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Temperature-induced neutral-ionic transition in 2-chloro-5-methyl-*p*-phenylenediamine-2,5-dimethyl-dicyanoquinonediimine

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A mixed-stack organic charge-transfer crystal of 2-chloro-5-methyl-*p*-phenylenediamine-2,5-dimethyl-dicyanoquinonediimine (CMePD-DMeDCNQi), which undergoes a temperature-induced neutral-ionic transition (TINIT), is reported. From infrared spectroscopy, the molecular ionicity (ρ) of CMePD-DMeDCNQi was found to change continuously from $\rho=0.3$ at 300 K to $\rho=0.6$ at 100 K. The neutral-ionic interface was crossed without a discontinuity in ρ at around 200 K, accompanied by stack dimerization. These features were quite different from the discontinuous change in ρ observed for the TINIT of tetrathiafulvalene-*p*-chloranil (TTF-CA) and tetramethylbenzidine-tetracyanoquinodimethane (TMB-TCNQ). The transition characteristics in CMePD-DMeDCNQi are discussed by drawing a comparison with those seen in TTF-CA and TMB-TCNQ. [S0163-1829(97)51030-7]

Since the discovery of neutral-ionic transitions (NIT's) in mixed-stack organic charge-transfer (CT) crystals,¹ extensive studies have been carried out. The NIT's found in several complexes are generally induced by lowering the temperature and/or applying hydrostatic pressure. To date, however, only a few CT complexes have been found to undergo a temperature-induced NIT (TINIT) at ambient pressure.²⁻⁴ Among these compounds, tetrathiafulvalene-*p*-chloranil (TTF-CA) was considered to be unique in undergoing the TINIT at the early stage of the studies on the NIT, although about ten CT complex systems were known to exhibit a pressure-induced NIT. As a consequence, many studies were concentrated on TTF-CA to elucidate the nature of its NIT. In the TINIT of TTF-CA, a first-order transition with a discontinuous change in molecular ionicity (ρ) of $\Delta\rho=0.3$ has been found to occur at the critical temperature of 81 K.⁵⁻⁷ It has been recognized that the effects of electrostatic Madelung interactions and electron-lattice interactions play crucial roles in the transition. The subsequent discovery of a new TINIT in tetramethylbenzidine-tetracyanoquinodimethane (TMB-TCNQ) has revealed other aspects of the transition.³ TMB-TCNQ crystals have been found to exhibit a first-order transition including an ionicity jump of $\Delta\rho=0.1$ and distinct

hysteresis effects. However, a detailed understanding of the NIT has not yet been reached. This is partly because little experimental evidence concerning TINIT's has so far been available, although existing theoretical studies have predicted the occurrence of various types of the transition.^{8,9} For this reason, new complexes exhibiting different features of TINIT have long been required to obtain a further understanding of the transition.

In this paper, we present an example of a mixed-stack CT complex, 2-chloro-5-methyl-*p*-phenylenediamine-2,5-dimethyl-dicyanoquinonediimine (CMePD-DMeDCNQi), which undergoes a TINIT at ambient pressure. A change in the molecular ionicity of CMePD-DMeDCNQi is observed at around 200 K, accompanied by dimeric distortions of the stacks at low temperatures. The most striking features of the transition are the continuous change in molecular ionicity. These characteristics are quite different from those observed in the TINIT's of TTF-CA and TMB-TCNQ. Therefore, studies of CMePD-DMeDCNQi may be quite useful to elucidate factors affecting the phase transition.

The starting materials of CMePD (Tokyo Kasei Co.) and DMeDCNQi (Aldrich) were purified by repeated recrystallization and vacuum sublimation. Needlelike crystals, typi-

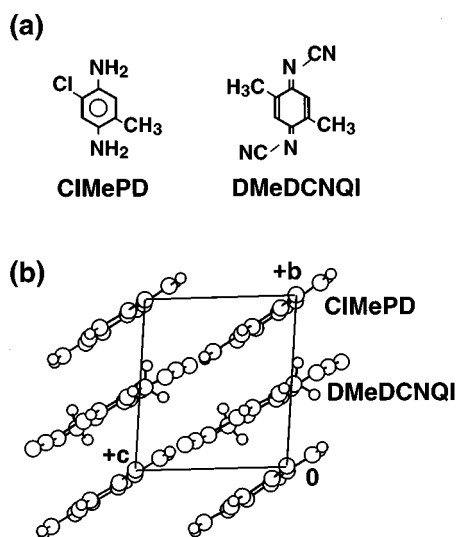


FIG. 1. (a) Molecular structures of ClMePD and DMeDCNQI. (b) Crystal structures of ClMePD-DMeDCNQI.

cally $1 \times 0.1 \times 0.1$ mm³ in size, were grown from dichloromethane solution. Crystal structure analysis was carried out using a diffractometer with an imaging plate (RIGAKU RAXIS IV). The infrared (IR) and visible absorption measurements were performed on powder samples obtained by pulverizing the crystals.

The crystal structure of ClMePD-DMeDCNQI is depicted in Fig. 1. The crystals are of triclinic form with a space group *P*1, and the lattice constants were as follows: $a=7.463$ Å, $b=7.504$ Å, $c=7.191$ Å, $\alpha=91.23^\circ$, $\beta=112.19^\circ$, $\gamma=96.91^\circ$, and $Z=1$. To obtain suitable values of thermal factors in the analysis, 2- and 5-substitutional sites in the parent *p*-phenylenediamine moieties were assumed to be occupied by chlorine atoms and methyl groups with equal probability. The number of unique reflections and the final *R* factor were 1223 and 0.049, respectively. ClMePD and DMeDCNQI molecules formed mixed-stack columns in a direction parallel to the *b* axes, as shown in Fig. 1.

Figure 2 shows the visible absorption spectra of ClMePD-DMeDCNQI powder at 300 and 100 K. The structure around 3.0 eV at 300 K, marked A in Fig. 2, was identified with the intramolecular excitation band of neutral DMeDCNQI molecules. The assignment was made from comparison with the corresponding spectra of neutral and ionic species in solutions.¹⁰ When the temperature was lowered to 100 K, a structure denoted by B appeared around 2.4 eV. This band, which characteristically appears in the low-energy region, can be safely assigned to the lowest intramolecular excitation of DMeDCNQI⁻ ions. Also the structure appearing around 2.9 eV at 100 K (the C band) might be ascribed to both the lowest intramolecular excitation of ClMePD⁺ and the second lowest intramolecular excitation of DMeDCNQI⁻.¹⁰ These spectral features in electronic excitation indicate a change in molecular ionicity of the complex with temperature, as also observed in the TINIT's of TTF-CA (Ref. 5) and TMB-TCNQ.³

Changes in molecular ionicity with temperature are more apparent in IR molecular vibration spectra. The IR absorp-

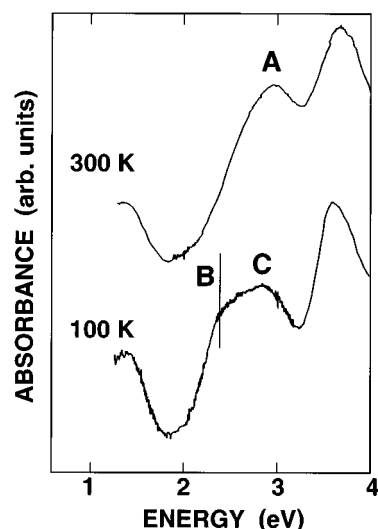


FIG. 2. Visible absorption spectra of ClMePD-DMeDCNQI powder.

tion spectra of ClMePD-DMeDCNQI powder at various temperatures are shown in Fig. 3 for the frequency range 1270–1700 cm⁻¹. Structure A in Fig. 3 is attributed to the C=C stretching vibration mode (b_u) of DMeDCNQI molecules, while the structures B and C are attributed to the a_g modes of DMeDCNQI.

The C=C stretching mode (A) well known to be useful for determining the degree of ionicity,^{11–13} exhibits marked changes with temperature. The A band of 1572 cm⁻¹ at 390 K shifted to 1553 cm⁻¹ at 97 K. Such a frequency shift indicates a change in molecular ionicity of the complex, since the C=C stretching frequencies in fully neutral and fully ionic DMeDCNQI are known to appear at 1591 cm⁻¹ and 1530 cm⁻¹, respectively.¹⁴ From the peak position of the A band, the degree of ionicity (p) was estimated to be 0.3 at

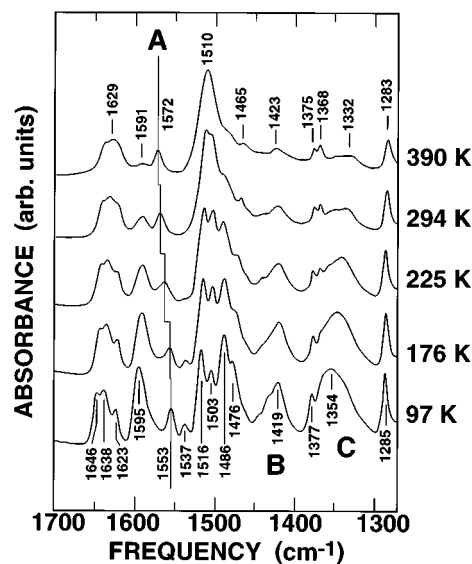


FIG. 3. IR absorption spectra of ClMePD-DMeDCNQI powder at various temperatures. Structure A is assigned to the b_u C=C stretching mode in DMeDCNQI molecules. Structures B and C are assigned to the a_g modes in DMeDCNQI molecules.

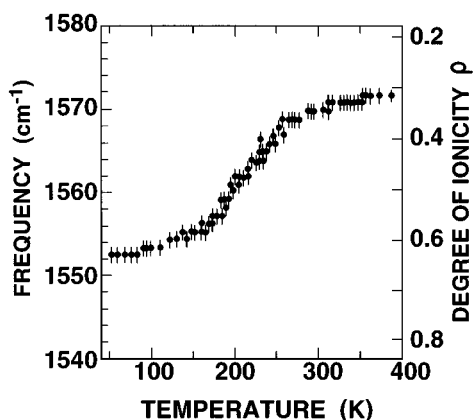


FIG. 4. Temperature dependence of b_u C=C stretching in DMEDCNQI molecules for powder samples.

390 K, and 0.6 at 97 K. An additional small band (1537 cm^{-1}) was also found to appear in the C=C stretching region at low temperatures, as shown in Fig. 3. However, this band can be ascribed to CIMEPD moiety, since such a band was not observed in the low-temperature phase of the deuterated complex, d_4 -N,N,N',N'-CIMEPD-DMEDCNQI.¹⁵

The change in molecular ionicity is also manifest in the temperature dependence of the peak frequencies of the A band, as given in Fig. 4. The A band shows a remarkable change in frequency across 200 K. Further, no distinct hysteresis effects between cooling and heating runs were detected. Therefore, the transition temperature of the TINIT in CIMEPD-DMEDCNQI is roughly estimated to be 200 K.

Note that the peak position of the A band changes continuously with temperature. These features have never been observed in the TINIT's of TTF-CA and TMB-TCNQ. In the case of the TINIT in TTF-CA, the C=O stretching vibration mode (b_{1u}) of CA molecules, suitable for determining the molecular ionicity, is known to change discontinuously at the critical temperature (T_c) of 81 K.⁷ Even in the powdered form, as employed in the present measurements, simultaneous appearance of both neutral and ionic vibration modes in TTF-CA was observed only around T_c . In the present case, however, the single vibrational structure of the C=C stretching mode (b_u) in CIMEPD-DMEDCNQI exhibited a relatively gradual shift over a wide frequency range across 200 K, as shown in Fig. 4. Thus, these features do not arise from inhomogeneity of the sample, but can be considered an essential ingredient of the transition. Therefore, either the TINIT of CIMEPD-DMEDCNQI exhibits no jump in ionicity, or the possible discontinuity in ρ is too small to be appreciated from the vibrational spectra. Such a continuous change in molecular ionicity may somewhat resemble that in the pressure-induced NIT in TTF-dichlorobenzoquinone (TTF-Cl₂BQ).¹⁶

Also shown in Fig. 3 is the remarkable enhancement of the a_g modes (B and C) at lower temperatures. Such activation of the a_g modes is attributed to the onset of dimeric distortion of the stacks. This was apparent from the temperature-dependent normalized intensity of the a_g bands, as given in Fig. 5. The intensity changed distinctly across 200 K, and was negligible at higher temperatures. The TINIT of CIMEPD-DMEDCNQI is therefore accompanied by lattice

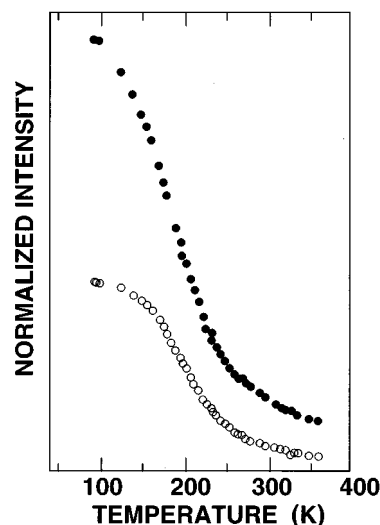


FIG. 5. Temperature dependence of normalized intensity of a_g modes in DMEDCNQI molecules for powder samples. Open circles: the B band in Fig. 3 (around 1420 cm^{-1}); closed circles: the C band in Fig. 3 (around 1350 cm^{-1}).

dimerization, while in the N phase the molecules are stacked almost regularly.

From the above results, the following features of the TINIT in CIMEPD-DMEDCNQI can be deduced. The transition is characterized by a continuous change in ionicity at around 200 K, accompanied by lattice dimerization. The degree of ionicity in the neutral phase is relatively large ($\rho=0.3$), while that in the ionic phase is small ($\rho=0.6$). Also, hysteresis effects were hardly detected. These features of the TINIT in CIMEPD-DMEDCNQI contrast with those observed in the TINIT's of TTF-CA and TMB-TCNQ, both of which include apparent jumps in ionicity at certain critical temperatures. According to previous theoretical studies,^{8,17,18} such continuous changes in ρ in CIMEPD-DMEDCNQI could be ascribed to the larger contribution of intermolecular transfer energy (t) between the constituent donor and acceptor molecules in comparison with that of intersite Coulomb energy (Madelung energy). In this case, it is predicted that, as the effects of t prevail, the jump in ρ decreases and finally vanishes; the transition becomes indistinct. Indeed, the evaluation of the transfer energy of CIMEPD-DMEDCNQI from the optical spectra might seem to support this conjecture. Following the procedure used in the theoretical studies by Painelli and Girlando,¹⁹ the transfer energy t of CIMEPD-DMEDCNQI can be estimated to be 0.6 eV from the peak energy of the CT band of 1.3 eV and the degree of ionicity of $\rho=0.3$ at 300 K. This value is considerably larger than the estimated value of 0.21 eV for TTF-CA.¹⁹ Such a large t in CIMEPD-DMEDCNQI might be related to the relatively small value of mean intermolecular distance of 3.15 \AA between CIMEPD and DMEDCNQI, compared to the reported values of 3.39 \AA for TTF-CA. Although intersite energy is also thought to be somewhat larger in CIMEPD-DMEDCNQI than in TTF-CA, as can be inferred from the energies of the CT bands (1.3 eV in CIMEPD-DMEDCNQI; 0.7 eV in TTF-CA), such a large value of transfer energy in CIMEPD-DMEDCNQI might still lead to a continuous change in molecular ionicity.

In conclusion, we have shown that ClMePD-DMeDCNQI undergoes a TINIT at about 200 K, accompanied by a lattice dimerization. The transition occurs with a continuous change of molecular ionicity, in contrast to those observed in TTF-CA and TMB-TCNQ. Such a feature, to our knowledge, has never before been observed in complexes reported to undergo TINIT's. In addition, no distinct hysteresis effects were observed in the TINIT of ClMePD-DMeDCNQI. Although the reason for these features of the TINIT have not been clarified yet, the larger contribution of intermolecular

transfer energy in comparison with the intersite Coulomb energy might be a plausible explanation. In any case, the discovery of a new complex might provide useful clues toward a further understanding of the NIT.

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