Crystal Structure and Conducting Property of a Metallic Charge-Transfer Complex Based on a Novel Tellurophene-Extended [3]Radialene Acceptor

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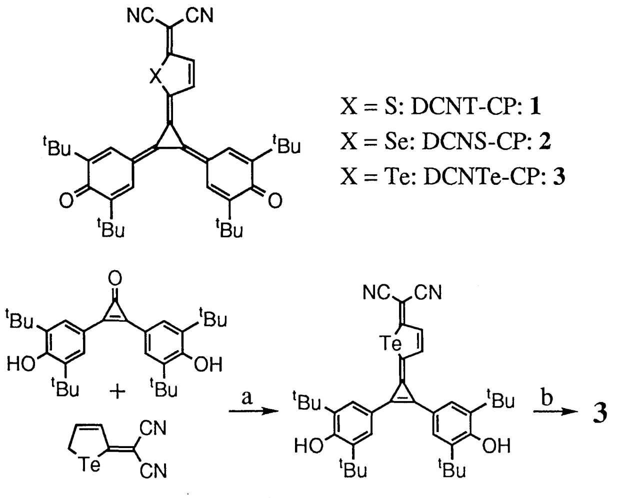
A metallic charge-transfer complex of a novel tellurophene-extended [3]radialene type acceptor with TTF was prepared. The one-dimensional metallic conduction was proved to occur through the acceptor column by X-ray crystal analysis and thermoelectric power measurement.

Although a large number of donor molecules have been prepared so far, investigations on the molecular design and synthesis of acceptor molecules for organic conductors are limited to those concerning TCNQ, DCNQI, and M(dmit)$_2$ families. Therefore, creation of novel acceptor molecules giving high conducting CT complexes or anion radical salts provides a significant impetus to the development in the field of organic conductors. We have recently synthesized new [3]radialene type electron acceptors, (**1**)[1] and (**2**)[2] and have demonstrated that single crystals of CT complexes of **2** with TTF and TTT show metallic properties with metal-to-insulator (M-I) transition temperatures of 182 and 80 K, respectively. However, the crystal structures of these complexes have not been determined so far. In continuous interest in investigation on the new metals composed of the functionally different type of organic acceptor molecules, we report now the preparation of a tellurium-containing [3]radialene acceptor DCNTe-CP (**3**), and the crystal structure and the electric property of [TTF][DCNTe-CP], proving the fact that the one-dimensional metallic conduction occurs through the column consisting of DCNTe-CP.

The new acceptor DCNTe-CP (**3**)[3] was synthesized in a fairly good overall yield by a convenient, short-step method according to the routes shown in Scheme 1.[4] The X-ray crystal structural analysis on a single crystal of DCNTe-CP (**3**) revealed that this compound is an essentially planar molecule[5] with dihedral angles between the mean planes of the neighboring two rings of 4.09—10.97 °. DCNTe-CP is quite stable and characterized as a strong electron acceptor exhibiting the first reduction potential E_1^{red} = +0.17 V *vs.* SCE in CH$_2$Cl$_2$, that is nearly identical with those of **1** (+0.20 V) and **2** (+0.19 V).



Scheme 1. a: catalytic *β*-alanine in Ac$_2$O, reflux (46%); b: K$_3$Fe(CN)$_6$/1N KOH aq in benzene, rt (quant).

Table 1. Conductivities and IR data of CT-salts of DCNTe-CP

Donor	D : A^a	$\sigma_{r.t.}{}^b$ / Scm^{-1}	$\nu_{CN}{}^c$ / cm^{-1}	$\nu_{CO}{}^c$ / cm^{-1}
TTF	1 : 1	62^d	2206	1535
TTT	1 : 1	2.9^e	2204	1539
BDTT	1 : 1	0.12^e	2187	1533

^{a}Determined by elemental analysis. ^{b}Measured by a four probe method. ^{c}Measured by FTIR using a KBr disk. ^{d}Measured on a single crystal. ^{e}Measured on a compressed pellet.

DCNTe-CP formed 1:1 CT complexes with TTF, TTT, and 2,5-bis(1,3-dithiol-2-ylidene)-2,5-dihydrothiophene (BDTT). As shown in Table 1, these complexes were proved to exist in a certain partial CT condition, since the CO and CN bands of the complexes shift to lower frequency regions than those of DCNTe-CP itself (1599 and 2208 cm^{-1}, respectively) in the IR spectra. The single crystal of [TTF][DCNTe-CP] exhibiting a room temperature conductivity of 62 Scm^{-1} was grown by cooling slowly the hot benzene solution of the 1:1 equiv. mixture of the two reactants.

The temperature dependence of the resistivity of the single crystalline [TTF][DCNTe-CP] is shown in Figure 1. It is metallic down to 175 K and the conductivity reaches maximum value of 75 Scm^{-1} at 220 K. A M-I transition occurred at 175 K. The profile of the temperature dependence of the resistivity shown in Figure 1 is analogous to that of [TTF][DCNS-CP], so

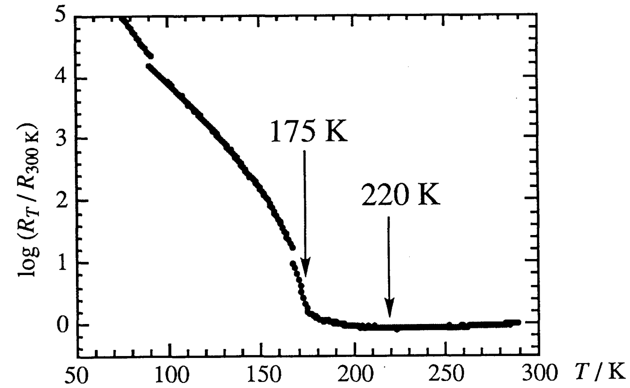


Figure 1. Temperature dependence of the resistivity of [TTF][DCNTe-CP].

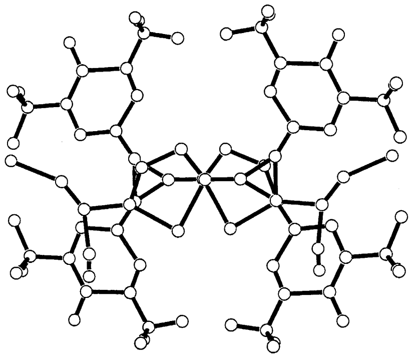


Figure 2. Overlapping mode of acceptor molecules in [TTF][DCNTe-CP].

that these two molecular metals may have similar crystal structures with each other.

The crystal structure of the metallic [TTF][DCNTe-CP] complex was determined preliminarily by X-ray crystal analysis,[6] although the full crystal structure analysis is not finally completed due to poor quality of the crystal. The donor and acceptor molecules stack in a segregated manner along the *a*-axis with a uniform interplanar distance of 3.432 Å, half of the cell constant *a* = 6.863(1) Å. The overlapping mode of the acceptor column is of so called head-to-tail type, directing the tellurium atom to the same side of the molecule (Figure 2). There exists strong intra-stack intermolecular LUMO-LUMO bonding interactions between each of the overlapping atoms because they have large π-LUMO coefficients.[2a] Although the Te---Te distance is slightly longer than those of the overlapping carbon atoms, the highly diffused *p*-orbitals of the tellurium atoms would allow a significant intra-stack Te---Te overlap. There is no inter-stack interaction because the periphery of the acceptor column is surrounded by the bulky *t*-butyl groups (Figure 3). The overlapping mode of the TTF molecules is of crisscross type with an eclipse angle of about 45°.

A definite information on the fact that the metallic conduction of [TTF][DCNTe-CP] occurs on the acceptor column is given by the measurement of the temperature dependence of the thermoelectric power, which showed a constant thermoelectric power in the high temperature region of 300 — 200 K (Figure 4) and the large negative value of –55 μVK^{-1} at room temperature. This fact indicates that the conduction carrier of the metallic [TTF][DCNTe-CP] should be electrons and this complex has a large electron correlation. Below 200 K, the absolute value of the thermoelectric power slightly decreased to around –40 μVK^{-1}, but noticeable change was not observed down to around 170 K. The metallic [TTF][DCNS-CP] also showed a negative value of –30 μVK^{-1} at room temperature. The metallic property of [TTF][DCNTe-CP] is also proved by the measurement of the magnetic susceptibility showing a Pauli paramagnetism in the temperature region of 300 — 182 K. Thus we have fully proved that the [3]radialene molecule can construct metallic conduction columns.

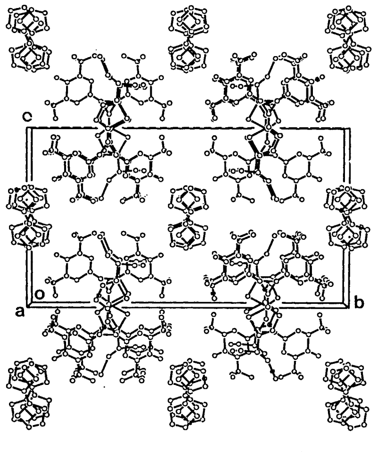


Figure 3. Crystal structure of [TTF][DCNTe-CP].

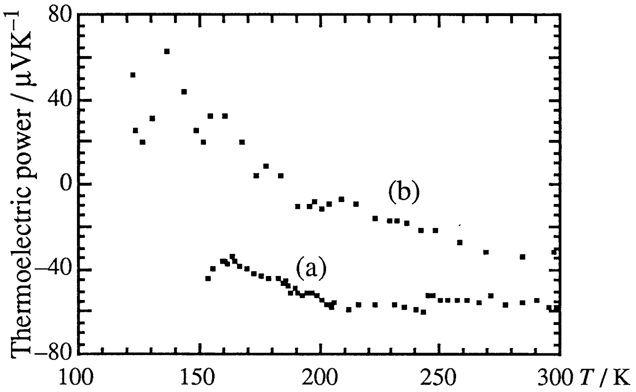


Figure 4. Temperature dependence of the thermoelectric power of (a): [TTF][DCNTe-CP]; (b): [TTF][DCNS-CP].

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References and Notes

1 K. Takahashi and S. Tarutani, *J. Chem. Soc., Chem. Commun.*, **1994**, 519.

2 a) K. Takahashi and S. Tarutani, *Adv. Mater.*, **1995**, 639; b) K. Takahashi and S. Tarutani, *Synth. Metals*, **70**, 1165 (1995).

3 Selected physical data of DCNTe-CP (**3**): dark blue plates, mp 266 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (1H, d, $J_{4''',3'''}$ = 6.25 Hz, H-4'''), 7.54 (1H, d, $J_{3''',4'''}$ = 6.25 Hz, H-3'''), 7.47 (1H, d, $J_{2'',6''}$ = 2.31 Hz, H-2"), 7.46 (1H, d, $J_{2',6'}$ = 2.31 Hz, H-2'), 7.42 (1H, d, $J_{6'',2''}$ = 2.31 Hz, H-6"), 7.04 (1H, d, $J_{6',2'}$ = 2.31 Hz, H-6'), 1.42, 1.40, 1.39, and 1.38 (each 9H, s, four *t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.7 (C-4"), 185.4 (C-4'), 171.9 (C-2'''), 137.7 (C-3'''), 151.7 (C-4'''), 118.9 (C-5'''), 131.8 (C-3), 128.1 (C-2), 126.9 (C-1), 82.0 ($\underline{C}$CNCN), 116.0 (CN), 112.7 (CN) (six-membered and *t*-butyl carbons are omitted); FTIR (KBr) ν 2952, 2208, 1599, 1506, 1456, 1363, 1090, 895 cm^{-1}; UV/vis/NIR (CH_2Cl_2) λ_{max}/nm (log ε) 845 (4.58), 749 (4.66), 422 (4.67), 321 (4.08).

4 The synthesis of 2-dicyanomethylene-2,5-dihydrotellurophene was reported: K. Takahashi and S. Tarutani, *Heterocycles*, **43**, 1927 (1996).

5 Details of the X-ray crystal analysis of DCNTe-CP (**3**) will be reported in a separate paper.

6 The single crystal of [TTF][DCNTe-CP] belongs to a orthorhombic cell, *Z* = 4, space group *C*mma, with cell dimensions *a* = 6.863(1), *b* = 33.87(1), *c* = 19.027(9) Å, *V* = 4 423(8) Å^3: *R* = 0.219 for observed 1129 reflections with *I* > 3.00σ(*I*).