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Novel Bis-fused π-Electron Donor Composed of Tetrathiafulvalene and Tetraselenafulvalene

Minoru Ashizawa,[1,2] Ken-ichi Ishidzu,[1] Masaki Watanabe,[1] Tetsuhiko Tanahashi,[1]
Takashi Shirahata,[1] Tadashi Kawamoto,[2] Takehiko Mori,[2] and Yohji Misaki*[1]
[1]*Department of Applied Chemistry, Graduate School of Science and Engineering, Ehime University,*
3 Bunkyo-cho, Matsuyama, Ehime 790-8577
[2]*Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,*
Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552

(Received June 28, 2010; CL-100589; E-mail: misaki.yohji@eng.ehime-u.ac.jp)

A new donor (ST-STP), in which tetrathiafulvalene and tetraselenafulvalene are fused, has been synthesized. This donor shows unexpectedly large on-site Coulomb repulsion compared with other bis-fused TTF systems. In (ST-STP)ReO_4, *intramolecular* charge disproportionation is suggested by the crystal structure and transport properties.

Bis-fused tetrathiafulvalene (TTF), 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) (Chart 1) has produced a large number of metallic charge-transfer salts stable down to low temperatures.[1] However, BDT-TTP and its derivatives have not produced superconductors except for the vinyl analog 2-bis(1,3-dithiol-2-ylidene)-5-(2-ethandiylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene (DTEDT).[2,3] Recent efforts to design molecular superconductors[4] have been devoted to reducing the π-framework for increasing the on-site Coulomb repulsion U and decreasing the band width W based on the prediction of the Kanoda diagram.[5] In contrast, the metallic state of most BDT-TTP conductors is excessively stabilized by reduced U at the $3/4$ band filling state as well as the large bandwidth. On the basis of these aspects, we have attempted chemical tuning of BDT-TTP conductors. For examples, increase of U can be achieved by full oxidation of the donor molecule, and BDT-TTP type conductors can keep high conductivity even in the fully oxidized state.[6,7] On the other hand, selenium replacement of sulfur atoms of the donor molecule, especially of the central TTP core, is effective to increase the bandwidth. To date, selenium replacement of two outer 1,3-dithiole rings has been performed,[8,9] but very few has been attempted for the central TTP core.[9,10] For the systematic investigations of selenium substitution effects on BDT-TTP derivatives, we herein report synthesis, structures, and properties of a bis-fused TTF molecule composed of TTF and tetraselenafulvalene (TSF), 2-(1,3-diselenol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene (ST-STP), and its radical cation salt, (ST-STP)ReO_4.

ST-STP was synthesized according to Scheme 1. A TSF derivative **1**[11] was reacted with $CsOH\cdot H_2O$, followed by treatment with $ZnCl_2$, n-Bu_4NBr, and triphosgen to provide **2** in 40% yield. A cross-coupling reaction between **2** and two equiv of 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**3**) mediated by trimethylphosphite in refluxing toluene gave the bis(methoxycarbonyl) derivative of ST-STP **4** in 79% yield on the basis of **2**. ST-STP was obtained in 49% yield by demethoxycarbonylation of **4** with an excess of $LiBr\cdot H_2O$ in hexamethylphosphoric triamide (HMPA).[12]

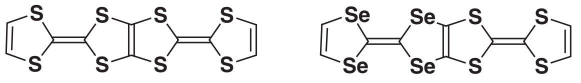
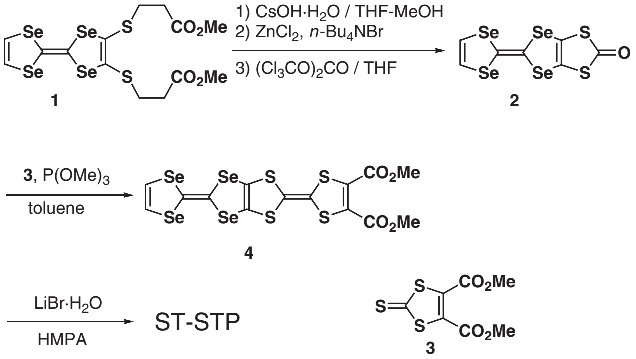

BDT-TTP ST-STP

Chart 1.



Scheme 1.

ST-STP exhibits four pairs of reversible one-electron redox waves at 0.00, 0.30, 0.56, and 0.74 V (V vs. Fc/Fc^+, in PhCN) corresponding to the four redox-active 1,3-dichalcogenole rings. The first redox potential of ST-STP (0.00 V) is almost the same as that of BDT-TTP (−0.01 V) under the identical conditions. In contrast, the second redox potential of ST-STP (0.30 V) is higher by 0.08 V than that of BDT-TTP (0.22 V). Considering TTF is a stronger donor than TSF, a positive charge formed by the first one-electron oxidation of ST-STP is expected to be mainly located on the TTF moiety, while the TSF moiety mainly contributes to the second oxidation. Consequently, $\Delta E = E_2 - E_1 = 0.30$ V of ST-STP, an electrochemical estimation of U, is considerably larger than that of BDT-TTP (0.23 V), and more close to that of BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene, 0.36 V]. This result indicates that fusion of TTF and TSF units is useful to increase U in the TTP-type conductors.

A single crystal of ST-STP suitable for X-ray diffraction analysis was grown by recrystallization from a CS_2–hexane solution. ST-STP crystallized in the monoclinic system with the space group $P2_1/a$, whose crystal structure is analogous to the neutral crystal of BDT-TTP.[2a,13] A whole molecule is crystallographically independent and located on a general position. The TTF and TSF parts are randomly distributed so that all chalcogen atoms are disordered. Attempts to solve the structure with a noncentrosymmetric space group are not successful. The molecule has a bent shape similar to the neutral state of BDT-TTP (Figure 1).

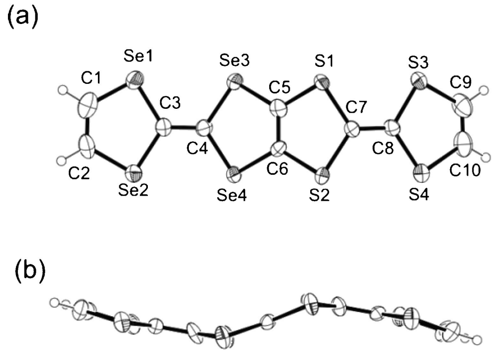


Figure 1. (a) Molecular structure of ST-STP and (b) the side view.

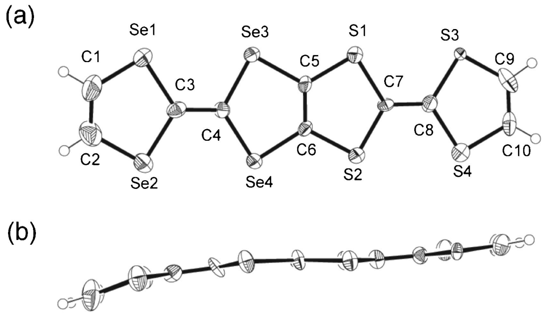


Figure 2. (a) Molecular structure of ST-STP in (ST-STP)-ReO_4, and (b) the side view.

Single crystals of (ST-STP)ReO_4 were grown by an electrochemical oxidation technique, and X-ray diffraction analysis was carried out.[14] The space group of (ST-STP)ReO_4 is $P2_1/c$. One donor molecule and one anion are crystallographically independent, and both the ST-STP molecule and the ReO_4^- anion are located on general positions. There is no positional disorder concerning the chalcogen atoms in contrast with the neutral ST-STP and the other known diselenadithiapentalene conductors, in which the chalcogen atoms are usually disordered.[10] Surprisingly, the TSF moiety adopts a boat-like conformation with dihedral angles of 10.1 and 16.4° with respect to the C3–C4 bond of the TSF moiety, while the TTF moiety is almost planar (Figure 2). This conformational difference between the TSF and TTF parts implies one positive charge on the ST-STP molecules disproportionately distribute on both the TTF and TSF parts. Namely, TTF moiety has more positive charge of $+(0.5 + \delta)$ while TSF one is less positive of $+(0.5 - \delta)$. The bond lengths are unfortunately not accurate enough to prove this assumption. The ST-STP molecules form a dimerized face-to-face π-stack along the a axis with interplanar distances of 3.33 and 3.62 Å. The π-stacks are arranged in a herring bone fashion in the bc plane (Figure 3a). The packing pattern of the donors is so-called β-type as shown in Figure 3b.[15] The donors show the overlapping pattern of a head-to-tail manner in the stack, indicating TTF and TSF moieties are effectively overlapped with each other. As a consequence, the positive charges are alternately arranged.

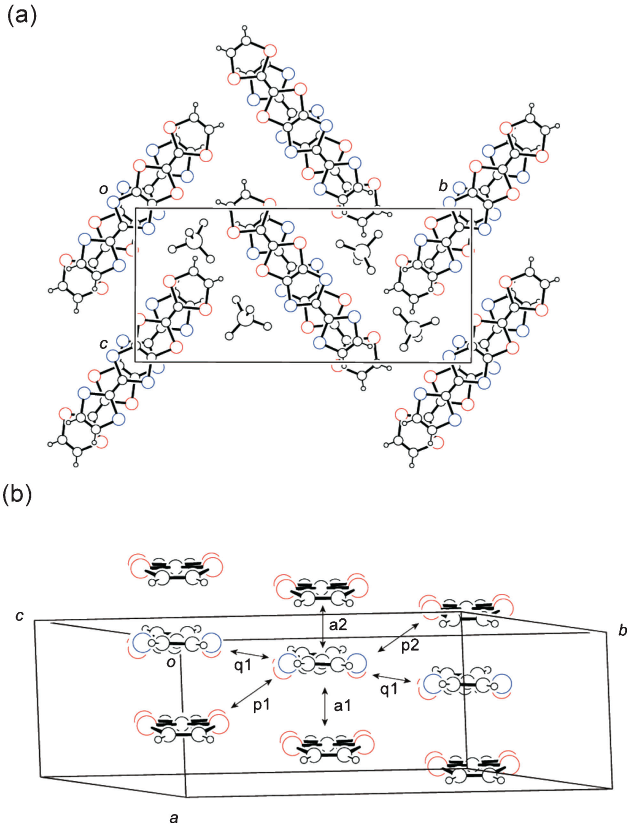


Figure 3. (a) Crystal structure of ST-STP in (ST-STP)ReO_4 viewed onto the bc plane and (b) donor sheet structure viewed along the donor long axis. The calculated overlap integrals are $a1 = 28.5$, $a2 = 35.9$, $p1 = 0.9$, $p2 = 4.1$, and $q1 = 2.4 \times 10^{-3}$.

The calculation of overlap integrals was carried out by using the HOMO estimated on the basis of the conventional extended Hückel method.[16–18] The largest interstack overlap ($p2$) is only 11% as large as that of the larger intrastack one ($a2$) owing to the large slip along the donor long axis. As a result, this system is highly one dimensional. A tight-binding calculation suggests this salt is a band insulator owing to the dimerized stack. (ST-STP)ReO_4 exhibits semiconductive behavior with low conductivity ($\sigma_{rt} = 7.7 \times 10^{-3}\,S\,cm^{-1}$ and $E_a = 0.14\,eV$). By contrast, (TTM-TTP)AuI_2, where TTM-TTP is tetrakis(methylthio)-TTP, exhibits comparatively high conductivity ($\sigma_{rt} = 10\,S\,cm^{-1}$ and $E_a = 0.03\,eV$) in spite of the energy gap originating from the dimerized stack similar to the present compound.[7] The high conductivity of (TTM-TTP)AuI_2 was understood as a result of the delocalization of HOMO over the whole molecule to reduce the band gap. Assuming the HOMO of ST-STP to be distributed over the whole molecule, (ST-STP)ReO_4 is expected to be more conductive, but (ST-STP)ReO_4 shows low conductivity with large activation energy. This discrepancy is best understood by concerning the *intramolecular* charge disproportionation considering the results of X-ray structure analysis.[9] Theoretical molecular orbital calculation of SOMO of ST-STP$^{+\bullet}$ would also imply this charge disproportionation.[18] Although intramolecular charge separation has been proposed in the low-temperature insulating phase of (TTM-TTP)I_3,[19] such charge separation as is obvious from the room-temperature molecular structure is the first observation.

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12 ST-STP: brown solid; mp 219–221 °C (dec); ^{1}H NMR (C_6D_6): δ 7.08 (d, 2H), 6.16 (d, 2H); MS (EI, m/z): 402 (M^+); Anal. Calcd for $C_{10}H_4S_4Se_4$: C, 21.14; H, 0.71%. Found: C, 21.37; H, 0.99%.

13 Crystal data of ST-STP: monoclinic, space group $P2_1/a$, $a = 12.813(2)$, $b = 9.255(2)$, $c = 12.277(3)$ Å, $\beta = 97.79(2)°$, $V = 1442.5(5)$ Å^3, $Z = 4$, $R = 0.0592$, $R_w = 0.0637$ for observed 2107 reflections ($I > 2\sigma(I)$). Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 789688.

14 Crystal data of (ST-STP)ReO_4: monoclinic, space group $P2_1/c$, $a = 6.9891(8)$, $b = 23.237(3)$, $c = 10.8494(11)$ Å, $\beta = 97.2809(9)°$, $V = 1747.8(4)$ Å^3, $Z = 4$, $R = 0.0938$, $R_w = 0.2682$ for observed 4726 reflections ($I > 2\sigma(I)$). Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 789689.

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