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Modulating the Ferroelectric Performance by Altering Halogen Anions in Crystals of Tetranuclear Copper–Clusters

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Contents

Table S1 Crystal data and structure refinement of complex **1** and **3**.

Table S2 Main bond lengths [Å] and angles [°] for complex **1** and **3.**

Table S3 Partial hydrogen bond data for complex **1** and **3**.

Fig. S1 The FT–IR spectra of complex **1**–**4**.

Fig. S2 [Cu_4O_4] boated–shape structure.

Fig. S3 The ORTEP of complex **1**

Fig. S4 The coordination mode of ligand L^{2-}.

Fig. S5 A chain structure of complex **1** in the direction of *a* axis.

Fig. S6 The ORTEP of complex **3**

Fig. S7 A zig−zag chain structure of complex **3** in the direction of *a* axis.

Fig. S8 The simulation and PXRD patterns for complex **1**–**4**.

Fig. S9 (a) TGA curves of complex **1** and **2**, (b) TGA curves complex **3** and **4**.

Fig. S10 Dielectric constant of complex **1** (a) and **3** (b) under different frequency in the temperature of 30−240℃.

Fig. S11 DSC curves of complex **1** (a) and **3** (b).

Fig. S12 Leakage curves of complex **1** (a) and **3** (b).

Table S1 Crystallographic data and structure refinement for complex **1** and complex **3**.

Name	Complex **1**	Complex **3**
Empirical formula	C_{70} H_{76} Cl_2 Cu_4 N_4 O_{14}	$C_{68.71}$ $H_{75.43}$ Br_2 Cu_4 N_4 O_{14}
Formula weight	1522.40	1595.25
Temperature/K	293.15	273.15
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
space group	*P2₁*	*P2₁*
a/Å	10.4998(19)	10.2904(5)
b/Å	25.108(5)	21.3262(9)
c/Å	15.766(3)	15.8441(7)
α/°	90	90
β/°	109.173(5)	93.987(2)
γ/°	90	90
Volume/Å^3	3925.8(13)	3468.7(3)
Z	2	2
ρ_{calc}mg/cm^3	1.288	1.527
Absorption coefficient/mm^{-1}	1.195	2.427
F(000)	1572	1627
Crystal size/ mm^3	0.06 × 0.05 × 0.03	0.09× 0.08 × 0.06
Theta range for data collection/°	2.736 to 25.200	2.75 to 25.50
Index ranges	−12<=h<=12 −30<=k<=30 −18<=l<=18	−12<=h<=12 −25<=k<=25 −19<=l<=19
Reflections collected	88529	86122
Independent reflections	13976 [R(int) = 0.0848]	12882 [R(int) = 0.0335]
Completeness to theta	99.4	99.8%
Absorption correction	Semi−empirical from equivalents	Semi−empirical from equivalents
Max. and min. transmission	0.7457 and 0.4291	0.7454 and 0.6234
Refinement method	Full−matrix least−squares on F^2	Full−matrix least−squares on F^2
Data/restraints /parameters	13976 / 565 / 832	12882 / 16 / 881
Goodness−of−fit on F^2	1.067	1.071
Final R indices [I>2sigma(I)]	R_1 = 0.1099, wR_2 = 0.2856	R_1 = 0.0307 wR_2 = 0.0681
R indices (all data)	R_1 = 0.1177, wR_2 = 0.2966	R_1 = 0.0408, wR_2 = 0.0723
Absolute structure parameter	0.250(9)	0.010(3)

Largest diff. peak/hole / e Å^{-3}	2.320 and −1.634	0.37 and −0.24

Table S2 Main bond lengths (Å) and angles (°) for complex **1** and complex **3**.

Bond lengths (Å)			
Complex **1**		Complex **3**	
Cu(1)−N(1)	1.90(2)	Cu(1)−N(4)	1.936(4)
Cu(1)−O(2)	1.956(14)	Cu(1)−O(6)	1.937(3)
Cu(1)−O(3)	1.987(18)	Cu(1)−O(8)	1.927(3)
Cu(1)−O(9)	1.935(17)	Cu(1)−O(9)	2.022(4)
Cu(1)−O(13)	2.260(19)	Cu(1)−O(14)	2.294(4)
Cu(2)−N(2)	1.913(18)	Cu(2)−N(3)	1.952(4)
Cu(2)−O(1)	2.400(18)	Cu(2)−O(8)	2.001(3)
Cu(2)−O(2)	1.942(13)	Cu(2)−O(11)	1.921(3)
Cu(2)−O(5)	1.920(15)	Cu(2)−O(12)	1.978(3)
Cu(2)−O(6)	2.011(17)	Cu(3)−N(2)	1.944(4)
Cu(3)−N(3)	1.910(18)	Cu(3)−O(1)	2.369(4)
Cu(3)−O(8)	1.954(14)	Cu(3)−O(2)	2.011(3)
Cu(3)−O(9)	2.014(17)	Cu(3)−O(5)	1.907(3)
Cu(3)−O(11)	1.993(15)	Cu(3)−O(6)	1.966(3)
Cu(4)−N(4)	1.82(3)	Cu(4)−N(1)	1.951(4)
Cu(4)−O(6)	1.907(16)	Cu(4)−O(2)	1.938(3)
Cu(4)−O(11)	1.922(15)	Cu(4)−O(3)	1.996(4)
Cu(4)−O(12)	1.989(19)	Cu(4)−O(12)	1.942(3)
Cu(4)−O(14)	2.248(18)	Cu(4)−O(13A)	2.34(5)
		Cu(4)−O(13B)	2.28(2)
Bond angles (°)			
Complex **1**		Complex **3**	
N(1)−Cu(1)−O(2)	94.2(8)	N(4)−Cu(1)−O(8)	92.34(15)
N(1)−Cu(1)−O(3)	82.0(9)	N(4)−Cu(1)−O(6)	164.41(14)
N(1)−Cu(1)−O(9)	163.1(7)	N(4)−Cu(1)−O(9)	82.85 (16)
N(1)−Cu(1)−O(13)	103.0(7)	N(4)−Cu(1)−O(14)	98.19 (15)
O(2)−Cu(1)−O(3)	176.2(7)	O(6)−Cu(1)−O(9)	97.13 (14)
O(2)−Cu(1)−O(13)	90.2(6)	O(6)−Cu(1)−O(14)	97.39(14)
O(3)−Cu(1)−O(13)	90.2(8)	O(8)−Cu(1)−O(6)	86.89(14)
O(9)−Cu(1)−O(13)	94.0(7)	O(8)−Cu(1)−O(9)	174.70(14)

O(9)−Cu(1)−O(2)	85.0(6)	O(8)−Cu(1)−O(14)	91.33(16)
O(9)−Cu(1)−O(3)	98.7(7)	O(9)−Cu(1)−O(14)	91.57(16)
N(2)−Cu(2)−O(1)	100.5(7)	N(3)−Cu(2)−O(8)	174.24 (16)
N(2)−Cu(2)−O(2)	171.4(7)	N(3)−Cu(2)−O(11)	92.34 (16)
N(2)−Cu(2)−O(5)	93.1(7)	N(3)−Cu(2)−O(12)	85.22(15)
N(2)−Cu(2)−O(6)	85.6(7)	O(11)−Cu(2)−O(8)	91.37 (14)
O(2)−Cu(2)−O(6)	88.7(6)	O(11)−Cu(2)−O(12)	173.67(16)
O(2)−Cu(2)−O(1)	73.3(6)	O(12)−Cu(2)−O(8)	91.54(14)
O(5)−Cu(2)−O(1)	93.6(7)	N(2)−Cu(3)−O(1)	101.11(16)
O(5)−Cu(2)−O(2)	93.3(6)	N(2)−Cu(3)−O(2)	172.74 (16)
O(5)−Cu(2)−O(6)	172.8(7)	N(2)−Cu(3)−O(5)	93.30(15)
O(6)−Cu(2)−O(1)	93.6(7)	N(2)−Cu(3)−O(6)	84.97(14)
N(3)−Cu(3)−O(8)	94.2(7)	O(2)−Cu(3)−O(1)	72.63(13)
N(3)−Cu(3)−O(9)	84.4(7)	O(5)−Cu(3)−O(1)	96.93(15)
N(3)−Cu(3)−O(11)	172.5(7)	O(5)−Cu(3)−O(2)	91.14(14)
O(8)−Cu(3)−O(9)	172.9(7)	O(5)−Cu(3)−O(6)	173.71(15)
O(8)−Cu(3)−O(11)	91.3(6)	O(6)−Cu(3)−O(1)	89.34 (13)
O(11)−Cu(3)−O(9)	90.8(6)	O(6)−Cu(3)−O(2)	91.21(13)
N(4)−Cu(4)−O(6)	160.6(10)	N(1)−Cu(4)−O(2)	91.68(17)
N(4)−Cu(4)−O(11)	92.3(8)	N(1)−Cu(4)−O(3)	82.35(19)
N(4)−Cu(4)−O(12)	83.1(9)	N(1)−Cu(4)−O(12)	167.20(15)
N(4)−Cu(4)−O(14)	103.0(9)	N(1)−Cu(4)−O(13A)	100.7(10)
O(6)−Cu(4)−O(11)	85.1(7)	N(1)−Cu(4)−O(13B)	95.3(5)
O(6)−Cu(4)−O(12)	98.7(8)	O(2)−Cu(4)−O(3)	171.46(16)
O(6)−Cu(4)−O(14)	96.2(7)	O(2)−Cu(4)−O(12)	86.43(14)
O(11)−Cu(4)−O(12)	175.1(8)	O(2)−Cu(4)−O(13A)	92.9(10)
O(11)−Cu(4)−O(14)	88.2(6)	O(2)−Cu(4)−O(13B)	94.7(6)
O(12)−Cu(4)−O(14)	94.5(8)	O(3)−Cu(4)−O(13A)	94.2(9)
		O(3)−Cu(4)−O(13B)	91.9(6)
		O(12)−Cu(4)−O(3)	98.03(17)
		O(12)−Cu(4)−O(13A)	92.0(10)
		O(12)−Cu(4)−O(13B)	97.5(5)

Table 3.3 Partial hydrogen bond data for complex **1** and complex **3**.

Complex **1**					
D	A	d(D−H)	d(H..A)	<DHA	d(D..A)

C8	Cl2	0.930	2.896	126.53	3.530
C59	Cl2	0.929	2.963	121.62	3.541
C60	Cl1	0.979	2.822	169.16	3.789
Complex **3**					
O3	Br4	0.863	2.139	166.58	2.985
C49	Br4	0.969	2.718	162.81	3.656
O14	Br2	0.911	2.675	148.06	3.481

D: Donor, A: Acceptor

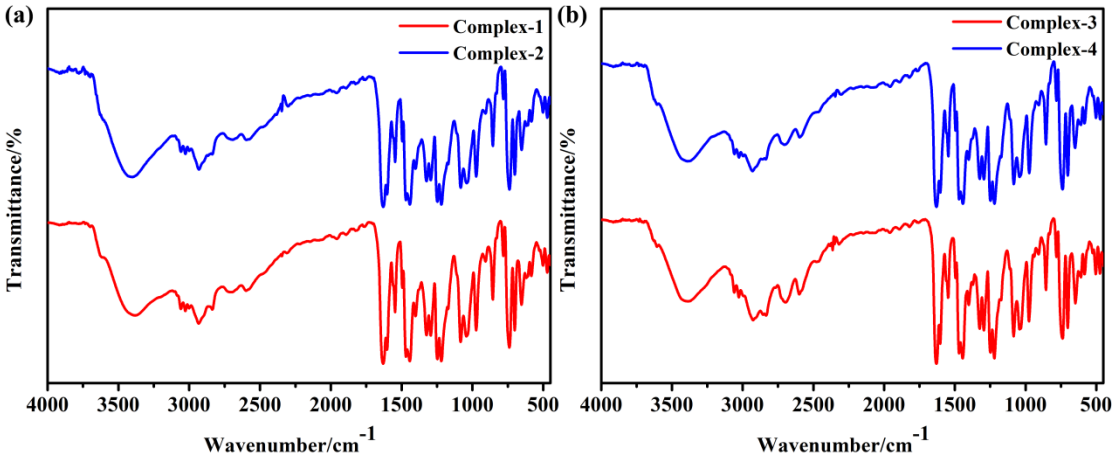

Fig. S1 The FT–IR spectra of complex **1**–**4**.

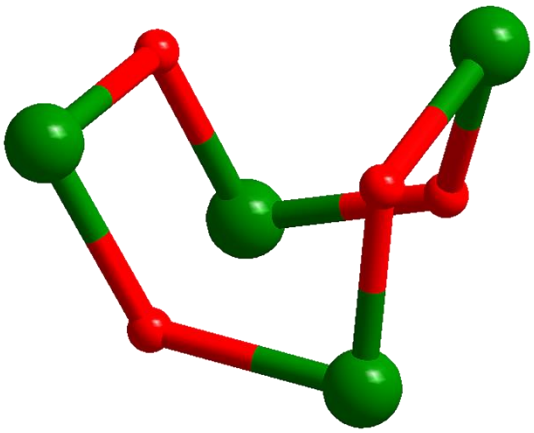

Fig. S2 [Cu_4O_4] boated–shape structure.

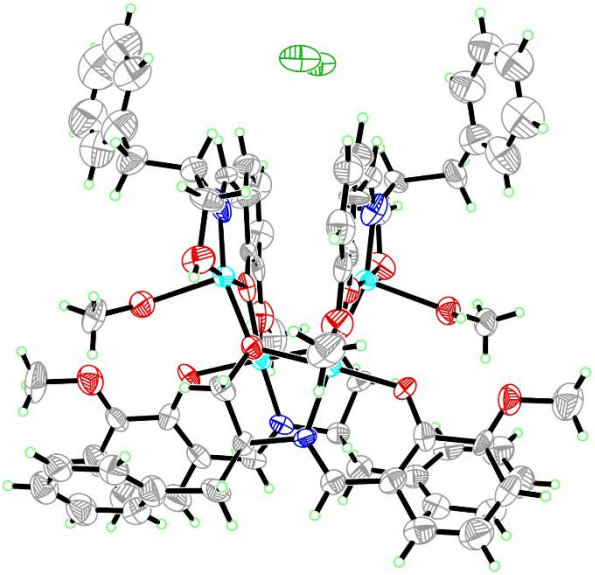

Fig. S3 The ORTEP of complex **1**.

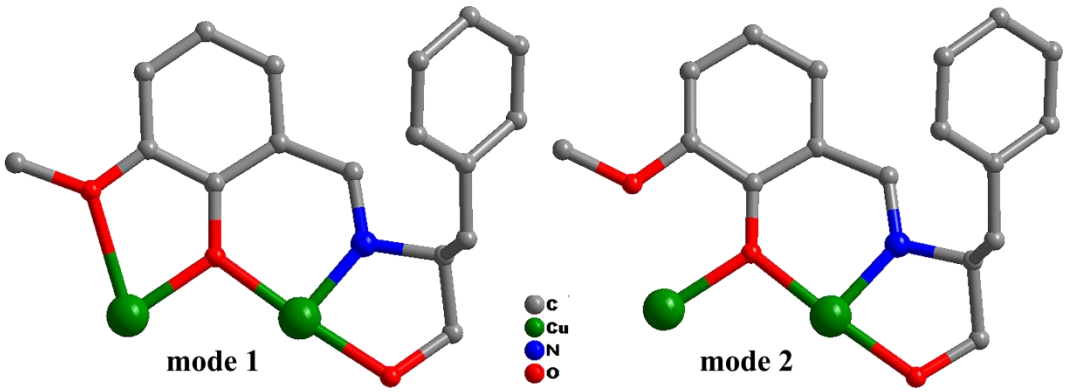

Fig. S4 The coordination mode of ligand L^{2-}.

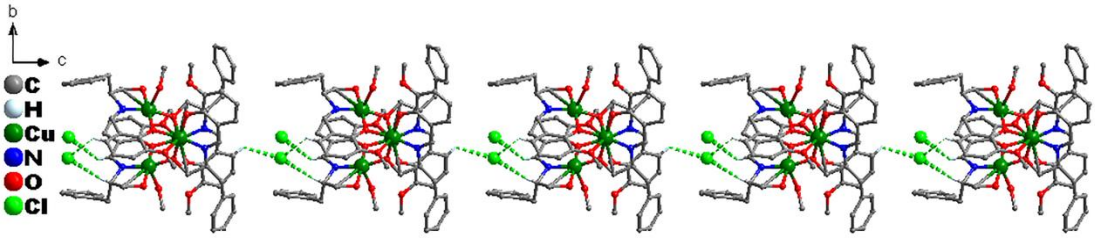

Fig. S5 A chain structure of complex **1** in the direction of *a* axis.

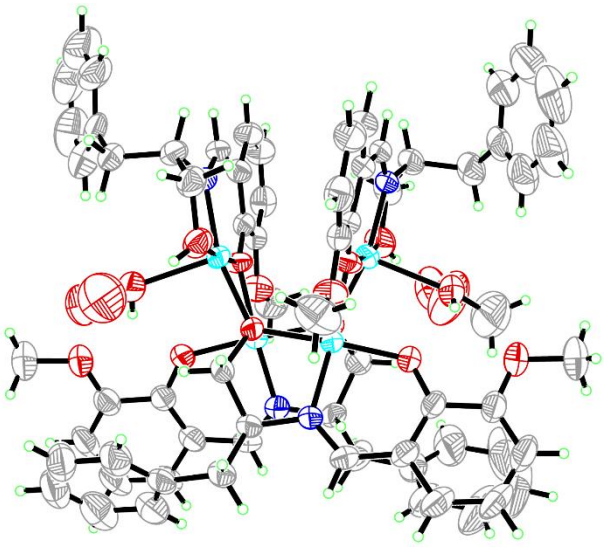

Fig. S6 The ORTEP of complex **3**.

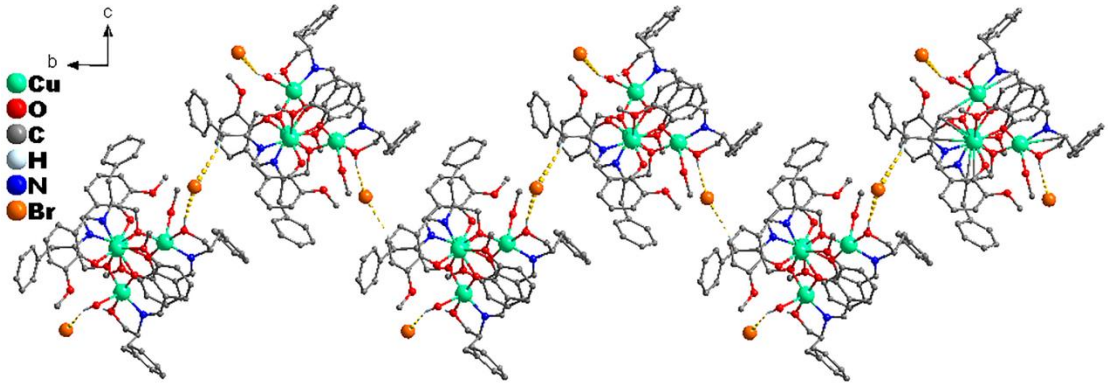

Fig. S7 A zig–zag chain structure of complex **3** in the direction of *a* axis.

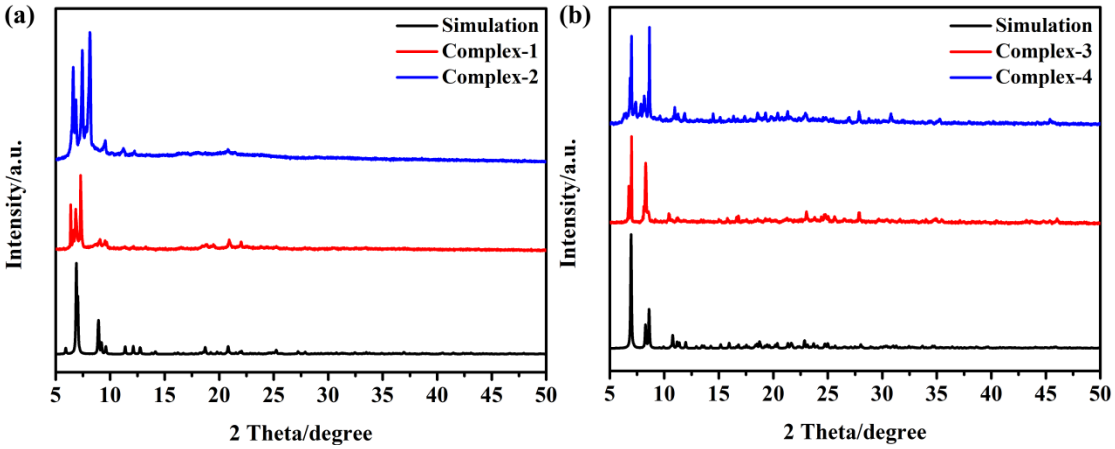

Fig. S8 The simulation and PXRD patterns for complex **1**–**4**.

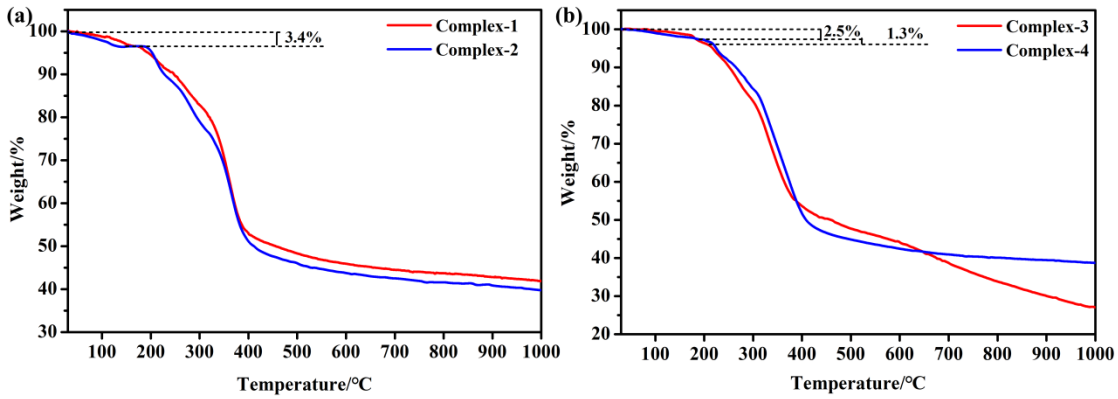

Fig. S9 (a) TGA curves of complex **1** and **2**, (b) TGA curves complex **3** and **4**.

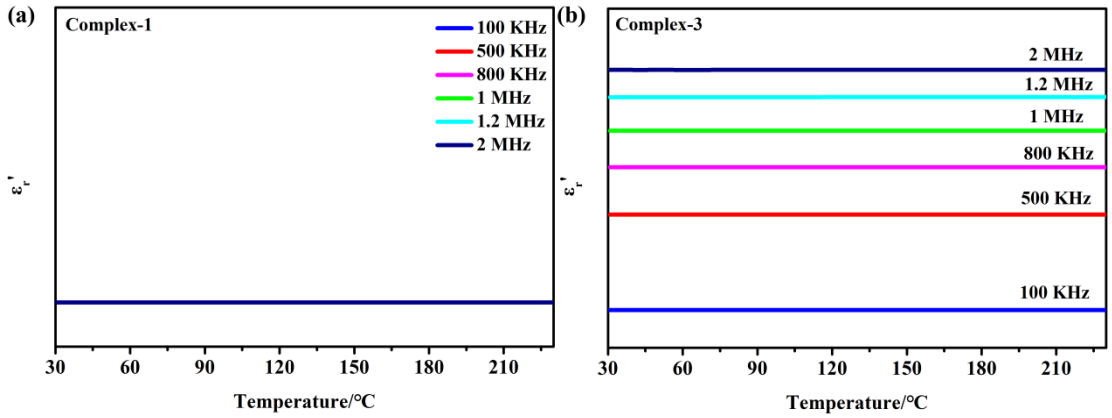

Fig. S10 Dielectric constant of complex **1** (a) and **3** (b) under different frequency in the temperature of 30−240°C.

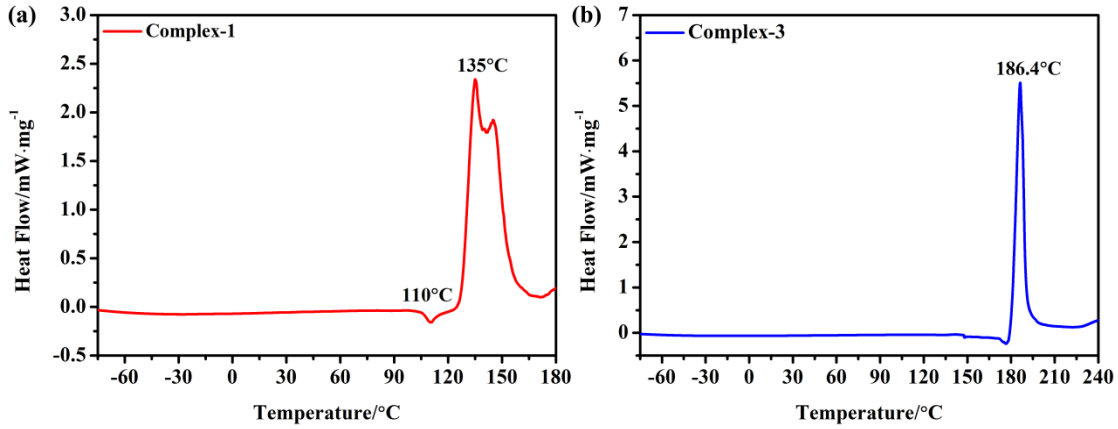

Fig. S11 DSC curves of complex **1** (a) and **3** (b).

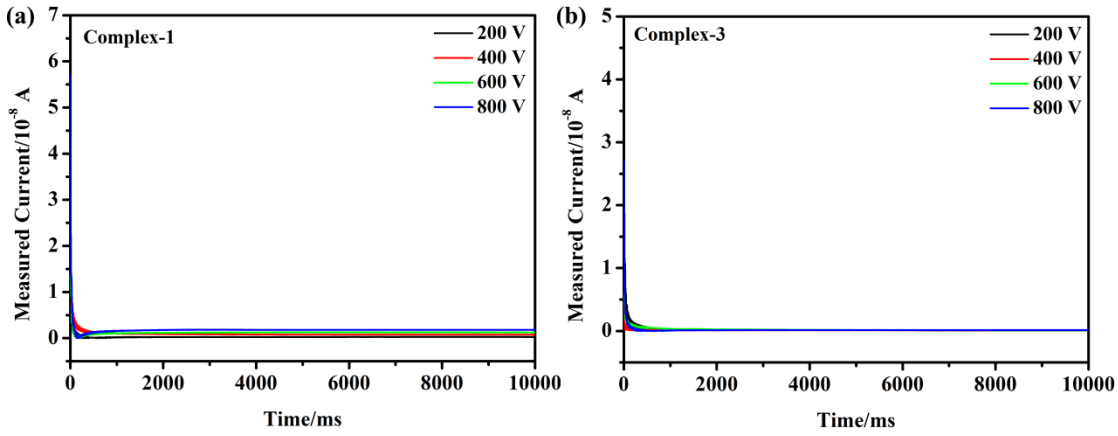

Fig. S12 Leakage curves of complex **1** (a) and **3** (b).