Electronic Supporting Information for

Polymorphism of chiral iron(II) complex: spin-crossover and ferroelectric properties

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1. Experimental Section

All reagents and solvents were reagent grade, purchased from commercial sources and used without further purification. 1-butyl-2-imidazolecarboxaldehyde was prepared according to the literature,^[1] and the corresponding characterization results were consistent well with that of reported in the literature.

Infrared spectra were measured on an ABB Bomem FTLA 2000-104 spectrometer with KBr pellets in the 500-4000 cm⁻¹ region. ¹H NMR spectra were recorded on AVANCE III (400 MHz) instrument at 298 K using standard Varian or Bruker software, and chemical shifts were reported in parts per milion (ppm) downfield from tetramethylsilane. The thermogravimetric analysis (TGA) were carried out by using TGA/1100SF thermo grabinetric analyzer with a heating rate of 15 °C min⁻¹ from 25 to 500 °C under anitrogen atmosphere. Power X-ray Diffraction (PXRD) data on the crystalline samples were collected on a D8 Advance X-ray diffractometer (Bruker AXS Germany) with Cu K α radiation in a 2 θ range from 3° to 50° at the speed of 2° min⁻¹ at room temperature. Variable-temperature magnetic susceptibility on polycrystalline samples were performed on a Quantum Design MPMS-XL-7 SQUID magnetometer over the temperature range 2-400 K with the applied magnetic field of 1000 Oe at a rate of 1 K min⁻¹. The molar susceptibility was corrected for diamagnetic contributions using Pascal's constants and the increment method. Samples (ca. 30 mg) were restrained with petroleum jelly to prevent decomposing of the crystallites. The ferroelectric properties of single crystals were recorded on a Ferroelectric Tester Precision Premier II made by Radiant Technologies, Inc. The single crystal with approximate size of 0.3mm×0.6mm×0.6mm of polymorph II was covered with conducting Ag-glue. The single crystal with Ag-glue was dried under irradiant lamp for half day. Using two steel needles to contact two electrodes faces under microscope while hysteresis loop was recorded at room temperature. When the applied electric field varied from positive to negative voltage, an electric hysteresis loop was observed.

2. Synthesis of polymorph I and II

1-butyl-imidazole-2-carbaldehyde (0.152 g, 1 mmol) and commercially available (*S*)- 1phenylethylamine (0.121 g, 1 mmol) were dissolved in 10 mL acetonitrile and heated to reflux for 2 h at 80 °C. Then cooling to room temperature, the solution of Fe(BF₄)₂·6H₂O (0.1124 g, 0.333 mmol) in 10 mL acetonitrile was added with drops to form a dark purple solution which was further stirred vigorously for 1 h under a nitrogen atmosphere and filtered. After slow diffusion of diethyl ether into the filtrate in a few days, dark purple tetrahedral crystals (polymorph I) and orange triangular crystals (polymorph II) were simultaneously crystallized. Hand separation of polymorph I and II were able to be carried out under a microscope due to the significant differences in crystal morphologies and color. Yield for polymorph I: 47%. IR (KBr, v cm⁻¹): 3140, 3117, 2961, 2933, 2873, 1609, 1574, 1488, 1453, 1380, 1308, 1056, 765, 703, 628. Elem. anal. calcd for C₄₈H₆₃B₂F₈FeN₉: C, 57.91; N, 12.66; H, 6.38; Found: C, 57.86; N, 12.58; H, 6.45. Yield for polymorph II: 21%. IR (KBr, v cm⁻¹): 3152, 3127, 2960, 2933, 2874, 1613, 1488, 1446, 1378, 1308, 1056, 769, 704, 628. Elem. anal. calcd for C₄₈H₆₃B₂F₈FeN₉: C, 57.91; N, 12.66; H, 6.38; Found: C, 57.83; N, 12.63; H, 6.42.

3. PXRD of polymorph I and II



Figure S1. Observed and simulated powder X-ray diffraction (PXRD) of polymorph I.



Figure S2. Observed and simulated powder X-ray diffraction (PXRD) of polymorph II.

4. Infrared (IR) spectra of polymorph I and II



Figure. S3. IR spectra of polymorph I and II.

5. Thermogravimetric analysis (TGA)



Figure S4. Thermogravimetric analysis (TGA) of polymorph I and II.

The weight of the two polymorphs (I and II) were nearly a constant following the increasing temperature until 281 °C, and then the complex started to decompose. Further heated to 500 °C, there were approximate 18 and 17 percent of weight residual for these two polymorphs, which possibly corresponded to the iron oxides.

6. Crystal structure and crystal packing of polymorph I and II



Figure S5. The pseudo-octahedral structure formed by Fe–N in (a) polymorph I and (b) polymorph II (N: blue; Fe:purple); (c) the dihedral angle θ between the plane which parallel with phenyl rings and the plane which perpendicular to C_3 axis (the ligands are in three different colors, green, yellow and black, and all H atoms and the anions have been removed for clarity).



Figure S6. The three-dimensional supramolecular framework of polymorph I, highlighting each cation unit is linked with adjacent six monomers at spherical position through C-H $\cdots\pi$ interactions.



Figure S7. The two-dimensional "layer by layer" supramolecular crystal packing of polymorph II, highlighting each cation unit is linked with adjacent six monomers in the same plane through C-H··· π interactions.

7. Simulated of the $\chi_{\rm M}T$ verus *T* curve of polymorph I

To analyze the SCO behavior, we have simulated the $\chi_M T$ verus *T* curves using a variant of the regular-solution model proposed by Slichter and Drickamer,^[2] and the relevant thermodynamic parameters have been deduced from the expression (eqn(1)),

$$\ln\left[\frac{1-\gamma_{HS}}{\gamma_{HS}}-f_{HS}\right] = \frac{\Delta H + \Gamma\left(1+f_{HS}-2\gamma_{HS}\right)}{RT} - \frac{\Delta S}{R} \quad (1)$$

where ΔH and ΔS are, respectively, the enthalpy and the entropy variations during the SCO, Γ represents the interaction energy between molecular (cooperativity), and *R* is the gas constant. The HS molar fraction, γ_{HS} , has been deduced from the magnetic susceptibility through (eqn(2)),

$$\gamma_{HS} \approx \frac{(\chi_M T)_{\rm m}}{(\chi_M T)_{HS}}$$
 (2)

where $(\chi_M T)_m$ is the value of $\chi_M T$ at any temperature, $(\chi_M T)_{HS}$ corresponds to the pure HS state. In the present case $(\chi_M T)_{HS}$ has been considered an adjustable parameter. The parameter f_{HS} accounts for the HS molar fraction at low temperature (eqn(3)),

$$f_{HS} \approx \frac{(\chi_M T)_{LS}}{(\chi_M T)_{HS}} \quad (3)$$

where $(\chi_M T)_{LS}$ corresponds to the value of $\chi_M T$ at low temperature once the SCO has been accomplished. We have considered the parameter $(\chi_M T)_{LS} = 0.02 \text{ cm}^3 \text{ K cm}^{-1}$ from the experimental curve. Simulation of the experimental data gives $\Delta H = 17.85 \text{ kJ mol}^{-1}$, $\Delta S =$ 59.12 J K⁻¹ mol⁻¹, $T_{1/2} = 301.9 \text{ K} (=\Delta H/\Delta S)$, $\Gamma = 1.20 \text{ kJ mol}^{-1}$, $(\chi_M T)_{HS} = 3.67 \text{ cm}^3 \text{ K cm}^{-1}$ (see blue line in *Figure S8*).



Figure S8. Experimental (black) and simulated (blue) $\chi_M T$ verus T plot for polymorph I.

8. Simulated of the $\chi_{\rm M}T$ verus *T* curve of polymorph II

The temperature dependence of the $\chi_M T$ value of polymorph II was analyzed based on the molecular-field approximation with a zero-field splitting (ZFS).^[3] The magnetic susceptibility ($\chi_M T$) for S = 2 centers associated with ZFS is expressed as follows:

$$(\chi_{M}T)_{ZFS} = \frac{\chi_{M}T_{P} + 2\chi_{M}T_{\perp}}{3} \quad (4)$$

with $\chi_{M}T_{P} = \frac{3}{4}g^{2}\frac{e^{\frac{-D}{k_{B}T}} + 4e^{\frac{-4D}{k_{B}T}}}{1 + 2e^{\frac{-D}{k_{B}T}} + 2e^{\frac{-4D}{k_{B}T}}} \quad (5)$
with $\chi_{M}T_{\perp} = \frac{1}{4}g^{2}\frac{k_{B}T}{D}\frac{9 - 7e^{\frac{-D}{k_{B}T}} - 2e^{\frac{-4D}{k_{B}T}}}{1 + 2e^{\frac{-4D}{k_{B}T}} + 2e^{\frac{-4D}{k_{B}T}}} \quad (6)$

where k_B is the Boltzmann constant ($k_B = 1.3807 \times 10^{-23}$ J K⁻¹), D is the magnitude of ZFS.



Figure S9. Experimental (red) and simulated (blue) $\chi_M T$ verus T plot for polymorph II.

9. The ferroelectric data of polymorph II at different voltages



Figure S10. *P-E* hysteresis loop for polymorph **II** based on single crystal measurements at room temperature under different amplitudes of electric field settings.

10. The unit cell of polymorph II at different temperature

	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	space group
100 K	12.4931(13)	12.4931(13)	28.1012(37)	90	90	120	R_3
145 K	12.5372(18)	12.5372(18)	28.1543(47)	90	90	120	R_3
296 K	12.6436(16)	12.6436(16)	28.035(3)	90	90	120	R_3

Table S1 The unit cell of polymorph II at different temperature





Figure S11. DSC curves of polymorph II.

12. X-ray crystallographic data

The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were retrieved using SMART software and refined using SAINT^[4] on all observed reflections. The highly redundant data sets were reduced using SAINT^[5] and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS^[5] supplied by Bruker. Structures were solved by direct methods using the program SHELXL-97.^[6] All of the non-hydrogen atoms except the anions were refined with anisotropic thermal displacement coefficients. Hydrogen atoms of organic ligands were located geometrically and refined in a riding model. Disorder was modeled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. For polymorph II, two tetrafluoroborate anions are disordered. Table S2 lists the crystallographic parameters concerning data collection and structure refinements for polymorph I and II while relevant bond lengths and angles (°) were listed in Table S3.

	Polymorph I	Polymorph II
formula	$C_{48}H_{63}B_2F_8FeN_9$	$C_{48}H_{63}B_2F_8FeN_9$
fw	995.54	995.54
<i>T</i> (K)	100(2) K	296(2) K
λ (Å)	0.71073	0.71073
crystal system	Cubic	Trigonal
space group	<i>P</i> 2 ₁ 3	R_3
<i>a</i> (Å)	17.0031(2)	12.6436(16)
<i>b</i> (Å)	17.0031(2)	12.6436(16)
<i>c</i> (Å)	17.0031(2)	28.035(3)
α (0)	90	90
eta (0)	90	90
γ (⁰)	90	120
$V(Å^3)$	4915.69(10)	3881.3(8)
Ζ	4	3
D_{calc} (Mg/m ³)	1.345	1.278
$\mu (\text{mm}^{-1})$	0.381	0.362
<i>F</i> (000)	2088	1566
heta (0)	3.39 - 25.62	2.00 - 27.70
	-4<=h<=17	-10<=h<=16
index ranges	-15<=k<=17	-16<=k<=14
	-15<=l<=20	-35<=1<=36
reflections collected	5438	8614
GOF (F^2)	1.017	1.013
R_1^a , wR_2^b (I>2 σ (I))	0.0241, 0.0530	0.0687, 0.1818
$R_1^{\rm a}, wR_2^{\rm b}$ (all data)	0.0261, 0.0535	0.0922, 0.1982

Table S2 Summary of crystallographic data for polymorph I and II.

 $R_{I}^{a} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma F_{o}|. \ wR_{2}^{b} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})]^{1/2}$

polyn	norph I	polymorph H			
Fe(1)-N(1)#5	1.9428(14)	Fe(1)-N(2)	2.151(4)		
Fe(1)-N(1)#6	1.9428(14)	Fe(1)-N(2)#1	2.151(4)		
Fe(1)-N(1)	1.9429(14)	Fe(1)-N(2)#2	2.151(4)		
Fe(1)-N(3)	2.0318(15)	Fe(1)-N(3)#1	2.267(4)		
Fe(1)-N(3)#6	2.0318(15)	Fe(1)-N(3)#2	2.267(4)		
Fe(1)-N(3)#5	2.0318(15)	Fe(1)-N(3)	2.267(4)		
N(1)#5-Fe(1)-N(1)#6	89.28(6)	N(2)-Fe(1)-N(2)#1	91.68(15)		
N(1)#5-Fe(1)-N(1)	89.29(6)	N(2)-Fe(1)-N(2)#2	91.68(15)		
N(1)#6-Fe(1)-N(1)	89.28(6)	N(2)#1-Fe(1)-N(2)#2	91.68(15)		
N(1)#5-Fe(1)-N(3)	169.51(6)	N(2)-Fe(1)-N(3)#1	96.41(13)		
N(1)#6-Fe(1)-N(3)	92.21(6)	N(2)#1-Fe(1)-N(3)#1	75.37(13)		
N(1)-Fe(1)-N(3)	80.35(6)	N(2)#2-Fe(1)-N(3)#1	164.87(12)		
N(1)#5-Fe(1)-N(3)#6	92.21(6)	N(2)-Fe(1)-N(3)#2	164.87(12)		
N(1)#6-Fe(1)-N(3)#6	80.35(6)	N(2)#1-Fe(1)-N(3)#2	96.41(13)		
N(1)-Fe(1)-N(3)#6	169.50(6)	N(2)#2-Fe(1)-N(3)#2	75.37(13)		
N(3)-Fe(1)-N(3)#6	98.28(5)	N(3)#1-Fe(1)-N(3)#2	97.99(12)		
N(1)#5-Fe(1)-N(3)#5	80.35(6)	N(2)-Fe(1)-N(3)	75.37(13)		
N(1)#6-Fe(1)-N(3)#5	169.50(6)	N(2)#1-Fe(1)-N(3)	164.87(12)		
N(1)-Fe(1)-N(3)#5	92.22(6)	N(2)#2-Fe(1)-N(3)	96.41(13)		
N(3)-Fe(1)-N(3)#5	98.28(5)	N(3)#1-Fe(1)-N(3)	97.99(12)		
N(3)#6-Fe(1)-N(3)#5	98.28(5)	N(3)#2-Fe(1)-N(3)	97.99(12)		

Table S3. Selected bond lengths [Å] and angles [°] for polymorph I and II.

Symmetry transformations used to generate equivalent atoms for polymorph I: #5 -z, x+1/2, -y+1/2 #6 - y-1/2, -z+1/2, -x; polymorph II: #1 - x+y, -x+1, z #2 - y+1, x-y+1, z

13. References

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