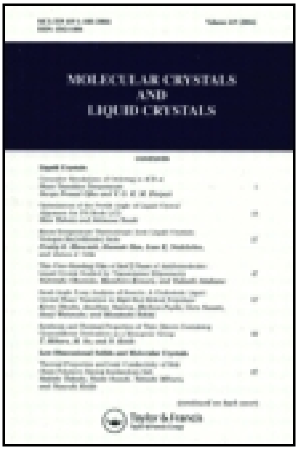

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Asymmetric tetrathiapentalene derivatives having long alkyl chains

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ASYMMETRIC TETRATHIAPENTALENE DERIVATIVES HAVING LONG ALKYL CHAINS

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Selenium-contained analogs of C_nTET-TTP, C_nTES-TTP ($n = 2, 3$), have been synthesized. A charge-transfer complex $(C_2TES\text{-}TTP)_2I_3$ shows lower conducting behavior than that of $(C_2TET\text{-}TTP)_2X$ ($X = BF_4$, ClO_4); C_3TES-TTP forms 1:1 complex with I_3, and is semiconductive from room temperature. X-Ray analysis revealed that $(C_3TET\text{-}TTP)I_3$ has a dimeric structure, but is not isostructual to $(C_4TET\text{-}TTP)I_3$.

Keywords: Tetrathiapentalene; Long alkyl chains; Charge-transfer complex

INTRODUCTION

Charge-transfer complexes based on tetrathiapentalene (TTP, Scheme 1) derivatives have been drawing a considerable attention due to the tendency toward the metallic behavior down to low temperatures. Although most TTP donors derived from usual TTF donors have been already synthesized, and their radical cation salts have been investigated [1], there is no TTP-based superconductor except for $(DTEDT)_3Au(CN)_2$ ($T_c = 4\,K$, DTEDT = 2-(1,3-dithiol-2-ylidene)-5-[2-(1,3-dithiol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene, Scheme 1)[2]. Therefore, it is necessary to modify TTP donors from the viewpoint of molecular design. We have chosen TMET-TTP (bis(methylthio) ethylenedithio-TTP, Scheme 1), which forms 4:1 salts regardless of anions [3], as a target of the modification. In order to increase the anion content, we have obtained analogs of TMET-TTP, C_nTET-TTP ($n = 2$–4, Scheme 1), having longer alkylthio groups [4].

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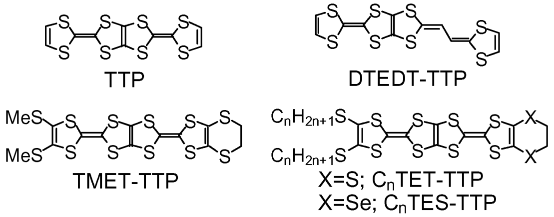


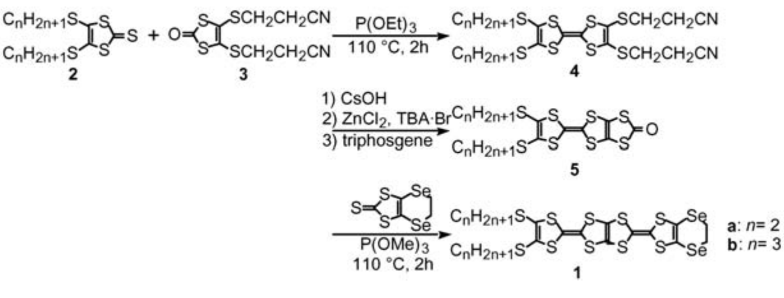
SCHEME 1 TTP derivatives.

It has been demonstrated that the long alkylthio chains of C_nTET-TTP are effective in increasing the anion content as expected; $(C_2TET\text{-}TTP)_2ClO_4$ has 2:1 composition and β-type uniform stacking, and $(C_4TET\text{-}TTP)I_3$ has 1:1 composition with a dimeric structure. These salts contrast with the salts of TMET-TTP, which have 4:1 composition with a θ-type structures. From these results, we have concluded that the attachment of longer alkyl chains is a promising tool for controlling the donor:acceptor ratio as well as the crystal structure.

In the case of $(C_2TET\text{-}TTP)_2X$ ($X = BF_4$, ClO_4), the metallic character seems to be too stable and no superconductivity has been found. In this context, introduction of some instability is necessary. For this purpose, we have designed new TTP donors, C_nTES-TTP ($n = 2$, 3, Scheme 1), where the ethylenedithio-rings of C_nTET-TTP are replaced by ethylenediseleno-rings. The outer selenium atoms are expected to decrease the side-by-side interactions of the charge transfer complexes, resulting in less metallic behavior.

RESULTS AND DISCUSSIONS

The synthesis of C_nTES-TTP is shown in Scheme 2. Compound **4** was obtained by the triethyl phosphite-mediated cross coupling between **2** and



SCHEME 2 The synthesis of C_nTES-TTP derivatives.

3. The treatment of **4** with triphosgene provided **5**. Compound **5** and 4,5-ethylenediseleno-1,3-dithiole-2-thione were cross-coupled in trimethyl phosphite-toluene (1:1, v/v) to give the corresponding C_nTES-TTP **1** derivatives in 25% yield for **a** and 15% yield for **b**.

The electrochemical properties of newly synthesized donors C_nTES-TTP were investigated by cyclic voltammetry: $E_1 = +0.44\,V$, $E_2 = +0.66\,V$, $E_3 = +0.92$, $E_4 = +1.08\,V$, $E_2 - E_1 = 0.22\,V$ for **1a**, $E_1 = +0.45\,V$, $E_2 = +0.68\,V$, $E_3 = +0.96\,V$, $E_4 = +1.12\,V$, $E_2 - E_1 = 0.23\,V$ for **1b**. These values almost correspond with those of C_nTET-TTP derivatives.

The donor molecules were as soluble in organic solvents as C_nTET-TTP derivatives. The I_3 salts of C_2TES-TTP and C_3TES-TTP were prepared by electrochemical oxidation in dichloroethane or 1,1,2-trichloroethane in the presence of tetrabutylammonium salt of I_3.

C_2TES-TTP and C_3TES-TTP formed 2:1 crystals in the form of black needles and 1:1 crystals in the form of black plates. X-Ray crystal analysis of (C_3TES-TTP)I_3 has been performed (Figure 1) [5]. It has a dimeric structure similarly to (C_4TET-TTP)I_3, but these salts are not isostructual judging from the lattice constants. The overlap integrals calculated from the overlap of HOMO are $p = -15.6$, $a1 = 1.78$, and $a2 = 0.119 \times 10^{-3}$; the large p interaction represents the strong dimerization.

The room-temperature conductivities are $1.4 \times 10^2\,Scm^{-1}$ for (C_2TES-TTP)$_2I_3$ and $2.7 \times 10^{-3}\,Scm^{-1}$ for (C_3TES-TTP)I_3. The resistivity of (C_2TES-TTP)$_2I_3$ makes minimum around 40 K and gradually increases below this temperature. As we have expected, the selenium atoms reduce side-by-side interactions compared with the salts of C_2TET-TTP. (C_3TES-TTP)I_3 is semiconductive from room temperature. The activation energy is 4.9×10^{-2} eV.

We are exploring other TTP derivatives having long alkyl chains.

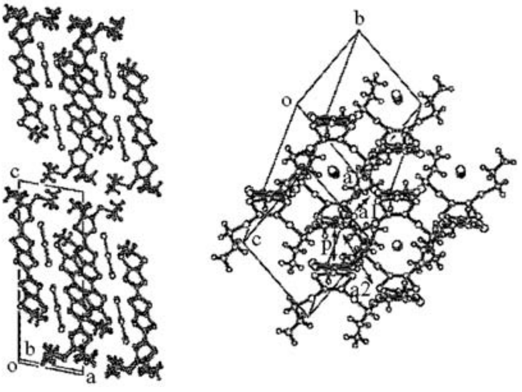


FIGURE 1 Crystal structure of (C_3TES-TTP)I_3.

SYNTHESIS

4a: Compounds **2** (500 mg, 1.97 mmol) and **3** (565 mg, 1.96 mmol) were refluxed in triethyl-phosphite (15 ml) under argon for 2 h. After the mixture was cooled to room temperature, the solvent was removed in vacuo. The residue was purified by column chromatography (silica, CH_2Cl_2-hexane) to afford **4a** (517 mg, 53%) as an orange solid. mp 91°C; ^1H NMR ($CDCl_3$) $\delta = 1.33$ (6H, t, $J = 7.4$ Hz), 2.74 (4H, t, $J = 7.2$ Hz), 2.87 (4H, q, $J = 7.4$ Hz), 3.09 (4H, t, $J = 7.2$ Hz).

4b: 58% yield; orange solid; mp 92 °C; ^1H NMR ($CDCl_3$) $\delta = 1.03$ (6H, t, $J = 7.4$ Hz), 1.68 (4H, m, $J = 7.2, 7.4$ Hz), 2.74 (4H, t, $J = 7.0$ Hz), 2.81 (4H, t, $J = 7.2$ Hz), 3.09 (4H, t, $J = 7.0$ Hz).

5a: To a mixture of **4a** (823 mg, 1.66 mmol) and cesium hydroxide (2.01 g, 13.4 mmol) were added acetone (5 ml) and methanol (5 ml) at 0°C under argon, and the reaction mixture was stirred for 30 min at room temperature. The mixture was treated at 0°C with zinc chloride (119 mg, 0.875 mmol) dissolved in methanol (4 ml) and with tetrabutylammonium bromide (544 mg, 1.69 mmol) dissolved in methanol (2 ml). After stirring at room temperature for 15 min, the reaction mixture was filtered. The residue was suspended in THF (15 ml) and an excess of triphosgene (362 mg, 1.22 mmol) dissolved in THF (4 ml) was added at −78°C. The reaction mixture was allowed to warm up to room temperature overnight and filtered. The residue was purified by short column chromatography (silica, CS_2) to afford **4a** (488 mg, 71%) as a red solid. mp 169°C; ^1H NMR ($CDCl_3$) $\delta = 1.32$ (6H, t, $J = 7.4$ Hz), 2.86 (4H, t, $J = 7.4$ Hz).

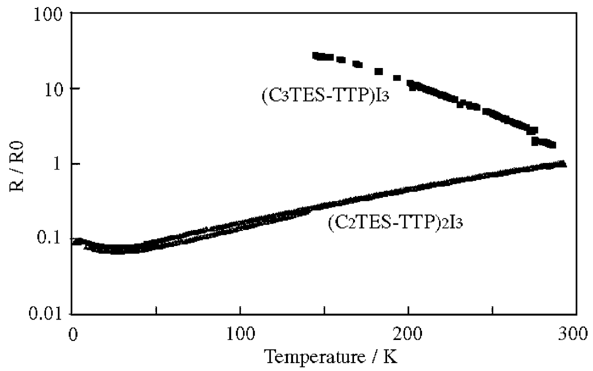


FIGURE 2 Temperature dependence of the resistivities of C_nTES-TTP salts (normalized to the values at room temperatures).

5b: 79% yield; red solid; mp 152°C; ^{1}H NMR ($CDCl_3$) $\delta = 1.02$ (6H, t, $J = 7.4$ Hz), 1.67 (4H, m, $J = 7.2$, 7.4 Hz), 2.81 (4H, t, $J = 7.2$ Hz).

1a: Compound **5a** (201 mg, 0.484 mmol) and 4,5-ethylenediseleno-1,3-dithiole-2-thione (388 mg, 1.06 mmol) were refluxed in trimethyl phosphite (8 ml) – toluene (8 ml) for 2 h. After the reaction mixture was cooled, the residue was filtered and purified by short column chromatography (silica, CS_2) to afford **1a** (84.1 mg, 25%) as a red solid. mp 184°C; ^{1}H NMR ($CDCl_3$) $\delta = 1.31$ (6H, t, $J = 7.4$ Hz), 2.82 (4H, q, $J = 7.4$ Hz), 3.29 (4H, s).

1b: 15% yield; red solid; mp 161°C; ^{1}H NMR ($CDCl_3$) $\delta = 1.01$ (6H, t, $J = 7.3$ Hz), 1.67 (4H, m, $J = 7.3$, 7.4 Hz), 2.79 (4H, t, $J = 7.4$ Hz), 3.54 (4H, s).

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[5] Crystal data of $(C_3TES\text{-}TTP)I_3$: $F_w = 1093.57$, triclinic, space group $P\bar{1}$, $a = 8.681(5)$, $b = 23.12(2)$, $c = 8.636(4)$ Å, $\alpha = 98.88(5)$, $\beta = 109.86(4)$, $\gamma = 91.84(6)°$, $Z = 2$, $\rho_{calc} = 2.264\ g\,cm^{-3}$, and $V = 1604(2)$ Å^3. The final $R = 0.070$ ($R_w = 0.080$) for independent 3731 reflections ($I > 3\sigma(I)$).