20(10)	77.17(19)	77.46(11)	77.40(13)
O(3)-M(1)-O(2)#4	117.84(11)	117.45(14)	117.33(11)	117.04(19)	116.49(12)	116.48(13)
O(7)#1-M(1)-Cl(1)	77.09(7)	77.67(9)	77.83(7)	78.22(11)	78.10(7)	78.18(8)
O(1)-M(1)-Cl(1)	156.52(7)	156.53(9)	156.60(7)	156.79(13)	156.72(8)	156.65(8)
O(5)#2-M(1)-Cl(1)	125.25(9)	125.25(11)	125.37(8)	125.25(14)	125.30(9)	125.56(10)
O(6)#3-M(1)-Cl(1)	89.80(8)	89.98(11)	89.94(8)	89.88(13)	90.07(9)	90.09(9)
O(3)-M(1)-Cl(1)	82.53(8)	82.33(10)	82.21(8)	81.87(13)	81.44(8)	81.62(9)
O(2)#4-M(1)-Cl(1)	73.20(7)	73.01(9)	73.23(7)	72.90(11)	73.15(8)	73.08(7)
O(4)-Gd(2)-O(10)#5	154.95(10)	155.60(13)	155.81(10)	156.17(17)	156.50(10)	156.65(12)
O(4)-Gd(2)-O(11)#1	97.78(10)	96.36(13)	95.61(10)	95.10(18)	94.75(11)	95.38(12)
O(10)#5-Gd(2)-O(11)#1	80.36(10)	80.88(14)	81.28(10)	81.45(18)	81.58(11)	81.96(12)
O(4)-Gd(2)-O(8)#1	76.96(9)	77.24(12)	77.52(9)	77.98(16)	78.30(10)	78.09(11)
O(10)#5-Gd(2)-O(8)#1	78.11(9)	78.40(12)	78.31(9)	78.20(15)	78.20(10)	78.61(11)
O(11)#1-Gd(2)-O(8)#1	80.39(9)	80.15(12)	80.12(9)	80.14(16)	80.26(10)	79.99(11)
O(4)-Gd(2)-O(9)	74.03(9)	74.29(12)	74.59(9)	74.46(16)	74.73(10)	74.68(11)
O(10)#5-Gd(2)-O(9)	128.35(9)	127.26(12)	126.71(9)	126.45(15)	125.81(10)	126.16(10)
O(11)#1-Gd(2)-O(9)	75.01(9)	75.11(12)	75.14(9)	75.47(16)	75.42(10)	75.40(11)
O(8)#1-Gd(2)-O(9)	138.57(10)	139.52(13)	140.29(9)	141.01(17)	141.66(10)	141.00(12)
O(4)-Gd(2)-O(12)#6	116.60(10)	117.82(13)	118.66(10)	119.05(17)	119.63(10)	118.77(12)
O(10)#5-Gd(2)-O(12)#6	84.07(11)	82.86(13)	82.01(10)	81.48(17)	80.80(10)	81.00(12)
O(11)#1-Gd(2)-O(12)#6	123.00(9)	122.98(13)	123.05(10)	123.21(16)	122.87(10)	123.05(11)
O(8)#1-Gd(2)-O(12)#6	147.71(10)	147.35(13)	146.72(10)	146.12(17)	145.79(10)	146.46(12)
O(9)-Gd(2)-O(12)#6	73.09(10)	72.69(13)	72.68(9)	72.59(17)	72.36(10)	72.30(12)
O(4)-Gd(2)-Cl(1)	83.09(7)	83.34(9)	83.17(7)	83.03(12)	82.86(8)	82.61(8)
O(10)#5-Gd(2)-Cl(1)	91.16(7)	91.87(9)	92.41(7)	92.96(12)	93.36(8)	92.70(8)
O(11)#1-Gd(2)-Cl(1)	161.84(7)	161.79(9)	161.85(7)	161.85(12)	161.70(7)	161.74(9)
O(8)#1-Gd(2)-Cl(1)	82.16(7)	82.05(9)	81.95(7)	81.82(11)	81.49(7)	81.85(7)
O(9)-Gd(2)-Cl(1)	122.23(7)	121.84(9)	121.47(7)	120.87(12)	120.88(7)	120.99(8)
O(12)#6-Gd(2)-Cl(1)	71.42(7)	72.04(9)	72.30(7)	72.43(11)	73.08(7)	72.78(7)

[a]Symmetry transformations used to generate equivalent atoms: #1 *x*,-*y*+1/2,*z*-1/2; #2 *x*, -*y*+1/2,*z*+1/2; #3 -*x*+1,*y*-1/2,-*z*-1/2; #4 -*x*+1,-*y*,-*z*; #5 -*x*,-*y*,-*z*; #6 -*x*,*y*-1/2,-*z*+1/2.



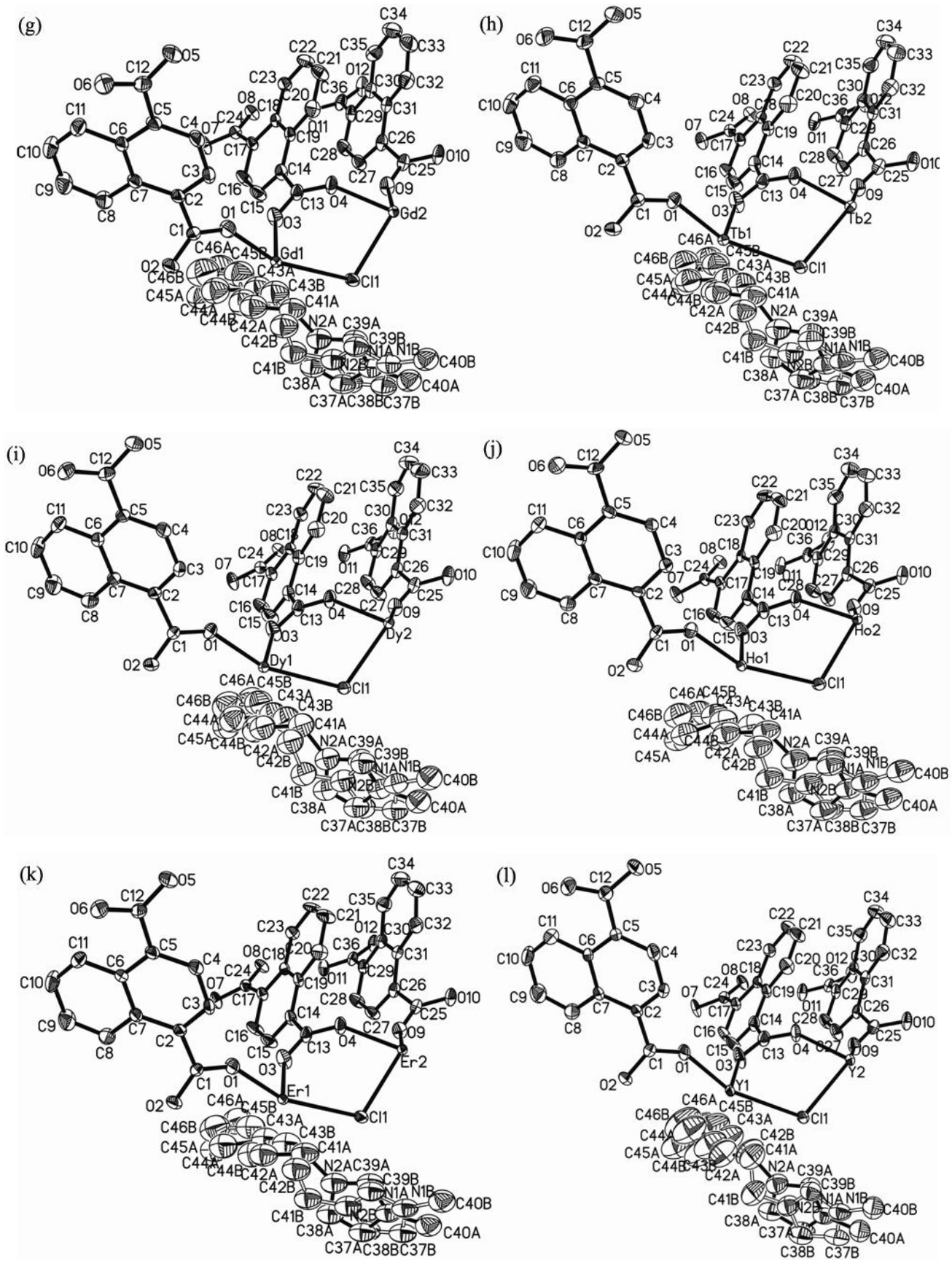


Figure S1. *ORTEP* plot showing the crystallographically asymmetric units in compounds **1**-**12**. Thermal ellipsoids are given at the 50% probability level.

In compounds **1**-**5** the RE(2)-O(11)#6 (symmetry code, #6: -*x*, *y*-1/2, -*z*+1/2) distance is less than 3.0 Å which could be viewed as a weak RE-O coordination bond. Taking account of this, the RE(2) ions are in a distorted bicapped triprismatic coordination geometry in **1**-**5** (Figure S2b), surrounded by one Cl^- ion, five 1,4-NDC ligands in monodentate mode and one 1,4-NDC in bidentate chelating fashion (Figure S2a). Consequently, one of the three crystallographic independent 1,4-NDC ligand then acts as a pentadentate metal linker in which the O(11) and O(12) chelate to a $RE(2)^{3+}$ ion (Figure S2c).

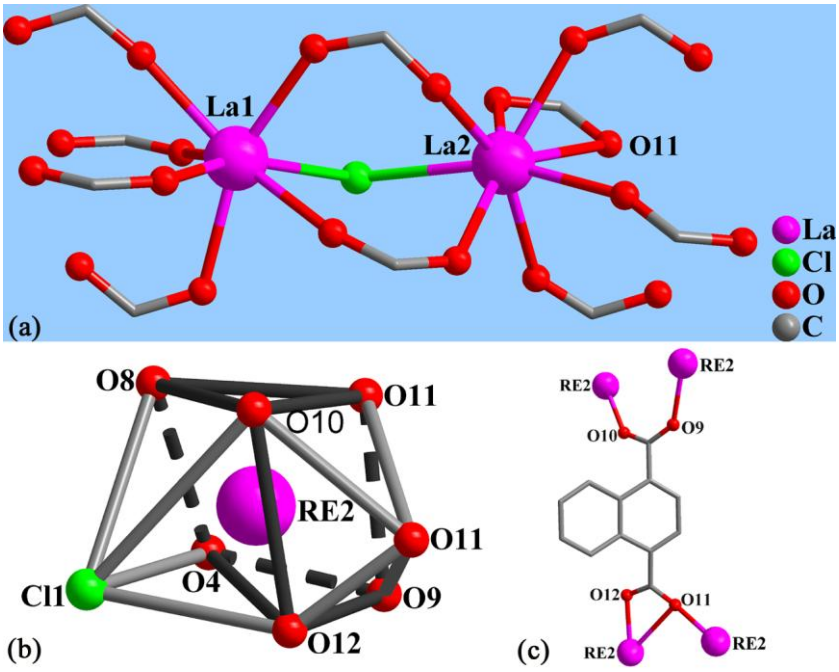


Figure S2. (a) The coordination environment of La^{3+} ions in **1** contains a long La(2)–O(11) #6 (symmetry code, #6: -*x*, *y*-1/2, -*z*+1/2) distance. (b) Distorted bicapped triprismatic coordination polyhedron of the RE^{3+} ions in **1**-**5**. (c) Coordination mode of a 1,4-NDC ligand in **1**-**5**

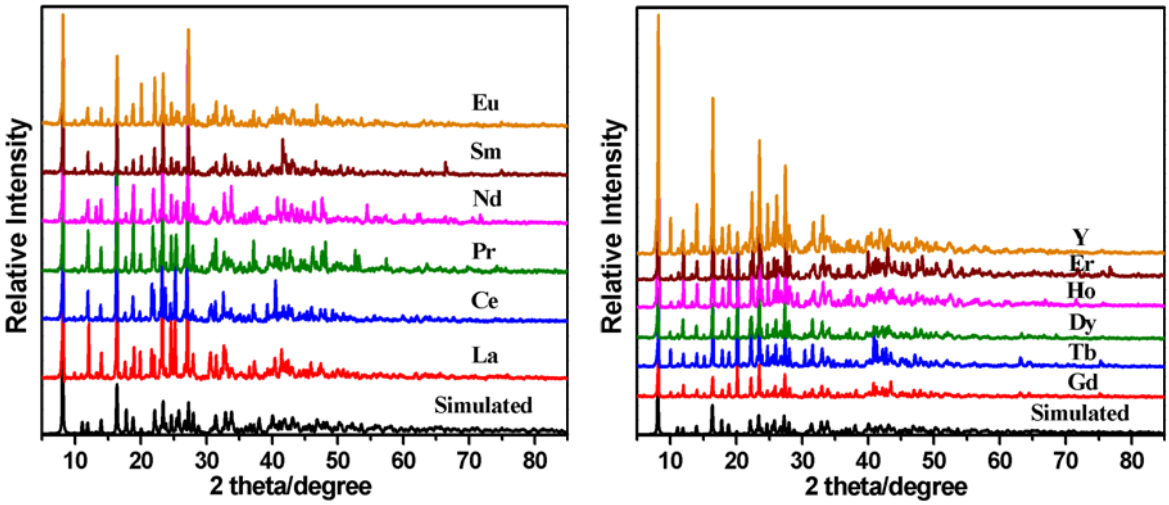


Figure S3. The PXRD patterns of compounds **1-12** are in good agreement with the simulated PXRD pattern calculated from the single crystal X-ray data of **6** (black) at room temperature.

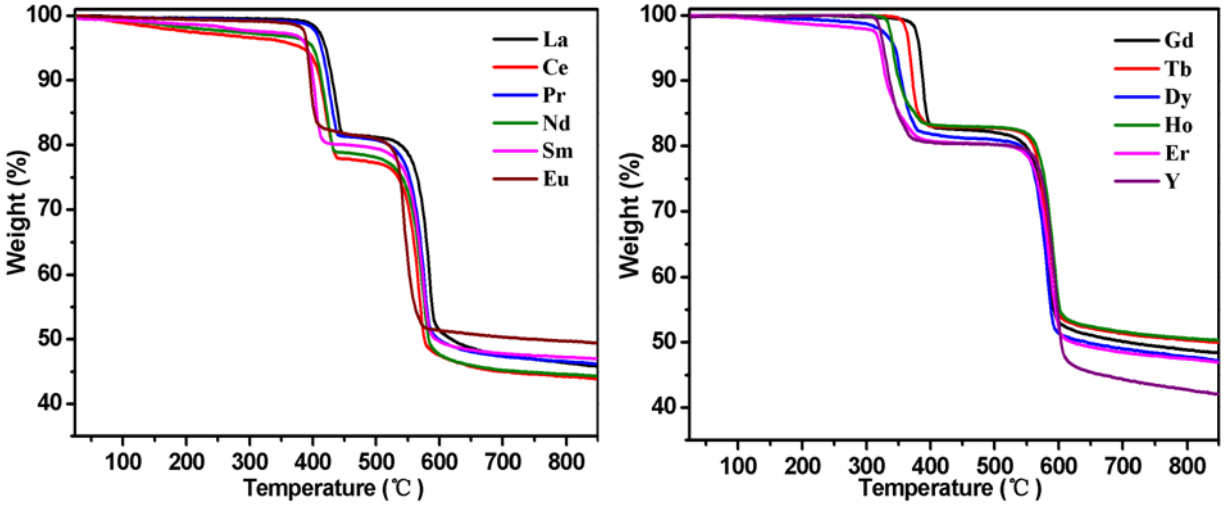


Figure S4. TGA curves of compounds **1-12**.

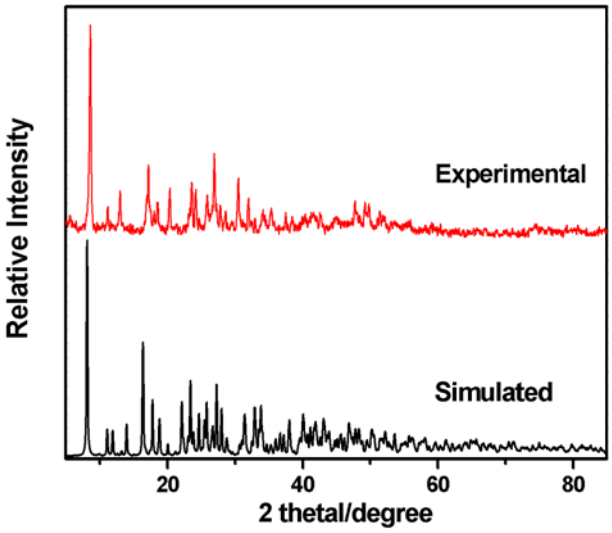
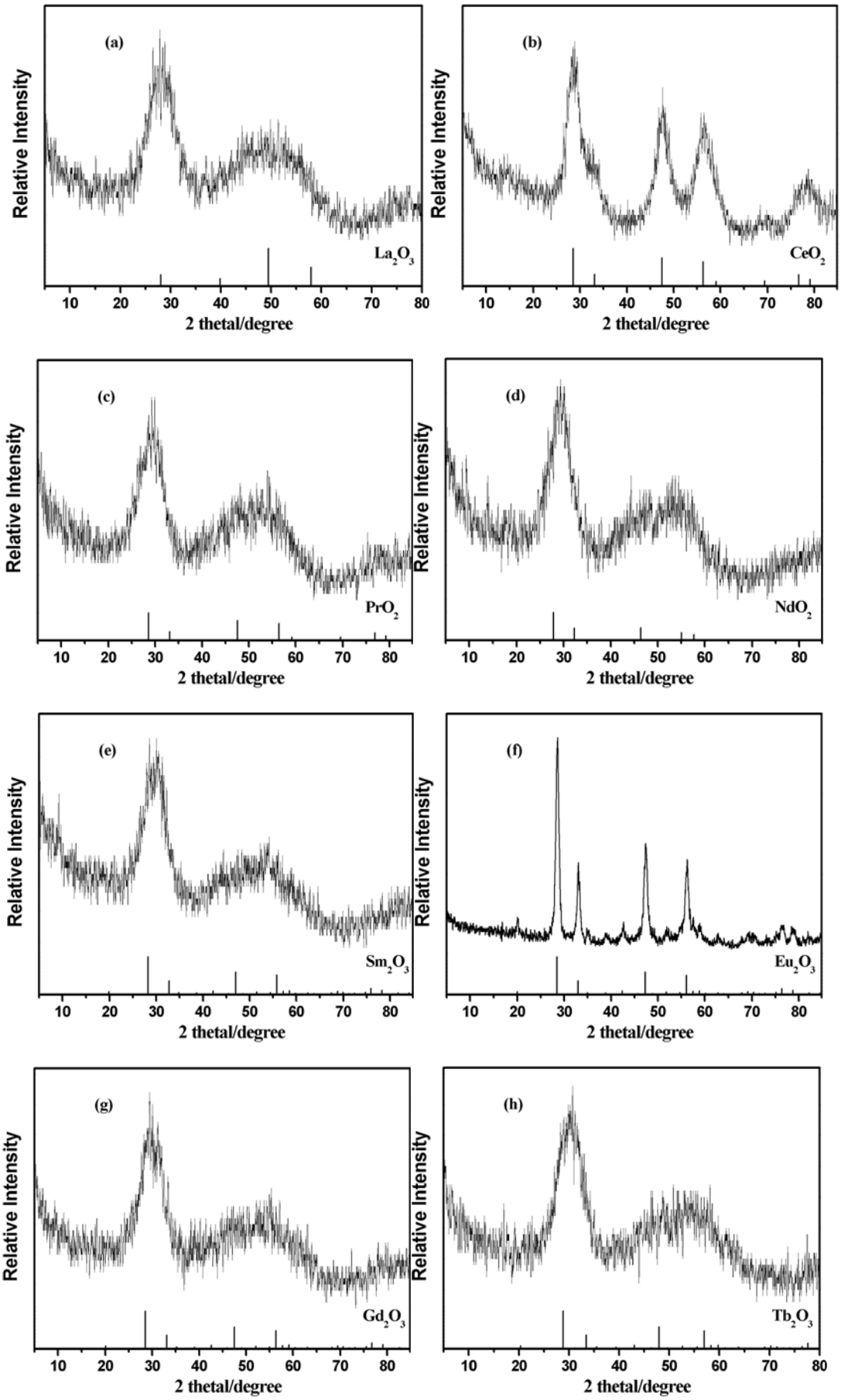


Figure S5. The PXRD patterns of the TG 400 °C residue of **6** and the simulated PXRD pattern calculated from the single crystal X-ray data of **6** (bottom) at room temperature.



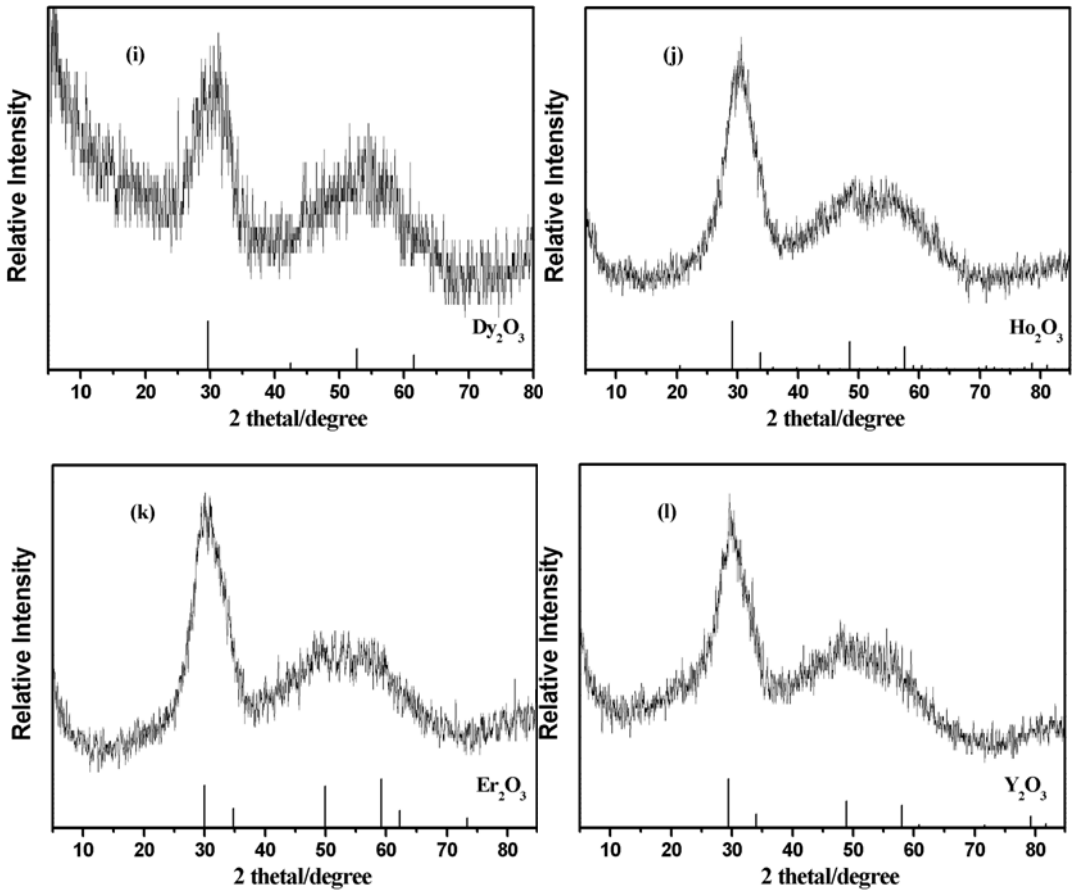


Figure S6. The PXRD patterns of the TG 850 °C residues of compounds **1-12** are in good agreement with the simulated PXRD patterns of La_2O_3 (**1**, **a**), CeO_2 (**2**, **b**), PrO_2 (**3**, **c**), NdO_2 (**4, d**), Sm_2O_3 (**5**, **e**), Eu_2O_3 (**6**, **f**), Gd_2O_3 (**7**, **g**), Tb_2O_3 (**8**, **h**), Dy_2O_3 (**9, i**), Ho_2O_3 (**10**, **j**), Er_2O_3 (**11**, **k**), Y_2O_3 (**1**, **l**) (bottom) at room temperature, respectively.

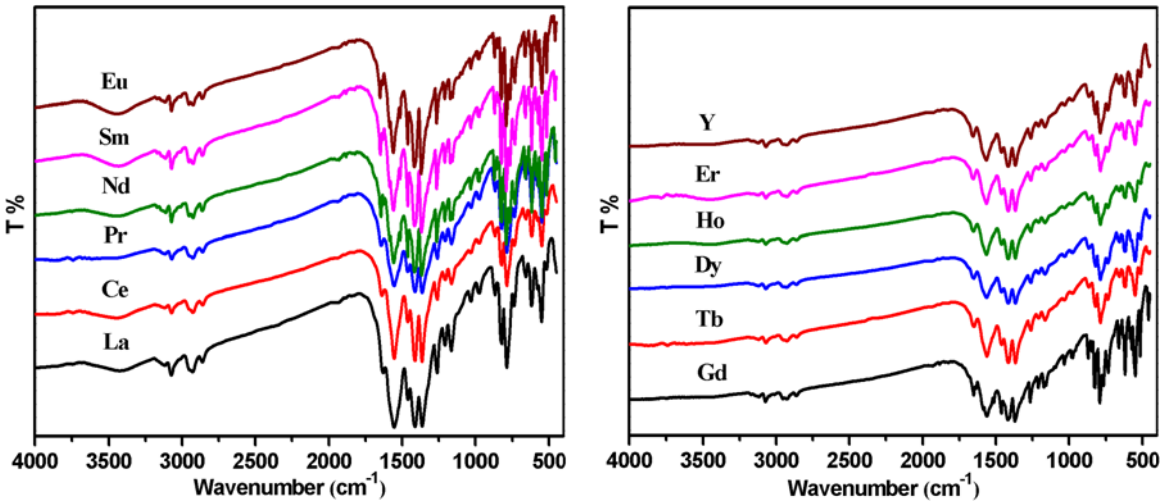


Figure S7. IR Spectra of compounds **1-12**.

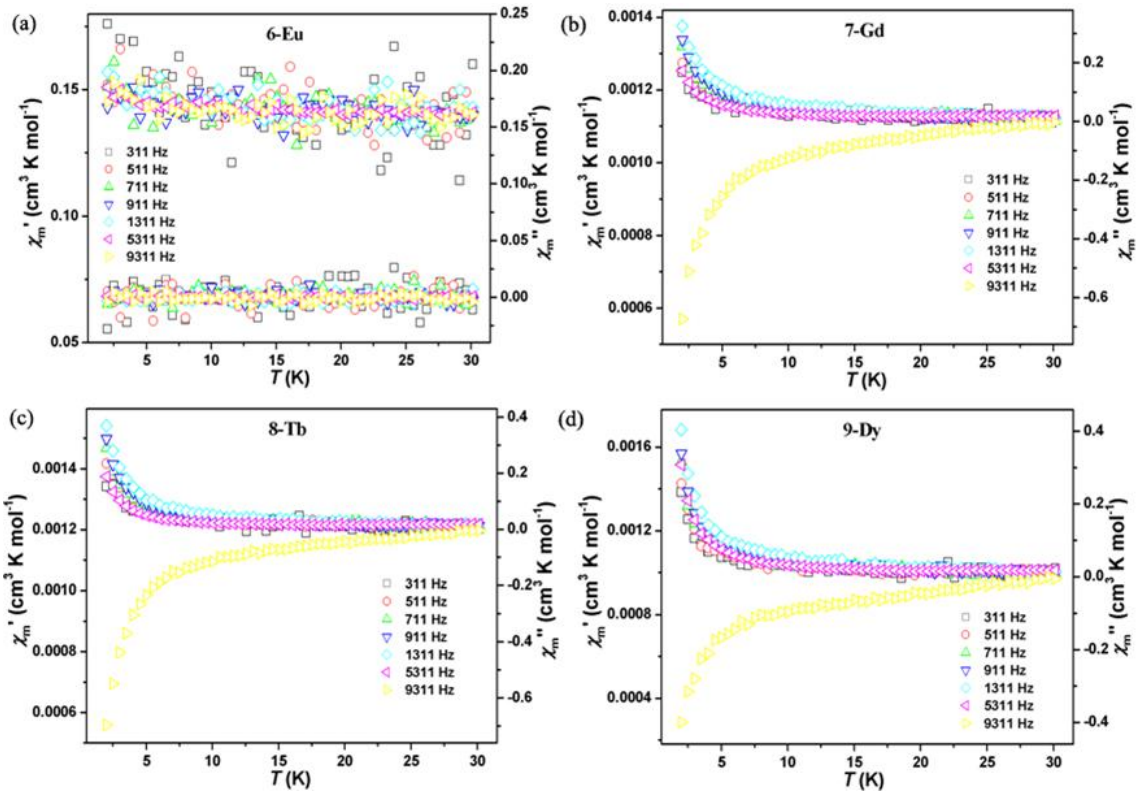


Figure S8. Temperature dependence of ac magnetic susceptibilities for [Hmim][$RE_2Cl(1,4\text{-}NDC)_3$] (RE = Eu (**6**), Gd (**7**), Tb (**8**), Dy (**9**)), under a zero dc field within the frequency range 311-9311 Hz.