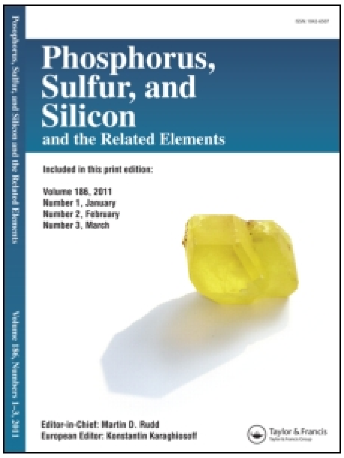

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CONDUCTIVE CHARGE-TRANSFER COMPLEXES OF ALKOXY SUBSTITUTED TETRATHIAFULVALENE, BEDO-TTF

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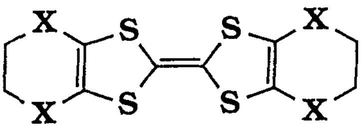
Abstract BEDO-TTF which is one of the oxygen substituted BEDT-TTF analogues, gave conductive organic charge transfer complexes in contrast to BEDT-TTF and other BEDT-TTF derivatives. Especially many complexes exhibit metallic temperature dependences even with the compressed disks. These facts suggest the remarkable tendency of BEDO-TTF to aggregate themselves.

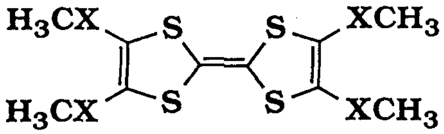
INTRODUCTION

Since the discovery of the first organic metal, (TTF)(TCNQ) in 1973, the chemical modifications of the donor and acceptor molecules have been carried out to stabilize the metallic state of the complexes. As the ultimate organic metal, the organic superconductors have been produced, most of which contain TTF derivatives as the conducting components. Among them, BEDT-TTF complexes are rich in variety concerning with the crystal structure and have been tempting us the syntheses of the derivatives of the donor molecule and their complexes. All of the superconductors based on BEDT-TTF so far prepared are the cation radical salts with inorganic counter anions. The introduction of the suitable organic acceptors as the counter part may bring about the following interesting issues: (1) the increment of the dimensionality due to the donor-acceptor interaction in the solid state, (2)



BEDX-TTF

X=O BEDO-TTF
S BEDT-TTF
Se BEDSe-TTF
Te BEDTe-TTF



TXC$_1$-TTF

X=S TTC$_1$-TTF
Se TSeC$_1$-TTF
Te TTeC$_1$-TTF

the stabilization of the metallic state due to the big polarizability of the organic compounds, and (3) two chain conductors like as (TTF)(TCNQ).

This paper presents our work on the BEDO-TTF complexes with organic acceptor molecules and the comparison of them with other complexes of BEDT-TTF derivatives.

RESULTS

Direct reaction between BEDO-TTF and the acceptors in appropriate solvents gave the charge transfer (CT) complexes listed in TABLE I. Variety of the acceptors were used in view of the electron affinity. The compositions were determined by the elemental analyses. Absorption spectra of the complexes were measured on the KBr pellets. Conductivity measurements were carried out on the compressed pellets by pseudo-four probe method, namely, each face of the pellet was painted with the gold paste and the current and voltage probes were attached to the same portion of the paste.

Most of the complexes showed the CT absorption peaks in the infra red region. Many of them exhibit the metallic behavior, even the conductivity measurements were carried out on the compressed pellets. The degree of CT of the TCNQ complex was determined as 0.55-0.64 from the CN stretching frequency.

DISCUSSION

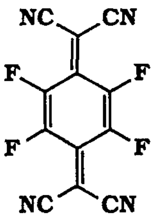
CT complexes of BEDT-TTF derivatives other than those of BEDO-TTF

Concerning the alkylchalcogeno groups attached to the TTF skeleton, there are mainly two groups of the donor molecules. One is the capped type compound, BEDX-TTF and the other is uncapped one, TXC_1-TTF. Excepting BEDTe-TTF, all the derivatives have been synthesized. Comparing to the cation radical salts with inorganic anions, the number of the CT complexes of BEDX-TTF and TXC_1-TTF with organic acceptors is rather small. For BEDT-TTF, BEDSe-TTF, TTC_1-TTF, $TSeC_1$-TTF, and $TTeC_1$-TTF, the numbers of the reported CT complexes are 18, 0, 11, 1, and 2, respectively. Among them, only the triclinic form of the (BEDT-TTF)(TCNQ) shows the metallic conductivity above room temperature. Most of the reported BEDT-TTF complexes have neutral ground states. For the TXC_1-TTF complexes, the steric effect of the methyl group is critical to produce the metallic CT complexes. Most of the complexes mentioned above do not satisfy the requirements for organic metals that is summarized as (1) having the partial charge transferred

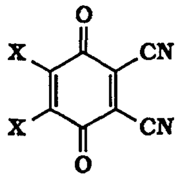
TABLE I Physical data of BEDO-TTF complexes

Acceptor	$E_{1/2}$[a)] /V	Composition (D : A)	$h\nu_{CT}$ $/10^3$ cm	Room temperature conductivity $/S\cdot cm^{-1}$
F4TCNQ	0.58	1:1	ca. 6[c)]	9.2×10^{-8}, Ea = 0.48 eV[e)]
F4TCNQ	0.58	9:5:4(THF)	1.8	1.1×10, metallic
DDQ	0.55	5:3:1(CH_3CN)	2.0	4.6×10, metallic[d)]
DBDQ	0.52	11:7:1(CH_3CN)	2.0	4.3×10, metallic[d)]
TCNE	0.25	> 2:1[b)]	2.1	8.1×10[d)]
TCNQ	0.20	1:1	4.5	8.3×10^{-2}, Ea = 0.07 eV[e)]
Me_2TCNQ	0.12	9:5:1(CH_3CN)	2.4	1.0×10, metallic
$(MeO)_2$TCNQ	0.03	2:1	2.5	4.6×10, metallic[d)]
DCNQ	0.18	2:1	3.0	1.1×10, metallic
BTDA-TCNQ	0.00	2:1[b)]	3.0	8.4×10[d)]
QCl_4	0.02	2:1	4.0	5.7×10, metallic[d)]
QF_4	0.02	11:5:6(CH_3CN)	1.8	2.2, metallic
QBr_4	0.01	7:4	3.5	4.7×10, metallic[d)]
DTNF	-0.03	2:1:1(CH_3CN)	1.8	6.5×10, metallic[d)]
TNF	-0.45	1:1	10	$< 3 \times 10^{-9}$

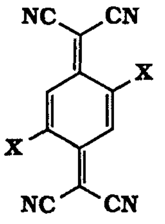
a) Determined by cyclic voltammetry: vs. SCE, 0.1 M $(Bu_4N)BF_4$ in CH_3CN. b) approximate values which have more than 0.3 % error in the C, H, N, S elemental analyses. c) The peak position is not clear. d) standard 4 probe method. e) 2 probe method.



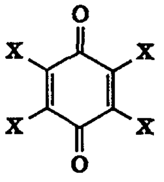
F4TCNQ



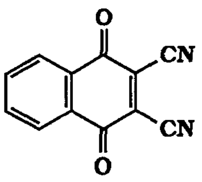
X=Cl DDQ
Br DBDQ



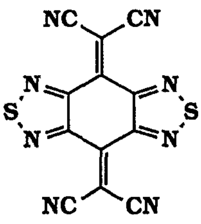
X=H TCNQ
CH_3 Me_2TCNQ
OCH_3 $(MeO)_2$TCNQ



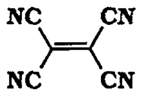
X=F QF_4
Cl QCl_4
Br QBr_4



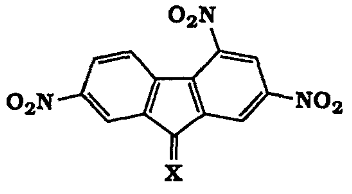
DCNQ



BTDA-TCNQ



TCNE



X=$C(CN)_2$ DTNF
O TNF

ground state and (2) having the appropriate conducting path.

CT complexes of BEDO-TTF

In contrast to the former donors, BEDO-TTF gave, at least, ten organic metals with the acceptors having rather wide range of the electron affinities. According to Lichitenberger et al.[1], virtually the ionization potential of BEDO-TTF (IPv = 6.46 eV) is less than that of BEDT-TTF (6.7 eV) and even less than TTF (6.70 eV). So, BEDO-TTF is a rather strong donor. When the donor is completely ionized in the solid, it can not be a conducting component even if the crystal structure is appropriate. Judging from the reduction potential of the acceptor, 1:1 F4TCNQ complex is the case of this situation. Whereas in the 9:5:4 F4TCNQ complex, even the acceptor is ionized completely to $(\text{acceptor})^{1-}$, the charge on the donor is still 5/9. In this complex, the CT absorption appears at around $1.8 \times 10^3\ \text{cm}^{-1}$. According to Torrance et al.[2], for the mixed stacked CT complexes, the transition energy must be higher than $5.65 \times 10^3\ \text{cm}^{-1}$. Also taking into account the conducting behavior, the segregated columnar structure or sheet structure suitable for the metallic conductivity are expected for 9:5:4 F4TCNQ complex. By analogy to this complex, other complexes except 1:1 F4TCNQ and TNF ones are expected to have the partial charge transferred ground state and the segregated column structures. The metallic conducting behaviors of the ten complexes in TABLE I support this postulate.

Characteristics of BEDO-TTF

As can be seen from TABLE I, the composition of 1:1 is rather rare and some of them have intricate donor:acceptor ratios in contrast to those (1:1 or 2:1) of the complexes of other BEDT-TTF derivatives. The non 1:1 composition is favorable to get organic metals in the combination of strong donors and strong acceptors as mentioned above. So long as presumed from TABLE I, BEDO-TTF tends to construct segregated columnar structures of the partially charged donor molecules. All the BEDO-TTF cation radical salts with inorganic and stable organic anions so far analyzed have similar packing motif in which the donor molecules form two dimensional sheets[3-5]. This indicates the strong tendency of the donor to pack in such fashion. One of the origins of the nature may be the existence of the weak hydrogen bond among the donor molecules as claimed by Williams et al.[3] In analogy with this, the tendency of BEDO-TTF to give conductive organic CT complexes can be regarded as the result of its strong ability to aggregate themselves which may work similarly both in the cation radical salts and in the CT complexes.

It is noteworthy that ten of the complexes listed in TABLE I exhibit the metallic behavior even the measurements were carried out on the compressed pellets. Commonly, even if the complex is an intrinsic metal, the compacted pellet of the organic complex shows the semiconductive temperature dependence due to the semiconductive nature of the contact resistances between the sample particles. To understand the abnormal behaviors of these BEDO-TTF complexes, the intrinsic anisotropy of the samples should be considered. According to Klanderman et al.[6], the most resistive component of the conductivity tensor mainly dominates the conductivity of the compressed pellet for the anisotropic material. $(\mathrm{BEDO\text{-}TTF})_5(\mathrm{HCTMM})(\mathrm{Ph\text{-}CN})_2$ salt (HCTMM = $[\mathrm{C}[\mathrm{C}(\mathrm{CN})_2]_3]^{2-}$) is the two dimensional metal of which the anisotropy of the conductivity is measured.[7] Even along the most resistive direction, the salt exhibits the metallic temperature dependence of the resistivity. Interestingly, also the compressed pellet of this salt behaves as a metal, however the variation of the resistivity with temperature is smaller than that of the single crystal. Thus, when the resistivity along the most resistive direction changes greater than those from the inter-particle contacts with temperature, the compressed pellet can behave as a metal. The metallic complexes in TABLE I can be regarded as the materials in which the intrinsic resistivities along the most resistive directions vary greater than the semiconductive inter-particle contacts with temperature.

Conclusion

BEDO-TTF gave the conductive complexes with the organic acceptors having various acceptor strength. The 1:1 ratio is rare for the composition of these complexes. The conductive complexes exhibit the CT absorption bands at very low energy region of 1.8 to 3.0 x 10^3 cm^{-1}. The metallic complexes exhibit the metallic behaviors even the measurements were carried out on the compressed pellets. This donor has the stronger tendency to form organic metals than the other alkylchalcogeno substituted TTF derivatives. The origins of this nature can be attributed to its low ionization potential and the ability of its self-aggregation.

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