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Electronic Structures of 2,7-Bis(methylthio)-1,6-dithiapyrene (MTDTPY) Charge Transfer Complexes

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Polarized reflection spectra were measured on two charge-transfer complexes of 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY) with chloranil and 7,7,8,8-tetracyanoquinodimethane (TCNQ), which showed metallic conductivity. In spite of short intercolumnar S-S contacts, the spectra showed a strong one-dimensional character. The optical conductivity spectra, $\sigma(\omega)$, and real part of the dielectric constant, $\varepsilon'(\omega)$, along the stack axis were obtained by means of Kramers-Kronig transformation. The conductivity spectra and the dielectric constant of both complexes substantially differ from the simple Drude model. These results were analyzed with a one-dimensional electron localization model in a disordered system with the optical parameters: $\omega_p=13500\ \mathrm{cm}^{-1}$, $\tau_i=1.6\times10^{-15}$ s ($\tau_i^{-1}=3300\ \mathrm{cm}^{-1}$) for chloranil complex and $\omega_p=12000\ \mathrm{cm}^{-1}$, $\tau_i=2.5\times10^{-15}$ s ($\tau_i^{-1}=2100\ \mathrm{cm}^{-1}$) for TCNQ complex.

The design and synthesis of new components for organic metals are important in order to find the mechanisms of metallic conductivity and superconductivity. Nakasuji et al. synthesized new donors, 3,10-dithiaperylene (DTPR) and 1,6-dithiapyrene (DTPY), which belong to a class of peri-condensed Weitz-type donors.1) The new donors were substituted with methylthio groups or etylenedithio groups in order to increase the dimensionality of the conducting chains. Actually, some charge-transfer complexes of 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY) showed metallic conductivity.2) Imaeda et al. reported from ESR studies that the metal-insulator (M-I) transition occurred around 110 and 240K for β-MTDTPY-TCNQ and MTDTPY-chloranil, respectively.3)

The reflection spectra of organic metals show a quasimetallic behavior along the stacking direction of molecules with a well defined plasma edge; sometimes, however, the spectra do not show a simple Drude behavior, in which the conductivity spectra have a maximum in the infrared region and the real part of dielectric constant shows a positive value, even in the low frequency region.

In this paper we explain the optical properties of these complexes in terms of the electron localization model in a one-dimensional disordered system,4—7) and characterize the behavior of conducting electron from the spectral properties.

Experimental

Reflection spectra were measured in the 700—20000 cm^{-1} frequency range using two different instruments with polarized light both parallel and perpendicular to the stack axis on the [010] and [100] faces, with typical areas of 0.1 mm^2 for TCNQ and chloranil complexes, respectively. For the mid-infrared region, 700—5000 cm^{-1}, a Fourier spectrometer with a HgCdTe detector was used. For the near-infrared and visible regions, a microspectrophotometer was used, which comprised of a Carl-Zeiss double monochromator with a PbS cell and a photomultiplier tube of HTV 928. An aluminum mirror and SiC were used as references in the infrared and visible regions, respectively.

Results

Reflection Spcectra: The reflection spectra of β-MTDTPY-TCNQ on the [010] face are shown in Fig. 1. For both parallel and perpendicular polarization directions, the reflection spectra are fairly low above~6000 cm^{-1} and broad peaks are observed in this region. A plasma edge can be seen along the stacking direction at 5000 cm^{-1}. The reflectance below 4000 to 800 cm^{-1} is 50—60%. In the transverse direction, no evident peaks can be observed.

The reflection spectra of MTDTPY-chloranil on the [100] face are shown in Fig. 2. Similar to β-MTDTPY-TCNQ, the spectra show a large anisotropy both parallel and perpendicular to the stacking direction; and the reflectance gradually rises at low frequencies. The plasma edge in the chloranil complex is more broad than in the TCNQ complex. Vibrational structures could not be clearly resolved in both complexes, except that the chloranil complex

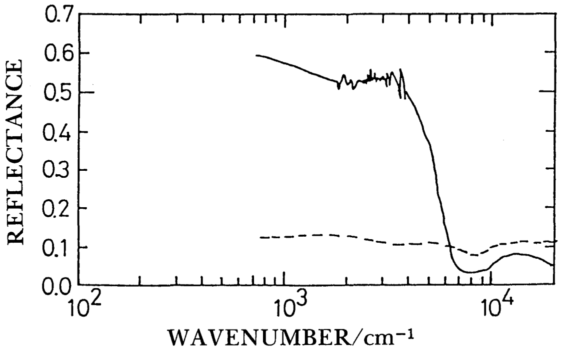

Fig. 1. Reflection spectra of β-MTDTPY-TCNQ on [010] face. solid line: parallel to the stack axis, dashed line: perpendicular to the stack axis.

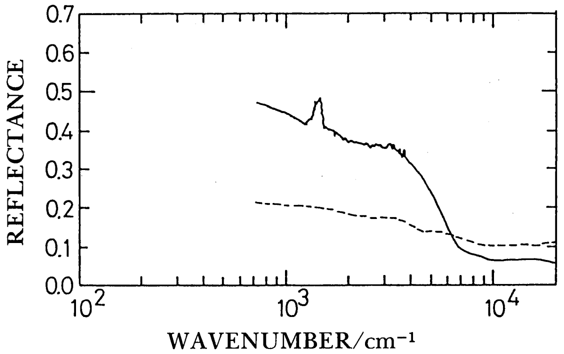

Fig. 2. Reflection spectra of MTDTPY-chloranil on [100] face. solid line: parallel to the stack axis, dashed line: perpendicular to the stack axis.

showed a strong vibrational structure at ~1430 cm^{-1}, corresponding to values of 1330 or 1420 cm^{-1} of the electron-molecular vibration coupled bands (emv-coupling) of MTDTPY molecules.[8]

Kramers-Kronig Analysis: The optical conductivity spectra, $\sigma(\omega)$, along the stacking axis were obtained by means of Kramers-Kronig transformation. In order to determine the phase shift, $\theta(\omega)$, upon reflection at both ends of the measurement, we extrapolated the reflectance, with Drude like ($R(\omega)=A-B\omega^{1/2}$) at low frequency and with an inverse fouth power ($R(\omega)=C/\omega^4$) at high frequency. Here, A, B, and C were determined with a least-square method in order to fit the experimental data in the low- and high-frequency regions.

Figures 3 and 4 show the optical conductivity and the real part of the dielectric constant for the TCNQ and chloranil complexes, respectively. Considering that the dc conductivities of TCNQ and chloranil complexes are values of 110 and 140 S cm^{-1}, respectively, both optical conductivity spectra fall with decreasing ω. The real part of the dielectric constant has a positive value and doesn't show any tendency of going to negative values. These results can not be explained by the simple Drude model, and will be discussed in more detail in the next section.

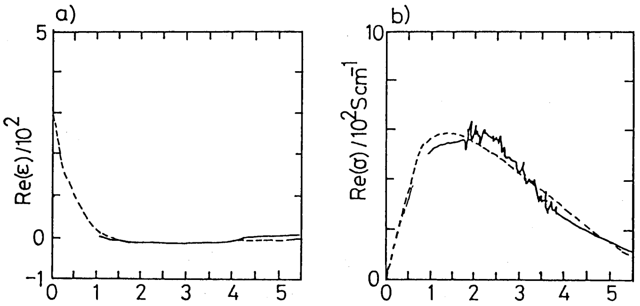

Fig. 3. Frequency dependence of a) $Re(\varepsilon)$ and b) σ for β-MTDTPY-TCNQ. The solid line represents experiment and the dashed line represents localization model.

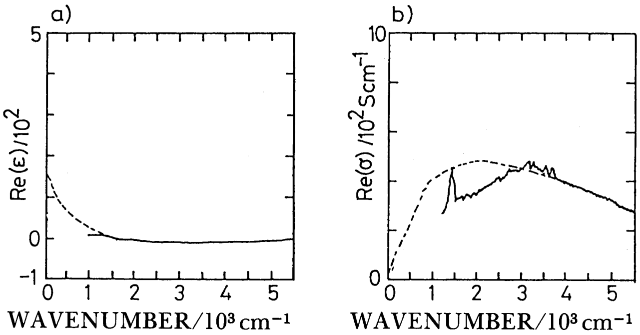

Fig. 4. Frequency dependence of a) $Re(\varepsilon)$ and b) σ for MTDTPY-chloranil. The solid line represents experiment and the dashed line represents localization model.

Discussion

Electronic Structure: X-Ray crystal structure analysis[2] showed that both β-TCNQ and chloranil complexes have a segregated column structure with interplanar distances of 3.48 Å of MTDTPY and 3.27 Å of TCNQ for β-MTDTPY-TCNQ, 3.47 Å of MTDTPY and 3.22 Å of chloranil for MTDTPY-chloranil; short S-S contacts were found between the MTDTPY columns. The degrees of charge transfer were estimated at ca. 0.6 in both complexes.[2] Although the TCNQ complex has two-dimensional networks in the crystals, the electronic structures has a strong one-dimensional character, as evidenced by the overlap integral calculated with the extended Hückel method.[3] For the chloranil complex, in spite of the small anisotoropy of the overlap integrals, the ESR spectra showed one-dimensional electronic structures.[3] As shown in Figs. 1 and 2, the one-dimensional electronic structures can be seen in the large anisotropy of the reflection spectra.

We neglected the intercolumnar interaction and treated the electronic structures of these complexes as one-dimensional metals.

Analysis with Localization Model: Since the optical conductivities and the real part of the dielectric constants are different from the simple Drude-like behavior, we must consider the localization effect.

Mott,[9] Berezinsky,[4] and Saso et al.[10] suggested that a one-dimensional system distinctly displays a localization effect which is not found in a three-dimensional system. One of them, the optical conductivity, $\sigma(\omega)$, in a one-dimensional metal disordered by impurities or lattice defects, has the form $\omega^2 \ln^2 \omega$ in the $\omega\tau_i \ll 1$ region.[8]

Berezinsky[4] derived values of $\sigma(\omega)$ and $\varepsilon'(\omega)$ which are valid at any ω at 0 K by following equations:

$$\sigma(\omega)=\sigma_0 Re \sum_{i=0}^{\infty} Q_m(R_m-R_{m+1}) \tag{1}$$

and

$$\varepsilon'(\omega)=\frac{-\varepsilon_0}{2\omega\tau_i} I_m \sum_{i=0}^{\infty} Q_m(R_m-R_{m+1}), \tag{2}$$

where σ_0 and ε_0 are the Drude values of the conductivity and the dielectric constant, respectively. R_m and Q_m satisfy the following recursion equations:

$$2i\omega\tau_i R_m + m(R_{m+1}+R_{m-1}-2R_m)=0,\ R_0=1 \tag{3}$$

and

$$2i\omega\tau_i(m+1/2)Q_m+(m+1)^2(Q_{m+1}-Q_m) \\ -m^2(Q_m-Q_{m-1})=R_{m+1}-R_m, \tag{4}$$

where τ_l is the mean lifetime with respect to scattering on a disordered system. At the limit $\omega\tau_l \gg 1$, this model shows $\sigma(\omega)$ and $\varepsilon(\omega)$ of the normal Drude type: $\sigma(\omega)\sim 2\sigma_0/(\omega\tau_i)^2$ and $\varepsilon(\omega)\sim -\varepsilon_0/(\omega\tau_i)^2$.

Numerical solutions of these formula were given by Gogolin,[5,7] who assumed $R_M=Q_M=1$ and $R_{M+1}=Q_{M+1}=0$, and solved the recursion equations down to R_0 and Q_0. Following Gogolin's numerical calculation method, the optical conductivity, $\sigma(\omega)$, and the real part dielectric constant, $\varepsilon'(\omega)$, were simulated, as shown in Figs. 3 and 4. As shown in Table 1, we determined three parameters in this simulation: τ_i, ω_p, and ε_{core}. Here, ω_p is the plasma frequency.

β-MTDTPY-TCNQ: Fitting parameters were determined as $\tau_i=2.5\times10^{-15}$ s ($\tau_i^{-1}=2100$ cm^{-1}), $\omega_p=12000$ cm^{-1} and $\varepsilon_{core}=3.5$. ε_{core} as typical values for an organic metal. The calculated values are shown in Fig. 3 by dashed lines; they fit well with the experimental curve. This result shows that the one-dimensional localization model is appropriate for describing the present system. However, the reflection spectra were measured at room temperature. Hence, the optical conductivity at $\omega\rightarrow 0$ didn't vanish.

According to a tight-binding approximation, the mean free path of a one-dimensional system is given by $l_i=v_F\tau_i$. The value of v_F is estimated as follows:

$$v_F=\frac{\rho^2\pi\hbar}{2\sqrt{2}\ m^*d\sin(\rho\pi/2)}, \tag{5}$$

Here, d is the spacing of stacked molecules, $\rho=0.6$ is number of carriers per site, and m^* is effective mass estimated from ω_p by

$$m^*=\frac{N e^2}{\pi c^2\omega_p^2}, \tag{6}$$

where c is the velocity of light. Here, l_i was estimated to be 2.6 Å. The electron localization length was given by $l_{loc}=4l_i$;[6] we then obtained $l_{loc}=10.5$ Å$=2.4\ d$.

The temperature dependence of the dc conductivity showed no obvious M-I transition and the maximum value was found at 275 K.[3] Gogolin,[6,7] and Kaveh et al.[11] pointed out that the temperature dependence of the dc conductivity in localization systems has a maximum value for the following reasons:

(1) At low temperatures, when $\tau_i \ll \tau_{ph}$, electron-phonon scattering gives rise to electron transitions between localized states, leading to hopping conductivity.

(2) At high temperature, the effective impurity mean free path is given by $l_{eff}^{-1}(T)=l_i^{-1}+(l_{ph}')^{-1}$; the drop in the conductivity is caused by a decrease in the localization length due to the influence of intramolecular phonons. Consequently, in the medium-temperature region, the dc conductivity has a maximum value.

We reported that MTDTPY molecules in PF_6^- salts showed strong emv-coupling.[8] Actually, the activation energy below 90 K was estimated to be 0.056 eV (452 cm^{-1}).[3] The value of $E_a=0.056$ eV is in the range of molecular vibration region. This picture may be too simple; nevertheless, it gives a qualitatively correct description of the features regarding the temperature dependence of dc conductivity.

MTDTPY-Chloranil: The fitting parameters were determined as being $\tau_i=1.6\times10^{-15}$ s ($\tau_i^{-1}=3300$ cm^{-1}), $\omega_p=13500$ cm^{-1}, and $\varepsilon_{core}=3.0$. Regarding β-MTDTPY-TCNQ, ε_{core} is a typical value for organic metals. The calculated curves didn't completely explain the experimental curves, as shown in Fig. 4; nevertheless, the overall feature is satisfactory. According to the tight-binding approximation, the electron localization length was determined as $l_{loc}=8.8$ Å$=2.3\ d$.

The value $\tau_i^{-1}=3300$ cm^{-1} was larger than that of β-TCNQ. The temperature dependence of dc conductivity clearly showed a M-I transition at 240 K. Hence, a Peierls gap may appear as the result of a one-dimensional fluctuation.[3] Considering that Berezinsky's equations are valid for a weak random potential, the potentials created by a Peierls fluctuation are so strong that Berezinsky's equations may not be valid. Gogolin applied the Berezinsky diagram technique to the case of a strong random potential.[7] However, the behavior of one-dimensional carriers in a strong random potential has not yet been made clear.

Recently, Saso et al. discussed both localization and interaction in a one-dimensional electron system.[10] The contribution of the interaction between electrons may be considered to describe a one-dimensional electron system.

Comparison with MTDTPY-$(PF_6)_{0.67}$: We previously reported on the one-dimensional localization characteristics of MTDTPY-$(PF_6)_{0.67}$ radical salts; parameters of $\tau_i^{-1}=2400$ cm^{-1} ($\tau_i=2.2\times10^{-15}$ s) and $\omega_p=14000$ cm^{-1} were obtained.[8] The large value of ω_p for MTDTPY-$(PF_6)_{0.67}$ is due to a small interplanar distance of 3.40 Å, compared with the value of 3.48 Å

Table 1. Fitting Parameters of Localization Model

	β-MTDTPY-TCNQ	MTDTPY-chloranil
ω_p/cm^{-1}	12000	13500
τ_i^{-1}/cm^{-1}	2100	3300
ε_{core}	3.5	3.0

in TCNQ complexes. The τ_i^{-1} of the TCNQ complexes is smaller than MTDTPY-$(PF_6)_{0.67}$. This result showed that the localization effects of the TCNQ complexes are smaller than those of MTDTPY-$(PF_6)_{0.67}$. The fluctuation of the Peierls instability may occur in a chloranil complex, since the localization effect is larger than in MTDTPY-$(PF_6)_{0.67}$.

Conclusion

The reflection spectra of charge-transfer complexes of MTDTPY with TCNQ and chloranil showed strong one-dimensionality, in spite of short intercolumn S-S contacts. The one-dimensional localization picture is suitable for describing the optical properties of a one-dimensional conducting electron, rather than the simple free-electron picture.

In β-MTDTPY-TCNQ, values of $\tau_i^{-1}=2100$ cm^{-1} ($\tau_i=2.5\times10^{-15}$ s) and $\omega_p=12000$ cm^{-1} were obtained for free carriers in the column. The electron localization length was estimated to be $l_{loc}=10.5$ Å.

On the other hand, in MTDTPY-chloranil, values of $\tau_i^{-1}=3300$ cm^{-1} ($\tau_i=1.6\times10^{-15}$ s), $\omega_p=13500$ cm^{-1} and $l_{loc}=8.8$ Å were obtained. The large τ_i^{-1} and optical conductivity spectra showed that fluctuation due to the Peierls instability may occur in this crystal.

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