Synthesis and Properties of Alkylthio-Substituted Tris-Fused Tetrathiafulvalenes

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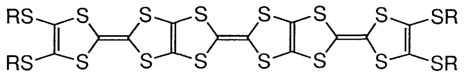
Several derivatives of title donors (**1a**-**c**) have been synthesized. The cyclic voltammogram of tetrakis(hexylthio) derivative **1c** exhibited three pairs of double-electron transfer waves. The iodine complexes of **1a**-**c** showed relatively high conductivities of 10^{-1} - 10^{1} S cm^{-1} at room temperature.

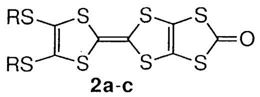
Bis- and tris-tetrathiafulvalene (TTF) systems have received current attention as potential donors for development of organic conductors and ferromagnets as well as multi-redox systems.[1,2] Among them, bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP), is a promising π-electron framework for the realization of two-dimensional electronic structure which is viable strategy for stabilizing metallic state down to a low temperature. Recently we have prepared various BDT-TTP derivatives,[3] several of which have produced many metallic cation radical salts with various anions.[3,4] A tris-fused TTF, 2,2'-bi[5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalenylidene] (BDT-TTPY, **1**) is of interest similar to BDT-TTP. Although the synthesis of BDT-TTPY substituted with strongly electron-withdrawing trifluoromethyl groups has already been reported,[5] its properties, especially redox behavior and preparation of its conducting salts have not been described. We report herein synthesis and redox behavior of tetrakis(alkylthio) derivatives of **1** (**1a**-**c**), and conducting properties of their iodine complexes.

The synthesis of the new donors was carried out by triethyl phosphite-mediated coupling reaction of 4,5-bis(alkylthio)-TTF fused with 1,3-dithiol-2-one (**2a**-**c**) at 100 °C in 30-46% yields.[6] The unknown derivatives of **2** (**2b**, **c**) were prepared by the method similar to that of **2a**.[3a] Thus, 4,5-bis(alkylthio)-1,3-dithiole-2-thione (**3b**, **c**) and 4,5-bis(*p*-acetoxybenzylthio)-1,3-dithiol-2-one (**4**) were cross-coupled in neat triethyl phosphite at 110 °C to give the corresponding 4,5-bis(*p*-acetoxybenzylthio)-4',5'-bis(alkylthio)-TTFs (**5b**, **c**) in 84 and 67% yields, respectively. The acetoxybenzyl groups of **5b**, **c** were removed by treatment with an excess of 28%-methanol solution of sodium methoxide in dichloromethane-methanol (1 : 3, v/v) and then with zinc chloride at room temperature. After addition of tetrabutylammonium bromide, the reaction mixture was treated with excess triphosgen in THF at -70 °C to afford **2b**, **c** in 54 and 77% yields, respectively. All of tris-fused TTF donors were obtained as stable solids which are sparingly soluble in organic solvents. A comparison of the electronic spectrum of **1c** with those of corresponding BDT-TTP **6**[7] and TTF **7**[8] revealed that there was no large shift of the absorption maxima among those donors (Table 1), although absorption coefficients tend to increase as the number of TTF units increases.

Cyclic voltammogram of **1c** in benzonitrile-carbon disulfide (1:1, v/v) consist of two pairs of quasi-reversible waves and a pair of irreversible one (Figure 1).[9] The first redox wave is broad and its peak current at a constant concentration is about twice as large as that of **6**. These results strongly indicate that the first and second oxidations occur in sequence with a small potential difference, resulting in an apparent overlap of two redox waves.[10] Furthermore the peak currents of all waves are almost equal to each other, suggesting that redox process of **1c** is probably composed of three stages of double-electron transfer to form a hexacation, which is in agreement with the fact that **1c** has six redox-active 1,3-dithiole rings. Table 1 shows its redox potentials together with those of **6** and **7** measured under the identical conditions. The first redox potential of **1c** is higher by 0.02 and 0.05 V than those of **6** and **7**, respectively. On the other hand, the E_2-E_1 value is getting smaller as the number of fused TTF units increases. In order to interpret the first double-electron oxidation, molecular orbital calculation of BDT-TTPY was carried out at the

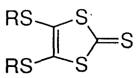


1a-c

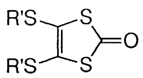


2a-c

a; R = Me
b; R = Et
c; R = *n*-C_6H_{13}



3b, c



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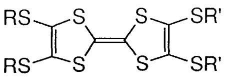


5b, c

R' = *p*-$AcOC_6H_4CH_2$

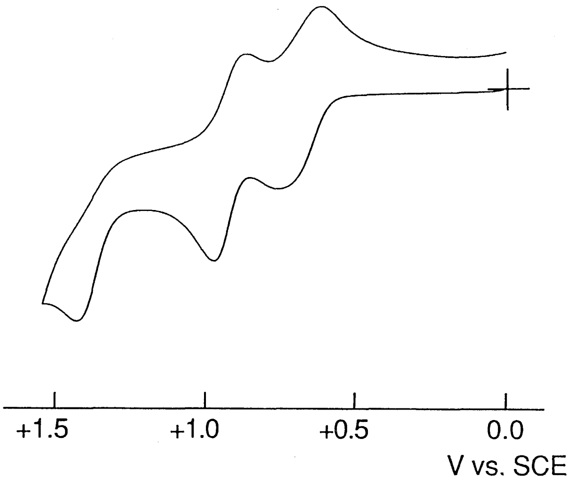
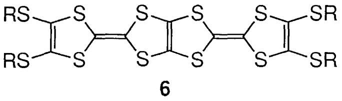


Figure 1. Cyclic voltammogram of **1c** in benzonitrile-carbon disulfide (1:1, v/v).

Table 1. Redox potentials[a] and absorption maxima[b] of **1c** and its related compounds

Compound	E_1/V	E_2/V	E_3/V	E_4/V	E_{m3}[e]	E_2-E_1/V	λ_{max}/nm(log ε)		
	E_{m1}[c]		E_{m2}[d]						
1c	+0.67		+0.92		+1.43[f]	—	370 (sh, 3.99)	325 (4.44)	284 (4.40)
6	+0.65	+0.81	+1.08	+1.20	—	0.16	380 (sh, 3.58)	324 (4.23)	290 (4.20)
7	+0.62	+0.86	—	—	—	0.24	390 (sh, 3.58)	335 (4.14)	310 (4.13)

[a] 0.1 M Bu_4NClO_4 in PhCN-CS_2 (1 : 1, v/v), V vs. SCE, Pt electrode, 25 °C. [b] In $CHCl_3$. [c] $E_{m1}=(E_1+E_2)/2$. [d] $E_{m2}=(E_3+E_4)/2$. [e] $E_{m3}=(E_5+E_6)/2$. [f] Irreversible step. Anodic peak potential.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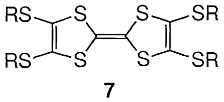
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R = n-C_6H_{13}

Hartree-Fock theory with a 6-31G* basis set (HF/6-31G*) under D_{2h} symmetry constraint.[11] As shown in Figure 2, the HOMO is a π orbital delocalized on the whole molecule, while the HOMO-1 is localized on the outer TTF moieties. Thus, a positive charge (and an odd electron) should delocalize on the whole molecule in the cation radical. The first ionization potentials obtained by using the Koopmans' theorem are 6.894 eV for BDT-TTPY, 6.820 eV for BDT-TTP, and 6.808 eV for TTF.[12] This agrees with that the electron donating ability estimated by cyclic voltammetry decreases as TTF units increase. It is noteworthy that BDT-TTPY has the significantly small orbital energy difference between HOMO and HOMO-1 (0.255 eV),[13] which may cause HOMO-HOMO-1 mixing in the dicationic state of BDT-TTPY. As a result, on-site coulomb repulsion in (BDT-TTPY)$^{2+}$ should considerably decrease because they are mainly located on the outer TTF moieties due to participation of HOMO-1. Therefore, the dicationic state of BDT-TTPY is largely stabilized, which may result in double-electron transfer at the first redox stage in the cyclic voltammogram.

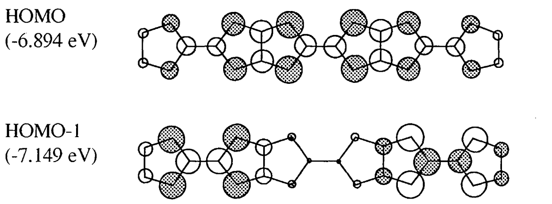

Figure 2. HOMO and HOMO-1 (HF/6-31G* level) of BDT-TTPY. The radii of circles are approximately proportional to the LCAO coefficients.

Charge-transfer complexes and cation radical salts of **1a-c** could not be prepared by the usual mixing or electrochemical oxidation method owing to their solubility problem. However, chloroform suspensions of them were doped with iodine to give the corresponding iodine complexes as black powder. The room temperature conductivities of these complexes on compressed pellets are relatively high values of 0.7-16 Scm^{-1} (see Table 2), all of which show semiconductive temperature dependence with small activation energies (0.03-0.055 eV).

Table 2. Electrical properties of I_2 complexes of **1a-c**

Donors	D : A[a]	σ_{rt} / Scm^{-1}	E_a / eV
1a	1 : 1	16	0.030
1b	3 : 4	2.0	0.033
1c	1 : 1	0.7	0.055

[a] Determined based on elemental analyses.

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6 **1a**: 45% yield: reddish brown microcrystals; mp 246-247 °C (decomp.); IR(KBr) 2914, 1306, 1417, 961 cm^{-1}; ^{1}H NMR(CS_2-C_6D_6) δ 2.41 (s). **1b**, 30% yield: mp. 217.0-217.5 °C (dec.); IR(KBr) 2924, 1449, 1434, 964 cm^{-1}; ^{1}H NMR(CS_2-C_6D_6) δ 1.25(t, J = 7.2 Hz, 12H), 2.75(q, J = 7.2 Hz, 8H). **1c**: 46% yield; reddish orange crystals; mp. 210.5-211.0 °C (dec.); IR(KBr) 2924, 1465, 1415, 966 cm^{-1}; ^{1}H NMR(CS_2-C_6D_6) δ 0.89(t, J = 7.3 Hz, 12H), 1.28(m, 16H), 1.42(m, 8H), 1.61 (m, 8H), 2.78(t, J = 7.3 Hz, 8H). Satisfactory elemental analyses were obtained for all compounds.

7 Compound **6** was obtained in 53% yield by cross-coupling between **2c** and 2 equiv of **3c** in P(OMe)$_3$-toluene (1:1, v/v) at 110 °C.

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9 Satisfactory voltammogram could not be obtained for **1a**, **b** owing to their low solubility in the same solvent.

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12 The details of molecular orbital calculations of multi-fused TTF donors will be reported elsewhere.

13 The orbital energy differences between HOMO and HOMO-1 of BDT-TTP and TTF are 0.558 and 2.259 eV, respectively.