

# Supplementary Information

## Synthesis, Structures, Thermal Decomposition Mechanism, and Luminescence Properties of Sm(III), Pr(III), Nd(III), and La(III) Complexes with Diverse Carboxylate Coordination Modes

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**Table S1** Crystallographic data for complexes **1-4**

Complex	1	2	3	4
Empirical formula	C <sub>72</sub> H <sub>68</sub> N <sub>4</sub> O <sub>13</sub> Sm <sub>2</sub>	C <sub>72</sub> H <sub>68</sub> N <sub>4</sub> O <sub>13</sub> Pr <sub>2</sub>	C <sub>72</sub> H <sub>68</sub> N <sub>4</sub> O <sub>13</sub> Nd <sub>2</sub>	C <sub>88</sub> H <sub>82</sub> N <sub>4</sub> O <sub>16</sub> La <sub>2</sub>
Formula weight	1498.00	1479.12	1485.78	1729.39
Temperature	293 (2) K	293 (2) K	293(2)K	293(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic	monoclinic
Space group	P-1	P-1	P-1	P2 <sub>1</sub> /n
Unit cell dimensions				
a(Å)	10.678(3) Å	10.739(3) Å	10.7209(10) Å	14.5700(15) Å
b (Å)	12.640(3) Å	12.608(4) Å	12.6673(12) Å	14.7415(16) Å
c (Å)	12.648(3) Å	12.675(4) Å	12.6770(13) Å	18.4795(18) Å
α (°)	89.183(9)°	89.093(10)°	88.981(4)°	90°
β (°)	66.989(8)°	67.669(10)°	67.262(3)°	89.995(4)°
γ (°)	82.021(8)°	81.574(11)°	81.700(3)°	90°
Volume	1554.6(7) Å <sup>3</sup>	1568.9(8) Å <sup>3</sup>	1569.8(3) Å <sup>3</sup>	3969.1(7) Å <sup>3</sup>
Z, Density (calculated)	1, 1.600Mg/m <sup>3</sup>	1, 1.566 Mg/m <sup>3</sup>	1,1.572 Mg/m <sup>3</sup>	2,1.447 Mg/m <sup>3</sup>
Absorption coefficient	1.941 mm <sup>-1</sup>	1.604 mm <sup>-1</sup>	1.705 mm <sup>-1</sup>	1.132 mm <sup>-1</sup>
F(000)	756.0	750	752	1760
Crystal size(mm <sup>3</sup> )	0.18 × 0.09 × 0.03	0.15 × 0.05 × 0.03	0.22 × 0.12 × 0.06	0.17 × 0.1 × 0.08
Theta range for data collection	5.644 to 50.05°	5.66 to 50.694°	5.65 to 52.742°	5.204 to 51.864°
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-17 ≤ h ≤ 17, -17 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected	22658	20464	24845	60189
Independent reflections	5467 (R <sub>(int)</sub> = 0.1204)	5720 (R <sub>(int)</sub> = 0.0920)	6409 (R <sub>(int)</sub> = 0.0464)	7653 (R <sub>(int)</sub> = 0.0699)
Completeness to theta = 25.05°	99.7 %	99.6 %	99.7%	98.9%
Max. and min. transmission	0.745 and 0.543	0.743 and 0.625	0.746 and 0.580	0.745 and 0.625
Data / restraints / parameters	5467/0/421	5720/0/420	6409/0/420	7653/0/514

Goodness-of-fit on F2	1.064	1.157	1.088	1.103
Final R indices (I>2sigma(I))	$R_I = 0.0780,$ $wR_2 = 0.1648$	$R_I = 0.0691,$ $wR_2 = 0.1237$	$R_I = 0.0451$ $wR_2 = 0.0987$	$R_I = 0.0575,$ $wR_2 = 0.1116$
R indices (all data)	$R_I = 0.1086,$ $wR_2 = 0.1864$	$R_I = 0.0933,$ $wR_2 = 0.1366$	$R_I = 0.0515,$ $wR_2 = 0.1033$	$R_I = 0.0777,$ $wR_2 = 0.1235$
Largest diff. peak and hole	2.24 and -2.11 e.Å <sup>-3</sup>	1.61 and -1.34 e.Å <sup>-3</sup>	1.47 and -1.68 e.Å <sup>-3</sup>	2.20 and -1.26 e.Å <sup>-3</sup>

**Table S2** Main bond lengths of complexes 1-4

complex1			
Sm(1)O(4)1	2.375(7)	O(5)Sm(1)N(2)	84.9(2)
Sm(1)O(5) <sup>1</sup>	2.798(7)	O(5)Sm(1)N(1)	143.9(3)
Sm(1)O(5)	2.380(7)	O(5)1Sm(1)C(9)	25.4(2)
Sm(1)O(3)	2.365(7)	O(5)Sm(1)C(9)	103.4(3)
Sm(1)O(6)1	2.413(7)	O(5)1Sm(1)C(1)	134.4(3)
Sm(1)O(1)	2.567(7)	O(5)Sm(1)C(1)	108.1(3)
Sm(1)O(2)	2.436(8)	O(3)Sm(1)Sm(1)1	68.02(17)
Sm(1)N(2)	2.614(9)	O(3)Sm(1)O(4)1	133.3(2)
Sm(1)N(1)	2.623(9)	O(3)Sm(1)O(5)	80.1(2)
O(4)1-Sm(1)-Sm(1)1	66.43(16)	O(3)Sm(1)O(5)1	66.8(2)
O(4)1Sm(1)O(5)	73.7(2)	O(3)Sm(1)O(6)1	82.2(2)
O(4)1Sm(1)O(5)1	70.3(2)	O(3)Sm(1)O(1)	146.6(2)
O(4)1Sm(1)O(6)1	84.0(2)	O(3)Sm(1)O(2)	142.1(2)
O(4)1Sm(1)O(1)	73.6(2)	O(3)Sm(1)N(2)	72.4(2)
O(4)1Sm(1)O(2)	73.9(2)	O(3)Sm(1)N(1)	77.3(3)
O(4)1Sm(1)N(2)	140.2(2)	O(3)Sm(1)C(9)1	70.2(3)
O(4)1Sm(1)N(1)	141.1(2)	O(3)Sm(1)C(1)	157.8(3)
O(4)1Sm(1)C(9)1	79.0(3)	O(6)1Sm(1)Sm(1)1	84.72(17)
O(4)1Sm(1)C(1)	68.7(3)	O(6)1Sm(1)O(5)1	49.5(2)
O(5)Sm(1)Sm(1)1	42.77(17)	O(6)1Sm(1)O(1)	81.9(2)
O(5)1Sm(1)Sm(1)1	35.27(14)	O(6)1Sm(1)O(2)	132.8(2)
O(5)Sm(1)O(5)1	78.0(2)	O(6)1Sm(1)N(2)	134.6(3)
O(5)Sm(1)O(6)1	127.4(2)	O(6)1Sm(1)N(1)	76.8(3)
O(5)Sm(1)O(1)	132.3(2)	O(6)1Sm(1)C(9)1	24.5(2)
O(5)Sm(1)O(2)	85.8(3)	O(6)1Sm(1)C(1)	84.9(2)
complex2			
Pr(1)O(1)	2.601(5)	O(3)Pr(1)C(1)	134.50(18)
Pr(1)O(2)	2.479(5)	O(3)Pr(1)C(9)1	108.4(2)
Pr(1)O(3)	2.435(5)	O(3)1Pr(1)C(9)1	103.15(19)
Pr(1)O(3)1	2.790(5)	O(4)1Pr(1)Pr(1)1	25.53(17)
Pr(1)O(4)1	2.464(5)	O(4)1Pr(1)O(1)	85.47(11)

Pr (1)O(5)	2.389(5)	O(4)1Pr(1)O(2)	82.29(18)
Pr(1)O(6)1	2.421(5)	O(4)1Pr(1)O(3)1	132.60(18)
Pr (1)N(1)	2.692(6)	O(4)1Pr(1)N(1)	49.86(14)
Pr (1)N(2)	2.668(6)	O(4)1Pr(1)N(2)	76.79(18)
O(1)Pr(1)Pr(1)1	139.18(12)	O(4)1Pr(1)C(1)	133.94(18)
O(1)Pr(1)O(3)1	121.43(16)	O(4)1Pr(1)C(9)1	106.6(2)
O(1)Pr(1)N(1)	70.29(18)	O(5)Pr(1)Pr(1)1	24.58(18)
O(1)Pr(1)N(2)	97.70(18)	O(5)Pr(1)O(1)	68.42(12)
O(1)Pr(1)C(1)	25.7(2)	O(5)Pr(1)O(2)	146.88(17)
O(1)Pr(1)C(9)1	103.5(2)	O(5)Pr(1)O(3)	141.25(18)
O(2)Pr(1)Pr(1)1	120.78(13)	O(5)Pr(1)O(3)1	79.81(17)
O(2)Pr(1)O(1)	51.55(18)	O(5)Pr(1)O(4)1	67.47(16)
O(2)Pr(1)O(3)1	143.71(16)	O(5)Pr(1)O(6)1	82.97(18)
O(2)Pr(1)N(1)	94.41(19)	O(5)Pr(1)N(1)	133.38(17)
O(2)Pr(1)N(2)	70.90(18)	O(5)Pr(1)N(2)	77.54(18)
O(2)Pr(1)C(1)	26.2(2)	O(5)Pr(1)C(1)	72.27(18)
O(2)Pr(1)C(9)1	147.21(19)	O(5)Pr(1)C(9)1	157.15(19)
O(3)1Pr(1)Pr(1)1	35.68(9)	O(6)1Pr(1)Pr(1)1	71.51(19)
O(3)Pr(1)Pr(1)1	41.95(12)	O(6)1Pr(1)O(1)	65.98(12)
O(3)Pr(1)O(1)	132.04(17)	O(6)1Pr(1)O(2)	74.13(17)
O(3)Pr(1)O(2)	86.18(18)	O(6)1Pr(1)O(3)1	74.17(17)
O(3)Pr(1)O(3)1	77.63(17)	O(6)1Pr(1)O(3)	70.12(16)
O(3)Pr(1)O(4)1	127.35(16)	O(6)1Pr(1)O(4)1	73.03(16)
O(3)Pr(1)N(1)	144.13(17)	O(6)1Pr(1)N(1)	84.35(17)
O(3)Pr(1)N(2)	86.25(17)	O(6)1Pr(1)N(2)	141.47(17)
O(3)1Pr(1)C(1)	134.50(18)	O(6)1Pr(1)C(1)	140.28(18)

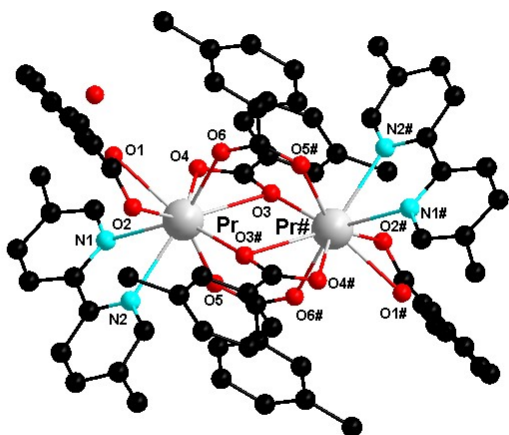
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**complex3**

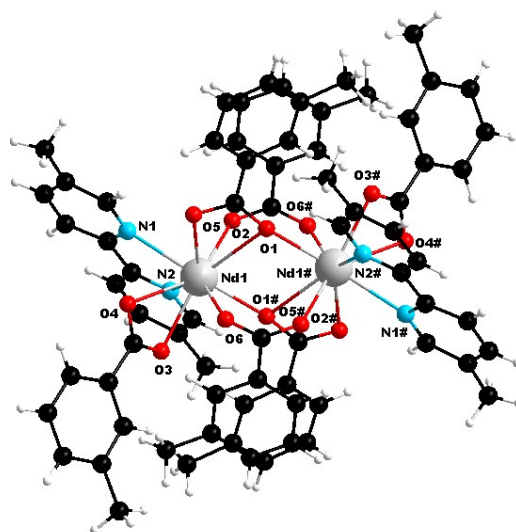
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Nd(1)O(1)1	2.785(3)	O(2) <sup>1</sup> Nd(1)O(4)	49.71(10)
Nd(1)O(1)	2.422(3)	O(2) <sup>1</sup> Nd(1)O(3)	82.12(12)
Nd(1)O(2)1	2.444(3)	O(2) <sup>1</sup> Nd(1)N(2)	132.33(11)
Nd(1)O(6)1	2.417(3)	O(2) <sup>1</sup> Nd(1)N(1)	134.33(12)
Nd(1)O(5)	2.399(3)	O(2) <sup>1</sup> Nd(1)C(1) <sup>1</sup>	76.48(11)
Nd(1)O(4)	2.590(4)	O(2) <sup>1</sup> Nd(1)C(9)	24.73(11)
Nd(1)O(3)	2.475(3)	O(6) <sup>1</sup> Nd(1)Nd(1) <sup>1</sup>	106.62(13)
Nd(1)N(2)	2.646(4)	O(6) <sup>1</sup> Nd(1)O(1) <sup>1</sup>	66.59(7)
Nd(1)N(1)	2.673(4)	O(6) <sup>1</sup> Nd(1)O(1)	70.65(10)
O(1) <sup>1</sup> Nd(1)Nd(1) <sup>1</sup>	35.77(6)	O(6) <sup>1</sup> Nd(1)O(2) <sup>1</sup>	73.51(11)
O(1)Nd(1)Nd(1) <sup>1</sup>	42.24(7)	O(6) <sup>1</sup> Nd(1)O(4)	84.41(11)
O(1)Nd(1)O(1) <sup>1</sup>	78.00(11)	O(6) <sup>1</sup> Nd(1)O(3)	73.72(11)
O(1)Nd(1)O(2) <sup>1</sup>	127.57(10)	O(6) <sup>1</sup> Nd(1)N(2)	73.74(11)
O(1)Nd(1)O(4)	132.18(11)	O(6) <sup>1</sup> Nd(1)N(1)	139.91(12)
O(1)Nd(1)O(3)	86.30(12)	O(6) <sup>1</sup> Nd(1)C(1) <sup>1</sup>	141.20(11)
O(1)Nd(1)N(2)	85.38(11)	O(6) <sup>1</sup> Nd(1)C(9)	79.05(12)
O(1)Nd(1)N(1)	143.97(11)	O(5)Nd(1)Nd(1) <sup>1</sup>	49.71(10)

O(1) <sup>1</sup> Nd(1)C(1) <sup>1</sup>	25.26(11)	O(5)Nd(1)O(1)1	68.65(12)
O(1)Nd(1)C(1) <sup>1</sup>	103.24(11)	O(5)Nd(1)O(1)	68.22(7)
O(1) <sup>1</sup> Nd(1)C(9)	134.59(11)	O(5)Nd(1)O(2)1	67.18(10)
O(1)Nd(1)C(9)	108.25(13)	O(5)Nd(1)O(6)1	79.93(11)
O(2) <sup>1</sup> Nd(1)Nd(1) <sup>1</sup>	85.41(7)	O(5)Nd(1)O(4)	82.69(11)
O(2) <sup>1</sup> Nd(1)O(1) <sup>1</sup>	35.77(6)	O(5)Nd(1)O(3)	133.73(11)
<hr/>			
complex4			
<hr/>			
La(1)O(5)	2.458(4)	O(7)La(1)N(1)	141.92(13)
La(1)O(5)1	2.767(4)	O(7)La(1)N(2)	135.43(13)
La(1)O(7)	2.508(4)	O(7)La(1)C(17)1	79.40(12)
La(1)O(3)	2.492(4)	O(3)La(1)La(1) <sup>1</sup>	72.15(13)
La(1)O(8)1	2.497(4)	O(3)La(1)O(5) <sup>1</sup>	115.88(9)
La(1)O(6)1	2.534(4)	O(3)La(1)O(7)	138.92(12)
La(1)O(1)	2.536(4)	O(3)La(1)O(8) <sup>1</sup>	72.91(12)
La(1)N(1)	2.722(4)	O(3)La(1)O(6) <sup>1</sup>	141.86(13)
La(1)N(2)	2.732(5)	O(3)La(1)O(1)	133.72(13)
O(5)La(1)La(1)1	40.74(9)	O(3)La(1)N(1)	72.41(13)
O(5)1La(1)La(1)1	35.43(7)	O(3)La(1)N(2)	104.20(13)
O(5)La(1)O(5)1	76.18(13)	O(3)La(1)C(17) <sup>1</sup>	69.75(13)
O(5)La(1)O(7)	77.47(12)	O(8) <sup>1</sup> La(1)La(1) <sup>1</sup>	142.80(14)
O(5)La(1)O(3)	83.24(12)	O(8) <sup>1</sup> La(1)O(5) <sup>1</sup>	66.67(8)
O(5)La(1)O(8)1	77.32(12)	O(8) <sup>1</sup> La(1)O(7)	66.78(12)
O(5)La(1)O(6)1	125.33(12)	O(8) <sup>1</sup> La(1)O(6) <sup>1</sup>	132.24(12)
O(5)La(1)O(1)	83.30(12)	O(8) <sup>1</sup> La(1)O(1)	83.73(13)
O(5)La(1)N(1)	147.09(13)	O(8) <sup>1</sup> La(1)N(1)	72.96(13)
O(5)La(1)N(2)	148.58(13)	O(8) <sup>1</sup> La(1)N(2)	77.62(13)
O(5)La(1)C(17)1	101.19(13)	O(8) <sup>1</sup> La(1)C(17) <sup>1</sup>	134.05(13)
O(5)1La(1)C(17)1	25.07(12)	O(6) <sup>1</sup> La(1)La(1) <sup>1</sup>	73.87(13)
O(7)La(1)La(1)1	67.69(8)	O(6) <sup>1</sup> La(1)O(5) <sup>1</sup>	84.66(8)
O(7)La(1)O(5)1	68.15(11)	O(6) <sup>1</sup> La(1)O(1)	49.29(11)
O(7)La(1)O(6)1	78.81(13)	O(6) <sup>1</sup> La(1)N(1)	138.15(13)

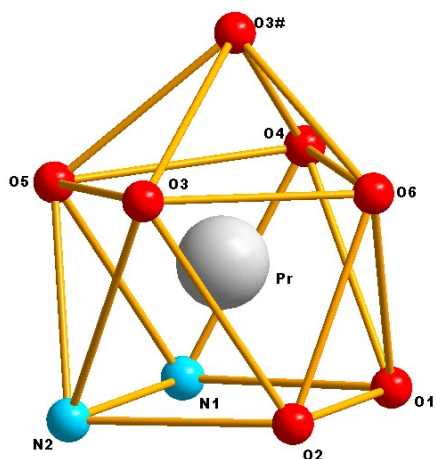


(a)

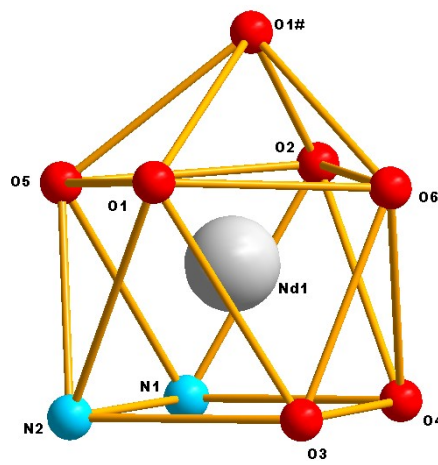


(b)

**Figure S1** Structural units of complex 2 (a) and complex 3 (b)

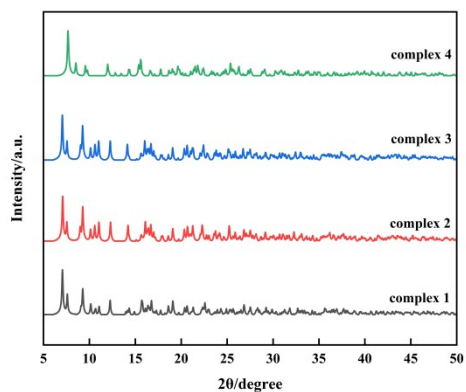


(a)

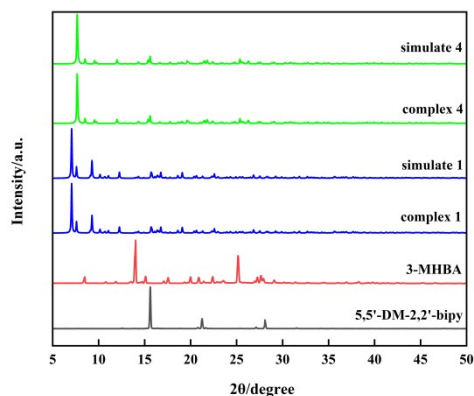


(b)

**Figure S2** Coordination environments of Pr(III) ion (a) and Nd(III) ion(b)

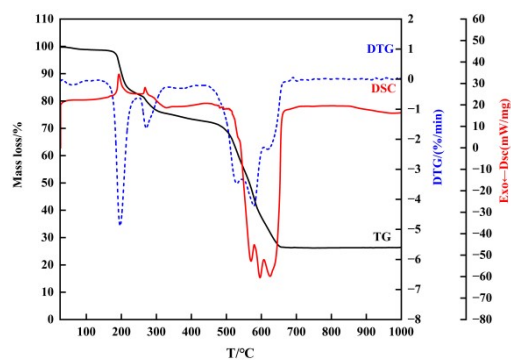


(a)

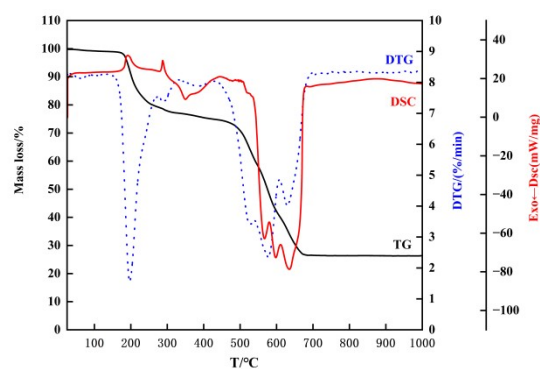


(b)

**Figure S3** (a) XRD patterns of complexes 1-4 (b) Experimental XRD patterns of complexes 1 and 4, simulated patterns from single-crystal data fitting, and XRD patterns of the ligands.

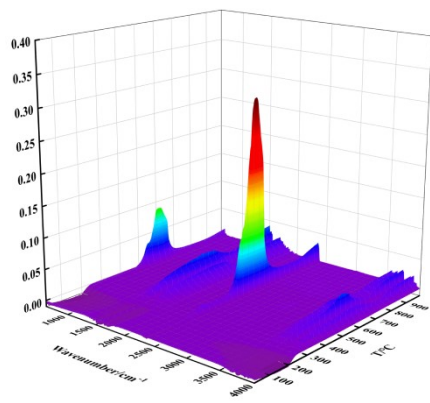


(a)

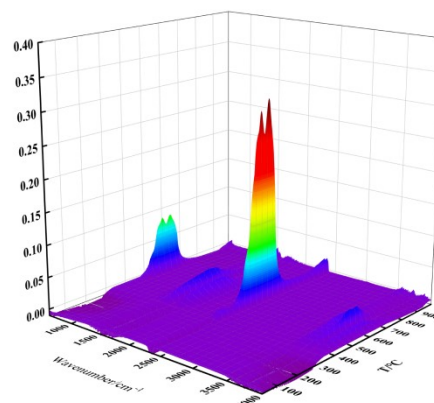


(b)

**Figure S4** TG-DTG/DSC curves of complex 2 (a) and complex 3 (b)

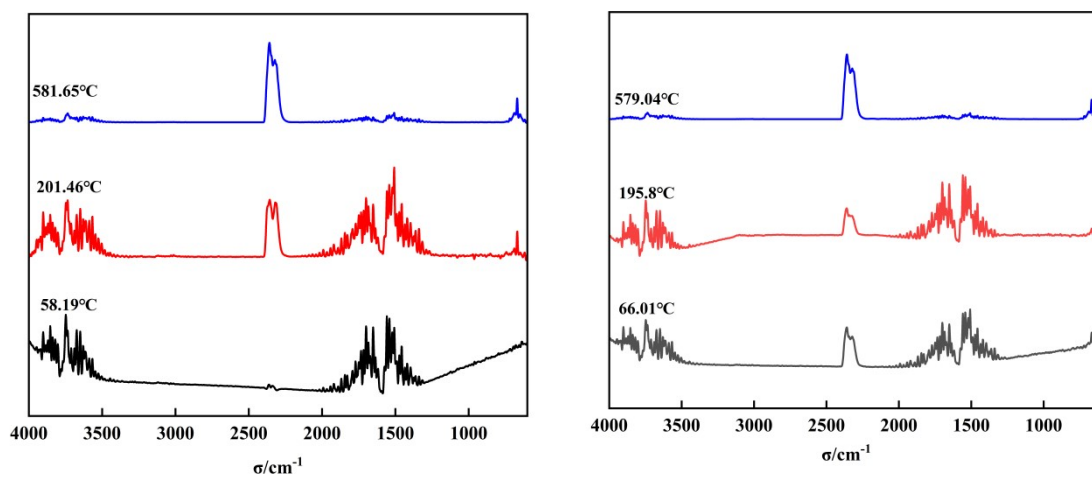


(a)



(b)

**Figure S5** 3D infrared spectra of evolved gases from complex **2** (a) and complex **3** (b)



(a)

(b)

**Figure S6** 2D infrared spectra of evolved gases from complex **2** (a) and complex **3** (b)