A Novel Organic Conductor with Two-Dimensional Molecular Array by the “Edge-to-Edge” Donor Interaction

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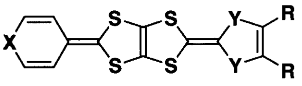
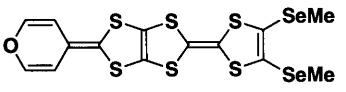
The title donor, where SM-PDT is 2-[4,5-bis(selenomethyl)-1,3-dithiol-2-ylidene]-5-(pyran-4-ylidene)-1,3,4,6-tetrathiapentalene, formed semiconducting 1:1 salts with various anions. The crystal structure analysis of (SM-PDT)$PF_6(PhCl)_x$ has revealed that an edge-to-edge chalcogen interaction gave two-dimensional sheet-like structure.

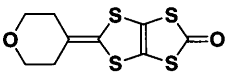
Since organic molecular components in molecular-based conductors usually have a plate-like structure and a ladder arrangement of sulfur, two directional interactions play an important role: One is π–π interaction perpendicular to molecular plane and another is chalcogen–chalcogen interaction along the transverse direction. Therefore, most organic conductors have one- or two-dimensional electronic structure. On the other hand, there are a few examples of realization of three-dimensional electronic structure in organic conducting materials.[1] In order to introduce the third directional interaction along the molecular long axis, we have recently reported synthesis and electrical properties of the cation radical salts of PDT-TTP derivatives,[2,3] which have chalcogen atoms in their edges. Among them, $(TM\text{-}TPDS)_2AsF_6$ gave three-dimensional donor array,[4] which is designated as a “windmill” arrangement, and its conductivity was metallic down to about 100 K. In order to stabilize a metallic state, substitution of sulfur with selenium atom in donor-edge is expected to realize larger overlaps between donor-edge and -side. In this letter, we report synthesis and electrochemical properties of a novel π-electron donor, 2-[4,5-bis(selenomethyl)-1,3-dithiol-2-ylidene]-5-(pyran-4-ylidene)-1,3,4,6-tetrathiapentalene (SM-PDT), which contains selenium atoms in its terminal, and crystal structure and electrical properties of its cation radical salts.



PDT-TTP : X = O, Y = S, R = H
TM-PDT : X = O, Y = S, R = SMe
TM-TPDT : X = Y = S, R = SMe
TM-TPDS : X = S,Y = Se, R = SMe



SM-PDT



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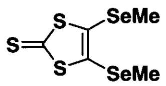

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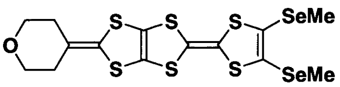

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SM-PDT was prepared according to modified procedure of synthesis of PDT-TTP derivatives.[3] Cross-coupling reaction between ketone **1**[3] and thione **2**[5] in neat triethylphosphite at 80 °C gave tetrahydro compound **3** in 37% yield. Target donor was obtained by dehydrogenation of **3** with DDQ in refluxing xylene (60%). Cyclic voltammetry revealed that SM-PDT exhibited two reversible one-electron oxidation waves and successively one irreversible two-electron one (E_1 = –0.05, E_2 = +0.22, E_3 = +0.68 V vs Fc/Fc^+, 0.1 M Bu_4NPF_6 in benzonitrile). Since TM-PDT showed similar voltammograms on the same condition (E_1 = –0.04, E_2 = +0.24, E_3 = +0.66 V vs Fc/Fc^+), the effect of substitution with selenium atoms at the thiomethyl moiety can be negligible.

Cation radical salts of SM-PDT were obtained by the electrochemical oxidation in the presence of corresponding tetrabutylammonium salts in chlorobenzene containing 5%(v/v) ethanol at room temperature (Table 1). Although TM-PDT mainly formed the 2:1 salts,[3] the compositions of the SM-PDT salts with octahedral anions were 1:1. The electrical conductivities of the SM-PDT salts are relatively high ($\sigma_{rt} = 10^0$ S cm^{-1}) at room temperature (Table 1). However, all of them showed a semiconducting behavior with an activation energy (~0.05 eV).

Crystal structure of (SM-PDT)$PF_6(PhCl)_x$ was determined by an X-ray analysis (Figure 1).[6] The PDT-TTP part is almost planar and the selenomethyl moieties are spread out nearly on the molecular plane. The donor molecules are stacked in a head-to-tail manner along the *c* axis. These donor columns are completely divided by counter anions and disordered solvents along the *a* axis. Thus, no interaction between donors was observed in the transverse direction. The donors are alternately strung along the molecular long axis, in other words, the same edge (pyran or selenomethyl moiety) faces each other (Figure 2). The short chalcogen–chalcogen contacts within the sum of the van der Waals radii were observed between selenomethyl

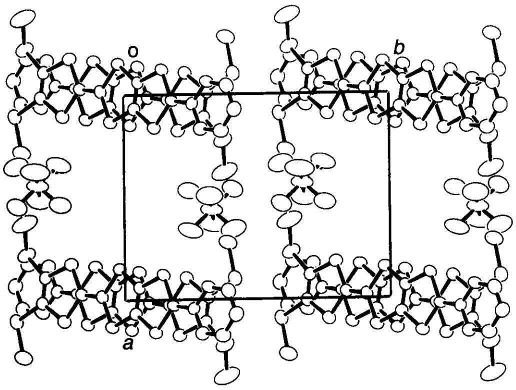

Figure 1. Crystal structure of (SM-PDT)$PF_6(PhCl)_x$ viewed along the *c* axis. Disorderd solvents are located on the cavity.

Table 1. Electrical properties of (SM-PDT)(Anion)$_m$(PhCl)$_x$

Anion	m^a	x^a	Form	σ_{rt} /S cm^{-1}	Conducting Behavior
BF_4	_^{b}	0.57(Cl)	needle	4.9	E_a = 40 meV
ClO_4	1.12(Cl)		needle	2.9	E_a = 48 meV
PF_6	1.14(P), 1.0^c	0.43(Cl), 0.33^c	needle	4.8	E_a = 50 meV
AsF_6	1.0^c	0.5^c	needle	8.3	E_a = 45 meV

^{a}Determined by energy dispersion spectroscopy (EDS) from ratio of sulfur and the element degignated in parenthesis. ^{b}The contents of light elements such as B and F could not be reliably determined by EDS. ^{c}Determined by an X-ray analysis.

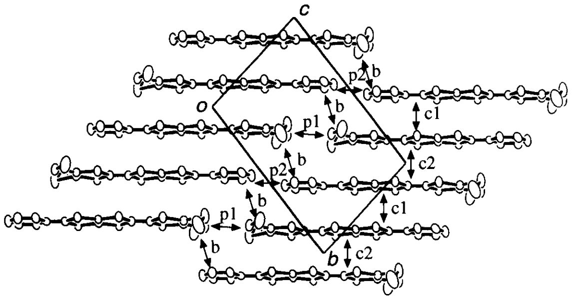

Figure 2. Donor column structure viewed along the *a* axis and definition of the overlap integrals of (SM-PDT)PF_6(PhCl)$_x$. The intermolecular overlap integrals are c1 = 6.3, c2 = 8.1, p1 = –2.3, p2 = 0.00, b = –0.8 (×10^{-3}).

moieties (Se(1)–Se(2')(–x,1–y,1–z), 3.738(2) Å; Se(2)–Se(2'), 3.694(2) Å).[7] One-dimensional donor columns are bridged by these Se···Se interactions, so that two-dimensional sheet-like structure was formed. Although there are a few examples of crystal structure of the cation radical salts based on the donors bearing selenomethyl functional groups,[8] this type of structure has never been observed and furthermore, to our knowledge, this is the first example of significant edge-to-edge chalcogen interaction among organic conductors. The Se···Se interaction between selenomethyl groups is considered to be relatively stronger in the present salt than the edge-to-side interactions through tetrathiapentalene moiety as seen in (TM-TPDS)$_2$$AsF_6$.[4] The donor molecules in the columns are weakly dimerized. As shown in Figure 3, the overlap of intra-dimer is usual ring-over-bond type with a slip of 1.42 Å. In contrast, the slip of inter-dimer is much larger (4.68 Å). The mean distances between molecular planes are 3.42 Å within a dimer and 3.41 Å between dimers. Inter-column overlap integral between selenomethyl groups is approximately one fourth as large as intra-column ones (Figure 2) and is significantly large as the longitudinal interaction. Compared with the interaction between oxygen atoms at pyran moieties, the inter-selenium interaction plays a dominant role for the formation of quasi-one-dimensional electronic structure effectively.

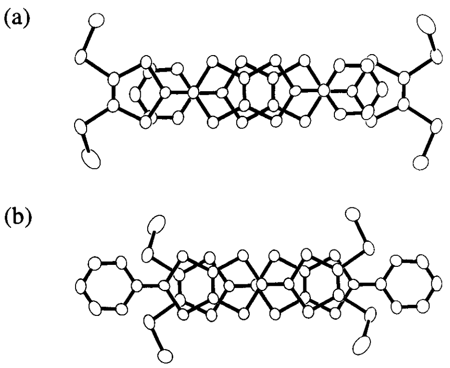

Figure 3. The overlap mode of (a) intra-dimer and (b) inter-dimer of (SM-PDT)PF_6(PhCl)$_x$.

Further investigations as well as preparation of selenium analogues replaced at the other side of molecular edge or the central tetrathiapentalene moiety are continuously in progress.

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References and Notes

1 Some examples indicating three-dimensional electronic structure in molecular-based conductor have been reported. However, in all cases the interaction between composed organic molecules and inorganic counter ions play an important role. The fact that three-dimensional electronic structure is achieved only by the interactions between pure organic molecules is unknown: S. Uji, T. Terashima, H. Aoki, J. S. Brooks, R. Kato, H. Sawa, S. Aonuma, M. Tamura, and M. Kinoshita, *Phys. Rev.*, *B*, **50**, 15597 (1994); T. Terashima, S. Uji, H. Aoki, M. Tamura, M. Kinoshita, and M. Tokumoto, *Solid State Commun.*, **91**, 595 (1994).

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6 Crystal data for (SM-PDT)PF_6(PhCl)$_x$: $C_{14}H_{10}F_6OPS_6Se_2$ FW = 689.51, triclinic, space group $P\bar{1}$, a = 10.467(2), b = 13.643(3), c = 9.161(2) Å, α = 100.53(2), β = 98.75(2), γ = 88.70(2)°, V = 1271.2(5) Å^3, Z = 2, R = 0.055, R_w = 0.060 for 2924 ($I \geq 3\sigma(I)$) observed reflections from 5857 unique data. Energy dispersion spectroscopy measurement indicated the existence of chlorobenzene and the ratio of sulfur to chlorine is 14 to 1. After determining all the atomic positions of donor and counter anion, the maximum peak was designated as chlorine. As the result of population analysis, the occupancy factor (x) was fixed to be 0.33 and the next two peaks were designated as carbon atoms. The positional parameters and isotropic temperature factors of these non-hydrogen atoms was refined, but we could not see the solvent structure as a discrete molecule owing to serious disorder.

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