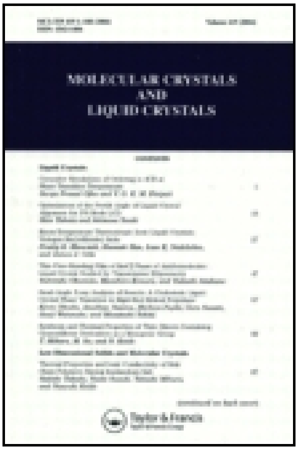

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# Synthesis and properties of TTP analog with a cyclohexene ring inserted

Yohji Misaki [a], Tadahiro Kaibuki [a], Kazyuki Takahashi [a], Hiroaki Tanioka [a] & Kazuyoshi Tanaka [a]
[a] Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto, 606-8501, Japan

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# SYNTHESIS AND PROPERTIES OF TTP ANALOG WITH A CYCLOHEXENE RING INSERTED

*Yohji Misaki,* Tadahiro Kaibuki, Kazyuki Takahashi,*
*Hiroaki Tanioka and Kazuyoshi Tanaka*
*Department of Molecular Engineering,*
*Graduate School of Engineering, Kyoto University, Yoshida,*
*Kyoto 606-8501, Japan*

*A new tetrathiapentalene (TTP) type donor, 2-(2-cyclohexenediylidene-1,3-dithiole)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (CHDTDT), has been prepared. Cyclic voltammogram of CHDTDT showed three pairs of redox waves at 0.00 (2e), +0.42 (1e) and +0.66 (1e) V (vs. Ag/Ag$^+$, in PhCN). CHDTDT has yielded several metallic radical cation salts. Among them, the $AsF_6$ salt exhibited metallic conductivity down to 4.2 K.*

Keywords: organic conductor; tetrathiapentalene; cyclic voltammetry; electrical conductivity

## INTRODUCTION

A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)1,3,4,6-tetrathia-pentalene (TTP) [1] and its vinylog DTEDT [2,3] are promising donors for organic metals because they have afforded many metallic radical-cation salts stable down to liquid helium and $(DTEDT)_3Au(CN)_2$ show superconductivity. In this context, development of new bis-fused $\pi$-electron system composed of an extended TTF donor is of particular interest. We report herein synthesis and properties of a new extended TTP 2-(2-cyclohexenediylidene-1,3-dithiole)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene CHDTDT, in which a cyclohexene ring is inserted, and a selenium analog CHDTDS [3].

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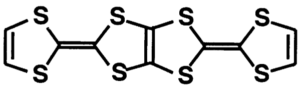
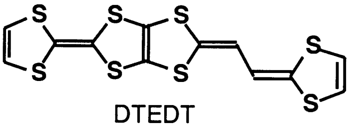
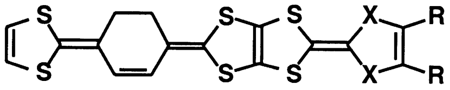
*Corresponding author. E-mail: misaki@mee3.moleng.kyoto-u.ac.jp



TTP



DTEDT



**1a**: X = S, R = H (CHDTDT)
**1b**: X = S, R = $CO_2Me$
**2a**: X = Se, R = H (CHDTDS)
**2b**: X = Se, R = $CO_2Me$

## RESULTS AND DISCUSSION

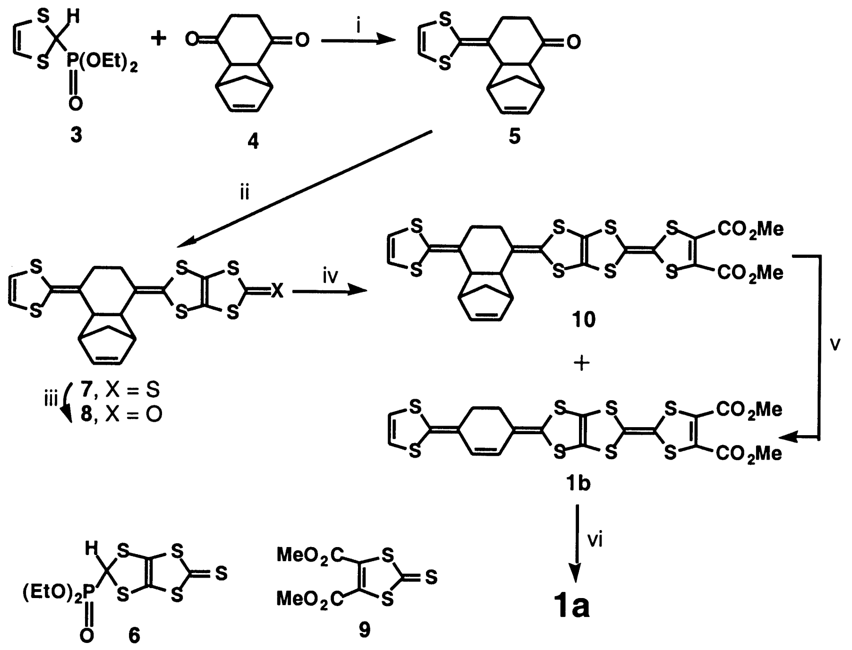
### Synthesis

Syntheses of CHDTDT was performed according to Scheme 1. A Wittig-Horner reagent **3** [4] was treated with diisopropylamide (LDA) in the presence of two equimolar amount of **4** [5] in THF at −78°C to give a monoaduct **5** in 72% yield (based on **3**) as shown in Scheme 1. Then subsequent Wittig-Horner reaction was carried out between **5** and **6** in the presence of LDA to afford **7** in 51% yield. The thione **7** was converted to the corresponding ketone (**8**, 60% yield), then cross-coupled with **9** with a large excess of trimethylphophite in refluxing toluene to give **10** and **11** in 27 and 10% yields, respectively. Compound **11** was also obtained in 93% yield by heating of **10** in solid state at 150°C under reduced pressure. Demethoxycarbonylation of a diester of CHDTDT **1b** with an excess of LiBr·$H_2O$ in HMPA at 90–130°C gave the target compound **1a** in 57% yield.

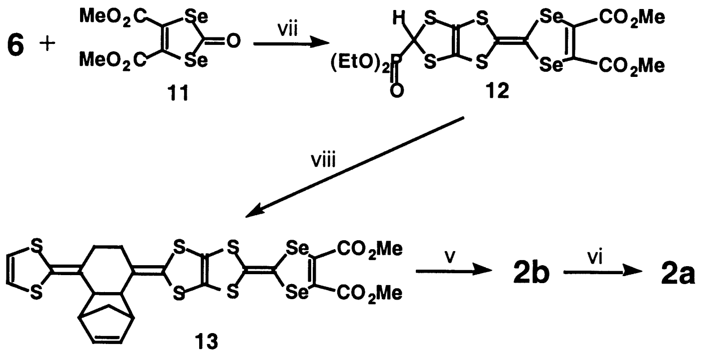
On the other hand, CHDTDS could not be obtained by the synthetic procedure similar to CHDTDT, therefore, an alternative method was adopted for the synthesis of CHDTDS as shown in Scheme 2. The trimethylphophite-mediated cross-coupling between **6** and **11** afforded a phosphonate fused with STF derivative **12** (64% yield), which was reacted with **5** in the presence of LDA to give **13** (40% yield). Compound **13** was heated at 150°C under reduced pressure to give bis(methoxycarbonyl) derivative **2b** (94% yield), which was converted to CHDTDS by treatment with an excess of LiBr·$H_2O$ in HMPA at 90–130°C (40% yield).

### Electrochemistry

Electrochemical properties of new donors were investigated by cyclic voltammetry.[6] Their redox potentials are summarized in Table 1 together



SCHEME 1



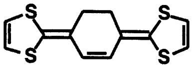
SCHEME 2

i) LDA, THF, −70°C; ii) Compound **6**, LDA, THF, −70°C; iii) $Hg(OAc)_2$, AcOH-$CHCl_3$, room temp.; iv) $P(OMe)_3$, toluene, 110°C; v) 1 mmHg, 150°C; vi) LiBr·$H_2O$, HMPA, 90–130°C; vii) $P(OMe)_3$, toluene, 110°C; viii) Compound **5**, LDA, THF, −70°C.

**TABLE 1** Redox Potentials of **1a, 2a** and Their Related Compounds in PhCN (V vs. Ag/Ag$^{+}$, Pt electrode, 25°C)

| Donor | $E_1$ | $E_m$$^{a}$ | $E_2$ | $E_3$ | $E_4$ |
|---|---|---|---|---|---|
| **1a** | | 0.00 | | +0.42 | +0.66 |
| **2a** | | +0.01 | | +0.48 | +0.65 |
| **14** | | −0.09 | | — | — |
| TTF | −0.04 | | +0.38 | — | — |
| TTP | +0.05 | | +0.34 | +0.61 | +0.82$^{b}$ |

$^{a}E_m = (E_1 + E_2)2$. $^{b}$Irreversible step. Anodic peak potential.



**14**

with several related compounds. Both CHDTDT and CHDTDS showed three pairs of reversible redox waves. The first redox waves were very broad or about to split to two waves, and their peak currents were considerably larger than the other stages. These results strongly indicate an apparent overlap of two redox single-electron waves due to occurrence of the first and second oxidations in sequence with a small redox potential differences. This is also reasonable considering that compound **14** [7] which consists of a half unit of CHDTDT shows only one-pair of redox wave corresponding to two-electron transfer. The first redox potential of CHDTDT ($E_m = 0.00$ V) is lower by 0.05 V than that of TTP, suggesting the donor ability is enhanced due to extension of $\pi$-conjugation. However, it is a little higher by 0.04 and 0.09 V compared with those of TTF and **14**, respectively, indicating the donor ability becomes rather weaker in spite of extension of apparent $\pi$-conjugation by fusing two donor units. On the other hand, the $E_1$ values of CHDTDS(**2a**) is almost same as that of **1a**. The above results suggest that the first two-electron oxidation mainly occur in the 2-cyclohexenediylidene-1,3-dithiole moiety, and TTF or STF unit acts as a sulfur-based substituent as is observed in usual extended TTP analogs [2a,8].

## Electrical Properties of Conducting Materials

CHDTDT and CHDTDS react with TCNQ to afford the corresponding CT complexes. Both complexes exhibited high conductivity of $\sigma_{rt} = 20$–$130$ S cm$^{-1}$ on a compressed pellet. Temperature dependence of resistivity revealed that they are semiconductor, but the activation energies were quite small (0.013–0.015 eV). Therefore, they are expected to show metallic

**TABLE 2** Electrical Properties of Radical Cation Salts of CHDTDT·$(A)_X$

| Acceptor | D : A[a] | $\sigma_{rt}$/ S cm$^{-1b}$ | Conducting behavior |
|---|---|---|---|
| $Au(CN)_2$ | 2 : 1 (Au) | 240 | Metallic down to 120 K[c] |
| $ClO_4$ | — | 260 | $T_{MI}$ = 160 K |
| $PF_6$ | 2 : 1 (P) | 490 | Metallic down to 100 K[c] |
| $AsF_6$ | 2 : 1 (As) | 320 | Metallic down to 4.2 K |

[a]Determined by the energy dispersion spectroscopy from the ratio of sulfur and the elements designated in the parentheses. [b]Measured on a single crystal. [c]The crystal was cracked at the temperature.

behavior on a single crystal. On the other hand, several cation radical salts based on CHDTDT were obtained by an electrochemical oxidation in the presence of the corresponding tetra-*n*-butylammonium salts in chlorobenzene at 50°C. Their electrical properties are summarized in Table 2. All of salts obtained so far show high conductivity of $\sigma_{rt} = 10^2$ S cm$^{-1}$ on a single crystal, and exhibited metal-like conducting behavior. Among them, the $AsF_6$ retain salt metallic conductivity down to 4.2 K though the resistivity increased a little at low temperature probably owing to low quality of crystal.

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[3] Abbreviations: DTEDT, 2-(2-ethanediylidene-1,3-dithiole)-5-(1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene; CHDTDS, 2-(2-cyclohexenediylidene-1,3-dithiole)-5-(1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene.

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