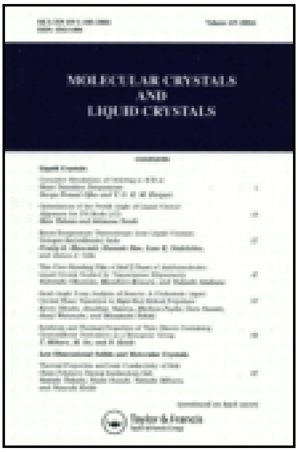

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Preparation and Physical Properties of Conductive EDO-TTF Complexes

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Preparation and Physical Properties of Conductive EDO-TTF Complexes

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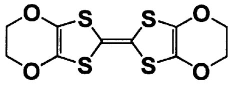
The charge-transfer complexes of EDO-TTF (EDO) with eight kinds of TCNQ derivatives were prepared. The electrical and optical properties were discussed and the crystal structure of $(EDO)_2(BTDA\text{-}TCNQ)_3$ was analyzed. The complexes with strong acceptors (F_2TCNQ, F_4TCNQ) or weak ones (BTDA-TCNQ, $(EtO)_2TCNQ$) were insulators with the conductivity of 10^{-7}-10^{-5} Scm^{-1}. Other TCNQ derivatives (FTCNQ, TCNQ, MeTCNQ, Me_2TCNQ) afforded first highly conductive EDO complexes (10^{-1}-10^{0} Scm^{-1}). These results were consistent with those of the optical measurements.

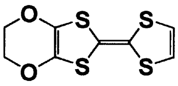
Keywords EDO-TTF; BEDO-TTF; TCNQ; Conducting Complexes; Charge Transfer (CT); Ionicity Diagram

INTRODUCTION

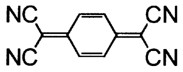
Owing to the strong self-assembling ability, the BEDO-TTF (BO) molecule has provided a number of organic metals with much weaker as well as stronger acceptors (A) than those expected for the typical quasi one-dimensional (1D) organic metals of (TTF)(TCNQ) family [1]. In the



BEDO-TTF (BO)



EDO-TTF (EDO)



TCNQ

BO system, however, the phase transition including superconducting one occurs rarely [2,3]. To realize the phase transitions, the chemical modifications of this donor molecule (D) have been carried out. One of the strategies for partial suppression of the self-assembling ability is the removal of one of the ethylenedioxy groups of BO, which leads EDO. However, only the semiconducting complexes had been reported without any structural and compositional information since the first synthesis of this donor molecule in 1990 [4,5]. In order to have deeper insights into the donor property and the self-assembling ability of EDO in formation of charge transfer (CT) complexes, we have done comprehensive study on complex formation of this donor molecule with TCNQ derivatives.

EXPERIMENTAL

EDO was prepared by slightly modified method from the reported one [3]. Cyclic voltammetry was measured in 0.1M solution of $(Bu_4N)\ BF_4$ in CH_3CN vs. SCE. CT complexes with TCNQ derivatives were prepared by mixing two hot solutions of each component. DC conductivities were measured with four- or two-probe method on compressed pellets.

RESULTS AND DISCUSSION

The values of the first and second redox potentials of EDO were $E^1_{1/2}(D) = 0.39$ V and $E^2_{1/2}(D) = 0.71$ V, respectively, which are consistent with the reported ones [6]. This result indicates that this donor molecule

Table 1 CT complexes of EDO.

#	Acceptor	$E^1_{1/2}$(A) /V	$h\nu_{\mathrm{CT}}$ /10^3cm^{-1}	D:A	σ_{RT} /Scm^{-1}	ε_a /meV
1	F_4TCNQ	0.60	7.5	1:1	$5.6\mathrm{x}10^{-7}$	
2	F_2TCNQ	0.41	11.5	1:1	$3.4\mathrm{x}10^{-5}$	
3	FTCNQ	0.32	3.5	1:1	$4.7\mathrm{x}10^{-1}$	31
4	TCNQ	0.22	3.5	1:1	7.3	22
5	MeTCNQ	0.15	3.4	1:1	$3.5\mathrm{x}10^{-1}$	
6	Me_2TCNQ	0.15	3.4	1:1	2.0	43
7	BTDA-TCNQ	0.03	8.0	2:3	$5.4\mathrm{x}10^{-7}$	
8	$(EtO)_2$TCNQ	0.01	8.0	1:1	$3.9\mathrm{x}10^{-7}$	

# indicates the entry number which represents both acceptor molecule and complex. The complexes are arranged according to redox potentials of acceptor molecules. The column of D:A shows the stoichiometry of the complex. The definitions of $E^1_{1/2}$(A), σ_{RT} and ε_{a} are given in text.

shows the intermediate character between BO and TTF in both the donor strength and difference between $E^1_{1/2}$(D) and $E^2_{1/2}$(D). Eight kinds of CT complexes were prepared between EDO and TCNQ derivatives. Table 1 summarizes their compositions and physical properties.

Ignoring the resonance energies between the donor and acceptor molecules, the CT band energy of the neutral ($h\nu_{\mathrm{CT}}{}^{\mathrm{N}}$) and ionic ($h\nu_{\mathrm{CT}}{}^{\mathrm{I}}$) solid complexes are represented as;

$$h\nu_{\mathrm{CT}}{}^{\mathrm{N}} = I_{\mathrm{D}} - E_{\mathrm{A}} - C' \tag{1}$$

$$h\nu_{\mathrm{CT}}{}^{\mathrm{I}} = -I_{\mathrm{D}} + E_{\mathrm{A}} + (2\alpha-1)C' \tag{2}$$

where I_{D}, E_{A}, C', and α are the ionization potential of the donor molecule, electron affinity of acceptor molecule, Coulomb attractive energy and Madelung constant, respectively [7]. The solid V-shaped line in Figure 1 depicts the eqs. (1) and (2) , where the difference between the first redox potentials of EDO and the acceptor molecule, ΔE (= $E^1_{1/2}$(D) - $E^1_{1/2}$(A)), is used instead of (I_{D} - E_{A}). This type of plot had been introduced by Torrance et al. [7] and helps us to predict the ionicity and stacking manner of a CT complex with some care. Accordingly, the complexes **7** and **8** are classified into neutral complexes with DADA type alternating stacks, since the CT bands of **7** and **8** are located close to the V-shaped line in Fig.1. The complex **1** belongs to ionic one. Although the complex **2** is located just on the border between ionic and partial CT complexes, the CT band energy resides far from the expected one from the V-shaped diagram.

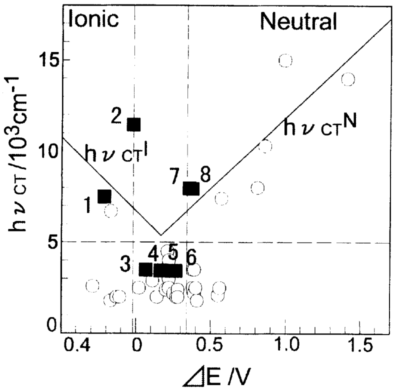


FIGURE 1 The plot of $h\nu_{CT}$ vs. ΔE. The closed squares represent EDO complexes, of which numbers correspond to those in Table 1. The open circles represent BO complexes [1].

The complexes **3-6** exhibit the characteristic low-energy absorption bands below 5 x 10^3 cm^{-1} (A-band, 3.4 - 3.5 x 10^3 cm^{-1}) in KBr pellet samples. It has been known that the (TTF)(TCNQ) type quasi 1D complexes, which are located between the two vertical lines in Fig. 1 ($-0.02 \leq \Delta E \leq 0.34$ V), have the partial CT states and segregated columns, resulting in the characteristic low energy CT bands below 5 x 10^3 cm^{-1}. Based on these facts, it is plausible that the complex **3-6** have both the partial CT state and segregated columns. Even though the ΔE region of BO complexes, which show A-band, is much wider than that of (TTF)(TCNQ) family (see Fig. 1), our experiments proved that the EDO complexes give A-band within the same ΔE region to that of (TTF)(TCNQ) family.

The room temperature conductivity (σ_{RT}) shows a good correlation with the ionicity of the component molecule. The partially ionic complexes, **3**-**6** are highly conductive and their conductivities at room temperature are more than 10^{-1} Scm^{-1}, which is higher by 10^5 orders of magnitude than those of fully ionic one (**1**) and neutral ones (**7**, **8**). The activation energies (ε_a) of complexes **3**, **4**, and **6** are 22 – 43 meV for the compressed pellets.

The formation of the alternating column in the neutral EDO complex is proved by the crystal structure analysis of $(EDO)_2(BTDA\text{-}TCNQ)_3$ (Fig. 2). In this complex, DADA type alternating columns along the *a*-axis are separated by additional acceptor molecules, molecular plains of which are parallel to the column.

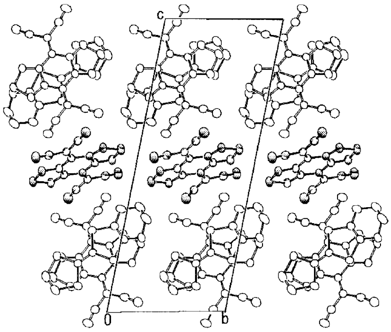


FIGURE 2 The projection along the *a*-axis of the crystal structure of **7**, $(EDO)_2(BTDA\text{-}TCNQ)_3$ [8]. The shaded BTDA-TCNQ molecules separate the DADA columns.

CONCLUSION

The CT complexes of EDO reported in this paper include the fully ionic, neutral and partially ionized ones. The range of ΔE value to afford the last ones is nearly the same as that for (TTF)(TCNQ) family. This fact indicates that the EDO molecule has much weaker self-assembling ability than that of BO molecule. As a result, EDO is expected to afford much (quasi) 1D conductive complexes with a variety of organic or inorganic counter components.

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