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New Organic Superconductors Consisting of an Unprecedented π-Electron Donor

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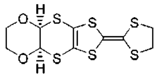
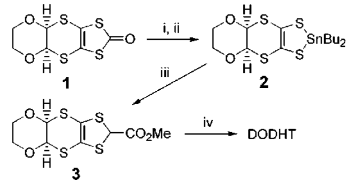
Since the discovery of superconductivity in a series of salts of TMTSF (see ref 1 for definition of abbreviations),[2] TCF derivatives have served as π-electron donors for the development of new organic superconductors.[3] Although considerable research effort in this field has focused on the construction of TCF-type donors with extended π-conjugation, these donors, except for the DTEDT donor,[4] failed to yield any organic superconductors.[5] Besides TCF derivatives, our reported BDA-TTP donor, which contains the bis-fused 1,3-dithiol-2-ylidene unit, gives superconducting salts,[6] but its π-electron system is the same as that of TCF derivatives. Then is it possible that donor molecules with a less extended π-system than that of TCF derivatives produce superconductors? We attempted to find an answer to this question in the DHTTF donor system. Our early study of this system enabled us to provide the metallic $(MDHT)_2AuI_2$ salt stable down to a very low temperature, but this salt failed to develop superconductivity.[7] Therefore, a further structural modification to the DHTTF donors examined would be required in achieving superconductivity. We thus designed a derivative of DHTTF with the appended dioxane ring by cis fusion, viz., DODHT, because we have found that the cis-fused dioxane ring, though bulky, on TTF derivatives does not necessarily break metallic electronic structures, as can be found in $(DOET)_2BF_4$ and $(DOES)_2(AuI_2)_{0.75}$.[8] Such a bulky donor containing only the 1,3-dithiol-2-ylidene unit as a π-system does not appear to hew to the conventional line of the molecular design for π-donors which are aimed at developing superconductors, hence the successful production of DODHT-based superconductors would lead to a new angle on the design of organic superconductors. Here we disclose new organic superconductors $(DODHT)_2X$ (X = AsF_6 and PF_6).



DODHT

The synthesis of DODHT was carried out as shown in Scheme 1. Conversion of the dioxane-fused ketone **1**[9] into tin dithiolate **2**, and transmetalation of **2** with *n*-BuLi (2 equiv) followed by treatment with methyl dichloroacetate gave ester **3** (74% overall yield). Reaction of **3** with bis(dimethylaluminum) 1,2-ethanedithiolate, generated from ethanedithiol and Me_3Al (2 equiv), furnished DODHT as yellow crystals in 46% yield.[10] Cyclic voltammetry of DODHT in PhCN showed two pairs of reversible redox waves at +0.64 (E_1) and +1.08 (E_2) V (vs SCE). The E_1 value is higher than that of its TTF analogue DOT[9] (+0.51 V) measured under the same conditions, and the $\Delta E(E_2 - E_1)$ value (0.44 V) is larger than that of DOT (0.33 V), indicating a decrease in the electron-donating ability and an increase in the on-site Coulombic repulsion due to a reduction in the π-system.

Scheme 1 [a]



[a] Reagents and conditions: (i) MeONa, MeOH, 0 °C, 1 h; (ii) Cl_2SnBu_2, THF, −78 °C → room temperature; (iii) *n*-BuLi (2 equiv), Cl_2CHCO_2Me, THF, −78 °C → room temperature, overnight (74% overall yield); (iv) bis(dimethylaluminum)1,2-ethanedithiolate, CH_2Cl_2, −78 °C → room temperature, overnight (46% yield).

Single crystals of the AsF_6 and PF_6 salts of DODHT were prepared by electrocrystallization at a constant current (1.0 μA) in PhCl at 25 °C, whose X-ray analyses revealed that both salts crystallize isostructurally and have the β''-type donor arrangement.[11,12] As shown in Figure 1a, the donor molecules in $(DODHT)_2AsF_6$ are stacked head-to-tail along the *b* axis. The interplanar distances (3.73 and 4.00 Å) within the stack are much longer than those in the metallic $(DOET)_2BF_4$ (3.50 and 3.77 Å) and $(DOES)_2(AuI_2)_{0.75}$ (3.47 and 3.78 Å) salts. There are several S···S contacts shorter than the sum of van der Waals radii (3.70 Å) between stacks, whereas no S···S contact is observed within the stack. This S···S contact pattern reflects the anisotropy of the intermolecular overlap integrals (Figure 1b), suggesting that the transverse interaction is superior to the interaction within the stack. Moreover, the two molecules with an interplanar distance of 4.00 Å are mutually slipped along both the molecular short and long axes, which causes the overlap integral b_2 to be almost zero. The intermolecular interaction in $(DODHT)_2AsF_6$ is much weaker compared to that in β''-$(BEDT\text{-}TTF)_2AuBr_2$;[13] that is, most of the overlap integrals in the former are smaller than the corresponding values in the latter. These structural characteristics hold also for the isostructural $(DODHT)_2PF_6$.

Figure 2 shows the four-probe dc resistivities of the AsF_6 salt ($\sigma_{300K} = 1.2$ S cm^{-1}) as a function of temperature under various pressures.[14] At ambient pressure, the resistivity of the AsF_6 salt was semiconductive with a broad shoulder around 120 K, and with increasing pressure, pronounced humps appeared at lower temperatures. At 16.5 kbar, the resistivity exhibited metallic behavior below room temperature and an abrupt drop attributable to a superconducting transition with an onset of 3.3 K. Superconductivity in this salt was confirmed by the magnetic field dependence of the

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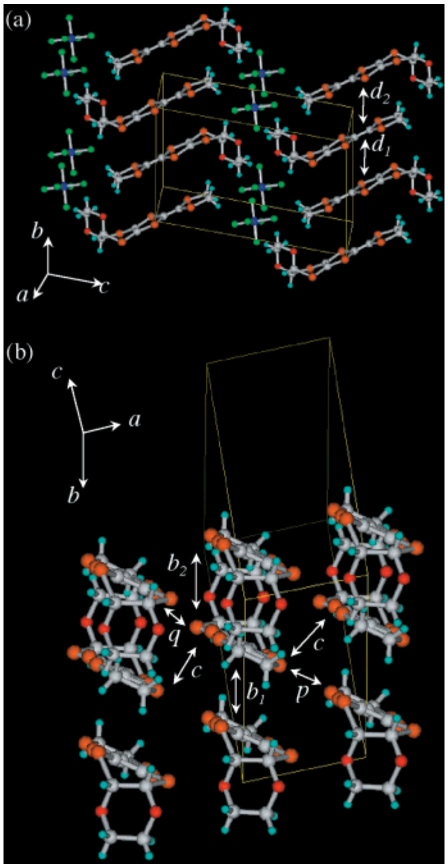

Figure 1. Crystal structure of $(DODHT)_2AsF_6$. (a) Intermolecular distances: $d_1 = 3.73$ and $d_2 = 4.00$ Å. (b) Intermolecular overlap integrals ($\times 10^{-3}$) b_1, b_2, c, p, and q are -2.81, -0.09, $-10.95-10.08$, and -6.28, respectively. Color scheme: S, orange; O, red; C, gray; H, light blue; As, blue; F, green.

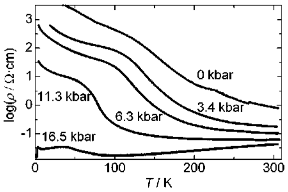

Figure 2. Temperature dependence of the resistivity for the $(DODHT)_2AsF_6$ at 0 kbar and under pressure up to 16.5 kbar.

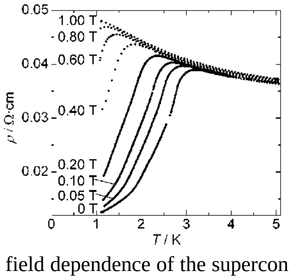

Figure 3. Magnetic field dependence of the superconducting transition of $(DODHT)_2AsF_6$ at 16.5 kbar.

drop of the resistivity measured for the AsF_6 salt at 16.5 kbar. With increasing the magnetic field, the superconducting transition of the AsF_6 salt shifted to a lower temperature, and was suppressed under 1 T (Figure 3).

Similarly to the AsF_6 salt, the PF_6 salt ($\sigma_{300K} = 0.92$ S cm^{-1}) exhibited semiconducting behavior at ambient pressure and metallic behavior at 11.3 kbar, and then underwent a superconducting transition with an onset of 3.1 K at 16.5 kbar, which disappeared under an applied magnetic field of 1 T.

In conclusion, we accomplished the synthesis of the DODHT donor with a reduced π-system as well as a bulky substituent, and demonstrated that this donor produces two superconductors, $(DODHT)_2X$ (X = AsF_6 and PF_6), which display a variety of the pressure-induced resistive behavior. It is an important subject of continued interest to reveal how structural change is brought about by applied pressures.

Supporting Information Available: Figures for the crystal structure, the resistive behavior, and the magnetic field dependence of the resistivity of $(DODHT)_2PF_6$; tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for $(DODHT)_2X$ (X = AsF_6 and PF_6) (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) TMTSF, tetramethyltetraselenafulvalene; TCF, tetrachalcogenafulvalene; DTEDT, 2-(1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylineneethylidene)-1,3,4,6-tetrathiapentalene; BDA-TTP, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene; DHTTF, dihydrotetrathiafulvalene; MDHT, methylenedithio(dihydro)tetrathiafulvalene; DODHT, (1,4-dioxane-2,3-diyldithio)dihydrotetrathiafulvalene; DOET, (1,4-dioxane-2,3-diyldithio)-ethylenedithiotetrathiafulvalene; DOES, (1,4-dioxane-2,3-diyldithio)-ethylenediselenotetrathiafulvalene; TTF, tetrathiafulvalene; DOT, (1,4-dioxane-2,3-diyldithio)tetrathiafulvalene; BEDT-TTF, bis(ethlylenedithio)-tetrathiafulvalene.

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(10) DODHT: mp 171−172 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38−3.51 (m, 4 H), 3.65−3.69 (m, 2 H), 4.03−4.08 (m, 2 H), 5.38 (s, 2 H); MS, *m*/*z* 354 (M$^+$). Anal. Calcd for $C_{10}H_{10}O_2S_6$: C, 33.87; H, 2.76. Found: C, 33.76 H, 2.84.

(11) Crystallographic data. $(DODHT)_2AsF_6$: $C_{20}H_{20}S_{12}O_4AsF_6$, FW = 898.00, triclinic, space group $P1$, $a = 5.7518(5)$ Å, $b = 9.4285(8)$ Å, $c = 15.8745(14)$ Å, $\alpha = 101.720(2)°$, $\beta = 98.150(2)°$, $\gamma = 107.282(2)°$, $V = 785.85(12)$ Å^3, $Z = 1$, $D_c = 1.898$ g cm^{-3}, $\mu = 1.95$ mm^{-1}, $R = 0.0450$, $R_w = 0.0987$, GOF = 0.812. $(DODHT)_2PF_6$: $C_{20}H_{20}S_{12}O_4PF_6$, FW = 854.05, triclinic, space group $P1$, $a = 5.7808(10)$ Å, $b = 9.2199(16)$ Å, $c = 15.784(3)$ Å, $\alpha = 101.222(3)°$, $\beta = 98.469(3)°$, $\gamma = 107.271(3)°$, $V = 768.9(2)$ Å^3, $Z = 1$, $D_c = 1.845$ g cm^{-3}, $\mu = 0.97$ mm^{-1}, $R = 0.0379$, $R_w = 0.1120$, GOF = 1.111.

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(14) The measurement under hydrostatic pressure was carried out using a clamped cell and Daphne 7373 oil (Idemitsu Co. Ltd.) as a pressure medium. The value of the pressure quoted here corresponds to that of the clamped pressure at room temperature.

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