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A Novel Family of 3D Photoluminescent Lanthanide–Bta–Flexible MOFs Constructed from 1,2,4,5-Benzenetetracarboxylic Acid and Different Spanning of Dicarboxylate Acid Ligands

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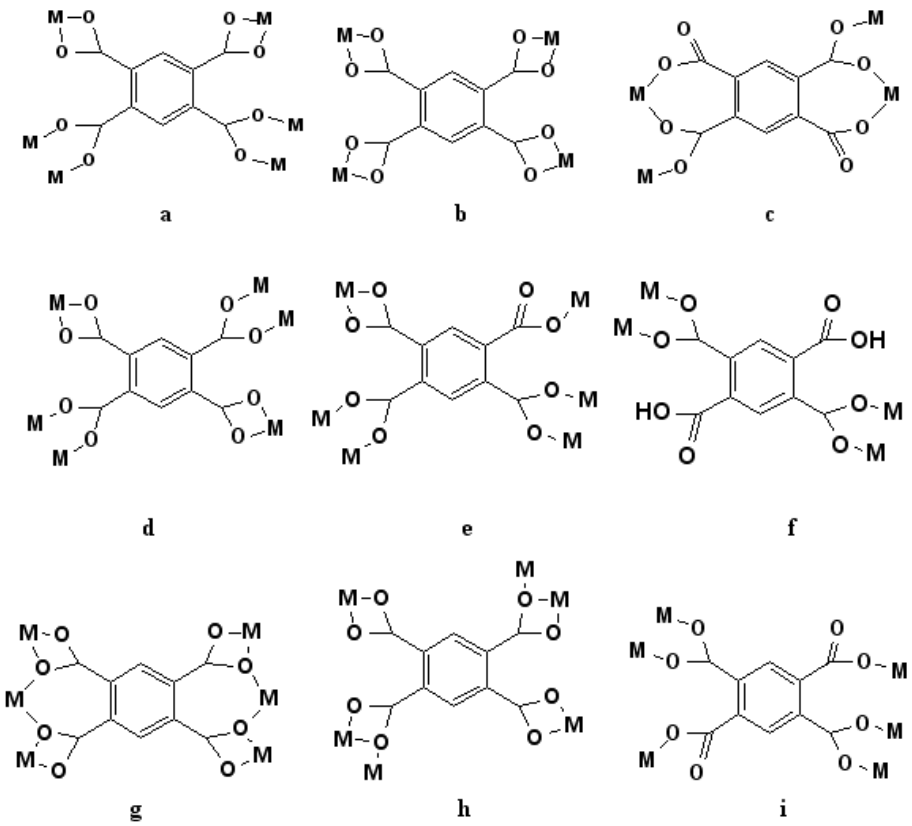

Scheme 1 The variety of coordination modes of 1,2,4, 5-benzenetetracarboxylic acid ligand coordinated to metals in the coordination polymer.

Text:

The Synthesis of complexes **2–4**, **6–8** and **10–12**.

$[Tb_2(ox)(bta)(H_2O)_4]$ (**2**) The compound was obtained by following a procedure similar to that used for **1** except that $EuCl_3·6H_2O$ was replaced by $TbCl_3·6H_2O$ (0.22 g 0.59 mmol). Colorless block single crystals for **2** were obtained in ca. 67.60 % yield (based on Tb). Anal. Calcd for $C_{12}H_{10}O_{16}Tb_2$ (728.04): Tb, 43.66; C, 19.78; H, 1.37 %. Found: Tb, 43.62; C, 19.83; H, 1.41 %. IR data (KBr pellet, ν[cm^{-1}]): 3328(s), 1686(m), 1581(s), 1485(w), 1434(w), 1397(s), 1324(m), 1142(w), 921(m), 873(m), 826(m), 800(w), 712(m), 573(m), 519(w), 438(m), 383(w).

$[Dy_2(ox)(bta)(H_2O)_4]$ (**3**) The complex was obtained by following a procedure similar to that used for **1** except that $EuCl_3·6H_2O$ was replaced by $DyCl_3·6H_2O$ (0.22 g 0.58 mmol). Primrose yellow block crystals for **3** were obtained in ca. 66.84 % yield (based on Dy). Anal. Calcd for $C_{12}H_{10}O_{16}Dy_2$ (735.20): Dy, 44.21; C, 19.59; H, 1.36 %. Found: Dy, 44.18; C, 19.65; H, 1.32 %. IR data (KBr pellet, ν[cm^{-1}]): 3341(s), 1687(m), 1583(s), 1487(w), 1435(w), 1397(s), 1325(m), 1142(w), 921(m), 873(m), 826(m), 799(w), 712(m), 572(m), 517(w), 437(m), 382(w).

$[Ho_2(ox)(bta)(H_2O)_4]$ (**4**) The synthesis procedure was prepared by a method similar to that used for **1** except that $EuCl_3·6H_2O$ was replaced by $HoCl_3·6H_2O$ (0.22 g 0.58 mmol). Rosiness block single crystals for **4** were obtained in ca. 64.56 % yield (based on Ho). Anal. Calcd for $C_{12}H_{10}O_{16}Ho_2$ (740.06): Ho, 44.57; C, 19.46; H, 1.35 %. Found: Ho, 44.52; C, 19.52; H, 1.31 %. IR data (KBr pellet, ν[cm^{-1}]): 3343(s), 1688(m), 1585(s), 1487(w), 1431(w), 1398(s), 1325(m), 1142(w), 921(m), 874(m), 827(m), 798(w), 713(m), 575(m), 517(w), 437(m), 382(w).

$[Eu_2(glu)(bta)(H_2O)_4]·(H_2O)$ (**6**) The complex was prepared by a method similar to that used for complex **5** but changing the $TbCl_3·6H_2O$ to $EuCl_3·6H_2O$ (0.22 g, 0.60 mmol). Colorless prismatic single crystals of **6** were obtained in ca.74.68 % yield (based on Eu). Anal. Calcd for $C_{15}H_{18}O_{17}Eu_2$(774.21): Eu, 39.25; C, 23.25; H, 2.32 %. Found: Eu, 39.28; C, 23.32; H, 2.38 %. IR data (KBr pellet, ν[cm^{-1}]): 3447(s), 2964(w), 1556(s), 1383(s), 1310(m), 1068(m), 946(m), 873(m), 823(m), 779(w), 647(w), 579(m), 510(m), 457(m), 402(w).

$[Dy_2(glu)(bta)(H_2O)_4]·(H_2O)$ (**7**) The complex was prepared by a method similar to that used for complex **5** but changing the $TbCl_3·6H_2O$ to $DyCl_3·6H_2O$ (0.22 g, 0.58 mmol), primrose yellow prismatic single crystals of **7** were obtained in ca. 77.25 % yield (based on Dy). Anal. Calcd for $C_{15}H_{18}O_{17}Dy_2$ (795.29): Dy, 40.87; C, 22.63; H, 2.26 %. Found: Dy, 40.83; C, 22.71; H, 2.22 %. IR data (KBr pellet, ν[cm^{-1}]): 3447(s), 2965(w), 1559(s), 1383(s), 1310(m), 1068(m), 949(m), 876(m), 825(m), 780(w), 649(w), 580(m), 510(m), 458(m), 404(w).

$[Ho_2(glu)(bta)(H_2O)_4]·(H_2O)$ (**8**) The synthesis procedure was similar to that used for complex **5** except that $TbCl_3·6H_2O$ was replaced by $HoCl_3·6H_2O$ (0.22 g, 0.58 mmol). Rosiness prismatic single crystals of **8** were obtained in ca. 79.24 % yield (based on Ho). Anal. Calcd for $C_{15}H_{18}O_{17}Ho_2$ (800.15): Ho, 41.22 ; C, 22.50; H, 2.25 %. Found: Ho, 41.27 ; C, 22.44; H, 2.28 %. IR data (KBr pellet, ν[cm^{-1}]): 3447(s), 2967(w), 1560(s), 1385(s), 1310(m), 1068(m), 949(m), 877(m), 826(m), 777(w), 650(w), 580(m), 511(m), 459(m), 405(w).

$[Eu_2(ad)(bta)(H_2O)_2]$ (**10**) The synthesis procedure was similar to that used for **9** except that $TbCl_3·6H_2O$ was replaced by $EuCl_3·6H_2O$ (0.22 g, 0.60 mmol). Spicule colorless single crystals for **10** were obtained in ca. 69.83 % yield (based on Eu). Anal. Calcd for $C_{16}H_{14}O_{14}Eu_2$ (734.19): Eu, 41.40; C, 26.15; H, 1.91 %. Found: Eu, 41.36; C, 26.23; H, 1.94 %. IR data (KBr pellet, ν[cm^{-1}]): 3449(s), 2964(w), 2922(w), 1565(s), 1496(m), 1431(w), 1386(s), 1148(m), 943(w), 882(m), 835(m), 779(m), 623(w) 588(m), 522(m), 370(w).

$[Dy_2(ad)(bta)(H_2O)_2]$ (**11**) The synthesis procedure was similar to that used for **9** except that $TbCl_3·6H_2O$ was replaced by $DyCl_3·6H_2O$ (0.22 g, 0.58 mmol). Spicule colorless single crystals for **11** were obtained in ca. 64.25 % yield (based on Dy). Anal. Calcd for $C_{16}H_{14}O_{14}Dy_2$ (755.27): Dy, 43.03; C, 26.48; H, 1.85 %. Found: Dy, 43.08; C, 26.39; H, 1.89 %. IR data (KBr pellet, ν[cm^{-1}]): 3459(s), 2963(w), 2922(w), 1572(s), 1496(m), 1427(w), 1386(s), 1149(m), 943(w), 885(m), 836(m), 780(m), 625(w), 588(m), 522(m), 373(w).

$[Er(ad)_{0.5}(bta)_{0.5}(H_2O)]$ (12) The synthesis procedure was similar to that used for **9** except that the $TbCl_3·6H_2O$ was replaced by $ErCl_3·6H_2O$ (0.22 g 0.58 mmol). Spicule Pink single crystals for **12** were obtained in ca. 62.88 % yield (based on Er). Anal. Calcd for $C_8H_7O_7Er$

(382.40): Er, 43.74; C, 25.10; H, 1.83 %. Found: Er, 43.70; C, 25.22; H, 1.78 %. IR data (KBr pellet, ν[cm^{-1}]): 3445(s), 2963(w), 2923(w), 1576(s), 1497(m), 1427(w), 1386(s), 1148(m), 943(w), 886(m), 837(m), 780(m), 626(w) 588(m), 521(m), 373(w).

Table S1 The selected bond angles (deg) of Complex **1, 5** and **9***

		Complex **1**			
O1–Eu–O4$^{\#2}$	144.40(8)	O1–Eu-O2W	141.36(9)	O4$^{\#2}$–Eu–O2W	70.70(8)
O1–Eu–O5	87.33(8)	O4$^{\#2}$–Eu–O5	88.74(9)	O2W–Eu–O5	75.63(9)
O1–Eu–O1W	71.29(9)	O4$^{\#2}$–Eu–O1W	140.92(8)	O2W–Eu–O1W	70.89(9)
O5–Eu–O1W	75.05(9)	O1–Eu–O2$^{\#3}$	105.90(8)	O2W–Eu–O2$^{\#3}$	72.54(9)
O5–Eu–O2$^{\#3}$	142.76(7)	O1W–Eu–O2$^{\#3}$	76.64(9)	O1–Eu–O6	74.79(8)
O4$^{\#2}$–Eu–O6	71.20(8)	O2W–Eu–O6	125.96(9)	O5–Eu–O6	66.67(8)
O1W–Eu–O6	129.25(8)	O2$^{\#3}$–Eu–O6	150.01(8)	O1–Eu–O3$^{\#4}$	76.44(8)
O2W–Eu–O3$^{\#4}$	135.40(8)	O5–Eu–O3$^{\#4}$	143.04(7)	O1W–Eu–O3$^{\#4}$	127.80(9)
O6–Eu–O3$^{\#4}$	77.03(7)				
		Complex **5**			
O3$^{\#1}$–Tb–O5	78.47(10)	O6$^{\#1}$–Tb–O5	135.04(11)	O4$^{\#2}$–Tb–O5	77.73(10)
O3$^{\#1}$–Tb–O1W	71.28(10)	O6$^{\#1}$–Tb–O1W	69.24(10)	O4$^{\#2}$–Tb–O1W	80.01(10)
O5–Tb–O1W	145.63(10)	O3$^{\#1}$–Tb–O2	144.58(10)	O6$^{\#1}$–Tb–O2	75.01(10)
O4$^{\#2}$–Tb–O2	123.80(10)	O5–Tb–O2	79.21(9)	O1W–Tb–O2	135.15(10)
O5–Tb–O2$^{\#1}$	67.53(10)	O1W–Tb–O2$^{\#1}$	115.96(10)	O2–Tb–O2$^{\#1}$	74.27(10)
O3$^{\#1}$–Tb–O2W	136.47(11)	O6$^{\#1}$–Tb–O2W	70.84(11)	O4$^{\#2}$–Tb–O2W	86.40(11)
O5–Tb–O2W	137.08(10)	O1W–Tb–O2W	66.23(11)	O2–Tb–O2W	77.18(10)
O2$^{\#1}$–Tb–O2W	136.36(10)	O3$^{\#1}$–Tb–O1	139.71(10)	O6$^{\#1}$–Tb–O1	117.19(10)
O4$^{\#2}$–Tb–O1	72.04(10)	O5–Tb–O1	70.10(10)	O1W–Tb–O1	126.30(10)
O2–Tb–O1	51.97(9)	O2$^{\#1}$–Tb–O1	115.78(10)	O2W–Tb–O1	67.09(11)
		Complex **9**			
O6$^{\#1}$–Tb–O5	143.16(9)	O2$^{\#1}$–Tb –O5	70.90(9)	O4$^{\#2}$–Tb–O5	78.17(9)
O6$^{\#1}$–Tb–O1W	73.56(12)	O2$^{\#1}$–Tb –O1W	132.27(11)	O4$^{\#2}$–Tb–O1W	78.21(11)
O5–Tb–O1W	138.11(11)	O6$^{\#1}$–Tb–O1	134.24(10)	O2$^{\#1}$–Tb–O1	140.89(9)
O4$^{\#2}$–Tb–O1	120.01(8)	O5–Tb–O1	76.08(9)	O1W–Tb–O1	86.62(11)
O6$^{\#1}$–Tb–O4	90.84(8)	O2$^{\#1}$–Tb–O4	71.45(8)	O4$^{\#2}$–Tb–O4	139.76(4)
O5–Tb–O4	72.86(8)	O1W–Tb–O4	141.21(11)	O1–Tb–O4	79.33(8)
O6$^{\#1}$–Tb–O2	137.35(9)	O2$^{\#1}$–Tb–O2	133.68(6)	O4$^{\#2}$–Tb–O2	69.80(8)
O5–Tb–O2	75.22(8)	O1W–Tb–O2	64.31(11)	O1–Tb–O2	51.59(8)
O4–Tb–O2	126.36(8)	O6$^{\#1}$–Tb –O3	72.55(9)	O2$^{\#1}$–Tb–O3	110.27(8)
O4$^{\#2}$–Tb–O3	165.89(8)	O5–Tb–O3	115.95(8)	O1W–Tb–O3	90.24(12)
O1–Tb–O3	66.61(8)	O4–Tb–O3	50.99(8)	O2–Tb–O3	112.57(8)

*****Symmetry transformations used to generate equivalent atoms:

#2: x, y, z–1; #3: –x+2, –y+1, –z+1; #4: –x+1, –y+1, –z+1 for **1**. #1 –x+1/2,–y+1/2,–z+1 ; #2 x,–y+1,z–1/2 for **5**. #1: –x+3/2, y+1/2, –z+1/2; #2 –x+3/2, y–1/2, –z+1/2 for **9**.

Table S2 Selected bond distances (Å) and angles (deg) of complex **2***

Bond Distances					
Tb–O1	2.433(3)	Tb–O2$^{\#2}$	2.329(3)	Tb–O3$^{\#3}$	2.409(3)
Tb–O4$^{\#1}$	2.328(3)	Tb–O5	2.365(3)	Tb–O6	2.421(3)
Tb–O1W	2.361(3)	Tb–O2W	2.408(3)		
Bond Angles					
O4$^{\#1}$–Tb–O1W	141.42(11)	O2$^{\#2}$–Tb–O1W	70.97(11)	O4$^{\#1}$–Tb–O5	87.78(12)
O2$^{\#2}$–Tb–O5	89.62(12)	O1W–Tb–O5	75.46(12)	O4$^{\#1}$–Tb–O2W	71.38(11)
O2$^{\#2}$–Tb–O2W	141.30(11)	O1W–Tb–O2W	70.82(11)	O5–Tb–O2W	75.19(11)
O1W–Tb–O3$^{\#3}$	72.64(12)	O5–Tb–O3$^{\#3}$	142.70(10)	O2W–Tb–O3$^{\#3}$	76.47(11)
O4$^{\#1}$–Tb–O6	74.84(11)	O2$^{\#2}$–Tb–O6	71.60(12)	O1W–Tb–O6	126.44(12)
O5–Tb–O6	67.41(10)	O2W–Tb–O6	129.80(11)	O3$^{\#3}$–Tb–O6	149.35(10)
O4$^{\#1}$–Tb–O1	76.34(10)	O2$^{\#2}$–Tb–O1	85.07(10)	O1W–Tb–O1	135.29(11)
O5–Tb–O1	143.26(10)	O2W–Tb–O1	127.75(11)	O3$^{\#3}$–Tb–O1	74.01(10)
O6–Tb–O1	76.45(10)				

*****Symmetry transformations used to generate equivalent atoms:

#1: x, y–1, z; #2: –x+1, –y+1, –z+1; #3: –x+2, –y+2, –z+2 for **2**.

Table S3 Selected bond distances (Å) and angles (deg) of complex **3***

Bond Distances					
Dy–O2$^{\#1}$	2.306(4)	Dy–O4$^{\#2}$	2.310(5)	Dy–O5	2.364(5)
Dy–O2W	2.357(5)	Dy–O1W	2.389(5)	Dy–O1	2.396(4)
Dy–O6$^{\#3}$	2.412(4)	Dy–O3$^{\#4}$	2.424(4)		
Bond Angles					
O2$^{\#1}$–Dy–O2W	141.51(18)	O4$^{\#2}$–Dy–O2W	70.65(17)	O2$^{\#1}$–Dy–O5	87.96(17)
O4$^{\#2}$–Dy–O5	90.34(17)	O2W–Dy–O5	75.31(18)	O2$^{\#1}$–Dy–O1W	70.81(18)
O4$^{\#2}$–Dy–O1W	141.70(17)	O2W–Dy–O1W	71.44(17)	O2$^{\#1}$–Dy–O6	75.19(16)
O4$^{\#2}$–Dy–O(6)	71.94(17)	O2$^{\#1}$–Dy–O3	76.18(16)	O5-Dy–O1W	74.96(17)
O2$^{\#1}$–Dy–O1)	104.89(15)	O4$^{\#2}$–Dy–O1	97.42(16)	O2W–Dy–O1	73.03(17)
O5–Dy–O1	142.61(16)	O1W–Dy–O1	76.51(17)	O2W–Dy–O6$^{\#3}$	126.35(17)
O5–Dy–O6$^{\#3}$	67.87(15)	O1W–Dy–O6$^{\#3}$	129.76(17)	O1–Dy–O6$^{\#3}$	149.05(16)
O2W–Dy–O3$^{\#4}$	135.37(16)	O5–Dy–O3$^{\#4}$	143.36(15)	O1W–Dy–O3$^{\#4}$	127.50(16)
O1–Dy–O3$^{\#4}$	73.96(16)				

*****Symmetry transformations used to generate equivalent atoms:

#1 –x+1, –y+1,-z+1 ; #2 x–1,y–1,z–1 ; #3 –x, –y, –z ; #4 –x+1, –y+2, –z+1for **3**.

Table S4 Selected bond distances (Å) and angles (deg) of complex **4***

Bond Distances					
Ho–O2$^{\#1}$	2.300(3)	Ho–O3$^{\#2}$	2.304(3)	Ho–O2W	2.341(3)
Ho–O6	2.351(3)	Ho–O1$^{\#3}$	2.382(3)	Ho–O1W	2.387(3)
Ho–O5	2.404(3)	Ho–O4	2.417(3)		
Bond Angles					
O2$^{\#1}$–Ho–O2W	141.87(12)	O3$^{\#2}$–Ho–O2W	70.80(12)	O2$^{\#1}$–Ho–O6	88.04(12)
O3$^{\#2}$–Ho–O6	90.75(13)	O2W–Ho–O6	75.55(13)	O2W–Ho–O1$^{\#3}$	73.18(13)
O6–Ho–O1$^{\#3}$	142.98(11)	O2$^{\#1}$–Ho–O1W	71.13(12)	O3$^{\#2}$–Ho–O1W	141.89(11)
O2W–Ho–O1W	71.44(12)	O6–Ho–O1W	75.02(12)	O1$^{\#3}$–Ho–O1W	76.62(12)
O2$^{\#1}$–Ho–O5	74.90(12)	O3$^{\#2}$–Ho–O5	72.13(12)	O2W–Ho–O5	126.56(13)
O6–Ho–O5	67.85(11)	O1$^{\#3}$–Ho–O5	148.75(11)	O1W–Ho–O5	129.78(12)
O2$^{\#1}$–Ho–O4	76.21(11)	O3$^{\#2}$–Ho–O4	84.36(11)	O2W–Ho–O4	134.83(11)
O6–Ho–O4	143.65(11)	O1$^{\#3}$–Ho–O4	73.30(11)	O1W–Ho–O4	127.45(11)
O5–Ho–O4	76.41(10)				

*****Symmetry transformations used to generate equivalent atoms:

#1: –x+2, –y+1, –z+1; #2: –x+2, –y+1, –z+2; #3: x–1, y, z for **4**.

Table S5 Selected bond distances (Å) and angles (deg) of complex **6***

Bond Distances					
Eu1–O3$^{\#1}$	2.357(2)	Eu–O6$^{\#1}$	2.386(2)	Eu–O4$^{\#2}$	2.423(2)
Eu1–O5	2.443(2)	Eu–O1W	2.462(2)	Eu–O2$^{\#1}$	2.482(2)
Eu1–O2	2.488(2)	Eu–O2W	2.558(3)	Eu–O1	2.563(2)
Bond Angles					
O3$^{\#1}$–Eu–O5	78.77(9)	O6$^{\#1}$–Eu–O5	134.70(8)	O4$^{\#2}$–Eu–O5	77.76(8)
O3$^{\#1}$–Eu–O1W	71.13(9)	O6$^{\#1}$–Eu–O1W	69.26(8)	O4$^{\#2}$–Eu–O1W	80.33(8)
O5–Eu–O1W	145.92(8)	O5–Eu–O2$^{\#1}$	67.43(8)	O1W–Eu–O2$^{\#1}$	115.49(8)
O3$^{\#1}$–Eu–O2	144.82(8)	O6$^{\#1}$–Eu–O2	74.84(8)	O4$^{\#2}$–Eu–O2	123.66(8)
O5–Eu–O2	79.11(8)	O1W–Eu–O2	134.96(8)	O2$^{\#1}$–Eu–O2	74.91(9)
O3$^{\#1}$–Eu–O2W	136.47(9)	O6$^{\#1}$–Eu–O2W	70.88(9)	O4$^{\#2}$–Eu–O2W	86.59(9)
O5–Eu1–O2W	136.96(9)	O1W–Eu–O2W	66.38(9)	O2$^{\#1}$–Eu–O2W	136.62(8)
O2–Eu1–O2W	76.90(8)	O3$^{\#1}$–Eu–O1	140.13(8)	O6$^{\#1}$–Eu–O1	116.77(8)
O4$^{\#2}$–Eu1–O1	72.42(7)	O5–Eu–O1	70.04(9)	O1W–Eu–O1	126.67(9)
O2$^{\#1}$–Eu1–O1	115.85(8)	O2–Eu–O1	51.45(7)	O2W–Eu–O1	67.03(9)

*****Symmetry transformations used to generate equivalent atoms:

#1 –x+1/2, –y+1/2,-z+1 #2 x, –y+1,z–1/2 for **6.**

Table S6 Selected bond distances (Å) and angles (deg) of complex **7***

Bond Distances					
Dy–O1$^{\#1}$	2.316(2)	Dy–O5$^{\#2}$	2.357(2)	Dy–O2$^{\#3}$	2.379(2)
Dy–O6	2.398(2)	Dy–O1W	2.427(2)	Dy–O4	2.442(2)
Dy–O4$^{\#2}$	2.451(2)	Dy–O2W	2.506(3)	Dy–O3	2.537(2)
Bond Angles					
O1$^{\#1}$–Dy–O6	78.29(8)	O5$^{\#2}$–Dy–O6	135.29(8)	O2$^{\#3}$–Dy–O6	77.83(8)
O1$^{\#1}$–Dy–O1W	70.72(8)	O5$^{\#2}$–Dy–O1W	69.19(8)	O2$^{\#3}$–Dy–O1W	80.00(8)
O6–Dy–O1W	145.08(8)	O1$^{\#1}$–Dy–O4	144.51(8)	O5$^{\#2}$–Dy–O4	74.97(8)
O2$^{\#3}$–Dy–O4	123.82(7)	O6–Dy–O4	79.32(7)	O1W–Dy–O4	135.61(8)
O6–Dy–O4$^{\#2}$	67.75(8)	O1W–Dy–O4$^{\#2}$	115.21(8)	O4–Dy–O4$^{\#2}$	74.37(8)
O1$^{\#1}$–Dy–O2W	136.04(9)	O5$^{\#2}$–Dy–O2W	70.89(9)	O2$^{\#3}$–Dy–O2W	85.76(9)
O6–Dy–O2W	137.28(9)	O1W–Dy–O2W	66.48(9)	O4–Dy–O2W	77.75(8)
O4$^{\#2}$–Dy–O2W	136.78(8)	O1$^{\#1}$–Dy–O3	139.54(8)	O5$^{\#2}$–Dy–O3	117.17(8)
O2$^{\#3}$–Dy–O3	71.93(8)	O6–Dy–O3	70.09(8)	O1W–Dy–O3	126.94(8)
O4–Dy–O3	52.09(7)	O4$^{\#2}$–Dy–O3	116.01(8)	O2W–Dy–O3	67.35(9)

*****Symmetry transformations used to generate equivalent atoms:

#1: x–1/2, y–1/2, z; #2: –x+1/2, –y+3/2, –z; #3: –x+1, y, –z+1/2 for **7**.

Table S7 Selected Bond distances (Å) and Angles (deg) of Complex **8***

Bond Distances					
Ho–O4$^{\#1}$	2.303(3)	Ho–O5$^{\#1}$	2.349(3)	Ho–O3$^{\#3}$	2.367(3)
Ho–O6	2.383(3)	Ho–O1W	2.416(3)	Ho1–O2	2.430(3)
Ho–O2$^{\#1}$	2.440(3)	Ho–O2W	2.501(4)	Ho1–O1	2.537(3)
Bond Angles					
O4$^{\#1}$–Ho–O6	78.30(10)	O5$^{\#1}$–Ho–O6	135.57(10)	O3$^{\#3}$–Ho–O6	77.80(9)
O4$^{\#1}$–Ho–O1W	71.00(11)	O5$^{\#1}$–Ho–O1W	69.29(10)	O3$^{\#3}$–Ho–O1W	79.69(10)
O6–Ho–O1W	145.13(10)	O4$^{\#1}$–Ho–O2	144.68(9)	O5$^{\#1}$–Ho–O2	75.04(9)
O3$^{\#3}$–Ho–O2	123.65(9)	O6–Ho–O2	79.36(9)	O1W–Ho–O2	135.50(10)
O6–Ho–O2$^{\#1}$	67.83(9)	O1W–Ho–O2$^{\#1}$	115.82(10)	O2–Ho–O2$^{\#1}$	74.25(10)
O4$^{\#1}$–Ho–O2W	136.24(10)	O5$^{\#1}$–Ho–O2W	70.82(12)	O3$^{\#3}$–Ho–O2W	85.61(12)
O6–Ho–O2W	136.94(11)	O1W–Ho–O2W	66.40(11)	O2–Ho–O2W	77.47(10)
O2$^{\#1}$–Ho–O2W	136.66(11)	O4$^{\#1}$–Ho–O1	139.27(10)	O5$^{\#1}$–Ho–O1	117.27(10)
O3$^{\#3}$–Ho–O1	71.63(9)	O6–Ho–O1	69.95(10)	O1W–Ho–O1	126.43(10)
O2–Ho–O1	52.20(9)	O2$^{\#1}$–Ho–O1	115.93(9)	O2W–Ho–O1	67.14(12)

*****Symmetry transformations used to generate equivalent atoms:

#1: –x+1/2, –y+3/2, –z; #3: x, –y+1, z+1/2 for **8**.

Table S8 Selected bond distances (Å) and angles (deg) of complex **10***

Bond Distances					
Eu–O6$^{\#1}$	2.339(3)	Eu–O2$^{\#1}$	2.383(3)	Eu–O3$^{\#2}$	2.403(2)
Eu–O5	2.410(3)	Eu–O1W	2.411(4)	Eu–O1	2.471(3)
Eu–O3	2.522(3)	Eu–O2	2.593(3)	Eu–O4	2.616(3)
Bond Angles					
O6$^{\#1}$–Eu–O1W	74.38(12)	O2$^{\#1}$–Eu–O1W	131.96(12)	O3$^{\#2}$–Eu–O1W	77.56(11)
O6$^{\#1}$–Eu–O5	142.66(10)	O2$^{\#1}$–Eu–O5	70.44(10)	O3$^{\#2}$–Eu–O5	77.85(10)
O5–Eu–O1W	137.43(10)	O6$^{\#1}$–Eu–O1	134.45(10)	O2$^{\#1}$–Eu–O1	140.98(10)
O3$^{\#2}$–Eu–O1	119.84(8)	O1W–Eu–O1	86.66(12)	O5–Eu–O1	76.29(10)
O6$^{\#1}$–Eu–O3	90.82(9)	O2$^{\#1}$–Eu–O3	71.59(9)	O3$^{\#2}$–Eu–O3	139.25(4)
O1W–Eu–O3	142.47(11)	O5–Eu–O3	72.53(9)	O1–Eu–O3	79.52(9)
O6$^{\#1}$–Eu–O2	138.20(9)	O2$^{\#1}$–Eu–O2	133.07(6)	O3$^{\#2}$–Eu–O2	70.03(8)
O1W–Eu–O2	64.24(11)	O5–Eu–O2	74.89(9)	O1–Eu–O2	51.11(8)
O3–Eu–O2	125.76(9)	O6$^{\#1}$–Eu–O4	72.58(10)	O2$^{\#1}$–Eu–O4	110.15(9)
O3$^{\#2}$–Eu–O4	166.52(9)	O1W–Eu–O4	91.78(11)	O5–Eu–O4	115.60(9)
O1–Eu–O4	66.94(9)	O3–Eu–O4	50.69(8)	O2–Eu–O4	112.93(8)

*Symmetry transformations used to generate equivalent atoms:
#1: –x+1/2, y–1/2, –z+1/2; #2 –x+1/2, y+1/2, –z+1/2 for **10**.

Table S9 Selected bond distances (Å) and angles (deg) of complex **11***

Bond Distances					
Dy–O1	2.561(3)	Dy–O2	2.434(3)	Dy–O3	2.608(3)
Dy–O4	2.475(3)	Dy–O5	2.369(3)	Dy–O1W	2.380(4)
Dy–O4$^{\#1}$	2.366(2)	Dy–O1$^{\#2}$	2.348(3)	Dy–O6$^{\#2}$	2.310(3)
Bond Angles					
O6$^{\#2}$–Dy–O5	143.32(10)	O1$^{\#2}$–Dy-O5	70.90(10)	O4$^{\#1}$–Dy–O5	78.29(10)
O6$^{\#2}$–Dy–O1W	73.44(13)	O1$^{\#2}$–Dy-O1W	132.49(12)	O4$^{\#1}$–Dy–O1W	78.19(13)
O5–Dy–O1W	138.18(13)	O6$^{\#2}$–Dy-O2	133.87(10)	O1$^{\#2}$–Dy–O2	141.01(10)
O4$^{\#1}$–Dy–O2	119.96(9)	O5–Dy–O2	76.30(10)	O1W–Dy–O2	86.31(13)
O6$^{\#2}$–Dy–O4	90.91(9)	O1$^{\#2}$–Dy–O4	71.39(9)	O4$^{\#1}$–Dy–O4	140.00(4)
O5–Dy–O4	72.83(9)	O1W–Dy–O4	141.02(13)	O2–Dy–O4	79.33(9)
O6$^{\#2}$–Dy–O1	137.06(10)	O1$^{\#2}$–Dy–O1	133.84(7)	O4$^{\#1}$–Dy–O1	69.58(8)
O5–Dy–O1	75.40(9)	O1W–Dy–O1	64.14(12)	O2–Dy–O1	51.71(9)
O4–Dy–O1	126.46(9)	O6$^{\#2}$–Dy–O3	72.31(10)	O1$^{\#2}$–Dy–O3	110.39(9)
O4$^{\#1}$–Dy–O3	165.49(9)	O5–Dy–O3	116.22(9)	O1W–Dy–O3	89.73(13)
O2–Dy–O3	66.48(9)	O4–Dy–O3	51.31(8)	O1–Dy–O3	112.43(9)

*Symmetry codes follow: #1: –x+3/2, y–1/2, –z+1/2; #2: –x+3/2, y+1/2, –z+1/2 for **11**.

Table S10 Selected Bond distances (Å) and Angles (deg) of Complex **12***

		Bond Distances			
Er–O1	2.447(3)	Er–O2	2.600(3)	Er–O3$^{\#3}$	2.547(3)
Er–O4$^{\#3}$	2.413(3)	Er–O1W	2.343(3)	Er–O6	2.348(3)
Er–O1$^{\#2}$	2.345(3)	Er–O3$^{\#2}$	2.323(3)	Er–O5$^{\#1}$	2.297(3)
		Bond Angles			
O5$^{\#1}$–Er–O6	143.30(11)	O3$^{\#2}$–Er–O6	71.04(11)	O1$^{\#2}$–Er–O6	78.27(10)
O5$^{\#1}$–Er–O1W	72.86(12)	O3$^{\#2}$–Er–O1W	132.57(12)	O1W–Er–O1$^{\#2}$	78.78(11)
O1W–Er–O6	138.87(11)	O5$^{\#1}$–Er–O4$^{\#3}$	133.92(11)	O3$^{\#2}$–Er–O4$^{\#3}$	141.00(11)
O1$^{\#2}$–Er–O4$^{\#3}$	119.97(10)	O6–Er–O4$^{\#3}$	76.36(11)	O1W–Er–O4$^{\#3}$	86.33(12)
O5$^{\#1}$–Er–O1	90.82(10)	O3$^{\#2}$–Er–O1	71.46(10)	O1$^{\#2}$–Er–O1	140.46(5)
O6–Er–O1	73.23(10)	O1W–Er–O1	139.89(11)	O4$^{\#3}$–Er1–O1	79.17(10)
O5$^{\#1}$–Er–O3$^{\#3}$	136.58(10)	O3$^{\#2}$–Er–O3$^{\#3}$	134.21(7)	O1$^{\#2}$–Er–O3$^{\#3}$	69.33(9)
O6–Er–O3$^{\#3}$	75.74(10)	O1W–Er–O3$^{\#3}$	64.35(11)	O4$^{\#3}$–Er–O3$^{\#3}$	52.04(9)
O1–Er–O3$^{\#3}$	126.89(10)	O5$^{\#1}$–Er–O2	72.33(11)	O3$^{\#2}$–Er–O2	110.69(10)
O1$^{\#2}$–Er–O2	164.90(10)	O6–Er–O2	116.81(10)	O1W–Er–O2	88.29(11)
O4$^{\#3}$–Er1–O2	66.26(10)	O1–Er–O2	51.63(9)	O3$^{\#3}$–Er–O2	112.07(9)

*Symmetry codes follow: #1 –x+1/2,y–1/2, –z+1/2 ; #2 –x+1/2,y+1/2, –z+1/2 ; #3 x,y+1,z for **12**.

Table S11 The comparison of the bond distance of rigid bta and glutarate ligands for Ln–bta–glu complexes

	Bta	Glutarate
Complexes	Ln–O (av)	Ln–O (av)
6	2.458(2)	2.415(2)
5	2.438(3)	2.387(3)
7	2.419(2)	2.378(2)
8	2.415(3)	2.366(3)

Table S12 The comparison of the bond distance of rigid bta and glutarate ligands for Ln–bta–ad complexes

	Bta	Adipate
Complexes	Ln–O (av)	Ln–O (av)
10	2.498(2)	2.375(3)
9	2.475(2)	2.351(3)
11	2.465(3)	2.340(3)
12	2.446(3)	2.323(3)

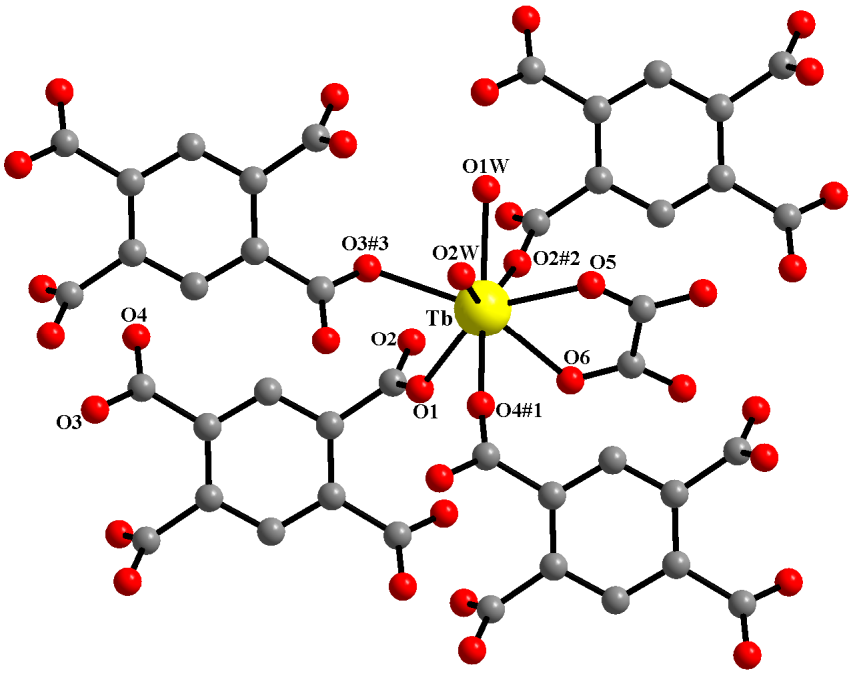

Figure S1 The coordination environment of Tb in complex **2**. (Symmetry codes follow: #1: x, y–1, z; #2: –x+1, –y+1, –z+1; #3: –x+2, –y+2, –z+2)

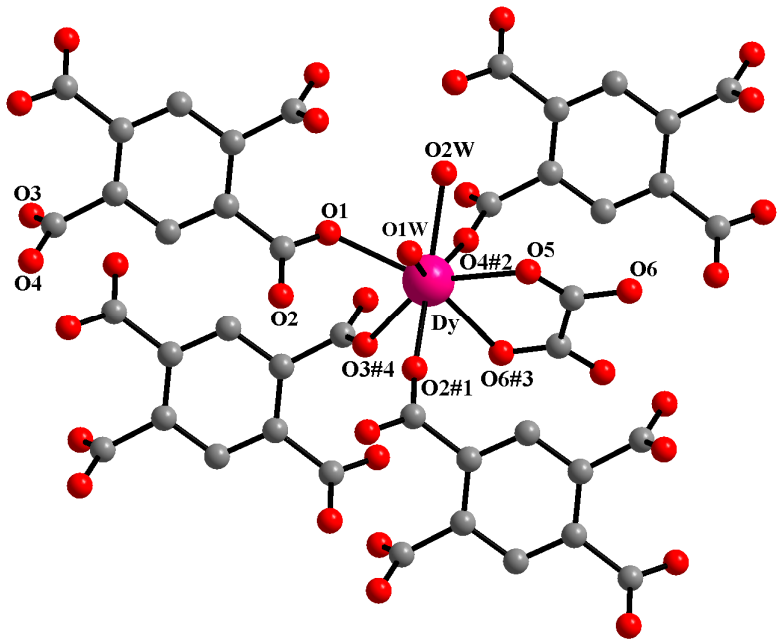

Figure S2 The coordination environment of Dy in complex **3**. (Symmetry codes follow: #1 -x+1,-y+1,-z+1; #2 x-1,y-1,z-1; #3 -x,-y,-z; #4 -x+1,-y+2,-z+1)

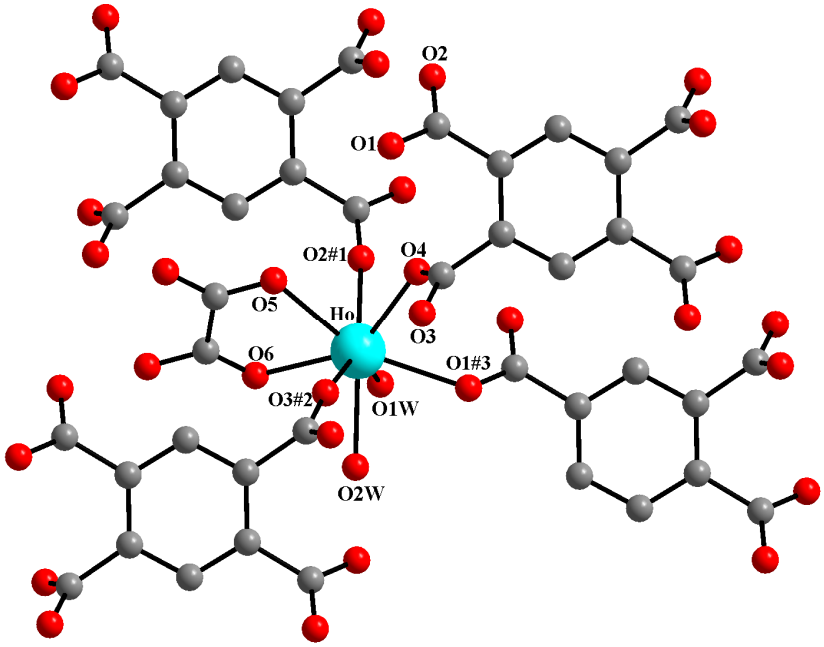

Figure S3 The coordination environment of Ho in complex **4**. (Symmetry codes follow: #1: –x+2, –y+1, –z+1; #2: –x+2, –y+1, –z+2; #3: x–1, y, z)

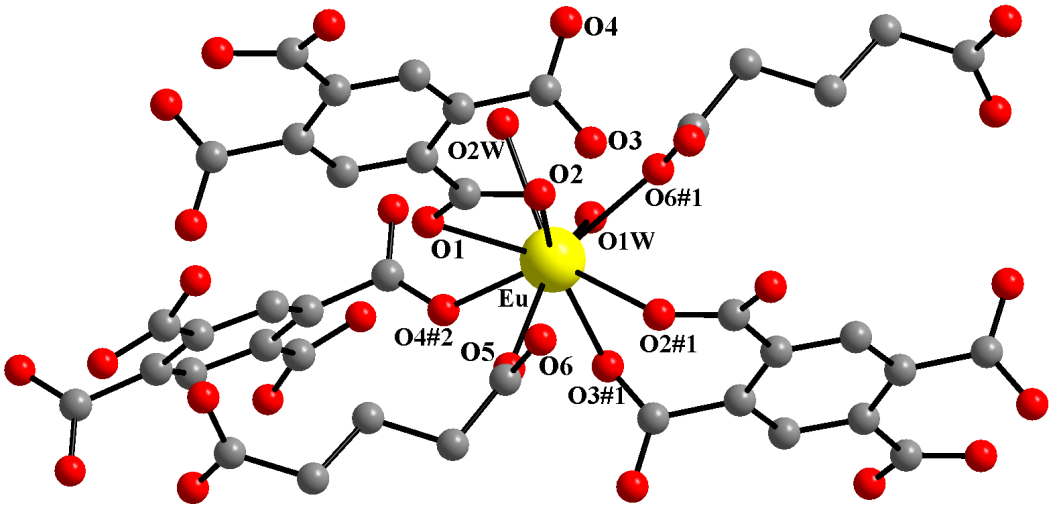

Figure S4 The coordination environment of Eu in complex **6**. (Symmetry codes follow: #1 –x+1/2, –y+1/2,-z+1; #2 x, –y+1,z–1/2)

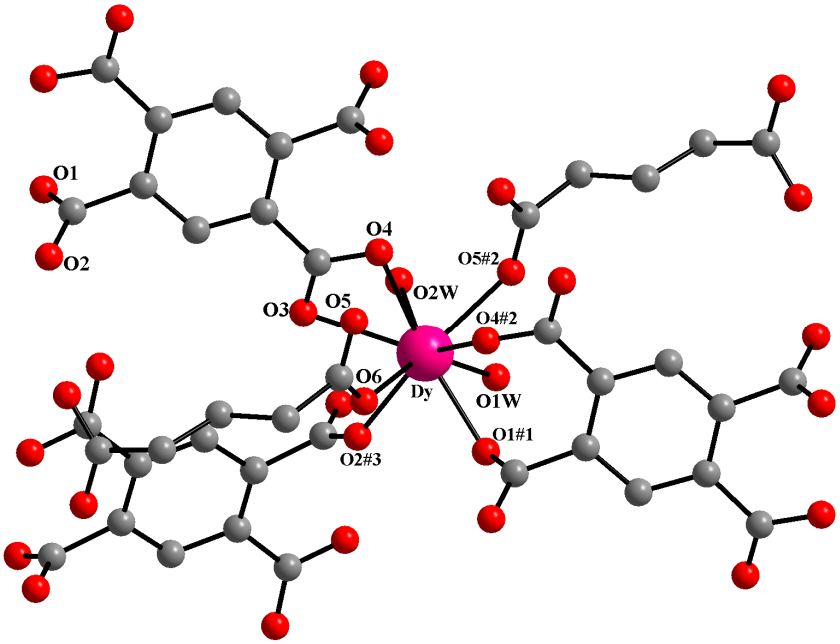

Figure S5 The coordination environment of Dy in complex **7**. (Symmetry codes follow: #1: x–1/2, y–1/2, z; #2: –x+1/2, –y+3/2, –z; #3: –x+1, y, –z+1/2)

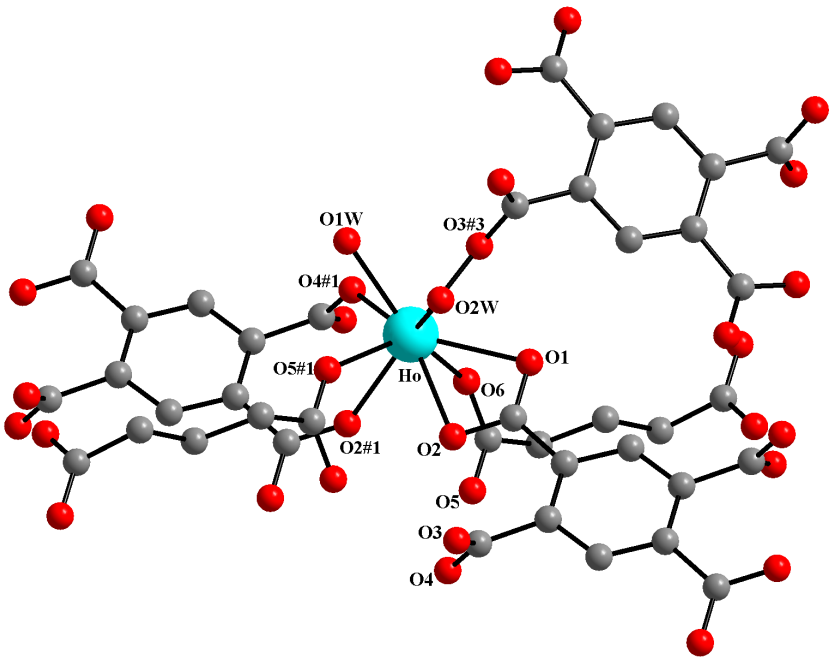

Figure S6 The coordination environment of Ho in complex **8**. (Symmetry codes follow: #1: –x+1/2, –y+3/2, –z; #3: x, –y+1, z+1/2)

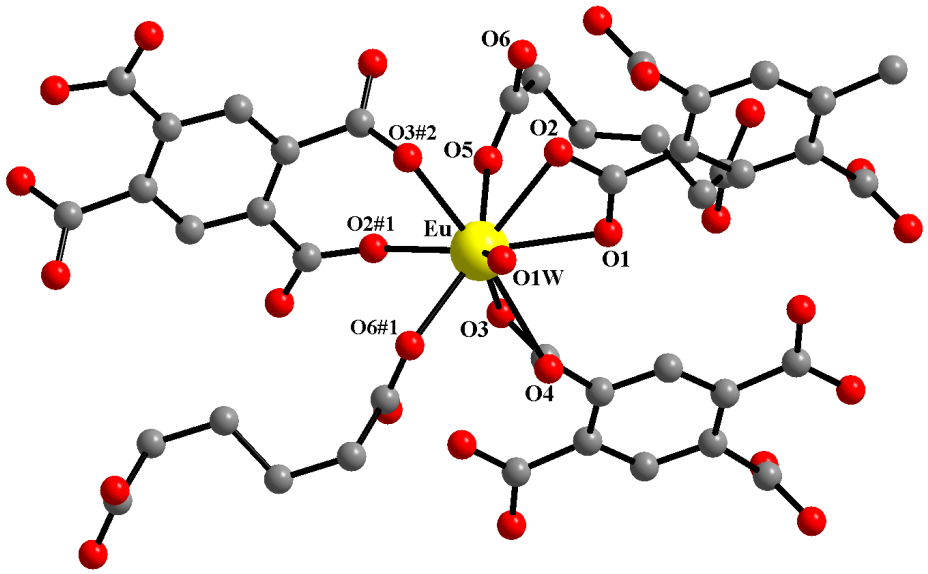

Figure S7 The coordination environment of Eu in complex **10**. (Symmetry codes follow: #1: –x+1/2, y–1/2, –z+1/2; #2 –x+1/2, y+1/2, –z+1/2)

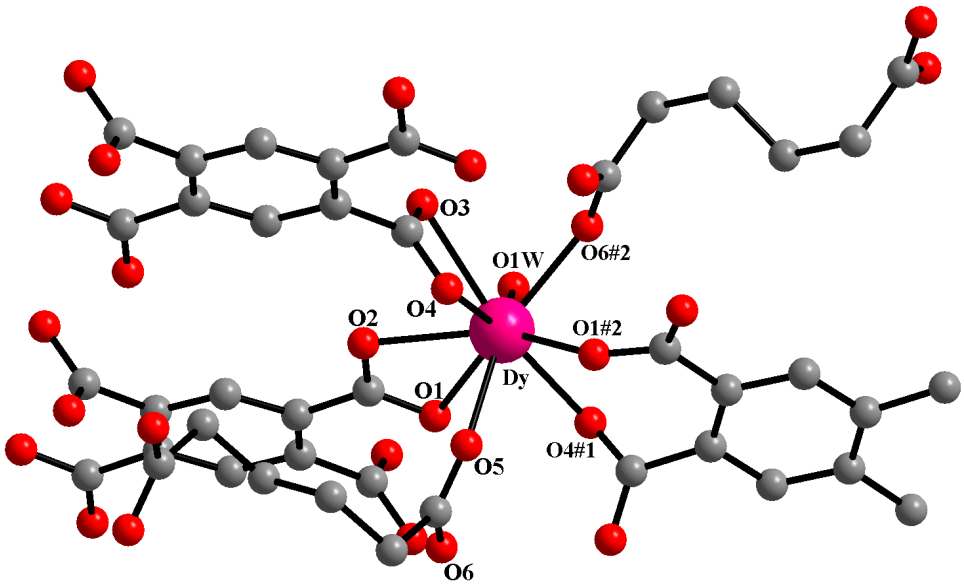

Figure S8 The coordination environment of Dy in complex **11**. (Symmetry codes follow: #1: –x+3/2, y–1/2, –z+1/2; #2: –x+3/2, y+1/2, –z+1/2)

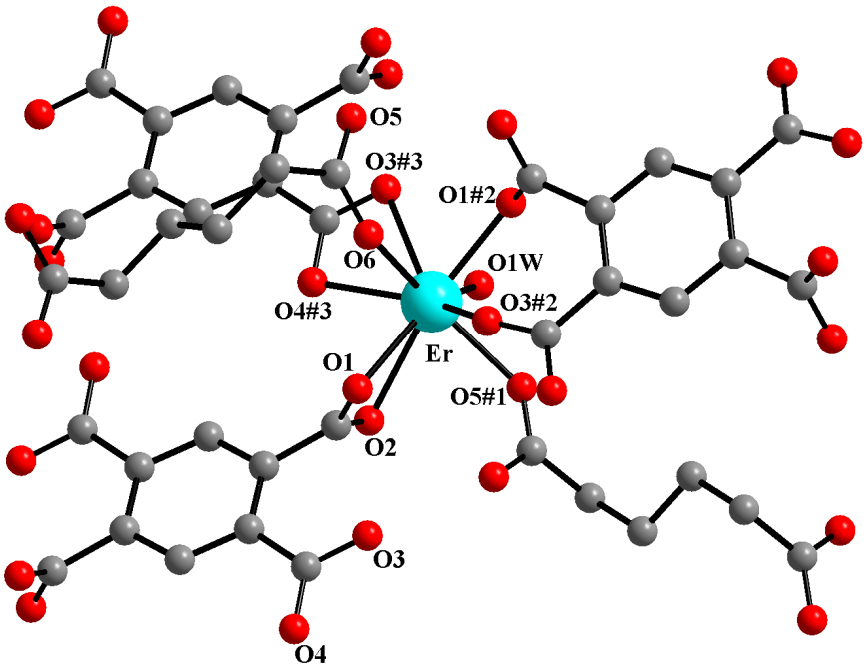

Figure S9 The coordination environment of Er in complex **12**. (Symmetry codes follow: #1 –x+1/2,y–1/2, –z+1/2 ; #2 –x+1/2,y+1/2, –z+1/2 ; #3 x,y+1,z.)

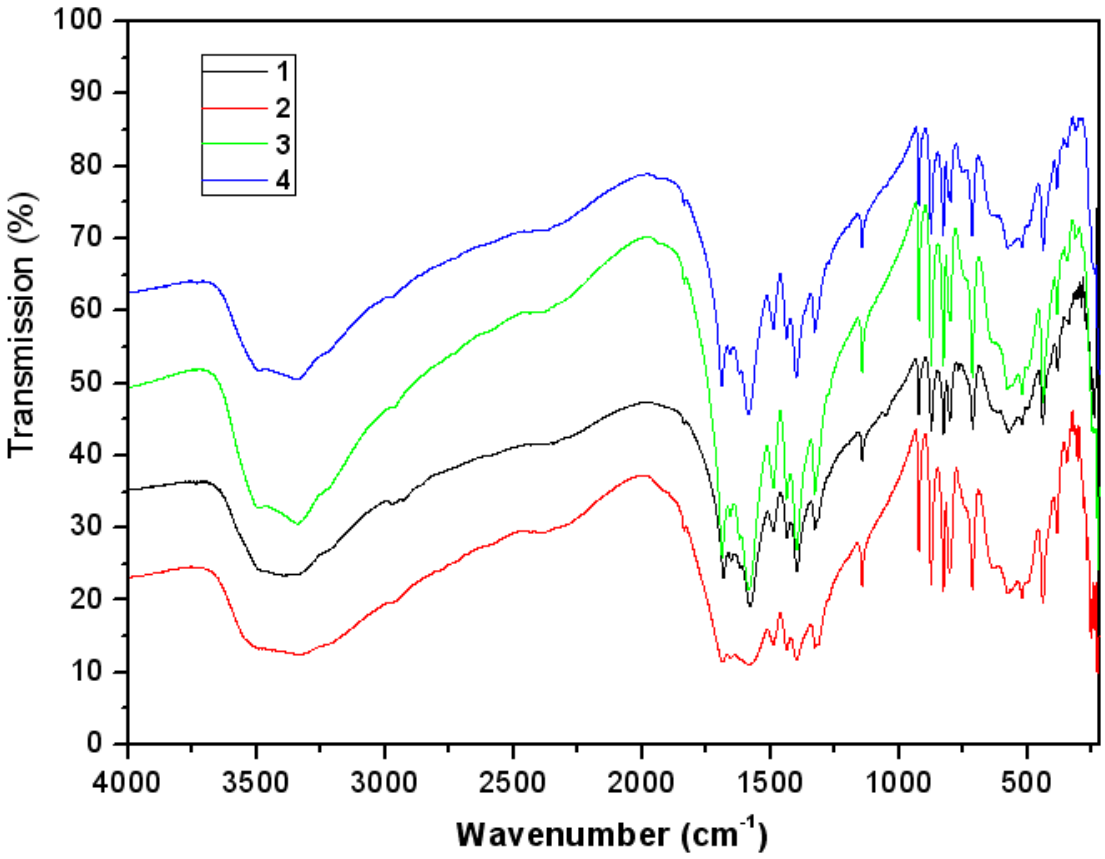

Figure S10 The infrared spectra for complexes **1**–**4**.

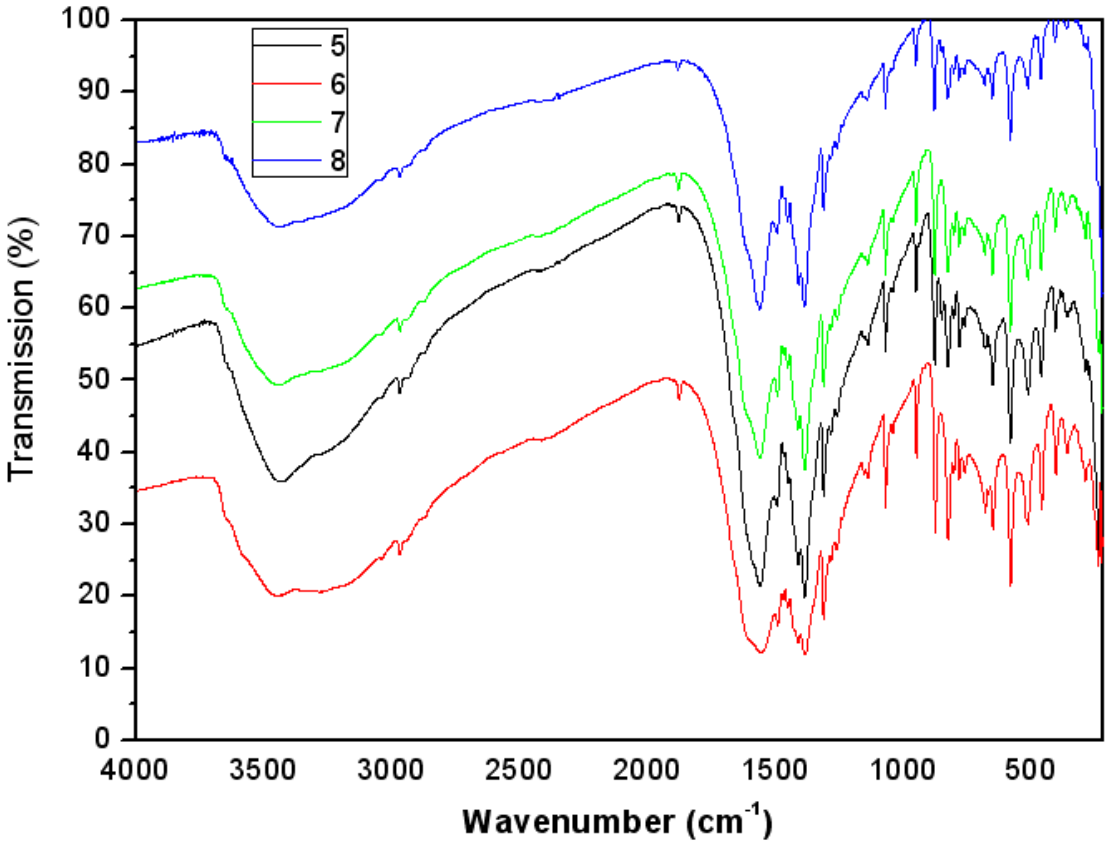

Figure S11 The infrared spectra for complexes **5**–**8**.

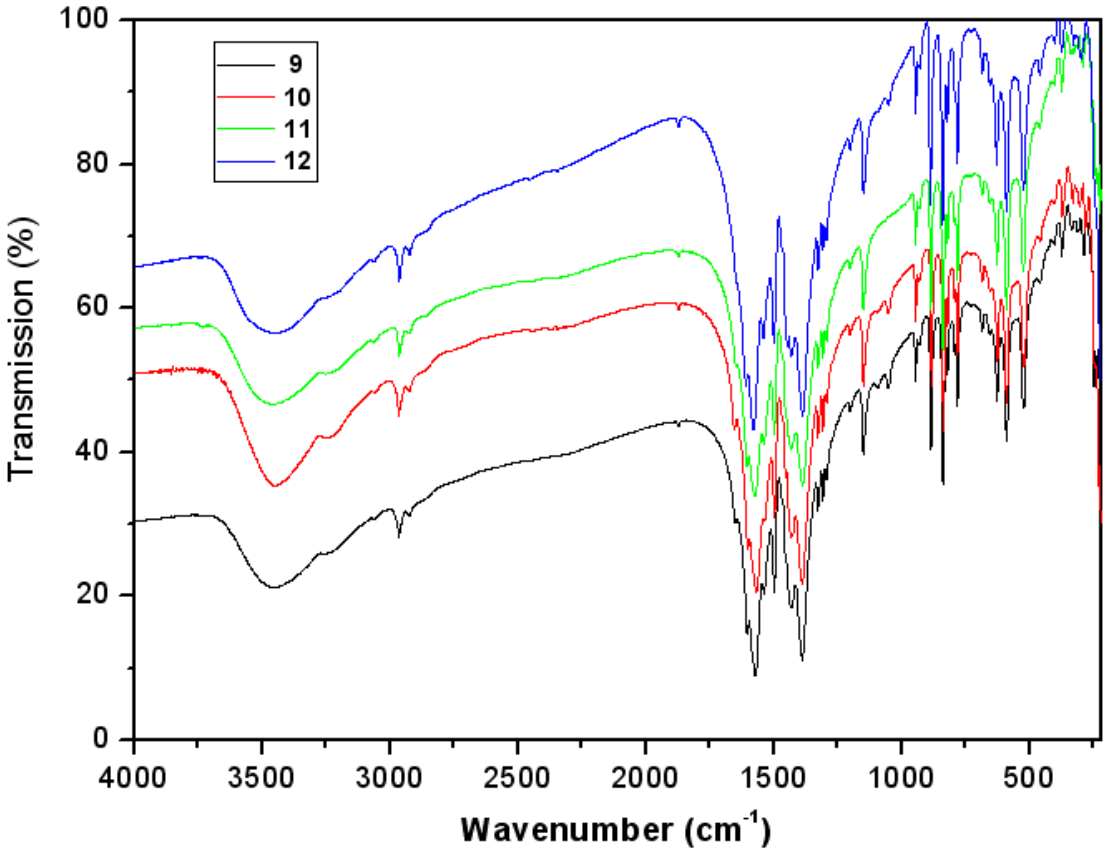

Figure S12 The infrared spectra for complexes **9**–**12**.