Bis(thioxo-diethylthiotetrathiafulvalenyl)ylidene, a New Donor Molecule with High Electron-Donating Ability Comparable to Tetrathiafulvalene

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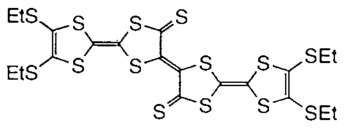
A new donor molecule, bis(thioxo-diethylthiotetrathiafulvalenyl)ylidene (**1**) was obtained by the iodine oxidation of bis(tetraethylammonium) bis(2,3-diethylthiotetrathiafulvalenyl-6, 7-dithiolato) zinc complex (**3**). The molecular skeleton of **1** except for the four ethyl groups is almost planar and significant intramolecular S-S contact is present. The redox process of **1** is composed of four electron-transfer steps, of which the first step has almost the same redox potential (+0.40 V vs. Ag/AgCl) to that of tetrakis(ethylthio)tetrathiafulvalene (TET-TTF). Very interestingly, **1** exhibited longest-wavelength electronic absorptions near 1100 nm.

Current interest is directed toward the synthesis and characterization of π/d molecular systems, in which conducting π electron and localized d spin coexist and interact significantly with each other.[1] The novel electrical conducting and magnetic properties are expected to emerge from the π/d molecular systems. A number of π/d molecular systems have so far been synthesized, most of which have, however, little interaction between both the electrons, except for [bis(ethylenedithio)tetrathiafulvalene]$_3$ • CuBr$_4$/CuCl$_2$Br$_2$,[2] [bis(ethylenedithio)tetraselenafulvalene]$_2$ • FeCl$_4$[3] and (dimethyldicyanoquinodiimine)$_2$ • Cu.[4] Under the circumstances new donor or acceptor molecules are now necessary, which can interact effectively with magnetic metal atoms. Very recently, we succeeded in the synthesis of such a new donor molecule, dimethylthiotetrathiafulvalenothioquinone-1,3-dithiolemethide (**2**) and investigated electrical conducting and magnetic properties of **2**•CuBr$_2$ complex.[5] In this communication we report the synthesis, molecular structure, and novel redox and electronic absorption properties of **1**, another donor molecule, which exhibits high electron-donating ability comparable to TET-TTF and is expected to capture several magnetic metal halides.



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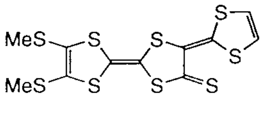

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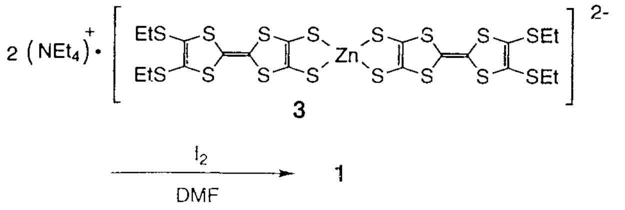
As is shown in Scheme 1, **1** was obtained by the reaction of **3**[6] with 2 equiv. of iodine in DMF at room temperature under argon. The crude product was recrystallized from CS$_2$/*iso*-PrOH to give black crystals (m.p. 190-192 °C) of **1** in 63% yield.[7] The X-ray structure analysis was successfully performed.[8] Figure 1 shows the molecular structure, in which the molecular skeleton except for four ethyl groups is almost planar as a result of tight intramolecular contact between the thiocarbonyl and 1,3-dithiolane sulfur atoms (2.84 Å, a markedly shorter distance than twice of van der Waals radius of sulfur atom (3.70 Å)).[9] The average of C=S bond distances (1.63 and 1.67 Å) is close to that of **2**



Scheme 1

(1.66 Å), and the central C=C bond (1.42 Å) has a similar distance to that of benzene (1.39 Å)[10], suggesting that there is very small contribution of a polar structure to the ground state of **1**. The following mechanism is most plausible as a formation of **1**. Thus, two 2,3-diethylthiotetrathiafulvalenyldithiolates in **3** are at first one-electron oxidized to produce the corresponding radical anions. The coupling of radical anions at the carbon atoms produces a dithiolate, which is converted to a disulfide by the second one-electron oxidation, followed by the elimination of two sulfur atoms to afford the final product.

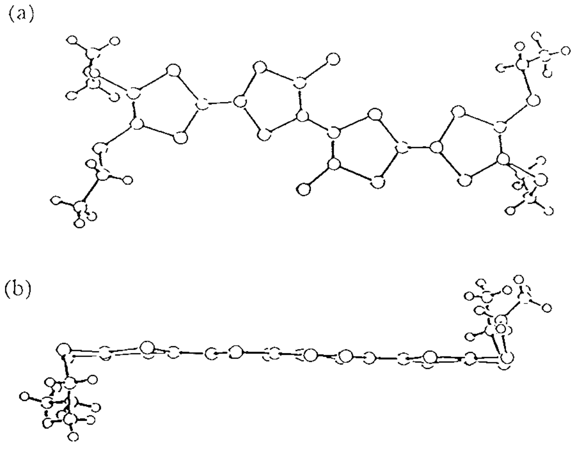


Figure 1. The molecular structure of **1**: (a) top and (b) side views.

The cyclic voltammetry measurement was performed for **1** and a reference compound, TET-TTF. The cyclic voltammogram (CV) of **1** measured in CH$_2$Cl$_2$ containing a supporting electrolyte, (n-Bu)$_4$NPF$_6$ at 0 °C showed four pairs of reversible redox waves at +0.40, +0.53, +0.88 and +1.01 V vs. Ag/AgCl. The four-step redox process can be reasonably understood as a sequential electron-transfer of $\mathbf{1} \rightleftarrows \mathbf{1}^{+\bullet} \rightleftarrows \mathbf{1}^{2+} \rightleftarrows \mathbf{1}^{3+\bullet} \rightleftarrows \mathbf{1}^{4+}$ ($\mathbf{1}^{+\bullet}$, $\mathbf{1}^{2+}$, $\mathbf{1}^{3+\bullet}$ and $\mathbf{1}^{4+}$ are radical cation, dication, radical

Table 1. Redox potentials[a] of **1**, **2** and **TET-TTF**

Donor	E^1	E^2	E^3	E^4
1[b]	+ 0.40	+ 0.53	+ 0.88	+1.01
2[c]	+ 0.61	+ 0.77		
TET-TTF[b]	+ 0.45	+ 0.78		

[a] V vs. Ag/AgCl. [b] Measured in CH_2Cl_2 at 0 ℃. [c] Measured in DMF at 0 ℃.

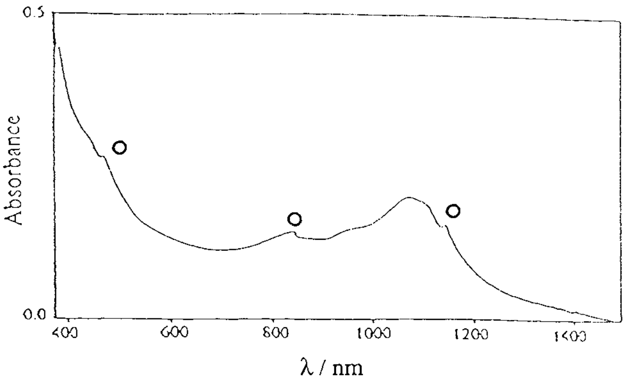
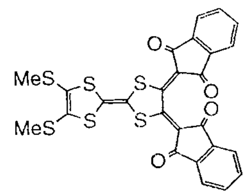


Figure 2. The electronic absorption spectrum of **1** (3.00×10^{-5} mol•dm^{-3}) in CH_2Cl_2: (o) denotes abberation in absorbance by the mirror change.

trication and tetracation of **1**, respectively). Under the same condition the CV of TET-TTF was also measured and two pairs of reversible redox waves due to the electron-transfer of TET-TTF $\leftrightarrows$ TET-TTF$^{+\bullet}$ $\leftrightarrows$ TET-TTF^{2+} (TET-TTF$^{+\bullet}$ and TET-TTF^{2+} are radical cation and dication of TET-TTF, respectively) appeared at +0.45 and +0.78 V. Table 1 summarizes the redox potentials (E's) of **1**, TET-TTF and **2**. From comparison of the first redox potentials (E^1's) between the three donors, the electron-donating ability of **1** is fairly higher than that of **2** and comparable to that of TET-TTF. Furthermore, very low second redox potential (E^2) of **1** as compared to that of TET-TTF suggests markedly decreased Coulomb repulsion between two positive charges residing in $\mathbf{1}^{2+}$.

Very interestingly, the longest-wavelength absorptions of **1** reached a near-infrared region (> 800 nm). The electronic absorption spectrum of **1** measured in CH_2Cl_2 is shown in Figure 2. In the near-infrared region three absorption maxima were observed at 956 ($\varepsilon_{max} = 4.07 \times 10^3$), 1084 ($6.55 \times 10^3$) and 1118 nm ($6.03 \times 10^3$), respectively. On the other hand, in the visible region of 400 to 800 nm there was no absorption maximum except for a shoulder absorption ($\varepsilon_{max} = 9.54 \times 10^3$) at 454 nm. We previously found out the similar phenomenon in a tetrathiafulvalenoquinodimethane derivative (**4**), whose longest-wavelength electronic absorption ($\varepsilon_{max} = 1.43 \times 10^4$) appeared at 850 nm.[11] Accordingly, the longest-wavelength electronic absorption of **1** is furthermore shifted by ca. 300 nm to the longer near-infrared region than that of **4**.



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In summary, **1** is promising as a reliable donor molecule for a new type of π/d molecular system and also as a purely organic near-infrared light-absorption material.[12] We are now investigating the possibilities as above.

References and Notes

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7 The satisfactory elemental analysis result was obtained. The new donor is very soluble in CS_2, and sparingly soluble in CH_2Cl_2, $CHCl_3$ and THF.

8 Crystal data for **1**: $C_{20}H_{20}S_{14}$, M =709.22, triclinic, space group $P\bar{1}$, a = 8.405(1), b = 17.604(3), c = 5.1846(9) Å, α = 97.64(2), β = 105.73(1), γ = 82.20(1)°, Z = 1, V = 727.8(2) Å^3, Dc = 1.618 g/cm^3. R = 0.057 and Rw = 0.075 for 1601 observed reflections with $I > 2\sigma(I)$. The measurements were made by Rigaku AFC7R diffractometer with graphite monochromated Cu-$K\alpha$ radiation (λ = 1.54178 Å).

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10 The five-membered ring composed of the central C=C and C=S bonds, and one sulfur atom might become aromatic, judging from the extraordinary distances of the central C=C bond and S-S contact.

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