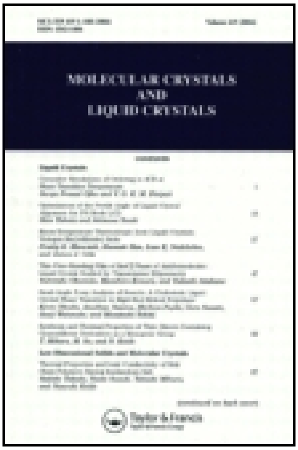

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Neutral-Ionic Transition, Ferroelectricity, and Field-Effect Transistors Based on Molecular Donor-Acceptor Compounds

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Versatile π-electronic functionality enabled by application of molecular donor(D)-acceptor(A) compounds are overviewed. These compounds are highlighted with respect to the quantum neutral-ionic phase transition, relaxor, displacive-type ferroelectricity, and also to the use in interface engineering of organic field-effect transistors (FETs).

Keywords: charge-transfer complexes; field-effect-transistor; hydrogen bond; neutral-ionic transition; organic ferroelectrics; organic semiconductors

INTRODUCTION

In an emergent field of "organic electronics," various types of functional organic materials are increasingly demanded from the industrial market as the disposable, light-weight, and flexible devices with ultimate goal for "all-organic" devices. The exploration of new materials and functionalities is a key step toward new applications as well as scientific progresses. Here we show some novel π-electronic

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functionality realized by the combinations of molecular donor (*D*)-acceptor (*A*) compounds, which include not only charge-transfer (CT) complexes but also the combination of proton-donor (acid) and acceptor (base). In addition some application of the molecular *DA* compounds is presented in organic field-effect transistors (FETs) that are known as key element devices in the organic electronics.

First, we demonstrate phase controls in the neutral-ionic phase transition (NIT) of *DA*-type system toward the zero Kelvin transition point (quantum critical point, QCP) and relaxor ferroelectrics. The proximity region of "QCP" has currently been one of the great scientific concerns in the correlated electron system. This is because many unconventional quantum phenomena are observed such as exotic superconductivity and non-Fermi liquid or magnetic instability behaviors of metal [1]. Meanwhile, "relaxor ferroelectric" is also a promising material as the ultrahigh dielectric and electromechanical responses are advantageous for many applications [2].

The ferroelectricity is a very important property, as has been versatile in applications to electronics and optics: capacitor, nonvolatile memories, piezoelectric transducers/actuators, pyroelectric sensors, high performance gate insulators in FET, nonlinear optics, and so on [3]. Whereas the purely organic ferroelectrics are quite few, we discovered the displacive-type ferroelectrics from the *DA*-type compounds, which are distinct from the conventional designs using polar organic molecules such as thiourea.

For exploring the electronics device applications, materials interfaces are of fundamental importance. For example, charge injections through the interface between metallic electrodes and semiconducting channels play crucial roles in the performance of organic (opto-)electronics devices, such as organic FETs, light-emitting diodes, photovoltaic cells, and so on [4,5]. We demonstrate here for some thin-film and single-crystal FETs that the use of molecular *DA* compounds can provide new functionality also to the interfaces of molecular materials.

PHASE CONTROLS OF NEUTRAL-IONIC TRANSITION

The NIT [6] is a unique valence transformation in the *DA*-mixed stack CT complexes. All the intriguing phenomena such as nonlinear electric transport [7], current-induced switching of the resistance by orders of magnitude [7], and photo-induced phase transformation [8] originate from such the valence instability of this one-dimensional system. Furthermore, the NIT materials are good candidates for ferroelectrics [9]. This is because the Peierls or spin-Peierls instability deforms the ionic lattice into the polar *DA*-dimerized chain. Indeed, the ferroelectric ordering in the prototype compound, TTF -*p*-chloranil (QCl_4), is accompanied by huge dielectric constant exceeding several hundreds [10–12].

The application of hydrostatic pressure and chemical modifications are useful for controlling valence instability through the change of electrostatic energy. The most successful example is the isomorphous series derived from the DMTTF (4,4′-Dimethyl-TTF)-QCl_4 complex showing the NIT at 65 K [13]. The four Cl sites can be substituted one by one with Br atoms, until the ionic phase with antiferroelectric (AFE) order disappears for the full substitution [14]. Conversely, when the lattice is compressed by applying hydrostatic pressure on the DMTTF-QBr_4 crystal, the NIT is recovered with the shift of dielectric peak from the low-temperature side (Fig. 1) [15]. In the pressure range near $P_c \sim 0.9$ kbar, which corresponds to QCP, the quantum paraelectricity is seen as the characteristic ε-saturation. It proves that the electric polarization experiences a quantum-fluctuation near $T = 0$ K.

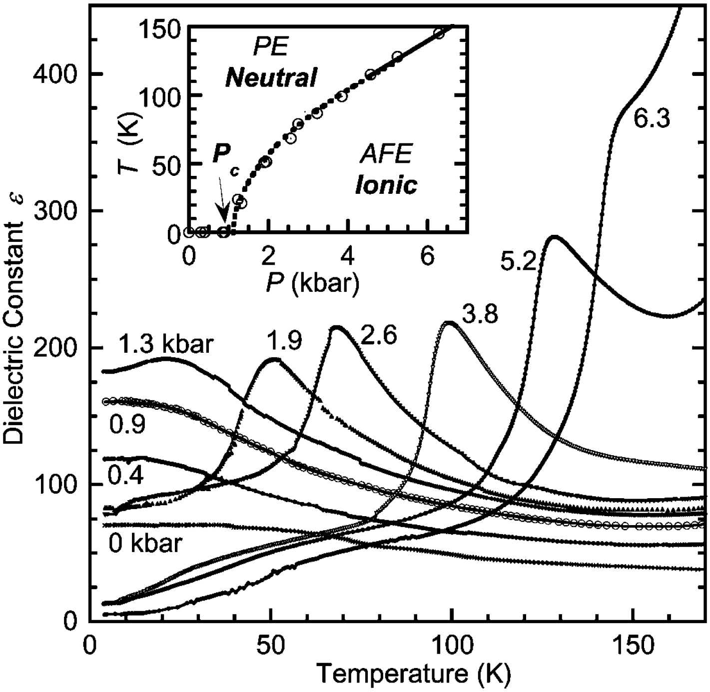

FIGURE 1 Temperature dependence of dielectric constant measured along the *DA* stack for a DMTTF-QBr_4 crystal under various hydrostatic pressures. (Inset) Pressure-temperature phase diagram.

Alternatively, without applying hydrostatic pressure, the 2,6-dibromo-substituted (2,6-QBr_2Cl_2) complex reproduced very similar quantum paraelectricity, manifesting itself in the very vicinity of the QCP. Furthermore, this compound experiences the fluctuation between the neutral and ionic states in both molecular charge and dimeric distortion at the lowest temperature as shown by the diffuse x-ray scattering and Raman scattering spectra [16]. Such the phase transition may be called a "quantum NIT."

The other interesting phenomenon arising from the NI transition is "relaxor," which is named after the "glassy" relaxational behaviors with strong frequency dispersion. This is clearly shown in Figure 2a for the TTF-QCl_4 crystal mixed with 12%-doped trichloro-*p*-benzoquinone (QCl_3) [17]. The dielectric peak height is several times amplified to a few thousand. Usually, the relaxor is realized by bringing the strong randomness or frustration into the ferroelectric system. Since the dopant with the weaker electron affinity favors the neutral state, the resultant destabilization of the ionic phase appears as the shift of dielectric peak to the low temperature (Fig. 2a). Beyond the critical QCl_3 content $y = 0.11$, the coexisting neutral and ionic species are found over wide temperature range as manifested by the ionicity (ρ)-sensitive phonon mode spectra (Fig. 2b). Therefore, the neutral regions around

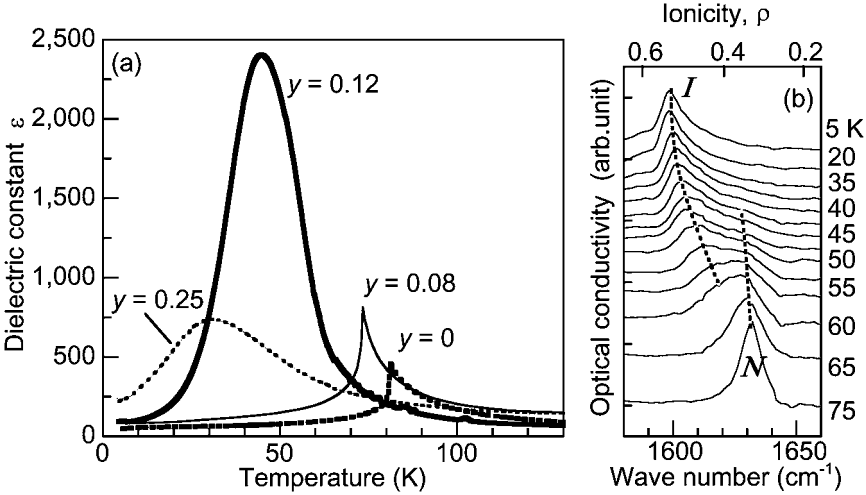

FIGURE 2 (a) Temperature dependence of dielectric constant ε for TTF-$(QCl_4)_{1\text{-}y}(QCl_3)_y$ crystals with various QCl_3 content, y. (Inset) The ε-T curves at various frequency of applied ac electric field for $y = 0.12$ crystal showing the relaxor behavior. (b) Thermal change of the C=O mode spectra showing the N-I phase segregation for $y = 0.12$ crystal.

the impurity sites should be locally embedded in the host ionic lattice, and weaken the dimeric distortion. According to the x-ray diffraction of the relaxor crystals, the long-range ferroelectric order appears to develop only along the *DA* stack direction. Such the dimensional crossover from 3D to 1D is an origin of the relaxor characteristics.

ROOM-TEMPERATURE FERROELECTRICITY

Although some CT complexes show the dielectric properties characteristic of a ferroelectric transition, none of them have so far shown the clear polarization hysteresis. They are usually bad insulators, and often suffer from the dielectric break down. To improve the electric leakage, we have developed a supramolecular approach using combination of proton D (=acid) and A (=base) as an alternative way.

The newly developed ferroelectrics are co-crystals of phenazine (Phz) and 2,5-dihalo-3,6-dihydroxy-*p*-benzoquinones (chloranilic acid (H_2ca) or bromanilic acid (H_2ba), designated as H_2xa) [18]. The H-bond between the hydroxy group and the nitrogen of Phz constructs an infinite supramolecular chain of the alternating D and A. At high temperature phase, both molecular structures are centrosymmetric and hence nonpolar. Furthermore, both molecules are not the in proton-transferred ionic state but electrically neutral. Even in the ferroelectric phase, all the molecules remain neutral and retain the nearly nonpolar structure. Only slight molecular displacement breaks the crystal symmetry.

Nevertheless, the Phz-H_2xa co-crystals reveal very large dielectric constant, which increases up to 2000–3000 at the transition point and exceeds 100 even at room temperature, as shown in Figure 3a. These values are the largest among the organic ferroelectrics. The transition temperature significantly increases, and especially for the Phz-H_2ca crystal, reaches the room temperature upon application of pressure (>6 kbar) [18] or deuteration of the H-bonds [19]. The deuterated Phz-D_2ca crystal displays the transition point at $T_c = 304\,\mathrm{K}$. Its clear polarization hysteresis curve observed at 300 K (Fig. 3b) evidences the room-temperature ferroelectricity. Spontaneous polarization (P_s) in the Phz-H_2xa crystals and their deuterated analogs reaches as large as 0.7–0.8 $\mu\mathrm{C/cm^2}$ at sufficiently low temperature below the transition point. The estimated P_s from the classical dipole model is too small to account for the large values as observed.

In this way, the above compounds seem to address new aspects of organic ferroelectrics in addition to the material design itself. According to the modern theory based on the Berry-phase picture [20], the importance of covalent bonding nature as the origin of electric polarization has already been recognized for the representative displacive-type ferroelectric oxides. The covalency in the molecular crystals should correspond to the significant charge density on the intermolecular space. This is actually observed for the intermolecular H-bonds, the importance of which is also suggested by the significant isotope effect on the ferroelectricity. The state-of-art first-principle calculation based on this model can quantitatively reproduce the ferroelectric feature of the present compounds [18,21]. In this sense, this compound could be viewed as a molecular-crystal version of "$BaTiO_3$," the most prototypical displacive-type ferroelectric.

FIELD EFFECT TRANSISTORS

In organic FETs, channels are usually composed of nominally intrinsic molecular semiconductors whose electrical contacts are formed directly with inorganic metal electrodes. This is significantly different from the case of inorganic semiconductor devices [22], mainly because of the difficulty in controlled chemical doping of molecular solids. Nevertheless, it is crucial to establish a reliable method of carrier doping in the active channel materials, in order to have precise control of the FET characteristics such as threshold gate voltage, which enables low-power device operations.

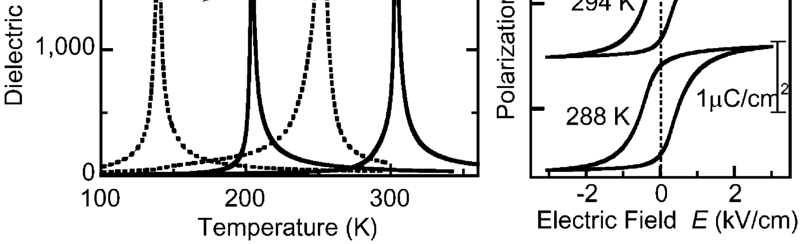

FIGURE 3 (a) Temperature dependence of dielectric constant of Phz-H_2ca, Phz-H_2ba (dotted curves) and their deuterated crystals (solid curves). (b) Thermal variation of hysteresis loops of electric polarization of the deuterated Phz-D_2ca crystal, showing the room-temperature ferroelectricity.

Our method of controlled carrier doping is based on the concept of "interlayer CT," as extended from the CT interaction in molecular *DA* compounds. It is found that the deposition of organic acceptor layers on top of the donor-based semiconducting channel layers provides mobile holes into the channels of organic thin-film FETs [23]. We used evaporated thin films of pentacene as active channel layers and F_4TCNQ, which is known to have large electron reduction potential, as additional organic acceptor layers. The illustration and typical transfer characteristics of the devices are presented in Figure 4. In the device whose channel is wholly covered by the acceptor layer, we observe large shift ($\sim 50\,V$) of the threshold gate voltage, with keeping the mobility constant ($1.0\,cm^2/Vs$). It is also found that the size of the shift can be predefined in the range of less than 50 V, by the local deposition of acceptor layers on top of the channels. From the variation of both the threshold gate voltage and the on/off current ratio with changing the coating area, we conclude that the holes are doped into the channels from the spatially-separated CT interface, where the doping

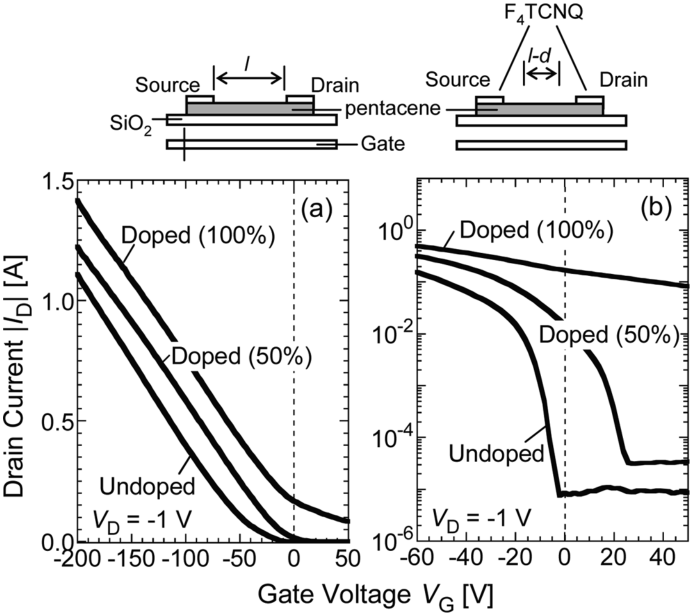

FIGURE 4 (Top) An illustration of carrier-doped pentacene thin film FETs by full and local (50%) deposition of acceptor layers on top of the channels. (a) Linear and (b) logarithmic plot of transfer characteristics for the doped and undoped pentacene thin film FETs, measured at $V_D = -1.0\,V$.

concentration is roughly proportional to the coating area on top of the channels. The method enables us to tune the threshold gate voltage as well as the film conductivity in pentacene thin film FETs, with keeping both the high field-effect mobility ($\sim 1\,\mathrm{cm}^2/\mathrm{Vs}$) and on/off current ratio ($> 10^5$).

Another fundamental issue in organic FETs is efficient carrier injections at the metal/semiconductor contacts. For this purpose a particular method is necessary suitable for molecular materials, because of the difficulty in such rich impurity doping at around the contacts as conventionally adopted in inorganic semiconductor devices. To achieve the tunable engineered contacts in organic FETs, we employ highly conductive molecular *DA* compounds as source and drain electrodes [24]. Using a prototypical single crystal FET based on DBTTF-TCNQ as channels it is demonstrated that the organic electrodes optimize the efficiencies in carrier injections. Figure 5 presents the transfer characteristics of the single crystal FETs with TTF-TCNQ, Au, and Ag electrodes, respectively. The device shows highest n-type mobility of approximately $1.0\,\mathrm{cm}^2/\mathrm{Vs}$, using TTF-TCNQ metallic thin-film electrodes. Comparing the present case with the devices with Au or Ag electrode, we conclude that the

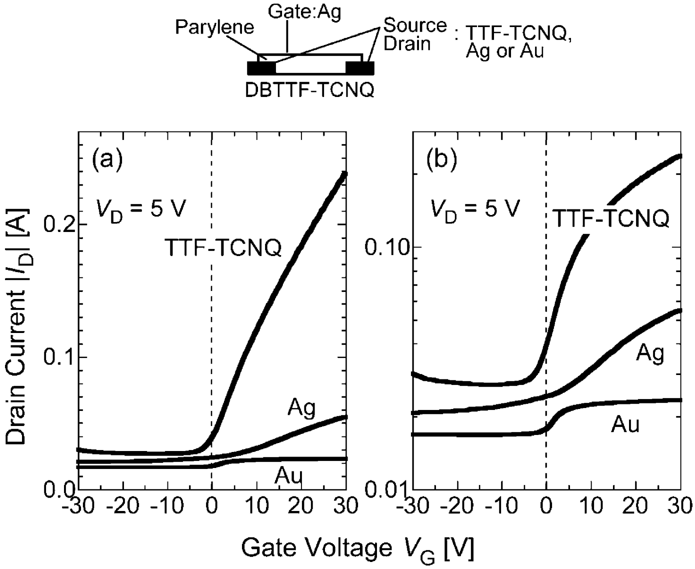

FIGURE 5 (a) Linear and (b) logarithmic plot of transfer characteristics for DBTTF-TCNQ single crystal FET's with the source and drain electrodes composed of Au, Ag, and TTF-TCNQ electrodes, measured along b-axes.

efficient electron injection with TTF-TCNQ electrode is associated with minimal contact potential at the metal/semiconductor interface, which is achieved through the nearly identical molecular levels between partially ionized TCNQ ($\mathrm{TCNQ}^{-\rho}$) as electrode and neutral TCNQ (TCNQ^{0}) as the channel. We propose that the use of organic metal electrodes could also lead to the prospective all-organic FETs with controllable characteristics. For example, Fermi energy can be finely tuned by chemical substitution of component donor and acceptor molecules, providing control of p- and n-type operations [25].

SUMMARY

The researches on solid-state CT complexes have been stimulated mostly by the interest in the organic (super)conductors and magnets. Meanwhile, as exemplified by the quantum phase transition and relaxor, our current studies extending to the dielectric properties have disclosed the novel phenomena implying possible new functionalities, which would awake concerns not only on the basic science but also on the potential applications. In particular, ferroelectricity and all-organic transistors would have high potential for diverse applications.

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