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Synthesis and Properties of (Propyleneditelluro)tetrathiafulvalene Donors

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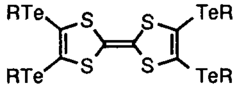
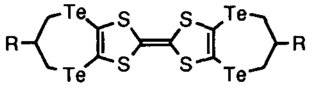
Abstract: The title (propyleneditelluro)tetrathiafulvalenes have been synthesized as the first examples of tellurocycle-fused TTF donors. They demonstrated characteristic multi-redox behavior due to both redox-active TTF and interactive tellurium parts. However, they, like tetrakis(alkyltelluro)TTFs, formed a mixed-stack type of charge-transfer complexes with TCNQ and TCNQF$_2$.

Among structural modifications of tetrathiafulvalene (TTF) in the search for superior electron donors forming organic conductors,[1] tellurium-containing TTF derivatives have drawn much attention, because the introduced tellurium atoms can contribute to marked intermolecular interactions essential to multidimensional conductors.[2] In this regard, several tellurium-substituted TTFs, such as tetrakis(alkyltelluro)- and (phenyltelluro)-tetrathiafulvalenes (**1**[3,4] and **2**[5]) have been investigated, leading to the discovery of tetrakis(methyltelluro)TTF (**1**, n=1) as a high-mobility single-component organic semiconductor owing to the two-dimensional tellurium network.[6] However, these compounds have not necessarily served as good electron donors for conducting molecular complexes.[7] Since structural studies of a number of organic superconductors based on bis(ethylenedithio)tetrathiafulvalene revealed that intermolecular contacts at the molecular long sides are as important as face-to-face interactions for the superconductivity,[8] similar heterocycle-fused TTFs have been actively studied, but tellurium-containing analogues have been so far unknown. We now would like to report bis(propyleneditelluro)tetrathiafulvalenes (**3** and **4**) and their derivatives as the first examples of tellurocycle-fused TTF donors.



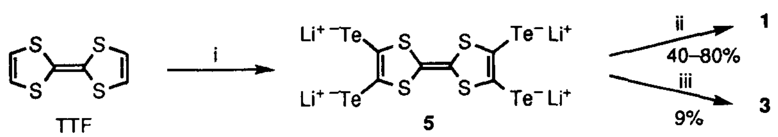
1 R = C$_n$H$_{2n+1}$, n = 1–18
2 R = Ph



3 R = H
4 R = CH$_3$

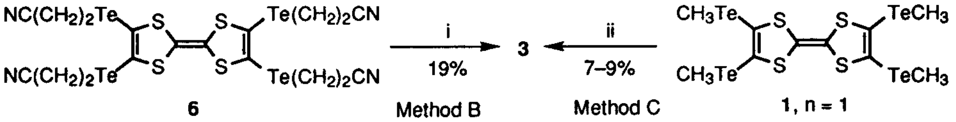
Aharon-Shalom and co-workers first reported that tetralithiation of TTF with lithium diisopropylamide (LDA) followed by treatment with elemental tellurium readily generated lithium tetrathiafulvalene-2,3,6,7-tetratellurolate (**5**), which reacted with ethyl iodide to give tetrakis(ethyltelluro)TTF (**1**, n=2) (Scheme 1).[3] Subsequently, this method allowed Saito's group to extensively study a series of **1** with different alkyltelluro groups.[4] However, Aharon-Shalom and co-workers commented that, when treated with dichloromethane or 1,2-dibromoethane, **5** did not give the corresponding alkyleneditelluro derivatives.[3]

For the synthesis of **3**, we have developed the following three approaches. First, we examined application of the Aharon-Shalom method and found that the intermediate **5** was reacted with 1,3-dibromopropane in THF–HMPA at room temperature to produce **3** in 9% yield (Scheme 1, Method A).[9] The low yield is in sharp contrast to good yields (40-80%) of the tetrakis(alkyltelluro)TTFs (**1**),[4] indicating the difficulty of the former cyclization



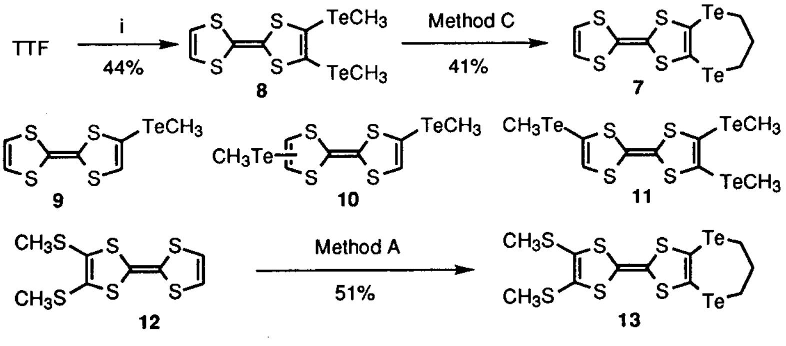
Scheme 1. Method A: (i) 1) 4 eq LDA, THF, -78 °C, 2.5 h, 2) 4 eq Te, -78 to 0 °C, 6 h; (ii) C$_n$H$_{2n+1}$I, -78 °C to rt, 1 h; (iii) 1) HMPA, 0 °C, 1 h, 2) Br(CH$_2$)$_3$Br, -78 °C to rt, 8 h.

reaction. In the second approach, we developed the effective generation of potassium tetrathiafulvalenetetratellurolate by retro-Michael addition reaction of tetrakis(2-cyanoethyltelluro)TTF (**6**) with potassium *t*-butoxide in DMF,[10] and conducted a similar reaction with 1,3-dibromopropane. This method led to enhanced yield (19%) of **3** (Scheme 2, Method B). The third approach involves the construction of a tellurocyclic system from two vicinal methyltelluro groups. This idea is based on transalkylation via a hypervalent telluronium salt.[11] Thus, treatment of tetrakis(methyltelluro)TTF (**1**, n=1) with either 1,3-dibromopropane-NaBr or 1,3-diiodopropane-NaI in DMF at 70 °C gave **3** in 7–9% yield (Scheme 2, Method C).[12]



Scheme 2. Method B: (i) 1) ^{t}BuOK, DMF, 0 °C, 0.5 h, 2) $Br(CH_2)_3Br$, 0 °C to rt, 4 h; Method C: (ii) $X(CH_2)_3X$, NaX (X = I or Br), DMF, 70 °C, 10 h.

These synthetic methods were successfully applied to the synthesis of the methyl derivative (**4**) using 1,3-dibromo-2-methylpropane instead of 1,3-dibromopropane: Method A, 58% yield; Method B, 25% yield; Method C, 12% yield. The advantage of the unique Method C was demonstrated in the synthesis of mono(propyleneditelluro)TTF (**7**). The compound **7** was obtained in only 5% yield by Method A treating TTF with 2 eq LDA, followed by 2 eq tellurium and finally 1,3-dibromopropane. This is apparently related to the statistical and regioisomeric problems for dilithiation at the four reaction sites of TTF, because quenching of the reaction mixture with methyl iodide produced the 2,3-bis(methyltelluro)TTF (**8**) (44%) together with the mono-substituted **9** (8%), the 2,6(7)-di-substituted **10** (11%), the tri-substituted **11** (17%), and the tetra-substituted **1** (n=1) (6%).[10] Alternatively, exchange reaction of **8** with 1,3-dibromopropane-NaBr gave **7** in 41% yield; thus, the Method C offers a better approach to **7** (Scheme 3). Since 2,3-bis(methylthio)TTF (**12**)[13] does not pose such problems for dilithiation, the Method A was directly applied to produce unsymmetrical 2,3-bis(methylthio)-6,7-(propyleneditelluro)TTF (**13**) in 51% yield.



Scheme 3. (i) 1) 2eq LDA, THF, -78 °C, 2.5 h, 2) 2eq Te, -78 to 0 °C, 6 h, 3) HMPA, 0 °C, 1 h, 4) CH_3I, 0 °C to rt, 8 h.

The cyclic voltammogram of **3** demonstrates three redox waves as shown in Fig. 1, and the half-wave oxidation potentials are summarized together with those of its derivatives in Table 1. The first redox at 0.39 V is estimated on the current intensity to correspond to one-electron transfer, the second at 0.79 V to three-electron, and the third at 0.94 V to two-electron. For comparison, Figure 1 also shows the cyclic voltammogram of tetrakis(methyltelluro)TTF (**1**, n=1), which demonstrates a different pattern but with three redox waves. Both the first redox at 0.37 V and the second at 0.70 V are apparently one-electron transfer from the TTF moiety.[3,4] Presumably, the third two-electron redox process at 0.99 V occurs at the tellurium atoms. On the other hand, the voltammogram of **3** is conveniently explained by superposition of the TTF- and tellurium-induced redox processes at the second wave. The fused cyclic system is presumed to promote a direct orbital interaction between the two vicinal tellurium atoms, leading to the facile oxidation.[14] Similar multi-redox voltammograms were also observed for the derivatives **4**, **7**, and **13** (Table 1).

An X-ray crystallographic analysis of **13** revealed a bent geometry of the TTF moiety as depicted in Figure 2.[15] The nonbonding distance between the two tellurium atoms in the tellurocycle is 3.88 Å. Considering the sum (4.12–4.40 Å) of van der Waals radius of tellurium, this supports that the electrochemically oxidized tellurium species can be stabilized by a neighboring tellurium-orbital interaction.

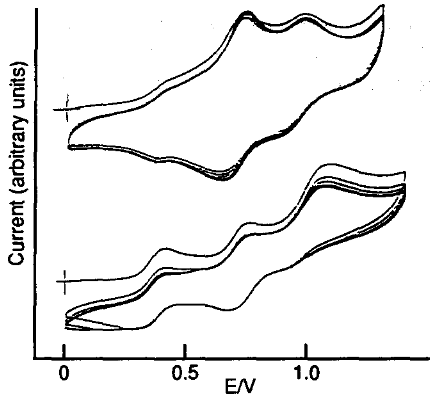


Fig. 1. Cyclic voltammograms of **3** (top) and **1** (n=1) (bottom)

The symmetrical TTFs **3** and **4** formed no charge-transfer complexes with TCNQ but with a stronger acceptor, $TCNQF_2$. On the other hand, the unsymmetrical TTFs **7** and **13** gave complexes with both acceptors. As seen from Table 1, the electrical conductivities of all the complexes are of the order of 10^{-3}–10^{-6} Scm^{-1}. The low conductivities are reminiscent of those of the TCNQ complexes of tetrakis(alkyltelluro)TTFs (**1**), which were explained by a mixed-stack crystal structure.[3,7] Similarly, the present complexes are thought to have mixed-stack crystal structures. In fact, the crystal structure of the **13**•$TCNQF_2$ complex comprises a DDAA type of stacking columns as shown in Fig. 3.[15] Within the column, the paired donors and acceptors are parallel with short interplanar average distances of 3.36 Å and 3.27 Å, respectively, but the donor and acceptor are stacked on the tilt, avoiding the effective interaction. On the other hand, there are marked Te•••Te interactions (4.12 Å)

Table 1. Half-Wave Oxidation Potentials[a] of the (Propyleneditelluro)TTF Donors and Electrical Conductivities of their Charge-Transfer Complexes[b] with TCNQ and $TCNQF_2$

Donor	Oxidation potential/V			Conductivity[c]/Scm^{-1}	
	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	TCNQ	$TCNQF_2$
3	0.39(1e)	0.79(3e)	0.94(2e)	non-complexation	3.8×10^{-4} [d]
4	0.38(1e)	0.72(3e)	0.94(2e)	non-complexation	5.8×10^{-6}
7	0.36(1e)	0.72(2e)	0.82(1e)	1.6×10^{-3}	8.3×10^{-4}
13	0.43(1e)	0.72(2e)	0.85(1e)	4.0×10^{-6}	2.8×10^{-5} [d]

a) V vs. Ag/AgCl in benzonitrile containing Bu_4NClO_4 as supporting electrolyte. b) Stoichiometry of donor and acceptor in all complexes is 1:1 except 2:1 of **7**•$TCNQF_2$ complex. c) Measured on a compressed pellet with a two-probe method at room temperature unless otherwise stated. d) Measured on a single crystal.

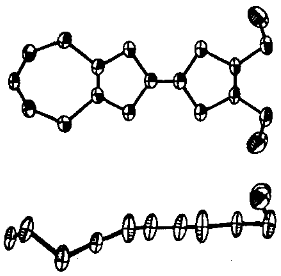


Fig. 2. ORTEP drawings of **13**; a top view (top) and a side view (bottom)

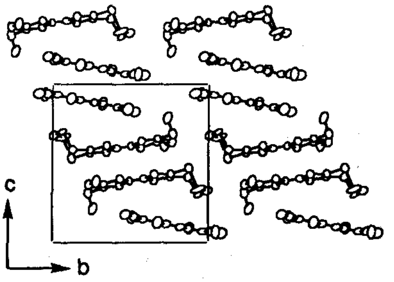


Fig. 3. Crystal structure of **13**•$TCNQF_2$ viewed along the *a* axis

between the neighboring donors in different columns. Further investigation to obtain conductive radical cation salts of the (propyleneditelluro)TTFs with a segregated-stack crystal structure is now under way.

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9. All (propyleneditelluro)TTF compounds were characterized by spectroscopic measurements and elemental analyses. **3**: orange crystals; dp 200 °C; ^{1}H-NMR ($CDCl_3$-CS_2) δ 2.78 (m, 4H) and 2.90 (m, 2H); MS m/z 796 (M^+). **4**: orange crystals; dp 203 °C; ^{1}H-NMR ($CDCl_3$-CS_2) δ 1.21 (d, J=6.6 Hz, 6H), 2.41 (m, 2H), 2.61 (dd, J=12.4 and 8.3 Hz, 4H), and 2.91 (dd, J=12.4 and 6.0 Hz, 4H); MS m/z 824 (M^+). **7**: orange needles; mp 176–177 °C; ^{1}H-NMR ($CDCl_3$-CS_2) δ 2.80 (m, 4H), 2.91 (m, 2H), and 6.23 (s, 2H); MS m/z 502 (M^+). **13**: orange needles; mp 147–148 °C; ^{1}H-NMR ($CDCl_3$-CS_2) δ 2.40 (s, 6H), 2.80 (m, 4H), and 2.91 (m, 2H); MS m/z 594 (M^+).
10. Tetrakis(2-cyanoethyltelluro)TTF (**6**) was prepared in 40% yield by treatment of **5** with 3-bromopropinonitrile. Use of similar tetrakis(2-cyanoethylthio)TTF for protection of tetrathiafulvalenetetrathiolate was recently developed by Becher's group; Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809–812.
    Selected data for new tellurium-containing TTF compounds are as follows. **6**: orange needles; mp 186–187 °C; ^{1}H-NMR (DMSO-d_6) δ 2.96 (t, J=7.5 Hz, 8H) and 3.10 (t, J=7.5 Hz, 8H); IR (KBr) 2245 cm^{-1}. **8**: orange needles; mp 102–103 °C; ^{1}H-NMR ($CDCl_3$) δ 2.23 (s, 6H) and 6.31 (s, 2H); MS m/z 488 (M^+). **9**: orange crystals; mp 183–184 °C; ^{1}H-NMR ($CDCl_3$) δ 2.17 (s, 3H), 6.24 (s, 2H), and 6.42 (s, 1H); MS m/z 348 (M^+). **10**: orange crystals; mp 125–126 °C; ^{1}H-NMR ($CDCl_3$) δ 2.18 (s, 6H) and 6.43 (s, 2H); MS m/z 488 (M^+). **11**: orange powder; mp 82–84 °C; ^{1}H-NMR ($CDCl_3$) δ 2.17 (s, 3H), 2.20 (s, 6H), and 6.41 (s, 1H); MS m/z 630 (M^+).
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15. Crystal data for **13**: orthorhombic, *P*nma, a=27.328(3), b=13.849(1), c=4.7087 Å, Z=4, R=0.057. Crystal data for **13**•$TCNQF_2$ complex: monoclinic, *C*2/*c*, a=26.695(4), b=14.562(2), c=19.681(3) Å, β=130.850(8) °, Z=8, R=0.051.

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