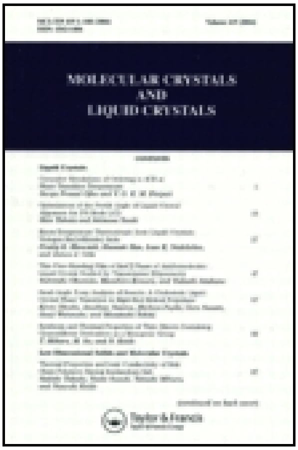

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SYNTHESIS AND PROPERTIES OF HIGHER HOMOLOGUES OF BIS-FUSED TTF

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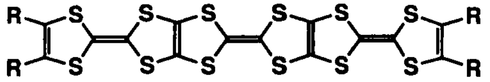
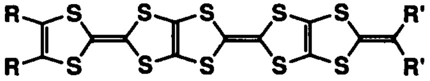
Abstract Several derivatives of higher homologues of bis-fused TTF, BDT-TTPY (**1**) and DT-TTP (**2**), have been synthesized. Cyclic voltammograms of **1** and **2** consist of three-pairs of double-electron and five-pairs of single electron redox waves, respectively. Most of cation radical salts obtained by the chemical doping with appropriate oxidants showed relatively high conductivity ($\sigma_{rt} = 10^{-2}$-10^{1} S cm^{-1} on compressed pellets).

INTRODUCTION

Multi-fused TTFs are of considerable interest as promising donors for organic metals that are stable down to low temperatures.[1,2] Recently we have prepared a bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) and its derivatives,[1] several of which have produced many metallic cation radical salts with various anions.[1,2] In this context, higher homologues of BDT-TTP are also interesting as promising donor components for organic metals as well as multi-redox systems. Among them, the synthesis of a tris-fused TTF, 2,2'-bi[5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalen-ylidene] (BDT-TTPY, **1**) substituted with strongly electron-withdrawing trifluoromethyl groups has already been reported,[3] its properties, particularly redox behavior and preparation of conducting salts have not been described. We report herein the synthesis and electrochemical properties of several derivatives of BDT-TTPY (**1A**-**E**) and BDT-



BDT-TTPY (**1**)
1A, R = H
1B, R = Me
1C, R = SMe
1D, R = SEt
1E, R = $SC_6H_{13}{}^n$



DT-TTP (**2**)
2Bb, R = Me, R' = Et
2Bc, R = Me, R' = Pr^n
2Ca, R = SMe, R' = Me
2Cb, R = SMe, R' = Et
2Cc, R = SMe, R' = Pr^n
2Da, R = SEt, R' = Me

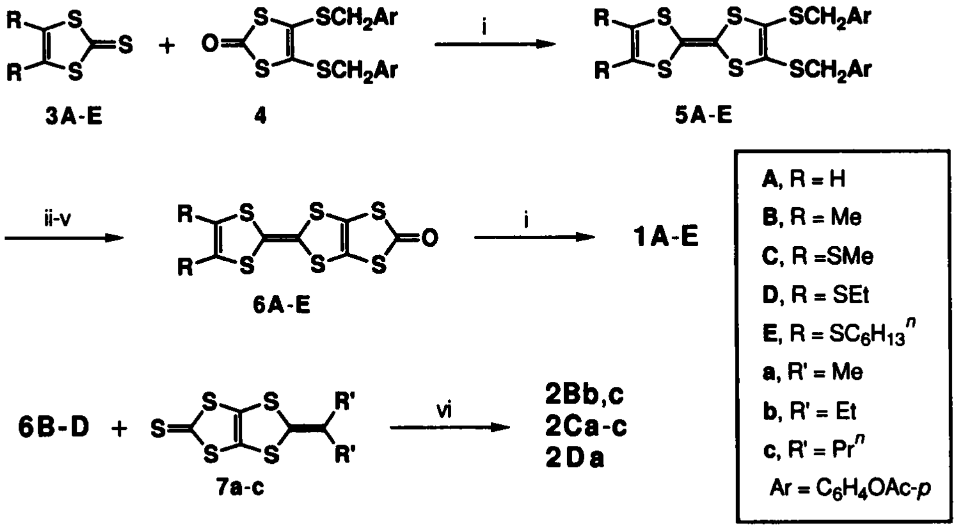
TTPs fused with 1,3-dithiol-2-ylidenes (DT-TTP, **2**). The latter ones are also regarded as higher homologues of 2-methylidene-1,3-dithiolo[4,5-*d*]-TTF (DT-TTF),[4] several of which have produced metallic cation radical salts down to low temperatures (≤4.2 K) with κ-type arrangement of donors.[5] Furthermore, conducting properties of their cation radical salts are reported.

RESULTS AND DISCUSSION

Synthesis

The synthesis of BDT-TTPYs and DT-TTPs was achieved as shown in Scheme I. 1,3-Dithiole-2-thione derivatives (**3A-E**) 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)-TTFs (**5A-E**) in 40-84% yields. The acetoxybenzyl groups of **5A-E** were removed by treatment with an excess 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 **6A-E** in 50-77% yields. The compounds

SCHEME I

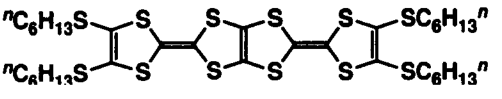


i, $P(OEt)_3$, 110 °C, 2 h; ii, NaOMe (8 equiv.), CH_2Cl_2-MeOH (1:3, v/v), room temp., 1 h; iii, $ZnCl_2$, 30 min; iv, *n*-Bu_4NBr, 30 min; v, $(Cl_3CO)_2CO$, THF, -78 °C - room temp., 1 h; vi, $P(OMe)_3$-toluene (1:1, v/v), 110 °C, 2 h.

6A-E were heated in neat triethyl phosphite at 110 °C gave the corresponding BDT-TTPY derivatives **1A-E** in 30-46% yields. On the other hand, DT-TTP derivatives **2** were obtained in 41-60% yields by cross-coupling between **6B-D** and 1,3-dithiol-2-thiones fused with 1,3-dithiol-2-ylidenes (**7a-c**) in trimethyl phosphite-toluene (1:1, v/v) at 110 °C. An attempt to introduce 1,3-dithiol-2-ylidene moiety by the alternate cross-coupling reaction between **7a** and **4** resulted in considerable decrease of the yield of the desired product (<10%). All the donors were obtained as stable solids which are sparingly soluble in organic solvents. A comparison of the electronic spectrum of **1E** with those of corresponding BDT-TTP **8**[6] and TTF **9**[7] revealed that there was no large shift of the absorption maxima among those donors (Table I), although absorption coefficients tend to increase as the number of TTF units increases.

TABLE I Absorption maxima of 1E and its related compounds in $CHCl_3$.

Compound	λ_{max}/nm(log ε)		
1E	370 (sh, 3.99)	325 (4.44)	284 (4.40)
8	380 (sh, 3.58)	324 (4.23)	290 (4.20)
9	390 (sh, 3.58)	335 (4.14)	310 (4.13)



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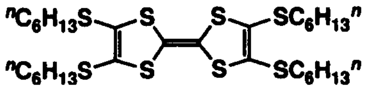

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Electrochemical Properties

Electrochemical properties of new donors were investigated by cyclic voltammetry, and the results are summarized in Tables II and III. Satisfactory voltammograms could be obtained only for **1E** and **2Cc** owing to solubility problem in organic solvents. Figure 1 shows cyclic voltammogram of **1E** in benzonitrile-carbon disulfide (1:1, v/v). Thus, two pairs of quasi-reversible waves and a pair of irreversible one were observed at +0.67, +0.92, and +1.43 V (vs. SCE), respectively. The first redox wave is broad and its peak current at a constant concentration is about twice as large as that of **8**. 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.[8] Furthermore, the peak currents of all waves are almost equal to each other, suggesting that redox process of **1E** is composed of three stages of double-electron transfer to form a hexacation, which is in agreement with the fact that **1E** has six redox-active 1,3-dithiole rings. The first redox potential of **1E** is higher by 0.02 and 0.05 V than those of the

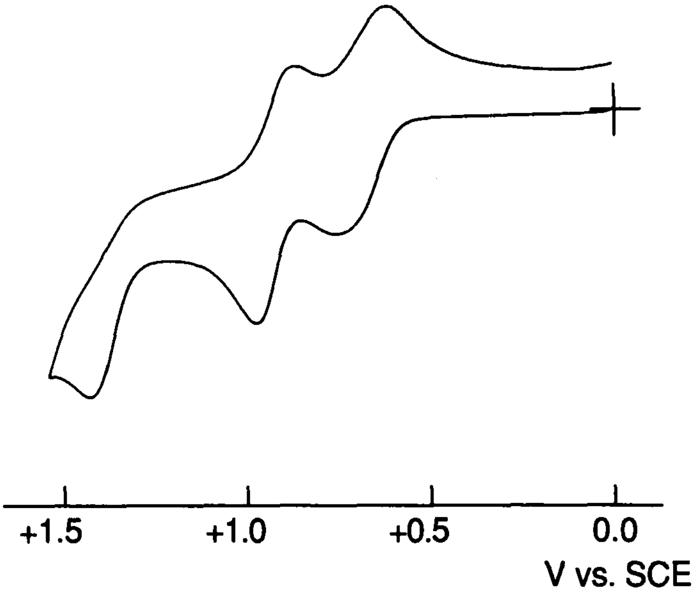


FIGURE 1 Cyclic voltammogram of **1E** in benzonitrile-carbon disulfide (1:1, v/v).

TABLE II Redox potentials of **1E** and its related compounds.[a]

Compound	E_1	E_2	E_3	E_4		E_2-E_1
	E_{m1}[b]		E_{m2}[c]		E_{m3}[d]	
1E	+0.67		+0.92		+1.43[e]	—
8	+0.65	+0.81	+1.08	+1.20	—	0.16
9	+0.62	+0.86	—	—	—	0.24

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

corresponding BDT-TTP (**8**) and TTF (**9**) derivatives, respectively. This result suggests that electron donating ability rather decreases by extension of apparent π-conjugation due to increase of TTF units. On the other hand, the E_2-E_1 value is getting smaller as the number of fused TTF units increases, indicating that the on-site Coulomb repulsion in dication decreases in the same order.

Cyclic voltammogram of **2Cc** in benzonitrile is shown in Figure 2. Thus, **2Cc** shows four-pairs of reversible redox waves and a irreversible one. The anodic peak current of the redox wave in the highest potential region is larger than those of the other redox waves. Considering the facts that this wave is irreversible and that **2Cc** has five

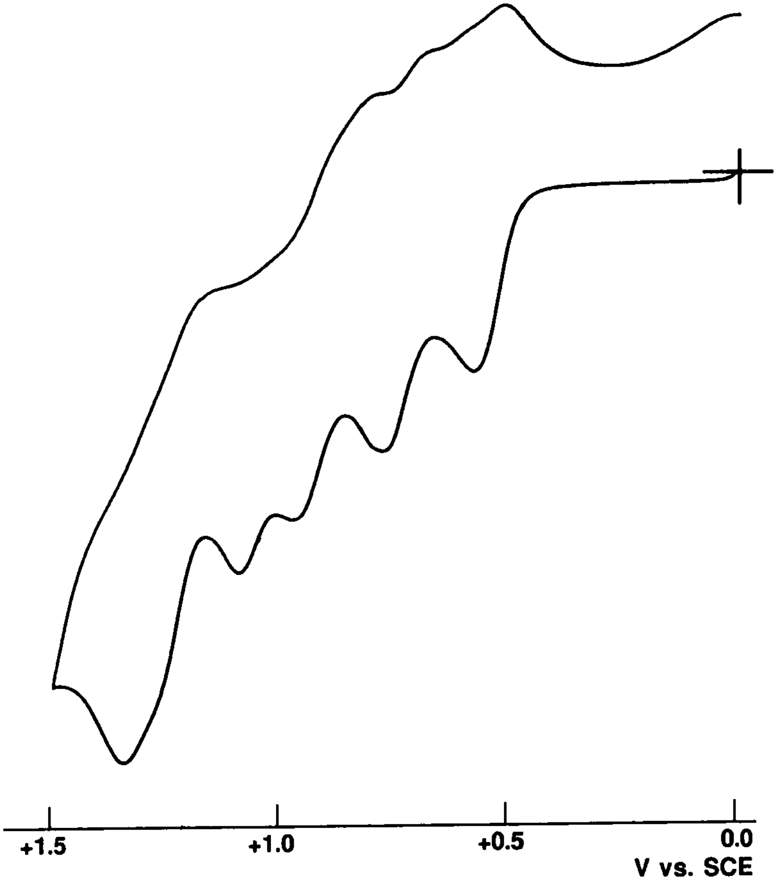
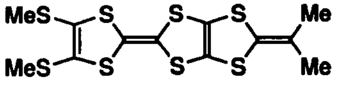


FIGURE 2 Cyclic voltammogram of 2Cc in benzonitrile.

TABLE III Redox potentials of 2Cc and their related compounds.[a]

Compound	E_1	E_2	E_3	E_4	E_5	$E_2 - E_1$
2Cc	+0.50	+0.70	+0.88	+1.06	+1.33[b]	0.20
10	+0.50	+0.75	+1.39[b]			0.25
11	+0.53	+0.72	+0.99	+1.11		0.19

[a] 0.1 M n-Bu$_4$NClO$_4$ in PhCN, V vs. SCE, Pt electrode, 25 °C. [b] Irreversible step. Anodic peak potential.



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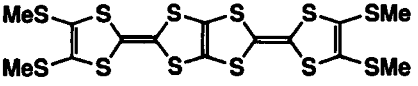

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redox-active 1,3-dithiol-2-ylidenes, the last stage of redox may correspond to one-electron transfer followed by an undefined chemical reaction. The redox potentials are listed in Table III along with those of a bis(methylthio) substituted DT-TTF (**10**) and tetrakis(methylthio)-BDT-TTP (**11**). The E_1 value of **2Cc** (+0.50 V) is comparable to those of **10** (+0.50 V) and **11** (+0.53 V) measured under the identical conditions, suggesting the donating ability is not enhanced by extension of π-conjugation similar to the case of BDT-TTPY. On the other hand, the E_2-E_1 value is smaller by 0.05 V than that of **10**, but is same as that of **11**.

Preparation and Conducting Properties of Cation Radical Salts

Charge-transfer complexes and cation radical salts of BDT-TTPY donors could not be prepared by the usual mixing or electrochemical oxidation method owing to their extremely low solubility in common organic solvents. However, chloroform suspensions of them were doped with *n*-Bu_4NI_3 or I_2 to give the corresponding iodine salts as black powder. In a similar manner, the SbF_6 salts of **1A** and **B** were obtained using the corresponding nitronium salt as the dopant. Because DT-TTP derivatives are more soluble than BDT-TTPYs, their iodine complexes were obtained by mixing with *n*-Bu_4NI_3 or I_2 in hot chlorobenzene solution.

TABLE IV Conducting properties of cation radical salts of **1** and **2** ($D \cdot A_x$).

Donor	Acceptor	x^a	σ_{rt} / Scm^{-1} [b]	E_a / eV
1A	I_3[c]	0.64(I)	2.4	0.017
	SbF_6	1.2(Sb)	1.8×10^{-1}	0.057
1B	I_3[c]	0.45(I)	2.1	0.041
	SbF_6	1.2(Sb)	3.5×10^{-5}	0.12
1C	I_3[d]	0.68(Anal.)	16	0.030
1D	I_3[d]	0.83(Anal.)	2.0	0.033
1E	I_3[d]	0.72(Anal.)	7.1×10^{-1}	0.055
2Bb	I_3[c]	0.43(Anal.)	1.6	0.026
2Ca	I_3[d]	0.48(I)	8.5×10^{-1}	0.033
2Cb	I_3[d]	0.71(I)	4.2×10^{-2}	0.088
2Da	I_3[d]	0.77(Anal.)	9.3×10^{-2}	0.049

[a] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. Anal. designates the value determined from elemental analyses. [b] Room temperature conductivity measured by four-probe technique on a compressed pellet. [c] Prepared using *n*-Bu_4NI_3. [d] Prepared using I_2.

Electrical conductivities were measured using a four-probe technique on compressed pellets, and the results are summarized in Table IV. Most of the salts based on BDT-TTPY derivatives showed relatively high conductivities of 10^{-1}-10^{1} Scm^{-1} at room temperature. However, all of them exhibited semiconductive temperature dependence with small activation energies (E_a = 0.017-0.055 eV). On the other hand, room temperature conductivities of I_3 salts based on DT-TTP donors were in the range of 10^{-2}-10^{0} Scm^{-1}. Among them, the salts of **2Bb** and **2Ca** showed high conductivities ($\sigma_{rt} \approx 10^{0}$ Scm^{-1}). Though both salts displayed semiconducting behavior with small E_a values (≈0.03 eV), they are expected to show metallic behavior on single crystals.

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