Supporting information:

Phase Transition Metal-Crown Ether Coordination Compounds Tuned by Metal ion

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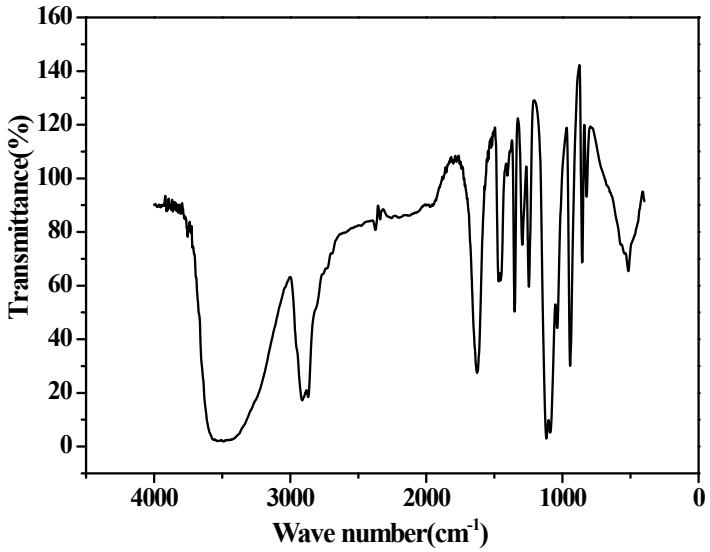


Figure S1 the IR spectrum of compound **1**, where the strong signal at 3500 cm-1 is due to the moisture of the KBr used for IR.

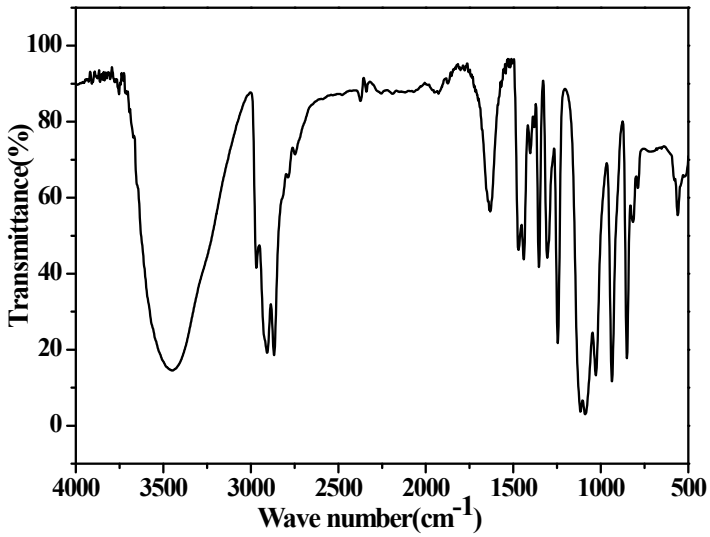


Figure S2 The IR spectrum of compound **2,** where the strong signal at 3500 cm-1 is due to the moisture of the KBr used for IR.

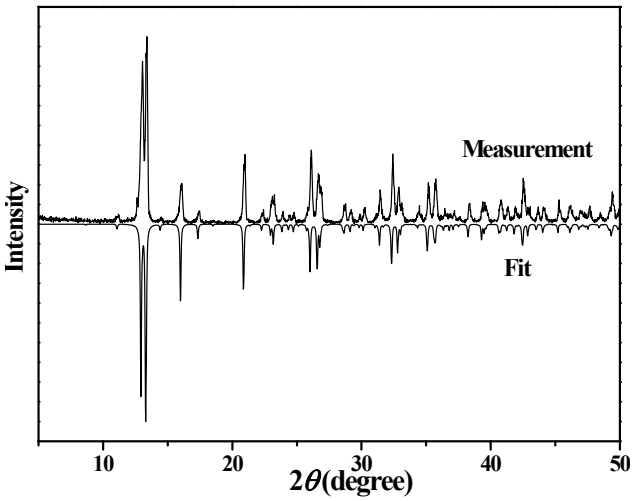


Figure S3 The powder XRD measurement result of compound **1**

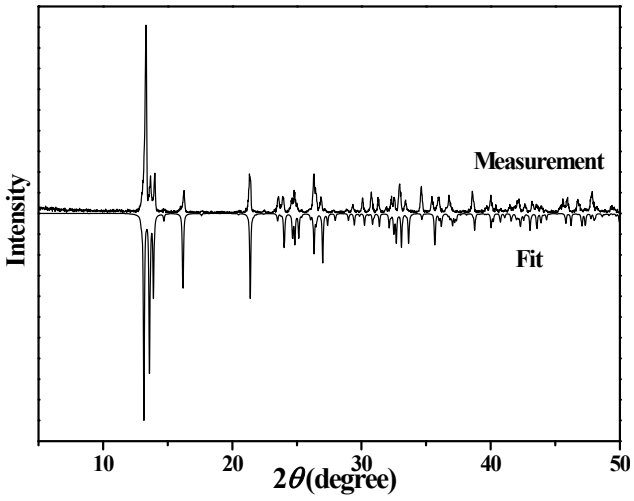


Figure S4 . The powder XRD measurement result of compound **2**

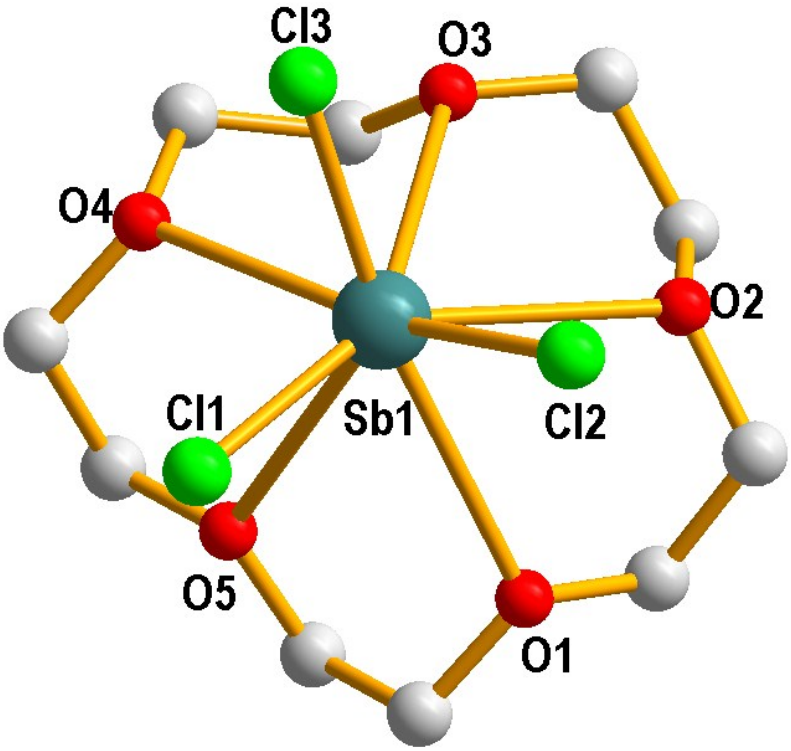


Figure S5 The molecular structure of compound **2**

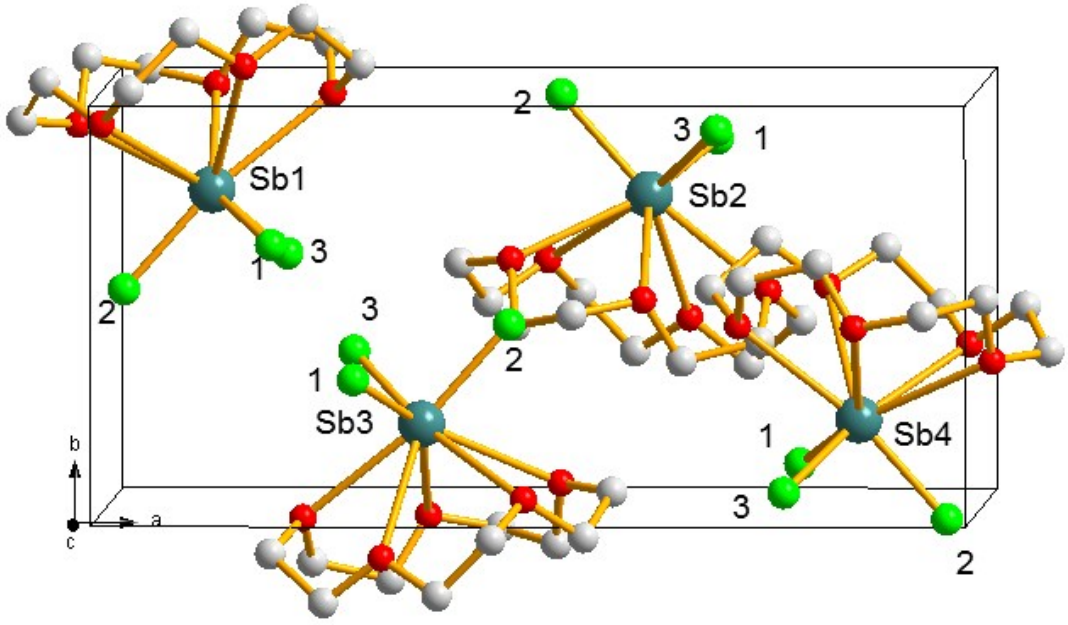


Figure S6 the cell packing view of compound **2** at 293K.

Table S1 The key bond distances and angels of compound **2** at 173 K, 273 K and 293 K

	173K	273K	293K
Sb1—Cl1	2.4078 (10)	2.4045 (12)	2.404(10)
Sb1—Cl2	2.4392 (9)	2.4334 (11)	2.429 (9)
Sb1—Cl3	2.4140 (9)	2.4118 (12)	2.409 (10)
Sb1—O1	2.9023 (18)	2.912 (3)	3.041(2)
Sb1—O2	2.943 (2)	2.941 (3)	2.831(1)
Sb1—O3	2.9387 (19)	2.960 (3)	2.958 (3)
Sb1—O4	2.807 (2)	2.829 (3)	2.937(2)
Sb1—O5	3.018 (2)	3.034 (3)	2.912(8)
Cl1—Sb1—Cl2	90.47 (3)	90.53 (4)	93.53 (4)
Cl1—Sb1—Cl3	93.37 (4)	93.48 (5)	90.61 (3)
Cl3—Sb1—Cl2	88.83 (3)	89.10 (4)	89.16 (4)
Cl1—Sb1—O1	90.15 (5)	90.75 (6)	78.25(2)
Cl1—Sb1—O2	147.24 (4)	147.56 (6)	89.10(1)
Cl1—Sb1—O3	149.85 (4)	149.44 (7)	167.37(1)
Cl1—Sb1—O4	88.94 (5)	89.20 (7)	132.75
Cl1—Sb1—O5	73.72 (5)	73.84 (6)	73.79 (5)
Cl2—Sb1—O1	82.63 (5)	82.94 (7)	134.98
Cl2—Sb1—O2	74.57 (5)	75.03 (6)	56.74(2)
Cl2—Sb1—O3	117.87 (4)	118.28 (7)	78.15(2)
Cl2—Sb1—O4	166.47 (4)	167.15 (6)	149.18(1)
Cl2—Sb1—O5	135.26 (4)	135.23 (6)	118.53(1)
Cl3—Sb1—O1	170.79 (4)	171.03 (6)	60.24(3)
Cl3—Sb1—O2	114.81 (5)	114.74 (6)	57.98(6)
Cl3—Sb1—O3	78.14(5)	78.06 (7)	170.96(1)
Cl3—Sb1—O4	77.72 (5)	78.09 (7)	90.92(5)
Cl3—Sb1—O5	132.66 (4)	132.54 (6)	82.91(4)
O1—Sb1—O2	59.56 (6)	59.17(8)	109.71(5)
O1—Sb1—O3	102.81 (6)	102.05 (8)	56.16(2)
O1—Sb1—O5	56.54 (5)	56.33 (8)	101.81
O2—Sb1—O5	96.38 (5)	58.06 (8)	59.14(3)
O3—Sb1—O2	58.27 (5)	95.96 (8)	118.53(2)
O3—Sb1—O5	90.75 (6)	90.24 (8)	60.23(8)
O4—Sb1—O1	110.88(6)	109.91 (9)	90.08(1)
O4—Sb1—O2	112.24 (6)	111.19 (9)	114.58(5)
O4—Sb1—O3	61.06(5)	60.41 (8)	147.76(2)
O4—Sb1—O5	57.18(5)	56.70 (8)	75.11(7)

Table S2 The Torsion angles of 15-crown-5 ether in compound 2 at 173 K, 273 K and 293 K

	173K	273 K	293 K
C1—C2—O2—C3	-79.1 (3)	-79.4 (4)	-79.4 (4)

C1—O1—C10—C9	-81.6(3)	-82.2 (4)	-82.1 (4)
C10—O1—C1—C2	178.5 (2)	178.5 (3)	178.5 (3)
C2—O2—C3—C4	-179.98 (19)	179.8 (3)	179.5 (3)
C4—O3—C5—C6	-169.3 (2)	-170.7 (3)	-170.2 (3)
C5—O3—C4—C3	-76.8 (3)	-78.1 (4)	-78.8 (4)
C6—O4—C7—C8	76.3 (3)	76.7 (5)	77.7 (4)
C7—O4—C6—C5	-109.4 (3)	-110.1 (4)	-110.4 (4)
C8—O5—C9—C10	-175.0 (2)	-175.6 (3)	-176.0 (3)
C9—O5—C8—C7	178.2 (2)	178.7 (3)	179.7 (3)
O1—C10—C9—O5	-58.9 (3)	-59.1 (4)	-59.3 (4)
O2—C2—C1—O1	-64.9 (3)	-64.8 (4)	-65.3 (4)
O3—C5—C6—O4	-66.9 (3)	-66.0 (5)	-65.4 (5)
O3—C4—C3—O2	-62.0 (3)	-61.0(5)	-61.2 (4)
O4—C7—C8—O5	59.4 (3)	59.8 (5)	59.3 (4)

Table S3 The average bond distances of compound **1** and **2**

	173K	293K	373K		173K	273K	293K
Bi—Cl	2.5407	2.535	2.5307	Sb—Cl	2.4203	2.4166	2.414
Bi—O	2.8414	2.8446	2.854	Sb—O	2.9218	2.9352	2.9358

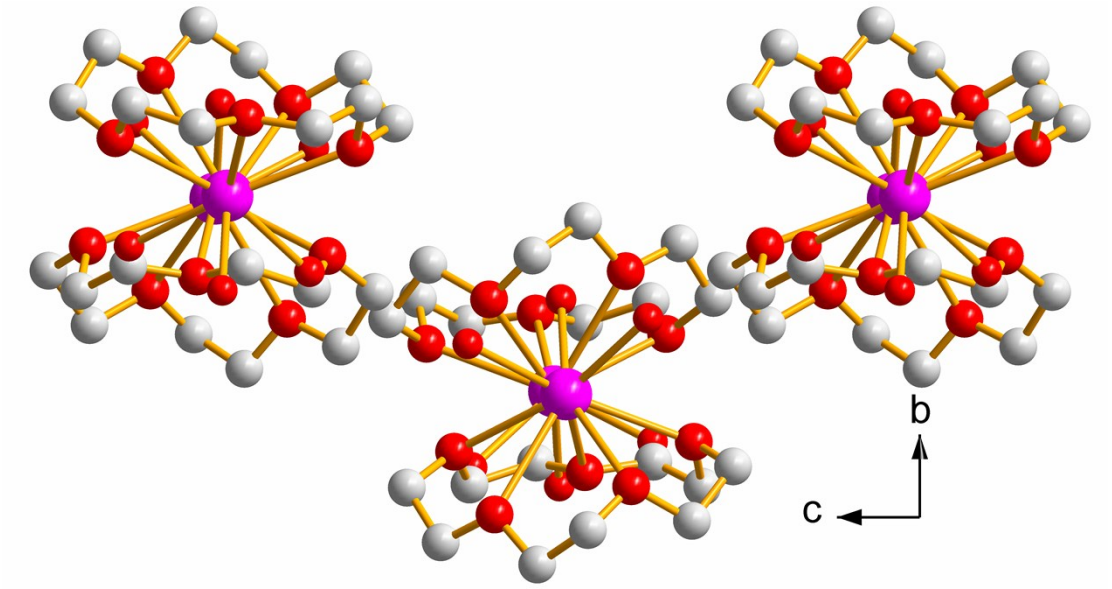


Figure S7 the packing view of compound **1** along *a* axis

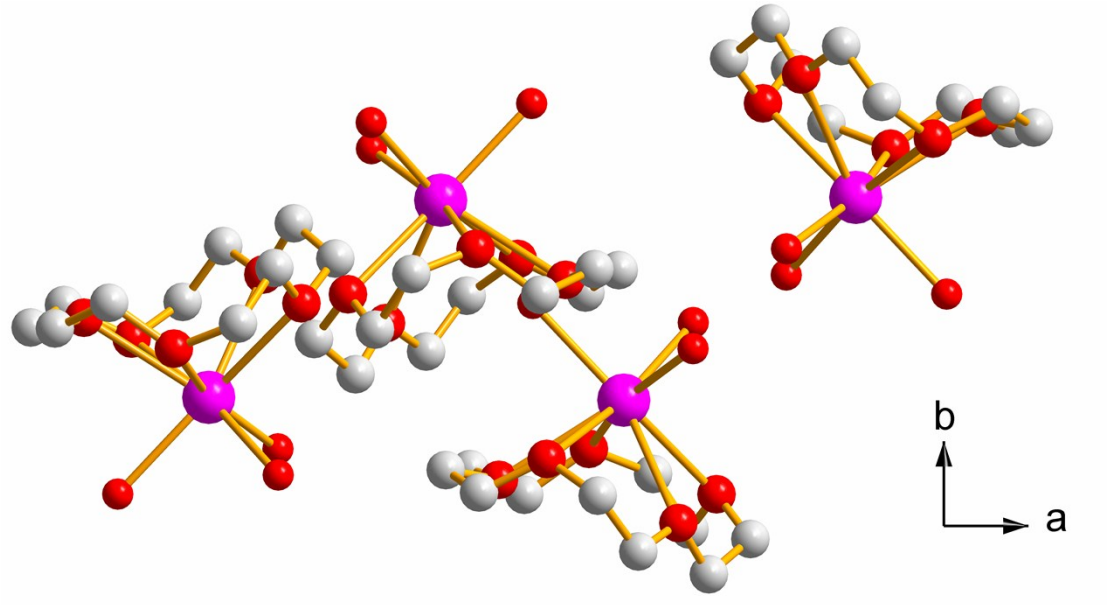


Figure S8 The packing view of compound **1** along *c* axis

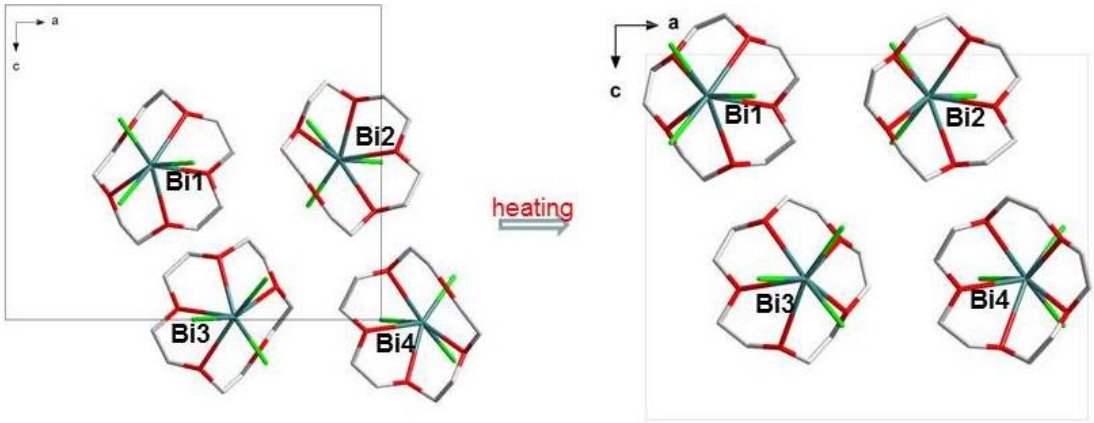


Figure S9 The packing view of compound **1** along *b* axis, where Bi1, Bi2, Bi3 and Bi4 correspond to the atoms listed in Table 3

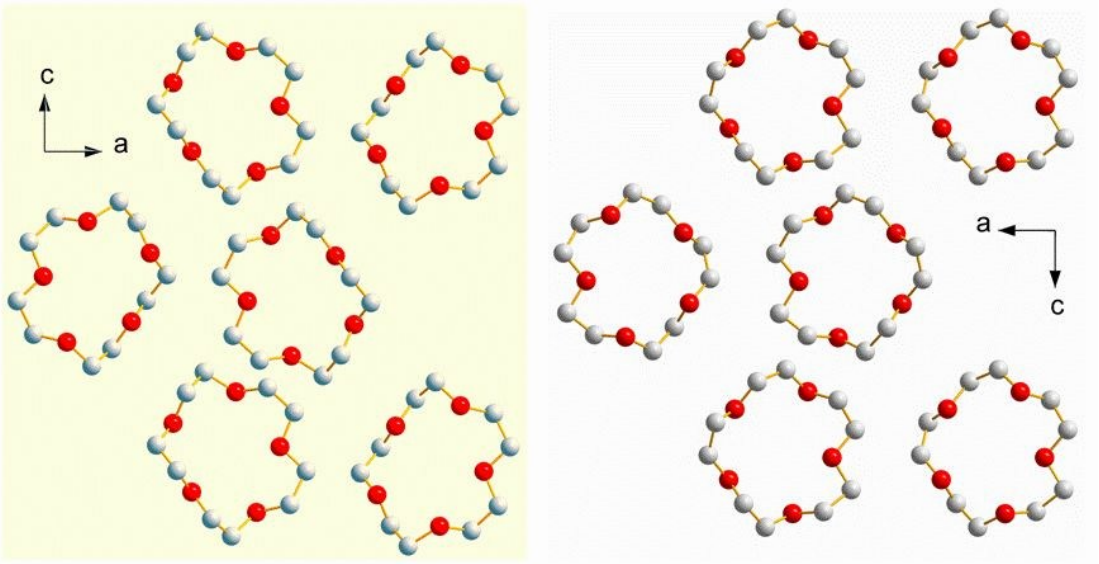


Figure S10 the packing view of 15-crown-5 at 173K(left) and 383K(right) along *b*

axis

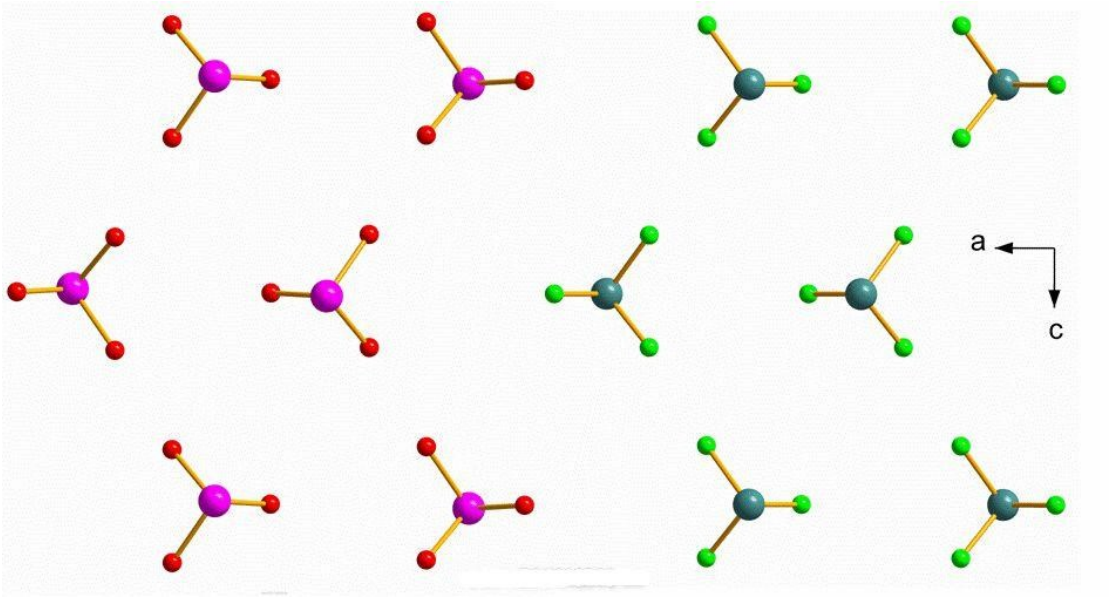


Figure S11 the packing view of compound **1** at 173K(left) and 383K(right) along b axis, where the 15-crown-5 have been omitted for clarity

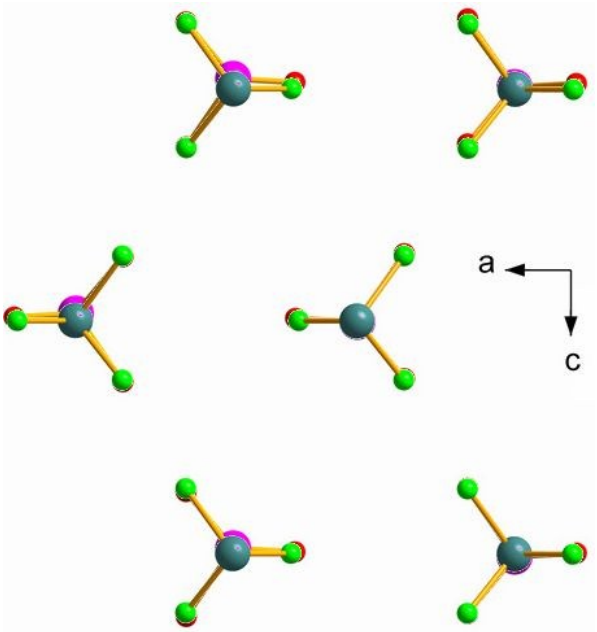


Figure S12 the overlap view of compound **1** in 173K low-temperature phase and 383K high-temperature phase along b axis, where the 15-crown-5 have been omitted for clarity

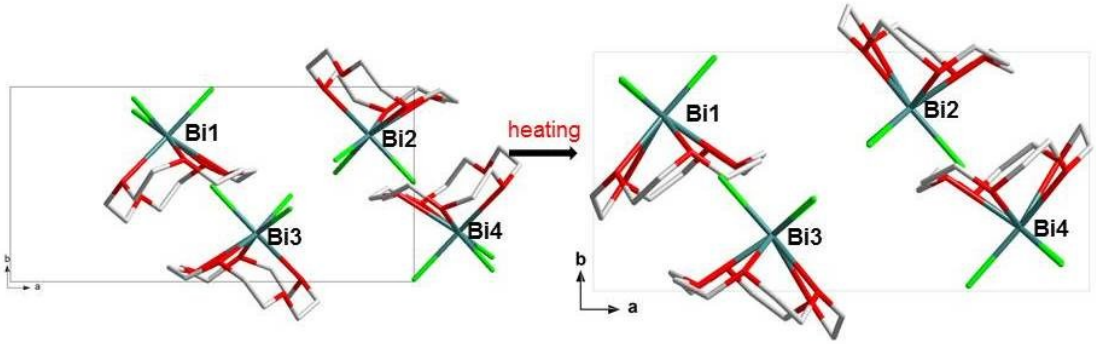


Figure S13 The packing view of compound **1** along *c* axis，where Bi1, Bi2, Bi3 and Bi4 correspond to the atoms listed in Table 3

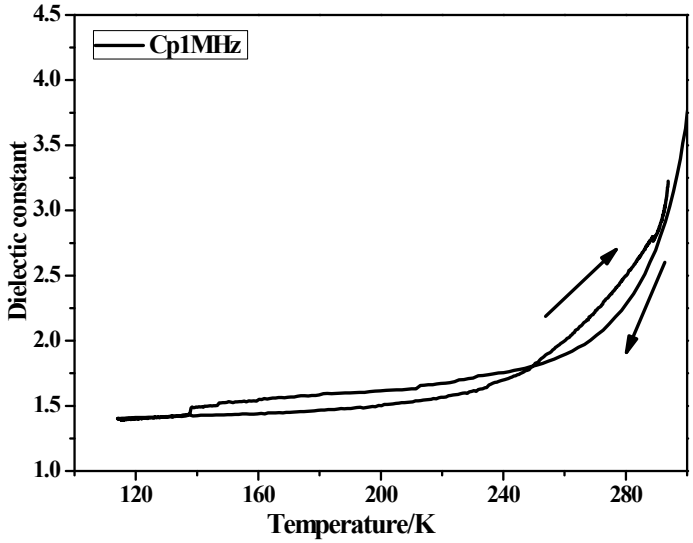


Figure S14 the dielectric constant of compound **1** from 110K to 300K

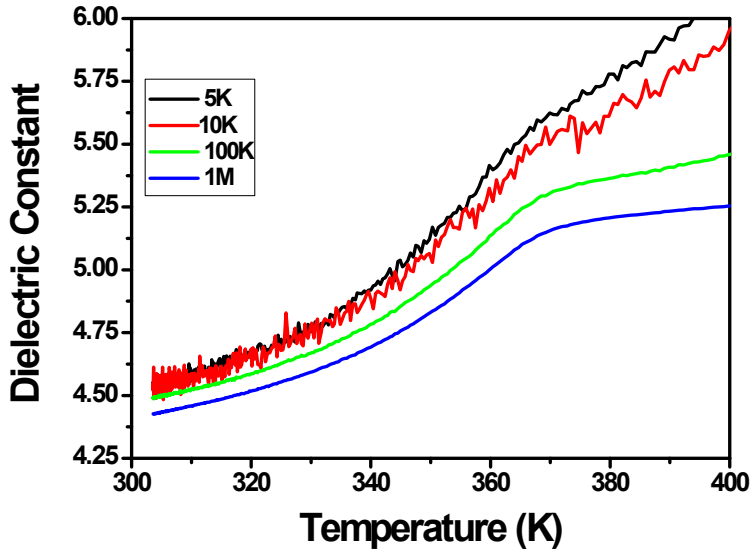


Figure S15 the temperature and frequency dependent dielectric constant of compound **1**

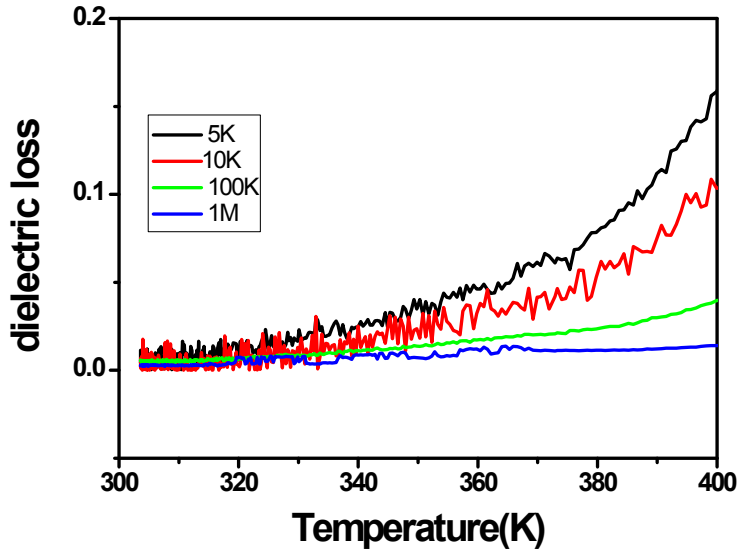


Figure S16 the temperature and frequency dependent dielectric loss of compound **1**

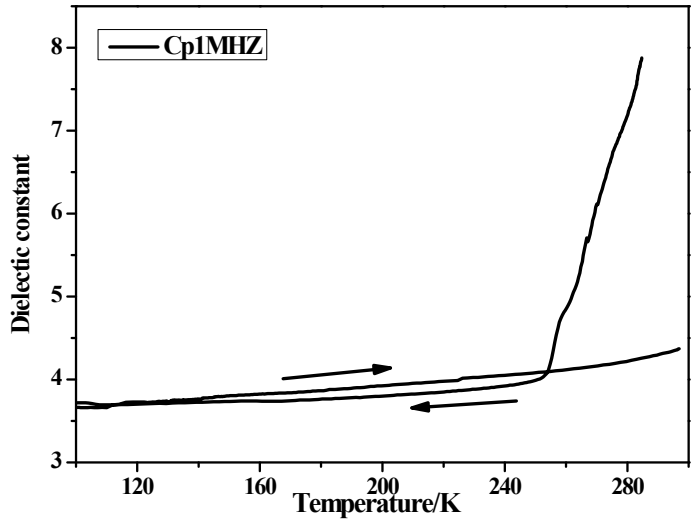


Figure S17 the dielectric constant of compound **2** from 100K to 300K

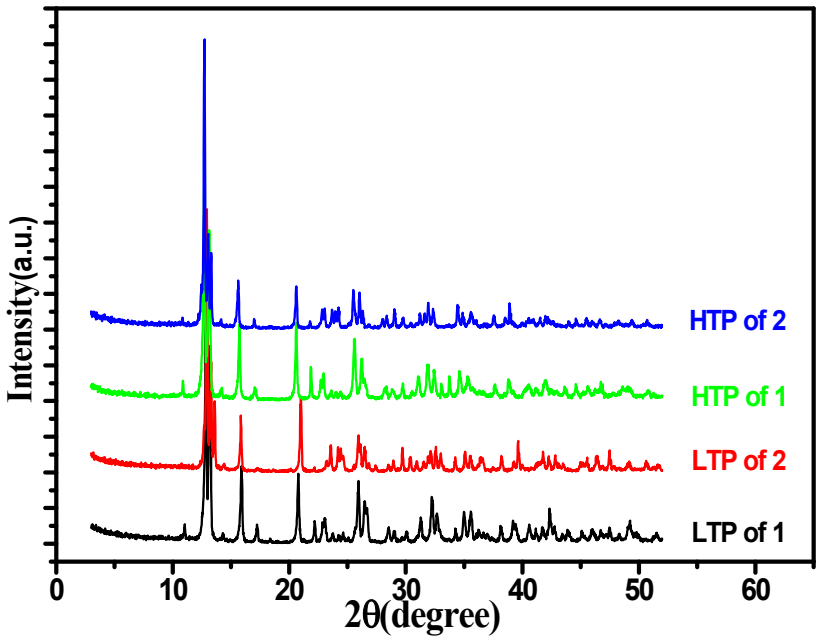
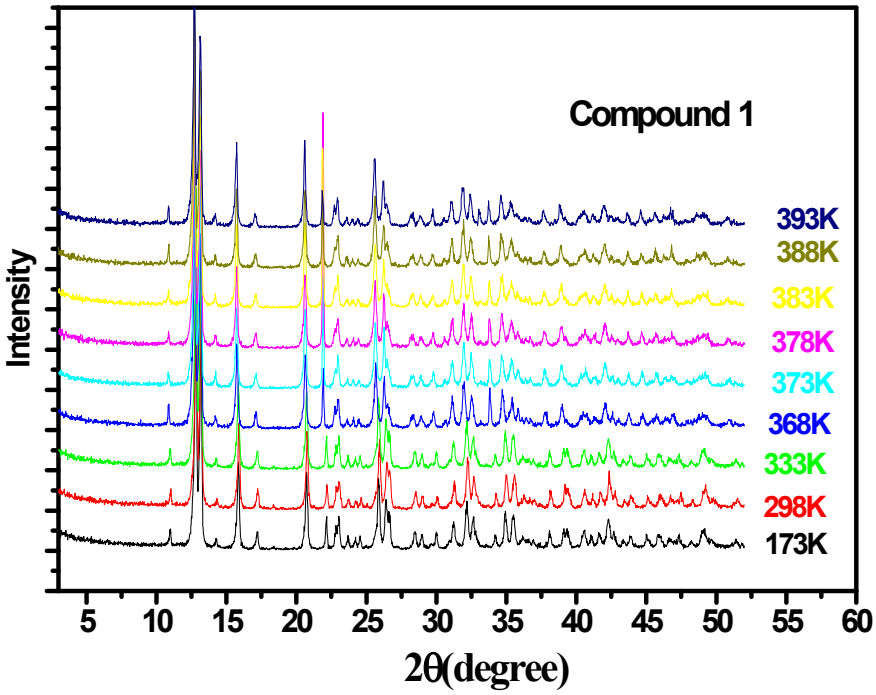


Figure S18 The powder X-ray diffraction of high temperature phases and low temperature phases of compounds **1** and **2**.



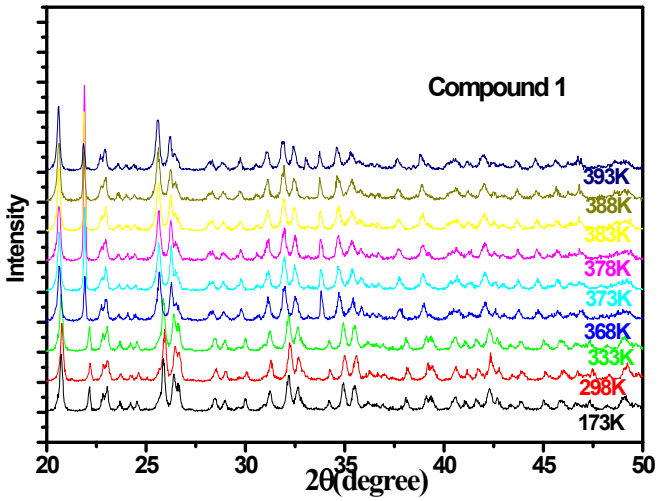
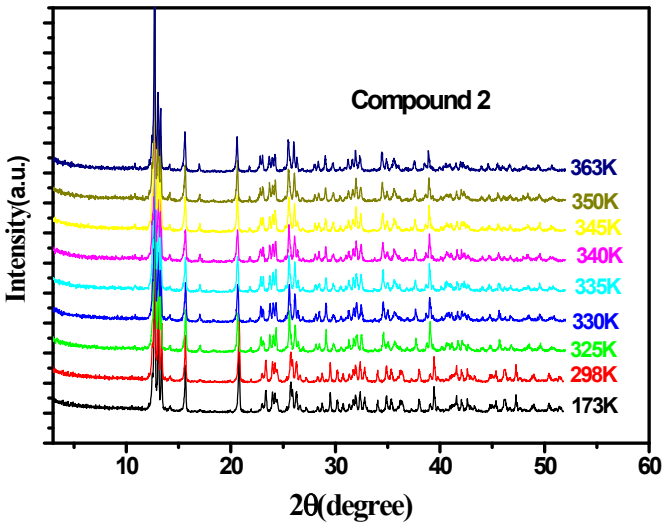


Figure S19 The temperature-variable powder X-ray diffraction of compound **1**.The spectrum shows slightly change in the 2θ range of 20-50°after the phase transition occurred.



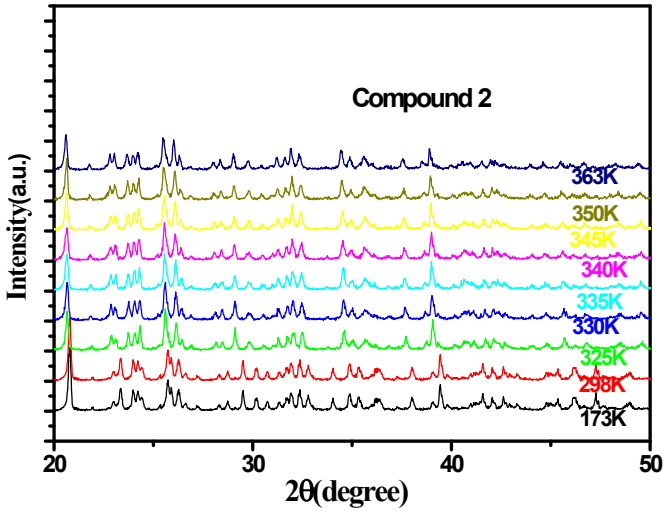
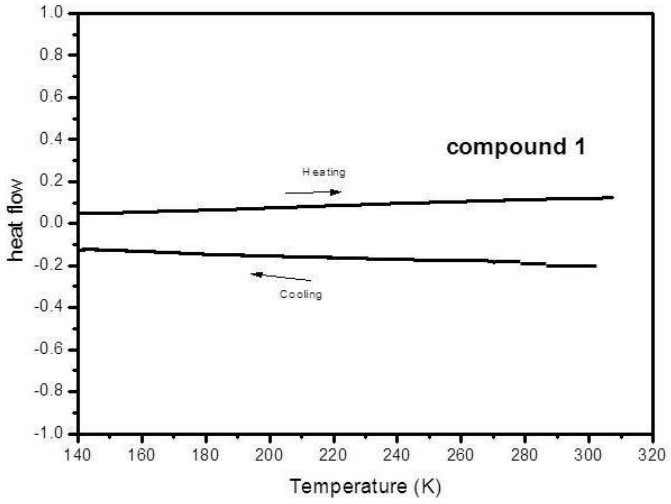


Figure S20 The temperature-variable powder X-ray diffraction of compound **2**.The spectrum shows slightly change in the 2θ range of 20-50° after the phase transition occurred.



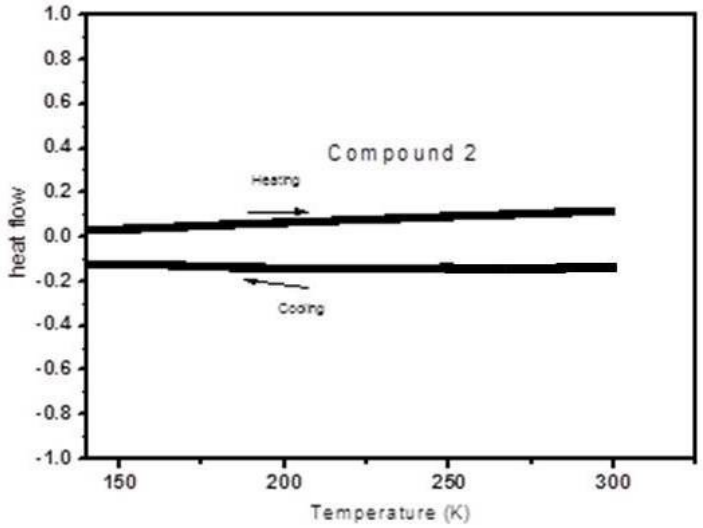


Figure S21 DSC measurement results of compound **1** and **2** from 140 to room temperature.