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Abstract

We report the infrared (IR) and Raman study of the 2:1 mixed-stack charge transfer salt $(EDT\text{-}TTF\text{-}I_2)_2TCNQF$, where EDT-TTF = ethylenedithiotetrathiafulvalene and TCNQ = tetracyanoquinodimethane, which undergoes a temperature induced neutral-ionic phase transition. Polarized infrared (IR) and Raman spectra of single crystals were measured in the 8-293 K temperature range. Temperature variations of vibrational modes that are assigned to both donors and acceptors show that the average degree of charge-transfer is growing continuously from about zero at room-temperature to about $1e$ at T = 8 K, nevertheless at about 100 K a regime change is observed. The coexistence of molecular species of different ionicity is detected in the whole temperature range. The IR vibrational features due to electron-molecular vibrational coupling increase their intensities considerably upon cooling giving an evidence of relatively small gradual distortions of crystal structure. Existence of ferroelectric domains is suggested. A scheme of the neutral-ionic phase transition in a 2:1 complex is proposed and discussed.

Introduction

Low dimensional organic charge-transfer (CT) salts provide a variety of structural and physical properties, which originate from strong electron correlations, intrinsic instabilities and an interplay between charge/spin and lattice degrees of freedom [1–3]. In particular, quasi-one dimensional mixed-stack CT crystals composed of π-electron donor (D) and acceptor (A) molecules alternating along a stack (...DADA...) attract much attention due to a possible neutral-ionic phase transition (NIT) [4,5]. Temperature- or pressure-induced increase of molecular ionicity (ρ) in these materials is the result of the competition between effective ionization energy of a DA pair and the long range electrostatic energy gained by the ionized lattice (Madelung energy). Passage from quasi-neutral (ρ<0.5e) to quasi-ionic state (ρ>0.5e) manifests itself by a change of CT degree and a dimerization distortion (...$D^{+\rho}A^{-\rho}$ $D^{+\rho}A^{-\rho}$ $D^{+\rho}A^{-\rho}$...) along the stacking axis. Therefore, the NIT transition can be presented as a complex interplay between the average site ionicity ρ and the stack dimerization δ. The ionicity may display a discontinuous change at critical temperature (T_c). Such a jump of ρ is favored by inter-site energy (V) and electron-molecular vibration (EMV) coupling which modulates the on-site energy (U). On the other hand, hopping integral (t) along the stack favors continuous ionicity change. The stack dimerization observed in the wide temperature range is then a result of coupling of electrons to lattice phonons. The NIT is associated to many intriguing phenomena like a dramatic increase in electrical conductivity and dielectric constant [5]. Among the methods used for investigations of the NIT, vibrational spectroscopy is one of the most reliable because it allows one to directly determine the charge on the donor and acceptor molecules based on its stretching modes [6,7]. The spectroscopy is also sensitive to the symmetry breaking associated with the stack distortions, that yields the intensity increasing of totally symmetric modes due to the EMV-coupling [8,9].

Tetrathiafulvalene-p-chloranil (TTF-QCl_4) is the prototypical material which exhibits the neutral-ionic phase transition [10]. There is a number of known NIT crystals with 1:1 stoichiometry [5,11]. Some of them are variants of TTF-QCl_4 like dimethyltetrathiafulvalene-chloranil (DMTTF-QCl_4), [12] DMTTF-QBr_xCl_{4-x} [13], and $TTF_{1-x}TSF_xQCl_4$ [14] where TSF = tetraselenofulvalene. Tetramethylbenzidine-

TCNQ[15,16], is another example of material with the discontinuous ionicity change. On the contrary to the TTF-QCl_4 salt with a first order NIT transition[17], the DMTTF-QCl_4 salt exhibits a second order phase transition with continuous change of ρ upon cooling[18]. A continuous ionicity change with T at ambient pressure has been observed in 2-chloro-5-methyl-p-phenylenediamine-2,5-dimethyl-dicyanoquinonediimine (ClMePD-DMeDCNQI)[19] where the enhancement of the stack dimerization under cooling is regarded as a driving force of the phase transition[20].

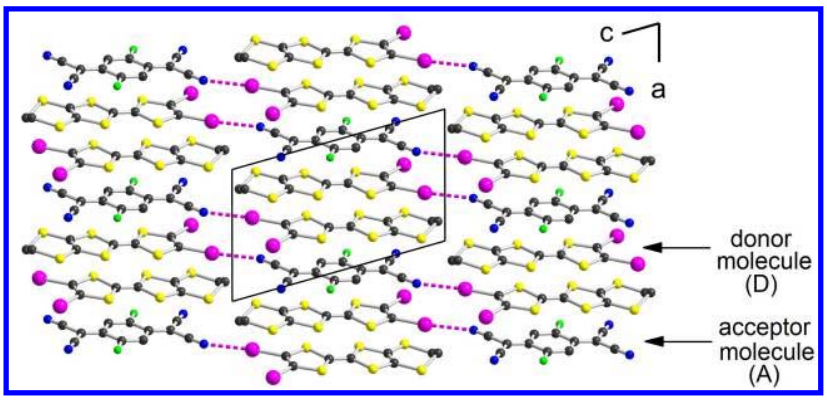

Figure 1: Projection view along *b* axis of the extended unit cell of (EDT-TTF-I_2)$_2$TCNQF, showing the alternated ...ADDADDA... stacks. The pink dotted lines indicate the halogen bond interaction between iodine and nitrogen atoms. The single fluorine atom is disordered on two positions related by inversion center.

Recently, for the first time the temperature-induced neutral-ionic phase transition has been reported in the (EDT-TTF-I_2)$_2$TCNQF mixed-stack charge-transfer complex characterized by 2:1 stoichiometry, formed by iodinated ethylenedithiotetrathiafulvalene (EDT-TTF-I_2) and tetracyanoquinodimethane derivative (TCNQF)[21]. The complex crystallizes in the triclinic system, space group $P\bar{1}$ with two TCNQF molecules on inversion centers and four EDT-TTF-I_2 molecules in general positions in the unit cell. Dyads of donor molecules in the "head-tail" configuration alternate with acceptor molecules along *a*-*b* axis. The resulting stacks (...ADDADDA...) interact with each other to form layers (Fig. 1). On the other hand, EDT-TTF-I_2 molecules link with TCNQF molecules along the *c* axis, by highly directional C$-$I$\cdots$N$\equiv$C halogen bonds. Infrared spectra of (EDT-TTF-I_2)$_2$TCNQF in the C$\equiv$N stretching vibration range of TCNQF molecule provided an evidence that the salt undergoes NIT transition with lowering temperature[21]. Based on the X-ray data, it has

been shown that the molecular ionicity increasing in (EDT-TTF-I_2)$_2$TCNQF does not induce a structural transition such as the loss of an inversion center, but is associated with a halogen bond strengthening and unit-cell contraction.

Here, we present a detailed spectral analysis of temperature induced neutral-ionic phase transition in the (EDT-TTF-I_2)$_2$TCNQF salt of 2:1 stoichiometry. In the first section of Results and Discussion, we compare the reflectance and absorbance spectra of (EDT-TTF-I_2)$_2$TCNQF in the broad frequency range at 8 and 293 K. In the second section, we concentrate on the origin of the temperature induced neutral-ionic phase transition in (EDT-TTF-I_2)$_2$TCNQF. The totally symmetric donor and acceptor modes, which are activated in the infrared spectra, show that molecular charge enhancement is associated with structure distortion. In the last section, we estimate the ionicity ρ based on the charge-sensitive stretching vibrations of the EDT-TTF-I_2 molecule. We show that ρ in (EDT-TTF-I_2)$_2$TCNQF gradually increases upon cooling, with remarkable enhancement below about 100 K. Our overall goal is to clarify the unknown aspects of the neutral-ionic phase transition in this mixed-stack material of 2:1 stoichiometry.

Experimental

Single crystals of (EDT-TTF-I_2)$_2$TCNQF were synthesized and crystallized according to a procedure described previously[21]. Typical dimensions of the elongated plates used in measurements were $0.5\times0.2\times0.02$ mm^3. The optical axes of the sample were determined as those displaying the largest reflectance anisotropy. The infrared spectra were measured along the *a*-*b* and *a*+*b* axes, that are nearly parallel and nearly perpendicular to the stacking direction, respectively. The polarized reflectance (from 600 to 12000 cm^{-1}) and transmittance (from 600 to 4000 cm^{-1}) spectra were recorded with a resolution of 4 cm^{-1} using a Bruker Equinox 55 FT-IR spectrometer equipped with a Hyperion 1000 infrared microscope and a set of suitable polarizers. The absolute values of reflectance were obtained using an aluminum mirror. The optical conductivity was calculated using Kramers-Krönig transformation of the reflectance data[22]. In the low frequency range, the data

were extrapolated assuming constant value appropriate for insulators, and in the high frequency range, the data were extrapolated assuming a ω^{-2} behavior (up to 10^6 cm^{-1}) and a ω^{-4} behavior (for higher frequencies). Raman spectra for the electric field vector of the laser beam polarized parallel to a+b axis were measured from 100 - 2300 cm^{-1} in a backscattering geometry with a Raman LABRAM HR800 spectrometer equipped with a microscope. Laser line of the 632.8 nm (He-Ne) was used with power reduced below 0.1 mW to avoid sample overheating. The spectra were recorded with a spectral resolution of 2 cm^{-1}.

Variable temperature IR and Raman spectra were measured with the help of a continuous-flow cold-finger cryostat manufactured by the Oxford Instruments. A good thermal contact between cold-finger and the sample was fulfilled using vacuum grease. The spectra were collected at several temperatures from 296 to 8 K. The rate of cooling/heating was 1 K/min. The complex vibrational features in the optical conductivity and transmittance spectra were decomposed by standard peak fitting techniques that allow to extract the center frequency and the integral intensity (oscillator strength). The oscillators were fitted using the Voigt spectroscopy function in the PeakFit program[23].

The theoretical calculations of normal vibrational modes for the TCNQF molecule with the charges 0 or -1e were performed with Gaussian 03[24], using the 6-31G(d) basis set and the hybrid Hartree-Fock density functional (B3LYP). The results of the structure optimization correspond to energy minima since no imaginary frequencies were found. C_1 symmetry of the molecule was identified at the level of the theory. On the basis of the optimized structure, the vibrational frequencies and Raman activities were calculated. The Raman activity was transformed to Raman intensity[25]. The frequencies computed with a quantum harmonic approximation tend to be higher than the experimental ones. Therefore the scaling factor 0.9614 has been used[26].

Results and discussion

Infrared spectra at 8 and 293 K

Figure 2 shows room-temperature and 8 K infrared spectra of single crystals of (EDT-TTF-I_2)$_2$TCNQF polarized along two mutually perpendicular directions in the frequency range 700 - 9000 cm^{-1}. The optical response of the material is characterized by a significant reflectance anisotropy. In the

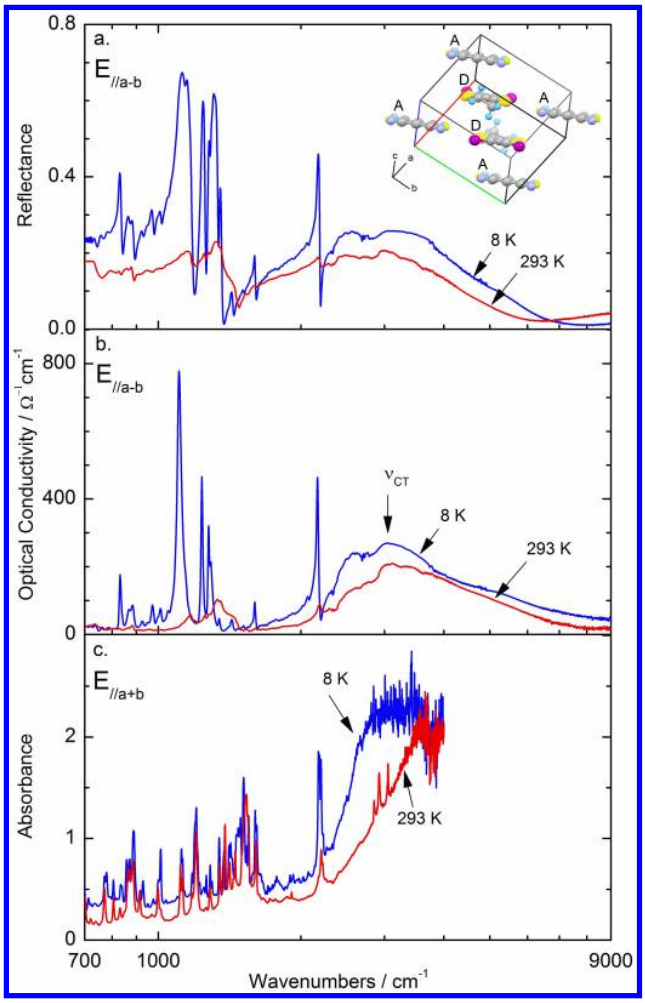

Figure 2: (a) Infrared reflectance spectra of (EDT-TTF-I_2)$_2$TCNQF at 293 K and 8 K polarized parallel to the stack; inset displays a schematic view of a single stack; (b) polarized optical conductivity spectra derived from the reflectance by the Kramers-Krönig transformation; ν_{CT} mark the position of the mid-infrared charge-transfer band; (c) infrared absorption spectra of (EDT-TTF-I_2)$_2$TCNQF at 293 K and 8 K polarized perpendicular to the stack (note the logarithmic frequency scale).

direction of the highest reflectance value, that is nearly parallel to *a*-*b* axis (stacking direction), we show the reflectance spectra (Fig. 2a), and in the *a*+*b* direction, we show the transmittance spectra (Fig. 2c).

The room-temperature reflectance spectrum polarized E||*a*-*b* displays semiconducting behavior, with the reflectance level of about 0.25 at low frequency and the reflectance edge at about 6500 cm^{-1} (Fig. 2a). In the 700 - 2300 cm^{-1} frequency range we observe rather weak and broad vibrational modes of EDT-TTF-I_2 and TCNQF molecules, activated due to the EMV-coupling[27–29]. Between 293 K and 8 K, the overall reflectance level increases slightly in the whole frequency range, and the reflectance edge is shifted about 1500 cm^{-1} toward higher frequencies. At the same time, we see a significant intensity enhancement of vibrational modes. The optical conductivity spectra of (EDT-TTF-I_2)$_2$TCNQF, obtained from the E||*a*-*b* reflectance spectra through the Kramers-Krönig transformation are shown in Fig. 2b. The room-temperature spectrum polarized in the stacking direction is dominated by the broad mid-infrared electronic band centered at around 3000 cm^{-1} that is attributed to a superposition of two charge transfer excitations, between the dyads of EDT-TTF-I_2 and TCNQF molecules and between the EDT-TTF-I_2 molecules themselves (Fig. 2b). Frequency of the maximum of the electronic CT band along stacking direction does not change much between 293 K and 8 K (Fig. 2b); a relatively small intensity increase and band broadening is found. On the other hand, in the spectra polarized perpendicularly to the stacking direction (E||*a*+*b*), the electronic band attributed to a side-by-side CT between EDT-TTF-I_2 and TCNQF is partially observed between 3000 and 4000 cm^{-1} (Fig. 2c). The measured crystals were not thin enough to perform transmittance investigations in higher frequency range.

Vibrational features observed both in the optical conductivity (E||*a*-*b*) and the transmittance spectrum (E||*a*+*b*) of (EDT-TTF-I_2)$_2$TCNQF in the range between 700 and 2300 cm^{-1} are related to both TCNQF and EDT-TTF-I_2 molecules. In the optical conductivity spectrum in the stacking direction, vibrational bands are rather broad and weak at room-temperature. These bands are mostly the consequence of the EMV-coupling. Between 293 K and 8 K, the most prominent EMV-coupled modes of EDT-TTF-I_2 and TCNQF molecules dramatically increase their intensity

and shift toward lower frequencies, as expected for a compound undergoing the neutral-ionic transition. On the other hand, vibrational bands in the absorbance spectrum in the interstack E||a+b direction are relatively narrow. These are mostly IR active modes of both TCNQF and EDT-TTF-I_2 but bands related to coupling with side-by-side CT transition are also possible. Temperature evolution of vibrational modes in (EDT-TTF-I_2)$_2$TCNQF, that is related with the changes of molecular ionicity and stack distortion, will be discussed in detail in the following sections.

Neutral-ionic phase transition

The structure of the mixed-stack CT materials is intrinsically unstable towards lattice distortion upon approaching an ionic phase with lowering temperature[2,3]. Such structural distortions are usually evidenced by intensity enhancement of the totally symmetric molecular vibrations, that are activated in the infrared spectra due to EMV-coupling[8,9]. Here, we focus on the C≡N stretching TCNQF modes in the spectral range 2100-2250 cm^{-1}, where no EDT-TTF-I_2 vibrational modes are present. It is known, that the C≡N stretching modes are charge-sensitive, so they are useful to molecular charge estimation[30–32]. As shown in our previous paper[21], investigations of these modes give an unambiguous evidence of the neutral-ionic phase transition. However, it should be also taken into account, that the C≡N stretching modes are sensitive to molecular environment like electrostatic potential and hydrogen (halogen) bonding[20,33]. This is particularly important from the point of view of relatively strong halogen bond interaction in (EDT-TTF-I_2)$_2$TCNQF[21].

Figure 3a shows the optical conductivity spectra of (EDT-TTF-I_2)$_2$TCNQF in the C≡N stretching region, polarized along stacking direction (E||a-b) at selected temperatures. The relatively weak and broad mode observed at about 2190 cm^{-1} at room-temperature is the counterpart of totally symmetric TCNQ mode $\nu_2(a_g)$, that is activated in the infrared spectra due to EMV-coupling. Schematic view of the mode, that we denote here as ν_g^A, is shown as the inset in Fig. 3b. During cooling from room-temperature down to about 100 K, maximum of the ν_g^A band centered at 2192 cm^{-1} at 293 K shifts continuously toward lower frequencies of about 25 cm^{-1} (Fig. 4a); below about 100 K, the band position changes slightly reaching 2166 cm^{-1} at 8 K. Softening of the ν_g^A

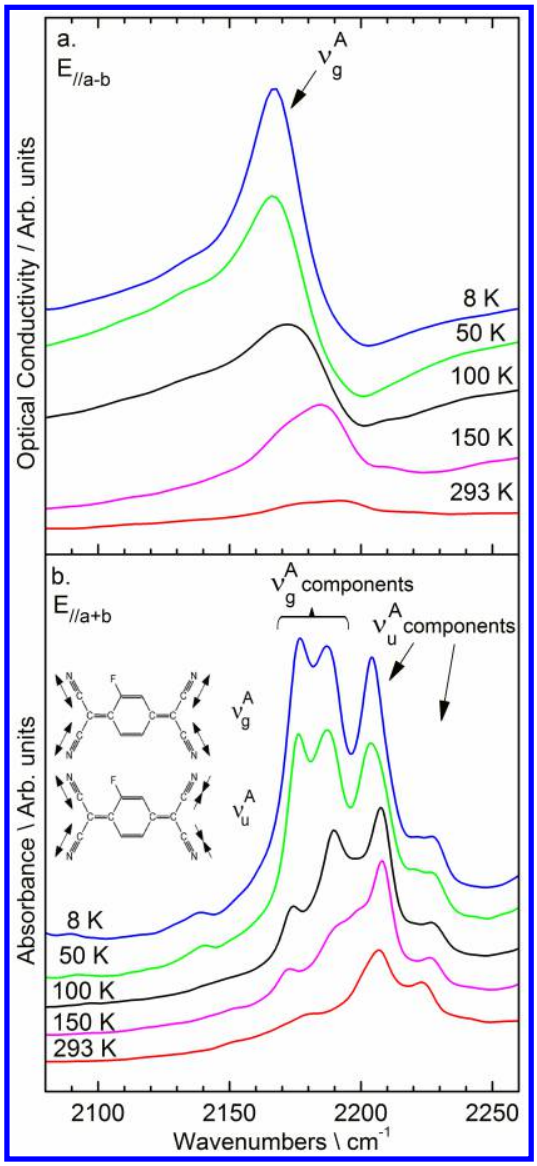

Figure 3: (a) IR optical conductivity and (b) absorbance spectra of (EDT-TTF-I_2)$_2$TCNQF in the frequency range of the stretching C≡N vibration at selected temperature (adopted from Ref.[21]).

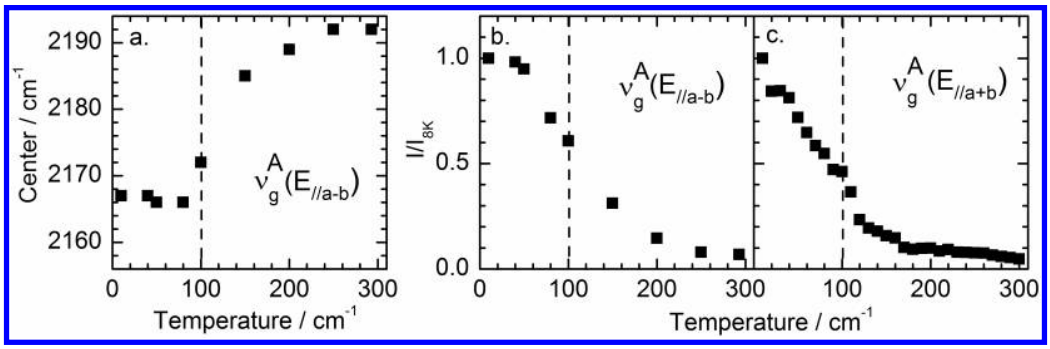

Figure 4: (a) Temperature evolution of the frequency of the TCNQF ν_g^A band observed in the optical conductivity spectra; (b) temperature dependence of the ν_g^A intensity normalized to the low-temperature value; (c) temperature evolution of the normalized intensity of the 2175 and 2185 cm^{-1} components of the C≡N spectral features observed in the absorbance spectra.

mode is mostly caused by the ionicity variation and the EMV-coupling. At the same time, we observe significant intensity enhancement of the ν_g^A band. As shown in Fig. 4b, intensity of ν_g^A (normalized to the 8 K value) increases gradually with lowering temperature. Such a temperature dependence of the mode intensity in (EDT-TTF-I_2)$_2$TCNQF, suggests a continuous increase of structure distortion in the *a*-*b* direction due to the neutral-ionic phase transition.

Figure 3b shows the absorbance spectra of (EDT-TTF-I_2)$_2$TCNQF in the C≡N stretching range, polarized perpendicular to the stacking direction (E$\|$*a*+*b*) at selected temperatures. In this frequency range, we observe a broad multi-component spectral feature, with four strongest components at about 2175, 2185, 2207 and 2223 cm^{-1} at room-temperature. Two bands observed at 2207 and 2223 cm^{-1} are assigned to two components of normally infrared active C≡N mode of TCNQF, that is counterpart of the unsymmetrical TCNQ $\nu_{19}(b_{1u})$ mode. Schematic view of the TCNQF mode, that we denote here as ν_u^A, is shown as the inset in Fig. 3b. The higher-frequency feature at 2223 cm^{-1} is assigned to ν_u^A mode of neutral TCNQF molecules. The band at 2207 cm^{-1} is related to ν_u^A which corresponds to small number of ionized $TCNQF^-$ molecules that can exist in the crystal at room-temperature. When temperature decreases the intensity of the $TCNQF^-$ band at 2207 cm^{-1} strongly grows giving thus a clear evidence of the neutral-ionic transition[21]. With decreasing temperature, two other bands grow at around 2175 and 2185 cm^{-1}, which can be related to the ν_g^A mode activated due to EMV-coupling. Fig. 4c shows temperature depen-

dence of the normalized integral intensity of the 2175 and 2185 cm^{-1} components of the broad C≡N stretching band in the absorbance spectra. As one can notice, we observe similar behavior as shown in Fig. 4b for the ν_g^A mode in E||*a*-*b* polarization. Therefore, the intensity enhancement of the ν_g^A components of the C≡N band in the spectra polarized perpendicular to the stacking direction is also related with a structure distortion that appears parallel to stacking direction (E||*a*-*b*). In this case the ν_g^A mode interacts most probably with the side-by-side CT, therefore temperature dependence of the ν_g^A suggests that it exists a relatively small distortion in the direction perpendicular to the stacks but it is significantly smaller than in the *a*-*b* direction. In fact, CT interaction in the mixed-stack materials is highly sensitive to a subtle structural change[30]. The doublet structure of the band can be interpreted as an indication that in the crystal exist molecules with different charges. The two components at 2175 and 2185 cm^{-1} can be related to $TCNQF^-$ and $TCNQF^0$ molecules, respectively.

Figures 5a, 5b and 6 show optical conductivity (E||*a*-*b*), absorbance (E||*a*+*b*) and Raman (E||*a*+*b*) spectra of (EDT-TTF-I_2)$_2$TCNQF in the frequency range 1000-1700 cm^{-1}, where both donor and acceptor bands are seen. Here, we analyze the stretching vibrations of TCNQF that are activated in the infrared spectra due to EMV-coupling. We assign the band at about 1170 cm^{-1} in the optical conductivity spectrum at room-temperature (Fig. 5a) to C−F and C−C stretching vibration of TCNQF, as shown in the inset in Fig. 7b. Here, we denote this mode as ν_a^A. For this polarization the 1170 cm^{-1} band has a clear doublet structure in the whole temperature range but the intensity of lower-frequency component grows stronger on cooling down. Analogously, the ν_a^A band has also a doublet structure in the absorption spectra polarized in the direction E||*a*+*b*, centered at 1177 and 1204 cm^{-1} (Fig. 5b) and in the Raman spectrum at 1177 and 1194 cm^{-1} at room-temperature (Fig. 6). Similar behavior to the ν_a^A band is also observed in the case of another TCNQF mode at 1605 cm^{-1} in the optical conductivity spectrum (E||*a*-*b*), which we assign to the totally symmetric C=C stretching vibration of the TCNQF ring, as shown in the inset in Fig. 7d. Here, we denote this band as ν_b^A. In the spectra polarized perpendicularly to the stack, the ν_b^A features are centered at 1607 and 1614 cm^{-1} in the absorbance spectrum (Fig. 5b) and at 1608

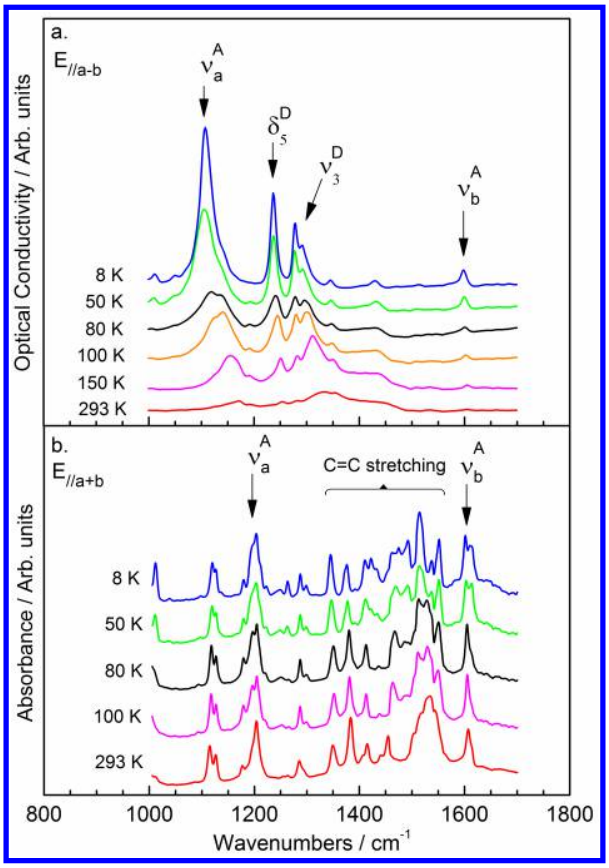

Figure 5: (a) IR optical conductivity, (b) absorbance spectra of (EDT-TTF-I_2)$_2$TCNQF in the 1000-1700 cm^{-1} frequency range at selected temperatures.

and 1612 cm^{-1} in the Raman spectrum (Fig. 6). We suggest that the doublet structure of the TCNQF bands in (EDT-TTF-I_2)$_2$TCNQF is due to coexistence of two species of TCNQF molecules of different ionicity.

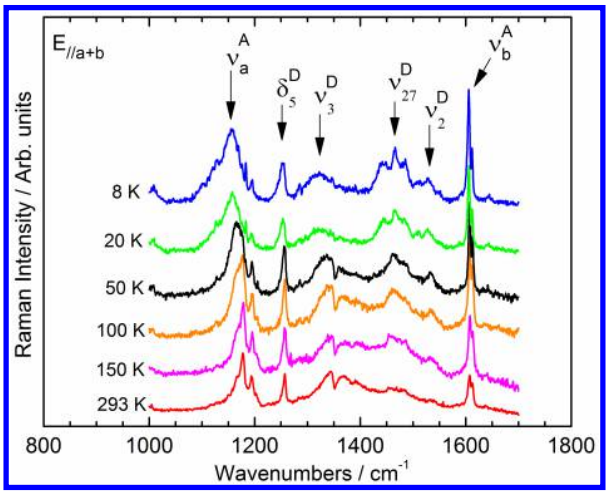

Figure 6: Raman spectra of (EDT-TTF-I_2)$_2$TCNQF in the 1000-1700 cm^{-1} frequency range at selected temperatures.

As results from our DFT calculations[34], when TCNQF molecule is ionized the frequencies of the ν_a^A and ν_b^A modes shift towards lower frequencies by 16 and 21 cm^{-1}, respectively. Upon cooling, maximum of the EMV-coupled ν_a^A mode shifts gradually from 1171 cm^{-1} at 293 K to 1107 cm^{-1} at 8 K (Fig. 7a) due to molecular ionicity variation and lattice distortion. At the same time, the ν_a^A band increases intensity (Fig. 7b), what is an indication of the structure distortion in (EDT-TTF-I_2)$_2$TCNQF. On the other hand, the ν_a^A band in the Raman spectrum exhibits moderate temperature changes down to about 100 K and then it shifts from 1176 cm^{-1} at 100 K to 1155 cm^{-1} at 8 K (Fig. 7a). The red-shift of ν_a^A in the Raman spectra is associated mostly with the ionicity change of TCNQF molecules. Frequency of the ν_b^A mode is also sensitive to ionicity variation in (EDT-TTF-I_2)$_2$TCNQF. The ν_b^A band shifts from 1607 cm^{-1} at 293 K to 1598 cm^{-1} at 8 K in the optical conductivity spectra (E||*a*-*b*). Only the 1607 cm^{-1} component of ν_b^A is temperature dependent in the absorbance spectra (E||*a*+*b*). Upon cooling, it shifts 6 cm^{-1} toward lower frequencies (Fig. 7c). At the same time, the ν_b^A band increases the intensity with lowering temperature (Fig. 7d). The temperature dependence of a band intensity that is similar to ν_a^A and

ν_b^A bands is also observed for C−S stretching band of EDT-TTF-I_2 at around 1000 cm^{-1} (see Fig. 9c).

In the whole temperature range we observe bands related to $TCNQF^-$ ions and to $TCNQF^0$ neutral molecules but on temperature decreasing the $TCNQF^-$ bands considerably grow as expected for neutral-ionic transition. Our analysis of the C≡N, C=C and C−S stretching modes shows that the transition in (EDT-TTF-I_2)$_2$TCNQF is related with the structure distortions both in the direction parallel (E||*a*-*b*) and perpendicular (E||*a*+*b*) to the stacks. The ionicity and lattice distortion change continuously with temperature decreasing, however these changes become stronger below about 100 K, i. e. there is an important regime change at this temperature. In case of the EDT-TTF-I_2 modes, δ_5^D is related to the bending vibration of CH_2 groups of EDT-TTF-I_2 molecules. Temperature dependence of the frequency and intensity of δ_5^D and other EDT-TTF-I_2 modes, like ν_3^D, ν_2^D and ν_{27}^D (corresponding to stretching C=C vibrations) are similar to the temperature behavior of TCNQF modes (Figs. 5a, 5b, 6).

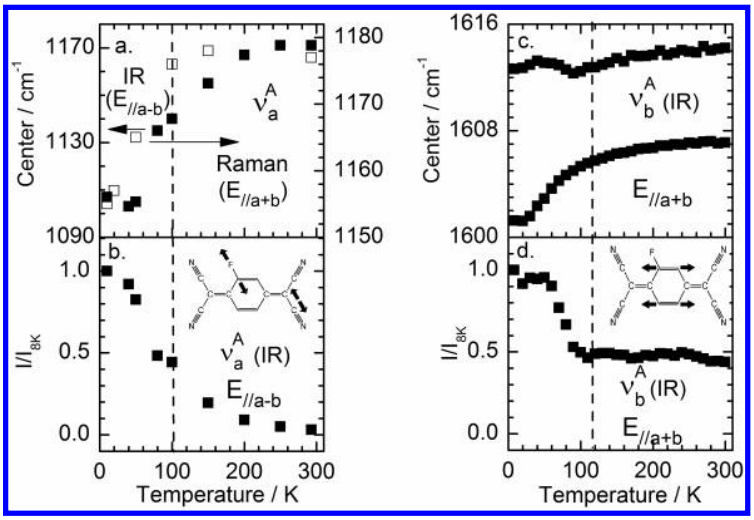

Figure 7: (a) Temperature evolution of the frequency of the TCNQF ν_a^A band observed in the optical conductivity spectra (■) and in the Raman spectra (□); (b) temperature dependence of the intensity (normalized to 8 K value) of the TCNQF ν_a^A band observed in the optical conductivity spectra; (c) temperature evolution of the frequencies of the two components of the TCNQF ν_b^A band observed in the absorbance spectra; (d) temperature dependence of the intensity (normalized to 8 K value) of the TCNQF ν_b^A doublet band observed in the absorbance spectra.

Figure 8 shows Raman spectra of (EDT-TTF-I_2)$_2$TCNQF polarized in E||*a*+*b* in the frequency

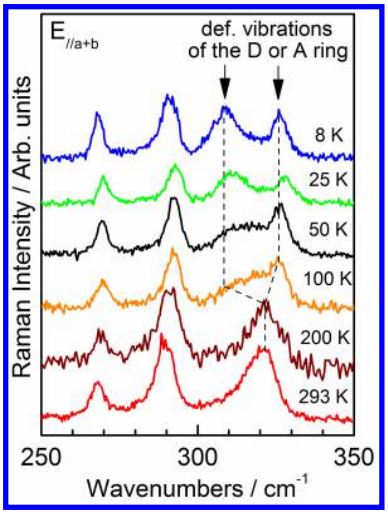

Figure 8: Raman spectra of (EDT-TTF-I_2)$_2$TCNQF in the range of the deformation vibrations of the donor and acceptor molecules at selected temperatures.

range 250-350 cm^{-1} at selected temperatures. We assign the bands at 268 and 290 cm^{-1} at room-temperature to deformation vibrations of EDT-TTF-I_2 rings[6]. The band at 320 cm^{-1}, that can be related to deformation modes of the TCNQF or EDT-TTF-I_2 splits in two components at 309 and 326 cm^{-1} with lowering the temperature. Significant changes of vibrational features in the low frequency Raman spectra of low-dimensional CT salts are usually related to structural transition. Thus, we suggest that the band splitting at around 100 K in (EDT-TTF-I_2)$_2$TCNQF is due to structure distortion.

Estimation of the charge on EDT-TTF-I_2

The most important parameter to discuss the neutral-ionic phase transition is the ionicity ρ of donor and acceptor molecules in the whole temperature range. In Ref.[21], the actual degree of charge transfer ρ was tentatively estimated from the evolution of the intramolecular bond lengths within the TCNQF molecule to exceed 0.5e. The evolution of the N$\cdots$I halogen bond distances with temperature indicate a larger charge transfer, closer to 0.7-0.8e. A more quantitative analysis based on the evolution of the C$\equiv$N stretching frequencies was not attempted at that time since, as mentioned above, these modes can be perturbed by the molecular environment and particularly

by the strong halogen bonding interaction taking place with the iodine atom of the EDT-TTF-I_2 molecules. In order to circumvent this problem, we have focused our attention on the charge localized on the (EDT-TTF-I_2)$_2$ dimer, which should be less sensitive to the influence of environment. Figure 9a shows the infrared spectra of (EDT-TTF-I_2)$_2$TCNQF, polarized perpendicular to the stacks (E$\|a+b$) in the spectral region of C−S, C−I vibrational modes of EDT-TTF-I_2. These modes are well separated from TCNQF vibrational modes. Based on the well-known behavior of the tetrathiafulvalene derivatives[35,36], we assume that an ionization of EDT-TTF-I_2 molecule leads to contraction of C−S bonds length, and therefore hardening of the corresponding charge-sensitive modes. Here, we assign the single peak observed at 914 cm^{-1} at room-temperature (Fig. 9a) as the IR active C−S, C−I stretching mode of EDT-TTF-I_2, marked as $\nu^{D}_{C\text{-}S,C\text{-}I}$.

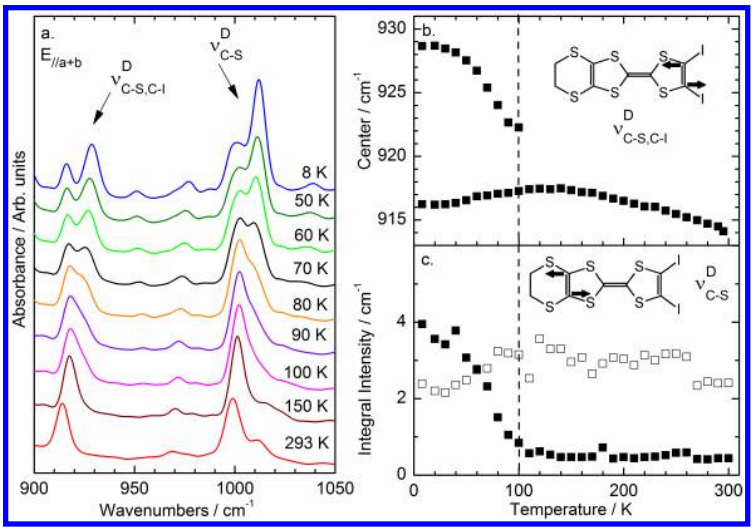

Figure 9: (a) IR absorption spectra of (EDT-TTF-I_2)$_2$TCNQF in the C−S stretching frequency range at selected temperatures; (b) temperature evolution of the frequency of the EDT-TTF-I_2 stretching $\nu^{D}_{C\text{-}S,C\text{-}I}$ mode; (c) the intensity change of the two components at 999 cm^{-1} (□) and 1011 cm^{-1} (■) of the EDT-TTF-I_2 stretching $\nu^{D}_{C\text{-}S}$ mode, that is related to the stack dimerization.

We compare the frequency of the $\nu^{D}_{C\text{-}S,C\text{-}I}$ mode in the absorbance spectra of (EDT-TTF-I_2)$_2$TCNQF polarized perpendicularly to the stack (E$\|a+b$) with frequency of $\nu^{D}_{C\text{-}S,C\text{-}I}$ in other two isostructural complexes: (EDT-TTF-I_2)$_2$TCNQ and (EDT-TTF-I_2)$_2$TCNQF$_2$. As results from our previous studies there is almost no charge-transfer in the (EDT-TTF-I_2)$_2$TCNQ salt, while the (EDT-TTF-I_2)$_2$TCNQF$_2$ salt is fully ionized, i. e. in these salts the (EDT-TTF-I_2)$_2$ dimers possess charges

0 and 1e, respectively[21]. It is to be emphasized that both salts are isostructural with (EDT-TTF-I_2)$_2$TCNQF. In the absorbance spectra (E$\|a$+b) of the (EDT-TTF-I_2)$_2$TCNQ neutral complex the $\nu^{D}_{C\text{-}S,C\text{-}I}$ mode is observed at 914 cm^{-1} at 293 K (See the Supporting Information, Figure S1, Table S1). In fact, for the neutral EDT-TTF-I_2 molecule[6], the experimental frequency of the mode is 917 cm^{-1}. On the other hand, in the absorbance spectra (E$\|a$+b) of the (EDT-TTF-I_2)$_2$TCNQF$_2$ ionic complex, the $\nu^{D}_{C\text{-}S,C\text{-}I}$ band has a doublet structure and the frequencies of the mode are 919 and 929 cm^{-1} (See the Supporting Information, Figure S1, Table S1); this is an indication that the charge 1e is distributed non-uniformly among molecules forming (EDT-TTF-I_2)$_2$ dimers. The $\nu^{D}_{C\text{-}S,C\text{-}I}$ mode in the (EDT-TTF-I_2)$_2$TCNQF shows a small shift towards higher frequencies upon cooling down to 110 K (Fig. 9a). Then below 110 K, the $\nu^{D}_{C\text{-}S,C\text{-}I}$ mode splits into two peaks centered at 916 and 929 cm^{-1} at 8 K. Hence, frequencies of the C$-$S, C$-$I stretching mode components of EDT-TTF-I_2 in (EDT-TTF-I_2)$_2$TCNQF indicate a change of ionicity ρ from about zero at room-temperature to about 1e at 8 K. Splitting of the $\nu^{D}_{C\text{-}S,C\text{-}I}$ band at 100 K suggests the simultaneous presence of quasi-neutral and quasi-ionic molecules in the ionic phase, which means that the charge distribution among molecules in EDT-TTF-I_2 dyad components is not uniform.

Let us focus on the possible charge distribution in the (EDT-TTF-I_2)$_2$TCNQF complex. According to our results, at room-temperature in the neutral ground state all the molecules are mostly neutral (Fig. 10a). Upon cooling the complex becomes ionic and two types of charge distributions in the 2:1 complex are possible, as shown in Figs. 10b and 10c. When the charge is uniformly distributed among molecules in the dimer (Fig. 10b), apparent inversion centers remain, but it is not the case in (EDT-TTF-I_2)$_2$TCNQF because we do not observe donors with charge +0.5. On the other hand, when the charge is localized on one of the donors in the dimeric unit (Fig. 10c), inversion centers no longer exist and the lattice should be deformed. The coexistence of molecules with different charges is indeed observed in our IR spectra. Therefore, we suggest that the charge distribution in the ionic state of (EDT-TTF-I_2)$_2$TCNQF can be represented by the model shown in the Fig. 10c. However, the structural investigations show that TCNQF molecules are located on an inversion center and no indication of any structural phase transition, such as the loss of

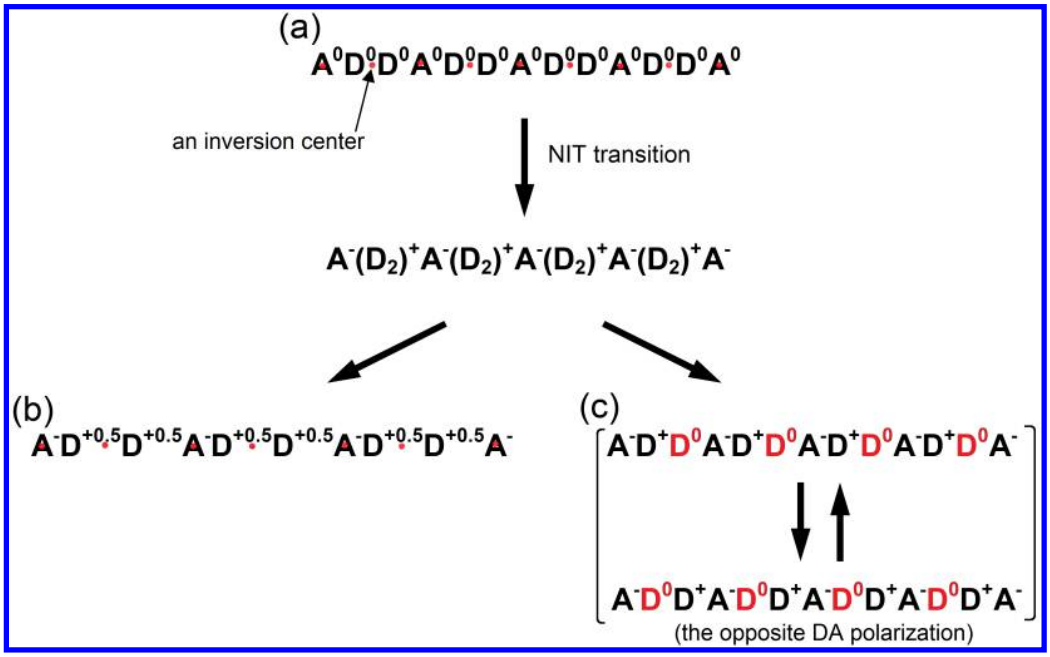

Figure 10: Schematic representation of the neutral-ionic phase transition (NIT) in the 2:1 material; mixed-stack in the neutral phase (a); two possibilities of charge distribution in the ionic phase (b), (c).

this center, was found down to T = 20 K[21]. Two possibilities depicted here in Fig. 10c most probably involve the presence of oppositely polarized ferroelectric domains in the structure, and also the domain walls that can be considered as solitons. It can be assumed that the polarization of domains fluctuates between opposite directions in the time scale which is larger than that one appropriate for IR spectroscopy. In this picture the distortion inside domains disappears in the time scale of the X-ray experiment, therefore the stack distortion and thus the lost of the inversion center is not seen in the structure data. It is also important that unpaired spins in the ionic state interact antiferromagnetically giving rise to magnetic phase transitions[21]. Such a scenario has been already discussed in case of 1:1 mixed stacked materials[37,38]. In case of (EDT-TTF-I_2)$_2$TCNQF characterized by stoichiometry 2:1, the situation is obviously more complex taking into account both charge-transfer between dimer of donor molecules and acceptors and non-uniform charge distribution within dimers. In fact, the non-uniform distribution of charge evidenced here also explains why the structural characteristics deduced from the X-ray diffraction studies (intramolecular bond lengths and halogen bond distances) give an averaged charge transfer less than 1e. The

non-uniform charge distribution among the EDT-TTF-I_2 molecules in the dimer is connected with the neutral-ionic transition observed here, involving a continuous and smooth increase of charged species with decreasing the temperature. The non-uniform charge distribution is also associated with the strong charge localization as shown by the insulating character of the salt down to the lowest temperatures.

Conclusion

In summary, using infrared and Raman spectroscopy we have investigated the neutral-ionic phase transition in (EDT-TTF-I_2)$_2$TCNQF, the first mixed-stack salt of 2:1 stoichiometry showing such transition. We estimated the molecular ionicity ρ in (EDT-TTF-I_2)$_2$TCNQF based on charge-sensitive stretching vibrations of EDT-TTF-I_2 molecules; ρ changes continuously from about zero at room-temperature to about 1e at 8 K but coexistence of two species of different ionicity persists down to the lowest temperature. Our spectroscopic data indicate that at about 100 K a regime change is found. The nominally totally symmetric TCNQF and EDT-TTF-I_2 modes, activated in the infrared spectra due to EMV-coupling, provide an evidence that stacks ...ADDADDA... are slightly distorted already at room-temperature. Intensity increasing of such modes indicates that ionicity enhancement in (EDT-TTF-I_2)$_2$TCNQF is associated with gradual increase of the structure distortion in the direction parallel to the stacks; in the direction perpendicular to the stacks a subtle structure distortion is also possible. We demonstrated and discussed a scheme of the charge distribution in the mixed-stack charge-transfer salt of a 2:1 stoichiometry that undergoes a neutral-ionic phase transition. We suggest that ferroelectric domains exist in (EDT-TTF-I_2)$_2$TCNQF and their polarization fluctuates between the opposite directions.

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Supporting Information Available

The following files are available free of charge.

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- Figure S1 shows the IR absorbance spectra of (EDT-TTF-I_2)$_2$TCNQ, (EDT-TTF-I_2)$_2$TCNQF and (EDT-TTF-I_2)$_2$TCNQF$_2$ in the C-S, C-I stretching frequency range with a brief description.
- Table S1 shows the frequency of the bands related to the C-S, C-I stretching vibrations at room-temperature.

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