Anion Dependant Self-assembly and the First X-Ray Structure of a Neutral Homoleptic Lanthanide Salen Complex $Tb_4(Salen)_6$)

Xiaoping Yang,[a] Richard A Jones,*[a] and Wai-Kwok Wong*[b]

§ Electronic supplementary information (ESI):

Figure S1. ^{1}H NMR spectrum of **1** in CD_3OD.

Crystallographic data for **1-5**

Tables of bond length and angles for **1-5**

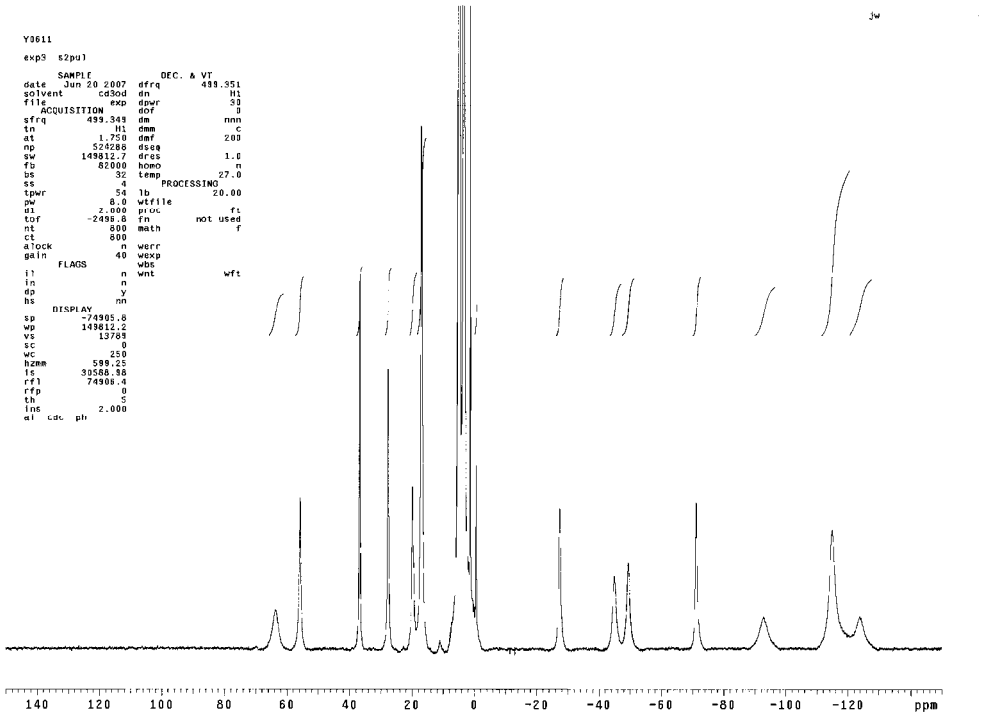

Figure S1. ^{1}H NMR spectrum of **1** in CD_3OD.

Crystallographic data for 1-5

‡ *Crystal data* for **1**: $C_{102}H_{116}N_{12}O_{22}Tb_4$, triclinic, space group $P\bar{1}$, a = 13.537(5), b = 14.101(6), c = 15.774(5) Å, α = 69.305(5)°, β = 78.510(6)°, γ = 63.050(5)°, V = 2508.1(1) Å^3, Z = 1, Dc = 1.654 g cm^{-3}, μ(Mo-Kα) = 2.862 mm^{-1}, F(000) = 1240, T = 153 K. R_1 = 0.0429, wR_2 = 0.1072 for 8772 independent reflections with a goodness-of-fit of 1.070. For **2**: $C_{50}H_{52}N_8O_{14}Tb_2$, monoclinic, space group P2(1)/c, a = 12.267(3), b = 10.542(2), c = 20.449(4) Å, β = 103.33(3)°, V = 2573.1(9) Å^3, Z = 2, Dc = 1.687 g cm^{-3}, μ(Mo-Kα) = 2.800 mm^{-1}, F(000) = 1300, T = 153 K. R_1 = 0.0320, wR_2 = 0.0797 for 4448 independent reflections with a goodness-of-fit of 1.046. For **3**: $C_{50}H_{52}Cl_2N_6O_8Tb_2$, monoclinic, space group P2(1)/c, a = 13.122(3), b = 10.038(2), c = 19.478(4) Å, β = 103.71(3)°, V = 2492.6 (9) Å^3, Z = 2, Dc = 1.670 g cm^{-3}, μ(Mo-Kα) = 2.980 mm^{-1}, F(000) = 1244, T = 153 K. R_1 = 0.0274, wR_2 = 0.0670 for 4399 independent reflections with a goodness-of-fit of 1.160. For **4**: $C_{50}H_{52}Cl_2N_6O_8Nd_2$, monoclinic, space group P2(1)/c, a = 13.124(3), b = 10.173(2), c = 19.757(4) Å, β = 104.76(3)°, V = 2550.7 (9) Å^3, Z = 2, Dc = 1.594 g cm^{-3}, μ(Mo-Kα) = 2.175 mm^{-1}, F(000) = 1224, T = 153 K. R_1 = 0.0272, wR_2 = 0.0608 for 4493 independent reflections with a goodness-of-fit of 1.057. For **5**: $C_{50}H_{52}Cl_2N_6O_8Yb_2$, monoclinic, space group P2(1)/c, a = 13.104(3), b = 10.018(2), c = 19.463(4) Å, β = 103.51(3)°, V = 2484.3 (9) Å^3, Z = 2, Dc = 1.714 g cm^{-3}, μ(Mo-Kα) = 3.908 mm^{-1}, F(000) = 1264, T = 153 K. R_1 = 0.0285, wR_2 = 0.0712 for 4354 independent reflections with a goodness-of-fit of 1.079. All data were collected on a Nonius Kappa CCD diffractometer and structures solved using the program SHELXL-97.. All data were collected on a Nonius Kappa CCD diffractometer and structures solved using the program SHELXL-97. CCDC reference numbers 680102 - 680106. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format.

Table 1. Bond Lengths (Å) and Angles (°) for **1**.

Tb(1)-O(2)	2.260(6)	O(1)-Tb(1)-N(2)	118.9(2)
Tb(1)-O(4)	2.267(6)	O(3)-Tb(1)-N(2)	77.2(2)
Tb(1)-O(1)	2.387(5)	N(1)-Tb(1)-N(2)	67.1(2)
Tb(1)-O(3)	2.394(5)	N(4)-Tb(1)-N(2)	159.9(2)
Tb(1)-N(1)	2.519(6)	O(2)-Tb(1)-N(3)	73.1(2)
Tb(1)-N(4)	2.520(7)	O(4)-Tb(1)-N(3)	124.3(2)
Tb(1)-N(2)	2.539(7)	O(1)-Tb(1)-N(3)	86.6(2)
Tb(1)-N(3)	2.551(7)	O(3)-Tb(1)-N(3)	69.3(2)
Tb(2)-O(5)	2.211(5)	N(1)-Tb(1)-N(3)	155.2(2)
Tb(2)-O(1)	2.330(6)	N(4)-Tb(1)-N(3)	66.1(2)
Tb(2)-O(6)	2.336(5)	N(2)-Tb(1)-N(3)	126.1(2)
Tb(2)-O(3)	2.343(5)	O(5)-Tb(2)-O(1)	81.45(19)
Tb(2)-O(6)#1	2.372(5)	O(5)-Tb(2)-O(6)	138.68(19)
Tb(2)-N(6)	2.492(7)	O(1)-Tb(2)-O(6)	85.55(19)
Tb(2)-N(5)	2.522(7)	O(5)-Tb(2)-O(3)	109.34(19)
O(2)-Tb(1)-O(4)	79.8(2)	O(1)-Tb(2)-O(3)	70.44(18)
O(2)-Tb(1)-O(1)	159.2(2)	O(6)-Tb(2)-O(3)	102.74(18)
O(4)-Tb(1)-O(1)	116.5(2)	O(5)-Tb(2)-O(6)#1	82.87(18)
O(2)-Tb(1)-O(3)	99.2(2)	O(1)-Tb(2)-O(6)#1	118.63(19)
O(4)-Tb(1)-O(3)	164.41(19)	O(6)-Tb(2)-O(6)#1	69.5(2)
O(1)-Tb(1)-O(3)	68.63(18)	O(3)-Tb(2)-O(6)#1	166.40(18)
O(2)-Tb(1)-N(1)	130.9(2)	O(5)-Tb(2)-N(6)	138.2(2)
O(4)-Tb(1)-N(1)	72.7(2)	O(1)-Tb(2)-N(6)	137.8(2)
O(1)-Tb(1)-N(1)	68.9(2)	O(6)-Tb(2)-N(6)	71.6(2)
O(3)-Tb(1)-N(1)	97.2(2)	O(3)-Tb(2)-N(6)	80.4(2)
O(2)-Tb(1)-N(4)	100.2(2)	O(6)#1-Tb(2)-N(6)	86.5(2)
O(4)-Tb(1)-N(4)	72.4(2)	O(5)-Tb(2)-N(5)	73.1(2)
O(1)-Tb(1)-N(4)	74.8(2)	O(1)-Tb(2)-N(5)	136.0(2)
O(3)-Tb(1)-N(4)	122.8(2)	O(6)-Tb(2)-N(5)	136.4(2)
N(1)-Tb(1)-N(4)	108.8(2)	O(3)-Tb(2)-N(5)	84.7(2)
O(2)-Tb(1)-N(2)	72.1(2)	O(6)#1-Tb(2)-N(5)	93.5(2)
O(4)-Tb(1)-N(2)	87.8(2)	N(6)-Tb(2)-N(5)	67.4(2)

Table 2. Bond Lengths (Å) and Angles (°) for **2**.

Tb(1)-O(1)	2.165(3)	O(1)-Tb(1)-O(3)	116.76(13)
Tb(1)-O(2)	2.190(3)	O(2)-Tb(1)-O(3)	80.50(13)
Tb(1)-O(1')	2.201(4)	O(1')-Tb(1)-O(3)	144.85(13)
Tb(1)-O(6)	2.360(3)	O(6)-Tb(1)-O(3)	118.69(12)
Tb(1)-N(1)	2.435(5)	N(1)-Tb(1)-O(3)	78.80(14)
Tb(1)-O(3)	2.450(4)	O(1)-Tb(1)-O(4)	80.56(14)
Tb(1)-O(4)	2.496(4)	O(2)-Tb(1)-O(4)	89.40(14)
Tb(1)-N(2)	2.502(4)	O(1')-Tb(1)-O(4)	161.47(14)
O(1)-Tb(1)-O(2)	144.77(13)	O(6)-Tb(1)-O(4)	75.42(12)
O(1)-Tb(1)-O(1')	92.15(14)	N(1)-Tb(1)-O(4)	102.42(14)
O(2)-Tb(1)-O(1')	86.84(14)	O(3)-Tb(1)-O(4)	51.57(12)
O(1)-Tb(1)-O(6)	75.46(13)	O(1)-Tb(1)-N(2)	140.33(15)
O(2)-Tb(1)-O(6)	69.33(12)	O(2)-Tb(1)-N(2)	73.37(15)
O(1')-Tb(1)-O(6)	86.28(13)	O(1')-Tb(1)-N(2)	76.25(14)
O(1)-Tb(1)-N(1)	73.82(14)	O(6)-Tb(1)-N(2)	139.46(13)
O(2)-Tb(1)-N(1)	141.40(14)	N(1)-Tb(1)-N(2)	68.86(15)
O(1')-Tb(1)-N(1)	91.72(14)	O(3)-Tb(1)-N(2)	68.73(14)
O(6)-Tb(1)-N(1)	149.11(14)	O(4)-Tb(1)-N(2)	119.90(14)

Table 3. Bond Lengths (Å) and Angles (°) for **3**.

Tb(1)-O(1)	2.191(4)	O(1')-Tb(1)-O(3)	95.42(13)
Tb(1)-O(1')	2.207(3)	O(2)-Tb(1)-O(3)	71.07(12)
Tb(1)-O(2)	2.237(3)	O(1)-Tb(1)-N(1)	73.47(14)
Tb(1)-O(3)	2.359(3)	O(1')-Tb(1)-N(1)	96.05(13)
Tb(1)-N(1)	2.467(4)	O(2)-Tb(1)-N(1)	142.55(13)
Tb(1)-N(2)	2.482(4)	O(3)-Tb(1)-N(1)	145.80(13)
Tb(1)-Cl(1)	2.6518(13)	O(1)-Tb(1)-N(2)	138.64(13)
O(1)-Tb(1)-O(1')	87.87(13)	O(1')-Tb(1)-N(2)	80.32(13)
O(1)-Tb(1)-O(2)	143.23(13)	O(2)-Tb(1)-N(2)	74.19(12)
O(1')-Tb(1)-O(2)	81.95(13)	O(3)-Tb(1)-N(2)	145.25(12)
O(1)-Tb(1)-O(3)	74.89(12)	N(1)-Tb(1)-N(2)	68.65(13)

Table 4. Bond Lengths (Å) and Angles (°) for **4**.

Nd(1)-O(1)	2.274(3)	O(2)-Nd(1)-O(3)	74.85(9)
Nd(1)-O(2)	2.311(3)	O(1')-Nd(1)-O(3)	96.33(9)
Nd(1)-O(1')	2.317(2)	O(1)-Nd(1)-N(1)	70.81(9)
Nd(1)-O(3)	2.484(3)	O(2)-Nd(1)-N(1)	138.05(9)
Nd(1)-N(1)	2.578(3)	O(1')-Nd(1)-N(1)	93.82(9)
Nd(1)-N(2)	2.594(3)	O(3)-Nd(1)-N(1)	146.89(9)
Nd(1)-Cl(1)	2.7681(10)	O(1)-Nd(1)-N(2)	134.44(9)
O(1)-Nd(1)-O(2)	149.42(9)	O(2)-Nd(1)-N(2)	71.60(9)
O(1)-Nd(1)-O(1')	88.72(9)	O(1')-Nd(1)-N(2)	79.02(9)
O(2)-Nd(1)-O(1')	80.62(9)	O(3)-Nd(1)-N(2)	146.45(9)
O(1)-Nd(1)-O(3)	77.99(9)	N(1)-Nd(1)-N(2)	66.53(10)

Table 5. Bond Lengths (Å) and Angles (°) for **5**.

Yb(1)-O(2)	2.163(3)	O(1')-Yb(1)-O(3)	95.03(12)
Yb(1)-O(1')	2.193(3)	O(1)-Yb(1)-O(3)	70.64(11)
Yb(1)-O(1)	2.206(3)	O(2)-Yb(1)-N(2)	73.59(12)
Yb(1)-O(3)	2.341(3)	O(1')-Yb(1)-N(2)	96.66(12)
Yb(1)-N(2)	2.451(3)	O(1)-Yb(1)-N(2)	142.99(12)
Yb(1)-N(1)	2.466(3)	O(3)-Yb(1)-N(2)	145.64(12)
Yb(1)-Cl(1)	2.6354(12)	O(2)-Yb(1)-N(1)	138.98(12)
O(2)-Yb(1)-O(1')	87.71(13)	O(1')-Yb(1)-N(1)	80.65(12)
O(2)-Yb(1)-O(1)	142.88(12)	O(1)-Yb(1)-N(1)	74.42(12)
O(1')-Yb(1)-O(1)	82.46(12)	O(3)-Yb(1)-N(1)	145.06(11)
O(2)-Yb(1)-O(3)	74.73(11)	N(2)-Yb(1)-N(1)	68.97(12)