Structure, Hydrogen Bonding and Other Exciting Effects in Low Dimensional TCNQ Salts. Recent Advances

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Abstract: Organic compounds have long been considered the most natural representatives of the insulating state. It started to change about fifty years ago, after the synthesis of an extraordinary organic molecule: tetracyano-*p*-quinodimethane (TCNQ). This molecule displays unique chemical and physical properties and give rise to a very rich class of organic conducting materials. The common feature of this conductors is high ordering of TCNQ molecules, very often in linear one-dimensional chains or columns. The physical properties of TCNQ salts are determined by two major points: 1) a restricted electronic dimensionality and 2) electronic correlations and electron-phonon interactions.

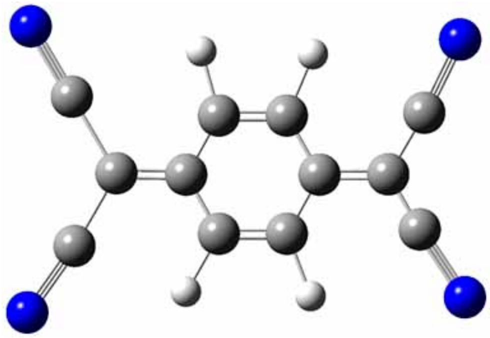
The aim of the paper is to review the influence of the properties and spatial structure of the cations on selected physical properties of adequate TCNQ complex salts. Some uncommon effects such as thin layer's molecular organization and anions orientation, multidimensionality of hydrogen bonded networks of the salts – their types and strengths, melting of organic composites based on TCNQ and photoinduced melting of spin-Peierls phase in CT compounds are discussed. Possible applications of TCNQ salts are also mentioned.

Keywords: Organic conductors, TCNQ salts, thin films, hydrogen bonding, melting.

1. INTRODUCTION

Organic compounds have long been considered the most natural representatives of the insulating state. It started to change about fifty years ago, after the synthesis in 1960 of an extraordinary organic molecule: tetracyano-*p*-quinodimethane (TCNQ) [1] (Scheme **1**). This molecule displays unique chemical and physical properties and give rise to a very rich class of organic conducting materials. TCNQ shows high molecular symmetry and planarity but its very strong electron accepting properties predispose this molecule to create charge transfer (CT) complexes and ion-radical salts with various electron donors. Usually, the TCNQ anions and donor's cations form two various sublattices differently organized. The common feature of the ion-radical salts is high ordering of TCNQ molecules, very often in linear one-dimensional chains or columns [2-4]. The distances between the planes of molecules creating such columns are generally smaller than the sum of the atomic radii of the largest atoms in the TCNQ molecule. The linear arrangement (Fig. **1**), as well as considerable distances between the adjacent columns are due to the fact that the prevailing interactions are those parallel to the column axis, whereas those in the perpendicular direction can be neglected. The physical properties of TCNQ salts are determined by two major points: 1) a restricted electronic dimensionality and 2) an evidence for electronic correlations and electron-phonon interactions in these narrow electronic band systems [5]. The experimental facts which characterize this class of materials are the electronic, magnetic and optical properties in relationship with their structural organization. A valuable electronic conductivity with a semiconducting behavior is a first evidence. A paramagnetic susceptibility, which is often strongly enhanced over Pauli value, is a second experimental key point. Finally, CT absorption bands in the IR range are the signatures of strong intermolecular interactions characteristic of this class of compounds.

TCNQ salts with regular quasi one-dimensional (Q1D) stacks show usually metallic properties but they undergo phase transitions becoming insulators below the transition temperature T_c. The one-dimensional (1D) organic metal is unstable to static lattice distortion [5]. If the lattice is subjected to periodic distortion the chain to be treated as a dimerized one with the energy gap 2Δ in the vicinity of the Fermi vector $\boldsymbol{k}_F$. This type of instability is referred to as Peierls transition [6].



Scheme 1. Molecular structure of the tetracyano-*p*-quinodimethane (TCNQ).

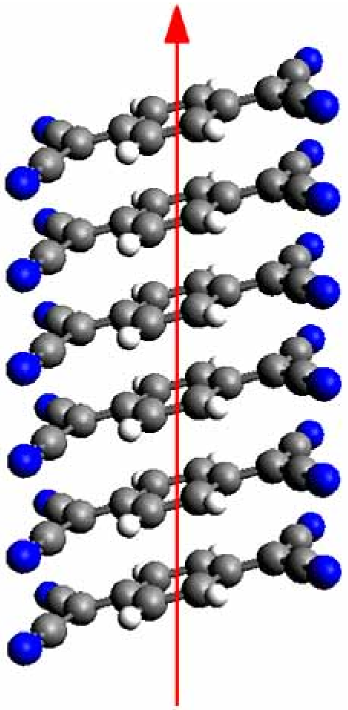


Fig. (1). Typical molecular arrangements in 1D regular chains of TCNQ anions.

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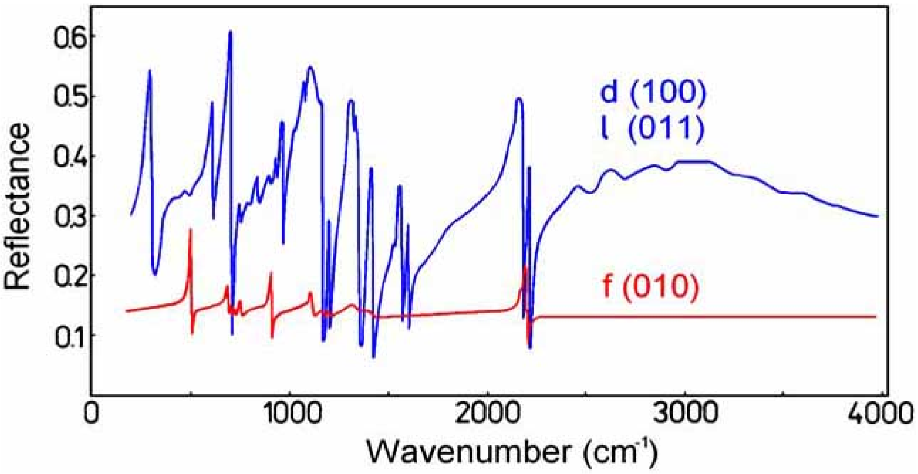


Fig. (2). Infrared reflectivity of the low-temperature phase of MTPP(TCNQ)$_2$ salt for different crystal faces. The electrical vector ***E*** is parallel to the TCNQ stacks direction in the case of faces d(100) and l(011) and is parallel to the TCNQ long axis for f(010) [7].

The feature of quasi-one-dimensional compounds most frequently emphasized is high anisotropy of their physical properties. For example, an optical reflectance (Fig. **2**) is small and almost frequency independent when the electric vector of external radiation is perpendicular to the stacks, but for parallel polarization one observes an overdamped electronic CT band and a number of lines with considerable half-width at frequencies close to those of totally symmetric (A_g) modes of isolated molecules [7-9]. Electron-molecular vibration (e-mv) coupling mentioned above determines the optical properties of low-dimensional organic conductors in the middle infrared region. It leads to the activation of modes that are normally nonactive in the IR and these modes dominate the spectrum. For TCNQ and other symmetrical molecules, π molecular orbitals occupied by the radical electron are nondegenerated; so linear e-mv coupling is possible only for the totally symmetric modes [10,11].

It is well known, that e-mv coupling constants in the anion radical salts of TCNQ depend indirectly on the molecular structure of electron donor species (cations). The cation structure influences indirectly other physical properties of TCNQ salts, in particular their structure and electrical conductivity. For example, it was shown for the family of TCNQ salts with N-methyl derivatives of pyridine [12 and Scheme **1**]. These pyridine derived cations contain various number of methyl groups, in different pyridine sites. Though all the salts show triclinic symmetry with nearly the same unit cell parameters and similar dimer structure, the d.c. electrical conductivity overcomes a range from $4 \cdot 10^{-5}$ Ω^{-1}cm^{-1} to $6 \cdot 10^{-3}$ Ω^{-1}cm^{-1} [12,13].

The aim of the paper is to review the influence of the spatial structure and properties of the cations on selected physical properties of adequate TCNQ complex salts; some novel developments and trends as well as uncommon effects occurring in these salts and their possible applications are also discussed.

2. NOVEL DEVELOPMENTS AND TRENDS IN TCNQ SALTS

2.1. Thin Layers of TCNQ Salts – Their Properties and Molecular Organization

In recent years, there has been a growing interest in organic electronic devices such as transistors, switching devices, sensors, light emitting diodes, and solar cells due to the unique electrical and optical properties of organic materials, between them the TCNQ semiconducting or metallic salts. Thin films of these materials are attractive as substrates for chemically modified interfaces because the molecular nature of the conducting TCNQ salts is amenable to synthetic manipulation. On the other hand the high charge densities and rapid charging characteristic of these films portend applications with excellent sensitivity, and the materials have a degree of biocompatibility due to their organic nature [14]. Commonly used way of preparation of thin organic films is the Langmuir-Blodgett (LB) technique which can be shortly defined as a way of arranging molecules in a fixed configuration which could not spontaneously come about. For more information on this technique see [15].

The comparison between LB conducting films and CT crystals has shown that the pertinent interactions i.e. the electronic correlations on one side and the electron-molecular vibrations on the other are very similar. The molecular parameters are not strongly modified even if a different structural organization is present in TCNQ films with the transfer integral values about the same order of magnitude [16].

Studies of LB films are currently very important not only from the viewpoint of practical applications but also from that of basic sciences. Compared to practical research, basic science studies have fallen behind, although there are many areas of sciences, which can benefit from studies of systems based on LB films of organic conductors. For example molecular organization of layers, ordering and orientation of molecules in thin films, nature of phase transitions in the films, photophysical and photochemical processes as well as interaction between substrate and monomolecular layer are good and very interesting examples of such areas.

The first studies concerning the conductive LB films using the CT complexes of TCNQ were performed by Ruaudel-Teixier *et al.* [17]. Since then, many kinds of CT complexes and ion-radical salts films have been prepared and their structure has been described. The analysis of both ESR line shapes and linear dichroism data in the UV-Vis and IR has been successful in providing information on the thin films organization hardly accessible by X-ray diffraction techniques [18-20]. Some supplementary information on the LB film organization comes from microscopic methods e.g. SEM or AFM.

Recently, researchers around the word have developed a number of surface-sensitive experimental methods for proving “in situ” the organization of molecules on the water surface. One of these techniques is UV-Vis reflection spectroscopy. This method has been applied for studying Langmuir and Langmuir-Blodgett films of viologen (see Table **1**) and viologen-TCNQ monolayers [21]. Properties of LB films of viologens have shown a great dependence on several parameters including the orientation of the molecules on the films as well as the type of counterion incorporated into the film

Table 1. Electron Donor and Acceptor Molecules Cited in the Paper

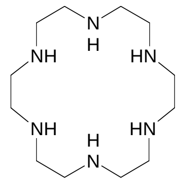
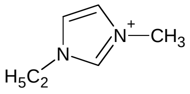
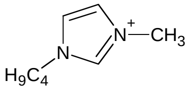
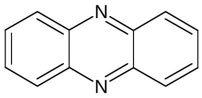
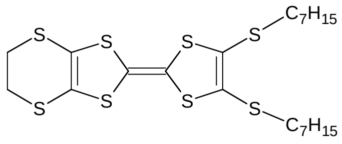
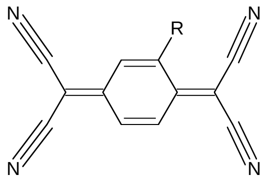
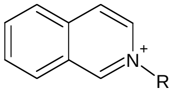
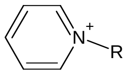
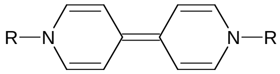
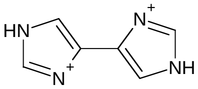
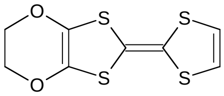
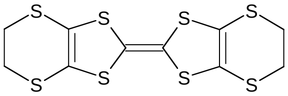
Chemical Structure	Chemical Name
	**[18]ane-N_6** hexaazamacrocycle- -1,4,7,10,13,16-hexaazacyclooctadecane
	**EMI** 1-ethyl-3-methylimidazolium
	**BMI** 1-buthyl-3-methylimidazolium
	**Ph** phenazine
	**C_7TET-TTF** bis(heptylthio)ethylenedithiotetrathiafulvalene
	**2-alkyl-TCNQ** R= $-C_{12}H_{25}$ (dodecyl) R= $-C_{15}H_{31}$ (pentadecyl) R= $-C_{18}H_{37}$ (octadecyl)
	**N-alkylisoquinolinium** R= $-CH_3$ (methyl) R= $-C_3H_7$ (prophyl)
	**N-alkylpyridinium** R= $-CH_3$ (methyl) R= $-C_{18}H_{37}$ (octadecyl) R= $-C_{22}H_{45}$ (docosyl)

Table 1. contd….

Chemical Structure	Chemical Name
	**viologen** R= -$C_{18}H_{37}$ (dioctadecyl-4,4′-bipyridinium)
	**4,4′-H_4-Bim** 4,4′-H_4-biimidazoles
	**EDO-TTF** ethylenedioxytetrathiafulvelene
	**BEDT-TTF** bis(ethylenedithio)tetrathiafulvalene

[22-24]. The organization of the viologen in the Langmuir monolayer was investigated upon the different states of compression, and the tilt angle of the viologen moieties with respect to the water surface was determined. In solution, the orientation of the viologen units is a random. Nevertheless, it was stated by Cea and coworkers [21] that at the air-water interface there is a preferential orientation of the viologen units which must change under compression, i.e., the more parallel the transition moment of the viologen to the water surface the higher the intensity of the reflection spectrum, and therefore an orientation factor can be defined. It was stated that at low surface density, the viologens are situated in a lying flat position, but as the surface pressure increases, the viologen units suffer a transition to a more vertical position. Before of the overshoot in the isotherm, the aromatic rings of the viologen derivative have a tilt angle Φ of ca. 43º with respect to the water surface; afterward, in the region after the overshoot, Φ gradually increases until it reaches ca. 50º. It indicates that the overshoot is caused by a reorganization of the viologen units but not a collapse. Hybrid viologen-TCNQ monolayers have been prepared and analyzed by means of various methods. A simultaneous quantitative analysis of the two active molecules in the UV-Vis region suggested an organization model at the air-water interface. In this model, a parallel arrangement of viologen and TCNQ units with a 1:2 stoichiometry was proposed [21]. After the overshoot this model is no longer valid and a possible explanation is that TCNQ units are ejected from their initial position in the monolayer, being just absorbed beneath the viologen units in a more horizontal position or even squeezed into the subphase [20]. The schematic models of organization of viologen-TCNQ monolayers at the air-water interface before and after the overshoot are shown in Figs. (**3a**) and (**3b**).

Richard *et al.* [19] have investigated the molecular constitution and ordering of LB films prepared by deposition of N-docosylpyridinium-TCNQ salts (see Table **1**) and their subsequent doping with iodine. UV-Vis and IR spectra of the salt show features typical of a system containing weakly interacting $(TCNQ^{-})_2$ dimers. The polar sheets in the precursor film consist of slipped $(TCNQ^{-})_2$ dimers with their molecular planes almost parallel to the plane of supporting slide. The spectroscopic and linear dichroism data allow the authors of the paper to monitor the changes induced by iodination process and to show that there is a complete change in the orientation of the TCNQ units. The TCNQ molecules stand edge on with their molecular planes roughly perpendicular to the plane of the slide and with their long axes close to being normal to it [19].

Investigation into the molecular organization of LB films of the 1:1 CT salt of N-octadecylpyridinium-TCNQ (see Table **1**) was reported by Dhindsa *et al.* [25]. Using a number of spectroscopic techniques (UV-Vis dichroism, attenuated total IR reflection, IR reflection-absorption and low-angle X-ray diffraction) it was indicated that the long axes of TCNQ molecules are aligned at an average angle of approximately 30º to the substrate normal and that the pyridine ring and associated hydrocarbon chain take up approximately the same orientation (Fig. **3c**). This is consistent with the relatively high lateral conductivity observed in the films.

For comparison with the above-cited structures of TCNQ salts, we would like to show the molecular orientation in the LB films of alkylated TCNQ derivatives (see Table **1**) according to studies of Nichogi *et al.* [26]. It was stated by the authors of the paper that the first lower layer is thicker than the upper layers. This indicates that the molecules in the first lower layers are less inclined with respect to the surface normal than those in the upper layers (Fig. **3d**). Probably, this difference of the molecular orientation is due to the interaction between the TCNQ chromophores and the substrate. This result is consistent with that of IR spectroscopy [27]. The authors of this paper shown that the TCNQ plane of molecular axis of the TCNQ chromophore changes with the ordinal number of the monolayer, at least up to the third monomolecular layer.

Some structure-property relationships for conducting LB films based on semiamphiphilic TCNQ salts with closed shell cations were investigate by Vandevyver *et al.* [28]. It was shown that formation of a three-dimensionally ordered phase containing $(TCNQ^{-})_2$

Fig. 3a

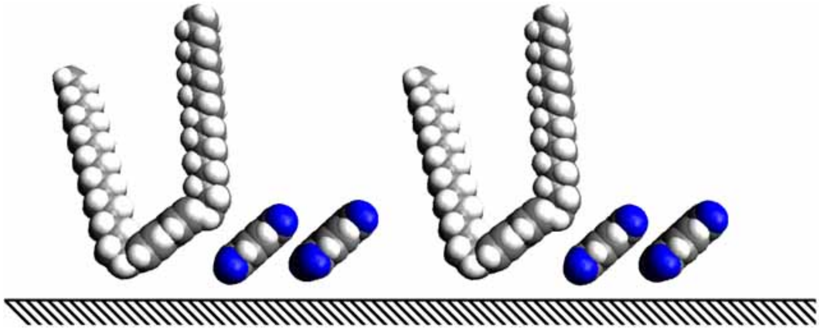


Fig. 3b

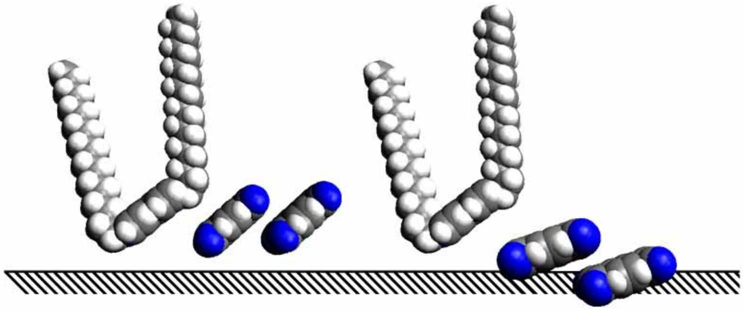


Fig. 3c

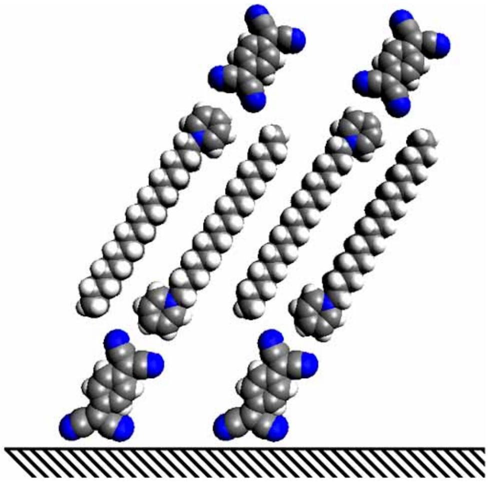


Fig. 3d

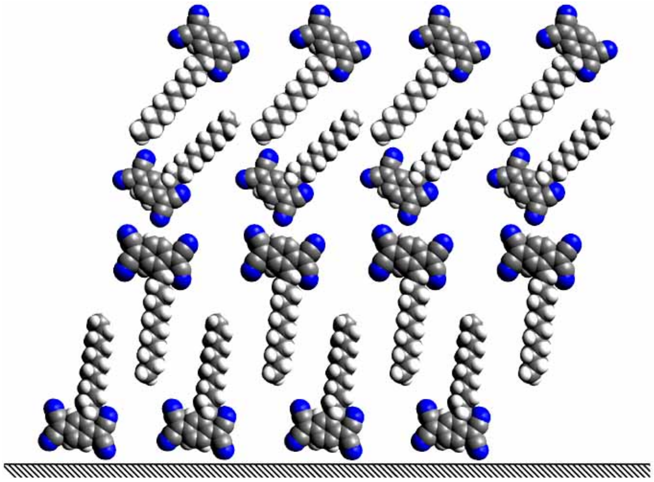


Fig. (3). Schematic model of organization of viologen-TCNQ monolayers at the air-water interface before (**a**) and after the overshoot (**b**), and the model of organization of N- octadecylpyridinium-TCNQ LB film (**c**). Section (**d**) of the figure shows a schematic representation of molecular orientation in the alkylated TCNQ films (C_{12}TCNQ). All figures are prepared after the data of the adequate papers [21,25,26].

dimers with their molecular planes parallel to the substrate is the primary structural requirement for observing conductivity. Upon treatment with iodine, this type of structure allows the necessary remarkable molecular reorganization of the films to occur [28].

As it was mentioned before, the preparation of thin films of TCNQ-based organic conductors is an important step towards the development of organic-based systems. For example, preparation and characterization of TTF-TCNQ highly oriented layers grown by organic CVD technique was elaborated by Caro *et al.* [29]. On the other hand, physical properties of similar, mixed LB conducting films based on TTF derivatives were studied by Dourthe *et al.* [30]. Some electroactive films from poly(ethylene oxide)-sodium iodide complexes with TCNQ was investigated by Siddiqui *et al.* [20]. The utility of TCNQ and p-chloranilic acid in analysis of pentazocine was presented by Abdel-Hamid *et al.* [31]. Switching effect in Cu-TCNQ thin films prepared by vacuum vapor codeposition was described and investigated by Oyamada *et al.* [32].

From various papers it is clear, that the TCNQ molecules orientation in thin films show a great dependence on several parameters. The molecule orientation is determined not only by the conditions of thin layers preparation (mainly the terms of compressions), but also the type of counter ions incorporated into the film. Presence of the counter ions forces the charge transfer from the electron donor to acceptor and formation of the TCNQ anions or their dimers. Depending on the spatial organization of the donors, including their sizes, the orientation of the TCNQ species on the films is self adapted.

It seems that the investigations of the molecular organization and structure of thin films of organic conductors should improve the technology of the films with better structural properties, in particular to obtain a well defined lamellar structure over the whole area of the sample. Building up other more conducting or optical active LB films may play useful roles in future molecular electronic devices such as transistors, switching devices, sensors, light emitting diodes, and solar cells.

2.2. Multidimensional Hydrogen-Bonded Networks of TCNQ Salts

The majority of ion-radical salts and conducting CT complexes in the solid state form segregated stacks of donors and acceptors but several complexes are also known to form mixed stacks where the donor and acceptor molecules are stacked alternately in infinite columns. The importance of stacking interactions in understanding physical properties of low-dimensional solids led to extended studies of these effects. The charges in the conducting molecular materials are transferred from electron donor moieties to electron accepting one. This is why the electrostatic interactions, similar to known from typical ionic crystals, should be taken into consideration. On the other hand the charges on the sites are distributed on the whole, usually big, organic molecule. Charges on the low-dimensional columns are delocalized along the stacks giving something like electron cloud determining electric conductivity of the material. Short distances between atoms of neighboring molecules or ions cause also that weak interactions as van der Waals interactions or hydrogen bonding (HB) should be included in evaluations [3-5]. It is necessary to notice, that some of these materials exhibit high electrical conductivity, magnetic ordering or other unique physical properties. In this regard, understanding lateral interactions within or between stacks is essential in order to control the stacking patterns in the solid state and thus to design new materials of desired properties. Though electrostatic interactions between anion radicals and cations are of fundamental importance much weaker hydrogen-bond interactions cannot be neglected.

Construction of ion-radical salts and CT complexes having well defined multidimensional H-bonding networks is an important issue in developing of organic conductors. Thus, the use of HB interaction to establish defined supramolecular architecture and control molecular organization of TCNQ salts is a major current topic [2-4,33-36]. In addition to structural aspects, HB exhibit abilities to control the electronic structure of ion-radical salts by i) regulation of charge distribution by electrostatic interaction, ii) control of the component ratio, and iii) enhancement of redox activity based on high polarizability.

An appearance and the role of HB in molecular conductors will be illustrated taking into consideration an organization and properties of selected ion-radical TCNQ salts. Just recently Murata *et al.* [37] have investigated H-bonded CT salts of protonated cations of R_2-4,4′-H_4-biimidazoles and oligo(imidazole)s (see Table **1**) with TCNQ. Chemical modifications of the 4,4′-H_2Bim skeleton, where Bim is biimidazole, demonstrated the diverse HB structures: chain-like motifs composed of imidazole-$(TCNQ)_2$-imidazole cyclic units in some salts (Figs. **4a** and **4b**) and two-dimensional sheets constructed by the alternation of R_2-4,4′-H_4Bim^{2+} and TCNQ in another.

(Me_2-4,4'-H_4Bim^{2+})$(TCNQ)_3(MeOH)_2$ salt shows one of the typical structures. The salt is composed of Me_2-4,4′-H_4Bim^{2+} cations, two crystallographically independent TCNQ molecules, and MeOH as crystalline solvent. TCNQ molecules form a segregated linear column along the *b*-axis (Fig. **4a**). Overlap pattern of both stacks is a ring-overbond mode. TCNQ columns are arranged along the *a*-axis to form a layered structure (Fig. **4c**). The intermolecular interaction of different TCNQ stack is adequate to the stack organization. This result indicates that the highly ionized TCNQ molecules form a dimer structure within the TCNQ column. Because intercolumnar interactions are very small, the salt has a one-dimensional electronic structure. HB distances are: N1-(H)····N3≡C – 2.85 Å; N2-(H)····O1 – 2.73 Å; O1-(H)····N6≡C – 2.93 Å and are shorter than the sums of van der Waals radii of two N atoms (3.10 Å) and N and O atoms (3.07 Å). These HBs form a one-dimensional chainlike motif along the [011] direction and connect TCNQ columns (Fig. **4b**) [37,38].

(Th_2-4,4′-H_4Bim^{2+})$(TCNQ)_2(MeOH)_2$ salt shows another crystal structure. The salt is composed of Th_2-4,4′-H_4Bim^{2+} cations having an inversion center and two crystallographically independent TCNQ molecules (TCNQ-A and TCNQ-B). Bond length analysis of TCNQ moiety indicates the fully ionic state of the salt. TCNQ molecules form a dimers with a ring-overbond overlap mode and an interplanar distances of 3.2 and 3.4 Å. Th_2-4,4′-H_4Bim^{2+} also stacks to form a uniform column parallel to the TCNQ column (Fig. **5a**). Th_2-4,4′-H_4Bim^{2+} has H-bonded interactions with both TCNQ-A and TCNQ-B molecules: N1-(H)····N3 (3.09 Å) and N2-(H)···· N7 (2.99 Å) (Fig. **5b**) [37].

It was also shown by Murata *et al.* [38] that the chemical modifications of the cation's skeleton lead the diverse HB structures: chain-like motifs composed of imidazole-$(TCNQ)_2$-imidazole cyclic units or two-dimensional sheets constructed by the alternation of R_2-4,4′-H_4Bim^{2+} cations and TCNQ columns. Furthermore, the strong cation-anion interaction *via* HB exhibits the pinning of the charges, and the HB patterns in two types of self assembled structures lead unique charge-distribution natures. In all salts investigated by Murata *et al.* [37] the hydrogen-bonding patterns regulate the electronic structures in TCNQ columns by strong cation-anion interaction, causing the nonuniform charge distribution and semiconducting behaviors with an electrical conductivity between 10^{-8} and 10^{-1} $S{\cdot}cm^{-1}$ and an activation energy between 0.07 and 0.23 eV. The authors of the paper [37] emphasize that the diverse HB architectures and electronic modulation effect of HBs observed in the TCNQ salts will provide a new strategy for the future molecular design of organic conductors.

Very interesting group of TCNQ salts containing hexaazamacrocyclic (see Table **1**) complexes was synthesized and characterized recently by Ballester *et al.* [39]. The crystal structure of hexaazama-

Fig. 4a

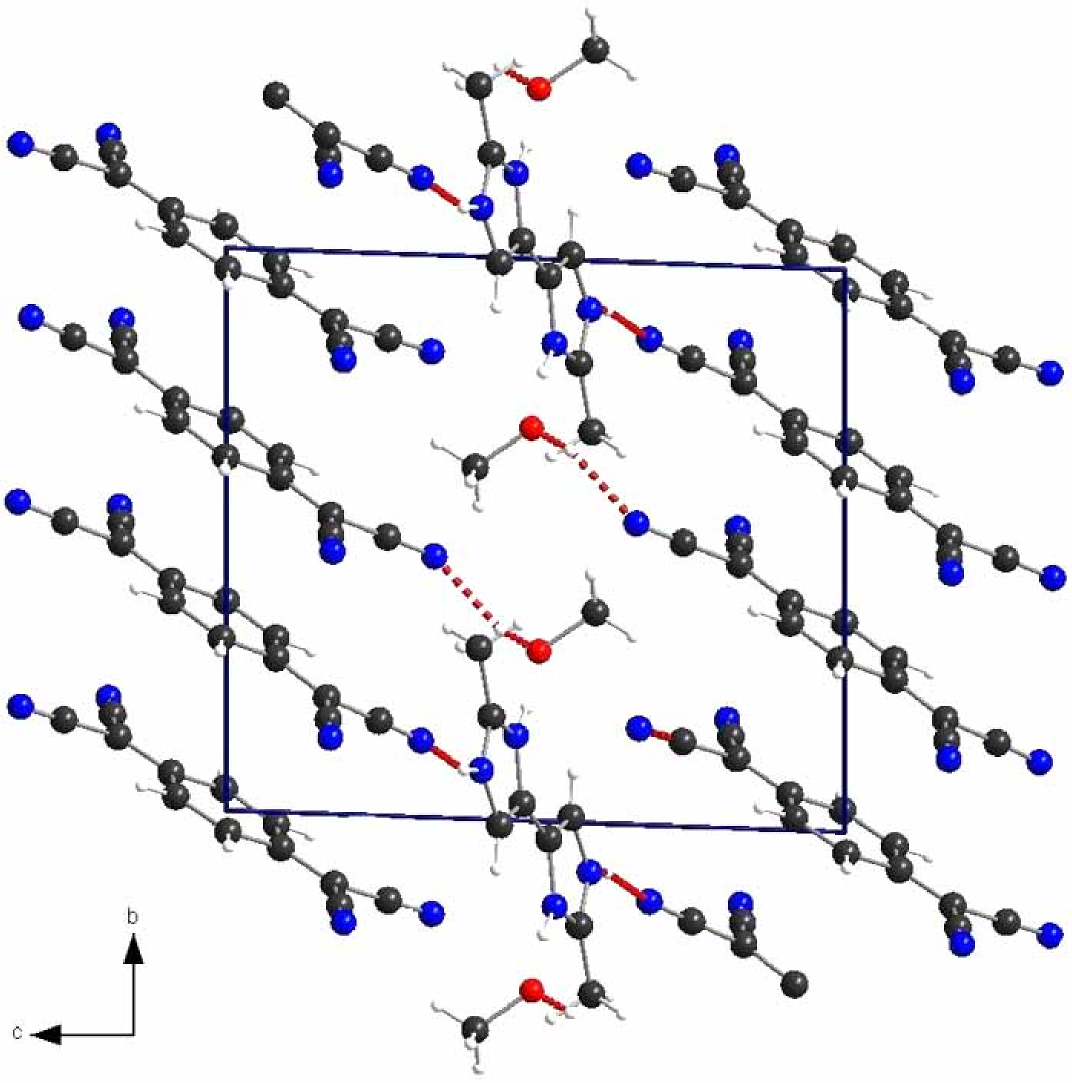


Fig. 4b

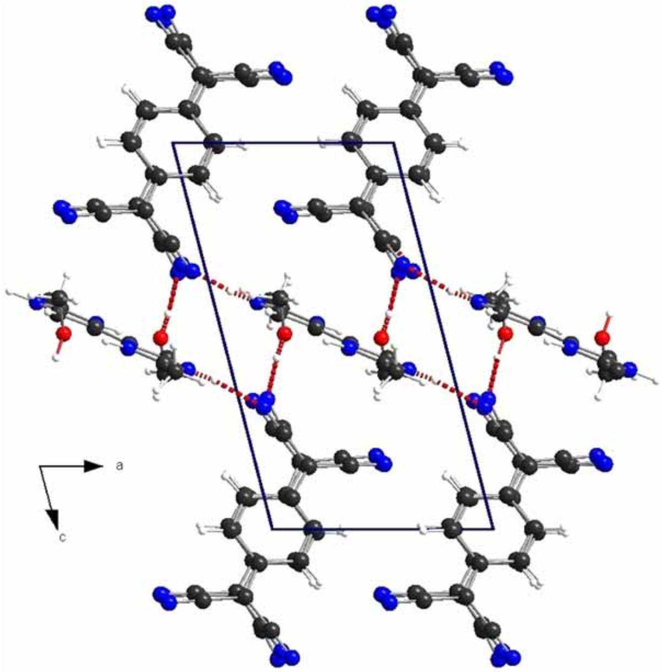


Fig. 4c

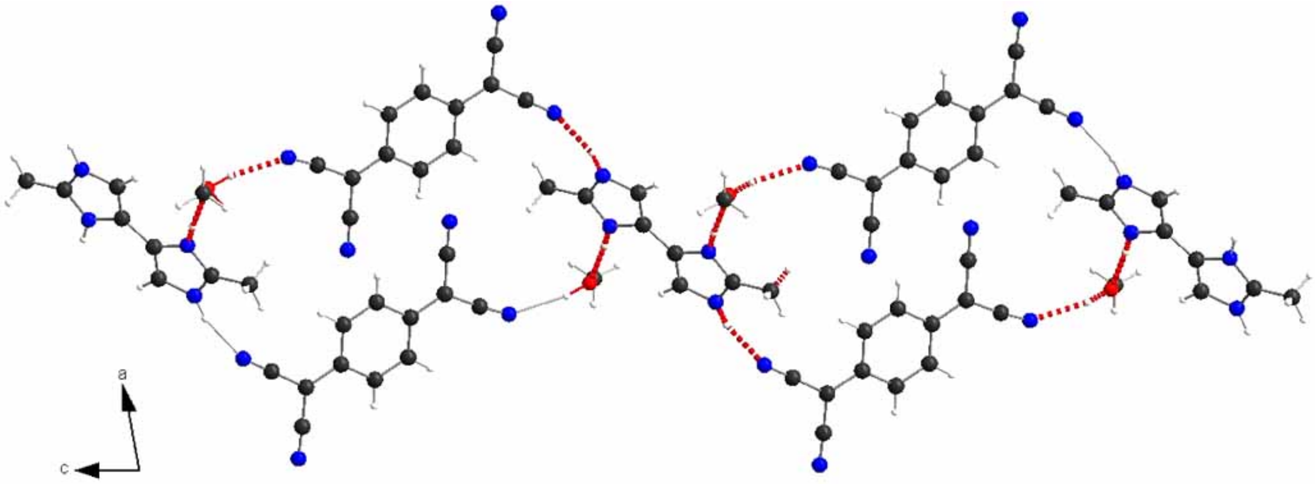


Fig. (4). Crystal structure of (Me_2-4,4'-H_4Bim^{2+})$(TCNQ)_3(MeOH)_2$ salt. 1D column of TCNQ molecules and HB (red points) of Me_2-4,4'-H_4Bim^{2+} along the *a*-axis (**a**), 1D chainlike motif by HB (**b**), and molecular packing along the *b*-axis (**c**) (figures are prepared tacking into consideration the crystal and molecular data of Brandenburg *et al.* [38]).

crocyclic complexes M([18]ane-N_6), where M is nickel or copper, is stabilized by a network of hydrogen bonds. These compounds react with TCNQ salts with formation of two types of derivatives, [M([18]ane-N_6)]$(TCNQ)_2$ and [M([18]ane-N_6)]$(TCNQ)_4$. The crystal structures of the nickel derivatives show that the former counter ions are built up by macrocyclic metal cations surrounded by dimeric dianions $(TCNQ)_2^{2-}$, either isolated or stacked along the crystal. The derivative with four TCNQ units consists of alternated chains of metallomacrocyclic cations and stacked TCNQ anions. The crystal parameters suggest that every TCNQ holds approximately 0.5 electrons and overlaps with a neighboring unit to form dimeric monoanions, $(TCNQ)_2^-$ [39].

The M([18]ane-N_6)]$(TCNQ)_2$ salt contains dimeric $(TCNQ)_2^{2-}$ anions alternating with [M([18]ane-N6)]$^{2+}$ cations. This structure is always associated with localized electronic charges leading to very low conductivity values well below 10^{-7} S·cm^{-1}. On the other hand, the M([18]ane-N_6)]$(TCNQ)_4$ salt shows the presence of partially reduced TCNQ stacks showing some degree of electronic delocalization. This is why these compounds have a semiconducting behavior with electrical conductivity of the order 10^{-4} S·cm^{-1} [39].

The [Ni([18]ane-N_6)]$(TCNQ)_2$ salt is built with four crystallographically different TCNQ species, identified by the authors of [39]. All the TCNQ are anion-radicals, as the IR spectrum suggests. The crystal packing (Fig. **6**) can be described as a bidimensional array of noninteracting metallomacrocyclic cations stacked along the [010] and [101] directions. The TCNQ units are located between the macrocyclic sheets forming dimeric dianions that stack in two different ways. Some TCNQs form infinite stacks built up of π overlapping TCNQ units. Another TCNQs form dimers stacked in the alternate sequence, but the interdimer distance is too long to consider the presence of π interactions between the dimers. The main interactions in the salt are the electrostatic attractions between cationic metallomacrocycles and dimeric dianions $(TCNQ)_2^{2-}$, which stack in the solid. These interactions are completed by various hydrogen bonds between the amine groups of the macrocycles and cyano groups in the TCNQ units [39].

The [Ni([18]ane-N_6)]$(TCNQ)_4$ salt is built with two crystallographically independent TCNQ molecules; both TCNQ show similar parameters and, within experimental error, they correspond to a formal charge of 0.5 electron. All the TCNQ species are stacked along the [100] direction interacting by π overlap with neighboring units (Fig. **7**). Crystallographically independent TCNQ alternate along the stack which can be alternatively seen as overlapping $(TCNQ)^{2-}$ dimers showing stronger interactions inside the dimer. The electrostatic interactions between the metallomacrocyclic cations and the TCNQ anionic stack are complemented by the

Fig. 5a

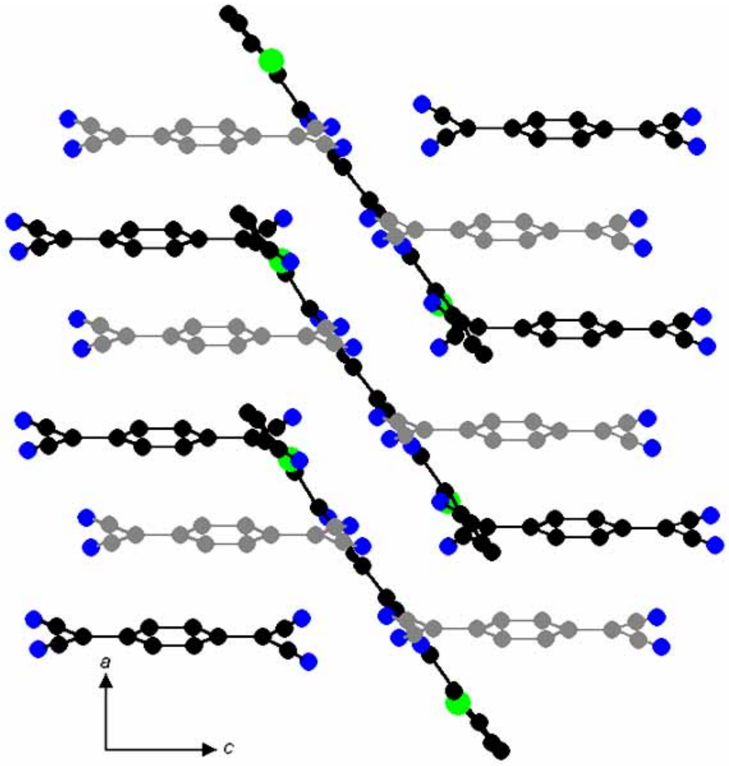


Fig. 5b

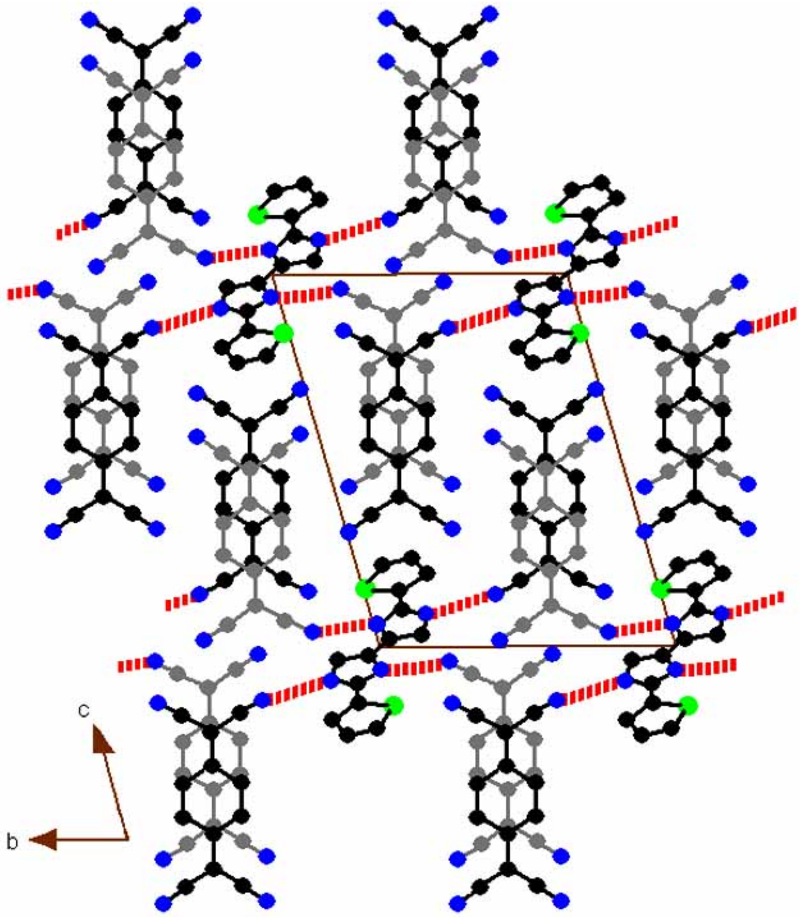


Fig. (5). Crystal structure of (Th$_2$-4,4$'$-H$_4$Bim^{2+})(TCNQ)$_4$ salt. 1D columns of Th$_2$-4,4'-H$_4$Bim^{2+} and TCNQ molecules viewed along the b-axis (black-colored are TCNQ-A molecules but grey-colored – TCNQ-B) (**a**) and molecular packing viewed along the a-axis (**b**) (according [37]).

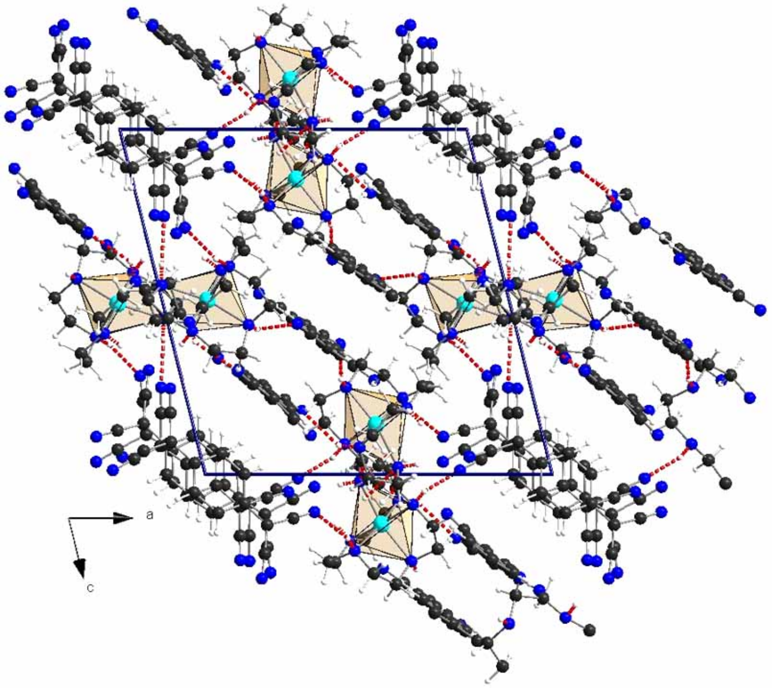


Fig. (6). View of the molecular packing of [Ni([18]ane-N_6)]$(TCNQ)_2$ modified salt containing supplementary oxygen atoms (figure is prepared tacking into consideration the crystal and molecular data of Brandenburg *et al.* [38]).

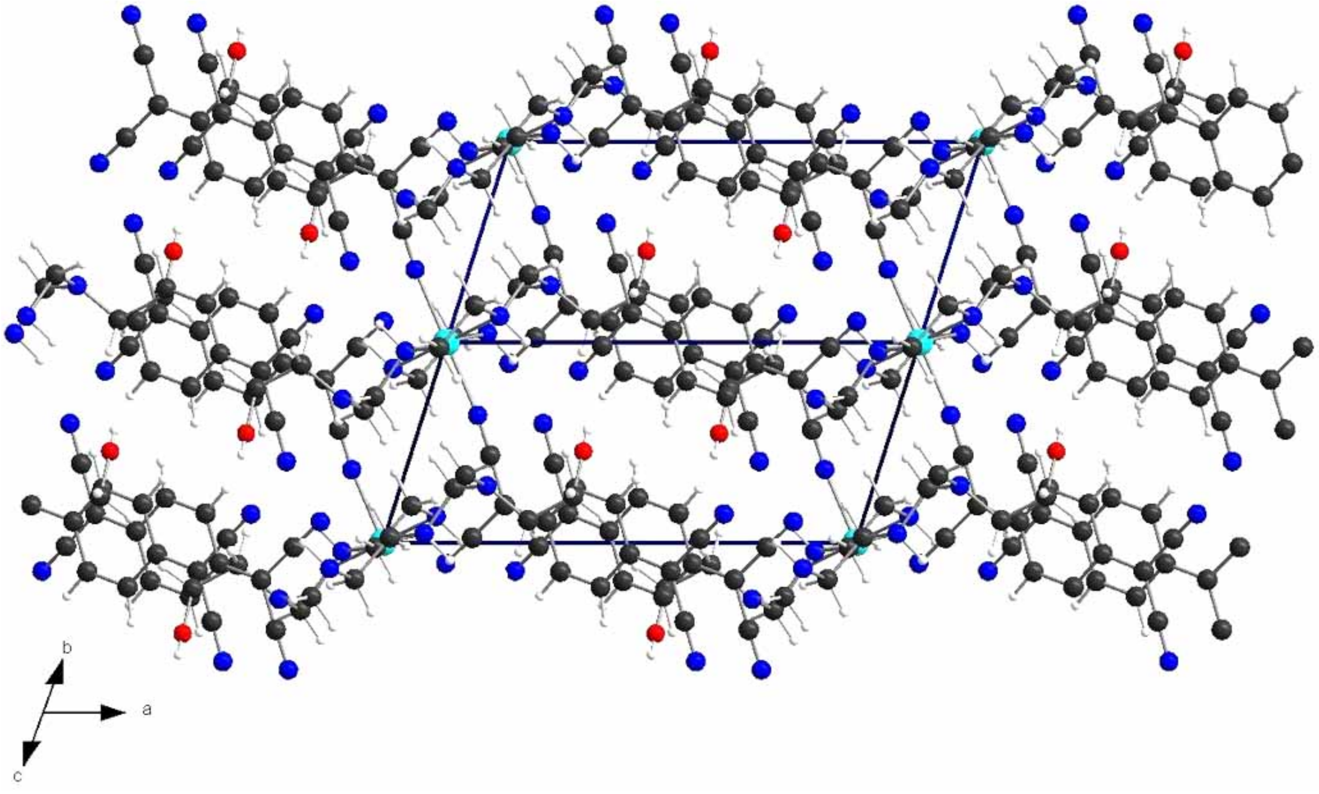


Fig. (7). View of the molecular packing of [Ni([18]ane-N_6)]$(TCNQ)_4$ salt (figure is prepared tacking into consideration the crystal and molecular data of Brandenburg *et al.* [38]).

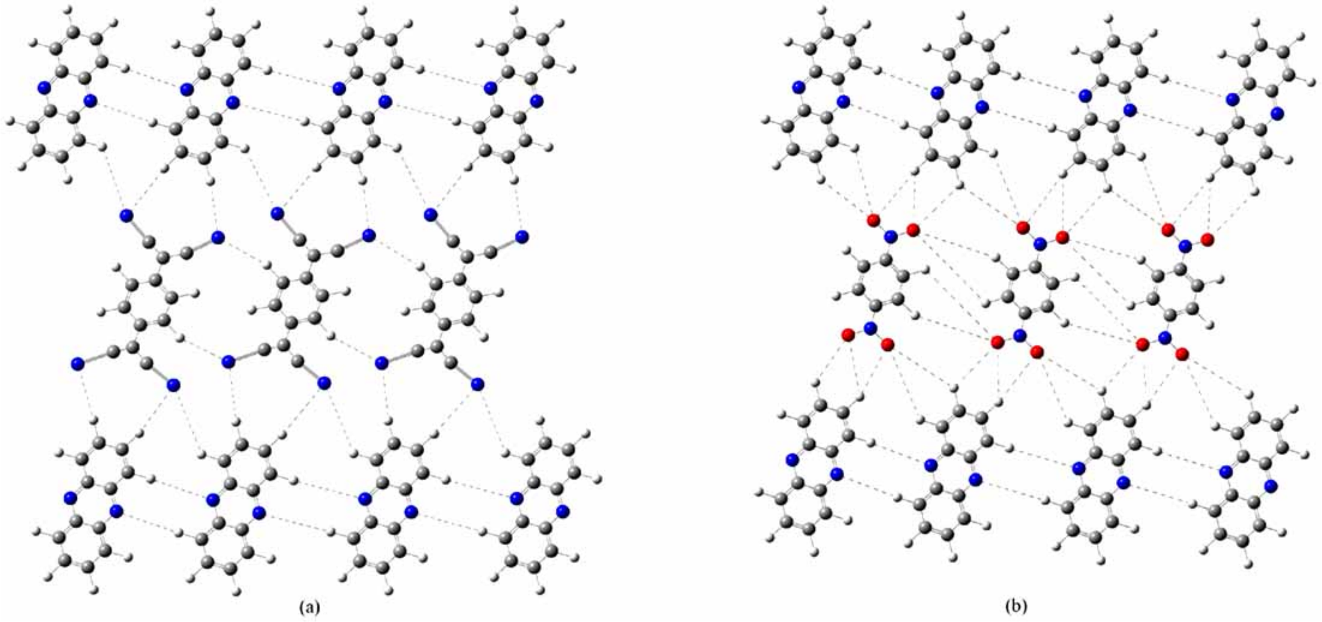


Fig. (8). The 2-D layer structures of the phenazine-TCNQ (**a**) and phenazine-1,4-dinitrobenzene (**b**) complexes (according [40]).

formation of several HB between the amine macrocyclic groups and the TCNQ cyano groups [38,39].

Ending the subject of hydrogen bonds in TCNQ salts we would like to pay attention to CT complexes, which form mixed stacks where the donor and acceptor molecules are stacked alternately in infinite columns. The phenazine-TCNQ complex (see Table **1**) illustrates it; for comparison a similar complex of phenazine-dinitrobenzene (DNB) is discussed [40].

There is a general consensus that weak hydrogen bonds such as C-H····X, where X is N or O, determine crystal packing, especially when strong interactions are absent. And more, many structures cannot be rationalized unless these hydrogen bonds are invoked [41]. In this context, above-mentioned CT complexes, which are essentially stabilized by stacking and C-H····X interactions, are good candidates to study the role of such interactions in determining the three-dimensional structural features.

The phenazine molecules in both complexes self-assemble through centrosymmetric C-H····N bonded dimers to form linear tapes C····N and C-H····N. The phenazine-TCNQ forms a 2D sheet structure but is exclusively stabilized by C-H····N bonds (Fig. **8a**). In the complex phenazine-DNB, the DNB molecules are held together by C-H····O HBs and are also hydrogen bonded to phenazine to form a planar two-dimensional sheet structure consisting of alternating 1D tapes of donor and acceptor molecules (Fig. **8b**) [40]. In both complexes the number of intermolecular interactions between donors and acceptors exceeds the intermolecular interactions between donor-donor and acceptor-acceptor. Thus, the authors of the paper [40] suggest that it is possible to control the geometrical arrangement of the molecules in lateral directions by manipulation of weak intermolecular interactions.

TCNQ ion-radical salts and CT complexes exhibit a wide variety of electronic characteristics depending of the cation present in the material. In addition, multiple phases exist with different physical properties. These properties derive primarily from the packing of the counter ions or cations in their crystal structure. The electronic interaction between both anions and cations are determined not only by the distances between them, but also by the spatial arrangement. It is by intuition clear that face-to-face interactions between rather flat TCNQ molecules along the stacks differ greatly from their side-to-side interactions or interactions between usually spatial cations. On the other hand, as it was signaled before, in TCNQ-derived materials the hydrogen bonds of various types and strengths play crucial role. All these effects appear together forming specific 2D or event 3D networks and determining crystal organization.

2.3. Melting of Organic Composites Based on TCNQ

In the end of the 1980s the Japanese scientists discovered the organic conductors that can be melt without decomposition [42,43]. These conductors were salts of TCNQ in which the cation may be N-alkylisoquinolinium or N-alkylpyridinium (see Table **1**). This discovery opened new avenues for practical use of such materials. Typical TCNQ salts have high melting temperature T_m (470 – 510 K) and are very viscous near the melting point. On the other hand, the decomposition temperature is very close to T_m. Distinctly lower melting temperature were observed in the complex salts of methyl-TCNQ (MeTCNQ) – an unsymmetrical electron acceptor. According to observation of Starodub *et al.* [44] the melting points of the MeTCNQ complex salts are 40 – 85 K lower than those of the analogous TCNQ salts but their electrical conductivity is lower by no more than an order of magnitude. These findings suggested the use of composites of TCNQ and MeTCNQ salts so as to obtain low melting but highly conducting organic materials. In fact, in the system $(\text{N-CH}_3\text{-iso-Qn})_{1-x}(\text{N-C}_3\text{H}_7\text{-iso-Qn})_x(\text{MeTCNQ})_{2-2x}(\text{TCNQ})_{2x}$, where Qn is the quinolinium (see Table 1), with x = 0.1, an eutectic is observed with a record $T_m = 353$ K [44]. In Q1D organic conductors the electrical conductivity is determined mainly by the electron transport along the TCNQ stacks. At the melting point the regular stacks disappear and the motion of the carriers can be accomplished only by thermally activated jumps or electron tunneling from one section of the deformed stack to another. Thus, it can result in an abrupt change of conductivity (Fig. **9**) and decrease of the activation energy. For $(\text{N-CH}_3\text{-iso-Qn})_{1-x}(\text{N-C}_3\text{H}_7\text{-iso-Qn})_x(\text{MeTCNQ})_{2-2x}$ $(\text{TCNQ})_{2x}$ salt value of E_a equals to 0.14 eV for the solid phase and 0.11 eV for the liquid phase [44].

Infrared spectroscopy is a perfect tool for detects the changes in the crystal structure, in particular in the molecular ordering of the TCNQ anions [3,4,9]. This method has been used by Świetlik and co-workers [45] for study a melting of $(\text{N-CH}_3\text{-iso-Qn})_{1-x}(\text{N-C}_3\text{H}_7\text{-iso-Qn})_x(\text{MeTCNQ})_2$ salt, with x = 0.8. IR absorption spectra of the salt at powdered sample dispersed in KBr pellet and thin film obtained by melting sample between KBr plates are shown in the Fig.

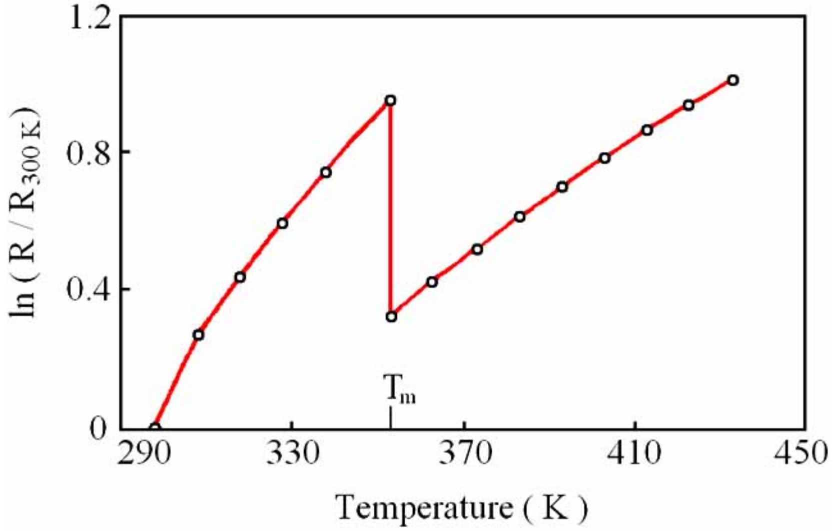


Fig. (9). Change of the resistance of the $(N\text{-}CH_3\text{-iso-Qn})_{1-x}(N\text{-}C_3H_7\text{-iso-Qn})_x(MeTCNQ)_{2-2x}(TCNQ)_{2x}$, composite with T_m = 353 K (according [44]).

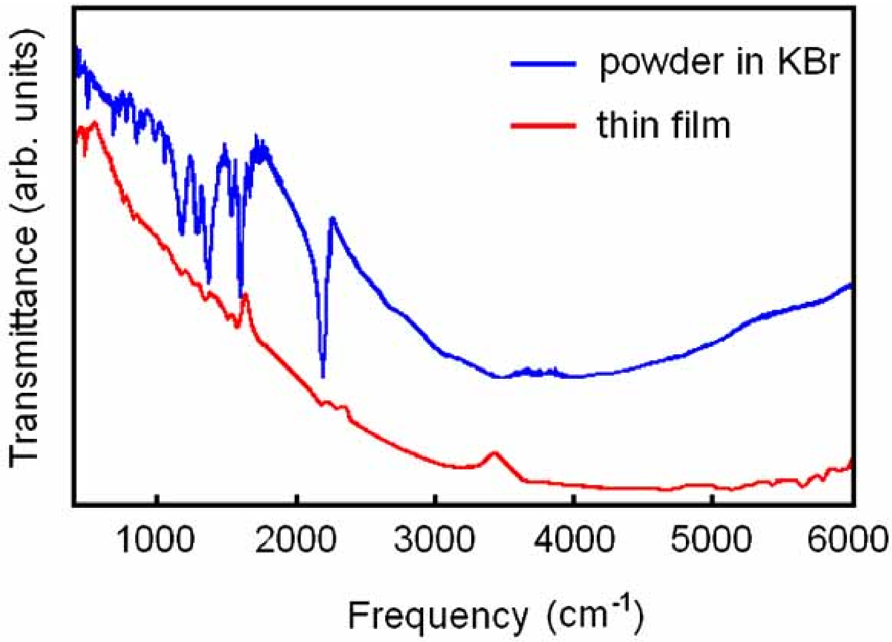


Fig. (10). IR absorption spectra of the $(N\text{-}CH_3\text{-iso-Qn})_{1-x}(N\text{-}C_3H_7\text{-iso-Qn})_x(MeTCNQ)_2$ salt, with x = 0.8, at powdered sample dispersed in KBr pellet and thin film obtained by melting sample between KBr plates (according [45]).

(**10**). The strongest vibrational bands related to totally symmetric A_g modes of TCNQ, activated by the coupling with its intramolecular vibrations, dominate the spectrum below the melting temperature. Above T_m these bands decrease gradually in intensity and nearly disappear. It confirms that as the temperature increases, the TCNQ stacks gradually break into segments, leading to electron localization. The effect of charge carrier's localization is supported by electrical conductivity data. Melting destroys irreversibly the conducting columns, and after cooling to room temperature, an amorphous phase is formed. The relatively high electrical conductivity of the molten phase could be explained by an existence of conducting paths in the amorphous sample. These paths are formed by strongly interacting TCNQ molecules and remain in the sample after cooling to room temperature [45].

Spectral methods have been used also by Morita *et al.* [46] for investigation of the thermal evolution of one-layer LB films of 2-pentadecyl-TCNQ (see Table **1**). The films shown gradual temperature-dependent changes below the melting point of the film, and then given dramatic spectral changes near the melting point. UV-Vis spectral changes of the film indicate that the morphological changes occur in domains of the film.

According to recently performed studies of the physical properties of anion radical salts having low melting points it is clear, that also asymmetric cations, such as quinolinium derivatives, give TCNQ salts with relatively low melting points [47]. Another example of the low melting salt is $(C_7TET\text{-}TTF)(TCNQ)$, where $C_7TET\text{-}TTF$ (see Table **1**) is bis(n-heptylthio)ethylenedithiotetrathiafulvalene. The salt is a neutral CT compound with alternating stacks, and quite low melting point at T_m = 328 K [48].

Four years ago Saito *et al.* investigated the thermal, electronic and magnetic properties of the anion radical salts of TCNQ with EMI and BMI (see Table **1**) in the liquid state [48]; EMI is 1-ethyl-3-methylimidazolium and BMI is 1-butyl-3-methylimidazolium. The EMI-TCNQ and BMI-TCMQ salts melt at 418 and 428 K, respectively. Except of symmetrical TCNQ the unsymmetrical acceptors with methyl (MeTCNQ) or ethyl (EtTCNQ) groups were used for preparation of melting TCNQ salts. The d.c. electrical

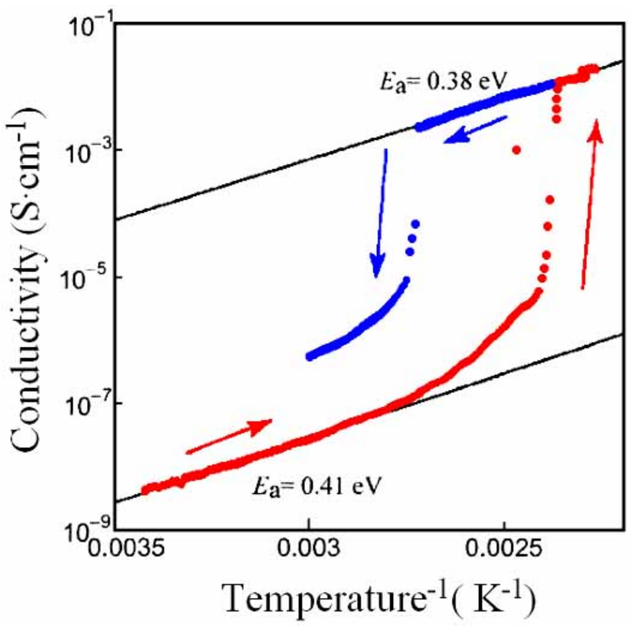


Fig. (11). Temperature dependence of d.c. electronic conductivity of EMI-TCNQ salt (the arrows show the hysteresis of the temperature dependence of the conductivity). The activation energies for both solid and liquid state are given. (according [47]).

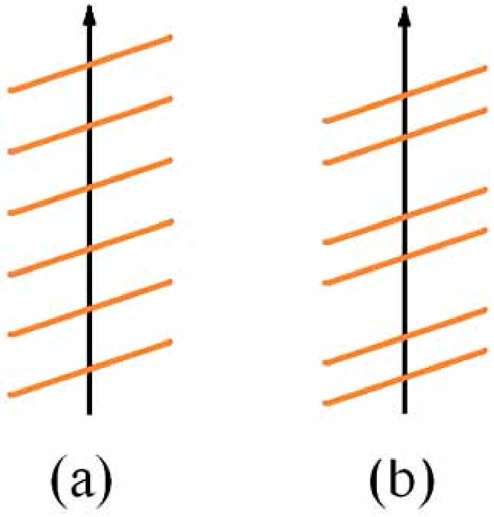


Fig. (12). Schematic view of the regular TCNQ$^-$ chain in the insulator phase (**a**) and in the conducting phase (**b**) of typical TCNQ ion-radical salts.

conductivity of EMI-TCNQ increases by four orders of magnitude at melting and decreases by three orders of magnitude at freezing (Fig. **11**). The salt shows semiconducting behavior with E_a = 0.41 and 0.34 eV for the solid and liquid state, respectively. The value of conductivity in the liquid state (≈ 10^{-2} S·cm^{-1}) is quite high compared to those of ordinary monovalent TCNQ salts, namely < 10^{-4} S·cm^{-1}. The observed hysteresis corresponds to the supercooled state observed in DSC measurements. When the constant voltage of 1.0 V was applied to EMI-TCNQ in the liquid state, the current decreases from 10^{-2} to 10^{-5} A in the first three hours then remained constant, whereas in the solid state the current was almost constant during the whole measurement. It was observed that high conductivity in the liquid state is realized by the increase of conducting carriers by the dissociation of dimers $(TCNQ^{\cdot-})_2 \rightarrow 2TCNQ^{\cdot-}$. This means that both ionic and electronic conductions contribute to the conducting mechanism in the liquid state [47].

Why the melting organic conductors are so interesting and important? The main reason of growing interest in such fusible conductive salts is their ability to form conducting layered electrodes of new types of capacitors. Such capacitors should be cheaper and better than the typical inorganic elements. The solid electrolytic capacitor also exhibits a large capacitance per unit area and a good frequency impedance response. As early as in the end of 80. all solid state capacitor composed of Al/TCNQ complex salt/Al_2O_3 insulator/Al showed an electric capacity of 7-8 μF [49]. On the other hand simple capacitor prepared with Cu: TCNQ thin films as an active layer shows reproducible resistive switching with distinctive reversible resistive switching effects. Three different states could be observed, a high resistance state (≈10^7 Ω), a low resistance state (≈10^4 Ω) and a very low resistance state with metallic like behavior (≈10^1 Ω). These properties of TCNQ-containing capacitors are also very promising.

2.4. Photoinduced Melting of Spin-Peierls Phase in CT Compounds

As it was mentioned, in majority of TCNQ ion-radical salts, TCNQ molecules stack face to face (Figs. **1** and **12**). An electron is transferred from a donor molecule or atom to a TCNQ molecule and a half-filled π-electron band is formed by the overlap of the π-orbital of neighboring TCNQ$^-$ anions. Purely 1D electronic system with nonzero on-site Coulomb repulsion energy U has a finite gap and becomes a Mott insulator (Fig. **12a**). Such systems undergo usually phase transition at T_c. Below T_c, two neighboring spins form a singlet state by molecular dimerization (spin-Peierls phase) (Fig. **12b**). 1D or better Q1D materials have strong instability inherent to electron-lattice (EL) and/or spin-lattice (SL) interactions and show characteristic phase transitions. The phase transitions in Q1D systems can be extorted by temperature, defects or irradiation. Strong femtosecond (fs) laser pulse can forced phase transition, so called photoinduced phase transition (PIPT). The PIPT is a process to the nonequilibrium phases generated from equilibrium by shining on high energy photons, and the nonequilibrium phase is a macroscopic excited domain that has new structural and electronic orders quite different from the starting ground state [50]. This phenomenon is important not only as the new subject in the field of physics but also as useful mechanisms for future optical switching devices.

One-dimensional correlated systems are good targets for the exploration of PIPTs. This is because photocarrier generations and/or charge transfer excitations by light can stimulate instabilities inherent to 1D nature of electronic states through strong electron-electron interactions and electron/spin-lattice interactions. There are three types of PIPTs which can be observed in selected 1D correlated electron systems: i) a photoinduced transition from a Mott insulator to a metal, ii) a photoinduced melting of a spin Peierls phase in organic CT compounds, for example in TCNQ ion-radical salts and iii) a photoinduced transition between neutral and ionic states in organic CT compounds.

Though the PIPT occur in various low-dimensional conductors, we will discuss this phase transition in M-TCNQ salts, where M is an alkali metal K or Na. The PIPT in these salts were recently investigated in detail by Japanese scientists [51,52] by a reflection-type femtosecond pump-probe spectroscopy. The spin-Peierls phase in these materials is destabilized by the generation of photocarriers through the breaking of the spin-singlet states in dimers. It results in the decrease of the dimeric molecular displacements within a few hundred of femtoseconds over several tens of TCNQ molecules. It is accompanied by the displacive-type coherent oscillations with the frequencies below 100 cm^{-1}, which are easily detectable by polarized Raman scattering spectroscopy.

As shown in Fig. (**13**), the temperature dependence of the x-ray reflection intensity activated by the dimerization gradually increases with decreasing temperature below T_c; the spin susceptibil-

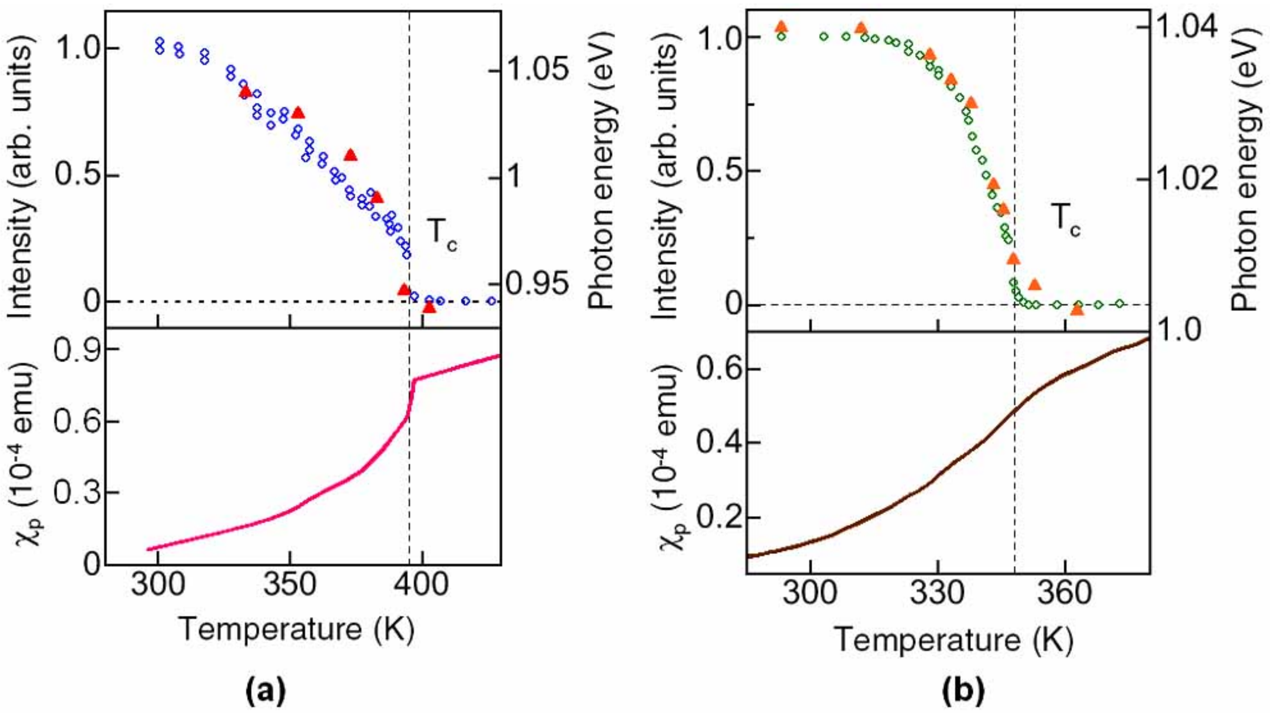


Fig. (13). Temperature dependence of the x-ray reflection intensity (open circles) reflecting the dimeric molecular displacements and the peak energy of the CT band (triangles) (upper panels) and temperature dependence of the spin susceptibility (lower panels) in K-TCNQ (**a**) and Na-TCNQ (**b**) (according [52]).

ity sharply decreases also below T_c [53]. It could be explained by assuming a uniform antiferromagnetic spin chain (S = ½), indicating the spin-Peierls nature of this transition. In the both salts the first-order phase transition from the paramagnetic phase to the dimerized diamagnetic phase occurs at T_c = 395 K (in K-TCNQ) and T_c = 348 K (in Na-TCNQ).

According to investigations of Ikegami *et al.* [52], photogenerated electrons and holes were instantaneously localized *via* the electron-lattice interaction, forming the polaronic states. Such polaronic carriers behaved as nonmagnetic impurities. Consequently, the SP phase was destabilized, and the dimeric molecular displacements decreased over 20-40 TCNQ molecules within a few hundred of femtoseconds. The photoinduced decrease of the dimeric molecular displacements was accompanied by the displacive-type coherent oscillations. A difference was observed in the nature of the coherent oscillations between K-TCNQ and Na-TCNQ salts. The former salt shows three coherent oscillations: 20, 49, and 90 cm^{-1} but the latter shows two oscillations: 49 and 99 cm^{-1}. By taking into account the temperature dependence of the Raman spectra, the mode with 20 cm^{-1} in K-TCNQ and the modes with 49 and 99 cm^{-1} in Na-TCNQ are assigned to the phonon modes in the SP ground state. By comparing the oscillations with the polarization dependence of the Raman scattering spectra, the authors of [52] assigned the 20 cm^{-1} mode of K-TCNQ, and the 49 cm^{-1} mode of Na-TCNQ to the longitudinal optical (LO) modes, whereas the 99 cm^{-1} mode of Na-TCNQ – to the transverse optical (TO) mode. The modes with 49 and 90 cm^{-1} in K-TCNQ are assigned to the local modes originated from the photoexcited states. The discussion in [52] suggests that for the stabilization of the spin-Peierls phase, the LO mode is important in K-TCNQ, whereas the LO and TO modes are important in Na-TCNQ. Such a difference can be explained by the differences of the crystal structures and the nature of the SP transitions in these two salts [52].

Summarizing, it was shown by Ikegami *et al.* [52], that photoirradiation of M-TCNQ salts using a femtosecond laser pulse induces the decrease of the dimerization within a few hundred of femtoseconds through the destabilization of the SP phase due to the photocarrier generations. Fig. (**14**) shows schematic illustration of the photoinduced melting of the SP phase: – photoexcitation of an electron-hole pair (a), the dissolution of the dimerization (b), and the generation of the coherent oscillations (c) [52].

Photoinduced melting of charge order has been recently investigated in several organic and inorganic low dimensional systems. An ultrafast, photoinduced phase transition from the insulator phase to the metal phase induced with very weak excitation intensity, at near room temperature in $(EDO\text{-}TTF)_2PF_6$, where EDO-TTF (see Table **1**) is ethylenedioxy-tetrathiafulvalene, was recently reported [54]. This effect was described in detail by using the exact many-electron wave function coupled with classically treated phonons in the one-dimensional quarter-filled Hubbard model with Peierls and Holstein types of electron-phonon couplings [55]. Comparative studies of two polytypes exhibiting large [Θ-$(BEDT\text{-}TTF)_2$ $RbZn(SCN)_4$] (see Table **1**) and small [α-$(BEDT\text{-}TTF)_2I_3$] molecular rearrangements through the charge-order transition were performed by Yakushi *et al.* [56]. The roles of the molecular rearrangements on the formation of the charge-order and the metallic domain are shown on the basis of low-frequency lattice dynamics. On the other hand, the major contributions of the electronic instabilities, which are due to Coulomb interaction, were shown. The PIPT in polymer suitable for optical sensors and data storage materials as well as in $K_{0.3}MoO_3$ were also investigated.

3. SUMMARY

In the paper we discussed some characteristic and important effects occurring in low-dimensional organic solids such as molecular organization of thin films of TCNQ salts, multidimensionality of hydrogen bonded networks of the salts – their types and strengths, melting of organic composites based on TCNQ and photoinduced melting of spin-Peierls phase in CT compounds.

The general trend in the study of organic conductors is to modify, through an imposed molecular organization, the physical properties of these materials on a mesoscopic or even microscopic scale. This is why the influence of the spatial structure and properties of

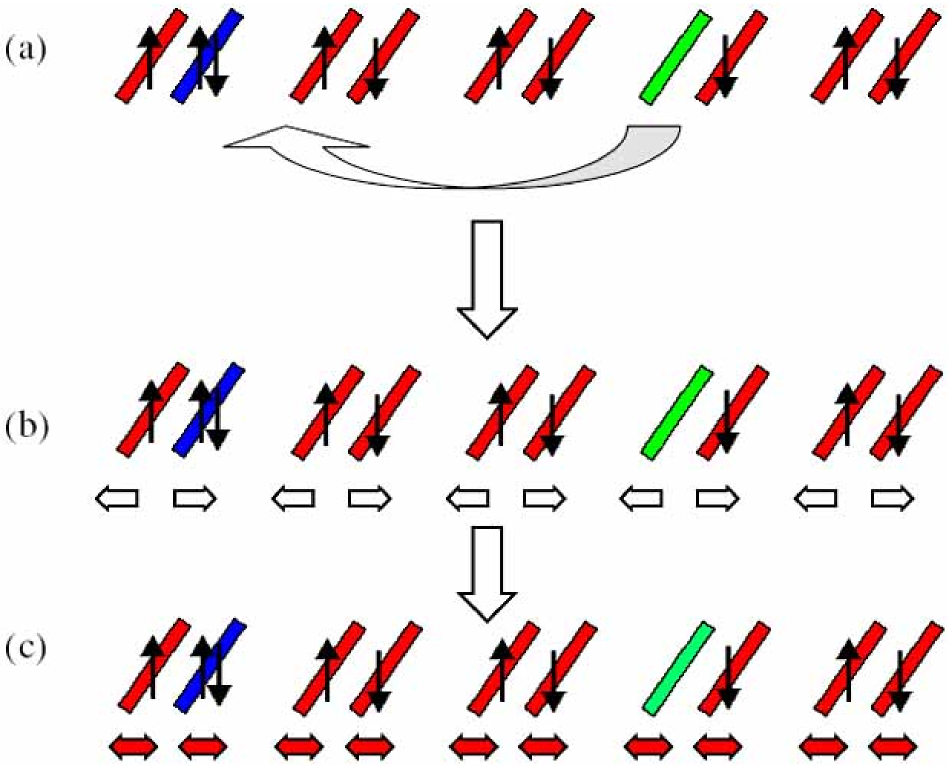


Fig. (14). Schematic illustration of the photoinduced melting of the spin-Peierls phase: photoexcitation of an electron-hole pair (**a**), the dissolution of the dimerization (**b**), and the generation of the coherent oscillations (**c**) (according [52]). Red molecules represent $TCNQ^{-1}$, green molecules – $TCNQ^{0}$, and blue molecules – $TCNQ^{-2}$.

the cations on selected physical properties of TCNQ complex salts and some uncommon effects occurring in these salts are shortly discussed in this article. It is necessary to notice, that the physical properties of low-dimensional organic conductors depend on several parameters, between them spatial organization, physical and chemical properties of electron-donors and acceptors, dominant interactions between them and so on. All these factors in organic materials can be relatively easily tailored according to our needs. It is of great importance because organic conductors, between them TCNQ salts, could be applied in various molecular electronics elements and devices such as high density and high-speed optical memories, photo- and electro-switches, organic light emitting diodes, bio-sensors, drain electrodes for bottom-contact transistors, thin-layer amperometric sensors and sensitive layer for gas (CO_2, NO_2, O_2, humidity) detection.

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Received: August 04, 2009 Revised: September 09, 2009 Accepted: October 05, 2009