Supplementary Material (ESI) for Dalton Transactions

Synthesis, Structure and Optical Properties of Rare-Earth Benzene Carboxylates

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ELECTRONIC SUPPLEMENTARY INFORMATION

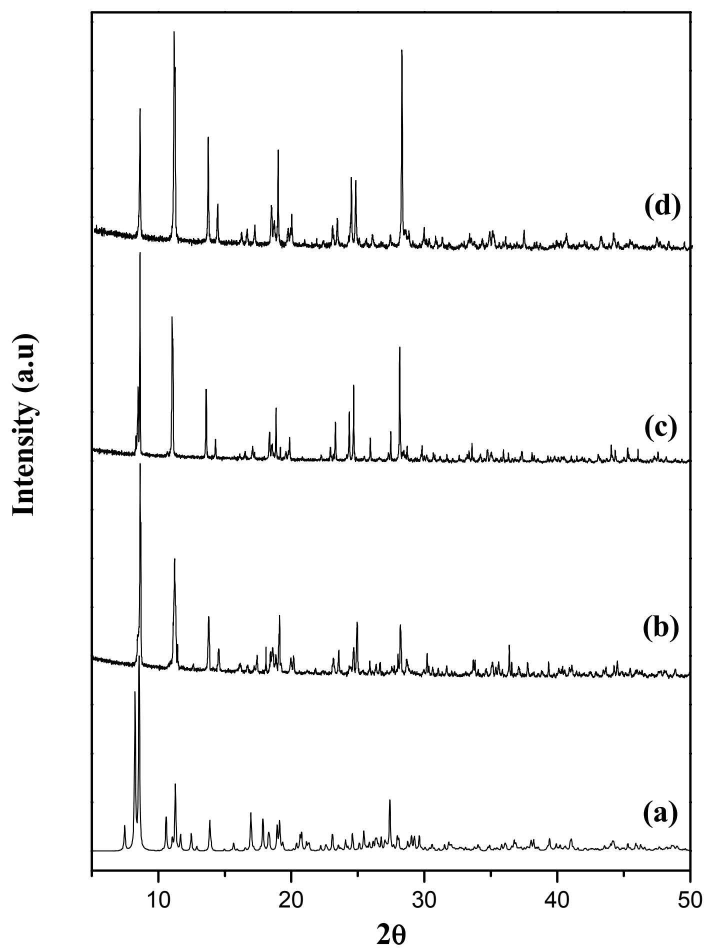


Fig. S1. Powder X-ray diffraction pattern (Cu Kα) for $[M_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$: (a) simulated of **I** (M = La)**,** (b) experimental of **I** (M = La)**,** (c) experimental of **Ia** (Pr) and (d) experimental of **Ib** (Nd)

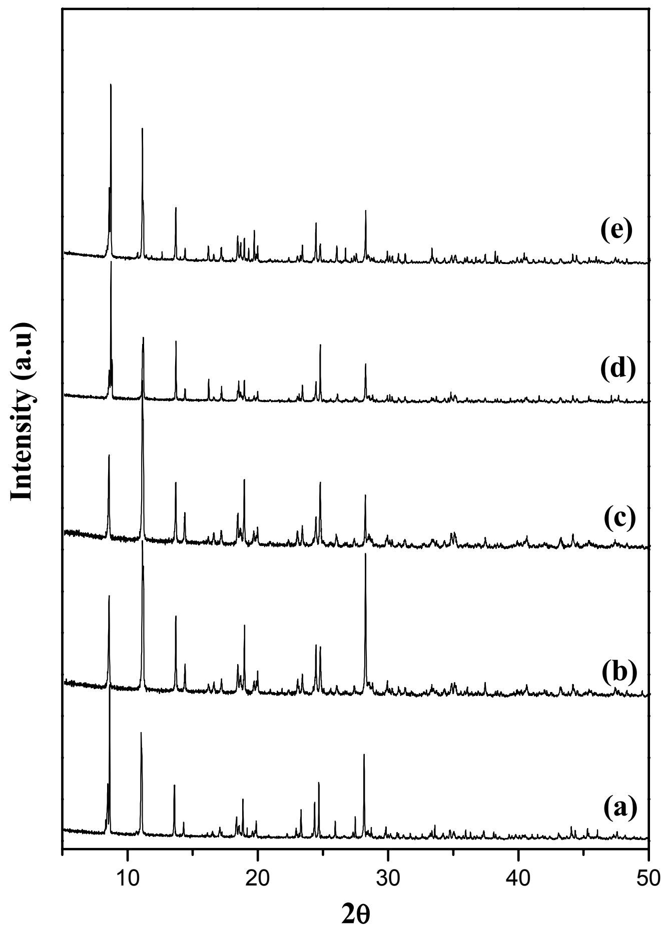


Fig. S2. Experimental Powder X-ray diffraction pattern (Cu Kα) for $[M_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$, (a) M = La (**1**), (b) M = $La_{0.98}Eu_{0.02}$ (**1c**), (c) M = $La_{0.96}Eu_{0.04}$ (**1d**), (d) M = $La_{0.98}Tb_{0.02}$ (**Ie**) and (e) M = $La_{0.96}Tb_{0.04}$ (**If**)

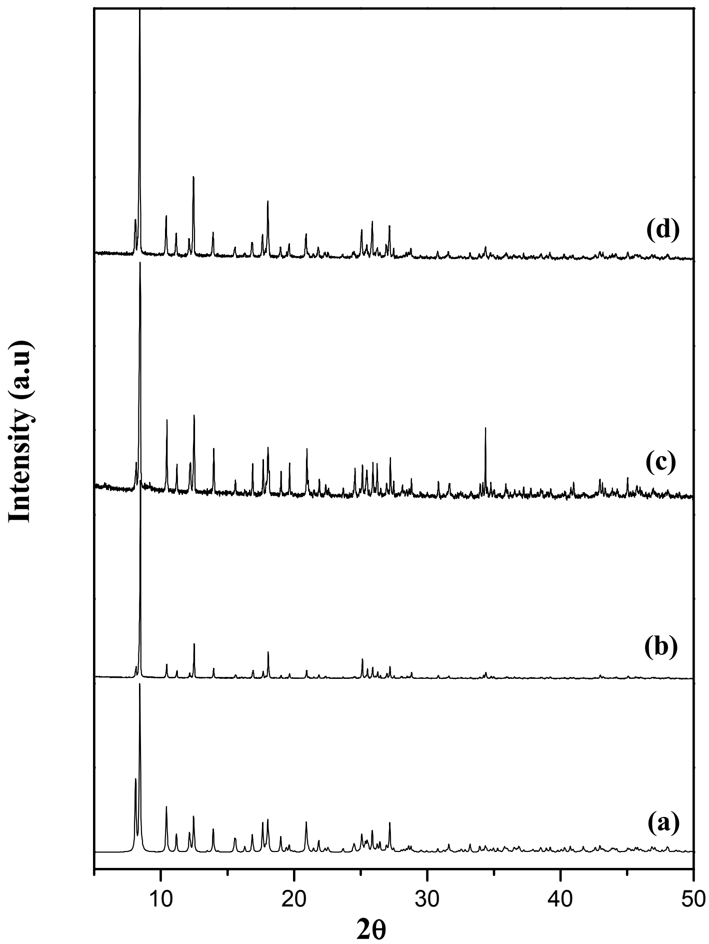


Fig. S3. Powder X-ray diffraction pattern (Cu Kα) for $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$: (a) simulated of **II** (M = Y)**,** (b) experimental of **II** (M = Y)**,** (c) experimental of **IIa** (Gd) and (d) experimental of **IIb** (Dy)

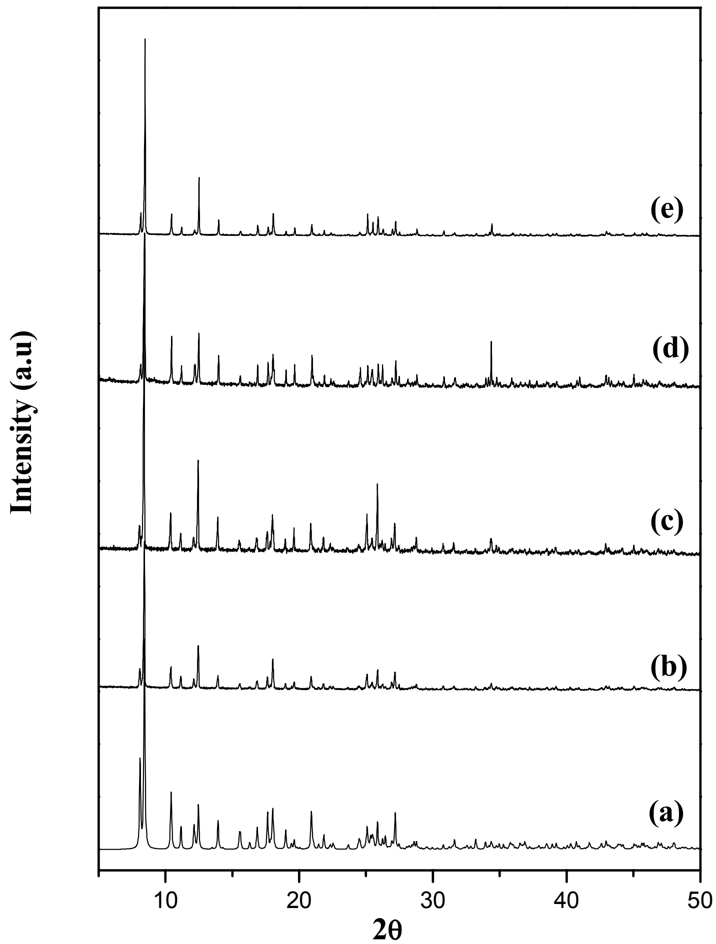


Fig. S4. Experimental Powder X-ray diffraction pattern (Cu Kα) for $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, (a) M= Y (**1I**), (b) M = $Y_{0.98}Eu_{0.02}$ (**1Ic),** (c) **M =** $Y_{0.96}Eu_{0.04}$ (**I1d**), (d) M = $Y_{0.98}Tb_{0.02}$ (**IIe**) and (e) M = $Y_{0.96}Tb_{0.04}$ (**IIf**)

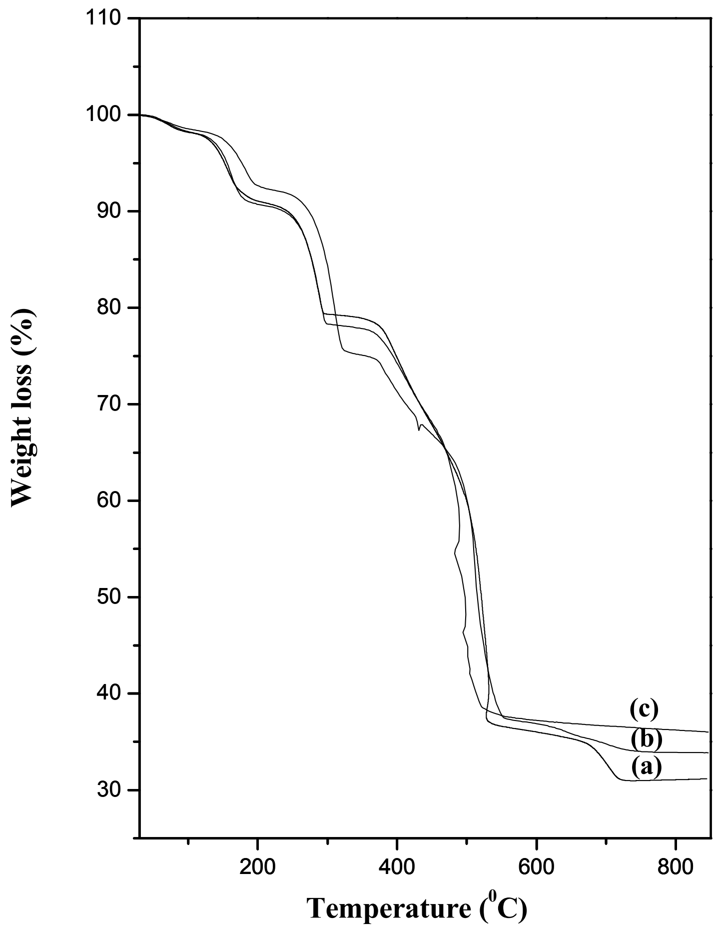


Fig. S5. TGA studies of[$M_2(H_2O)$][{$C_6H_4(COO)_2$}$_2${$C_6H_4(COOH)(COO)$}$_2$].H_2O, (a) M = La (**I**), (b) M = Pr (**Ia**) and (c) M = Nd (**Ib**).

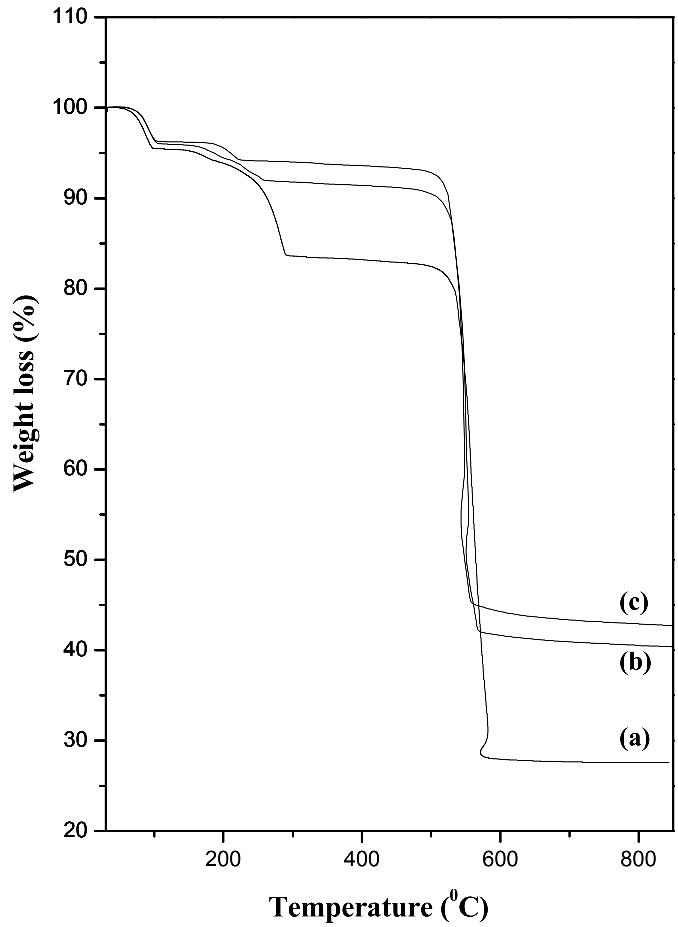


Fig. S6. TGA studies of $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, (a) M = Y (**II**), (b) M = Gd (**IIa**) and (c) M = Dy (**IIb**).

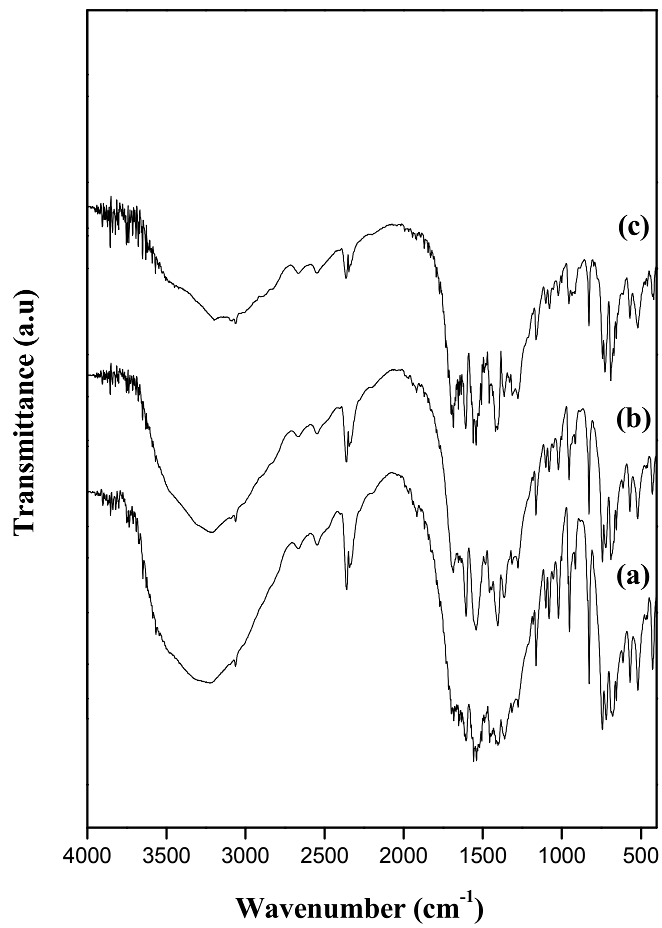


Fig. S7. IR spectra of $[M_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$, (a) M = La (**I**), (b) M = Pr (**Ia**) and (c) M = Nd (**Ib**).

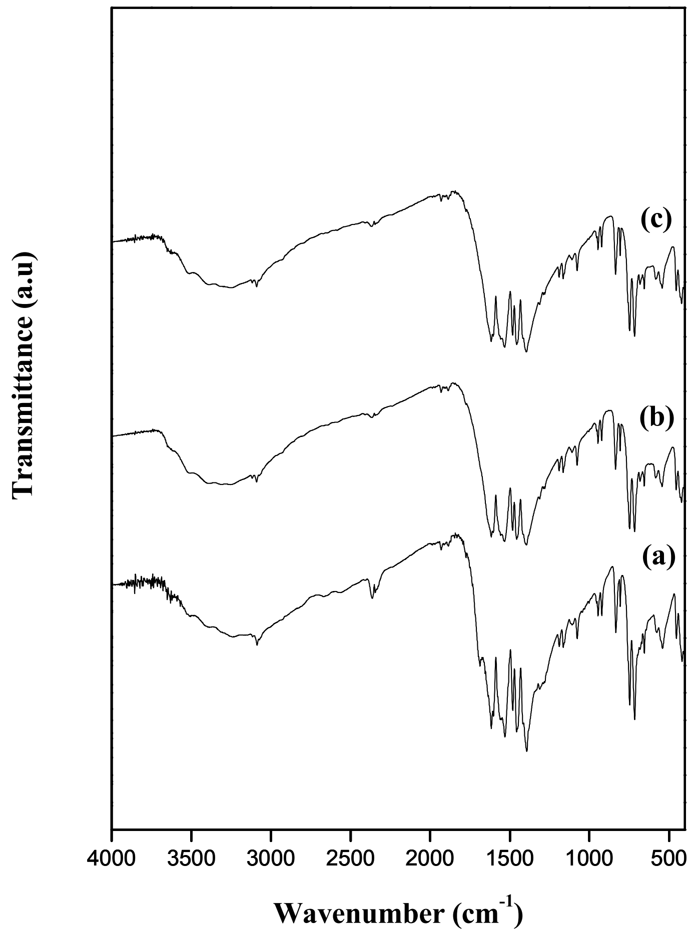


Fig. S8. IR spectra of $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, (a) M = Y (**II**), (b) M = Gd (**IIa**) and (c) M= Dy (**IIb**).

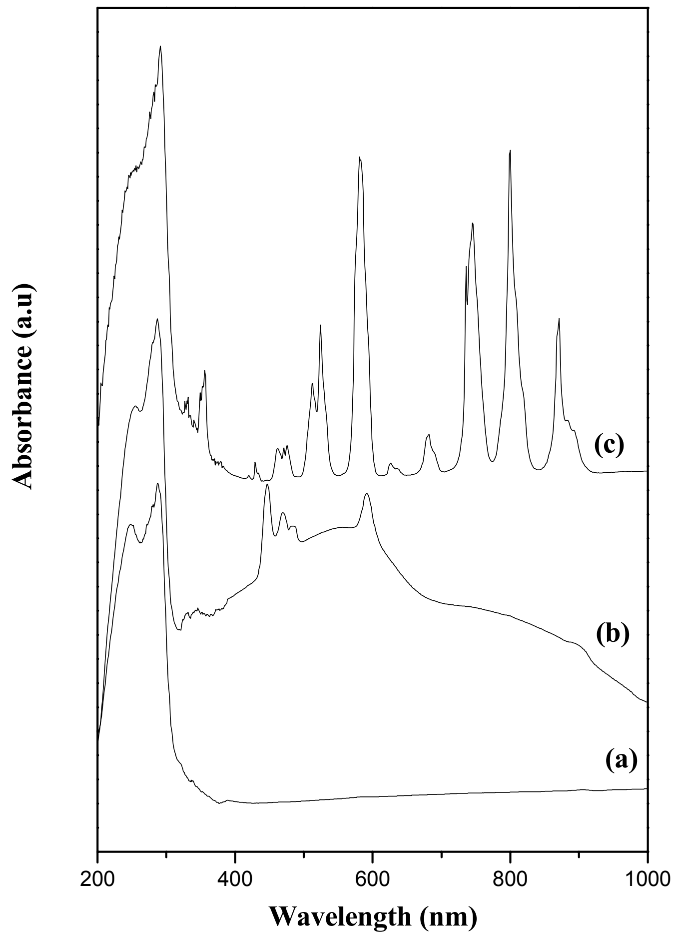


Fig. S9. UV-Vis spectra of $[M_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$, (a) M = La (**I**), (b) M = Pr (**Ia**) and (c) M = Nd (**Ib**).

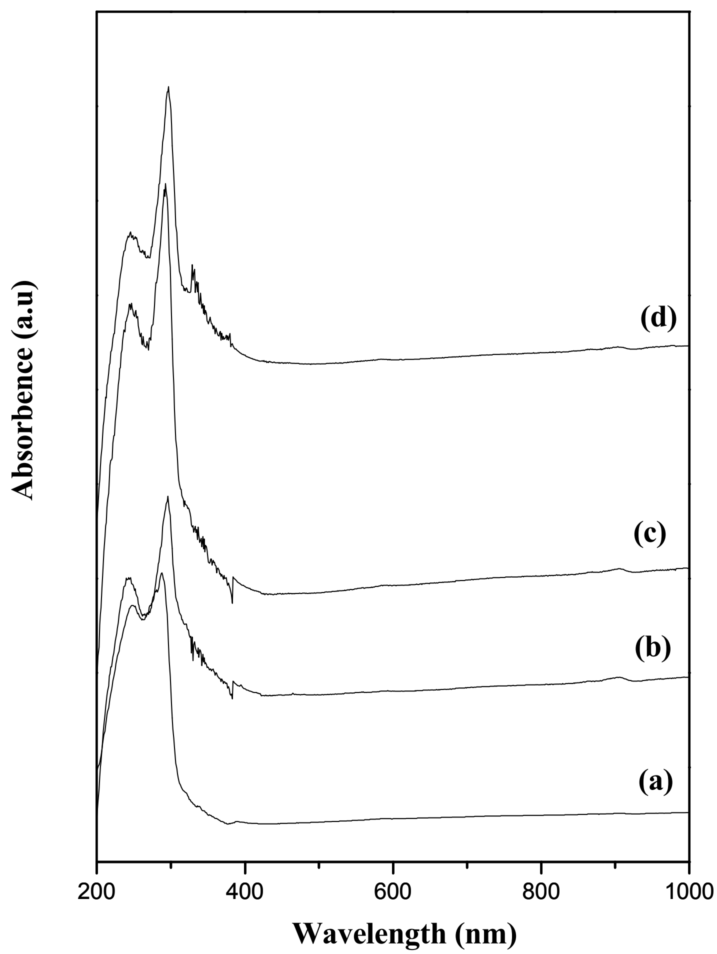


Fig. S10. UV-Vis spectra of $[M_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$ (a) M = $La_{0.98}Eu_{0.02}$ (**1c**)**,** (b) M = $La_{0.96}Eu_{0.04}$ (**1d**), (c) M = $La_{0.98}Tb_{0.02}$ (**Ie**) and (d) M = $La_{0.96}Tb_{0.04}$ (**If**)

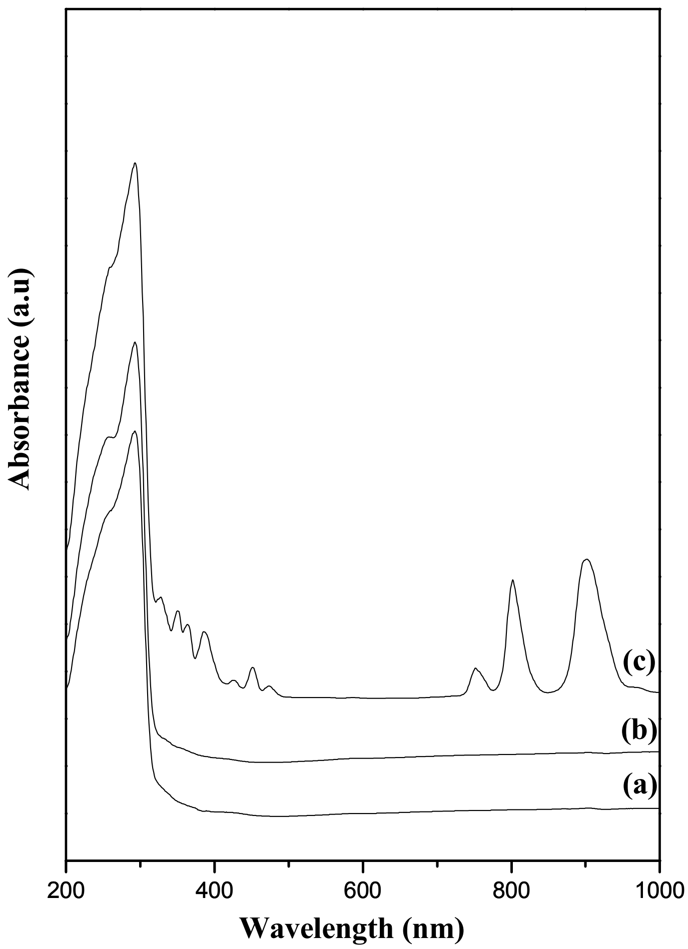


Fig. S11. UV-Vis spectra of $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, (a) M = Y (**II**), (b) M = Gd (**IIa**) and (c) M= Dy (**IIb**).

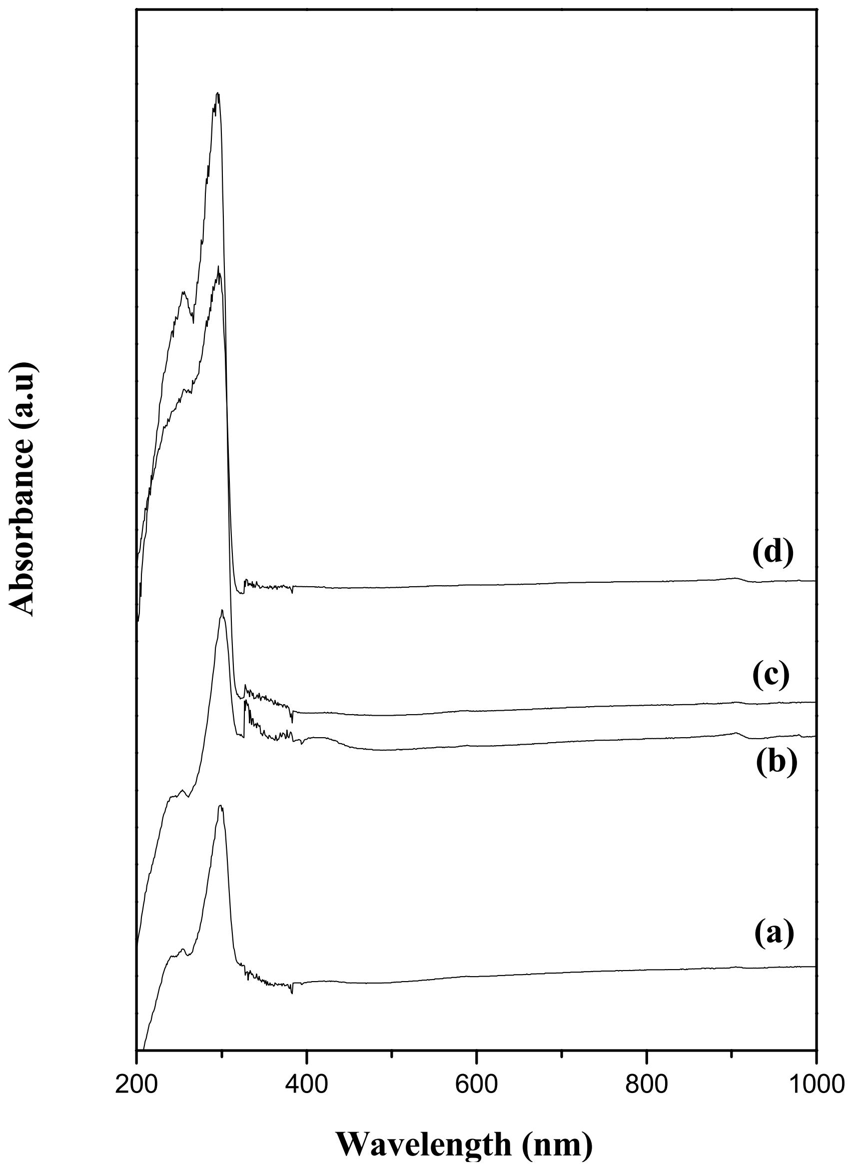


Fig. S12. UV-Vis spectra of $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, (a) M = $Y_{0.98}Eu_{0.02}$ (**1Ic),** (b) M = $Y_{0.96}Eu_{0.04}$ (**I1d**), (c) M = $Y_{0.98}Tb_{0.02}$ (**IIe**) and (d) M = $Y_{0.96}Tb_{0.04}$ (**IIf**)

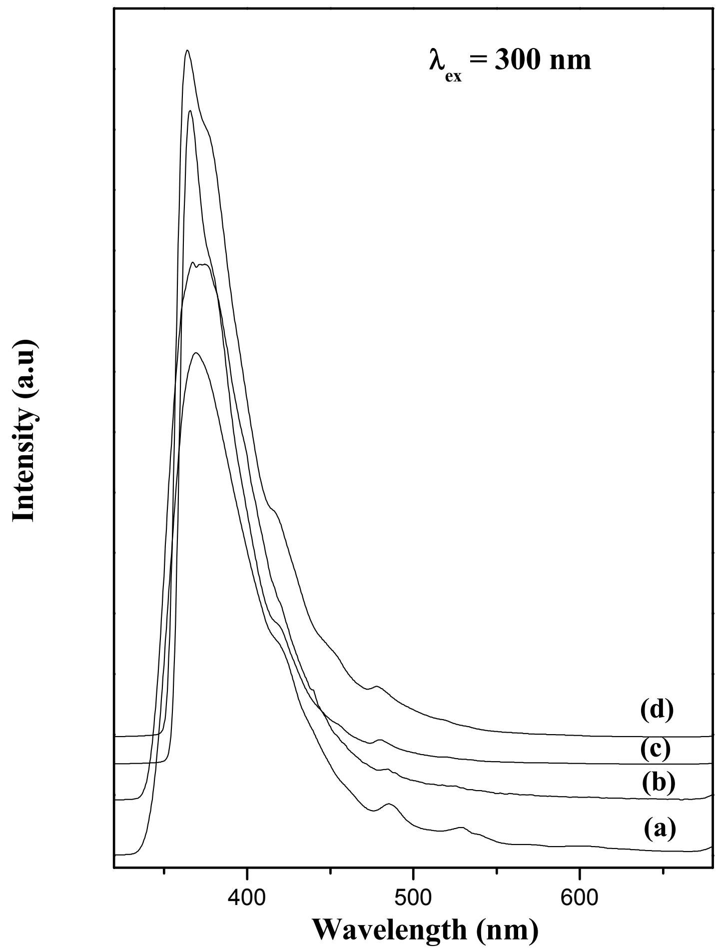


Fig. S13. Photoluminescence spectra of $[M_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$, (a) Sodium isophthalate, (b) M = La (**I**), (c) M = Pr (**Ia**) and (d) M = Nd (**Ib**).

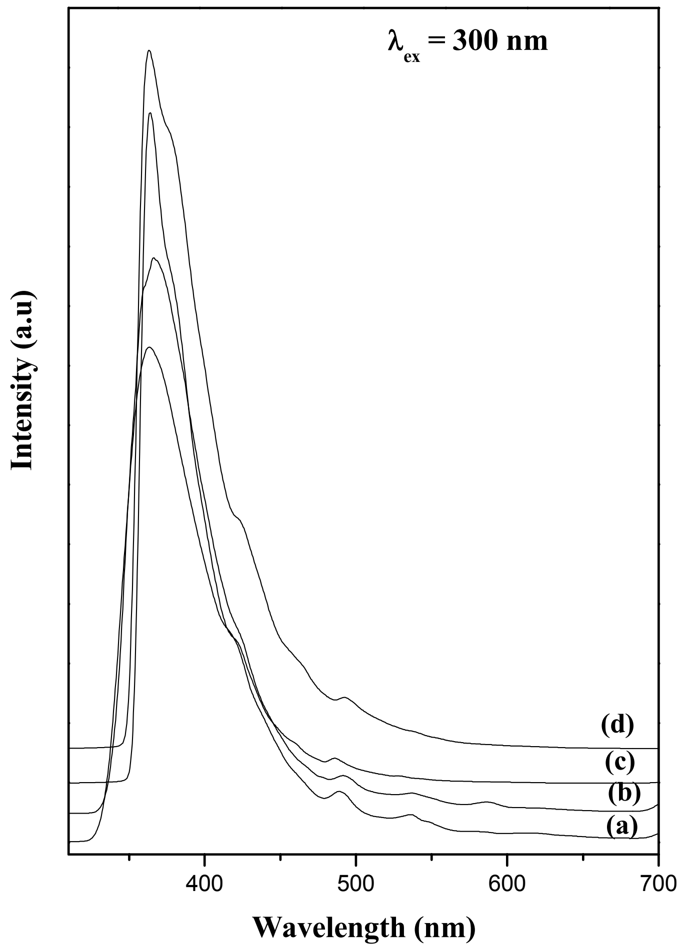


Fig. S14. Photoluminescence spectra of $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, (a) sodium isophthalate, (b) M = Y (**II**), (c) M = Gd (**IIa**) and (c) M= Dy (**IIb**).

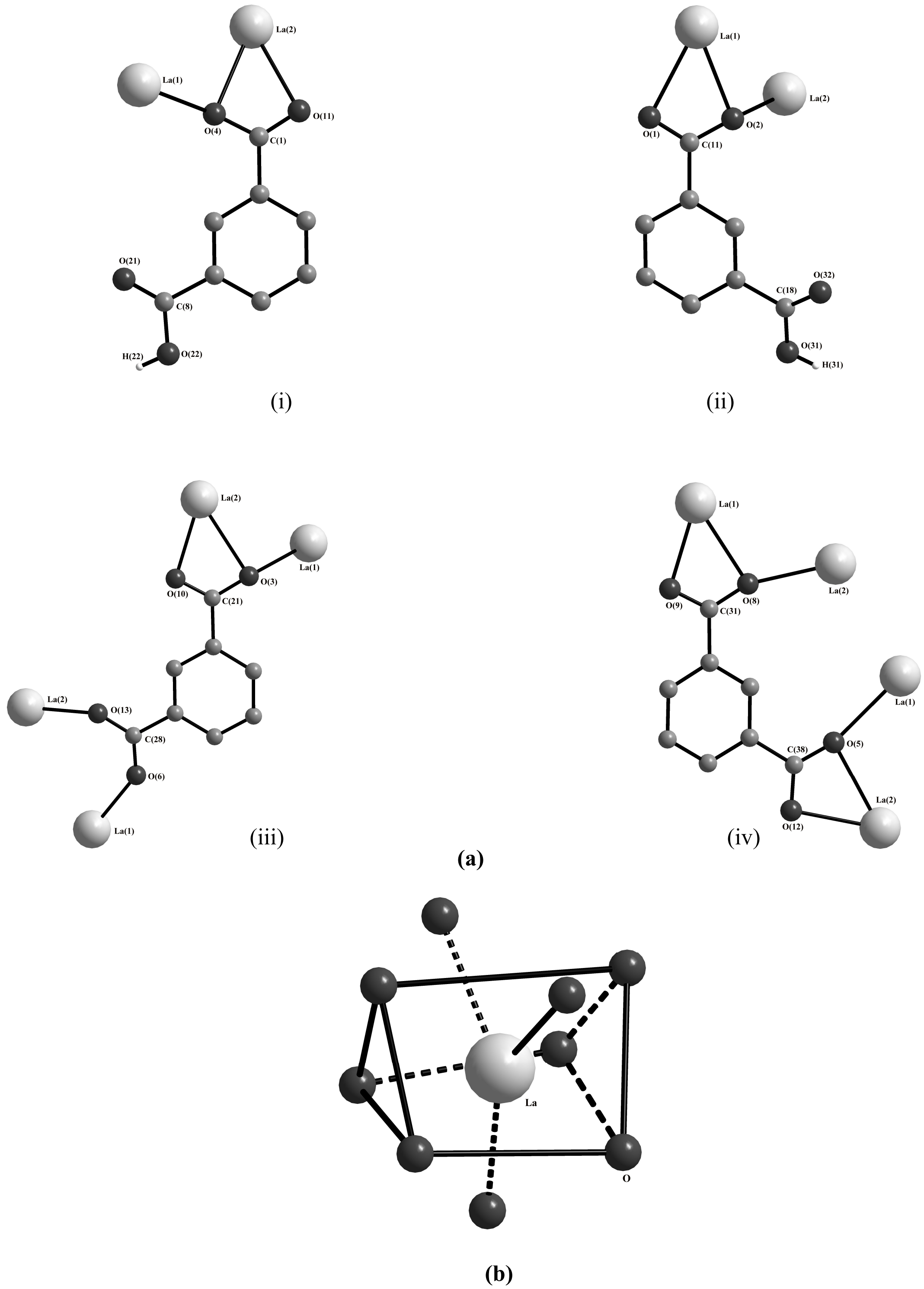
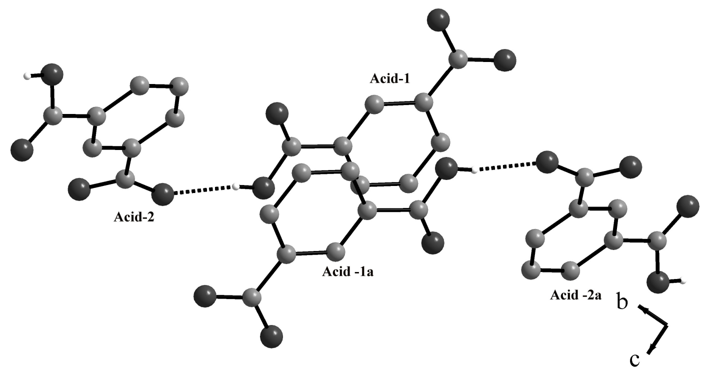
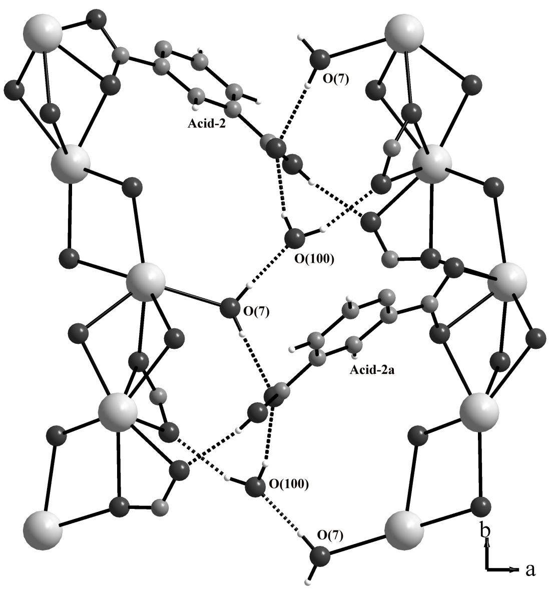


Fig. S15. (a) The various coordination modes of the isophthalate anions observed in $[La_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$, **I** (i) acid-1, (ii) acid-2, (iii) acid-3, and (iv) acid-4. (b) The tricapped trigonal prismatic geometry around the La^{3+} ions in **I**.



(a)



(b)

Fig. S16. (a) Figure showing the hydrogen bond interactions between the monoanionic isophthalate units (intra-layer). Note that the hydrogen bonds are formed between C-OH and bonded C-O units. The coordinating La^{3+} ions are not shown for clarity. Symmetry transformations used to generate equivalent acids: Acid-1 -x, -y, 1-z; Acid-1a x, -1+y, 1+z; Acid-2 -x, -1/2 +y, 1/2 - z; Acid-2a x, -1/2-y, 1/2 +z.

(b) View of the fragment of the structure of **I** showing the various inter-layer hydrogen bond interactions (see text).

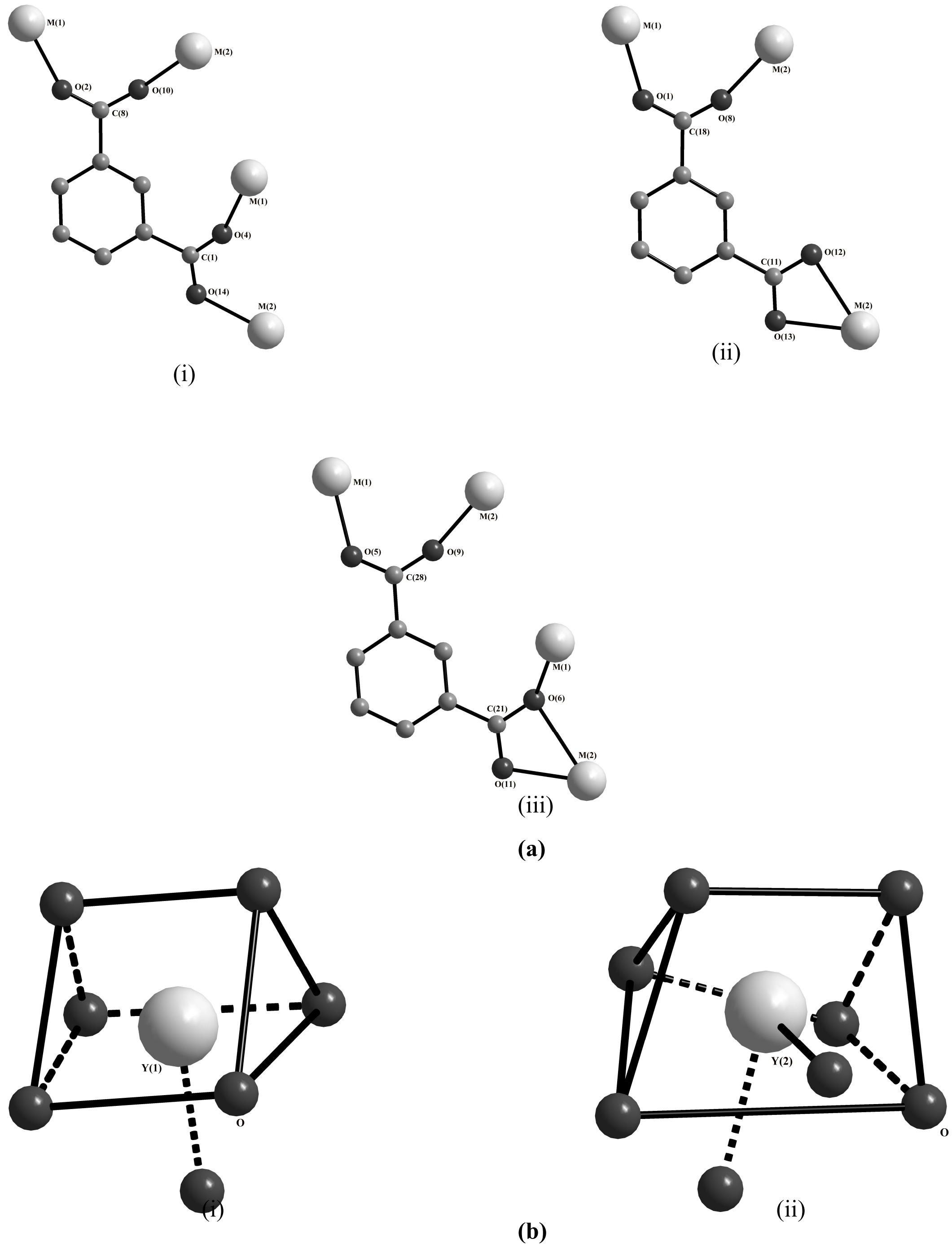


Fig. S17. (a) The various coordination modes of the isophthalate anions observed in $[Y_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, **II** (i) acid-1, (ii) acid-2, and (iii) acid-3.

(b) The coordination geometry around Y observed in **II** (i) monocapped trigonal prismatic, $Y(1)O_7$ and (ii) distorted bicapped trigonal prismatic, $Y(2)O_8$.

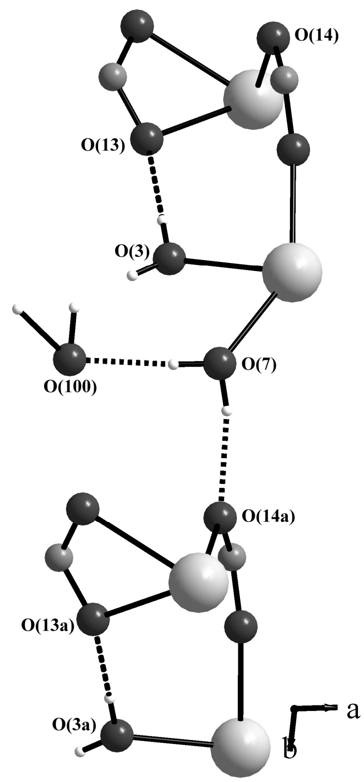


Fig. S18. Figure showing the hydrogen bond interactions between the coordinated and lattice water molecules in $[Y_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$ (see text). Symmetry transformations used to generate equivalent acids: O(13) -x, -1/2+y,1/2-z; O(14a) x,1/2-y, -1/2+z; O(13a) x, 1/2-y, 1-z, O(3a) x, 1.5-y, 1/2+z.

Table S1: Selected bond angles observed in $[La_2(H_2O)][\{C_6H_4(COO)_2\}_2\{C_6H_4(COOH)(COO)\}_2].H_2O$, **I**.

Angle	Amplitude	Angle	Amplitude
O(6)-La(1)-O(4)	90.11(8)	O(3)-La(1)-O(7)	68.82(8)
O(6)-La(1)-O(9)	87.82(9)	O(6)-La(1)-O(5)	75.12(8)
O(4)-La(1)-O(9)	148.25(7)	O(4)-La(1)-O(5)	89.49(7)
O(6)-La(1)-O(3)	139.22(8)	O(9)-La(1)-O(5)	120.37(7)
O(4)-La(1)-O(3)	73.65(7)	O(3)-La(1)-O(5)	139.65(7)
O(9)-La(1)-O(3)	87.55(7)	O(7)-La(1)-O(5)	142.49(9)
O(6)-La(1)-O(7)	70.94(9)	O(6)-La(1)-O(2)	139.96(7)
O(4)-La(1)-O(7)	75.24(9)	O(4)-La(1)-O(2)	65.64(7)
O(9)-La(1)-O(7)	74.15(9)	O(9)-La(1)-O(2)	129.68(8)
O(3)-La(1)-O(2)	66.24(7)	O(5)-La(1)-O(8)	70.99(6)
O(7)-La(1)-O(2)	126.54(8)	O(2)-La(1)-O(8)	113.38(7)
O(5)-La(1)-O(2)	73.41(7)	O(1)-La(1)-O(8)	71.33(7)
O(6)-La(1)-O(1)	146.07(7)	O(13)-La(2)-O(8)#1	78.22(8)
O(4)-La(1)-O(1)	113.78(7)	O(13)-La(2)-O(10)	75.51(8)
O(9)-La(1)-O(1)	83.63(8)	O(8)#1-La(2)-O(10)	149.40(8)
O(3)-La(1)-O(1)	73.25(7)	O(13)-La(2)-O(2)	86.40(8)
O(7)-La(1)-O(1)	136.38(9)	O(8)#1-La(2)-O(2)	84.60(7)
O(5)-La(1)-O(1)	81.11(7)	O(10)-La(2)-O(2)	78.41(8)
O(2)-La(1)-O(1)	48.78(6)	O(13)-La(2)-O(12)	98.18(8)
O(6)-La(1)-O(8)	78.16(7)	O(8)#1-La(2)-O(12)	121.03(7)
O(4)-La(1)-O(8)	159.18(7)	O(10)-La(2)-O(12)	78.39(8)
O(9)-La(1)-O(8)	49.52(7)	O(2)-La(2)-O(12)	154.38(7)
O(3)-La(1)-O(8)	126.09(7)	O(13)-La(2)-O(11)	146.81(8)

O(7)-La(1)-O(8)	115.91(8)	O(8)#1-La(2)-O(11)	79.06(8)
O(10)-La(2)-O(11)	131.26(8)	O(2)-La(2)-O(11)	115.12(7)
O(12)-La(2)-O(11)	73.59(7)	O(10)-La(2)-O(3)	49.47(7)
O(13)-La(2)-O(4)	144.16(8)	O(2)-La(2)-O(3)	65.34(7)
O(8)#1-La(2)-O(4)	77.43(7)	O(12)-La(2)-O(3)	91.15(7)
O(10)-La(2)-O(4)	116.91(7)	O(11)-La(2)-O(3)	91.82(7)
O(2)-La(2)-O(4)	65.50(7)	O(13)-La(2)-O(3)	120.84(7)
O(12)-La(2)-O(4)	116.87(7)	O(8)#1-La(2)-O(3)	141.36(7)
O(11)-La(2)-O(4)	49.73(7)	O(4)-La(2)-O(3)	68.47(6)
O(13)-La(2)-O(5)#1	76.05(8)	O(5)#1-La(2)-O(3)	140.59(6)
O(8)#1-La(2)-O(5)#1	73.07(7)	La(2)-O(2)-La(1)	100.27(7)
O(10)-La(2)-O(5)#1	114.68(7)	La(1)-O(3)-La(2)	97.28(7)
O(2)-La(2)-O(5)#1	153.86(7)	La(1)-O(4)-La(2)	102.69(8)
O(12)-La(2)-O(5)#1	49.73(6)	La(1)-O(5)-La(2)#2	105.72(7)
O(11)-La(2)-O(5)#1	74.38(7)	La(2)#2-O(8)-La(1)	106.95(7)
O(4)-La(2)-O(5)#1	120.49(7)	O(4)-La(2)-O(3)	68.47(6)
O(13)-La(2)-O(3)	120.84(7)	O(5)#1-La(2)-O(3)	140.59(6)
O(8)#1-La(2)-O(3)	141.36(7)		

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

Table S2: Selected bond angles observed in $[M_2(H_2O)_2][\{C_6H_4(COO)_2\}_3].H_2O$, M = Y(**II**), Gd(**IIa**)

Angle	M = Y(**II**)	M = Gd(**IIa**)
O(2)-M(1)-O(5)	157.66(13)	153.44(11)
O(2)-M(1)-O(1)	80.83(13)	79.24(10)
O(5)-M(1)-O(1)	120.90(13)	126.30(11)
O(2)-M(1)-O(7)	111.00(15)	113.18(12)
O(5)-M(1)-O(7)	74.88(15)	74.02(11)
O(1)-M(1)-O(7)	71.41(14)	71.72(11)
O(2)-M(1)-O(4)	81.46(12)	80.37(10)
O(5)-M(1)-O(4)	82.52(12)	81.10(10)
O(1)-M(1)-O(4)	143.52(12)	142.44(10)
O(7)-M(1)-O(4)	145.03(13)	145.77(11)
O(2)-M(1)-O(3)	81.21(14)	80.10(11)
O(5)-M(1)-O(3)	80.18(14)	77.76(12)
O(1)-M(1)-O(3)	130.37(14)	127.56(11)
O(7)-M(1)-O(3)	72.74(16)	73.30(13)
O(4)-M(1)-O(3)	77.42(13)	78.79(11)
O(5)-M(1)-O(6)	88.85(12)	92.16(10)
O(1)-M(1)-O(6)	73.75(11)	74.58(10)
O(7)-M(1)-O(6)	125.24(15)	123.60(12)
O(4)-M(1)-O(6)	79.76(11)	79.79(9)
O(3)-M(1)-O(6)	155.75(13)	157.48(11)
O(8)-M(2)-O(10)#1	150.81(12)	151.20(10)
O(8)-M(2)-O(9)	86.04(12)	86.31(10)
O(10)#1-M(2)-O(9)	78.99(12)	79.04(11)
O(8)-M(2)-O(14)#1	86.82(12)	83.93(10)
O(10)#1-M(2)-O(14)#1	115.48(12)	118.79(10)

O(9)-M(2)-O(14)#1	82.51(13)	84.81(11)
O(8)-M(2)-O(11)	80.64(12)	79.86(10)
O(10)#1-M(2)-O(11)	88.93(12)	88.82(10)
O(9)-M(2)-O(11)	127.86(12)	125.93(10)
O(14)#1-M(2)-O(11)	145.63(11)	143.65(9)
O(8)-M(2)-O(13)	129.09(11)	128.08(9)
O(10)#1-M(2)-O(13)	76.64(11)	76.87(9)
O(9)-M(2)-O(13)	137.46(12)	138.80(10)
O(14)#1-M(2)-O(13)	77.34(12)	78.30(11)
O(11)-M(2)-O(13)	86.03(12)	86.50(10)
O(8)-M(2)-O(12)	76.33(12)	76.34(10)
O(10)#1-M(2)-O(12)	126.36(12)	125.14(10)
O(9)-M(2)-O(12)	150.70(13)	152.82(11)
O(14)#1-M(2)-O(12)	73.42(11)	72.83(10)
O(11)-M(2)-O(12)	72.56(11)	71.82(9)
O(13)-M(2)-O(12)	52.82(11)	51.86(9)
O(8)-M(2)-O(6)	72.12(11)	72.32(9)
O(10)#1-M(2)-O(6)	80.04(11)	79.96(9)
O(9)-M(2)-O(6)	76.50(11)	75.00(9)
O(14)#1-M(2)-O(6)	151.00(11)	149.48(10)
O(11)-M(2)-O(6)	51.41(10)	50.96(8)
O(13)-M(2)-O(6)	131.47(11)	131.58(9)
O(12)-M(2)-O(6)	118.53(10)	117.90(9)
M(1)-O(6)-M(2)	117.65(12)	115.35(10)

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