A bis(maleonitriledithiolato)nickelate charge-transfer salt with mixed stacks exhibiting novel non-ferroelectric-type dielectric phase transition and bistability

Yao Chen,[a] Shun-Ping Zhao, [a] Jian-Lan Liu,*[a] Wei-Hua Ning, [a] Xiao-Mei Sun[a] and Xiao-Ming Ren*[a,b]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering and College of Science, Nanjing University of Technology, Nanjing 210009, P. R. China

[b] College of Material Science and Engineering, Nanjing University of Technology, Nanjing 210009, P. R. China

Tel.: +86 25 58139476

Fax: +86 25 58139481

Email: xmren@njut.edu.cn

Experimental section

Chemicals and reagents

All chemicals and reagents were purchased from commercial sources and used without further purification.

Preparation of compound

[C_8-4, 4'-Bipy][Ni(mnt)$_2$] (**1**): Na_2mnt (372 mg, 2 mmol) and $NiCl_2 \cdot 6H_2O$ (237 mg, 1 mmol) were mixed under stirring in 100 mL H_2O at room temperature, subsequently, a solution of 1, 1'-dioctyl-4, 4'-bipydinium dibromide (540 mg, 1 mmol) in H_2O (30 mL) was added to the mixture; the brown precipitate immediately formed was filtered off, washed with a little amount of H_2O. The crude product was further recrystallized in DMF/acetonitrile mixed solution to give red crystals, and the yield is *ca.* 83%.

Anal. Calcd. for $C_{34}H_{42}N_6S_4Ni$: C, 56.58; H, 5.86; N, 11.64%. Found: C, 56.93; H, 5.53; N, 11.78%. IR spectrum (KBr, cm^{-1}): 2193.9s for $\nu_{C\equiv N}$; 1458.2s for $\nu_{C=C}$ of mnt^{2-}; 1147.6s for ν_{C-S}.

Physical measurements

The elemental analyses for C, H, and N were performed on an Elementar Vario EL III analytic instrument. The IR spectra in the range 4000-400 cm-1 were recorded on a Bruker Vector 22 Fourier transform infrared spectrometer (170SX) using KBr disk. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 diffract meter with Cu Kα radiation (λ = 1.5418 Å) at ambient temperature. Thermogravimetric (TG) analyzer experiments were performed using a simultaneous SDT 2960 thermal, the sample was held in a platinum pan under nitrogen flow in the rate of 100 $mL \cdot min^{-1}$ and heated at a ramping rate of 20 $°C \cdot min^{-1}$ from ambient temperature to 700 °C. Differential scanning calorimeter (DSC) experiments were carried out on Shimadzu DSC-60 differential scanning calorimeter in the temperature range of 186-573 K (from -87 to 300 °C). Dielectric constant and loss measurements were carried out using Concept 80 system (Novo control, Germany) in the ranges of 1-10^7 Hz and 173-403 K; the pressed powder pellet sample, with a thickness of ca. 0.52 mm and a

area of 133 mm^2, was sandwiched by the copper electrodes under alternate current (ac) field, and the temperature sweep was undertaken at a rate of 5 $K \cdot min^{-1}$ during heating process.

X-Ray crystallography

The diffraction data for **1** were collected with graphite-monochromated Mo Kα (λ = 0.71073 Å) on a CCD area detector (Bruker SMART). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively. Structures were solved by the direct method and refined by the full-matrix least-squares procedure on F^2 using SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at calculated positions. The crystallographic details about data collection and structure refinements are summarized in Table S1 and the selected bond parameters for the moieties of anion are listed in Table S2.

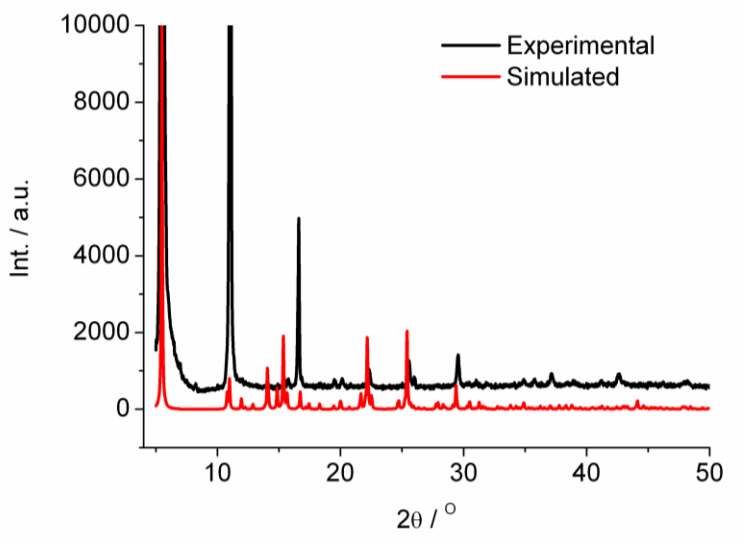

Figure S1 Experimental and simulated PXRD profiles of **1** at room temperature, showed that charge-transfer salt **1** possesses high phase purity.

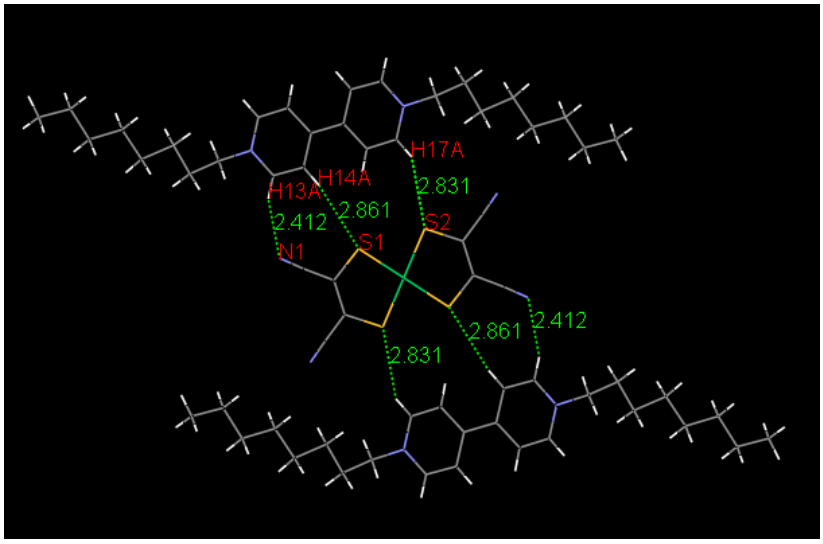

Figure S2 Illustration for the interatomic distances between the coplanar anion and cations in crystal **1**.

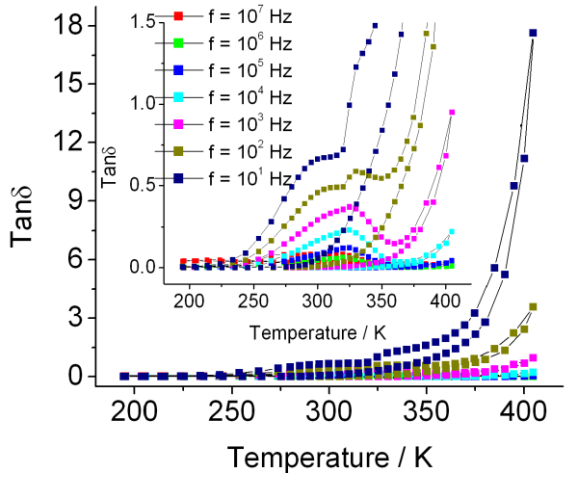

Figure S3 Temperature dependences of dielectric loss in the frequency range of 10-10^7 Hz for **1**.

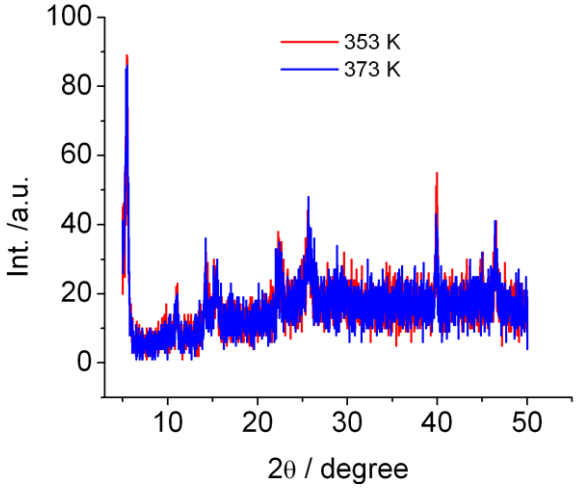

Figure S4 PXRD profiles of **1** in high temperature phase at 353 and 373 K, respectively.

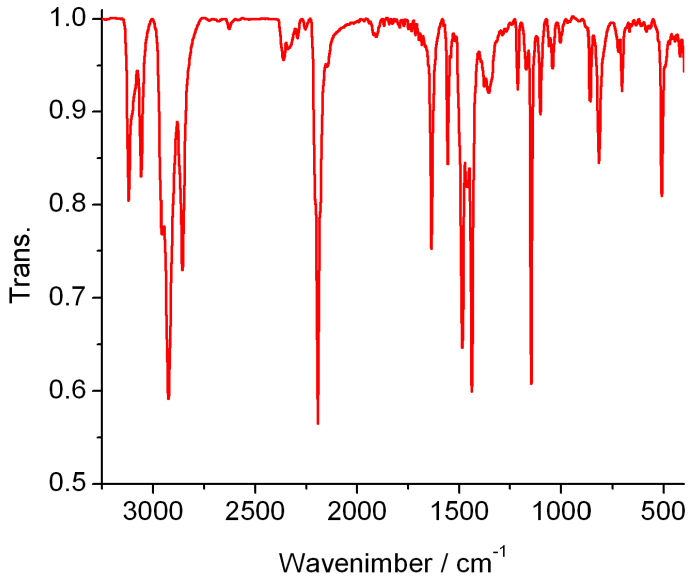

Figure S5 IR spectrum of **1**.

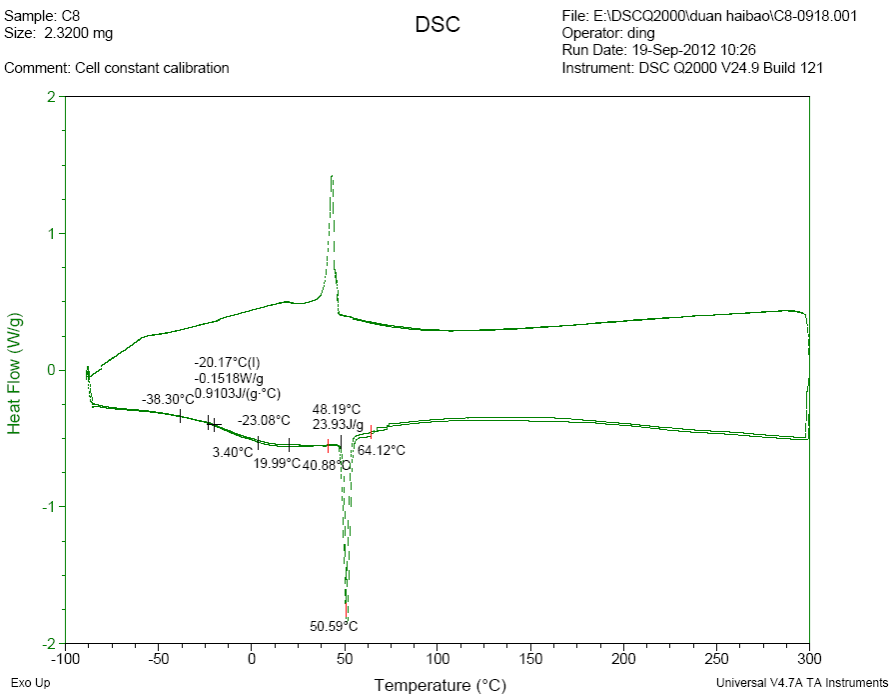

Figure S6 DSC plots of **1**.

Table S1 Crystal data and structure refinement parameters for **1**

Chemical formula	$C_{34}H_{42}N_6NiS_4$
CCDC number	929581
Formula weight	721.69
Temperature (K)	296(2) K
Wavelength(Å)	0.71073
Crystal system	triclinic
Space group	P -1
a (Å)	7.217(2)
b (Å)	8.617(3)
c (Å)	16.124(5)
α (°)	87.616(4)
β (°)	87.800(5)
γ (°)	72.222(4)
V(Å^3) / Z	953.7(5) / 1
Dcalc (g/cm^3)	1.257
Absorption coefficient (mm^{-1})	0.758
F(000)	380
θ Range for data collection	1.26 - 27.49
Index range	$-8 \le h \le 8$
	$-10 \le k \le 10$
	$-19 \le l \le 17$
Reflections collected	7258
Independent reflections	3527
R_{int}	0.0579
Refinement on F^2	Full-matrix least-squares
Data / restraints / parameters	3527 / 0 / 205
Goodness-of-fit on F^2	0.883
Final R indices [I > 2σ(I)]	R1 = 0.0568, wR2 = 0.1367
R indices (all data)	R1 = 0.1759, wR2 = 0.1886
Residual (eÅ^{-3})	0.478 and -0.341

$R_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0|$, $wR_2 = \Sigma w(|F_0|^2-|F_c|^2)^2/\Sigma w\ (|F_0|^2)^2]^{1/2}$

Table S2 Selected bonding lengths (Å) and angles (°) in the anion of **1**

Ni(1)–S(1)	2.1656(16)	Ni(1)–S(2)	2.1698(17)
S(1)-Ni(1)-S(2)	88.02(6)	S(1)-Ni(1)-S(1)#1	180.000

Symmetric code #1 = 1-x, -y, 1-z