

Order–Disorder Transition of Nonplanar Molecules and Dielectric Anomaly in a Crystal of Charge-Transfer Complex

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Solid-state chemistry and physics of charge-transfer (CT) complexes have been developing molecular conductors/superconductors and magnets of current interest,¹ but little has been exploited as ferroelectrics, one of the most important phases among solid-state properties. Ferroelectric/antiferroelectric phase transition in the organic molecular system has mostly been realized in hydrogen-bonded molecular crystals with mobile protons.² Nevertheless, CT complexes are also good candidates for molecular ferroelectrics with use of strong electron–lattice interactions. In particular, lattice dimerization in semiconducting crystals of alternately stacked donor and acceptor molecules results in creation of a ferroelectric chain with a large electric dipole.³ A typical example is the spin-Peierls-like dimerization in ionic D^+A^- chains with $S = 1/2$ spins on the respective donor (D) and acceptor (A) molecules. The neutral–ionic transition with the change in the molecular valence also accompanies analogous dimeric displacement, as typically seen in a ferroelectric transition in tetrathiafulvalene-*p*-chloranil crystals.^{4,5}

Besides the molecular displacement mentioned above, deformation of flexible constituent molecular moiety could generate a ferroelectric chain in a mixed-stack architecture, although such molecular-crystal engineering has not been employed yet. The motivation of the present study arises from the observations that the planar conformation is accessible in the CT complex even for some π -electron molecules which are bent in their neutral state. The phenazine-based donor molecule is one such example, because the folding pyramidal deformation around the nitrogen atoms in the neutral state⁶ is released by the delocalization of unpaired electrons upon oxidation.⁷ In this paper, we present structural, optical, and dielectric properties of a new complex of 5,10-dihydro-5,10-dimethylphenazine (M_2P) with 2,5-dimethyl-

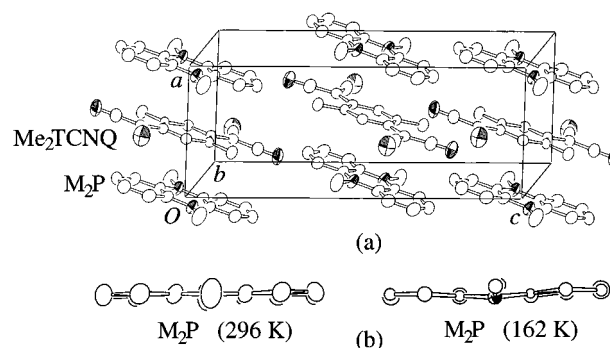
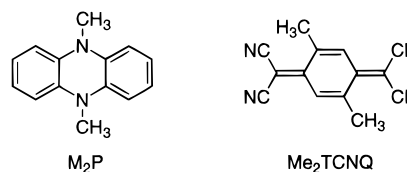


Figure 1. (a) Crystal structure of M_2P - Me_2TCNQ at room temperature (296 K). (b) M_2P molecules projected along the molecular short axis at 296 (left) and 162 K (right).

7,7,8,8-tetracyano-*p*-quinodimethane (Me_2TCNQ) as an example of dielectric phase transition accompanied by the order–disorder phenomenon of the deformation of fractionally charged molecules.



Rod-shaped black crystals of M_2P - Me_2TCNQ were grown by diffusion of the purified components in acetonitrile solution. The crystal structure determined by X-ray diffraction measurements⁸ at room temperature (296 K) belongs to the monoclinic $P2_1/c$ space group, and contains alternate stacks of DA molecules along the *a* axis with uniform separation of 3.37 Å (Figure 1a). The M_2P molecules (Figure 1b) as well as Me_2TCNQ are located on the center of inversion, and appear to be planar.

Low-temperature X-ray diffraction measurements displayed a sudden appearance of (*h*0*l*) (*l* = odd) reflections at 170 K (Figure 2a) and preserved the systematic absence of the (0*k*0) reflections (*k* = odd), indicating the symmetry change into the $P2_1$ space group. The lattice parameters exhibit a cusp-like anomaly at the same temperature, in particular for the stack spacing (*a*) showing the largest thermal variation (Figure 2b). These observations signal the structural phase transition. The critical phenomenon is characteristic of a continuous (second-order-like) phase transition, as the intensity of (*h*0*l*) (*l* = odd) reflections, which is proportional to the square of an order parameter for the symmetry breaking, shows linear temperature dependence without discontinuous jump below T_c (Figure 2a). According to the structural analysis at 162 K^{8,9} below $T_c = 170$ K, the M_2P molecule is slightly bent around the N–N line with a dihedral angle of 175.3°, and the methyl group deviates by about 0.3 Å from the molecular plane. Molecular deformation toward the chain axis corresponds to a ferroelectric arrangement in each stack, and the polarization is opposite for the neighboring stacks related by the 2_1 screw axis. These features result in an antiferroelectric three-dimensional arrangement of the polar stacks.

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(8) Crystal data of M_2P - Me_2TCNQ : $C_{28}H_{22}N_6$, fw 442.52. At 296 K, space group $P2_1/c$, $a = 7.013(7)$ Å, $b = 8.917(6)$ Å, $c = 17.753(6)$ Å, $\beta = 93.67(5)^\circ$, $V = 1107(1)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.33$ g cm⁻³, $R = 0.073$, $R_w = 0.078$. At 162 K, space group $P2_1$, $a = 6.913(4)$ Å, $b = 8.898(6)$ Å, $c = 17.661(4)$ Å, $\beta = 93.32(3)^\circ$, $V = 1084.6(9)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.35$ g cm⁻³, $R = 0.085$, $R_w = 0.098$.

(9) Measurements on single crystals are limited down to 130–150 K, around which temperature a crystal is broken into pieces presumably by another transition of the crystal structure.

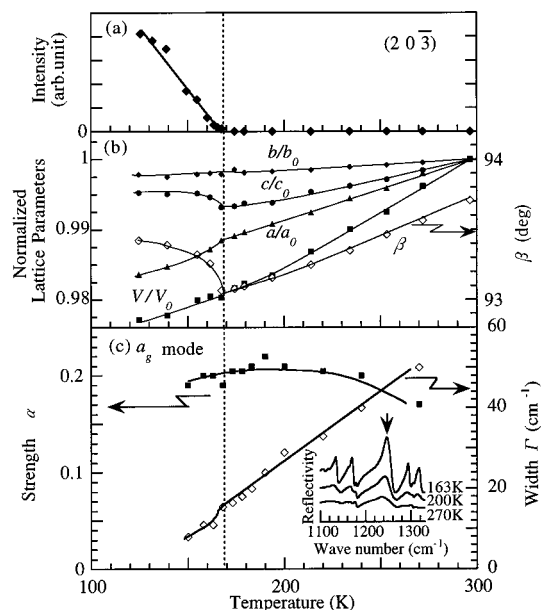


Figure 2. Temperature dependence of (a) the integrated intensity of (2 0 3) reflection, (b) the lattice parameters a , b , c , V (normalized to 296 K), and β , and (c) line width Γ and intensity α of the a_g mode at 1242 cm^{-1} . The inset to part c exemplifies the temperature variation of infrared reflection spectra for the a_g mode (indicated by an arrow).

The infrared absorption spectrum of $\text{M}_2\text{P-Me}_2\text{TCNQ}$ powder shows the $\text{C}\equiv\text{N}$ stretching mode of Me_2TCNQ as a sharp band at 2202 cm^{-1} . The frequency, which is known to shift linearly with the molecular valence ($-\rho$) for the TCNQ family,¹⁰ corresponds to an intermediate degree of CT ($\rho = 0.5$) on the basis of comparison between the neutral Me_2TCNQ molecule (2223 cm^{-1} for $\rho = 0$) and its potassium salt (2184 cm^{-1} for $\rho = 1$). The infrared reflection spectra polarized along the stack ($E//a$) of a single crystal of $\text{M}_2\text{P-Me}_2\text{TCNQ}$ have revealed some broad peaks, which are sharpened as the temperature is lowered, as shown in the inset to Figure 2c. These bands, which are strongly polarized along the DA stack and hence mixed with the electronic CT excitation between D and A, are ascribed to the totally symmetric a_g modes¹¹ activated in the noncentrosymmetric state.¹² Therefore, these a_g mode spectra enable one to monitor the thermal behavior of the molecular deformation and resultant lattice distortion breaking the local centrosymmetry. The line width Γ and intensity α of the a_g mode were analyzed by fitting to the Lorentz oscillator model, which describes the frequency (ω)-dependent dielectric function,

$$\epsilon(\omega) = \epsilon_\infty + 4\pi\omega_0^2\alpha/(\omega_0^2 - \omega^2 - i\omega\Gamma)$$

where ϵ_∞ is the high-frequency dielectric constant. As shown in Figure 2c for the most intense a_g mode at $\omega_0 = 1242 \text{ cm}^{-1}$, the α value, which is proportional to the squared amplitude of local distortion, is nearly constant across and even above T_c , whereas the steep increase in line width Γ proves a rapid fluctuation in the lattice distortion at high temperature. The phase transition in $\text{M}_2\text{P-Me}_2\text{TCNQ}$ can thus be considered as the order–disorder

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(11) The time-averaged molecular geometry of M_2P determined by the X-ray structural analysis at room temperature is planar with effective D_{2h} symmetry. The notation of the a_g mode in the text is based on the totally symmetric mode assuming this symmetry.

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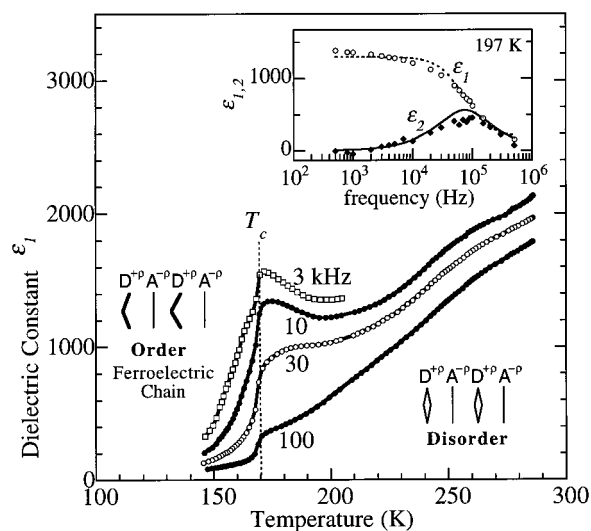


Figure 3. Temperature dependence of the real part (ϵ_1) and frequency dispersion of real and imaginary parts of the dielectric constant ($\epsilon = \epsilon_1 + i\epsilon_2$) at 197 K (inset). Solid and dotted curves in the inset are least-squares fits based on the Debye model (see text).

type. It becomes evident from the X-ray structure analysis of the M_2P molecule that the out-of-plane vibration of the methyl groups accompanied by a slight pyramidal distortion on the nitrogen atoms is frozen below T_c . This was also evidenced by the large thermal factors on the methyl carbon atoms at room temperature.

The temperature-dependent dielectric constant (ϵ_1) was measured with use of an LCR meter at different frequencies (0.5–500 kHz). The ϵ_1 along the stacking direction shows an anomaly associated with the phase transition at 170 K (Figure 3). The peak value of ϵ_1 at low frequencies is huge (about 1600) along the DA stack, being about 2 orders of magnitude larger than those along the interstack (b and c) directions. Such a one-dimensional dielectric response is ascribed to the creation of a polar chain with large dipoles by the collective molecular deformation. The relaxational behavior, which suppresses the anomaly with increasing frequency, is also characteristic of the order–disorder transition. The inset to Figure 3 shows the frequency dependence of real and imaginary parts of the dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$). The observed frequency dispersion (note that $\omega \ll \omega_0$ in this case) can be approximately described by the Debye-type relaxation model,

$$\epsilon(\omega) = \epsilon_\infty' + (\epsilon_0 - \epsilon_\infty')/(1 - i\omega\tau)$$

where the ϵ_0 and ϵ_∞' are static and high-frequency (but far below molecular vibrational frequencies) dielectric constants, respectively. The relaxation time τ obtained by the least-squares fit is found to obey the thermal activation behavior, $\tau^{-1} = \tau_0^{-1}\exp(-E_a/k_B T)$. The activation energy E_a of 0.14 eV (14 kJ/mol) for 170–200 K is attributed to the energy barrier for the motion of the methyl group in M_2P . On the basis of CT complexes, the use of such flexible π -electron molecules has been found to produce a new class of molecular dielectrics with very large dielectric susceptibility.

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Supporting Information Available: Tables of crystal data, structure solution, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for $\text{M}_2\text{P-Me}_2\text{TCNQ}$ at 296 and 162 K (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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