Novel Sulfur–Selenium Exchange in Ethylenedioxy- and Ethylenedithio-dithiadiselenafulvalenedithiolates

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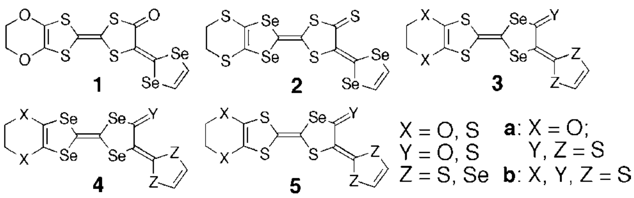
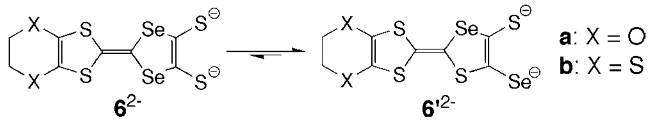
Ethylenedioxy- and ethylenedithiodithiadiselenafulvalenedithiolates are subjected to sulfur–selenium exchange, in which one selenium atom in the molecular skeleton is replaced by an outside sulfur atom. The reaction of the exchanged dithiolates with 2-methylthio-1,3-dithiolylium ion gives the corresponding thioquinone-1,3-dithiolemethides as new donor molecules.

Tetrathiafulvalene (TTF) and its derivatives still continue to play a crucial role in the generation of molecular metals and superconductors and also magnetic molecular conductors.[1] Molecular metals and superconductors endowed with antiferromagnetic or ferromagnetic ordering are already generated by use of charge-transfer (CT) salts between bis(ethylenedithio)-TTF or bis(ethylenedithio)tetraselenafulvalene (BETS) and magnetic anions with d spins.[2–6] However, the interactions between the conducting π electrons on the donor columns and the localized d spins of the counter anions are very weak in the CT salts other than λ-(BETS)$_2$•FeCl$_4$,[3] which possesses such a comparatively strong π–d interaction as to display a metal–insulator transition and a magnetic field-induced superconductivity. Very recently, we observed comparatively strong π–d interactions and high antiferromagnetic ordering temperatures increased up to 4.5 K in antiferromagnetic molecular metals based on the CT salts of two bent donor molecules, ethylenedioxytetrathiafulvalenoquinone-1,3-diselenolemethide (**1**)[7] and ethylenedithiodiselenadithiafulvalenothioquinone-1,3-diselenolemethide (**2**) with FeBr$_4^-$ ion (Scheme 1).[8]



Scheme 1. New bent donor molecules.

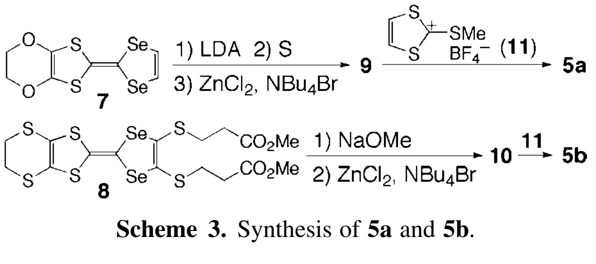
Our target is to prepare ferromagnetic molecular metals and semiconductors, which could be used as key parts in a molecular-based spin field-effect transistor.[9] To this end we noticed new bent donor molecules, ethylenedioxy- and ethylenedithiodithiadiselenafulvalenoquinone(-thioquinone)-1,3-dithiole(-diselenole)methides **3** and their tetraselenafulvaleno derivatives **4**. During the preparation of ethylenedioxy- and ethylenedithiothioquinone-1,3-dithiolemethides of **3a** (X = O; Y, Z = S) and **3b** (X, Y, Z = S), we found out that ethylenedioxy- and ethylenedithiodithiadiselenafulvalenedithiolates **6a**$^{2-}$ (X = O) and **6b**$^{2-}$ (X = S) were converted to the corresponding isomers **6′a**$^{2-}$ and **6′b**$^{2-}$ via sulfur–selenium exchange (Scheme 2), which gave such bent donor molecules **5a** and **5b** that one selenium atom in the molecular skeleton was replaced by an outside sulfur atom.



Scheme 2. Sulfur–selenium exchange between **6**$^{2-}$ and **6′**$^{2-}$.

Ethylenedioxydithiadiselenafulvalene (**7**) was treated with LDA (2.1 equiv) in dry THF at −78 °C, followed by the addition of sulfur (2.0 equiv) and then of ZnCl$_2$ (1.0 equiv) and NBu$_4$Br (2.0 equiv) at rt (Scheme 3). On the other hand, after ethylenedithiodicarbomethoxyethylthiodithiadiselenafulvalene (**8**) was reacted with NaOMe (2.1 equiv) in THF/MeOH (10:1, v/v) at rt, ZnCl$_2$ (1.0 equiv) and NBu$_4$Br (2.0 equiv) were added. The bis(NBu$_4^+$) salts of bis(ethylenedioxy)dithiadiselenafulvalenedithiolato) and bis(ethylenedithio)dithiadiselenafulvalenedithiolato)zinc complex dianions **9** and **10** were precipitated, and the salts were reacted with 2-methylthio-1,3-dithiolylium tetrafluoroborate (**11**) in DMF to give black solids in overall yields of 30% and 15%, respectively.[10] The mass spectra of the solids did not show molecular ion peaks due to **3a** and **3b** at all, and instead the peaks due to **5a** and **5b** were observed at 442 and 474, which are not molecular weights of **3a** and **3b** as expected, but those of **5a** and **5b**. In order to confirm molecular structures of **5a** and **5b** numerous attempts were made to get single crystals suitable for the X-ray structure analyses. Unfortunately, it has not yet been successful. Since **5a** and **5b** have electron-donating abilities ($E^1 = 0.60$ and 0.66 V and $E^2 = 0.90$ and 0.93 V vs. Ag/AgCl) comparable to those of **1** and **2**, they were subjected to electrochemical oxidation with a constant current of 0.2 µA in PhCl/EtOH (9:1, v/v) containing a supporting electrolyte of NBu$_4$FeCl$_4$ or NBu$_4$FeBr$_4$ at 35–45 °C, and after a few weeks black-colored single crystals were sticked on the surface of the Pt electrode used.

The crystal structure analyses showed that the crystals have 1:1 compositions of **5a** molecule and FeCl$_4^-$ ion, and of **5b** molecule and FeBr$_4^-$ ion, respectively.[11] The molecular



Scheme 3. Synthesis of **5a** and **5b**.

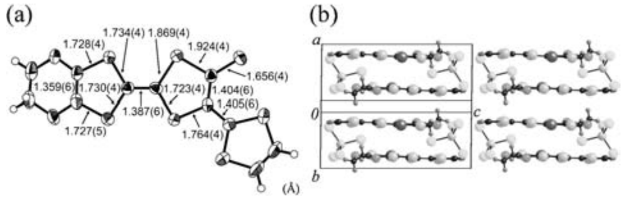
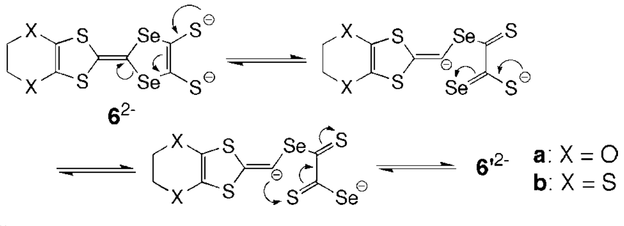


Figure 1. (a) Molecular structure of **5a** in **5a**•$FeCl_4$ and (b) crystal structure of **5a**•$FeCl_4$.

structure of **5a** in **5a**•$FeCl_4$ is shown in Figure 1a. Obviously, in the **5a** (and also **5b**) molecule only the selenium atom located near the 1,3-dithiole ring is replaced by a sulfur atom, as evidenced by the shorter C–S bond distances of 1.72–1.76 Å compared with the C–Se bond distances of 1.87–1.92 Å. In addition, the five-membered ring including one sulfur atom and one selenium atom is largely distorted compared with the five-membered ring including two sulfur atoms. On the other hand, Figure 1b shows the crystal structure of **5a**•$FeCl_4$, which resembles that of **5b**•$FeBr_4$.[16] The crystals are composed of an alternate arrangement of donor layers and $FeCl_4^-$ or $FeBr_4^-$ ion layers. In each of the donor layers the neighboring donor molecules are parallel to each other for **5a**•$FeCl_4$, while inclined to each other by 38° for **5b**•$FeBr_4$.[16] In each of the donor columns the donor molecules form a tight dimer with an interplanar distance (3.42 Å) comparable with π-cloud thickness (3.40 Å).[12] The interdimer distances are 3.64–3.69 Å. The $FeCl_4^-$ or $FeBr_4^-$ ions are located near the **5a** or **5b** molecules. As expected from the crystal structures the electrical conductivities at room temperature were very low (ca. $10^{-5}\,S\,cm^{-1}$) for both the crystals.

A plausible reaction mechanism is shown in Scheme 4. Thus, one C–Se bond of $\mathbf{6a}^{2-}$ ($\mathbf{6b}^{2-}$) in the side opposite to the formation of a C=S group is cleaved to produce a vinylidene anion, which preferentially attacks the S atom of a $(S{=}C{-}Se)^-$ group and gives $\mathbf{6'a}^{2-}$ ($\mathbf{6'b}^{2-}$) by a ring closure. The driving force of this S–Se exchange is due to the difference in the thermodynamic stability between $\mathbf{6a}^{2-}$ ($\mathbf{6b}^{2-}$) and $\mathbf{6'a}^{2-}$ ($\mathbf{6'b}^{2-}$), in which the latter dianion is more stable than the former dianion. Under the same reaction condition, an ethylenedithiotetrathiafulvalenediselenolate was not subjected to the S–Se exchange even at room temperature. A similar S–Se exchange has been recognized in the conversion of 1,3-diselenole-2-thione to 1,3-thiaselenole-2-selenone in the mono- and dianion states.[13–15] The reverse reaction of 1,3-thiaselenole-2-selenone to 1,3-diselenole-2-thione also did not proceed. It is probable that the following reaction of $\mathbf{6'a}^{2-}$ ($\mathbf{6'b}^{2-}$) with 2-methylthio-1,3-dithiolylium ion to give **5a** (**5b**) occurs in the following scheme. Thus, the C atom at the 2-position of the 1,3-dithiolylium ion preferentially attacks the C atom attached to the Se atom of $\mathbf{6'a}^{2-}$ ($\mathbf{6'b}^{2-}$), and **5a** (**5b**) is obtained through the formation of an episelenide intermediate and the following extrusion of S atom.



Scheme 4. A plausible reaction mechanism in the sulfur–selenium exchange between $\mathbf{6}^{2-}$ and $\mathbf{6'}^{2-}$.

The **5a** and **5b** molecules accidentally obtained in this study have a distorted and bent molecular skeleton in contrast to the previous bent donor molecules, so that in their CT salts with magnetic FeX_4^- (X = Cl and Br) ions the donor molecules and the FeX_4^- ions might have such a desirable arrangement with each other as to achieve our proposed ferromagnetic interactions between the metallic or semiconducting π electrons on the donor columns and the localized d spins of the FeX_4^- ions. We are now under investigation of the preparation of their CT salts with the other molecular compositions.

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11 Crystal data for **5a**•$FeCl_4$: $C_{11}H_6O_2S_6SeFeCl_4$, $M_r = 639.15$, triclinic, $P\bar{1}$, $a = 7.4517(6)$, $b = 9.3293(9)$, $c = 15.7297(12)$ Å, $\alpha = 92.998(2)$, $\beta = 90.3246(19)$, $\gamma = 108.953(3)°$, $V = 1032.52(15)$ Å^3, $\mu = 36.207\,cm^{-1}$, $Z = 2$, $D_{calcd} = 2.056\,g\,cm^{-3}$, 10172 reflections measured, 4672 unique ($R_{int} = 0.054$). Final R indices [$I > 3\sigma(I)$]: $R1 = 0.044$, $wR2 = 0.049$. Crystal data for **5b**•$FeBr_4$.[16] $C_{11}H_6S_8SeFeBr_4$, $M_r = 849.07$, monoclinic, $P2_1/c$, $a = 15.457(7)$, $b = 7.525(4)$, $c = 19.239(9)$ Å, $\beta = 92.1680(17)°$, $V = 2236.0(18)$ Å^3, $\mu = 102.154\,cm^{-1}$, $Z = 4$, $D_{calcd} = 2.522\,g\,cm^{-3}$, 21948 reflections measured, 5104 unique ($R_{int} = 0.161$). Final R indices [$I > 3\sigma(I)$]: $R1 = 0.083$, $wR2 = 0.074$.

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