Synthesis and Electrochemical Studies of Tetrathiafulvalene Derivatives (TTF's) as Redox Active Ligands

Abd El-Wareth A. O. Sarhan*, Makoto Murakami and Taeko Izumi

Department of Chemistry and Chemical Engineering
Faculty of Engineering, Yamagata University, 3-16 Jonan 4-Chome
Yonezawa 992-8510, Japan

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A simple route for synthesis of new tetrathiafulvalene dimethyl ester (TTF-DME) is reported. The tetrathifulvalene dimethylester (TTF-DME) has been prepared by introducing an ester coordination function as a bifunctional new donor. The redox behavior of the TTF-DME was investigated in comparison to the well-known dibenzotetrathiafulvene (DB-TTF) by cyclic voltammetry. A two-electron redox behavior was observed as a two waves.

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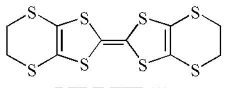
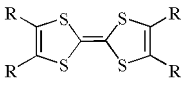
Since the discovery of the conducting properties of the tetrathiafulvalene and its derivatives it has become a subject of great interest for electrochemical studies [1]. Chemical modifications of the tetrathiafulvenes (TTF's) framework have been added to improve their electrical conductance properties. Several tetrathiafulvalenes TTF's were previously prepared *via* one step reaction with different yields [2].

Bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (1) has been widely used for the preparation of different organic superconductors [3]. TTF's containing two or more fused or covalently attached TTF's units have been also used for preparing super conducting salts [4].



BEDT-TTF (1)



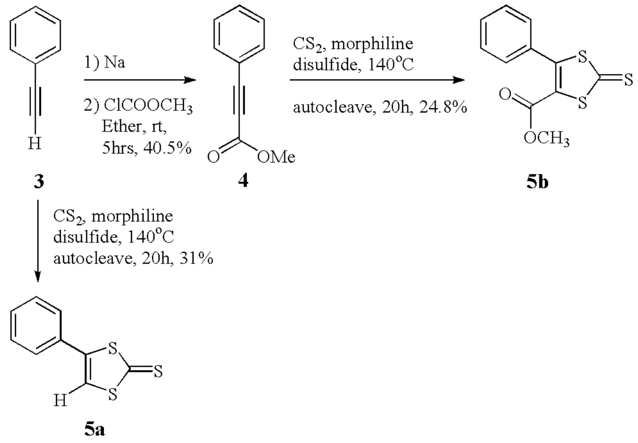
TTF (2)

Recently, Martin Bryce *et al.* reported the synthesis of a crown-annulated derivative of TTF (2) as a redox active ligand system [5]. The preparation of modified TTF's has focused on dimeric TTF units [6], for example bis-TTF's, higher oligomers [7] as well as polymers [8] and dendrimers [9]. In addition, intensive studies on TTF derivatives having more than one TTF unit with quinonoid structure as a conjugated spacer have been reported [10-13]. Tetrathiafulvalene substituted by coordination functions such as dithiolene or phosphine ligands, which are not the only ligands showing chelating ability towards various transition metals have been described [14]. β-Diketones and their enolate ions also show powerful chelating properties and form complexes with transition metals and main group elements [15]. Tetrathifulvalenes substituted with two electron-withdrawing ester groups are therefore perhaps potential ligands, which can be involved in the formation of organic-inorganic materials [16].

Results and Discussions.

In this work we focused on synthesis of tetrathiafulvalene TTF with appropriate coordination functions and study of the electrochemical behavior in comparison with the well-known dibenzotetrathiafulvene (DB-TTF) donor **11**. We report the synthesis of the first example of TTF substituted by two carboxylate coordination functions. Introducing of two carboxylate esters into the TTF core was also described. Methyl phenylpropiolate **4** was obtained (40.5% yield) *via* reaction of phenyl acetylene **3** with methyl chloroformate in the presence of sodium metal as shown in Scheme 1.

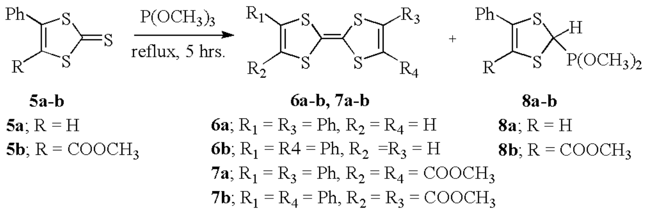
Scheme 1



The synthetic strategy described by Benitez and Grunwell for the preparation of 1,3-dithiole-2-thione derivative **5a** [17] was adapted for compound **5b** as shown in Scheme 1. Treatment of Phenyl acetylene **3** or related ester **4** with carbon disulfide at 140 °C using an autoclave in the presence of bis-morphiline disulfide gave the corresponding 1,3-dithiole-2-thione derivatives **5a-b** as shown in Scheme 1.

1,3-Dithiole-2-thiones **5a-b** were refluxed with trimethylphosphite for 5 hours to afford a mixture of *cis-trans* isomers of the corresponding TTF's **6a-b** and **7a-b**, in addition to the formation of 2-dimethoxyphosphinyl-1,3-dithioles (**8a-b**) in relatively good yield [18], Scheme 2.

Scheme 2



The tetrathiafulvalenes **6a-b** and **7a-b** obtained were a mixture of *cis-trans* isomers in a ratio of (86:14) and (55:45) respectively (^{1}HNMR analysis), Chart 1. The *cis*-isomers **6a** and **7a** could only be obtained as single isomers by column chromatography using silica gel (hexane/chloroform 2:1) and used for cyclic voltammetric studies. Furthermore, the *trans*-isomers **6b** and **7b** could not be obtained as single isomers.

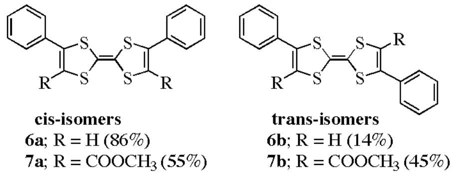
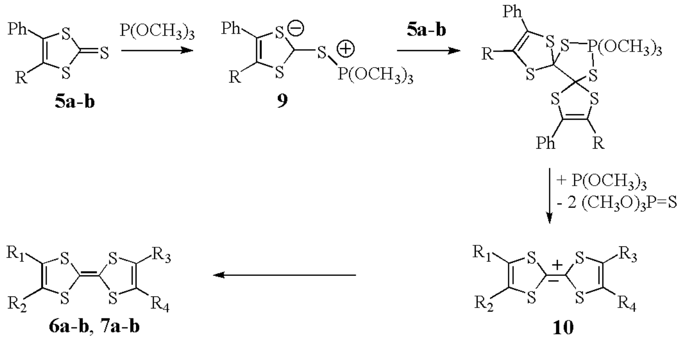


Chart 1

Formation of *cis-trans* isomers in this reaction was expected and this presumably involves initial thiophilic addition of trialkyl phosphite to the thione, to give the 1,3-dipolar intermediate **9**. Reaction of **9** with further thione leads to the intermediate **10,** which is easily rationalized to the *cis-trans* isomers **6a-b** and **7a-b** following the established mechanism of this reaction [18], Scheme 3.

Scheme 3



The DB-TTF **11** was prepared according to the method previously described [19] for comparison study of the electrochemical behavior using the cyclicvoltammetry spectra with the synthesized TTF's. Attempts are now underway to synthesize the tetrazafulvalenes (TAF) **12** for a comparison study of the electrochemical properties of both DTF's, TTF's and TAF, Chart 2.

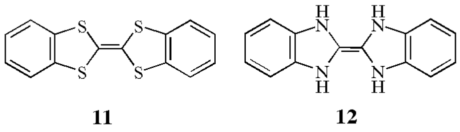


Chart 2

Electrochemistry.

The redox behavior of diphenyltetrathiafulvene (DPh-TTF **6a**), tetrathifulvalene dimethylester (TTF-DME **7a**) and DB-TTF **11** was investigated by cyclicvoltammetry and the results are listed in Table 1. As usually observed for TTF's, these derivative exhibit two reversible mono-electronic waves. One can see that the presence of the two electron withdrawing groups (ester groups) slightly decrease the donor ability of the TTF-DME compound 7a compared with the DPh-TTF **6a** and DB-TTF **11**. The value of $\Delta E^{1/2}$ decreases in the direction of DB-TTF **11** > DPh-TTF **6a** > TTF-DME **7a** suggesting that the intramolecular Columbic repulsion energy decrease in this series.

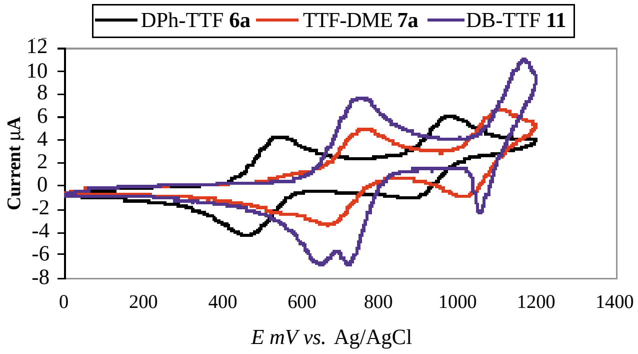


Figure 1. Cyclic volatmmogram of DPh-TTF **6a** TTF-DME **7a**, and DB-TTF **11** in CH_2Cl_2 on a platinum electrode, concentration of ($4.0x10^{-5}$ *M*). Scan rate 200 mVs^{-1}, base-electrolyte TBAP 0.1 *M*.

Table 1

Cyclic Voltammetry Data, of TTF's **6a**, **7a** and **11** in CH_2Cl_2 on a Platinum Electrode, Concentration of ($4.0x10^{-5}$ *M*), Scan rate 200mVs^{-1}, Base-Electrolyte TBAP 0.1 *M*

TTF	$E^{1/2}$ (1)/V	$E^{1/2}$ (2)/V	$\Delta E^{1/2}$/V
DB-TTF **11**	7.79	11.72	2.94
DPh--TTF **6a**	4.21	6.04	1.83
TTF-DME **7a**	4.91	6.53	1.62

As shown in Figure 2, increasing the scan rate from 20 mVs^{-1} to 400 mVs^{-1} leads to the increasing of the oxidation potential wave. Compounds **6a** and **7a** also showed some common features depending on the scan rates effect. In CH_2Cl_2 on a Pt electrode and at ambient temperature the TTF **6a** and **7a** showed two oxidation waves at peak potentials of 550 mV, 979 mV for **6a**, and 763 mV, 1108 mV for **7a** at scans rates 200 mVs^{-1}. For **6a** and **7a**, such a process is electrochemically reversible or quasi-reversible (ΔEp^1 85 mV and ΔEp^2 97 mV) for **6a** and (ΔEp^1 90 mV and ΔEp^2 92 mV) for **7a** respectively. The ΔEp^2 was also observed with the increase of scan rate from 20 mV to 400 mVs^{-1} at ambient temperature as shown in Figure 2.

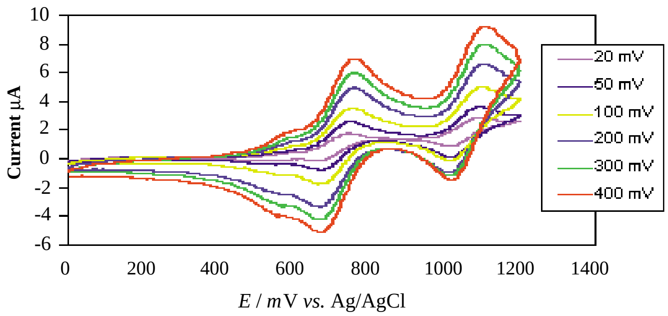


Figure 2. Cyclic volatmmogram of TTF-DME **7a** in CH_2Cl_2 on a platinum electrode, concentration of ($4.0x10^{-5}$ *M*). Scan rate 20 ~ 400 mVs^{-1}, base-electrolyte TBAP 0.1 *M*.

Conclusion.

The TTF's **6a**, **7a** and **11** were synthesized using the methods described in this text and their structures were confirmed by spectral analyses. The electrochemical behaviors of these compounds were studied using cyclic voltammetry at ambient temperature on a Pt working electrode, using TBAP as the supporting electrolyte. The CV exhibited good donor properties, showing a two-electron quazireversible oxidation wave to the dications TTF^{2+}. The oxidation potential values, and in a larger extent the reduction potential values processes, are strongly influenced by the scan rates. A two-electron redox behavior was observed as two waves. The advantage of introducing the electron-withdrawing ester substituents into the donor **7a** is that ester group raises the oxidation potentials relative to TTF [20].

Considering the fact that these donors contain two similar types of donor moieties, it was important to determine the oxidation/reduction process by changing the scan rates. Thereby a double two-electron oxidation process encountered quasireversible process in CH_2Cl_2 as a solvent.

EXPERIMENTAL

Melting points were recorded on a Gallencamp melting point apparatus and are uncorrected. Infrared spectra (IR) were measured on a Hitachi 260-10 spectrometer (Hitachi Ltd, 1-5-1, Marunouchi, Chiyod-ku, Tokyo, Japan). ^{1}HNMR and ^{13}CNMR spectra were recorded at room temperature on INOVA-Varian Nuclear Magnetic Resonance Spectrometer (500 MHz). Chemical shifts are denoted in δ units (ppm), relative to tetramethylsilane (TMS) as internal standard, J values are given in Hz. $CDCl_3$ is used as a deuterated solvent unless otherwise stated. MS and FAB-MS spectra were obtained using a JEOL JMS-AX505HA (Nihon Denshi Ltd, 3-1-2, Musashino, Akishima-shi, Tokyo, Japan). Cyclic voltammetry was measured on a cyclic voltammogram spectrometer (Model CS-1090/Model CS-1087, Cypress System Inc., Lawrence, Kansas, USA). Column chromatography was performed on silica gel 60 (230-400 Mesh ASTM). Solvents were distilled before use. 4-Phenyl-1,3-dithiole-2-thione (**5a**) was obtained according to the reported method as yellow crystals in 44% yield, mp 117-118 °C, lit. 117-118 °C [17].

Methyl phenylpropiolate (**4**).

A mixture of phenyl acetylene (**3**; 1.02 g, 10.0 mmol) and sodium metal (0.26 g, 11.3 mmol) was stirred at room temperature for one hour. The sodium acetylide thus formed is dissolved in ether (25 ml) and methyl chloroformate (1.0 ml) in ether (10 ml) was added drop wise with stirring over a period of 15 minutes. The reaction mixture is stirred at room temperature for further 5 hours. The ether is removed under vacuum and the residue washed with water, the dark brown oil thus formed is extracted by ether and dried over sodium sulfate. The reaction mixture is filtered off and chromatographed on silica gel using hexane/ethyl acetate mixture (10:3) to give 0.630 g of yellow oil of the corresponding methyl phenylpropiolate (**4**) in 40.5% yield; ir (neat) ν 3023w, 2952m, 2225m, 1712s, 1596w, 1496s, 1434s, 1288s, 1201s, 1170s, 757s, 688s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.6-7.5 (dd, J = 8 Hz, J = 1 Hz, 2H, aromatic-H), 7.4 (m, 3H, aromatic-H), 3.84 (s, 3H, OCH_3); ms: m/z 160 (M^+).

4-Methoxycarbonyl-5-phenyl-1,3-dithiole-2-thione (**5b**).

Following the method reported in reference [17], a mixture of methyl phenylpropiolate (**4**; 2.73 g, 17 mmol) and bis-morphiline disulfide (1.0 g, 4.0 mmol) in a 4:1 molar ratio was dissolved in 75 ml of CS_2, and the resulting solution was poured in a one liter Parr bomb reactor (autoclave). The apparatus was flushed with N_2 and heated to 140 °C for 24 hours. The Pressure was raised to 140 psi. After cooling, the apparatus was opened, the brown solution was transferred to a round-bottom flask, and the excess carbon disulfide was removed under vacuum. The dark residue was chromatographed on silica gel using hexane/chloroform as an eluent to give in the second fractions the 4-methoxycarbonyl-5-phenyl-1,3-dithiole-2-thione (**5b**) as yellow crystals, 1.3 g, 28.4% yield, mp. 87-89 °C; ir (KBr): ν 3060m, 3027m, 2962s, 1727s, 1577m, 1544s, 1488s, 1434s, 1268s, 1211s, 1083s, 761s, 732s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.4 (m, 5H, aromatic-H), 3.7 (s, 3H, OCH_3); ms: m/z 268 (M^+).

Synthesis of Tetrathiafulvalenes (TTF-DME) **7a-b** and 2-Dimethoxyphosphinyl-1,3-dithiole derivatives (**8b**).

A sample of **5b** (0.2 g, 0.74 mmol) was refluxed in trimethylphosphite (3.0 ml) for 2 hours. The reaction mixture was cooled, diluted with methanol and kept over night at room temperature. The brown crystals thus formed, were collected by filtration to give 36 mg, 10% yield of *cis-trans* isomers of TTF-DME **7a-b** (M^+ = 472). The residue was concentrated under vacuum and chromatographed on silica gel, hexane/chloroform 1:1 to give **8b** as brown yellow oil, 95 mg 37% yield, M^+ = 346.

cis-trans-Tetrathiafulvalenes (**7a-b**).

Compounds **7a-b** have ir (KBr): ν 1722s, 1637s, 1556m, 1430m, 1257s, 1203s, 1058w, 738s, 688s cm^{-1}; ^{1}H nmr ($CDCl_3$, 500 MHz): δ 7.41-7.39 (m, 10H, aromatic-H), 3.67 (s, 6H, OCH_3), 3.65 (s, OCH_3); ^{13}C nmr ($CDCl_3$, 125 MHz): δ 159.82 (CO, ester), 148.67, 148.29 (C-4), 131.22, 129.89, 129.87, 128.99, 128.96, 128.28 (aromatic-C), 119.96, 119.60 (C-5), 108.57, 108.40 (C=C), 52.43 (OCH_3); ms: m/z 472 (M^+).

cis-Tetrathiafulvalene (TTF-DME **7a**).

Compound **7a** has ir (KBr): ν 1722s, 1637s, 1556m, 1430m, 1257s, 1203s, 1058w, 738s, 688s cm^{-1}; ^1H nmr ($CDCl_3$, 500 MHz): δ 7.41-7.39 (m, 10H, aromatic-H), 3.65 (s, 6H, OCH_3); ms: m/z 472 (M^+).

4-Methoxycarbonyl-5-phenyl-2-dimethoxyphosphinyl-1,3-dithiole (**8b**).

Compound **8b** has ir (neat): 3056w, 2954s, 2925s, 2854s, 1731s, 1563m, 1461s, 1376s, 1294s, 1259s, 1039s, 755m cm^{-1}; ^1H nmr ($CDCl_3$, 500 MHz): δ 7.39-7.35 (m, 5H, aromatic-H), 4.82-4.81 (d, J = 5Hz, 1H, CH-$2_{AB\ system}$), 3.96-3.76 (m, 2 OCH_3 and 1H, CH-$2_{AB\ system}$) 3.62 (s, 3H, OCH_3); ^{13}C nmr ($CDCl_3$, 125 MHz): δ 160.84 (CO, ester), 147.22 (C-4), 131.11, 129.82, 129.11, 128.18 (aromatic-C), 117.11 (C-5), 55.03, 54.38 (2 OCH_3), 52.2 (OCH_3), 41.68 (PCH-2); ms: m/z 346 (M^+).

Synthesis of Tetrathiafulvalenes (DPh-TTF) **6a-b** and 2-Dimethoxyphosphinyl-1,3-dithiole derivatives (**8a**).

According to the method described for synthesis of TTF-DME **7a-b** and 1,3-dithiole derivative **8b**, the DPh-TTF **6a-b** and **8a** were obtained after chromatography using silica gel (hexane/chloroform 1:1) in 26% and 35.9% respectively

cis-trans-Tetrathiafulvalenes (DPh-TTF) **6a-b**.

Compounds **6a-b** were obtained in 26% yield (40 mg), mp 206-208 °C, Lit [2a], mp 208 °C; ir (KBr): ν 1590m, 1565s, 1548s, 1488s, 1440s, 1250m, 1205m, 1031m, 921s, 823s, 738s, 698s cm^{-1}; ^1H nmr ($CDCl_3$, 500 MHz): δ 7.43-7.25 (m, 10H, aromatic-H), 6.55 (s, 2H, trans-CH-5), 6.52 (s, 2H, cis-CH-5); ^{13}C nmr ($CDCl_3$, 125 MHz): δ 136.10 (C-4), 132.47, 128.96 (aromatic-C), 128.47, 126.28 (aromatic-CH), 113.37, 113.30 (C=C), 110.52 (CH-5); FAB-ms: m/z 356 (M^+).

cis-Tetrathifulvalenes (DPh-TTF) (**6a**).

Compound **6a** has ^1H nmr ($CDCl_3$, 500 MHz): δ 7.43-7.29 (m, 10H, aromatic-H), 6.52 (s, 2H, CH-5 and CH-5').

4-Phenyl-2-dimethoxyphosphinyl-1,3-dithiole (**8a**).

Compound **8a** was obtained in 35.9% yield (250 mg), mp 85-87 °C, Lit. mp 87-88 °C[21]; ir (KBr): 3054w, 2950m, 2850w, 1560m, 1462s, 1372s, 1290s, 1251s, 1064s, 1037s, 746s, 665s cm^{-1}; ^1H nmr ($CDCl_3$, 500 MHz): δ 7.40-7.31 (m, 5H, aromatic-H), 6.23 (s, 1H, CH-5), 5.06-5.05 (d, J = 4.5 Hz, CH-2), 3.91 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3).

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* E-mail: elwareth@acc.aun.eun.eg; Permanent Address: Chemistry Department, Faculty of science, Assiut University, Assiut 71516, Egypt.

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