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#### ABSTRACT

Two nickel-bis-1,2-dithiolene salts,  $[1,4-dimethyl-DABCO][Ni(mnt)_2]$  (1) and  $(TMSF)_2[Ni(mnt)_2]$  (2)  $(mnt^{2-} = maleonitriledithiolate, 1,4-dimethyl-DABCO^{2+} = 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane and TMSF<sup>+</sup> = trimethylsulfonium), were synthesized and characterized by elemental analysis, IR spectra, thermal analysis and single crystal structures. Both$ **1**and**2**crystallize in monoclinic space group*C2/c* $, with a formula and cell parameters of <math>C_{16}H_{18}N_6NiS_4$ , a = 16.9688(8) Å, b = 9.3003(5) Å, 13.4090(6) Å and  $\beta = 103.244(2)^{\circ}$  for **1** at 293 K versus  $C_{14}H_{18}N_4NiS_6$ , a = 17.108(3) Å, b = 10.2932(16) Å, 14.071(2) Å and  $\beta = 118.845(4)^{\circ}$  for **2** at 293 K. Moreover, two salts show similar packing structure, with the arrangements of alternating layer of anions and cations, and the layers are parallel to the crystallographic *ab*-plane. Both **1** and **2** display analogous dielectric behavior, which dielectric permittivity is almost a constant with  $\varepsilon' \approx 12$  at the temperature below 270 K for **1** versus 215 K for **2**, and two steps of dielectric relaxations appear in the higher temperature regime, which originate from the molecular dipole orientation and the ion migration.

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### 1. Introduction

Bis-1,2-dithiolene complexes of transition metals have been widely studied since 1960s. This type of complex has planar and electronically delocalized core, which is comprised of the central metal, four sulfurs and the C=C units (in most cases, the central metal is Ni, Pd or Pt ion), and the unique molecule geometry and electronic structure endow a bis-1,2-dithiolene complex of transition metal with lots of distinctive properties and promising application in the areas of conducting and magnetic materials, dyes, non-linear optics, catalysis and others [1–19].

In the family of bis-1,2-dithiolene complexes of transition metals, it is well known that the salts of  $[M(mnt)_2]^- (mnt^{2-} = maleoni$ triledithiolate) show diverse and novel magnetic and conducting natures [20–28]. The salt  $[NH_4][Ni(mnt)_2] \cdot H_2O$  exhibits Heisenberg antiferromagnetic chain behavior around room temperature and the singlet ground state with the monoanions associated as dimer at low temperatures [20]. Interestingly, this salt, with localized spins, shows long-range ferromagnetic order at the temperatures below 4.5 K and the Curie temperature demarcating the transition to ferromagnetic order abruptly disappears at 6.8 kbar applied pressure [20]. A series of one-dimensional salts, [R-BzPy][M  $(mnt)_2$  (BzPy<sup>+</sup> and R represent the benzylpyridinium and substituent; M = Ni or Pt), display spin-Peierls instability in a wide temperature ranges [29–31], and the significant isotopic effect of spin-Peierls transition temperature is observed in this series of salts [32,33]. In addition, the salt,  $[H_3O]_{0.33}Li_{0.8}[Pt(mnt)_2]$ . 1.67H<sub>2</sub>O, shows metallic properties at room temperature but undergoes the Peierls instability at ca. 220 K to become a semiconductor [34,35] and the non-stoichiometric salt, Cs<sub>0.82</sub>[Pd(mnt)<sub>2</sub>]. 0.5H<sub>2</sub>O, is the first palladium dithiolene complex to exhibit metallic behavior under pressure [21]. In recent years, some novel physical properties have been found in the transition metal bis-1,2-dithiolene complexes [36-38]. For instance, the quantum coherence was observed in  $(PPh_4)_2[Cu(mnt)_2]$  (mnt<sup>2-</sup> = maleonitriledithiolate) doped into the diamagnetic isostructural host  $(PPh_4)_2[Ni(mnt)_2]$  as a very promising quantum bit, and very long quantum coherence times was found of 68 s at low temperature (qubit figure of merit QM = 3400) and 1 s at room temperature,





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much higher than previously reported values for such systems [36].

With respect to  $[M(mnt)_2]^-$  (M = Ni or Pt) salts widely studied, the  $[M(mnt)_2]^{2-}$  salts have been rare investigated. Recently, we have synthesized and characterized a series of salts of  $[Ni(mnt)_2]^{2-1}$ with pyridinium derivatives, and found that the molecule structure and charge of the counter cation strongly influence on the crystal structure and dielectric properties and ionic liquid crystal nature of  $[Ni(mnt)_2]^{2-}$  salts [39,40]. The dielectric phase transition is one of the most attractive features of material since the conversion between the distinct high and low dielectric states has succeeded in photoelectronic fields. As one of the most promising strategies to assemble such a functional material, usually, to design and synthesize molecule compounds with structural transformations effectively acquires the typically temperature-dependent dielectric states. To continuously explore this context, herein, we present our study of the crystal structures and dielectric properties of two [Ni(mnt)<sub>2</sub>]<sup>2-</sup> salts containing noncentrosymmetric organic cations 1,4-dimethyl-DABCO<sup>2+</sup> and TMSF<sup>+</sup>. The two cations maybe show order-disorder structural transformation in their crystals with the temperature changes. Two new salts show similar packing structure and novel dielectric properties.

#### 2. Experimental

#### 2.1. Chemicals and materials

All reagents and chemicals, including 1,4-diazoniabicyclo[2.2.2] octane (abbr. DABCO), trimethylsulfonium bromide (abbr. [TMSF] Br) and iodomethane, were purchased from commercial sources and used without further purification.

Disodium maleonitriledithiolate (Na<sub>2</sub>mnt) was synthesized following the procedure published [41].

The typical process is described for the preparation of (1,4dimethyl-DABCO)I<sub>2</sub>. 1,4-diazabicyclo[2.2.2]octane (112 mg, 1 mmol) was solved in 20 mL acetone, and iodomethane (300 mg, 2.1 mml) was added into the above solution drop by drop and stirring at room temperature. The white precipitate formed gradually, and the mixture was further stirred for 30 min, and the precipitate was separated by suction and washing by absolute ethanol for three times, and dried at 60 °C overnight. Yield ca. 85% (based on DABCO). The final product was characterized by <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz; ref. Fig. S1) with  $\delta$ : 4.8 (s, D<sub>2</sub>O-D), 4.13 (S, 12H, H-CH<sub>2</sub>), 3.43 (S, 6H, H-CH<sub>3</sub>).

# 2.2. Preparation of 1 and 2

#### 2.2.1. [1,4-Dimethyl-DABCO][Ni(mnt)<sub>2</sub>] (1)

A H<sub>2</sub>O solution of Na<sub>2</sub>mnt (186 mg, 1 mmol) was added to a H<sub>2</sub>O solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (120 mg, 0.5 mmol), the mixture was stirred at room temperature for 10 min, and then filtered. To the filtrate was added dropwise a H<sub>2</sub>O solution of (1,4-dimethyl-DABCO)I<sub>2</sub> (200 mg, 0.5 mmol), the immediately formed dark red precipitate was filtered out, washed with H<sub>2</sub>O up to the filtrate being colorless. The precipitate was collected and dried at 60 °C in vacuum for 2 h. Yield ca. 58% (calculation based on NiCl<sub>2</sub>6H<sub>2</sub>O). Calc. for C<sub>16</sub>H<sub>18</sub>N<sub>6</sub>-NiS<sub>4</sub>: C, 39.93; H, 3.770; N, 17.46%; Found: C, 40.00; H, 3.86; N, 17.85%.

### 2.2.2. (TMSF)<sub>2</sub>[Ni(mnt)<sub>2</sub>] (2)

This salt was prepared following a similar process for preparation of **1**, just replaced (1,4-dimethyl-DABCO)I<sub>2</sub> by [TMSF]Br. Yield ca. **77**%. Calc. for  $C_{14}H_{18}N_4NiS_6$ : C, 34.08; H, 3.677; N, 11.36%; Found: C, 33.33; H, 3.73; N, 11.33%. The single crystals suitable for X-ray analysis for **1** and **2** were achieved via a diffusion process, namely, the powdered sample of **1** or **2** were dissolved in the minimum amount of DMF, and absolute ethanol diffuses into the DMF solution of **1** or **2** to give the corresponding crystals.

#### 2.3. Physical measurements

Elemental analyses (C, H and N) were carried out on a Perkin Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm<sup>-1</sup> region. The UV–vis-NIR absorption spectra in solid state were taken using a Shimadzu UV-3100 spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Riga-Ku/max-2550 diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). Thermogravimetric (TG) experiments were performed with a TA2000/2960 thermogravimetric analyzer from 293 K to 1063 K at a heating rate of 20 K min<sup>-1</sup> under a nitrogen atmosphere, and the polycrystalline samples were placed in an aluminum crucible. Differential scanning calorimetry (DSC) was carried out for 1 and 2 on a Pyris 1 power-compensation differential scanning calorimeter with a warming rate of 10 K min<sup>-1</sup> during the heating process. Temperature- and frequency-dependent dielectric permittivity and AC impedance measurements were carried out on a Concept 80 system (Novocontrol, Germany) in 153-403 K and 153-373 K for 1 and 2, respectively. The powdered disc, with a thickness of ca. 1.68 mm (for 1) and 1.36 mm (for 2) as well as a diameter of 7.0 mm, was coated by gold films on the opposite surfaces and sandwiched by platinum electrodes and the AC frequencies span from 1 to  $10^7$  Hz.

#### 2.4. X-ray single crystallography

The single crystal X-ray diffraction data were collected for **1** and **2** with graphite monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) on a CCD area detector (Bruker-SMART). Data reductions and absorption corrections were performed with the SAINT [42] and SADABS [43] software packages, respectively. Structures were solved by direct methods using the SHELXL-97 software package [44]. The non-H atoms were anisotropically refined using the full-matrix least squares method on F<sup>2</sup>. All H atoms were placed at calculated positions and refined riding on the parent atoms. The crystallographic details about data collection and structure refinement are summarized in Table 1.

## 3. Results and discussion

#### 3.1. Crystal structure analysis

Salt **1** crystallizes in monoclinic space group  $C^2/c$ . As shown in Fig. 1a, an asymmetric unit of **1** contains one half of  $[Ni(mnt)_2]^{2-}$  dianion and one half of divalent 1,4-Dimethyl-1,4-diazoniabicy-clo[2.2.2]octane (abbr. Me<sub>2</sub>-DABCO<sup>2+</sup>) cation. The Ni<sup>2+</sup> ion locates at an inversion center, which lead to the NiS<sub>4</sub> core being cofacial in  $[Ni(mnt)_2]^{2-}$ . The  $[Ni(mnt)_2]^{2-}$  has  $C_i$  point group symmetry, and the planar mnt<sup>2-</sup> ligand makes a dihedral angle of 7.8° with the plane of NiS<sub>4</sub> core. Two crystallographically inequivalent Ni-S bond lengths are 2.1753(6) and 2.1780(6) Å, respectively; and the S-Ni-S bite angle is 92.59(2)°. These bond parameters in  $[Ni(mnt)_2]^{2-}$  are comparable to that in other  $[Ni(mnt)_2]^{2-}$  salts reported [39,40]. The Me<sub>2</sub>-DABCO<sup>2+</sup> shows the C<sub>2</sub> point group symmetry, and the twofold rotation axis is parallel to the *b*-axis and passes through the midpoint of a segment connecting N3 and N3#1 with the symmetric code #1 = 1 - x, y, 0.5 - z.

 Table 1

 Crystallographic data and structural refinement data for 1 and 2.

Compound	1	2
Temperature/K	293 K	293 K
Chemical formula	$C_{16}H_{18}N_6NiS_4$	C14H18N4NiS6
Formula weight	481.31	493.40
Wavelength (Å)	0.71073 0.71073	
CCDC numbers	1 841 125 1 841 126	
Crystal system	monoclinic monoclinic	
Space group	C2/c C2/c	
a (Å)	16.9688(8)	17.108(3)
b (Å)	9.3003(5)	10.2932(16)
<i>c</i> (Å)	13.4090(6)	14.071(2)
α (°)	90	90
β(°)	103.244(2)	118.845(4)
γ (°)	90	90
$V(Å^3)/Z$	2059.86(17), (4)	2170.4(6), (4)
$ ho~({ m g} imes { m cm}^{-3})$	1.552	1.510
$F(0\ 0\ 0)$	992	1016
Abs. coeff. (mm <sup>-1</sup> )	1.361 1.477	
θ Ranges (data collection°)	2.4661–27.5287 2.4005–27.4663	
Index range	$-22 \le h \le 18$ $-20 \le h \le 22$	
	$-10 \le k \le 12$	$-10 \le k \le 13$
	$-16 \le l \le 17$	$-18 \leq l \leq 18$
R <sub>int</sub>	0.0264	0.0302
Independent reflections/restraints/parameters	2376/0/126	2496/0/118
Refine method	Full-matrix least-squares	
Goodness-of-fit (GOF) on $F^2$	1.210	1.088
$R_1, wR_2 [I > 2\sigma(I)]$	$R_1 = 0.0377$	$R_1 = 0.0293$
	$wR_2 = 0.0941$	$wR_2 = 0.0712$
$R_1$ , $wR_2$ [all data]	$R_1 = 0.0485$	$R_1 = 0.0421$
	$wR_2 = 0.0985$	$wR_2 = 0.0755$

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



Fig. 1. (a) Molecular structure of 1 and the non-H atoms in an asymmetric unit are labeled (b) packing diagram of 1 viewed along [-100] direction (All H atoms are omitted for clarity).

As shown in Fig. 1b, the  $[Ni(mnt)_2]^{2-}$  anions adopt parallel arrangement to form a layer, which is parallel to the crystallographic *ab*-plane, and the anions in the neighboring layers make an angle of 77.6°. The Me<sub>2</sub>-DABCO<sup>2+</sup> cations locate at the corner made by the neighboring anions.

Salt **2** crystallizes also in monoclinic space group *C*2/*c*. The asymmetric unit of **2** is depicted in Fig. 2a, which contains on TMSF<sup>+</sup> cation and one half of  $[Ni(mnt)_2]^{2-}$  anion. The Ni<sup>2+</sup> ion locates on an inversion center, which gives rise to the NiS<sub>4</sub> being cofacial, and the mean-molecular plane of mnt<sup>2–</sup> ligand makes a dihedral angle of 9.2° with the plane of NiS<sub>4</sub> plane. Two crystallographically different Ni–S bond lengths are 2.1658(5) and 2.1746

(6) Å, respectively, and the bite angle of S–Ni–S is 92.01(2)°. These bond parameters in **2** are rather similar to those in **1**. The TMSF<sup>+</sup> cation shows trigonal pyramid molecule geometry and the C–S bond lengths range from 1.782(2) to 1.786(2) Å, falling within the typical single bond of C–S distances. It is worth noting that the C–S bond distances in TMSF<sup>+</sup> cation is slight longer than that in [Ni(mnt)<sub>2</sub>]<sup>2–</sup> anion, ranging from 1.728(2) to 1.742(2) Å, and this situation is relevant to the fact that the [Ni(mnt)<sub>2</sub>]<sup>2–</sup> anion is a conjugated system and the conjugated effect leads to the single bonds enlarging while the double bonds shortening. As displayed in Fig. 2b, salt **2** shows analogous packing structure to **1**, and the [Ni(mnt)<sub>2</sub>]<sup>2–</sup> anions align into a layer, which is parallel to the



Fig. 2. Molecular packing of (a) and (b) 2 viewed along *b*-axis and *a*-axis, respectively.

crystallographic *ab*-plane, and the anions in the neighboring layers make an angle of  $17.3^{\circ}$ . The TMSF<sup>+</sup> cations locate at the sits near to the CN groups of  $[Ni(mnt)_2]^{2-}$  anions.

# 3.2. IR spectrum

Both IR spectrum of **1** and **2** are displayed in Fig. S2 and the characteristic vibration bands together with the assignments are summarized in Table 2. In the IR spectrum of **1**, an intense absorption band, centered at ca. 2187 cm<sup>-1</sup>, corresponds to the stretching vibration of  $C \equiv N$  in the mnt<sup>2–</sup> ligand. The stretching vibration of  $C \equiv C$  in the mnt<sup>2–</sup> ligand is seen at ca. 1472 cm<sup>-1</sup>. The characteris-

#### Table 2

Characteristic vibration bands (cm<sup>-1</sup>) and assignments in IR of **1** and **2**.

1	2	Assignment [45-47]
2997(w)	3006 (m)	$v_{C-H}$
2199.8(s)	2197(s)	Vc=N
1496(s)	1486(s)	V <sub>C=C</sub>
1414(m)	-	V <sub>C-C</sub>
746(m) and 847(w)	940(w)	$\delta_{C-S}$
	1066(s)	V <sub>C-S</sub>
1148(w)	-	V <sub>C-N</sub>



tic v<sub>C-S</sub> bands locate at 1048 cm<sup>-1</sup> in mnt<sup>2-</sup> ligand. In the Me<sub>2</sub>-DABCO<sup>2+</sup> cation, the stretching vibration bands of C–H appear at ca. 2987 cm<sup>-1</sup>, respectively, and the v<sub>C-N</sub> band is found at ca. 1142 cm<sup>-1</sup>.

Salt **2** shows rather similar IR spectrum to **1**, where the bands of stretching vibration of C=N, C=C and C-S in the mnt<sup>2–</sup> ligand appear at ca. 2196, 1481 and 1039 cm<sup>-1</sup>, and the bands of  $v_{C-H}$  and  $v_{C-S}$  in the cation appear at ca. 3015 and 935 cm<sup>-1</sup> [45–47], respectively.

# 3.3. PXRD and TG analyses

The experimental PXRD patterns of **1** and **2** are displayed in Fig. **3** together with the corresponding theoretically simulated profiles, which are obtained from the single crystal X-ray diffraction data using Mercury 3.0 program. It is found that both the experimental PXRD profiles of **1** and **2** are well agreement with the corresponding simulated PXRD patterns, suggesting that both **1** and **2** have high phase purity.

The TG plots of **1** and **2** in 299–1059 K are displayed in Fig. 4, which revealed that **1** and **2** are thermally stable up to ca. 406 K and ca. 383 K, respectively, indicating that two salts possess poor thermal stability.



Fig. 3. PXRD patterns of (a) 1 and (b) 2, respectively.



Fig. 4. TG plots of (a) 1 and (b) 2, respectively.

#### 3.4. Dielectric properties

The plots of real part of dielectric permittivity ( $\varepsilon'$ ) versus temperature (*T*) and frequency (*f*) are shown in Fig. 5a (Fig. S6a) and Fig. 5b (Fig. S6b) for **1**, respectively. The dielectric permittivity is temperature-independence with  $\varepsilon' \sim 12$  as the temperature is

below 270 K (Figs. 5a and S6a), which indicates the dynamical dipole motion is suppressed in the low temperature regime. With increasing temperature, the dielectric permittivity,  $\varepsilon'$ , rapidly increases and strongly depends on the AC frequency, for example, the  $\varepsilon' \approx 12$  and 60 under the frequency  $1.0 \times 10^7$  Hz and 1 Hz, respectively, at 403 K. The AC frequency dependent dielectric



**Fig. 5.** Plots of (a)  $\varepsilon' - T$  in 153–403 K at the selected frequencies (b)  $\varepsilon' - f$  in 1–10<sup>7</sup> Hz at the selected temperatures for **1** and (c) plots of  $\varepsilon' - T$  in 153–373 K at the selected frequencies (d)  $\varepsilon' - f$  in 1–10<sup>7</sup> Hz at the selected temperatures for **2**.

behavior is due to the dynamical dipole motion being thermally activated in the high temperature region and also reveals the dielectric relaxation occurring in the high temperature region. In Fig. 5b (Fig. S6b), it is more clear that the  $\varepsilon'$  is strongly relevant to the AC frequency at the frequency  $f < 10^5$  Hz, however, the  $\varepsilon'$  tends to a constant at high frequency  $(f > 10^5$  Hz), indicating that the dynamical dipole motion cannot follow the switching of the AC electric field at the frequency higher than  $10^5$  Hz.

The plots of  $\varepsilon'$ –*T* and  $\varepsilon'$ –*f* are depicted in Fig. 5c (Fig. S7a) and Fig. 5d (Fig. S7b) for **2**, respectively. The whole trends of  $\varepsilon'$  against *T* and *f* in **2** are analogous to that in **1**, namely, the  $\varepsilon'$  remains a constant value of 12 and is almost independent on the AC frequency below ca. 215 K, as well as the  $\varepsilon'$  is not significantly affected by temperature change when the AC frequency is higher than 10<sup>6</sup> Hz (as shown in Figs. 5d and S7b). The most distinction of plots of  $\varepsilon'$ –*T* and  $\varepsilon'$ –*f* between **1** and **2** concerns that the dielectric relaxation occurs at lower temperature (ca. 215 K) and higher frequency (10<sup>6</sup> Hz) in **2** than that (ca. 270 K and 10<sup>5</sup> Hz) in **1**, and such differences are probably related to the dynamical dipole motion of different cations in the lattices of **1** and **2**.

The characteristic AC frequency of dielectric relaxation occurred in **1** and **2** falls within the ranges  $<10^6$  Hz, indicating that the dielectric relaxation process underwent in both **1** and **2** arises probably from the molecular dipole orientation, ionic migration, the electrode polarization and space charge injection effect [48]. The molecular dipole orientation and the ion migration, all of which are the intrinsic nature, in a dielectric material, as well as the space charge injection and the electrode polarization effects, which belong to the extrinsic effects and undergo especially in the case at the low-frequency and the high-temperature regimes.

The contribution of electrode polarization and space charge injection effect to total dielectric relaxation process can be significantly reduced if the dielectric relaxation is analyzed using dielectric modulus, as a result, the intrinsic dielectric relaxation can be revealed more clearly. The electric modulus ( $M^*$ ) is calculated by Eq. (1) [49,50],

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = \frac{\varepsilon' - j\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + jM''$$
(1)

where M' and M'' are the real and imaginary parts of the complex modulus  $M^*$ , respectively. Figs. 6a and S6c show the relationship of M''-T in **1** at the selected frequencies, and it is clearly that a serials of round peaks together with a shoulder in the high temperature side locate in the range of  $10^0-10^5$  Hz and 314–403 K, moreover, the maximum of the round peak and the shoulder go towards higher temperature as frequency increasing, which presents typical two-steps of thermal-activated dielectric relaxations in **1**. Since it is hard to determine the exact value of the corresponding temperature at the maximum of peak for a shoulder-shape dielectric relaxation process, only the dielectric relaxation process with the round peaks is further analyzed using Arrhenius equation.



**Fig. 6.** Plots of (a) M''-T in 153-403 K at the selected frequencies (b) plot of  $\ln f - 1000/T$  for **1** and (c) plots of M''-T in 153-373 K at the selected frequencies (d) plots of  $\ln f - 1000/T$  for **2**.



Fig. 7. The short contacts between the (a) Me<sub>2</sub>-DABCO<sup>2+</sup> and (b) TMSF<sup>+</sup> cations with the  $[Ni(mnt)_2]^{2-}$  anions for 1 and 2, respectively.

$$f = f_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{2}$$

In Eq. (2),  $f_0 = 1/\tau_0$  and  $\tau_0$  is the macroscopic relaxation time,  $E_a$ denotes the activation energy of relaxation process, and other symbols in Arrhenius equation have normal meanings. The *f* against *T* is plotted in the form of ln f vs. 1000/T in the range of 314–403 K for the dielectric relaxation process with round peaks in 1, which is displayed in Fig. 6b. The best fit was performed for the plot of  $\ln f$  vs. 1000/*T*, to give the parameters  $E_a = 0.735$  eV and  $\tau_0 = 1.9 \times 10^{-12}$  s for the dielectric relaxation process with round peaks in 1. The plots of M''-T at the selected frequencies in 153– 373 K is shown in Figs. 6c and S7c for 2, indicating clearly two round peaks. This observation demonstrates that 2 has two steps of dielectric relaxations in 153–373 K and 1–10<sup>7</sup> Hz, and the best fit for the corresponding plot of  $\ln f$  vs. 1000/T gave the parameters  $E_a = 0.552 \text{ eV}$  and  $\tau_0 = 2.0 \times 10^{-13} \text{ s}$  for the dielectric relaxation process in the lower temperature region and  $E_a = 0.680 \text{ eV}$  and  $\tau_0 = 7.2 \times 10^{-13}$  s for the dielectric relaxation process in the higher temperature region in 2. The dielectric relaxation activation and macroscopic time in 1 and 2 are comparable to that in other molecule compounds [51] and fall in the typical ranges of the molecular dipole orientation and the ion migration relaxation activation and macroscopic time, further disclosing that the dielectric relaxations in both 1 and 2 originate from the molecular dipole orientation (for example, the dipole orientation of C-H bonds in methyl groups under the applied electrical field in **1** and **2**) and the ion migration (e.g. the relative displacement of cation with the anions under the applied electrical field in 1 and 2).

# 3.5. Correlation analyses between crystal structure and dielectric properties

The electric polarizability represents the tendency of a material to allow an externally applied electric field to induce electrical dipoles (separated negative and positive charges) in a material. The induced electrical dipoles, the externally applied electrical field, and the dielectric permittivity are related by the equation below,

$$Np = \varepsilon_0(\varepsilon_r - 1)E \tag{3}$$

where the symbol p is the induced dipole moment, N represents the density of induced dipoles, and the symbols  $\varepsilon_0$  and  $\varepsilon_r$  represent the permittivity of a material in the free space and the relative dielectric constant, respectively. The relative dielectric permittivity of a mate-

rial corresponds to the induced dipole moment per volume, which is generally related to the crystal structure of a material.

The order–disorder transformation in crystal generally induces the dielectric phase transition [52–55]. Several DABCO<sup>2+</sup> compounds show structural disorder in their crystals, and exhibit ferroelectric behavior [56] and dielectric phase transition [57]. Besides, the hybrid inorganic–organic frameworks containing triethylmethylammonium (Et<sub>3</sub>NMe<sup>+</sup>) and tetramethylphosphonium ((CH<sub>3</sub>)<sub>4</sub>P<sup>+</sup>) cations show above-room-temperature magnetodielectric coupling and switchable dielectric, magnetic, and optical properties [58,59].

In crystal structures of **1** and **2**, the cations Me<sub>2</sub>-DABCO<sup>2+</sup> and TMSF<sup>+</sup> without disorder nature in their crystals result in no obvious anomalies of dielectrics when the temperature changes, which can be further confirmed by DSC analysis in ESI. The cations Me<sub>2</sub>-DABCO<sup>2+</sup> and TMSF<sup>+</sup> are order in 293 K, and the anisotropic displacement parameters of them undertake change with the change of temperature. The anisotropic displacement parameters of the two cations are low, and the dynamical dipole motion of the cations is suppressed in the low temperature regime. Therefore, the dielectric permittivity is temperature-independence with  $\varepsilon' \sim 12$  as the temperature is below 270 K. With increasing temperature, the anisotropic displacement parameters of the two cations become high and the dielectric permittivity rapidly increases and strongly depends on the AC frequency.

Besides, the S···S, N···S, C–H···N and C–H···S short contacts between the cations Me<sub>2</sub>-DABCO<sup>2+</sup> and TMSF<sup>+</sup> and the anions [Ni (mnt)<sub>2</sub>]<sup>2-</sup> were observed in the crystal packing arrangement (Fig. 7a and b). The short contacts between the cations and anions may change with the change of temperature under the applied electrical field. Consequently, the molecular dipole orientation (for example, the dipole orientation of C–H bonds in methyl groups) and the ion migration (the displacement of the cation with the cations) result in the dielectric relaxations in the high-temperature regime.

# 4. Conclusion

In this study, two salts of  $[Ni(mnt)_2]^{2-}$  with two different asymmetric organic cations have been prepared and characterized by single crystal structure. Two salts show analogous packing structure, namely, the  $[Ni(mnt)_2]^{2-}$  anions and the asymmetric cations align into alternating layers, which are parallel to the crystallographic *ab*-plane. Two salts show similar dielectric properties, with frequency independent dielectric permittivity in the low temperature regime and two steps of dielectric relaxations in the high

temperature regime, corresponding to the molecular dipole orientation and the ion migration. The correlation analyses between crystal structure and dielectric properties demonstrated that the dielectric relaxations in the high temperature regime for 1 and 2 originated from the molecular dipole orientation (for example, the dipole orientation of C-H bonds in methyl groups) and the short contacts change between the cations and anions with the change of temperature under the applied electrical field.

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#### Appendix A. Supplementary data

CCDC 1841125 and 1841126 contains the supplementary crystallographic data for 1 and 2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10. 1016/j.poly.2018.08.029.

#### References

- [1] N. Robertson, L. Cronin, Coord. Chem. Rev. 227 (2002) 93.
- [2] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark, A.E. Underhill, Coord. Chem. Rev. 110 (1991) 115.
- [3] P. Cassoux, Coord. Chem. Rev. 185-186 (1999) 213.
- [4] A.E. Pullen, R.-M. Olk, Coord. Chem. Rev. 188 (1999) 211.
- [5] T. Akutagawa, T. Nakamura, Coord. Chem. Rev. 198 (2000) 297.
- [6] E. Canadell, Coord, Chem. Rev. 186 (1999) 629.
- [7] P.I. Clemenson, Coord. Chem. Rev. 106 (1990) 171.
- [8] R. Kato, Chem. Rev. 104 (2004) 5319.
- [9] M. Fourmigué, Acc. Chem. Res. 37 (2004) 179.
- [10] A. Kobayashi, E. Fujiwara, H. Kobayashi, Chem. Rev. 104 (2004) 5243.
- [11] L. Ouahab, Coord. Chem. Rev. 178 (1998) 1501. [12] R.-M. Olk, B. Olk, W. dietzsch, R. Kirmse, E. Hoyer, Coord. Chem. Rev. 117
- (1992) 99.
- [13] R.P. Burns, C.A. McAuliffe, Adv. Inorg. Chem. Radiochem. 22 (1979) 303.
- [14] J.A. McCleverty, Prog. Inorg. Chem. 10 (1968) 49.
   [15] U.T. Mueller-Westerhoff, B. Vance, D.I. Yoon, Tetrahedron 47 (1991) 909.
- [16] M. Tamura, R. Kato, Sci. Technol. Adv. Mater. 10 (2009) 024304. [17] E.B. Lopes, H. Alves, I.C. Santos, D. Graf, J.S. Brooks, E. Canadell, M. Almeida, J.
- Mater, Chem. 18 (2008) 2825. [18] R. Perochon, L. Piekara-Sady, W. Jurga, R. Clérac, M. Fourmigué, Dalton Trans. (2009) 3052.
- [19] E. Tomiyama, K. Tomono, D. Hashizume, T. Wada, K. Miyamura, Bull. Chem. Soc. Jap. 82 (2009) 352.
- [20] A.T. Coomber, D. Beljonne, R.H. Friend, J.L. Bredas, A. Charlton, N. Robertson, A. E. Underhill, M. Kurmoo, P. Day, Nature 380 (1996) 144.
- [21] I.D. Parker, R.H. Friend, P.I. Clemenson, A.E. Underhill, Nature 324 (1986) 547.

- [22] J. Nishijo, E. Ogura, J. Yamaura, A. Miyazaki, T. Enoki, T. Takano, Y. Kuwatani, M. Iyoda, Solid State Commun. 116 (2000) 661.
- [23] A.E. Pullen, C. Faulmann, K.I. Pokhodnya, P. Cassoux, M. Tokumoto, Inorg. Chem. 37 (1998) 6714.
- [24] D. Arcon, A. Lappas, S. Margadonna, K. Prassides, Phys. Rev. B 60 (1999) 4191.
- [25] E. Ribera, C. Rovira, J. Veciana, J. TarreÂs, E. Canadell, R. Rousseau, E. Molins, M. Mas, J.-P. Schoeffel, J.-P. Pouget, J. Morgado, R.T. Henriques, M. Almeida, Chem. Eur. J. 5 (1999) 2025.
- [26] J.C. Dias, X. Ribas, J. Morgado, J. Seica, E.B. Lopes, I.C. Santos, R.T. Henriques, M. Almeida, K. Wurst, P. Foury-Leylekian, E. Canadell, J. Vidal-Gancedo, J. Veciana, C. Rovira, J. Mater. Chem. 15 (2005) 3187.
- [27] X. Ribas, A. Sironi, N. Masciocchi, E.B. Lopes, M. Almeida, J. Veciana, C. Rovira, Inorg. Chem. 44 (2005) 2358.
- [28] R.A.L. Silva1, M.L. Afonso1, I.C. Santos1, D. Belo1, R.R. Freitas1, E.B. Lopes1, J.T. Coutinho1, L.C.J. Pereira, R.T. Henriques, M. Almeida, C. Rovira, Phys. Status Solidi C 9 (2012) 1134.
- [29] H.B. Duan, X.M. Ren, Q.J. Meng, Coord. Chem. Rev. 254 (2010) 1509.
- [30] J.L. Xie, X.M. Ren, Y. Song, W.W. Zhang, W.L. Liu, C. He, Q.J. Meng, Chem. Commun. (2002) 2346.
- X.M. Ren, Q.J. Meng, Y. Song, C.S. Lu, C.J. Hu, X.Y. Chen, Inorg. Chem. 41 (2002) [31] 5686.
- [32] G.J. Yuan, S.P. Zhao, C. Wang, X.M. Ren, J.L. Liu, Chem. Commun. 47 (2011) 9489
- [33] G.J. Yuan, S.P. Zhao, C. Wang, J.L. Liu, X.M. Ren, Chem. Asian J. 8 (2013) 611.
- [34] A.E. Underhill, M.M. Ahmad, J. Chem. Soc. Chem. Commun. (1981) 67. [35] M.M. Ahmad, D.J. Turner, A.E. Underhill, C.S. Jacobsen, K. Mortensen, K. Carneiro, Phys. Rev. B 29 (1984) 4796.
- [36] K. Bader, D. Dengler, S. Lenz, B. Endeward, S.D. Jiang, P. Neugebauer, J. Slageren. Nat. Commun. 5 (2014) 5304.
- [37] J.M. Zadrozny, J. Niklas, O.G. Poluektov, D.E. Freedman, ACS Cent. Sci. 1 (2015) 488.
- [38] L. Escalera-Moreno, N. Suaud, A. Gaita-Ariño, E. Coronado, J. Phys. Chem. Lett. 8 (2017) 1695
- [39] Y. Chen, J.L. Liu, S.P. Zhao, W.H. Ning, X.M. Sun, X.M. Ren, RSC Adv. 4 (2014) 9178
- [40] H.B. Duan, X.M. Ren, J.L. Liu, Soft Mater. 12 (2014) 166.
- [41] A. Davison, R.H. Holm, Inorg. Synth. 10 (1967) 8.
- [42] Bruker, APEX 2, SAINT, XPREP, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
  - [43] Bruker, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
  - [44] G.M. Sheldrick, SHELXS97 and SHELXL97. Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.
  - [45] C.W. Schläpfer, K. Nakamoto, Inorg. Chem. 14 (1975) 1338.
  - [46] X.R. Chen, C. Xue, S.X. Liu, B. Cai, J. Wang, J.Q. Tao, Y.S. Xue, X.C. Huang, X.M. Ren, J.L. Liu, Polyhedron 132 (2017) 12.
  - [47] X.R. Chen, X.Y. Xu, X.C. Huang, F.F. Ren, J. Wang, S.X. Liu, C. Xue, J.Q. Tao, Polyhedron 147 (2018) 55.
  - [48] Q. Chen, P.C. Guo, S.P. Zhao, J.L. Liu, X.M. Ren, CrystEngComm 15 (2013) 1264. [49] P.B. Macedo, C.T. Moynihan, R.A. Bose, Role of ionic diffusion in polarization,
  - Phys. Chem. Glasses 13 (1972) 171.
  - [50] F.S. Howell, R.A. Bose, P.B. Macedo, C.T. Moynihan, Electrical relaxation in a glass-forming molten salt, J. Phys. Chem. 78 (1974) 639.
  - [51] K.M. Wan, Y.B. Tong, L. Li, Y. Zou, H.B. Duan, J.L. Liu, X.M. Ren, New J. Chem. 40 (2016) 8664.
  - [52] W. Zhang, Y. Cai, R.G. Xiong, H. Yoshikawa, K. Awaga, Angew. Chem., Int. Ed. 122 (2010) 6758.
  - [53] D.W. Fu, W. Zhang, H.L. Cai, J.Z. Ge, Y. Zhang, R.G. Xiong, Adv. Mater. 23 (2011) 5658.
  - [54] S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai, Y. Tokura, Nature 463 (2010) 789.
  - [55] R. Shang, G.C. Xu, Z.M. Wang, S. Gao, Chem, Eur. J. 20 (2014) 1146.
  - [56] M. Szafrański, A. Katrusiak, G.J. McIntyre, Phys. Rev. Lett. 89 (2002) 215507.
  - [57] W.H. Ning, L. Zhai, X.M. Ren, RSC Adv. 4 (2014) 30993.
  - [58] H.L. Cai, Y. Zhang, D.W. Fu, W. Zhang, T. Liu, H. Yoshikawa, K. Awaga, R.G. Xiong, J. Am. Chem. Soc. 134 (2012) 18487.
  - [59] P.P. Shi, Q. Ye, Q. Li, H.T. Wang, D.W. Fu, Y. Zhang, R.G. Xiong, Chem. Mater. 26 (2014) 6042.