

What is the origin of anomalous dielectric response in 2D organic dimer Mott insulators κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl and κ -(BEDT-TTF)₂Cu₂(CN)₃

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ABSTRACT

Novel forms of the low-temperature phases in the two-dimensional molecular solids with competing interactions between charges, spins and lattice, in particular those featuring anomalous dielectric relaxation, have been the focus of intense activity in recent years. Open issues concern the nature of collective charge excitations as well as their coupling to applied ac and dc electric fields. The charge response is reasonably well understood by now in the charge-ordered phase with the formation of ferroelectric-like domains below the metal-to-insulator phase transition. Conversely, the dielectric response observed in dimer Mott insulator phases with no complete evidence for charge ordering is rather intriguing. We overview our recent results of anisotropic complex conductivity (dc – MHz) in the magnetic phase of κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl and in the spin-liquid phase of κ -(BEDT-TTF)₂Cu₂(CN)₃. We discuss possible explanations for the observed dynamics within current theoretical models and compare them with the well-known fingerprints of the spin density wave response to ac electric fields.

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1. Introduction

Strongly correlated low-dimensional molecular systems show a number of diverse charge structures and complex nonlinear dynamics [1]. Conventional charge and spin density waves established in the presence of prevailing electron–phonon interactions feature the collective phason mode with well established signatures in ac and dc electric fields [2,3]. Since the phason is pinned to random impurities or the commensurate lattice, it can be observed as a narrow resonance at terahertz frequencies and as a broad loss peak in audio-frequency range [4]. On the other hand, novel forms of electronic phases with spatially inhomogeneous charge structures giving rise to electronic ferroelectricity are found in the presence of strong onsite and intersite Coulomb repulsion [5]; the interplay with magnetic frustration found on molecular triangular lattices causes exotic phases such as Mott insulator and

quantum spin-liquid [6,7]. All these phases show a rich variety of nonlinear properties and complex dielectric and charge response whose full understanding is still missing.

In this paper, we address the issue of anomalous dielectric response and discuss different scenarios which may explain intriguing features detected at audio-frequency range. We first briefly review the case of charge ordering driven ferroelectricity and then address the dielectric response observed in dimer Mott insulator phases in which structural and spectroscopic evidence for charge ordering is still missing.

2. (TMTTF)₂X and α -(BEDT-TTF)₂I₃

Electronic ferroelectricity commonly arises due to charge ordering in which non-equivalent sites and bonds are formed. These structural changes break the inversion symmetry yielding a net dipole moment so that ferroelectricity can be developed at long range scales. Prominent examples are one-dimensional (TMTTF)₂X with anions X such as PF₆ and AsF₆ and two-dimensional

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α -(BEDT-TTF)₂I₃ molecular solids. TMTTF stands for tetramethyltetrafulvalene and BEDT-TTF is bis-(ethylenedithio)tetrafulvalene. In these materials most of the signatures of electronic ferroelectricity such as structural changes and charge disproportionation yielding symmetry breaking, as well as large dielectric constant with characteristic dielectric dispersion, have been observed.

(TMTTF)₂X solids are dimerized Mott insulators at room temperature, and the charge is equally distributed: there is a one hole per molecular dimer site [8]. The ferroelectric phase transition due to charge ordering sets in at lower temperatures. Structural changes involving the shift of the anion lattice as a whole have been detected by inelastic neutron scattering [9], while charge disproportionation has been established by nuclear magnetic resonance (NMR) [10,11] and infrared vibrational spectroscopy measurements [12]. The main features of the observed dielectric response, Curie-like peak of the real part of the dielectric function and the peak of the mean relaxation time, corresponded to what is expected within the theory of a conventional ferroelectric phase transition. The dielectric constant is huge, of the order of 10⁶, close to the transition point. Remarkably, in some nominally pure single crystals the signatures of the relaxor ferroelectricity have been detected: the peaks of the real part of the dielectric function and the mean relaxation time are much smaller and widened and dispersion is clearly detected. Nad and collaborators suggested that the heterogeneity might be associated with the random distribution of anions in the TMTTF lattice [13]. As we will show later, it appears that the heterogeneity in nominally pure single crystals may be a general property of low-dimensional molecular solids.

α -(BEDT-TTF)₂I₃ (abbreviated as α -ET) consists of stacks of anion layers and two kinds of cation stacks in which BEDT-TTF molecules are arranged in anisotropic triangles. In stack 1, BEDT-TTF molecules are dimerized, while within stack 2 molecules are equally spaced. The system is a semimetal at room temperature with one hole per molecular dimer site [14]. A metal-to-insulator ferroelectric phase transition due to charge ordering sets in at 136 K. Structural changes, involving mainly changes in dihedral angles, have been evidenced by X-ray diffraction data showing inversion symmetry breaking between BEDT-TTF molecules within stack 1 [15]. The charge disproportionation has been detected by several techniques including X-ray diffraction, NMR, Raman and infrared vibrational spectroscopy [14–17], while the generation of the net dipole moments and ferroelectric polarization was demonstrated by time-resolved pump and probe measurements of the optical second harmonic [18]. The observed dielectric response within molecular planes is complex and here we describe only features directly related to the ferroelectric nature of the low temperature electronic phase. The dielectric response is characterized by a small dielectric constant of the order of 400 and by the mean relaxation time, which is temperature-independent at least below 75 K (Fig. 1). This non-dispersive mode is clearly the manifestation of the ferroelectricity and bears features of domain-wall relaxation: twinned domains form due to the loss of inversion centers within molecular stack 1 [15,14]. Due to relatively high in-plane dc conductivity we were not able to do measurements in the vicinity of the phase transition point of 136 K, so that the Curie-like peak of the real part of the dielectric function and the peak of the mean relaxation time were not detected [14]. Interestingly, a recent study of the out-of-plane dielectric response in the temperature-domain indicated a strongly dispersive peak of the real part of the dielectric function, which seems to develop below 80 K, i.e. far below the phase transition point [19].

Above we have taken a look at the dielectric response of two established charge-ordered phases. For both phases, long-range charge ordering stabilizes by some structural changes: an uniform anion shift in (TMTTF)₂X, and the change of dihedral angles in

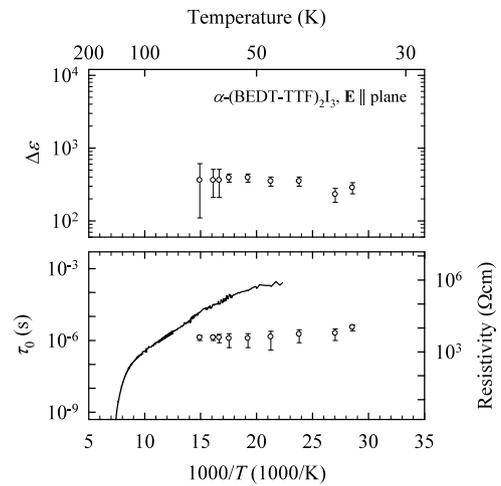


Fig. 1. In-plane dielectric strength (upper panel) and mean relaxation time together with dc resistivity (lower panel) of α -ET as a function of inverse temperature. DC resistivity is represented with a full line. Above 75 K the mode is not discernable any more in the fit.

α -ET. In contrast, the dimer Mott insulator phases on the triangular lattice present a rather intriguing case of anomalous dielectric response, in the absence of structural changes and with no evidence for charge disproportionation. In what follows we address the two examples, κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl (abbreviated as κ -Cl) and κ -(BEDT-TTF)₂Cu₂(CN)₃ (abbreviated as κ -CN); the results accumulated until now indicate the important role of internal heterogeneity in the determination of the dielectric dispersion, similarly as found in (TMTTF)₂X.

3. κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl and κ -(BEDT-TTF)₂Cu₂(CN)₃

κ -Cl consists of conducting BEDT-TTF layers separated by insulating anion layers (Fig. 2, left panel) [20]. The space group is Pnma with inversion centers between two BEDT-TTF molecules within the dimer, and in between parallel zig-zag anion chains. BEDT-TTF molecules form face-to-face dimers which themselves are rotated by about 90° with respect to neighboring dimers. The charge is equally distributed: there is one hole per molecular dimer site. BEDT-TTF dimers are arranged in anisotropic triangles with medium frustration: $t'/t \approx 0.5$ (Fig. 3, left panel).

The system is a dimerized insulator at room temperature, which crosses over into the Mott insulator below 40 K [21]. An insulator-to-insulator phase transition around that temperature was first reported by Williams et al. [20] and verified later in our measurements (Fig. 4, full line) [22]. A rather broad anomaly in the resistive derivative observed on our samples indicates that the phase transition develops only at short range scales. It is noteworthy that a sharp change in the resistivity was recently found in some single crystals of κ -Cl pointing the possible variations in internal homogeneity of the nominally pure single crystals [23]. As demonstrated by SQUID, ESR, NMR and magnetic torque measurements, κ -Cl presents an antiferromagnetic (AF) ground state with canted spins, so that the magnetic state is actually a weak ferromagnetic state [24–27]. Recently, a charge ordering phase transition into a ferroelectric state associated with the magnetic transition was proposed by Lang and collaborators [23]. According to this proposal, the charge ordering gives rise to non-equivalent BEDT-TTF dimer sites. Supporting evidences for this proposal are Curie-like peak of the out-of-plane real part of the dielectric function, hysteresis, non-linear response and time-dependent phenomena observed at the transition point. However, no charge

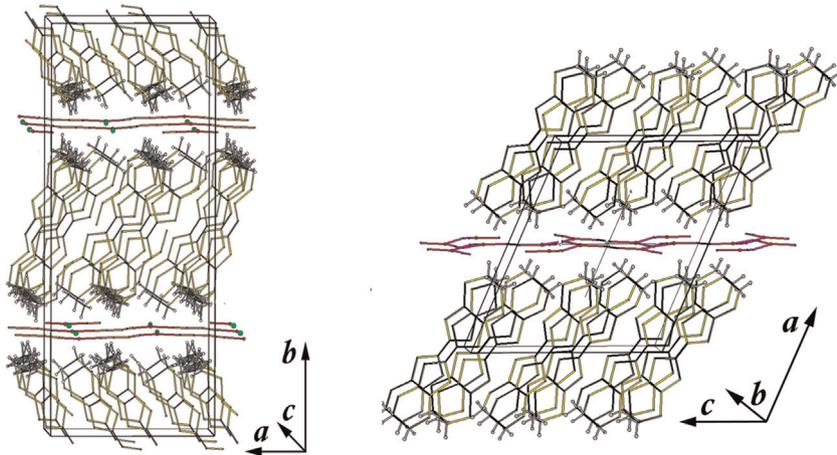


Fig. 2. Side view of unit cell of κ -Cl (left panel) and side view of extended unit cell of κ -CN (right panel). The unit cell is marked as a rectangle.

disproportionation and no structural changes indicating the symmetry breaking have been found until now. The spectroscopic result excludes static electric dipoles on dimers as predicted theoretically but left a possibility for fast temporal fluctuations of the order of 10^{11} Hz [28]. Namely, there are several theoretical approaches to describe the spin–charge coupling and to explain the experimentally observed dielectric response observed in κ -Cl, as well as in κ -CN we address later. Hotta and independently Naka and Ishihara suggested that quantum electric dipoles on dimers interact via dipolar-spin coupling [29,30]. Mazumdar and collaborators suggested a paired electron crystal due to frustration-induced charge disproportionation [31].

Due to this reason, we have developed an alternative scenario to explain the dielectric response within molecular planes (Fig. 5) [22] in analogy with spin-density waves in which the dielectric response has been explained by invoking second-order harmonic charge modulation coupled with magnetic order of itinerant spins [3]. In κ -Cl the ferromagnetic domains with equivalent spin configurations develop below about 25 K as demonstrated by magnetic field reversal of FM magnetization and hysteresis in the spin-flop transition [26]. We expect that the domain walls between ferromagnetic domains in addition to spin also carry charge which accumulates at the domain boundaries in order to promote the formation of magnetic order. These charged domain walls respond to the applied ac field and give rise to the observed dielectric response. It is noteworthy that the dielectric response emerges below about 50 K, concomitantly with antiferromagnetic fluctuations, and displays a maximum right in the region of the broad

anomaly in the resistive derivative. One explanation may be that indeed there is a charge ordering phase transition [23] which is smeared out and shifted to higher temperatures in single crystals we have studied due to internal inhomogeneities. However, it is noteworthy that the 40 K transition point observed in our dc and optical studies (as well as in previous studies by Williams et al., [20]) is quite close to the ordering of ethylene end groups of BEDT-TTF molecules, detected as anomalies in the thermal expansion of the lattice parameters and specific heat [32,33]. As a final remark we would like to point out that the overall charge and spin response in κ -Cl indicates the presence of unconventional spin–charge coupling, as well as an important role of interaction with randomly distributed pinning centers. This may cause areas of fluctuating electronic dipoles on dimers to couple to ferromagnetic domains; the intriguing question whether softening to audio frequencies is possible remains open [34].

Next, we address the case of the κ -CN system. Structurally, it has a simpler unit cell (Fig. 2, right panel), but otherwise it resembles κ -Cl with one important distinction: the BEDT-TTF dimers are arranged in almost isotropic triangles, yielding a much stronger frustration $t'/t \approx 0.8$ (Fig. 3, right panel) [35,36]. The charge is also equally distributed: there is a one hole per molecular dimer site. Most importantly, it is considered as the most prominent example of quantum spin liquid (QSL) system characterized by the absence of magnetic order due to the interplay of quantum effects and frustration occurring on the triangular lattice [37]. The κ -CN system displays insulating behavior over the wide temperature-range measured. Our dc resistivity data together with Hall

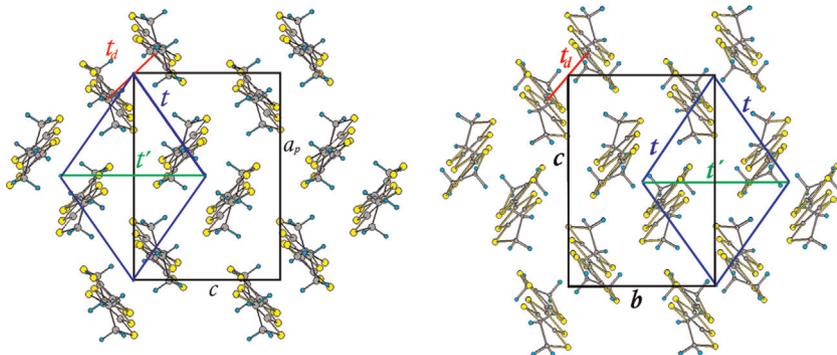


Fig. 3. Left panel: View of BEDT-TTF dimers of κ -Cl in the (c,a) plane projected along the direction tilted of the b -axis by 24° . For clarity reasons only one out of two cation layers constituting the unit cell along the b -axis is shown. An anisotropic triangular lattice is denoted by full thick lines; the interdimer transfer integrals are labeled by t and t' , while the intradimer transfer integral is labeled by t_d . Right panel: View of BEDT-TTF dimers of κ -CN in the bc plane projected along the a -axis; an almost isotropic triangular lattice is denoted by full thick lines; the interdimer transfer integrals are labeled by t and t' , while the intradimer transfer integral is labeled by t_d . In both cases, the unit cell is marked as a rectangle.

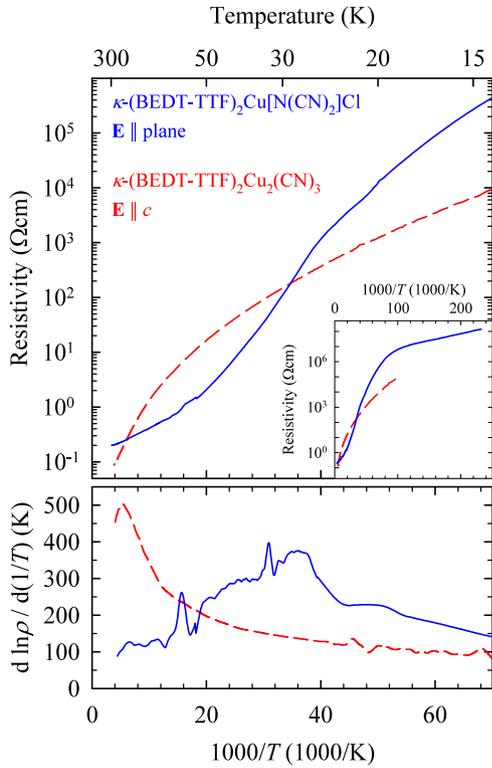


Fig. 4. In-plane resistivity (upper panel) and with derivative (lower panel) of κ -Cl (blue solid line) and κ -CN (red dashed line). The resistivity derivative of κ -Cl shows a distinctly broad maximum centered around 40 K, which indicates a phase transition at short-range scales at low temperatures. On the other hand, the derivative of κ -CN has a maximum around the high temperature of 185 K and steadily decreases with cooling down to the lowest temperature measured. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

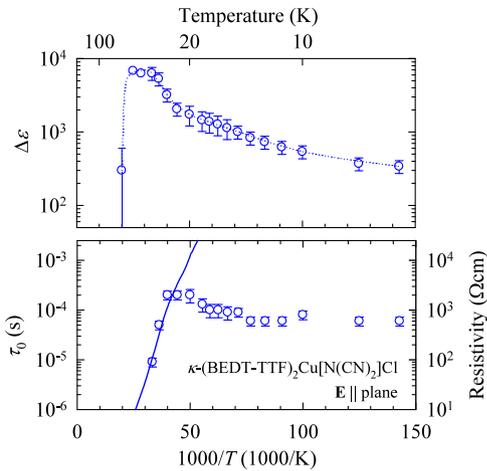


Fig. 5. In-plane dielectric strength (upper panel) and mean relaxation time together with dc resistivity (lower panel) of κ -Cl as a function of inverse temperature. DC resistivity is represented with a full line. The dotted line is a guide for the eye. Above 30 K the mode is outside the frequency window and only the dielectric strength can be extracted.

coefficient and magnetoresistance data suggest that the charge transport takes place via 2D variable-range hopping among localized states [38,39]. We note that Kawamoto and collaborators pointed out previously the presence of the charge inhomogeneity based on their NMR and dc data on κ -CN [40]. Lang and collaborators were the first who suggested, on the basis of strong lattice effects, that there is a phase transition at 6 K in which charge degrees of freedom may be involved [41]. Unfortunately, we could

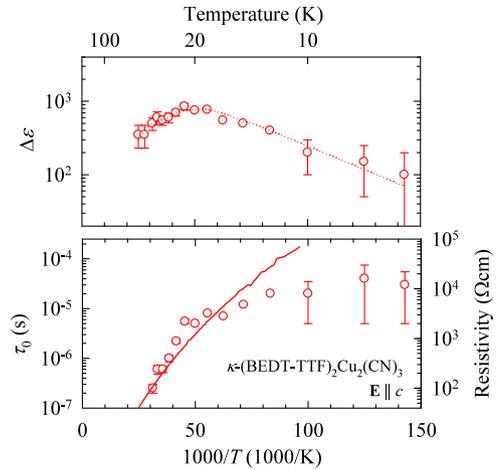


Fig. 6. Dielectric strength (upper panel) and mean relaxation time together with dc resistivity (lower panel) of κ -CN for $E \parallel c$ as a function of inverse temperature. DC resistivity is represented with a full line. The dotted line is a guide for the eye. Above 32 K the mode is outside the frequency window and only the dielectric strength can be extracted.

not do proper dc resistivity measurements in this low temperature range to check the behavior of the resistive derivative. However, note that the dc resistivity displays a peak around 185 K which may be associated with the ordering of ethylene groups of BEDT-TTF molecules (Fig. 4, dashed line). Later Abdel-Jawad and collaborators proposed on the basis of dielectric relaxation measurements for fields perpendicular to molecular planes that 6 K point may be associated with ferroelectric Curie and relaxor-like freezing of dipoles on BEDT-TTF dimers [42]. Lack of spectroscopic evidence for the static electric dipoles on the dimers made it clear that further experimental efforts were needed in order to better understand the origin of the dielectric and charge response in this system. Our dielectric spectroscopy data for ac electric fields along the in-plane c -axis showed the presence of one dielectric mode described well by a Cole–Cole function [38]. The dielectric strength $\Delta\epsilon$ and the mean relaxation time τ_0 for single crystal of κ -CN are shown in Fig. 6. Although the density of points in the measured temperature range is not high enough, two features can be immediately noticed: first is an anomaly of dielectric strength around 20 K, and second is an apparent deviation of $\tau_0(T)$ at high temperatures from the behavior of the dc resistivity. At lower temperatures $\tau_0(T)$ levels off. The broadening parameter $1 - \alpha \approx 0.5$ (not shown). This behavior indicates the relaxor-like response in the system and 20 K point below which the freezing develops so that only a tunneling-like process may become relevant. Strong softening of fluctuating dipoles on dimers may cause the dielectric response [34]. However, relaxor dielectric response indicates that disorder again plays an important role.

In the remaining part of the paper, we briefly discuss possible causes of the disorder in the nominally pure single crystals by exploring the anion subsystem of κ -Cl and κ -CN. In Fig. 7 we show the view of the single anion layer projected along the b -axis tilted by 23.4° ([110] direction) for κ -Cl (left panel), and projected along the a -axis ([100] direction) which itself is tilted by 23.4° of the layer's normal for κ -CN (right panel). It is noteworthy that in the case of κ -Cl, all CN groups between Cu atoms are ordered in zig-zag line along the a -axis so that the anion network forms chains in one dimension. On the other hand, in the case of κ -CN, in addition to ordered CN groups positioned between Cu atoms, there are CN groups located at inversion centers (black symbols), which also connect Cu atoms so that the anion network is formed in two dimensions. Interestingly, in the view shown in Fig. 8 where stacking of two subsequent anion layers are shown, a seemingly

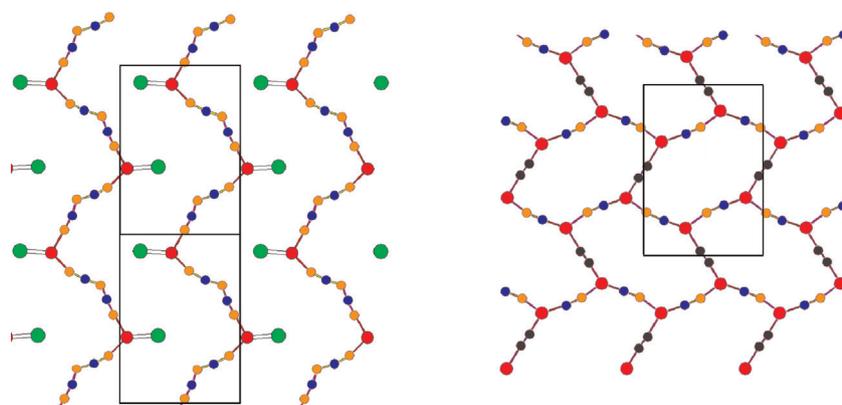


Fig. 7. *Left panel:* View of the anion network of κ -Cl in the ac plane projected along the b -axis tilted by 23.4° . For clarity reasons only one out of two anion layers constituting the unit cell along the b -axis is shown. Copper is colored in red; chlorine in green, carbon of CN groups is colored in blue, while nitrogen of CN^- groups as well as single nitrogen are colored in orange. The unit cell is marked as a double rectangle. *Right panel:* View of the anion network of κ -CN in the bc plane projected along the a -axis. Copper is colored in red; carbon and nitrogen of ordered CN^- groups are colored in blue and orange, while they are denoted by black in the case of CN^- groups located at inversion centers. The unit cell is marked as a rectangle. Note that for κ -Cl the anion network reveals a kind of linear bonding scheme, while for κ -CN the anion network displays 2D bonding arrangement. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

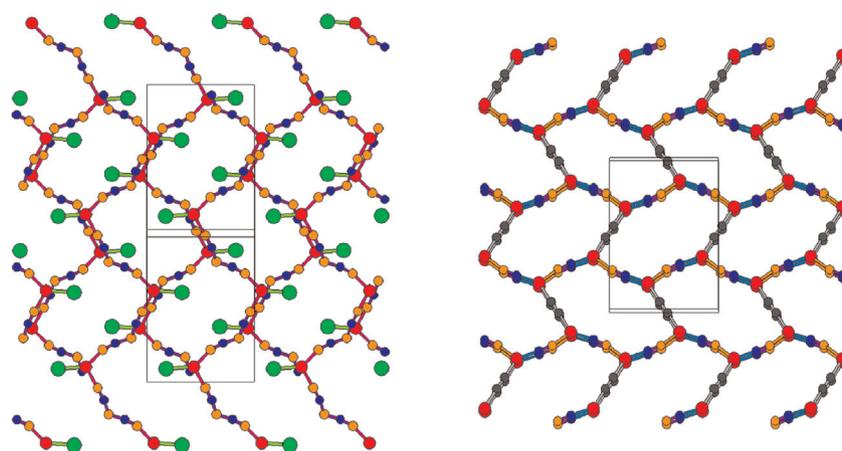


Fig. 8. Stacking of two subsequent anion layers for κ -Cl (left panel) and for κ -CN (right panel) in view along the direction as explained in Fig. 7.

2D bonding scheme shows up for κ -Cl. Another important distinction between the anion networks in κ -Cl and κ -CN concerns the triangular coordination of the copper atoms. While in κ -Cl each Cu atom is coordinated with two N atoms and one Cl atom, in κ -CN the Cu configuration is uniquely defined only in the high $P21/c$ symmetry. In this symmetry, two out of six C–N pairs (per unit cell) are considered as disordered over split-sites related by an inversion center point; each Cu atom is coordinated with one N atom, one C atom and with each atom of the CN group with 50–50% probability. Obviously, while there is disorder in the copper triangular coordination in the anion network of κ -CN [38], it is difficult to see any in κ -Cl. Thus, the source of internal inhomogeneity in κ -Cl single crystals should be explored further.

4. Conclusion and prospects

While in 1D $(\text{TMTTF})_2\text{X}$ charge order is stabilized by the shift of the anion sublattice as a whole, in 2D $(\text{BEDT-TTF})_2\text{X}$ organic compounds, the interaction between electronic and lattice subsystems being stronger, charge order is stabilized by structural changes involving mainly changes in dihedral angles as observed in α - $(\text{BEDT-TTF})_2\text{I}_3$. In these systems, dielectric response is rather well understood and tightly related with charge order driven electronic ferroelectricity established at low temperatures. Dimer Mott insulator with magnetic

ground state $\kappa - (\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ system presents a beautiful candidate for multiferroicity, the coexistence of magnetism and ferroelectricity. The dielectric response bears features expected in the presence of charge order. In view of the fact that the evidence for charge discommensuration in molecular dimers and structural changes indicating that symmetry breaking is still missing, we have advanced an alternative scenario invoking charge-domain walls in the weak-ferromagnetic structure at low temperatures. Dimer Mott insulator with quantum spin liquid state $\kappa - (\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3$ shows dielectric response whose signatures indicate relaxor-like ferroelectricity despite missing symmetry breaking evidences. Overall, results in these solids indicate that internal inhomogeneity in nominally pure single crystals play an important role in determination of low-frequency charge response. A growing body of experimental results emphasizes the importance of cation–anion coupling in low-dimensional molecular solids [43]. Clearly, more experimental and theoretical efforts are needed in order to visualize charge inhomogeneity, domains and charge boundaries and to improve the microscopic understanding of charge–spin coupling in the presence of disorder.

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