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Temperature-induced neutral-ionic transition in dimethyltetrathiafulvalene-*p*-chloranil

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A new 1:1 mixed-stack organic charge-transfer crystal of 2,6-dimethyltetrathiafulvalene-*p*-chloranil (DMTTF-CA), which undergoes a temperature-induced neutral-ionic transition (TINIT), was reported. At a critical temperature of 65 ± 5 K the molecular ionicity and the stack dimerization were found to change discontinuously. A most striking feature in the phase transition of DMTTF-CA was that a neutral-ionic coexisting phase did appear at lower temperatures, unlike the homogeneous ionic phase observed for the TINIT of tetrathiafulvalene-*p*-chloranil (TTF-CA). These transition characteristics were discussed by taking into account the structural differences between these two complexes composed of similar constituents.

Since the discovery of neutral-ionic transitions (NIT) in mixed-stack organic charge-transfer (CT) crystals,¹ extensive theoretical and experimental studies have been carried out. The NIT found in several CT complexes, which have critical points, have been induced usually by lowering the temperature and/or applying hydrostatic pressure. Until recently, the CT complex of tetrathiafulvalene-*p*-chloranil (TTF-CA) was considered to be unique in undergoing a temperature-induced NIT (TINIT) at ambient pressure,² although about ten CT complex systems are known to exhibit a pressure-induced NIT.¹ Hence the earlier studies on TINIT have been devoted mainly to TTF-CA. As for the transition, it has been thought that the effects of Coulomb interactions and electron-lattice interactions play important roles. However, a detailed understanding of the transition behaviors has not yet been reached. This is partly because little experimental evidence concerning TINIT has been available, despite much effort to discover new CT complexes including TTF-CA analogues.

More recently, Iwasa *et al.* have reported that 3,3',5,5'-tetramethylbenzidine-tetracyanoquinodimethane (TMB-TCNQ) is another CT complex system exhibiting TINIT at ambient pressure.³ Somewhat different features of the transition to those in TTF-CA have been found. Of particular interest in the transition of TMB-TCNQ is that a quasineutral (*N*) and quasi-ionic (*I*) coexisting phase appears at low temperatures, while a homogeneous ionic phase is observed for the TINIT in TTF-CA. In this respect, the possibility of a staging effect, originally proposed by Hubbard and Torrance,⁴ was pointed out.^{3,5} These behaviors are primarily attributable to the different molecular and structural parameters. A detailed description of these aspects, however, still seems to remain in question. Other CT complex sys-

tems exhibiting TINIT have therefore been required to obtain a further understanding of these transition phenomena.

In this paper, we present a third example of a mixed-stack CT complex, 2,6-dimethyltetrathiafulvalene-*p*-chloranil (DMTTF-CA), undergoing a TINIT at ambient pressure. Experimental evidence for the transition of coexisting *N* and *I* phases is also described. A discontinuous change in the molecular ionicity of DMTTF-CA was observed at $T_c = 65 \pm 5$ K, accompanied by dimeric distortions of the stacks at low temperatures. These characteristics are quite similar to those observed in TTF-CA,⁶⁻⁸ as can be predicted from their molecular properties, whereas the coexistence of both *N* and *I* molecules of DMTTF-CA even at temperatures lower than T_c is unexpected. In the case of TTF-CA, the first-order phase transition takes place at $T_c = 81$ K, and only the homogeneous ionic ground state is observed at $T < T_c$. Therefore, comparative studies of DMTTF-CA and TTF-CA may be very useful to elucidate the factors affecting the phase transitions.

The starting materials of DMTTF (Tokyo Kasei Co.) and CA were purified by repeated recrystallization and vacuum sublimation. As for DMTTF, special care was taken to characterize the positions of methyl groups substituted in the parent TTF moieties, and the plausible 2,7-dimethyl isomers⁹ were confirmed to be never obtained. Single crystals of 1:1 DMTTF-CA complex were grown by a cosublimation method; the purified powders were located at different positions in a sealed Pyrex glass tube, and placed in an electric furnace for several days at the sublimation temperature of about 70°C. Needlelike single crystals, typically $1 \times 0.5 \times 0.5$ mm³ in size, were obtained. Crystal structure analyses were carried out using an automated four-circle diffractometer (RIGAKU

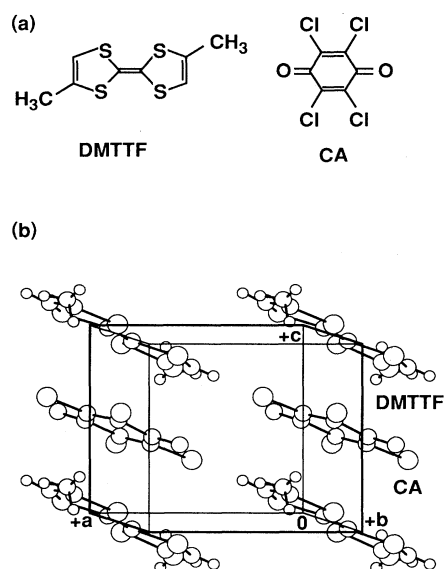


FIG. 1. (a) Molecular structures of DMTTF and CA. (b) Crystal structures of DMTTF-CA.

AFC5R). Polarized optical reflection measurements in the visible region were performed on the single crystals, while for IR absorption measurements the powder samples obtained by pulverizing the crystals were employed.

The crystal structure of DMTTF-CA is depicted in Fig. 1. The crystals were in the triclinic form with space group $P\bar{1}$, and the lattice constants were as follows: $a = 7.666 \text{ \AA}$, $b = 8.512 \text{ \AA}$, $c = 7.272 \text{ \AA}$, $\alpha = 103.89^\circ$, $\beta = 91.89^\circ$, $\gamma = 95.91^\circ$, and $Z = 1$. The number of unique reflections and the final R factor were 1355 and 0.036, re-

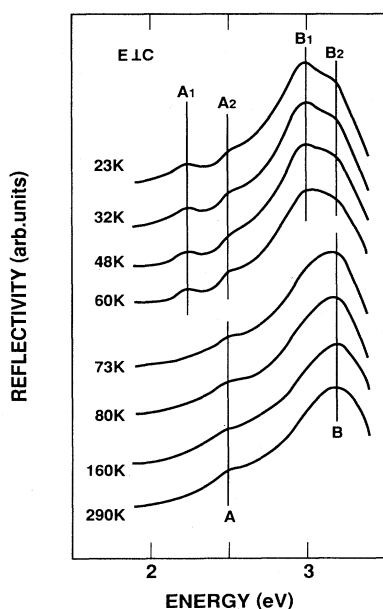


FIG. 2. Temperature dependence of polarized visible reflection spectra of DMTTF-CA, for the electric vector perpendicular to the stack-axis c .

spectively. DMTTF and CA molecules formed mixed-stack columns in the direction parallel to the c axes and the DMTTF molecular planes were inclined to the stacking axes by 21.8° . The structure is thus different from that of TTF-CA, which is reported to be in the monoclinic form ($P2_1/n$).¹⁰ It should also be noted that the ab planes (perpendicular to the stacking axes) are formed from only one kind of molecule; for example, each DMTTF molecule has the same kind of donors as its nearest neighbors in the plane. Hence the molecular arrangements of DMTTF-CA are considerably different from those of TTF-CA, in which the bc planes (normal to the stacking a axes) consist of interstacked donors and acceptors.

Figure 2 shows the temperature dependence of polarized reflection spectra of a DMTTF-CA crystal, for the electric vector perpendicular to the stack-axis c . The structures around 2.5 and 3.2 eV at 290 K, denoted by A and B , respectively, were identified with the intramolecular excitation bands of DMTTF molecules. The assignments were made from comparison with the corresponding spectra of the neutral and ionic species in solutions. These bands were strongly polarized for $E \perp c$, as expected from the structure shown in Fig. 1. The respective intramolecular excitation bands of TTF molecules in the TTF-CA complex are observed at 2.5 and 3.3 eV when polarized for $E \perp a$ (stack axis), and their energies and intensities depend markedly on the CT states of the molecules.^{6,11} Accordingly the spectral features of DMTTF-CA were almost the same as those of TTF-CA.

When the temperature was lowered, these excitation bands exhibited sudden changes at about 65 K. The A band split into two peaks (A_1 at 2.25 eV and A_2 at 2.5 eV); A_1 shifted towards lower energies and A_2 being almost at the same position as A . The B band at 3.2 eV, on the other hand, shifted to B_1 at 3.0 eV, with a shoulder B_2 nearly at B . Distinct hysteresis between cooling and heating runs was not observed when the temperatures exceeded 65 ± 5 K. The energies and intensities of these bands remained almost unchanged both in the low-temperature region (23–60 K) and also in the high-temperature region (73–290 K). These spectral features exhibited a discontinuous change of molecular ionicity with temperature, similar to the TINIT observed for TTF-CA and TMB-TCNQ.^{3,6} The existence of binary structures in the spectra at the low temperatures showed that two inequivalent DMTTF molecules having different degrees of ionicity were coexisting in the ground state. Such coexistence was considered to be of intrinsic origin, not to arise from macroscopic inhomogeneities of the samples, since these spectral changes were well reproducible.

The change of the molecular ionicity with temperature will be more apparent in IR molecular vibrational spectra. The IR absorption spectra of DMTTF-CA powder at various temperatures are shown in the frequency ranges around 1600 cm^{-1} in Fig. 3(a), and around $900\text{--}1000 \text{ cm}^{-1}$ in Fig. 3(b). The structures A and B in Fig. 3(a) were attributed to the $\text{C}=\text{O}$ stretching vibration modes (b_{1u}) of CA molecules, while the structure C in Fig. 3(b) was assigned to the a_g mode of CA. These

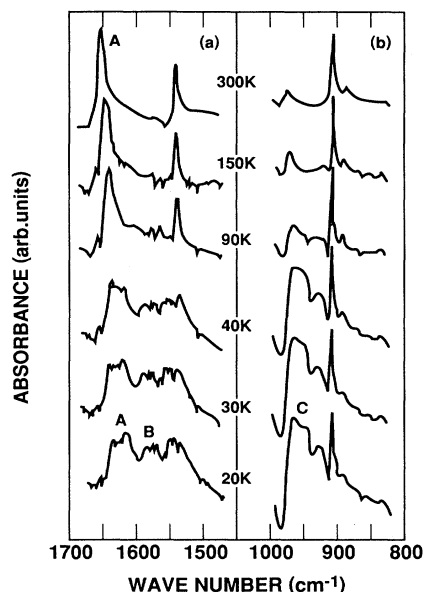


FIG. 3. IR absorption spectra of DMTTF-CA powder at various temperatures. The structures *A* and *B* are assigned to the b_{1u} C=O stretching modes in CA molecules. The structure *C* is assigned to the a_g mode in CA molecules.

vibration modes are well known to be particularly useful for determining the degree of ionicities and the stack distortions, respectively.^{7,8,12-14}

The structures in Fig. 3(a) indicated marked changes with temperature. Above T_c , the b_{1u} mode denoted by *A* at about 1650 cm^{-1} showed only gradual shifts with temperatures. From the peak position of the *A* band, the degree of ionicity (ρ) was estimated to be 0.2 at 300 K, and 0.3 at 90 K. On the other hand, below T_c the b_{1u} mode (*B*) due to the quasi-ionic CA molecules appeared at about 1580 cm^{-1} , whereas the original *A* band still remained with rather broadened structures. The coexistence of two molecular species having different ionicities in the low-temperature phase was thus clearly seen from the simultaneous appearance of the *A* and *B* bands. The ρ value at 20 K was estimated from the *B* band to be about 0.6–0.7 for the ionic species, and from the *A* band to be 0.3–0.4 for the neutral ones.

Also shown in Fig. 3 is the remarkable enhancement of the *C* band below T_c . Such activation of the a_g mode is attributed to the onset of the dimeric distortion of the stacks.⁷ This was manifested from the temperature-dependent normalized intensity of the *C* band, given in Fig. 4. The intensity changed drastically across T_c , and was negligibly small at higher temperatures than T_c . The TINIT of DMTTF-CA was therefore accompanied by lattice dimerization, while in the *N* phase the molecules were almost regularly stacked.

Note that the transition observed in the IR measurements across T_c was somewhat broadened in temperature by several tens of degrees in width, compared with the reflection measurements. This may be due to the powdered form of the samples used in the IR measurements. In fact, in visible absorption measurements on

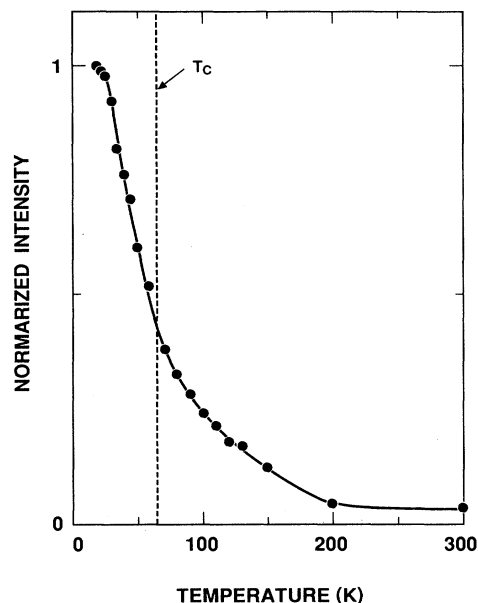


FIG. 4. Temperature dependence of the normalized intensity of the a_g mode in CA molecules on powder samples.

powder samples, such a blurred transition was found, so that the transition was strongly influenced by the form of samples, as frequently observed in TTF-CA.^{6,11}

From the above results, the following features for the TINIT in DMTTF-CA can be drawn. The transition was characterized by discontinuous change of molecular ionicity at about 65 K, accompanied by lattice dimerization. The ionicity change across T_c evaluated from the *A* and *B* band in Fig. 3 is fairly large (0.3–0.4), indicating a large ionicity jump at T_c . In addition, distinct hysteresis effects at T_c were not detected. According to the existing theories, these features may be described in terms of intracolumn parameters such as Coulomb energy, transfer energy, electron-lattice interaction, and of the inherent molecular parameters. We should note first, that the constituent DMTTF molecules possess almost the same chemical properties including the ionization potential as those of the authentic TTF molecules.¹⁵ Second, the molecular configurations of donors and acceptors within a single stacked column were similar to those of TTF-CA, and the mean intermolecular distance between DMTTF and CA, by which the CT interactions are markedly influenced, is estimated to be 3.39 \AA and identical with the reported value for TTF-CA.¹⁰ Therefore it could be said that at least for the intracolumn parameters both CT complexes are almost the same.

Nevertheless, the distinct feature in the TINIT of DMTTF-CA was the coexistence of *N* and *I* molecules in the ground state, which appeared in the low-temperature phase. These transition behaviors have never been observed yet in the TINIT of pure TTF-CA crystals. Furthermore, such coexistence was also different from the cases for the pressure-induced NIT in TTF-CA and the related compounds, where the binary phase merely appeared at the intermediate pressures midway toward the

eventual homogeneous *I* phase.^{12,14,16} According to previous theoretical studies by Nagaosa,¹⁷ the thermal excitation of ionic domains in a single column rather than the relatively weak intercolumn interactions would be an indication of coexistence behavior. In the present case, however, the effect of thermal excitations can be excluded, since the relative amount of *N* and *I* molecules in the low-temperature phase remained almost unchanged with temperature (Fig. 2).

Close resemblances between DMTTF-CA and TMB-TCNQ were found in that the NIT was accompanied by the coexisting phases. TMB-TCNQ is known to be in the monoclinic form and have almost equivalent molecular arrangements to those in TTF-CA except the different intermolecular distances in each axis.³ Considering these facts Iwasa and co-workers have pointed out that the staging effect proposed by Hubbard and Torrance can be applicable to describe the coexistence in the NIT of TMB-TCNQ.^{3,5} As described above, the crystallographic structure of DMTTF-CA was triclinic and the molecular configurations in the planes (normal to the stacking axes) were considerably different from those of TTF-CA and TMB-TCNQ. Despite such discrepancies, the staging effect, which is essentially ascribed to the frustration in the intercolumn Coulomb interactions caused by molecular arrangements, may become a possible explanation for the coexistence phenomenon. As for DMTTF-CA, in the directions of the *a* and *b* axes (normal to the stacking axis) the intercolumn interactions are both repulsive. On the other hand, the interactions in TTF-CA are repulsive along the *b* axis but attractive along the *c* axis; the former is relatively small and the latter is predominant. In the

case of DMTTF-CA, therefore, the frustration of Coulomb interactions between the adjacent columns will be considerably large. Consequently, mixed states of *N* and *I* columns appear exclusively in the DMTTF-CA crystal, rather than uniform ionic states. The different properties in the low-temperature phase between these otherwise very similar compounds seem to offer a useful way to investigate the crucial factors determining the coexistence phenomenon.

In conclusion, we have shown that DMTTF-CA undergoes a TINIT at about 65 K, accompanied by a lattice dimerization. The transition occurred with a discontinuous change of molecular ionicity, similar to those observed in TTF-CA and TMB-TCNQ. Unlike the case of TTF-CA, the low-temperature phase of DMTTF-CA was characterized by the appearance of the *N* and *I* coexisting state. To the best of our knowledge, this is the third compound which has been reported to exhibit a TINIT at ambient pressure. It was also suggested that the differences in the three-dimensional molecular arrangements were the most plausible origin for the coexisting phase, although further extensive studies have to be made. In any case, the findings presented here will offer some useful clues to investigate the TINIT in mixed-stack CT complexes including the coexistence phenomena.

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