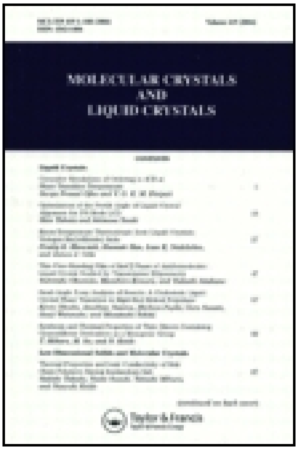

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The Study of Charge Transfer Complexes of Bedt-TTF Derivatives

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THE STUDY OF CHARGE TRANSFER COMPLEXES OF BEDT-TTF DERIVATIVES

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Abstract We have synthesized BEDT-TTF derivatives, which include eight sulfur atoms per molecule, and prepared several charge transfer (CT) complexes with TCNQs, p-quinones, and TCNEs in order to clarify the steric effect of substituents; R. Some of the CT complexes revealed high conductivities.

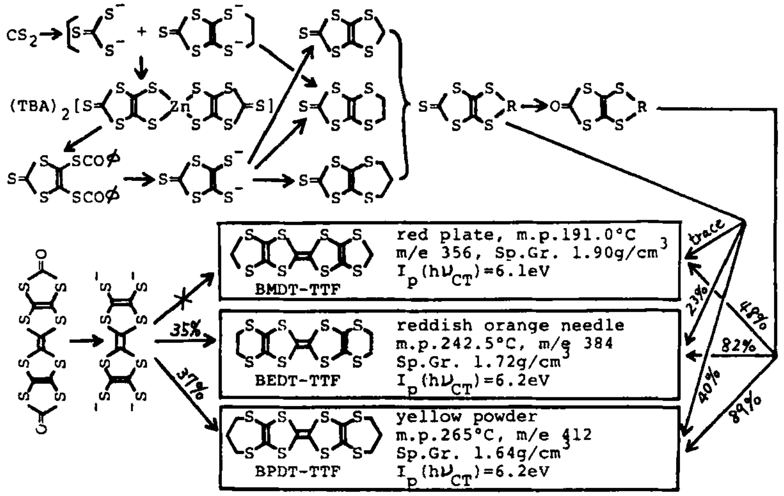
INTRODUCTION

It has been well demonstrated that the extension of TTF skeleton by alkylthio groups makes the donor excellent even than TMTSF concerning the on-site Coulomb repulsion, ionization potential, and polarizability. Furthermore, the alkylthio substituted TTF derivatives are promising donors to yield new organic metals in which the increased dimensionality is expected.[1] In this study we will make a survey of CT complexes of BEDT-TTF derivatives.

RESULTS

BEDT-TTF derivatives are synthesized according to a combination of several reported procedures as shown in Figure 1 and some properties of them are listed.[2] All these donors have the same ionization potential, and are expected to have the same polarizability, and on-site Coulomb repulsion. In Table 1 are summarized conductivity data, CT energies, and other properties of the CT complexes on powdered samples. From the Table, the following remarks can be withdrawn;

Figure 1

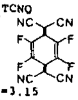
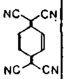
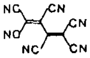
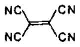
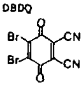
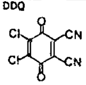
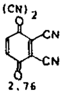


1. with TCNQ and F$_4$TCNQ···All TCNQ complexes are good conductors and the order of the conductivity is BMDT- >BEDT- >BPDT-TTF complex reflecting the bulkiness of the substituents; R. Our TCNQ complexes are not so conductive as reported by Mizuno et al.[3] Also BMDT-TTF·F$_4$TCNQ is rather conductive among several F$_4$TCNQ complexes of TTF derivatives, which are usually poor conductors. From IR spectrum, this complex is confirmed to be fully ionic. The good conductivity may come from the decreased on-site Coulomb repulsion, increased band width due to the increased dimensionality and also to the molecular flattness.

2. with HCBD and TCNE···BMDT-TTF gives conductive complexes with HCBD and TCNE in which the stoichiometry is 2:1. The high conductivity may be ascribed to the partial CT. Other donors give insulators of 1:1 stoichiometry with nominally ionic ground state.

3. with p-quinones···All p-quinone complexes in Table 1 are insulators except BEDT-TTF·Q(CN)$_2$ in which the donor component is excess.

TABLE I Physical data of CT complexes of BEDT-TTF derivatives.

	BMDT-TTF	BEDT-TTF	BPDT-TTF
F_4TCNQ  E_A=3.15	dark green powder D:A=1:1 ρ_{RT}=2.1x10^2(Ωcm; E_a=0.15eV) $h\nu_{CT}$=5.3x10^{3}cm^{-1})	dark green powder 1:1 6.7x10^4 0.29 6.1	black powder 1:1 3.7x10^6 0.56 9.1
TCNQ  2.83	dark blue needle 1:1 3.4 0 3.2	dark green needle 1:1 6.1 0.01 5.7, 3.6	black powder 1:1 1.6x10 0.06 3.2
HCBD  3.22	dark green powder 2:1 8.8 0.16 5.0	dark blue powder 1:1 3.3x10^6 0.34 6.0	dark blue needle 1:1 1.5x10^6 0.37 6.2
TCNE  2.76	dark purple plate 2:1 4.0x10 0.07 3.2	dark green needle 1:1(solv. 0.3) 5.3x10^5 0.30 5.7	———
DBDQ  3.00	dark green powder 1:2 5.9x10^{12} 0.43 5.9	black powder 1:1 2.7x10^5 0.26 6.0	black needle 1:2 1.7x10^7 0.45 7.7
DDQ  2.99	dark green granule 1:2 4.7x10^8 0.88 8.0	black powder 1:1 1.2x10^5 0.27 6.5	dark green needle 1:2 1.1x10^8 0.60 7.7
Q(CN)$_2$  2.76	dull brown powder 1:1(solv. 0.5) 1.3x10^8 0.65 7.7	brown granule 1:0.72 2.3x10^2 0.08 3.4	———

It is well known that the vibrational spectrum of the complex can be used to identify the ionicity of the ground state of the complex. In Figure 2, IR spectra of several TCNQ complexes are compared on KBr pellet. BMDT-TTF gives very broad structureless spectrum due to overlapping of electronic absorption with the peak at ca.3200cm^{-1} (curve b). This feature is characteristic of high conductive material. BEDT-TTF gives two forms, one shows broad spectrum due to partial CT (curve c) and the other shows sharp spectrum (curve d) which is a superimpose of those of neutral components. Reproducibility of yielding of the latter phase is very poor. BPDT-TTF also gives broad spectrum due to partial CT. All the complexes investigated in this work except the TCNQ complex represented by curve d are judged to be nominally ionic. Among them, BMDT-TTF·HCBD, BMDT-TTF·TCNE, and BEDT-TTF·Q(CN)$_2$ exhibit electronic absorption bands extending to IR region, in addition to above three TCNQ complexes.

There is a good correlation between the conductivity (or activation energy) and the position of the CT band of the powdered samples as is depicted in Figure 3, which demonstrates that there are high possibility of getting metallic single crystals in the com-

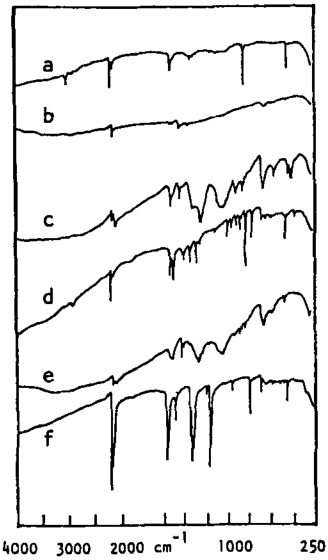


FIGURE 2 IR spectra of TCNQ complexes of BEDT-TTF derivatives.

a; TCNQ, b; BMDT-TTF.TCNQ,
c,d; BEDT-TTF·TCNQ,
e; BPDT-TTF·TCNQ,
f; K·TCNQ.

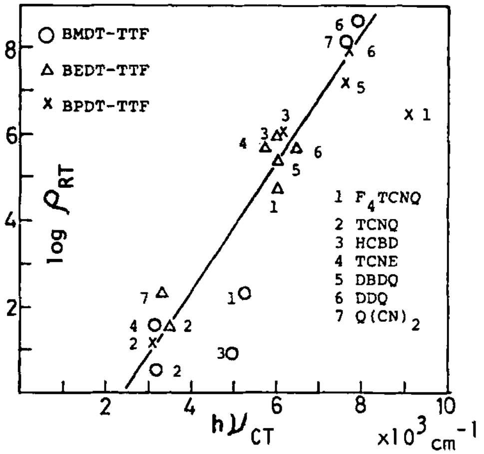


FIGURE 3 logρ_{RT} vs $h\nu_{CT}$
Line is a guide to the eye.

plexes BMDT-TTF·TCNQ, BMDT-TTF·HCBD, BMDT-TTF·TCNE, BEDT-TTF·TCNQ, BEDT-TTF·Q(CN)$_2$, and BPDT-TTF·TCNQ.

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