

# ORGANIC CHARGE TRANSFER SYSTEMS: THE NEXT STEP IN MOLECULAR ELECTRONICS?

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*Received: 6<sup>th</sup> December 2012 / Published: 13<sup>th</sup> December 2013*

## ABSTRACT

Since the 1950s a lot of effort has been devoted into the development of organic conductors. By a substantial degree this has been inspired by W. A. Little's theoretical analysis of London's idea that superconductivity might occur in organic macromolecules or polymers [1]. Over time this has resulted in the discovery of several organic metals and superconductors, albeit not with spectacularly high critical temperatures. The dominating material class in this respect are the organic charge transfer (CT) compounds which have provided an extended playground for studying the physics of low-dimensional, strongly correlated electron systems [2]. On the other hand, the practical application of organic materials relies on organic semiconductors rather than organic metals. Presently, polymers have found access to the semiconductor industry in capacitors and rechargeable batteries. Current research interests, which have been initiated already in the 1980s, are devoted to an application-oriented development for the growing market of organic electroluminescence devices, field effect transistors and solar cells. These devices are largely based on one-component organic materials or blends. Quite recently the research field of single-molecule electronics becomes increasingly popular.

There is a certain irony in the fact that by far the largest fraction of organic CT systems is semiconducting or insulating, whereas only a small fraction shows conducting properties or even becomes superconducting. As a consequence, research on this material class has

chiefly been devoted to studying the properties of the small subset of conducting representatives of this material class. From the crystal structure point of view semiconducting or insulating CT compounds are mostly of the mixed-stack type, which means that donor and acceptor molecules are alternately arranged in one-dimensional chains. Via hybridization of the highest occupied molecular orbital (HOMO) of the donor with the lowest unoccupied molecular orbital (LUMO) of the acceptor a fully occupied binding molecular orbital results which causes a filled valence band in the solid and renders the material semiconducting or insulating. On the one hand, organic CT systems might become interesting alternatives to the one-component organic semiconductors. This is due to the fact that the additional Coulomb contribution to the binding energy in the CT compounds causes a somewhat larger electronic bandwidth as compared to the one-component molecular crystals which promotes an enhanced charge carrier mobility. More important, however, is the additional functionality which can be gained from the CT systems, e. g. a nonlinear conductivity behavior reminiscent of a Gunn diode or a thyristor.

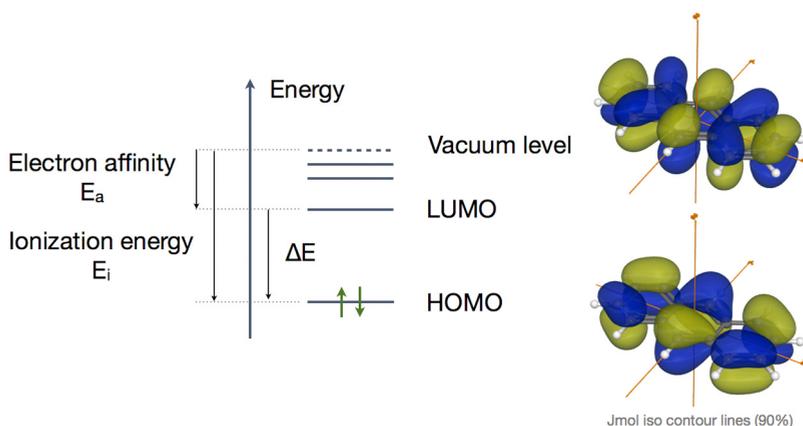
This presentation gives a very brief introduction into some aspects of organic CT systems and will provide a short overview of the different electronic structures which can be observed in this material class. The major part will be devoted to introducing the so called neutral-ionic phase transition CT systems which are of the mixed-stack type and show a pressure- or temperature-driven transition between two different charge transfer states. This gives rise to a wealth of unconventional charge transport phenomena which might have a role to play in future organic electronics.

## INTRODUCTION

### *Organic solids*

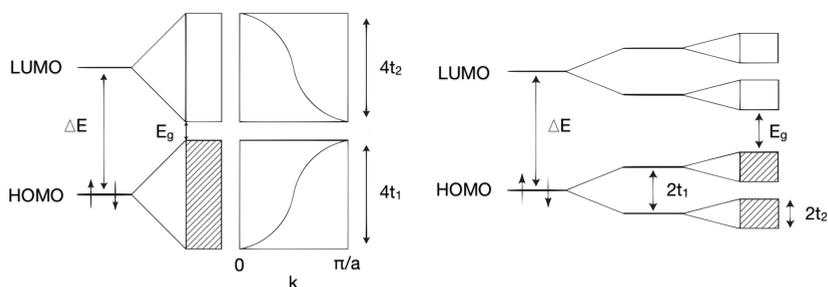
Constituents of organic solids are molecules or their ions (molecular ions or radical ions). They form single crystalline, polycrystalline or glass-like structures. In the following the focus will be on crystalline materials. The most important energy scales relevant for the formation of the crystals and their ensuing electronic band structure in close proximity to the Fermi level are the electron affinity  $E_A$  and ionization energy  $E_I$ . Both are measured from the vacuum level  $E_{vac}$ .  $E_A$  denotes the energetic position of the lowest unoccupied molecular orbital (LUMO) and  $E_I$  the position of the highest occupied molecular orbital (HOMO) below  $E_{vac}$ . Figure 1 shows this schematically for anthracene, a polycyclic aromatic hydrocarbon, which forms an organic semiconductor in its crystallized form.

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**Figure 1.** Schematic representation of relevant energy levels in donor or acceptor molecules. On the right, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of anthracene is exemplarily depicted as electron density iso-contour lines using Jmol.

With regard to their electronic properties the molecular energy scales defined by the HOMO and LUMO positions are essential for the ensuing electronic band structure in the crystal. Above all, Van-der-Waals interactions provide the most important contribution to the binding energy in molecular solids. As a consequence, intermolecular overlap and transfer integrals are small which results in rather narrow HOMO- and LUMO-derived bands with typical band widths in the range of 0.1 to 0.3 eV, whereas the energy gaps reflect the typical HOMO-LUMO energy differences of up to several eV.

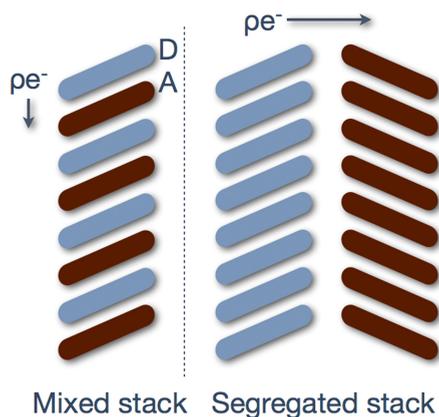


**Figure 2.** Schematic of the HOMO and LUMO level splitting towards weakly dispersing energy bands as a molecular crystal is assembled (left). The indicated band widths or band dispersions are highly exaggerated with typical band width of about 0.2 eV and band gaps in the eV range. On the right the band structure for a molecular crystal with dimerization is schematically indicated. This leads to additional band splittings.

Figure 2 depicts these aspects of the band structure in a qualitative fashion and also takes the consequences of dimerization of molecules into account which is of particular relevance in strong donor-acceptor crystals and radical ion salts to be introduced next. Many more details concerning the properties and applications of organic solids can be found in [3].

### *Organic charge transfer systems*

In organic charge transfer systems (CTS), which result from the co-crystallization of donor (D) and acceptor (A) molecules, the crystal structures are determined by the strongly increased Coulomb and dipolar interactions. TTF-TCNQ (TTF: tetrathiafulvalene, TCNQ: tetracyanoquinodimethane), a one-dimensional metal that shows a Peierls transition below 54 K [4], is probably the most studied system within this material class. A low ionization energy of the donor accompanied by a large electron affinity of the acceptor favors the formation of a CTS. Spatial proximity for sufficient overlap between the respective donor and acceptor molecular orbitals of, ideally, similar symmetry is also necessary. This does already provide a first indication for the preferred spatial arrangement of the donor and acceptor molecules in the prevailing number of known CTS, namely the so-called mixed stack arrangement which will be discussed in somewhat more detail later. Figure 3 provides a schematic overview of the principal stacking arrangements to be found in the organic CTS.



**Figure 3.** Schematic stacking arrangements of donor (D) and acceptor (A) molecules in a quasi one-dimensional crystal of an organic charge transfer system.

The discrimination between a weak and a strong CTS is represented by the nature of its ground state wave function which is a resonant state  $\Phi_G$  between the neutral  $\Phi_{DA}$  and ionized  $\Phi_{D+A-}$  states

$$\Phi_G = a\Phi_{DA} + b\Phi_{D+A-} \quad (1)$$

For  $a \gg b$  the CTS is of the weak type. These systems are not considered here. The actual degree of charge transfer between donor and acceptor is given as a fraction of an elemental charge  $\delta$  per donor-acceptor pair.

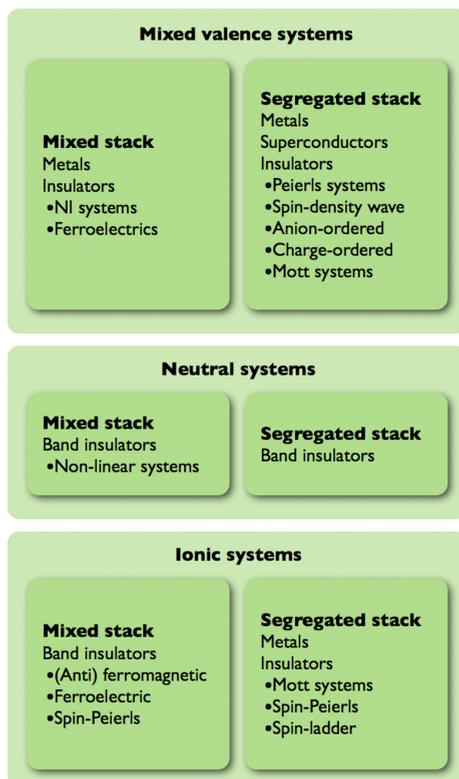
As mentioned above, Coulomb and dipolar interactions are important in CTS which has to be taken into account in the calculation of the binding energy  $E_B$  per D/A pair which is given by

$$E_B = (E_I - E_A)\delta - M\delta^2 \quad (2)$$

The ionic contribution to the binding energy is reflected in the Madelung energy  $E_M = M\delta^2$  (M: Madelung sum per D/A pair).  $E_M$  is the decisive factor in temperature- or pressure-driven (sudden or gradual) changes of the charge transfer degree  $\delta$  which will be discussed in the next section on neutral-ionic phase transition systems.

In the case of a mixed-stack CTS a first qualitative description of the band structure can be obtained from assuming that inter-stack interactions can be neglected, so that the structure is that of a one-dimensional chain of D/A pairs. The resulting valence (VB) and conduction band (CB) are then derived from the overlap of the donor's HOMO and the acceptor's LUMO which are themselves formed by linear combinations of  $p_z$  atomic orbitals perpendicular to the molecular planes. Since the  $p$  orbitals have a node in the molecular plane, the quantum mixing of the D and A molecular orbitals depends on their relative lateral position perpendicular to the stacking axis, as well as on the inclination angle of the molecules towards this axis. As a consequence, the maximum dispersion of the bands need not be at the Brillouin zone center. Also, the weight of the donor's HOMO and the acceptor's LUMO in the VB and CB will vary in  $k$ -space, depending in parallel on the degree of charge transfer. This has been very transparently described by Katan and Koenig for the structurally simple organic charge transfer system TTF-2,5Cl<sub>2</sub>BQ (2,5Cl<sub>2</sub>BQ: 2,5-dichloro-*p*-benzoquinone) [5].

Besides the stacking type, the functional properties of organic CTS is strongly determined by the degree of charge transfer. This leads to the concept of ionicity. Full ionicity is obtained for  $\delta = 1$ . In the range  $\delta_c < \delta < 1$  with  $\delta_c \approx 0.5$  a CTS is said to be of the mixed-valence type. For  $\delta < \delta_c$  a system is classified as neutral. This concept can be extended to the more general class of CTS of the type  $(D^{\delta+})_m(A^{\delta-})_n$ . Based on the stacking type and ionicity, Saito and Murata suggested a family tree of organic CTS which is reproduced in a different form in Fig. 4 [6]. Thus, the wealth of different ground states and associated functionalities of this material class becomes directly apparent. For further reading a recent comprehensive review by Saito and Yoshida is highly recommended [7]. In the next section the focus will be on the class of insulating mixed-valence systems with alternate stacking which can exhibit a so-called neutral-ionic phase transition which leads to a ferro- or antiferroelectric ground state.

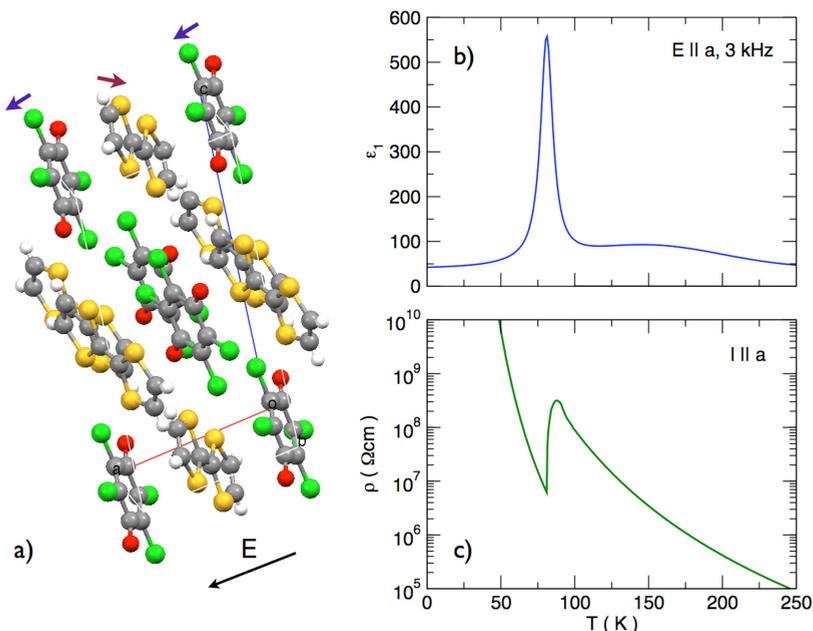


**Figure 4.** Hierarchical representation of organic charge transfer systems depending on the stacking type and degree of charge transfer.

## NEUTRAL-IONIC PHASE TRANSITION SYSTEMS

In mixed-stack organic CTS a conversion from the neutral to the ionic phase (NIT: neutral-ionic transition) can occur, depending on the D and A type, as well as on the packing motif. The NIT can be driven by temperature, pressure and also by photo-irradiation [8, 9, 10]. Different continuous or discontinuous types of NIT have been reported with varying degree of charge transfer between donor and acceptor. The transitions are often accompanied by D/A dimerization along the stacking axis. The mixed stack system TTF-CA (CA: p-chloranil) can be considered the prototypical compound of this material class. Under ambient pressure its NIT is of first order and shows a change of the charge-transfer degree from about 0.3 in the neutral phase to about 0.7 in the ionic phase. In electron spin resonance experiments a Curie-Weiss law is observed below the transition indicating the existence of unpaired spins. From these observations it can be concluded that the NIT in TTF-CA (and others) involves charge, spin and lattice degrees of freedom which renders the development of a microscopic understanding of this material both, interesting and complex.

The phase transition at 81 K is accompanied by a loss of inversion symmetry resulting in a ferroelectric low-temperature phase of slightly deformed and dimerized D/A molecules [11]. In Fig. 5a the crystal structure of TTF-CA in the neutral phase is shown in conjunction with a qualitative indication of the structural changes associated with the NIT. Temperature-dependent anomalies in the dielectric constant and the electrical resistivity are schematically sketched in Figs. 5b and 5c.



**Figure 5.** (a) Representation of the crystal structure of TTF-CA in the neutral phase. The arrows indicate the weak distortion in the molecular positions of about 1% in the ionic phase. (b) Qualitative plot of the temperature-dependent real part of the dielectric function  $\epsilon_1$  at moderate frequency, as indicated. The NI-transition is clearly visible as a sharp peak-like feature with  $\epsilon_1$  reaching values of several 100. (c) Qualitative plot of the temperature-dependent resistivity. At the NI-transition the resistivity shows a sharp anomaly.

The by far dominating amount of theoretical work trying to understand the underlying microscopic mechanisms that drive the NIT are based on modifications of the one-dimensional Hubbard model. TTF-CA can be considered essentially as one-dimensional system due to the  $\pi$ -orbital overlap which is, to a very large degree, restricted to the stacking direction. As a matter of fact, the narrow-band ideal of the Hubbard model is more closely realized by the electronic states in molecular crystals than in the d-electrons for which the Hubbard model is most often applied. A detailed account on the necessary modifications of the simple 1D-Hubbard model to take the D/A stacking and the Madelung energy (in a mean-field fashion) into account is given in [12]. This was later augmented by an electron –

molecular vibration coupling term which is also important for the NIT. The resulting modified Hubbard Hamiltonian has been shown to describe valence transitions and provides a good starting point for the description of the electron-phonon coupling in correlated systems. A recent example for the application of this Hubbard Hamiltonian approach on the symmetry crossover and excitation thresholds in the NIT can be found in [13]. The model-immanent limitation to treating the inherently long-ranged Madelung energy in a mean-field fashion represents one drawback in the Hubbard approach to the NIT. In fact, an *ab-initio* treatment of the problem without any prior assumptions of the relative strengths of the electronic interactions would also be desirable. It has been only rather recently that first-principles density functional theory calculations have become possible for organic CTS. Recent work in this regard has studied TTF-CA and found, e.g., that within the neutral phase just above the NIT the indirect band gap between the VB and CB tends to close as a consequence of thermal contraction of the lattice [14]. Interestingly, with the gap closing an increased charge transfer necessarily arises, so that one may argue that the NIT prevents the system from developing a metallic state.

At this stage we leave these rather general deliberations and focus on two properties of the NIT-systems which hold some promise with regard to applications: (i) the ferroelectric ground state and (ii) the electrical properties associated with domain formation in the neutral and ionic phase.

### ***Ferroelectricity in TTF-CA***

Switchable ferroelectric materials are very interesting for a range of electronic applications, such as in storage devices and sensor development. In this regard organic CTS of the NIT type hold some promise. At the same time, this material class also clearly reflects the complexities which arise in the proper definition and microscopic treatment of ferroelectricity. Before briefly discussing the ferroelectric properties of TTF-CA, a few words are in order to clarify the concept of ferroelectricity in general.

Macroscopic electric polarization  $\mathbf{P}$  can in most instances not be simply defined via the dipole of a unit cell of a lattice. It is only in the limit of purely ionic, localized charges without a continuous electrical charge distribution between the lattice sites that such a definition holds. As reviewed by Resta [15] a proper definition takes both, the ionic and charge distribution components into account

$$\mathbf{P} = \frac{1}{V} \left[ -e \sum_j \mathbf{Z}r_j + \int d^3r r \rho(r) \right] \quad (3)$$

where the sum describes the ionic contribution given by the ions on lattice sites indexed with  $j$  and  $\rho(\mathbf{r})$  is the charge density of a sample with volume  $V$ . Ultimately, the charge density is obtained from the quantum mechanical wave function, so that polarization must be considered as a quantum mechanical phenomenon. Due to the continuity equation for the charge,

the macroscopic polarization is associated with a macroscopic (displacement) current density which in turn is governed by the phase of the wave function. From this viewpoint it becomes apparent that the concept of a geometrical Berry phase is a suitable starting point for a microscopic understanding of ferroelectricity.

When considering the two classes of orientational “order-disorder”-like transitions of permanent dipoles and “displacive”-type transitions, organic ferroelectrics belong to the latter type. Moreover, the rather strong hybridization between the donor and acceptor molecular orbitals lends special importance to the electronic charge density contribution to the polarization. This is particularly true for TTF-CA, as has been recently shown by Kabayashi and collaborators [16]. They found the ferroelectricity of TTF-CA to be dominated by the D/A charge transfer and only to a small degree by the contribution of localized ionic charge dipole moments. In low-stress single crystals of TTF-CA they measured the dielectric constant at several hundred kHz along the stacking direction and found a clear Curie-Weiss behavior of the type  $\epsilon_r = C/(T - \theta)$  above the NIT temperature with a large Curie-Weiss constant  $C$ . This is indicative of a large polarization in the ferroelectric phase. However, the observation of a clear  $P$ - $E$ -hysteresis, a fingerprint of a ferroelectric material, is hindered in TTF-CA due to a large non-linear conductance contribution (see also next subsection) causing leakage currents already at a moderate electric field strength of 10 kV/cm. The authors were nevertheless able to measure hysteresis loops at temperatures below about 60 K. By carefully analyzing the data they found clear evidence that the electronic contribution to polarization exceeds the ionic part by a factor of about 20. This labels the ferroelectric state in TTF-CA as an emergent phenomenon resulting from electronic correlation effects. Also, the associated weak lattice distortion in this type of ferroelectric leads to high resonance frequencies for the polarization response. NIT-systems with ferroelectric ground state and transition temperatures above room temperature are therefore very promising for high-frequency applications, such as in Fe-RAM devices operating at high switching speeds.

### ***Charge-transport phenomena in TTF-CA***

In TTF-CA single crystals the conductivity  $\sigma$  in the ionic phase, as well as in the neutral phase, is dominated by strong non-linear effects already at rather small electric fields  $E$ . This is schematically shown in Fig. 6 for the ionic phase at a temperature close to the NIT. An ohmic behavior at low fields is followed by a quasi-linear  $\sigma(E)$  behavior which shows a sudden switching to an “on”-state with three orders of magnitude larger conductivity at fields above about 10 kV/cm, depending on temperature. The transition to the less conducting “off”-state occurs at a slightly smaller field as the field is reduced again, i.e. the switching is hysteretic. Similar switching effects can be observed in the neutral phase. The rather complex interplay of charge, spin and lattice degrees of freedom is ultimately responsible for these effects. In order to understand some important aspects of the type of charge-carrying excitations in this material it is useful to briefly discuss a theoretical model of the NIT-systems introduced by Nagaosa [17].

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We neglect possible inter-stack interactions and investigate a one-dimensional model based on the following Hamiltonian [17]

$$\begin{aligned}
 H = & - \sum_{l,s} t_{l,l+1} \left[ c_{l,s}^+ c_{l+1,s} + c_{l+1,s}^+ c_{l,s} \right] \\
 & + \frac{\Delta_0}{2} \sum_l (-1)^l n_l + U \sum_l n_{l,\uparrow} n_{l,\downarrow} \\
 & + V \left[ \sum_{l \text{ even}} n_l (n_{l+1} - 2) + \sum_{l \text{ odd}} (n_l - 2) n_{l+1} \right] \\
 & + \frac{2}{5} \sum_l (u_l - u_{l+1})^2
 \end{aligned} \tag{4}$$

The first term describes charge carrier hopping along the stack. The transfer is assumed to have the form  $t_{l,l+1} = T + (u_l - u_{l+1})$  with a transfer integral  $T$  and a linear electron-lattice coupling that tends to enhance or dampen the transfer depending on the sign of the relative lattice displacements on neighboring sites. The electron lattice coupling strength is set to  $S$ .  $n_l = n_{l,\uparrow} + n_{l,\downarrow}$  and  $n_{l,s} = c_{l,s} + c_{l,s}^+$  denote the fermionic number operators. The second term reflects the difference in ionization potential and electron affinity on the D sites (odd) and A sites (even), respectively, with  $\Delta_0 = E_I - E_A + U$ .  $U$  denotes the on-site Coulomb repulsion. The Madelung energy is taken into account on a nearest-neighbor level via the third term in the Hamiltonian. Finally, the last term gives the direct energy contribution to the electron system by way of the electron-phonon coupling. Since the lattice dimerization in the ionic phase amounts to only about 1% this last term is rather small. However, the transfer modulation due to the lattice dimerization is much more relevant being essentially a phase-factor effect in the hybridization of neighboring sites. Without going into more detail, which can be obtained from Nagaosa's excellent paper [17], some important statements can be made from this Hamiltonian in the case of half filling, i.e. the number of electrons corresponds to the number of lattice sites  $N$ .

(a) Neglecting the transfer and lattice term, some simple algebra on the then classical Hamiltonian shows that the energies per site in the ionic and neutral phase are

$$E_i/N = (U - \Delta_0)/2$$

$$E_n/N = -V$$

The phase transition occurs for  $E_i = E_n$  from which the condition  $(E_I - E_A)/2 = V$  is readily obtained, with the neutral phase being more stable for  $(E_I - E_A)/2 > V$ . This states that under lattice contraction the increase of the Madelung energy favors the ionic state.

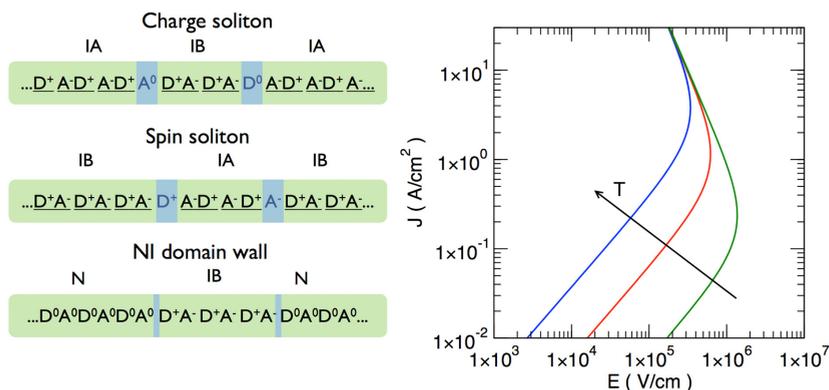
(b) If the transfer term is taken into account, the ionic phase exhibits a gapless spin excitation (magnon) as is also the case in the one-dimensional Heisenberg model.

(c) The NIT is first order in this model.

(d) In the neutral phase the energy for a magnetic excitation rises steeply. The charge-transfer energy, on the other hand, is minimal at the phase boundary.

From these observations Nagaosa concluded that the lowest lying charge excitation in TTF-CA at the NIT are neutral-ionic phase domain boundaries with an energy about four times smaller than the energy necessary to split a charge-transfer excitation into a separated electron-hole pair. Due to the transfer term, the domain wall excitations acquire a dispersion. For further details the reader is referred to [17].

Based on Nagaosa's analysis Tokura and collaborators interpreted their observations of non-linear effects in the field-dependent conductivity of TTF-CA single crystals in a domain-wall picture [18], as is also schematically indicated in Fig. 6 using a phenomenological model for the current-voltage characteristics introduced by Iwasa *et al.* [19]. In order to account for the non-linearity they assumed a positive feedback effect caused by the electric field in the excitation process of the domain walls.



**Figure 6.** Schematic representation of domain-like excitations of a NI-transition systems with ionic ground state according to [18]. The dynamics of these excitations leads to a strongly non-linear current-voltage characteristics, as schematically indicated on the right.

From the point of view of using the ferroelectricity in NIT-systems for applications in which field-induced polarization reversal is necessary, the presence of low-lying charge excitations based on the domain-wall mechanism is unfavorable. However, in other NIT-systems, such as TTF-QBrCl<sub>3</sub>, these conductance contributions are less pronounced [16]. Furthermore, applications can be envisioned for which the field-induced conductivity switching itself can

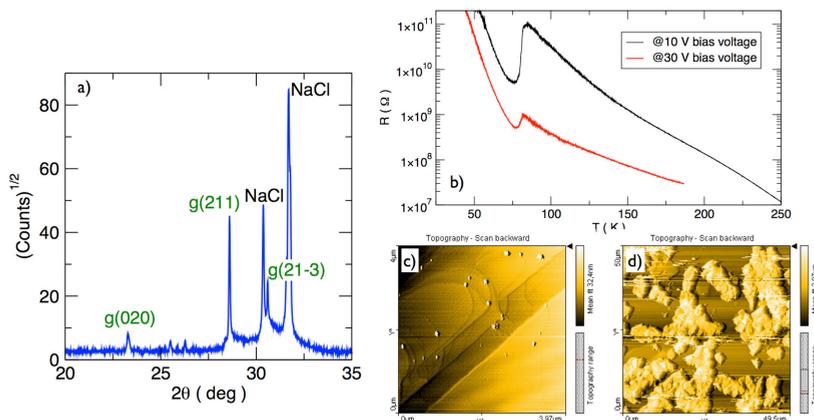
provide a useful thyristor-like functionality. In any case, the availability of thin films is mandatory, if NIT systems are to be used in organic electronics. This aspect is discussed next.

### THIN FILMS OF NIT SYSTEMS

Thin film deposition of organic CTS has so far not received a lot of attention. This may to some degree be attributed to the fact that crystalline organic thin film growth poses some additional complications when compared to the more classical (inorganic) semiconductor and metal epitaxy. Nevertheless, thin film growth studies of TTF-TCNQ have been reported quite early after the discovery of this one-dimensional organic metal [20] and have been also actively pursued in some recent works [21–24]. With a view to the promising functionalities provided by this material class, e. g. in photovoltaics [25], this is likely to change soon. Some of our recent work has also been dealing with other D/A systems, such as (BEDT-TTF)TCNQ (BEDT-TTF: bisethylene-TTF) [26] or also new organic CTS [27]. In the following some very recent and so far unpublished results on the thin film growth of TTF-CA are presented [28].

The films have been prepared from mixed powders of TTF and CA in stoichiometric proportions by sublimation from one effusion cell at cell temperatures between 95 °C and 105 °C. Different substrate materials with different crystallographic orientations have been used. The substrates have been held at room temperature. The film growth was performed under ultra-high vacuum conditions at a base pressure of about  $10^{-7}$  mbar. Figure 7 shows an X-ray diffractogram of a TTF-CA thin film grown on NaCl (100) (annealed). The preferential growth orientation is (211) which corresponds to the D/A molecules lying flat on the substrate surface. As evident from atomic force microscopy scans, also shown in Fig. 7, the growth proceeds by island formation. Interestingly, a partial wetting layer of 3 to 4 nm height forms between the islands. The composition of this layer is still under investigation. First temperature-dependent resistivity measurements have been performed on films grown on SiO<sub>2</sub>/Si(100), as also shown in Fig. 7. Apparently, the NIT is not suppressed in the layers and occurs at about 81 K (onset) as in single crystals. Further work is in progress to optimize the growth and also study the dielectric properties of the TTF-CA thin films.

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**Figure 7.** (a) X-ray diffractogram of TTF-CA thin film on annealed NaCl (100). The reflexion of the NI-phase are indicated. A (211) growth preference is observed which corresponds to a flat-on arrangement of the donor and acceptor molecules of the two non-equivalent D/A stacks (see Fig. 5a for reference). (b) Temperature-dependent resistivity of TTF-CA thin film grown on amorphous SiO<sub>2</sub>/Si(100). The data was taken under constant bias voltage conditions, as indicated. The NI-transition is clearly visible. The phase transition signature is suppressed at higher bias voltage. (c) Atomic force microscopy (AFM) image of the annealed NaCl(100) substrate used for the film growth. (d) AFM image of the island growth of TTF-CA layers on NaCl(100). The data was taken in non-contact mode.

## CONCLUSION

NIT-systems represent a highly interesting material class from the group of mixed-stack organic charge transfer systems. Until recently the number of representatives has been rather small but a systematic search has resulted in a significant number of new neutral-ionic phase transition systems [29]. In the future, the thin film route will provide a valuable extension of this research with regard to tuning the NIT by film-specific factors, such as biaxial-strain formation via clamping, and the realization of device structures, such as field-effect transistors. In this sense, NIT-systems represent exciting materials for studying electronic correlation effects under partially competing couplings between the charge, spin and lattice degrees of freedom. At the same time, their application potential is significant and could be appreciably enhanced, if it turned out to be possible to shift the NIT to above room temperature.

## ACKNOWLEDGMENTS

The author acknowledges financial support by the Beilstein-Institut, Frankfurt am Main, within the research collaboration NanoBiC. Financial support by the DFG through the transregional collaborative research center TR-SFB 49 is also gratefully acknowledged.

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