Supporting Information

Ionic Ferroelectrics Based on Nickel Schiff Base Complexes

Yan Sui, * Dong-Ping Li, Cheng-Hui Li, Xin-Hui Zhou, Tao Wu, and Xiao-Zeng You*

[†]State Key laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures Nanjing University,Nanjing 210093, People's Republic of China. E-mail: ysui@163.com (Y. Sui), youxz@nju.edu.cn (X.-Z. You.)

X-ray crystallography

Single-crystal X-ray diffraction measurements for complexes **1** and **2** were carried out on a Bruker SMART APEX CCD based on diffractometer operating at room temperature. Intensities were collected with graphite monochromatized Mo $K\alpha$ radiation (λ = 0.71073 Å), using φ-ω scans scan mode. The data integration and empirical absorption corrections were carried out by SAINT program.[1] The structures were produced by direct methods (SHELXS 97).[2] All the non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques (SHELXL 97).[3] Hydrogen atoms bonded to the carbon atoms were generated geometrically and refined isotropically using the riding mode.

Physical property measurements

Elemental analyses of the complexes were performed on a perkin-Elmer 240C analyzer. Infrared spectra were recorded in KBr pellet on a vector22 Bruker spectrophotometer in the range of 4000-400 cm^{-1}. The CD spectra were recorded on a JASCO J-810 Spectropolarimeter. The Electric hysteresis loops were recorded on a Ferroelectric Tester Precision Premier II made by Radiant Technologies, Inc. The temperature dependence of the dielectric constant and dielectric loss at 10^2-10^6 Hz frequencies were measured by using a dielectric impedance analyzer, Concept 80 system (Novocontrol, Germany) at Soochow University.

Semi- empirical calculations

Only the dipole moment for complexes **1** was calculated since complexes **1** and **2** are enantiomers and should have the same values. The calculation of dipole moment of complex **1** were carried out at the semi-empirical PM6 level[4] using the MOPAC program[5] and using Winmostar[6] as GUI interface. The dipole moment is about 41.161 D with the approximate direction from the S atom to the Na atom (Figure S10), which is almost parallel to b axis. Under the symmetry operation of 2-fold screw axes, the components of the dipole vector are cumulative along b axis and cancellative along other axis (Figure S11). Therefore, complexes **1** and **2** should have significant ferroelectric effect along b axis.

Table S1 Hydrogen-bond geometry (Å, °) of **1** and **2**

Complex		D—H	H...A	D...A	D—H...A
1	O10—H10A...N8[#1]	0.82	2.12	2.894 (12)	156.7
	C30—H30B...O3	0.96	2.56	3.274 (8)	131.2
	C31—H31A...O9[#2]	0.96	2.53	3.179 (9)	125.2
	C53—H53...N8[#3]	0.93	2.60	3.489 (9)	159.7
	C60—H60B...O7	0.96	2.54	3.252 (7)	130.6
2	O10—H10A...N5[#4]	0.82	2.18	2.979 (18)	164.7
	C48—H48B...O2	0.96	2.58	3.285 (11)	130.8

Symmetry codes: #1: -1+x, y, z; #2: 1+x, y, z; #3: 1-x, -1/2+y, 1-z.; #4: -1+x, -1+y, z
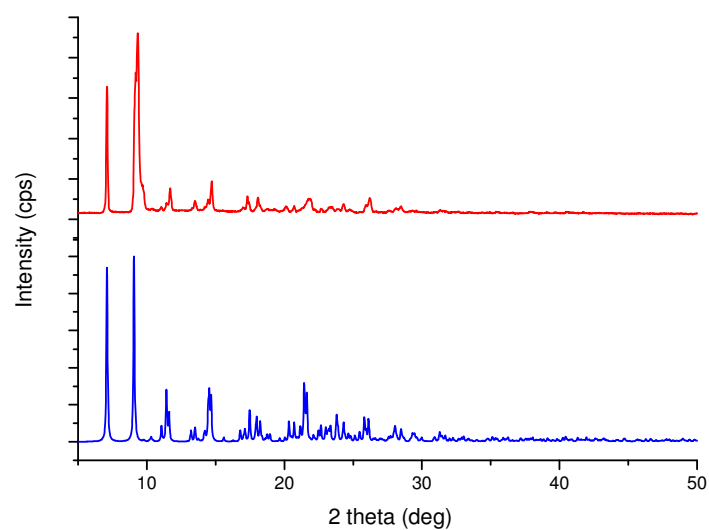

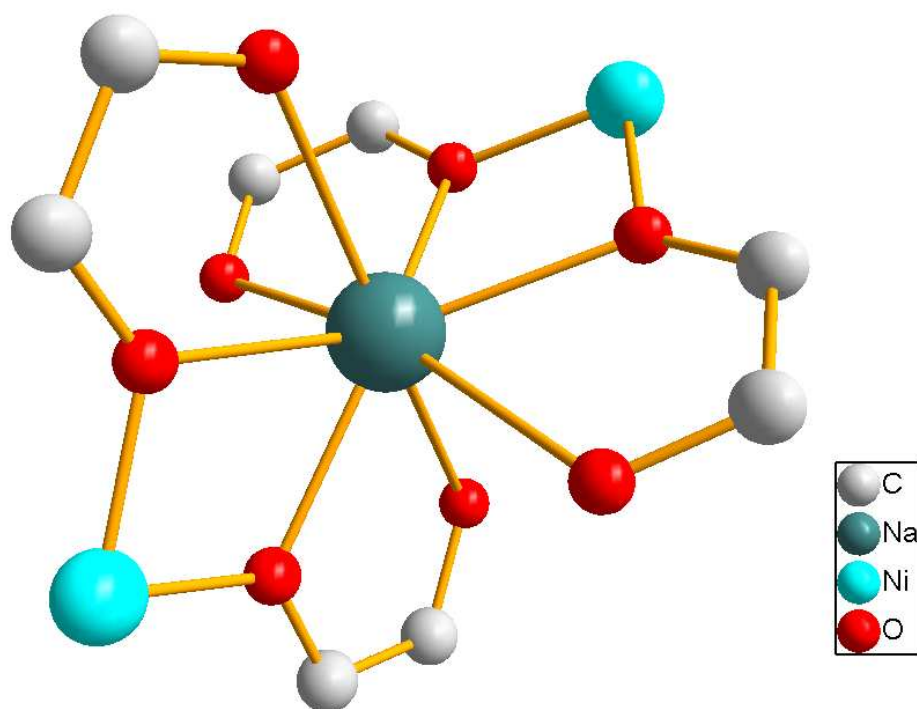**Figure S1.** The experimental (upper) and simulated (lower) powder X-ray diffraction patterns of complex **2**.

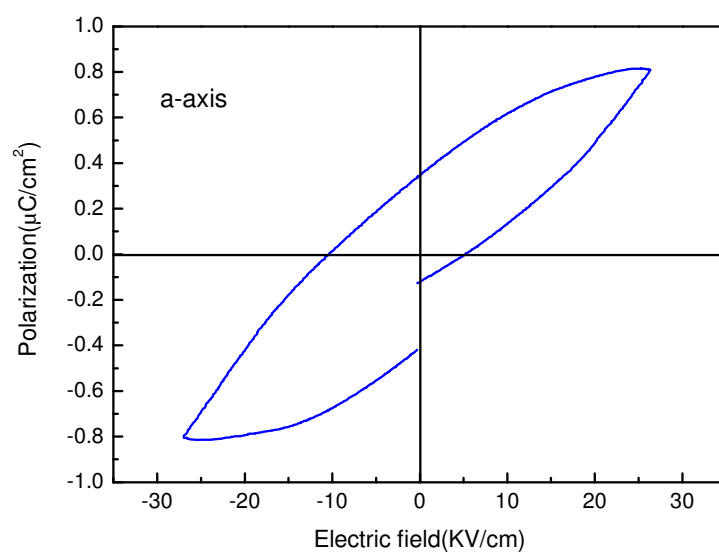**Figure S2.** The coordination environment of Na in complex **1**.

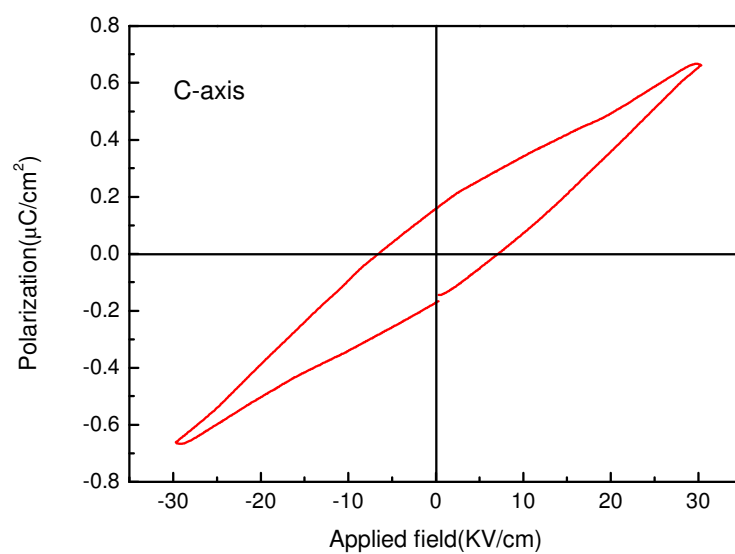**Figure S3.** E-P hysteresis loops for single crystal sample of **1** along *a* axis at room temperature

Figure S4. E-P hysteresis loops for single crystal sample of **1** along *c* axis at room temperature
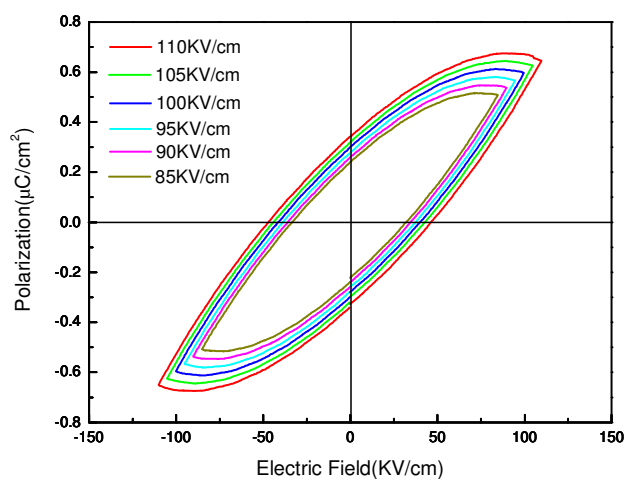

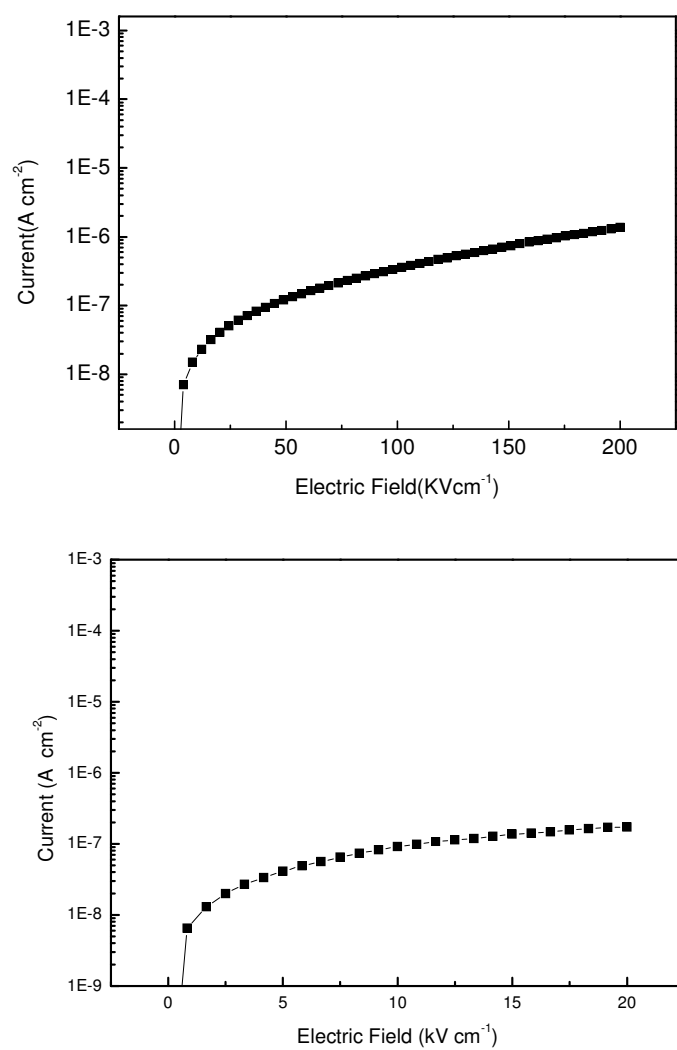**Figure S5.** E-P hysteresis loops on powered samples of **1** at room temperature.

Figure S6. Plots of leakage current versus electric fields for powered samples (top) and single crystal sample (bottom).
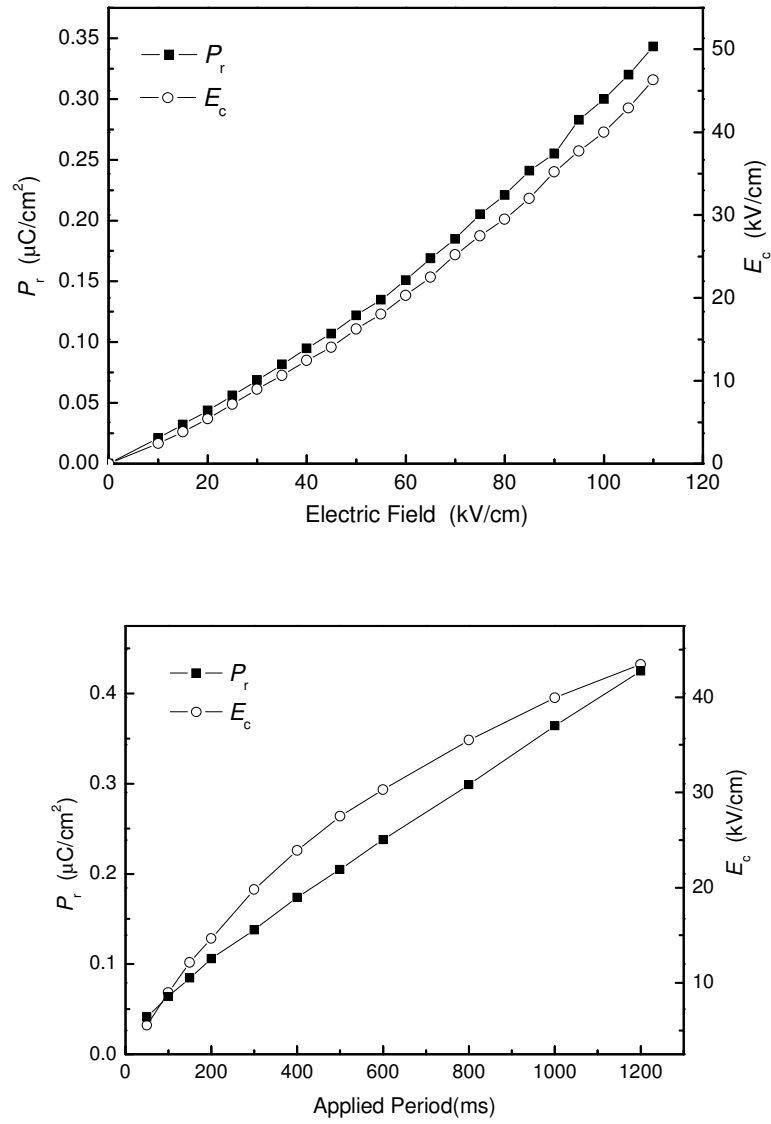
Figure S7. (top) The relationships between remnant polarization (*P*r) (or coercive field (*E*c)) and electric field at the frequency of 2Hz. (bottom) The relationships between remnant polarization (*P*r) (or coercive field (*E*c)) and applied period at the setting applied electric field of 75kV.
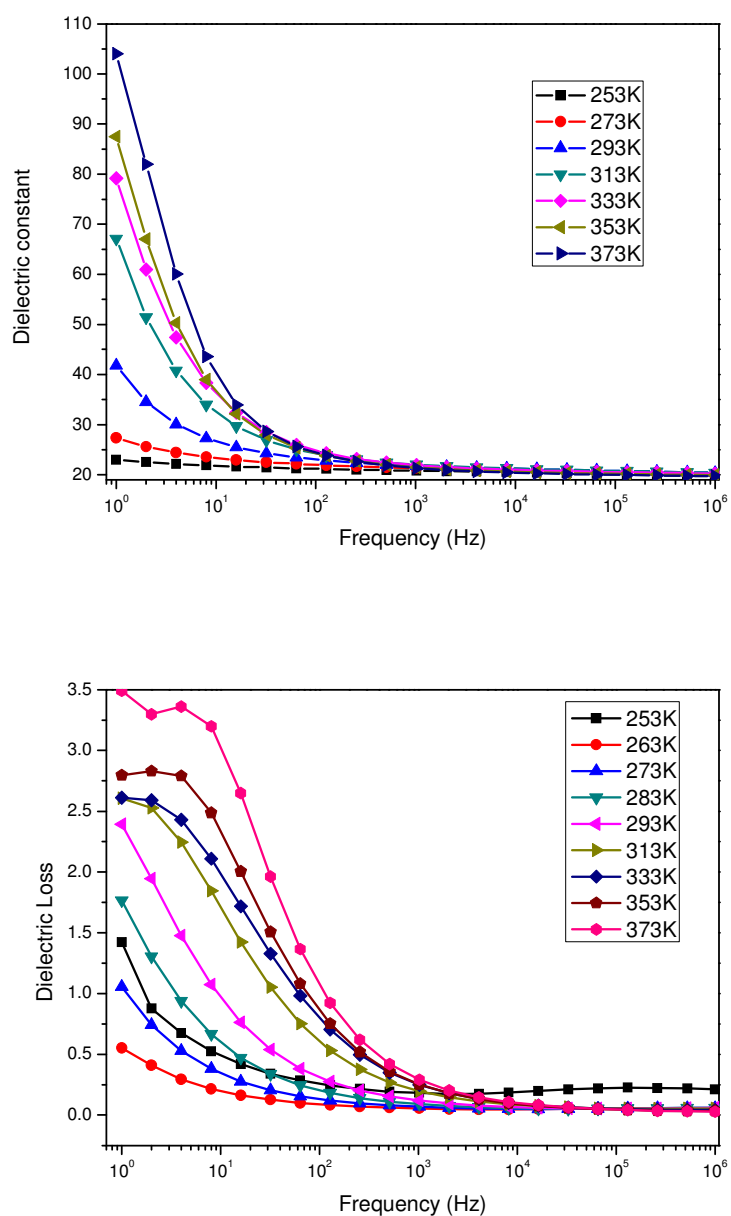
Figure S8. (top) Frequency dependence of the dielectric constant ε´ (real part) of complex **1** at various temperature (253-373K). (bottom) Frequency dependence of the dielectric loss ε˝/ε´, where ε˝ and ε´ are the imaginary and real parts of dielectric constant for complex **1**, at various temperature (253-373K).
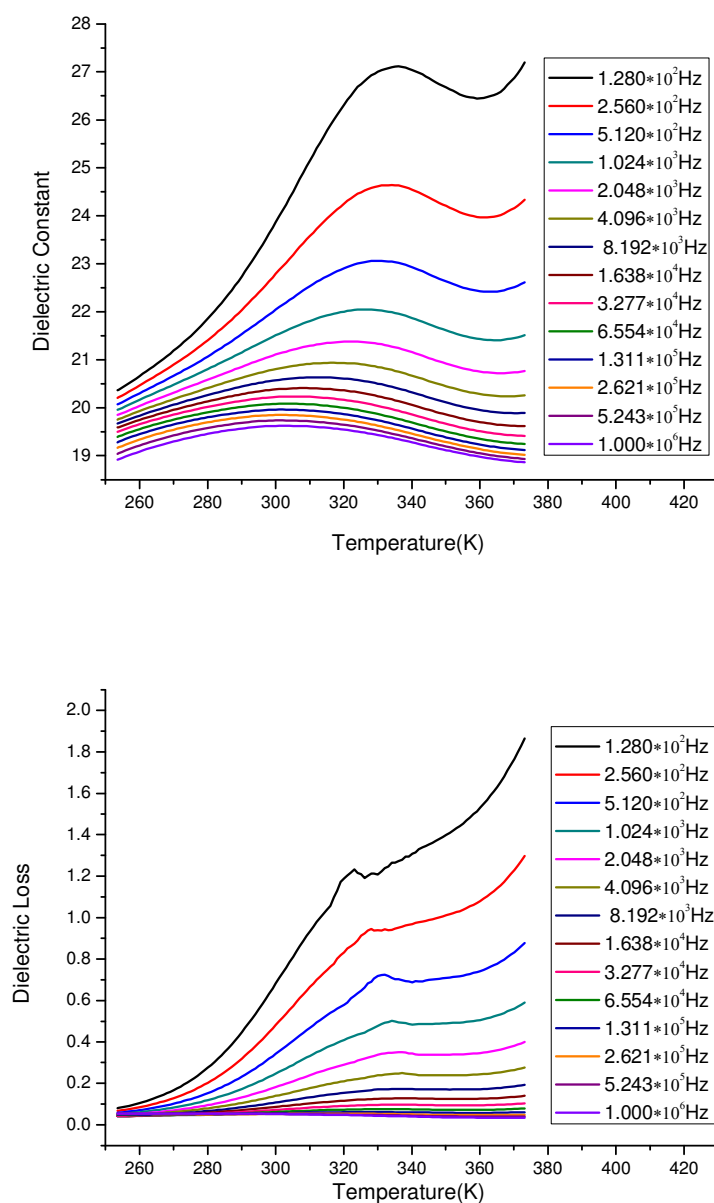
Figure S9. (top) Temperature dependence of the dielectric constant ε´ (real part) of complex **2** at various frequencies (10^2-10^6 Hz). (bottom) Temperature dependence of the dielectric loss ε˝/ε´, where ε˝ and ε´ are the imaginary and real parts of dielectric constant for complex **2**, at various frequencies (10^2-10^6 Hz).
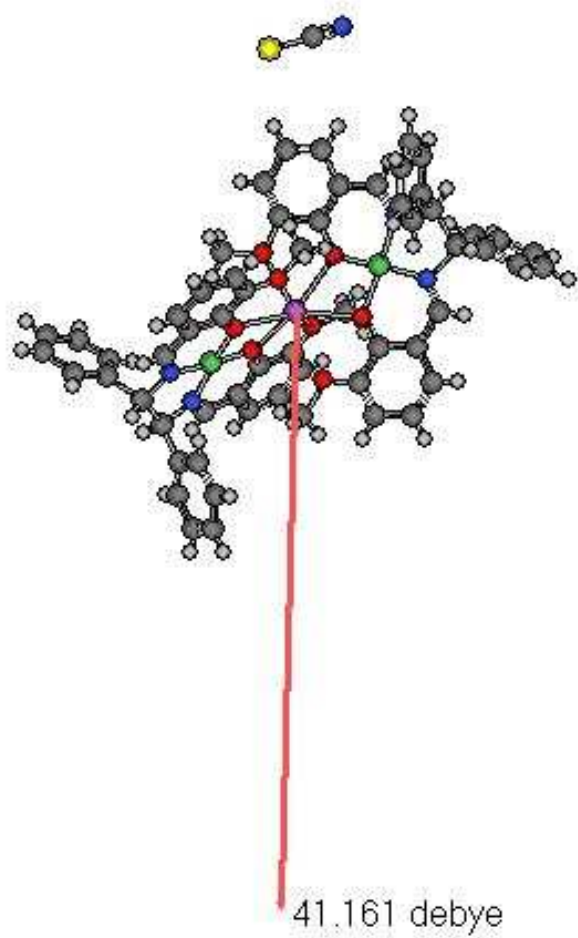
Figure S10. The calculated direction and value of the dipole moment of molecules.
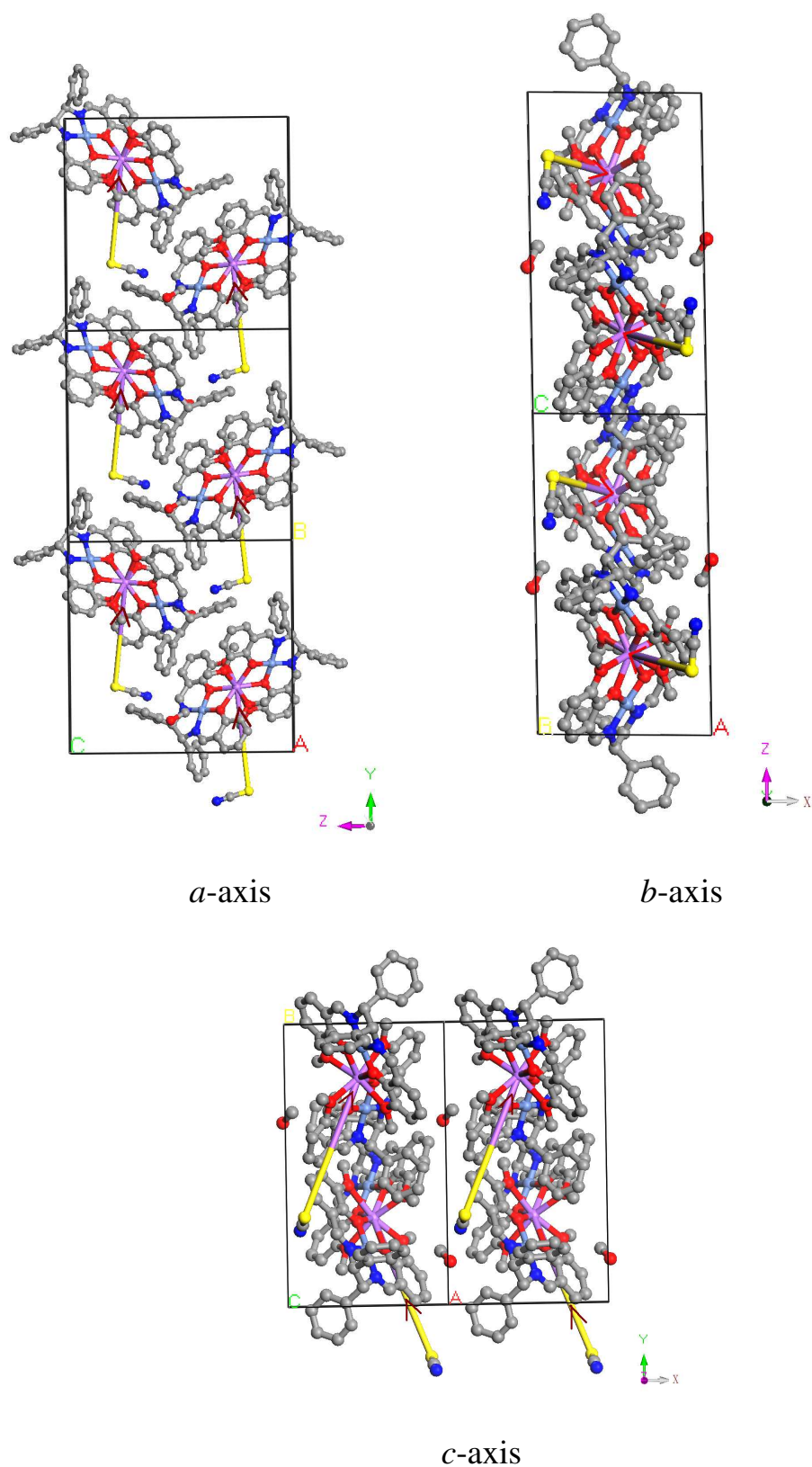
a-axis

b-axis

c-axis

Figure S11. Packing diagrams along *a*, *b* and *c* axises

The S atoms and the Na atoms are connected together, which represent the approximate directions of dipole moment of molecules. Red arrows are added to indicate that the directions of dipole moment of molecules are from the negative to the positive.

Reference

(1)   SAINT. Pragram for data extraction and reduction. Bruker AXS, Madison Inc: WI, **2001.**

(2)   G. M. Sheldrick, SHELXS-97, Program for the solution of crystal ctructures. University of Göttingen, Germany, **1997**.

(3)   G. M. Sheldrick, *SHELXTL-97*, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany,1997.

(4)   J. J. P. Stewart, *J. Mol. Mod.*, **2007**, 13, 1173-1213.

(5)   MOPAC2009, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, HTTP://OpenMOPAC.net **2008**.

(6)   Norio Senda. 3D-Graphics program for Molecular Modelling and Visualization of Quantum Chemical Calculations, http://winmostar.com/index_en.html.