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Multi-Tetrathiafulvalene Systems. New Donors Containing Two or Three Tetrathiafulvalene-Substituents at 1,3- and 1,3,5-Positions of Aromatic Rings

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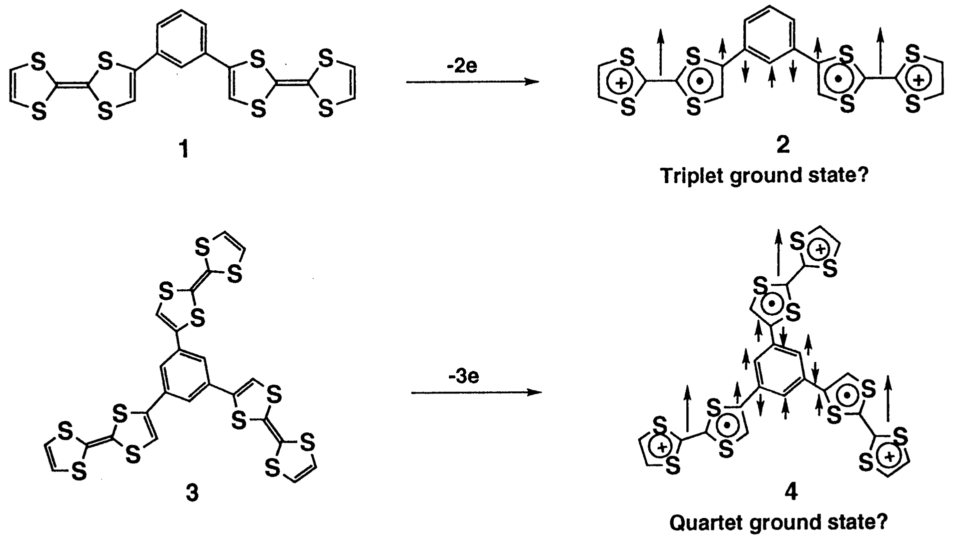
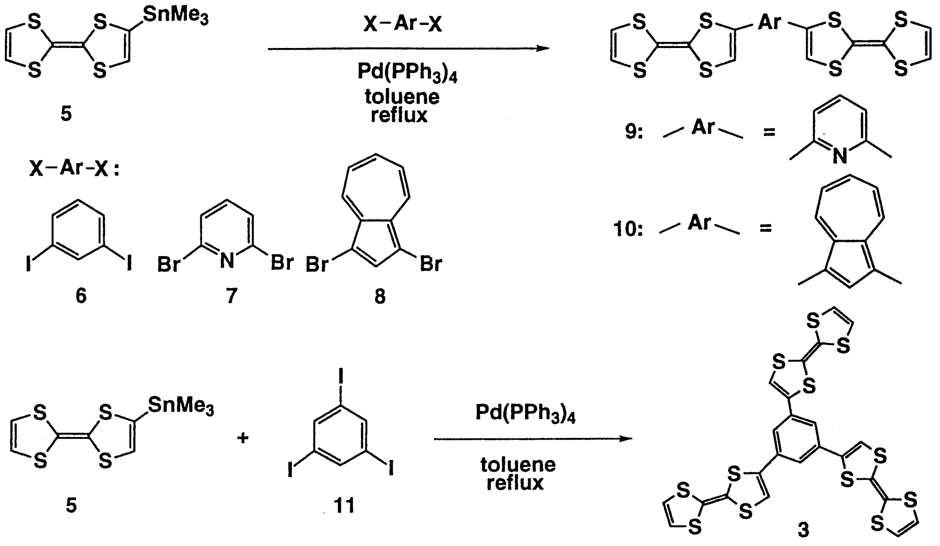
New donors having two or three tetrathiafulvalene moieties at 1,3- and 1,3,5-positions of the aromatic rings have been synthesized in order to examine the interactions of tetrathiafulvalene radical-cations in the diradical-dication or triradical-trication states. The molecular structures of two neutral donors have been determined and the conductivity of the CT complexes of the new donors have been measured.

Conjugated systems containing two or three tetrathiafulvalene (TTF) units can be expected to show intramolecular and intermolecular interactions of TTF units either in solution or in solid state.1) If two or three TTF units are introduced at 1,3- or 1,3,5-position of aromatic rings, a ferromagnetic interaction between TTF units might occur in the CT complex or radical-cation salts which are usually known to show high conductivity.2) Thus, the diradical-dication **2** and the triradical-trication **4** derived from **1** and **3** would be expected to have triplet and quartet ground states, respectively, if two and three TTF radical-cations show a ferromagnetic interaction shown in Scheme 1.3)



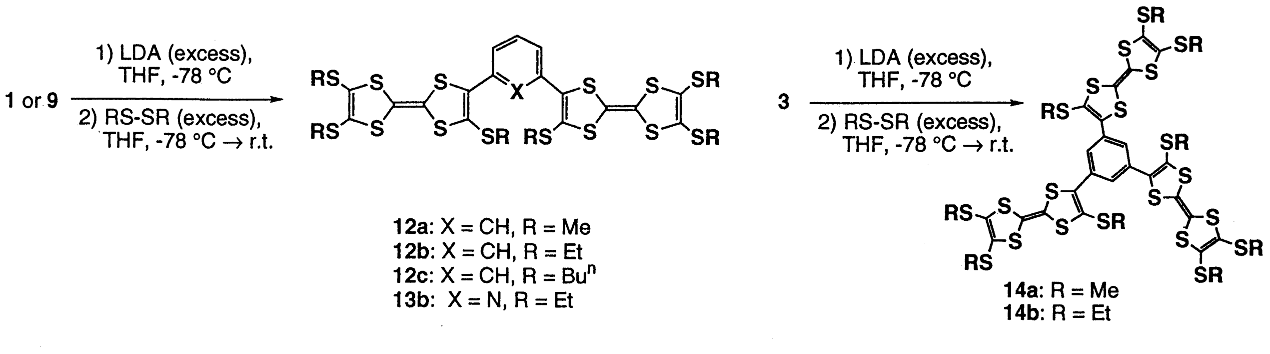
Scheme 1. Possible interaction between TTF radical-cations.

For constructing frameworks of the title compounds, we applied the palladium-catalyzed cross-coupling reaction as shown in Scheme 2.4) The reaction of aryl dihalides (**6**-**8**) with 2 equiv. of trimethylstannyl-TTF **5** in refluxing toluene in the presence of $Pd(PPh_3)_4$ (10-20 mol%) gave the desired products [**1** (77%), **9** (72%), and **10** (74%)].[5] In a similar manner, the palladium-catalyzed cross-coupling reaction of 1,3,5-triiodobenzene (**11**) with **5** in refluxing toluene for 5 h afforded **3** in 72% yield.[5]



Scheme 2. Synthesis of **1**, **3**, **9**, and **10**.

Because of the very low solubility of **1**, **3**, **9** and **10** in common organic solvents, TTF moieties of these compounds were converted into the corresponding alkylthio derivatives using lithiation of TTF parts, followed by treatment with dialkyldisulfides (Scheme 3). Thus, **1** was allowed to react with 10-12 equiv. of lithium diisopropylamide (LDA) at -78 °C in THF, followed by treatment with 10-12 equiv. of RSSR in THF at -78 °C to room temperature to produce the corresponding hexaalkylthio derivatives (**12a**: 54%; **12b**: 55%; **12c**: 63%).[5] Similary the reaction of **9** and **3** with excess amounts of LDA in THF at -78 °C, followed by treatment with excess amounts of RSSR afforded the corresponding hexaalkylthio and nonaalkylthio derivatives, respectively (**13b**: 48%; **14a**: 49%; **14b**: 53%).[5]



Scheme 3. Preparation of alkylthio derivatives (**12a-c**, **13b**, and **14a,b**).

As shown in Table 1, the oxidation potentials of the donor molecules measured by cyclic voltammetry indicate that the donors **1**, **3**, **9** and **10** possess the oxidation potentials similar to that of TTF, whereas the alkylthio derivatives **12a-c**, **13b** and **14a,b** indicate a little lower donor ability. All compounds reported here show only two oxidation waves. Therefore, **1**, **9**, **10**, **12a-c** and **13b** are oxidized by two two-electron steps, **3** and **14a,b** being oxidized by two three-electron steps.

Table 1. Cyclic voltammetric[a)] and melting point data for TTF derivatives

Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V	Mp/°C	Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V	Mp/°C
TTF	0.36	0.74	—	**12a**	0.53	0.79	141-142
1	0.40	0.81	196-197	**12b**	0.54	0.82	reddish orange oil
9	0.29	0.87	214-215	**12c**	0.54	0.79	reddish orange oil
10	0.37	0.75	245 (decomp.)	**13b**	0.54	0.82	120-121
3	0.29	0.77	235-240 (decomp.)	**14b**	0.54	0.81	128-129

a) Conditions: n-Bu_4NClO_4 (0.1 mol dm^{-3}), benzonitrile, 20 °C, Pt working and counter electrodes. Potentials were measured against a Ag/Ag^+ electrode and converted to the value *vs* SCE (Fc/Fc^+ = 0.31 V).

The molecular structures and packing diagrams of the neutral donors **12a**[6)] and **14b**[7)] were determined by X-ray analysis (Figures 1 and 2). As shown in Figure 1, two TTF parts in **12a** are near planar with the maximum atomic deviations from the least-squares plane of 0.05 and 0.14 Å. Interestingly, the TTF parts are oriented in a twisted conformation, and the dihedral angles of two TTF parts to benzene ring are 34 and 55°. The bond distances and angles in TTF and benzene parts of the molecule have the normal values. The crystal structure shows that one TTF unit comes closer to another TTF unit of the neighboring molecule with SMe groups in opposite directions. Thus, TTF units form a dimeric structure and benzene ring only takes part in the packing as a spacer or a binder.

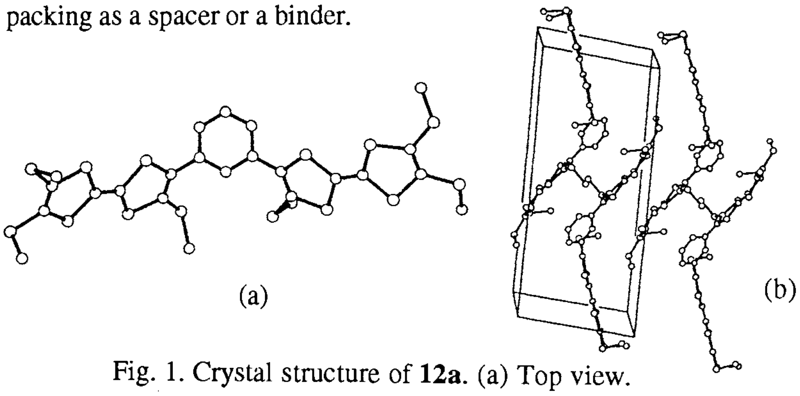

(a) (b)

Fig. 1. Crystal structure of **12a**. (a) Top view. (b) View from the c-axis.

Figure 2 shows the molecular structure of **14b**. Three TTF parts in **14b** are located randomly, forming no propeller structure. This irregular arrangement of the TTF units may be due to the steric repulsion between bulky ethylthio groups.

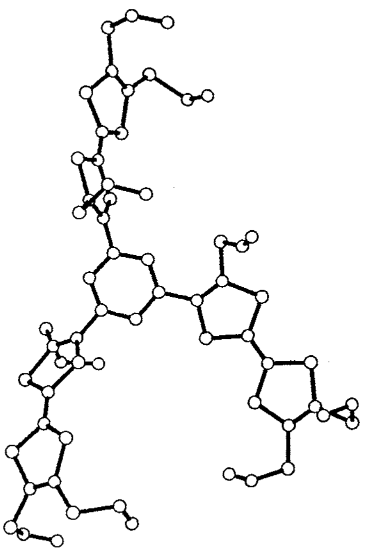


Fig. 2. Molecular structure of **14b**.

The donor molecules (**1**, **3**, **9**, and **10**) gave CT-complexes with tetracyano-*p*-quinodimethane (TCNQ), whereas **12a-c**, **13b**, and **14a,b** produced CT-complexes with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). Interestingly, the CT-complexes of **1**,**3**,**9**, and **10** with TCNQ showed an electrical conductivity, the CT-complex of **3** with TCNQ (**3** : TCNQ = 1 : 2) indicating a fairly high conductivity of 30 S cm^{-1} (room temp., compressed pellet, 4 probes).

Electrolytic oxidation of all donors reported here gave the corresponding radical-cation salts. The interactions of TTF units in the radical-cation salts are now under investigation.

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5) The structures of all new compounds reported here were fully characterized by the spectroscopic analysis. The selected data are as follows. **1**: orange fine cryst., ^{1}H NMR (400 MHz, CD_2Cl_2-CS_2) δ 7.35-7.28 (m, 4H), 6.50 (s, 2H), 6.29 (s, 4H); FAB MS (*m*-nitrobenzylalcohol) *m/z* 482 (M^+); **3**: orange fine cryst., ^{1}H NMR (400 MHz, CD_2Cl_2-CS_2) δ 7.29 (s, 3H), 6.59 (s, 3H), 6.33 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2-CS_2) δ 132.47, 132.40, 131.44, 121.02, 117.18, 117.07, 114.25, 93.55; FAB MS (*m*-nitrobenzylalcohol) *m/z* 684 (M^+); **12a**: red cryst., ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.50-7.44 (m, 3H), 2.37 (s, 6H), 2.44 (s, 6H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.78, 132.52, 130.52, 130.27, 129.04, 127.98, 123.92, 119.62, 111.26, 109.82, 20.06, 19.50; FAB MS (*m*-nitrobenzyl-alcohol) *m/z* 758 (M^+); **14b**: orange needles, ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.62 (s, 3H), 2.87 (q, J = 7.3 Hz, 6H), 2.86 (q, J = 7.3, 6H), 2.81 (q, J = 7.3, 6H), 1.31 (t, J = 7.3, 9H), 1.30 (t, J = 7.3, 9H), 1.24 (t, J = 7.3, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 134.23, 132.75, 130.96, 128.38, 128.27, 123.43, 110.22, 109.95, 31.27, 30.93, 15.34, 15.16; FAB MS (*m*-nitrobenzylalcohol) *m/z* 1225 (M+1).

6) Crystal data for **12a**: $C_{24}H_{22}S_{14}$, FW = 759.28, triclinic, space group $P\bar{1}$; $a = 9.892(2)$ Å, $b = 21.919(2)$ Å, $c = 7.6922(6)$ Å, $\alpha = 94.918(7)°$, $\beta = 101.643(9)°$, $\gamma = 98.29(1)°$, $V = 1605.0(3)$ Å^3, Z = 2, $d_{\text{calcd}} = 1.571$ g cm^{-3}. The structure was solved by direct method using MULTAN88.$^{8)}$ Full matrix least-squares refinement yielded the final R value of 0.066 ($R_w = 0.058$) for 3029 independent reflections [$2\theta \leq 120.2°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.548$ Å) and ω-2θ scan.

7) Crystal data for **14b**: $C_{42}H_{48}S_{21}$, FW = 1226.10, monoclinic, space group $P2_1/n$; $a = 25.947(1)$ Å; $b = 8.184(4)$ Å, $c = 27.502(1)$ Å, $\beta = 100.761(3)°$, $V = 5737(2)$ Å^3, Z = 6, $d_{\text{calcd}} = 2.1298$ g cm^{-3}. The structure was solved by direct method using MULTAN88.$^{8)}$ Full matrix least-squares refinement yielded the final R value of 0.070 ($R_w = 0.072$) for 3561 independent reflections [$2\theta \leq 120.1°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using $Cu_{K\alpha}$ radiation and ω-2θ scan.

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