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Synthesis of New Unsymmetrical Multi-Sulfur TTF Derivatives

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Synopsis. Multi-sulfur TTF derivatives with eight or nine sulfur atoms were synthesized for the development of new conducting organic salts. Their oxidation potentials were measured, and compared with those of the related donor molecules. The electrical conductivities of some of the ion radical salts were measured.

Most of the metallic conducting and superconducting organic solids have been made as the charge-transfer complexes or ion radical salts of tetrathiafulvalene (TTF) and its derivatives.[1] Although a number of studies have been done on complexes of symmetrical TTF derivatives, unsymmetrical TTF derivatives have also drawn much attention because of the discovery of the superconducting ion radical salts of DMET[2] and MDT-TTF.[3] The synthesis of the unsymmetrical TTF derivatives[4] is important, because the kind of the donor molecules can be extended widely by the cross-coupling reaction of known precursor molecules. Furthermore, the effects of the modification of the symmetrical donor site on the structural and electrical properties of the complexes have not been studied in detail. This paper reports the synthesis and oxidation potentials of the unsymmetrical multi-sulfur TTF derivatives, 4,5-trimethylenedithio-4′,5′-(vinylenedithio)tetrathiafulvalene (TMVT), 4,5-[thiobis(methylenethio)]-4′,5′-(vinylenedithio)tetrathiafulvalene (TMTVT), 4,5-[thiobis(methylenethio)]-4′,5′-(ethylenedithio)tetrathiafulvalene (TMTET), 4,5-ethylenedithio-4′,5′-(methylvinylenedithio)tetrathiafulvalene (EMVT), and 4,5-ethylenedithio-4′,5′-(dimethylvinylenedithio)tetrathiafulvalene (EDMVT). We have also tried to synthesize 4,5-methylenedithio-4′,5′-(vinylenedithio)tetrathiafulvalene (MVT) (Chart 1). Electrochemical crystallization of these donor molecules gave several ion radical salts, and their electrical conductivities were measured at room temperature.

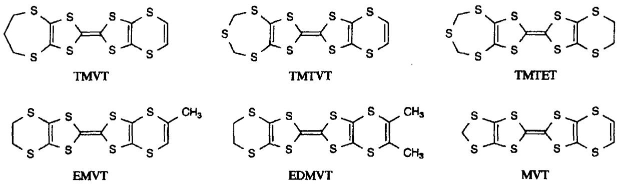
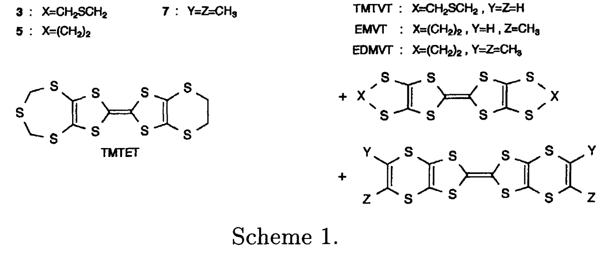


Chart 1.

Results and Discussion

Synthesis of Unsymmetrical TTF Derivatives. Cross-coupling reactions of 4,5-methylenedithio-1,3-dithiole-2-thione (**1**),[5] 4,5-trimethylenedithio-1,3-dithiole-2-thione (**2**),[6] and 1,3-dithiolo[4,5-*f*][1,3,5]trithiepin-2-thione (**3**)[7] with 4,5-vinylenedithio-1,3-dithiol-2-one (**4**)[8] gave MVT, TMVT, and TMTVT respectively (Scheme 1). TMVT and TMTVT were obtained as main products. On the other hand, MVT and bis(vinylenedithio)tetrathiafulvalene (VT) were obtained in almost comparable yields, judging from a mass spectrum; bis(methylenedithio)tetrathiafulvalene (MT) were not obtained. TMTET was obtained as a main product by the cross-coupling reaction of **3** with 4,5-ethylenedithio-1,3-dithiole-2-thione (**5**). EMVT and EDMVT were obtained as main products by the cross-coupling reactions of **5** with 4,5-(methylvinylenedithio)-1,3-dithiol-2-one (**6**)[8] and 4,5-(dimethylvinylenedithio)-1,3-dithiol-2-one (**7**)[9] respectively. It is fortunate that, although the reaction products have similar molecular structures, the cross-coupling product (unsymmetric product) can easily be separated from the homocoupling products (symmetric products) by silica-gel column chromatography for TMVT, TMTVT, TMTET, EMVT, and EDMVT.

Oxidation Potentials of Unsymmetrical TTF Derivatives. Cyclic voltammetries of TMVT, TMTVT, TMTET, EMVT, and EDMVT were measured for THF solutions by using tetrabutylammonium perchlorate as an electrolyte and platinum plates as electrodes. All of them gave only one redox wave. Figure 1 shows the first-wave oxidation potentials ($E_{1/2}(1)$ vs. SCE) of symmetrical[8,9] and unsymmetrical TTF derivatives[10] measured in THF solutions. This figure clearly shows that $E_{1/2}$ of an unsymmetrical TTF derivative is between those of the corresponding two



Scheme 1.

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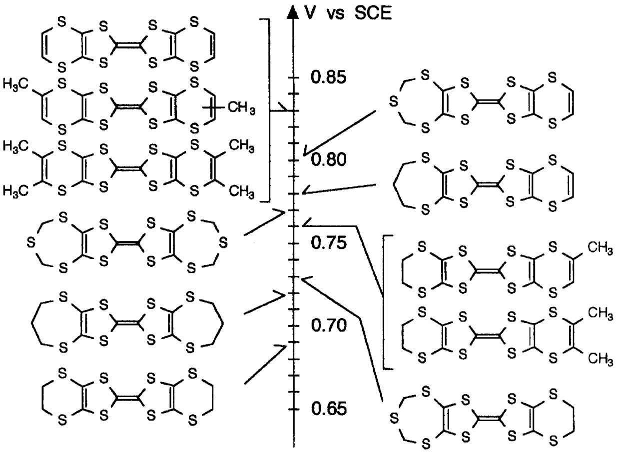

Fig. 1. First half-wave oxidation potentials (V vs. SCE) of symmetric and unsymmetric multi-sulfur TTF derivatives in THF solution.

symmetrical TTF derivatives.

Electrical Conductivities of Ion Radical Salts. Electrochemical crystallization of these donor molecules was done in several solvents. Only TMVT and TMTET gave several good quality single crystals. Table 1 summarizes ion radical salts, solvents used for the electrochemical crystallization, electrical conductivities at room temperature measured by the four-probe method, and crystal shapes. The compositions of the ion radical salts were identified by elemental analysis. TMVT salts were poor conductors with the conductivities of the order of 10^{-4} S cm^{-1}. On the other hand, TMTET salts were much more conductive with conductivities of 10^{-1}—10^{0} S cm^{-1}.

Experimental

4,5-Trimethylenedithio-4′,5′-(vinylenedithio)tetrathiafulvalene (TMVT). To a mixture of 4,5-trimethylenedithio-1,3-dithiole-2-thione[6] (0.52 g, 2.2 mmol) and 4,5-vinylenedithio-1,3-dithiol-2-one[8] (0.45 g, 2.2 mmol), we added triethyl phosphite (10 ml) that had been freshly distilled. The temperature of the solution was elevated gradually to 110 °C with stirring under a nitrogen atmosphere; the solution was stirred for another 2 h at 110 °C. After cooling to room temperature, the precipitate was collected, washed with methyl alcohol, and dried under vacuum. The crude products were then chromatographed on a silica-gel column by using carbon disulfide as an eluent; the second main fraction gave almost pure TMVT (0.51 g, 58%). Recrystallization from benzene gave yellow needles. Mp 231—232 °C (decomp). MS m/z 396 (M^+). Calcd for $C_{11}H_8S_8$: C, 33.30; H, 2.30; S, 64.67%. Found: C, 33.37; H, 1.94; S, 64.43%. ^{1}H NMR (CS_2) $\delta=2.50$ (2H, m), 2.72 (4H, t), 6.52 (2H, s). $\lambda_{\max}^{\mathrm{THF}}$ ($\log\varepsilon$) 338.8 (4.15), 308.0 nm (4.13).

Other TTF Derivatives. MVT, TMTVT, TMTET, EMVT, and EDMVT were synthesized under similar reaction conditions to those described for TMVT by the cross-coupling reactions shown in Scheme 1. MVT could not be separated well from VT by column chromatography or HPLC.

Table 1. Ion Radical Salts, Solvents for Electrochemical Crystallization, Electrical Conductivities at Room Temperature, and Crystal Shapes of TMVT and TMTET Salts

Salts	Solvents	Conductivities	Shapes
		S cm^{-1}	
$TMVT_2PF_6$	THF	8.8×10^{-4}	Plates
$TMVT_2AsF_6$	THF	4.5×10^{-4}	Plates
$TMTET_2PF_6$	C_6H_5Cl	2.5×10^{-1}	Plates
$TMTET_2AsF_6$	C_6H_5Cl	2.0	Plates
$TMTET_2IBr_2$	THF	1.2	Needles
$TMTET_2AuBr_2$	o-$C_6H_4Cl_2$	2.1×10^{-1} [a]	Powders
$TMTET_2AuCl_2$	o-$C_6H_4Cl_2$	1.9	Needles

a) Measured on compressed pellet samples.

TMTVT: Yield 45%. Orange needles. Mp 225—227 °C (decomp). MS m/z 414 (M^+). Calcd for $C_{10}H_6S_9$: C, 28.96; H, 1.46; S, 69.58%. Found: C, 28.95; H, 1.33; S, 69.81%. ^{1}H NMR (CS_2) $\delta=3.94$ (4H, s), 6.52 (2H, s). $\lambda_{\max}^{\mathrm{THF}}$ ($\log\varepsilon$) 338.2 (4.14), 306.6 nm (4.14).

TMTET: Yield 58%. Orange needles. Mp 233—235 °C (decomp). MS m/z 416 (M^+). Calcd for $C_{10}H_8S_9$: C, 28.82; H, 1.93; S, 69.25%. Found: C, 28.93; H, 1.78; S, 68.82%. ^{1}H NMR (CS_2) $\delta=3.28$ (4H, s), 3.90 (4H, s). $\lambda_{\max}^{\mathrm{THF}}$ ($\log\varepsilon$) 342 (4.08), 316 nm (4.20).

EMVT: Yield 61%. Orange needles. Mp 210 °C (decomp). MS m/z 396 (M^+). Calcd for $C_{11}H_8S_8$: C, 33.30; H, 2.03; S, 64.66%. Found: C, 33.40; H, 1.89; S, 64.39%. ^{1}H NMR (CS_2) $\delta=2.23$ (3H, s), 3.26 (4H, s), 6.02 (1H, s). $\lambda_{\max}^{\mathrm{THF}}$ ($\log\varepsilon$) 346 (4.02), 318 nm (4.12).

EDMVT: Yield 49%. Yellow needles. Mp 217 °C (decomp). MS m/z 410 (M^+). Calcd for $C_{12}H_{10}S_8$: C, 35.09; H, 2.45; S, 62.46%. Found: C, 35.08; H, 2.30; S, 62.35%. ^{1}H NMR (CS_2) $\delta=2.03$ (3H, s), 3.28 (2H, s). $\lambda_{\max}^{\mathrm{THF}}$ ($\log\varepsilon$) 347 (4.06), 318 nm (4.15).

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