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Spectroscopic Evidence for the Inter-Chain Charge-Transfer Interaction in Copper-bis(2,5-dimethyl-N,N'-dicyanoquinonediimine), Cu(2,5-DM-DCNQI)$_2$

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Polarized reflectance spectra of the single crystals of Cu(2,5-DM-DCNQI)$_2$ and Na(2,5-DM-DCNQI)$_2$ were measured at room temperature. The spectrum of Cu(2,5-DM-DCNQI)$_2$ clearly indicated the inter-chain interaction through the coordinate bonds, whereas the spectrum of Na(2,5-DM-DCNQI)$_2$ showed a typical one-dimensional feature along the stacking direction.

Recently, Aumüller and Hünig synthesized a new class of electron acceptors, N,N'-substituted dicyanoquinonediimines, which have similar chemical properties to the corresponding quinones having the functional groups, =O or =C(CN)$_2$.[1,2] Especially, the anion radical salt, Cu(2,5-dimethyl-N,N'-dicyanoquinonediimine)$_2$ (Cu(2,5-DM-DCNQI)$_2$) has attracted much attention because of its highly metallic electrical conductivity down to 1.3 K.[3] The unique structure of this material is the coexistence of the partially reduced one-dimensional column and the coordinate bond which connects the adjacent columns through the Cu cation and the cyano groups of 2,5-DM-DCNQI. The stable metallic behavior down to low temperature is expected to be related to this inter-chain interaction.[3] However, no direct experimental evidence is given as to the interaction between the metal ion and the cyano groups except for the short interatomic distances between copper and nitrogen atoms. We examined the inter-chain interaction of Cu(2,5-DM-DCNQI)$_2$ by comparing the optical spectrum of the single crystal with that of Na(2,5-DM-DCNQI)$_2$ which does not have a coordinate bond with cyano groups.[4]

2,5-DM-DCNQI was synthesized by the one-step reaction reported by Aumüller

and Hünig.[5] Single crystals of Cu(2,5-DM-DCNQI)$_2$ were prepared by the same method given in the reference.[3] Single crystals of Na(2,5-DM-DCNQI)$_2$ were prepared by the electrochemical reduction of 2,5-DM-DCNQI in the acetonitrile solution of $NaClO_4$. The dimensions of the crystal were $0.02\times0.02\times10$ mm^3 for Cu(2,5-DM-DCNQI)$_2$ and $0.1\times0.3\times0.3$ mm^3 for Na(2,5-DM-DCNQI)$_2$. The polarized reflectance spectrum of Na(2,5-DM-DCNQI)$_2$ was measured from 750 cm^{-1} to 25000 cm^{-1} using a single crystal. The spectrum of Cu(2,5-DM-DCNQI)$_2$ was measured using a single crystal in the spectral region from 4200 cm^{-1} to 25000 cm^{-1}, but the infrared spectrum was measured using an array of crystals having their c-axis in a common direction. The absolute reflectivity in the infrared region was calibrated by comparing the reflectivity around 4200 cm^{-1} with the measured reflectivity data of the single crystal. Although the absolute reflectivity of the Cu salt in the infrared region should be remeasured using a single crystal, these data is available for the qualitative discussion. The reflectance spectra were measured at room temperature.

The reflectance spectrum of Na(2,5-DM-DCNQI)$_2$ is shown in Fig. 1a. The strong anisotropy as to the dispersion in the infrared region indicates the existence of a one-dimensional conducting path along the stacking direction, since the crystal structure is nearly tetragonal and 2,5-DM-DCNQI's are stacking along the b-axis.[4] Although Na(2,5-DM-DCNQI)$_2$ is metallic at room temperature, the shape of the infrared conductivity spectrum is not Drude-like but has a peak at about 3200 cm^{-1} as shown in Fig. 1b. This kind of line shape is often observed in the one-dimensional organic metals, and it is connected with a strong

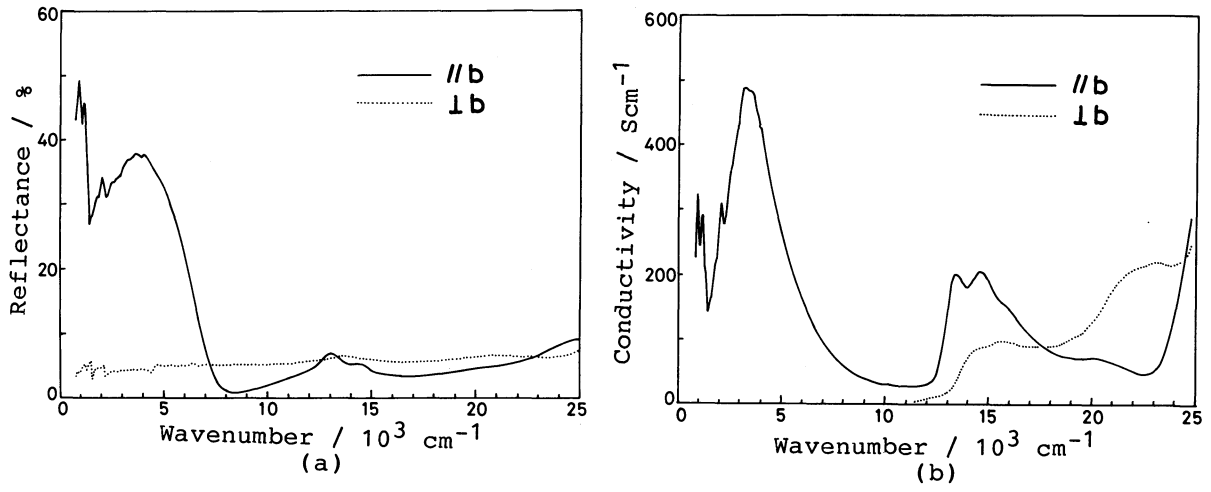

Fig. 1. (a)Reflectance and (b)conductivity spectra of Na(2,5-DM-DCNQI)$_2$.

electron-electron interaction.[6-8] The dispersion around 13000 cm^{-1} is assignable to the lowest intramolecular excitation of 2,5-DM-DCNQI$^-$, since the excitation energies (13200 cm^{-1}, 14600 cm^{-1}, and 16000 cm^{-1}) and the line shape accompanied by a characteristic vibrational structure are quite similar to those (15000 cm^{-1}, 16500 cm^{-1}, and 17900 cm^{-1}) of 2,5-DM-DCNQI$^-$ which were measured with the acetonitrile solution.

Figure 2a shows the reflectance spectrum of Cu(2,5-DM-DCNQI)$_2$, which is remarkably different from that of Na(2,5-DM-DCNQI)$_2$. First of all, the $\perp$c spectrum exhibits a very broad dispersion, which indicates the inter-chain interaction. Second, the reflectivity minimum which existed around 8000 cm^{-1} in the //c spectrum of Na(2,5-DM-DCNQI)$_2$ fades away in this material, and the vibrational structure of the intramolecular transition disappears. Finally, the slope of the infrared dispersion in the //c spectrum is gentle as compared with that of Na(2,5-DM-DCNQI)$_2$. These spectral characteristics are related to the appearance of an additional absorption band around 12000 cm^{-1}, which is isotropic and extraordinarily broad as shown in Fig. 2b. This notable spectroscopic feature should be attributed to the contribution of the coordinate bond between Cu and the cyano groups of 2,5-DM-DCNQI, because the crystal structure of this material is nearly the same as that of Na(2,5-DM-DCNQI)$_2$ except for the coordinate bonds. This new broad band would be associated with the charge-transfer transition between Cu and tetrahedrally coordinating 2,5-DM-DCNQI's, although it is not clear at present what orbitals are involved in the charge-transfer transitions. The intervalence transition between Cu(I) and Cu(II) may

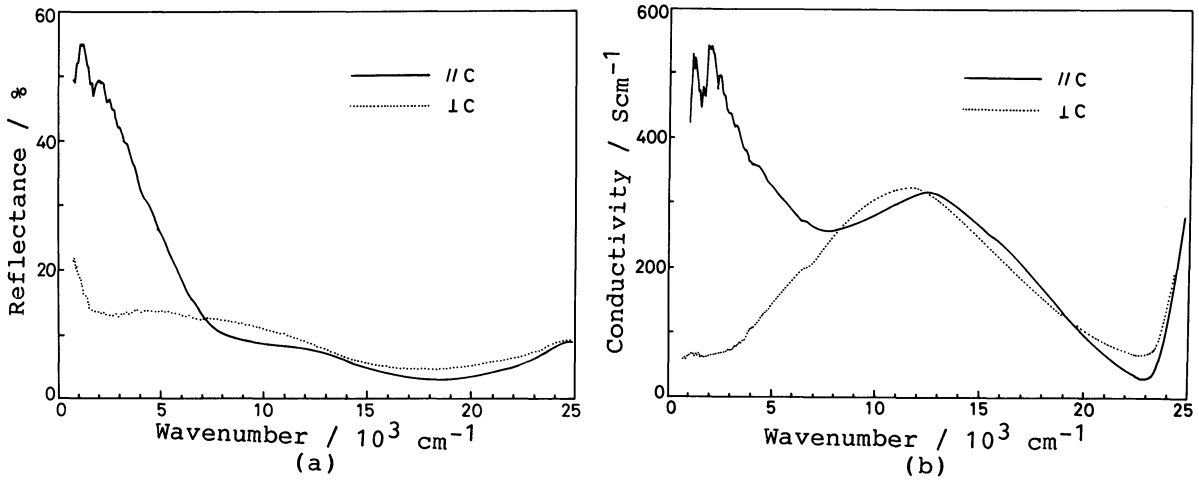

Fig. 2. (a)Reflectance and (b)conductivity spectra of Cu(2,5-DM-DCNQI)$_2$.

also contribute to this broad absorption band, since the recent XPS experiment indicates that the valency of Cu is not +1 but mixed valent between +1 and +2.[9] The mixed-valent state of the Cu cation means that the charge transfer takes place partially from Cu(I) to 2,5-DM-DCNQI and the electronic configuration of Cu 3d electrons is $(3d)^{10-x}$. Therefore, the energy level of the uppermost d-orbital is expected to be located near the Fermi level of the conduction band which is mainly derived from the lowest unoccupied molecular orbital of 2,5-DM-DCNQI. Hence the conduction band possibly has three-dimensional character through the interaction between Cu and N atoms. The steep rise of the reflectivity from 1500 cm^{-1} to low-wavenumber side in the $\perp c$ spectrum is probably related to the intraband transition along the inter-chain direction.[10] If this is the case, this would be the first experimental evidence for the three-dimensional character of the conduction band of $Cu(2,5\text{-DM-DCNQI})_2$.

References

1) A. Aumüller and S. Hünig, Liebigs Ann. Chem., 1986, 142.
2) A. Aumüller and S. Hünig, Liebigs Ann. Chem., 1986, 165.
3) A. Aumüller, P. Erk, G. Klebe, S. Hünig, J. U. von Schutz, and H.-P. Werner, Angew. Chem., Int. Ed. Engl., 25, 740 (1986).
4) R. Kato, H. Kobayashi, A. Kobayashi, T. Mori, and H. Inokuchi, Chem. Lett., 1987, 1579.
5) A. Aumüller and S. Hünig, Angew. Chem., Int. Ed. Engl., 23, 447 (1984).
6) C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, Phys. Rev. Lett., 28, 7019 (1983).
7) C. S. Jacobsen, I. Johansen,and K. Bechgaard, Phys. Rev. Lett., 53, 194 (1984).
8) K. Yakushi, S. Aratani, K. Kikuchi, H. Tajima, and H. Kuroda, Bull. Chem. Soc. Jpn., 59, 363 (1986).
9) H. Kobayashi, private communication.
H. C. Wolf, private communication.
10) The reflectivity in this region significantly increased at low temperature according to the preliminary low-temperature experiment.

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