CHEMISTRY LETTERS, pp. 503-506, 1983.

ORGANIC CONDUCTORS: ELECTRICAL PROPERTIES OF HMTTeF(HEXAMETHYLENETETRATELLURAFULVALENE) COMPLEXES

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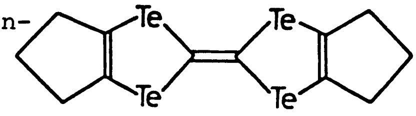
Several charge transfer complexes of HMTTeF(hexamethylenetetratellurafulvalene) with TCNQs, p-quinones, and other π-acceptors were prepared and electrical resistivities were measured with compaction samples. Some of them revealed very low resistivities(ρ_{RT}<1Ωcm) and low activation energies(ε_a<0.01eV). Intermolecular interaction through tellurium atoms seems to play an important role in the conduction.

One of the most effective ways to suppress the Peierls transition in low-dimensional organic metals, thiafulvalene or thianaphthacene complexes has been the replacement of sulfur by selenium atoms. Of these, TMTSF(tetramethyltetraselenafulvalene) was the most fascinating because ClO_4, PF_6, or AsF_6 salt of TMTSF became an organic superconductor with $T_c \sim 1K$. In the TMTSF salts, the increased interchain interaction caused by close intermolecular Se···Se contact plays a crucial role to stabilize the superconducting state.1) Moreover, in the two-chain complex of HMTSF(hexamethylene-TSF)·TCNQ, an enhanced intermolecular interaction due to Se(HMTSF)···N(TCNQ) contact makes the complex quasi two-dimensional and suppresses the Peierls transition to lower temperature.2) Taking into account the van der Waals radius of charcogenide atoms(S:1.80, Se:1.90, and Te:2.06Å),3) it is more promising to use tellurium analogues in the study of low-dimensional organic metals in order to obtain a complex with strong interchain interaction. In addition to this, using tellurium analogues will increase the conduction band width and polarizability, and hence an enhancement of metallic character is expected. Recent excellent success by Wudl and Aharon-Shalom4) in preparation of HMTTeF(**1**) prompted us to elucidate the physical properties of charge transfer(CT) complexes of HMTTeF.

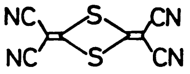


1 HMTTeF

HMTTeF was prepared as black needles starting from cyclopentanone according to the method of Wudl and Aharon-Shalom and purified by recrystallization from chlorobenzene(mp ca.260°C decomp., density 2.95g/cm^3, and elemental analysis C:21.69(calcd 21.60), H:1.77(1.80%)).5) CT complexes with several π-acceptors were prepared by mixing hot solution of each component. In Table 1, the acceptors, their electron affinities(E_A) determined from their CT band with pyrene complexes in chloroform taking E_A of TCNQ as 2.83eV, the color of the complexes, and the molecular ratio(HMTTeF:acceptor) are presented.

The resistivity was measured by a two- or four-probe method from room temperature to 77K using silver paste Du Pont #4922. Some of these complexes were quite sensitive to the electrical contacts and showed gradual resistivity increase by using silver paste Du Pont #4817. The results of the resistivity measurements were summarized in Table 1 together with those of TTF·TCNQ as a reference.

Table 1. Electrical Properties of HMTTeF Complexes

π-Acceptor	E_A(eV)	Color	Ratio	ρ_{RT}(Ωcm)	ε_a(eV)
TCNQs					
1. F_4	3.15	dark blue	1:1	3.3	0.034
2. F	2.92	dark blue	1:1	2.7	<0.001
3. TCNQ	2.83	dark blue	1:1	0.14 0.6~1 4)	0.0030
4. 2,5-dimethyl	2.74	green	2:1	0.22	0.0024
5. 2,5-dimethoxy	2.56	blue	1:2	1.7x10^{9}	0.30
p-quinones					
2,3-dibromo-5,6-dicyano(DBDQ)	3.00	black	1:1	4.9x10^{2}	0.079
2,3-dichloro-5,6-dicyano(DDQ)	2.99	black	1:1	8.3x10	0.046
2-bromo-5,6-dicyano	2.88	black	~1:2	1.6x10^{4}	0.045
2-chloro-5,6-dicyano	2.87	black	2:3	2.3x10^{3}	0.092
2,3-dicyano	2.76	brown	2:3	2.7x10^{5}	0.23
2,3-dicyano-1,4-naphthoquinone(DCNQ)	2.64	brown	1:1	1.2x10^{2}	0.071
others					
9-dicyanomethylene-2,4,5,7-tetranitrofluorene(DTENF)	2.69	black	3:2	4.1x10^{2}	0.080
9-dicyanomethylene-2,4,7-trinitrofluorene(DTNF)	2.52	black	1:1	3.7x10^{11}	0.50
tetracyanoethylene(TCNE)	2.76	dull green	~1:1	1.4x10^{3}	0.069
2,4-bisdicyanomethylene-1,3-dithietan 	2.04 6)	dark brown	1:1	3.0x10^{8}	0.49
TTF·TCNQ		black	1:1	0.19	0.0053

According to our diagram to predict electrical properties of the TTF·TCNQ system, the oxidation potential of HMTTeF(0.40V) 4) makes this donor form metallic complexes with the TCNQ type acceptors in the range of $2.72<E_A<3.07$eV if the ratio is 1:1, as far as the partial CT is the dominating factor. 7) Therefore, it is quite reasonable that FTCNQ and TCNQ give highly conductive complexes, while 2,5-dimethoxy-TCNQ gives neutral insulating complex. Though the molecular ratio of 2,5-dimethyl-TCNQ complex is not simple, this acceptor satisfies the above electron affinity criterion, and so enough degree of CT between the components is taking place. Relatively high conductivity of F_4TCNQ complex, IR spectrum of which is mainly composed of that of $F_4TCNQ^{\overline{\cdot}}$, cannot be explained from its degree of CT. This result and its considerably small activation energy suggest that the increased band width due to big tellurium atoms plays an important role in the conduction, together with the small on-site Coulomb energy of HMTTeF. 8) A comparison with the electrical properties of TTF·TCNQ indicates that the complexes with FTCNQ, TCNQ, and 2,5-dimethyl-TCNQ are considered to be organic metals, supporting validity of our diagram(Figure 1).

Since the discovery of highly conducting complexes of TTFs with tetrahalo-p-quinone,9) the electrical properties of the TTF·p-quinone system have received great attention in connection with the neutral-to-ionic phase transition10) and the metallic character. All of the p-quinone complexes studied in this work (Table 1) are not highly conductive. In Table 2, 1:1 HMTTeF complexes are compared with those of thiafulvalenes to look into characteristic properties of the HMTTeF complexes.11) A single crystal of DBTTF·DDQ was investigated on its structure and electrical properties by Kobayashi and Nakayama12) and was considered to be an organic metal(ρ_{RT}=0.013 Ωcm). A value of 0.13Ωcm was reported by Mayerle and Torrance for a compressed sample.13) Compared with those values, our resistivity of 3.7Ωcm for the compressed DBTTF·DDQ is pretty high due to some unknown reason. In the Table, TMTTF·DCNQ shows twice smaller resistivity and an order smaller activation energy than those of our DBTTF·DDQ, therefore we may expect that TMTTF·DDQ is also an organic metal. It is noteworthy that activation energies of HMTTeF complexes are appreciably smaller than those of thiafulvalene semiconductive complexes, indicating a contribution of tellurium atoms to the conduction. The resistivities of DBDQ and DDQ complexes are decreasing as increasing oxidation potentials of the donors, and this tendency satisfies the diagram proposed to predict the electrical properties of the TTF·p-quinone system from their redox potentials.11)

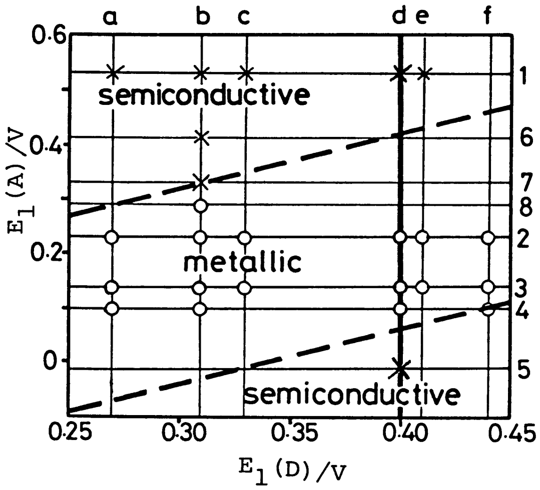


Fig. 1. Conductivity of complexes plotted as E_1(A) vs E_1(D); x=insulators or semiconductors, and o=highly conducting complexes. Donor; a:TMTTF, b:TTF, c:HMTTF, d:HMTTeF, e:HMTSF, f:TMTSF. Acceptor; 1~5:see Table 1, 6:2,5-dichloro-, 7:2,5-difluoro-, 8:chloro-TCNQ. E_1(A):first reduction potential of acceptor and E_1(D):first oxidation potential of donor.

Table 2. Electrical Properties of p-Quinone Complexes: ρ_{RT}(Ωcm)(ε_a(eV))

	TMTTF(0.27V^a)	HMTTF(0.33V)	HMTTeF(0.40V)	DBTTF(0.53V)
DBDQ	1.7×10^4 (0.26)	7.4×10^4 (0.24)	4.9×10^2 (0.079)	2.9×10 (0.15)
DDQ	3.1×10^4 (0.27) 10^3 (0.31)14)	8.3×10^5 (0.20)	8.3×10 (0.046)	3.7 0.1313), 0.01312,b)
DCNQ	1.9 (0.01)	1.0×10^{12} (0.59)	1.2×10^2 (0.071)	————

a:oxidation potential, b:single crystal

DTNF and DTENF have not been used frequently as acceptors to get highly conductive complexes because these acceptors have big on-site Coulomb repulsive energies, and so tend to form Mott insulators. So far, trimethyl-1,2,3-benzimidazolium$(\mathrm{DTENF})_2$ in which the formal charge of DTENF is 0.5 has been the most conductive complex(ρ_{RT}=50Ωcm, ε_a=0.085eV)15) to our knowledge. In this anion radical salt, it is assumed that stacking manner is segregated. HMTTeF·DTENF shows the resistivity only eight times bigger than that of the above benzimidazolium complex and the activation energy almost the same. In HMTTeF·DTENF, an alternating stacking manner is more probable than the segregated one. Even in the alternating type, partial CT is a critical factor which governs the conductivity. The relatively good conductivity of this complex is mainly due to the partial CT and fairly small activation energy(usual DTENF and DTNF anion radical salts show $\rho_{RT}>10^4\Omega$cm and ε_a= 0.15~0.46eV)[15] may also be ascribed to the participation of tellurium atoms into the conduction mechanism. DTNF is a little weaker as an acceptor to fulfill partial CT. TCNE is an unfavorable acceptor for the purpose of pursuing highly conductive 1:1 CT complexes, since the two electron-accepting groups are too proximate to diminish the on-site Coulomb repulsion. Concerning to the on-site Coulomb energy, 2,4-bisdicyanomethylene-1,3-dithietan is more favorable than TCNE, and besides a reinforcement of intermolecular interaction caused by Te···S contacts is possible in its HMTTeF complex, but unfortunately the electron accepting strength of this exotic compound is miserable(almost comparable to that of chloro-p-benzoquinone). Reflecting these features on the conductivity of the complexes, TCNE gives a semiconductor in which CT is moderate and 2,4-bisdicyanomethylene-1,3-dithietan and DTNF give insulators with almost no CT.

This research was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

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(Received January 5, 1983)