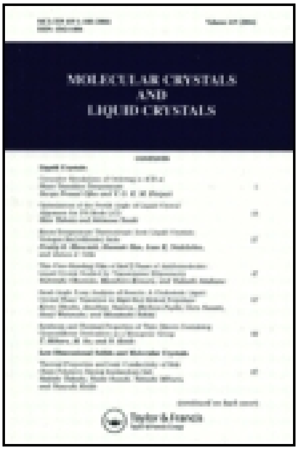

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Organic Metals Based on Hexamethylenetetratellurafulvalen (HMTTeF)

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ORGANIC METALS BASED ON HEXAMETHYLENETETRATELLURAFULVALENE (HMTTeF)

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Abstract Several CT complexes of HMTTeF with TCNQs, quinones, and other acceptors were prepared and electrical and optical properties were examined. A linear correlation between the resistivities and the position of CT bands was observed. In general, 1:1 complexes with strong acceptors(E_A>2.60eV) show relatively high conductivity with low activation energy as well as strong electronic absorption extending to IR region. Single crystals of TCNQ and 2,5-dimethylTCNQ complexes show metallic character, in which Peierls transition is strongly suppressed.

INTRODUCTION

To obtain an organic metal with enhanced metallic character, usage of tellurium atoms instead of sulfur in TTF is quite effective, because van der Waals radius increment is 14% and atomic electronegativity decrement is 16%. Therefore, one may expect increased polarizability, band width, and interchain interaction, also decreased on-site Coulomb repulsion in HMTTeF complexes.

RESULTS

Electric Properties···Comparison of the electric properties of HMTTeF complexes on compaction samples(Table 1) with the data of TTF·TCNQ(σ_{RT}=5.3Scm^{-1}, ϵ_a=0.005eV) suggests that FTCNQ, TCNQ, and Me_2TCNQ complexes may be metallic. Single crystals of TCNQ and Me_2TCNQ complexes, in the latter complex the stoichiometry is different from that in the powder, show


HMTTeF

metallic behavior(σ_{RT}=1400 and 1800Scm^{-1}). Although they have maximum in conductivity at 243 and 130K, the conductivity decrease below the maximum is very gradual(σ_{77K}=600 and 2600 Scm^{-1}, respectively) indicating strong suppression of the Peierls transition(Figure 1). With other acceptors, HMTTeF also produces conductive complexes, but only with strong ones(E_A>2.60eV). These results are in good agreement with our diagram proposed for the requirement for an organic metal.

Acceptor	E_A(eV)	D:A	σ_{RT}(Scm^{-1})	$\mathcal{E}_a$(eV)	$h\nu_{CT}$ x10^{3}cm^{-1}	Ionicity IR	UV-VIS
1 F_4TCNQ	3.15	1:1	3.0x10^{-1}	0.034	3.2	I	I
2 DBDQ	3.01	1:1	2.0x10^{-3}	0.079	3.9	I	I
3 DDQ	2.99	1:1	1.2x10^{-2}	0.046	3.6	I	I
4 FTCNQ	2.92	1:1	3.7x10^{-1}	0.0010	2.8	I	I
5 TCNQ	2.83	1:1	7.1	0.0030	2.9	I	I
6 Me_2TCNQ	2.74	2:1	4.5	0.0024	2.7	I	I
7 DCNQ	2.64	1:1	8.3x10^{-3}	0.071	3.8	I	I
8 $(MeO)_2$TCNQ	2.56	1:2	5.8x10^{-10}	0.30	6.7	N	N
9 DTNF	2.52	1:1	2.7x10^{-12}	0.50	6.8	N	N
10 BODT	2.04	1:1	3.3x10^{-9}	0.49	6.3	N	N

TABLE I Summary of conductivity, electronic spectra, and judgement of ionicity by IR, UV-VIS(I:nominally ionic, N:neutral).

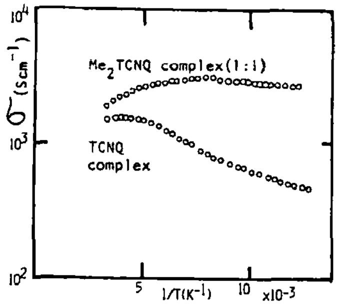

FIGURE I Single crystal data of the TCNQ and Me_2TCNQ(1:1 form) complexes.

UV-VIS and IR Spectra···The electronic spectra of several TCNQs complexes are compared in Figure 2. The weakest TCNQ; $(MeO)_2$TCNQ, exhibits ordinal CT band at 6.7x10^{3}cm^{-1} in the complex. On the other hand, the complexes with strong TCNQs reveal characteristic bands extending below 4x10^{3}cm^{-1}, leading that they have nominally ionic ground state(0.5≲degree of CT≲1). IR spectra tell us again that the $(MeO)_2$TCNQ complex is neutral and other TCNQs complexes to be nominally ionin. Especially the FTCNQ, TCNQ, and Me_2TCNQ complexes display characteristic structureless spectra caused by partial CT (Figure 2). The ionicity of the complexes is summarized in Table 1.

Plot of logσ_{RT} (or $\mathcal{E}_a$) vs $h\nu_{CT}$ clearly devides the two groups; one is nominally ionic and the other neutral, in Figure 3. High conductivity, low activation energy, and electronic absorption band ex-

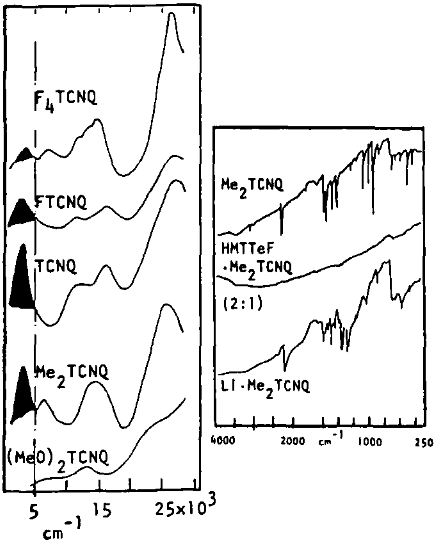

FIGURE 2 UV-VIS, and IR spectra of HMTTeF complexes with several TCNQs(in KBr).

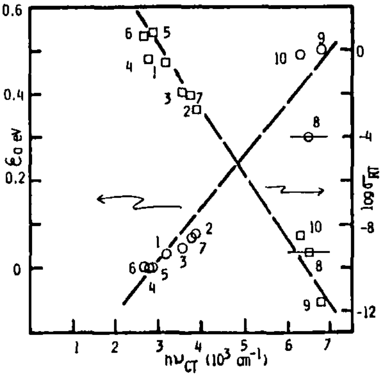

FIGURE 3 Empirical relationship between $h\nu_{CT}$ and $\log\sigma_{RT}$ or ε_a.

tending below $4\times10^3 cm^{-1}$ can be observed in nominally ionic HMTTeF complexes.

HMTTeF·F_4TCNQ complex···This complex is unique among the F_4TCNQ complex ever obtained(Table 2). 1:1 F_4TCNQ complexes are insulators due to complete CT usually, and sometimes Mott insulators. But the only exception is the HMTTeF complex. In general, completely ionic complex exhibits a sharp IR spectrum which can be a superimpose of the ionized components(donor^{+} and acceptor^{-}). While, in the case of highly conductive partial CT complexes like HMTTeF complexes of FTCNQ, TCNQ, and Me_2TCNQ, the IR spectrum is completely obscured by the invasion of intraband transition band. Although the IR spectrum of HMTTeF·F_4TCNQ is broadened by overlapping of the electronic absorption band in IR region, the spectrum is definitely sharper than that in Figure 2 and total feature is much similar to that of ionized F_4TCNQ(Figure 4). Therefore it is likely to conclude that the ionicity of this F_4TCNQ complex is very close to unity.

The redox parameters(Table 2) predict that this complex is fully ionic. Actually a preliminary Raman experiment estimates the ionicity to be unity for the complex. Nevertheless the complex is conductive. In the electronic spectra, the HMTTeF·F_4TCNQ is the only one which exhibits a band below $4\times10^3 cm^{-1}$ among the F_4TCNQ complexes in Table 2. Other absorptions in HMTTeF·F_4TCNQ are assigned to those observed in K·F_4TCNQ (Figure 4). At this moment the assignment of the low energy band of the HMTTeF complex cannot be made. Eventhough, we can give the following remarks: The 1:1 F_4TCNQ complexes in Table 2 are insulators mainly due to complete CT and U≫4t. In the case of the HMTTeF complex, however, it is plausible that effective U is decreased and band width 4t is increased due to big polarizability, big orbital overlap, and small electronegativity resulting in U≈4t; very narrow gap semiconductor. We need more study to confirm this.

TABLE 2 F4TCNQ complexes.

F_4TCNQ complex	E_{ox}(V)	degree of CT	property
TMTTF	0.27		insulator
	0.28		$\rho_{RT}\sim4\times10^{5}$
TTF	0.31	1	dimerized segregated, $\rho_{RT}\sim3.8\times10^{3}$
HMTTF	0.33	1	Mott insulator $\rho_{RT}\sim10^{4}$
HMTTeF	0.40		conductive $\rho_{RT}\sim3.3$
HMTSF	0.41	1	Mott insulator
TMTSF	0.44		insulator
DBTSF	0.47	1	Mott insulator
DBTTF	0.53	1	dimerized segregated, Mott insulator >390K
	0.65		α form $\rho_{RT}\sim1.4\times10^{3}$

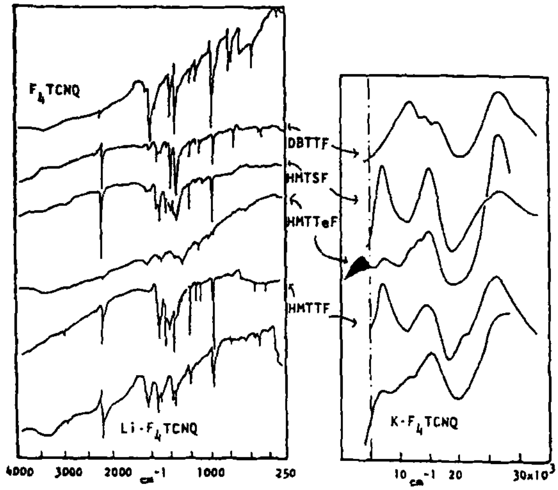

FIGURE 4 UV-VIS and IR spectra of F_4TCNQ complexes(in KBr).