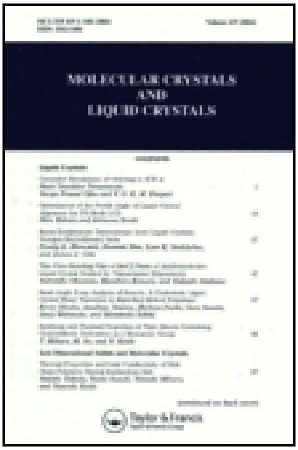

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Properties and Crystal Structure of Charge-Transfer Complex of Tetramethoxydibenzotetrathiafulvalene-Tetracyanoquinodimethane, $(MeO)_4$DBTTF-TCNQ

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PROPERTIES AND CRYSTAL STRUCTURE OF CHARGE−TRANSFER COMPLEX OF TETRAMETHOXYDIBENZOTETRATHIAFULVALENE−TETRACYANOQUINODIMETHANE, $(MeO)_4$DBTTF−TCNQ

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Abstract A novel electron donor, $(MeO)_4$DBTTF (D) forms two kinds of charge−transfer(CT) complexes, black powdered 1:1 (DA) and black needle single crystalline 2:1 (D_2A) complexes, with TCNQ (A). The electrical conductivities are 1.5 Ωcm for DA and 67 Ωcm for D_2A. For D_2A, a single crystal X ray diffraction analysis was performed. It is found that two kinds of D molecules exist in a unit cell and the positive charge inhomogeneously distributed over the two D molecules. For DA, the degree of charge−migration from D to A is estimated to be ~0.6 from the Raman spectrum.

INTRODUCTION

During the past two decades, many experimental data have been accumulated on the organic electrical conducting materials, among which TTF−TCNQ (tetrathiafulvalene−tetracyanoquinodimethane) radical salts and its related compounds have attracted much attention.[1-7] It has been reported that CT complex between DBTTF (dibenzotetrathiafulvalene) and TCNQ shows low conductivity ($\rho_{rt} \approx 10^6$ Ωcm)[8] and forms a mixed−column structure.[9] In the present investigation, using a novel electron donor, $(MeO)_4$DBTTF (D), which is one of the DBTTF derivatives and may show a more excellent property as an electron donor,[10] we prepared 1:1 and 2:1 CT complexes (DA and D_2A) with TCNQ (A). To elucidate physicochemical properties of the complexes we determined the temperature dependence of electrical conductivities, the electronic absorption, and Raman spectra of the complexes. Furthermore, a single crystal X ray diffraction analysis has been performed for D_2A.

EXPERIMENTAL

The 1:1 complex (DA): two hot 1,2-dichloroethane solutions of (MeO)$_4$DBTTF and TCNQ were mixed, then a black powdered 1:1 complex was immediately precipitated out. mp >300 ℃; ir 2199, 2162 cm^{-1}; found C 56.48, H 3.40, N 8.91, S 20.32 % calcd C 57.31, H 3.21, N 8.91, S 20.40 %.

The 2:1 complex (D$_2$A): D$_2$A has been prepared by the electrochemical oxidation of (MeO)$_4$DBTTF,[11] i.e., passing 1 μA of DC current for 5 weeks through a 1,1,2-trichloroethane solution dissolved in (MeO)$_4$DBTTF (1 mmol dm^{-3}) and N-methylquinolinium tetracyanoquinodimethane (1 mmol dm^{-3}), in the presence of a trace amount of a powdered DA, one can obtain a black needle single crystalline 2:1 complex. mp >300 ℃; ir 2178, 2146 cm^{-1}.

DC electrical resistivities were measured by a conventional four probe method using gold paste and gold wire of 50 μm diameter.

The Raman spectrum of the powdered 1:1 complex was recorded on a Jobin Yvon RAMANOR-U1000 double-monochromator. The sample-rotating technique was used to avoid thermal decomposition of the sample. Electronic absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer.

Diffracted data were collected on a Mac Science MXC18 diffractometer ($2\theta_{max} < 130°$, Cu$K\alpha$(λ=1.54178Å) with a graphite monochromator at room temperature. The reflections were scanned at the rate of 8° min^{-1}. A crystal of D$_2$A with approximate dimensions, 0.40×0.15×0.04mm^3 was used for the measurement. C$_{48}$H$_{36}$O$_8$N$_4$S$_8$, formula weight, 1053.36. Crystal data: triclinic, P-1, a=7.198(3), b=9.821(4), c=16.873(6)Å, α=103.99(3), β=91.15(3), γ=94.48(4)°, V=1152.9(8)Å^3, D$_{obs}$=1.50, D$_{calc}$=1.51g/cm^3, Z=1. Number of reflections total 4271, unique 3798; No. observations ($I>3.00\sigma(I)$) 2660; R(Rw) 0.065(0.076). We used Crystan-GM as a computer program for the solution and refinement of crystal structure and solved the structure by a direct method (SIR 92). The structure was refined using a full-matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic one for hydrogen atoms. $\Sigma[W(|F_o|^2-|F_c|^2)^2]$ was minimized, where $W=1.0/[\sigma|F_o|^2+0.0007|F_o|^2]$.

RESULTS AND DISCUSSION

The temperature dependence of DC electrical conductivities of the compressed pellet of DA and the single crystal of D$_2$A are shown in Fig. 1. As seen from this figure, both complexes behave as semiconductors, i. e., the resistances increase with a decrease in temperature. The room temperature conductivity and the activation energy of the pellet are 1. 5 Ωcm and 0. 066 eV, respectively.

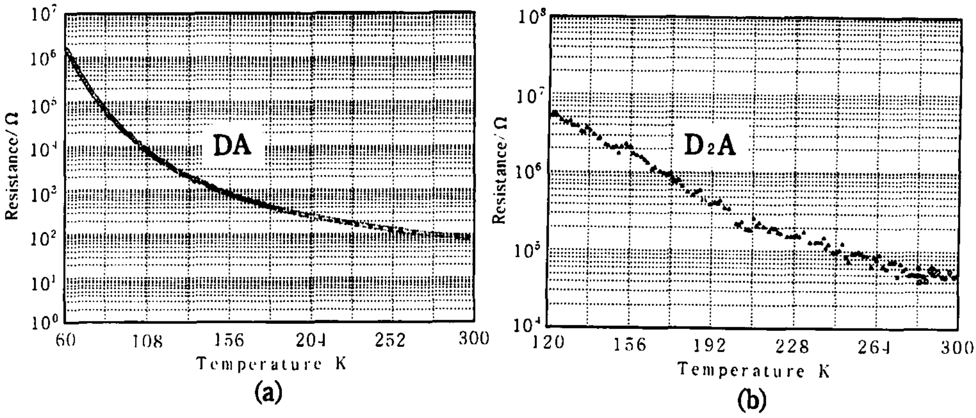

FIGURE 1 Temperature dependence of electrical resistivities of (a) powdered 1:1 complex (DA), and (b) single crystalline 2:1 complex (D$_2$A).

The corresponding values for the single crystalline complex, on the contrary, are relatively high values, 67 Ωcm and 0. 113 eV. This indicates that the two complexes take different column structures in the crystals. In order to know a more detailed information on the crystalline state of the complex, we performed an X ray diffraction measurement for a single crystal of D$_2$A (Fig. 2).

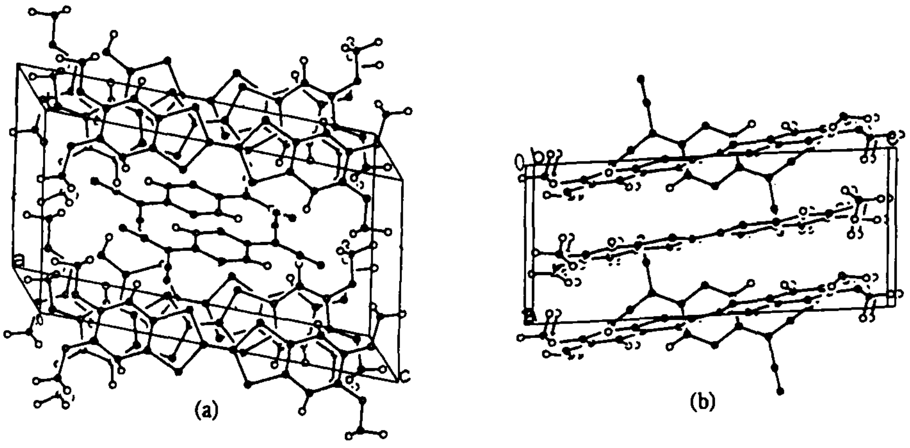

FIGURE 2 Projection of the crystal structures (D$_2$A) viewed along the (a)a– and (b) b–axes.

The X ray measurement clearly shows that the donor–acceptor molar ratio is 2:1, and two types of donor exist in a unit cell, i. e., the positive charge is inhomogeneously distributed over the two donor molecules. The above results of the X ray diffraction analysis for D_2A may be interpreted as follows: in the crystalline state, (1) one D molecule interacts directly with A, TCNQ, $D+A \rightarrow D^+ \cdot A^-$, (2) the produced D^+ behaves as an electron acceptor with respect to the other D molecule, $D+D^+ \cdot A^- \rightarrow D^{+x} \cdot D^{+(1-x)} \cdot A^-$, and (3) $D^{+x} \cdot D^{+(1-x)}$ in $D^{+x} \cdot D^{+(1-x)} \cdot A^-$ makes columns along the a–axis ($0<x<1$). Thus, the columns consisting of two types of D molecules may be regarded as a kind of mixed columns, resulting in relatively high resistance for the 2:1 complex D_2A compared with that of the 1:1 complex DA. Figure 3 shows the electronic absorption spectra of DA and D_2A measured in the transparent KBr disks.

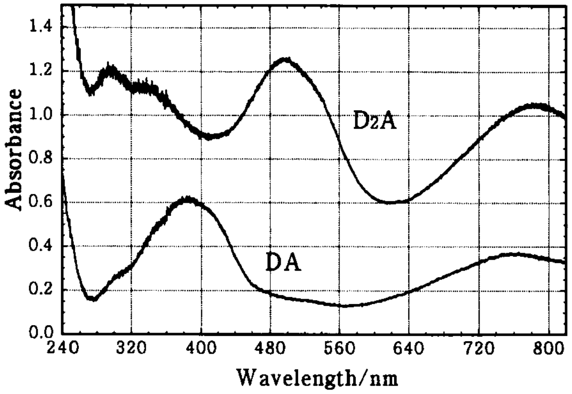

FIGURE 3 Electronic absorption spectra of the powdered (DA) and single crystalline (D_2A) complexes in the KBr disks.

DA shows absorption bands at 755, 522, 385, and 310 nm, and D_2A at 780, 500, 340, and 295 nm. The 755 nm band of DA may be mainly due to the transition localized on the donor moiety D^+, and concerned with the electrical conductivity of this complex. According to Melby et al., an electronic transition localized on the acceptor TCNQ exists in the wavelength region 700–900 nm.[12] The corresponding band does not, however, observed apparently in the spectra of DA and D_2A. In the case of D_2A, the first band (755 nm) is redshifted compared with that of DA, and an additional strong band appears at 500 nm.

It may be interesting to know the degree of a charge migration from D to A in the complex state. According to Matsuzaki, Kuwata, and Toyoda, the Raman shifts of TCNQ ν_4 (C=C stretching) bands are linearly dependent on the degrees of charge migrations of TCNQ and its salts.[13] The ν_4 band of DA is observed at 1451 cm^{-1} (Fig. 4).

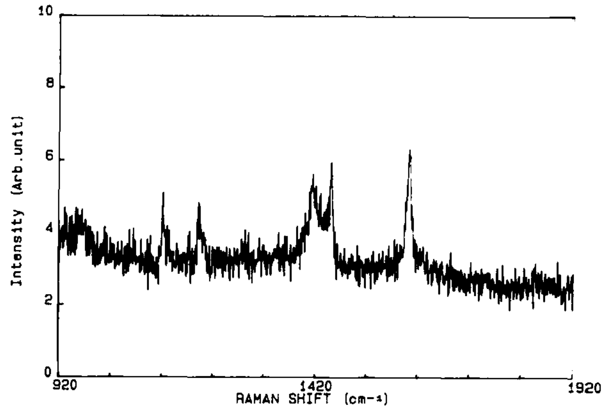

FIGURE 4 The Raman spectrum of powdered complex (DA).

The Raman shifts of the ν_4 bands are plotted with respect to the degrees of the charge migration ρ in Fig. 5, from which ρ is estimated to be ~0.6 for DA.

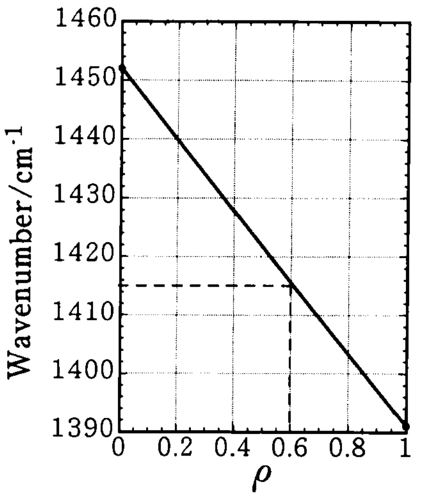

FIGURE 5 Plots of the Raman wavenumber of powdered complex (DA) vs. the degree of charge migration ρ.

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