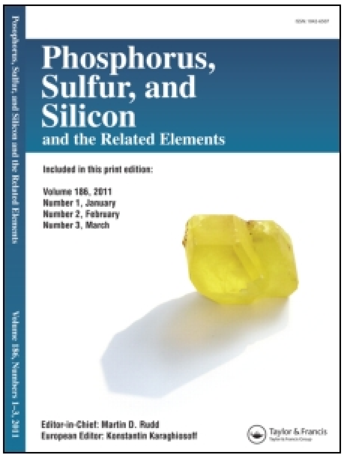

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Structural and Functional Aspects of Tetrathiafulvalene Derivatives and Analogues

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STRUCTURAL AND FUNCTIONAL ASPECTS OF TETRATHIAFULVALENE DERIVATIVES AND ANALOGUES

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New tetrathiafulvalene (TTF) derivatives and analogues were synthesized, which might serve as a promising donor for developing organic materials with electrical conducting and magnetic properties superior to those hitherto obtained. The charge-transfer (CT) complexes and cation radical salts prepared from the donors exhibited comparatively high electrical conductivities. The CT complex between ethanediylidene-2,2'-bis(1,3-dithiole) and TCNQ was obtained as single crystals, whose temperature dependence of electrical conductivity was surely metal-like. Several attempts to get organic ferromagnets, ferrimagnets and magnetic metals using the new donors were also made. To be noted, ferromagnetic interaction was first found out in the CT complexes between the trimethylenemethane dication substituted with 1,3-dithiole groups and dianionic donors. By taking this opportunity the first purely organic ferromagnets came out, which are based on the CT complexes with a definite composition.

Key Words tetrathiafulvalene, derivatives, analogues, donor, electrical conductivity, magnetism

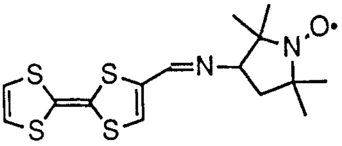
INTRODUCTION

Since the discovery of metal-like conductivity in the charge-transfer (CT) complex between tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) in the early 1970's,[1,2] active search with the aim at acquring a first organic superconductor has been initiated. To this end mainly two different approaches to develop new donors in place of TTF were carried out. One approach is based on the introduction of several substituents into the olefinic carbon atoms of a TTF skeleton as well as the substitution of the sulfur atoms in TTF with the other chalcogen atoms, selenium and tellurium. Some of these new TTF derivatives , especially bis(ethylenedithio)-substituted TTF and tetramethyltetraselena-fulvalene, have served as reliable donors, whose cation radical salts exhibited superconductivity at the highest metal-superconductor transition temperature (T_c) of 12.5 K.[3] Recently, some new TTF derivatives are also devoted to use in molecular sensors, molecular shuttles and second-order nonlinear optical materials.[4] We very recently succeeded in the synthesis of two kinds of TTF derivatives, which might be applicable as a promising donor for organic ferrimagnets and ferromagnetic metals. The other approach involves the introduction of conjugated spacer groups between two and more 1,3-dithiole groups to give new TTF analogues with one- or two-dimensional arrangement of 1,3-dithiole groups. We have been concerned in this work since 1980 and till now have synthesized more than twenty TTF analogues.[5] These donors exhibited different redox properties from that of TTF, and a most unique case was observed in 1,3-dithiole [5]radialene, where only one redox peak involving transfer of four electrons appeared. This redox anomaly is related to remarkable conformational change accompanied with progress of oxidation. In some cases the oxidized intermediates, the cation radicals, dications and tetracations were isolated, whose optical or magnetic properties were quite unique. No organic superconductor still emerges out of the new TTF analogues syntheiszed by us and the other groups. It needs some time till fruitful results will come out. The odd-numbered [n]radialenes (n=3,5) and trimethylenemethane substituted with 1,3-dithiole group or the other groups with its isoelectronic structure can be expected as a promising donor, whose CT complexes and cation radical salts might become an organic ferromagnet. The results on these works are presented in this paper.

NEW TTF DERIVATIVES AS A DONOR FOR ORGANIC MAGNETIC MATERIALS

In contrast to the considerable developments that have occurred in organic materials with electrical conductivity, and especially superconductivity, ferromagnetism, another very important and useful physical properties, can not be said to have been achieved in organic materials in spite of remarkable progress recently. The increase of a ferromagnetic phase transition temperature is an urgent problem to be solved. We are now making much effort on this research project by using two organic materials obtained from new TTF derivatives: (1) CT complexes and cation radical salts in which itenerant and localized electrons coexist and (2) oxidatively doped TTF polymers.

The two TTF derivatives bearing a stable nitroxide radical substituent (**1** and **2**) are donor candidates for the preparation of cation radical salts and CT complexes involving itenerant and localized electrons in coexistence (Figure 1), because they have advantages of preserving a comparable donating ability with that of TTF as well as of not interferring



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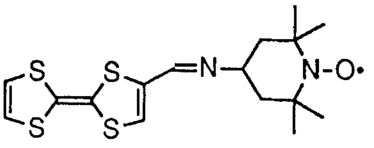

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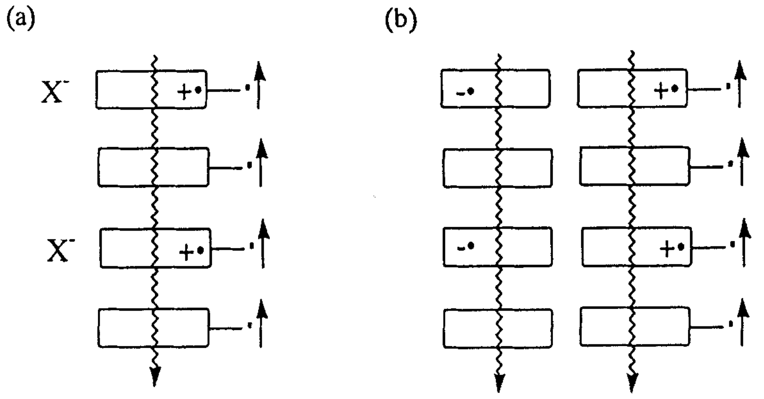
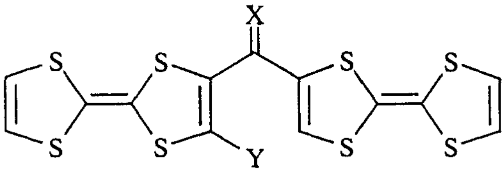


FIGURE 1 (a) Cation radical salts and (b) CT complexes involving itenerant and localized electrons in coexistence.

a contact with an acceptor. On the other hand, there is however a problem on the weak spin interaction between the TTF cation radical and the nitroxide radical, since the radical centers are too apart from each other. In fact, the magnitude of interaction is too small (ca. 30 cal/mol), so that the alignment of the nitroxide spins can not be achieved in the CT complexes and cation radical salts.[6,7] The molecular design and preparation of new donors in this kind are needed with taking account this result into account.

Bis(tetrathiafulvenyl) derivatives bridged with 1,1-vinylene, carbonyl and thiocarbonyl groups (**3**) are the other target molecules, since the triplet nature of the



$X = CH_2$, O, S

3 $Y = H, CO_2Me, CONMe_2$

ground state of their dications has been theoretically predicted.[8] If this prediction could be also confirmed experimentally, these triplet dications might serve as building blocks for the production of stable high-spin organic oligomers and polymers (Figure 2). At the start of this study **3** (X=O), and its monocarbomethoxy ($Y=CO_2Me$) and monodimethylcarbamoyl ($Y=CONMe_2$) derivatives were synthesized and the ground spin states of their dications were investigated.[9] Contrary to the theoretical prediction the ground state of their dications is in all cases a singlet with its triplet state lying ca. 3.0

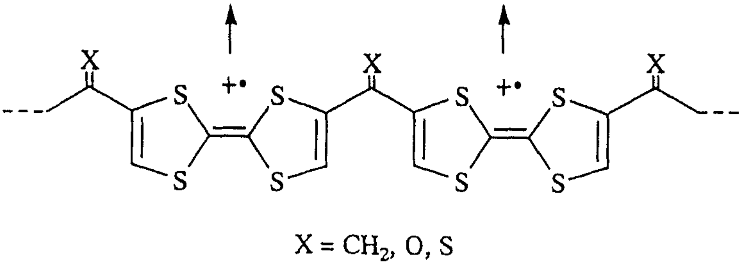


FIGURE 2 Oxidatively-doped high-spin organic oligomers and polymers.

kcal/mol higher in the frozen solution, where the two TTF planes are fixed by the dihedral angle of ca. 50°, as shown by the X-ray structure of **3** (X=O, Y=CONMe$_2$) (Figure 3).

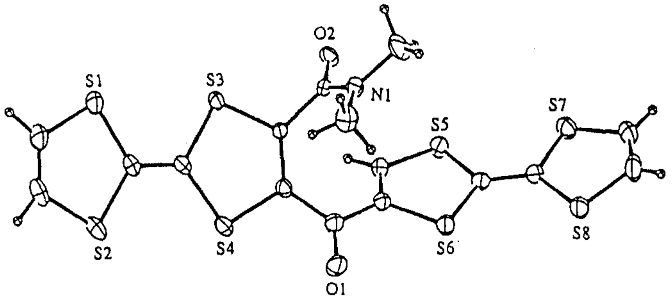
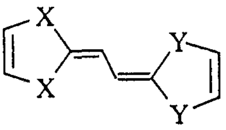


FIGURE 3 ORTEP Drawing of **3** (X=O, Y=CONMe$_2$).

The fixed geometry leads to a strong spin interaction between the two TTF cation radicals. The theoretical calculations in consideration of the polarization of the carbonyl group suggest more stabilization of the singlet. Our next aim is focusing on the synthesis of **3** (X = CH$_2$, S), whose dications should exhibit the more preferential triplet nature in the ground state.

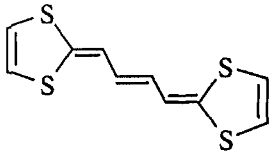
ONE-DIMENSIONALLY ARRANGED TTF ANALOGUES

The new donors with skeletal structures different from that of TTF will be needed, if high-T$_c$ organic superconductors are ultimately to be achieved. Based on this view, research has begun on synthesizing new types of donors, in the belief that they will lead to the preparation of organic conductors and superconductors with properties superior to those hitherto obtained. For this purpose we synthesized apparently one-dimensionally arranged TTF analogues, ethanediylidene-2,2'-bis(1,3-dithiole)[10] and its derivatives substituted with selenium atoms in place of the corresponding sulfur atoms (**4**),[11] 2-butene-1,4-diylidene-2,2'-bis(1,3-dithiole) (**5**),[12] ethenediylidene-2,2'-bis(1,3-dithiole)



X = Y = S
X = S, Y = Se
X = Y = Se

4



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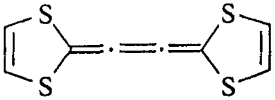

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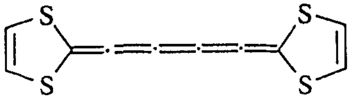

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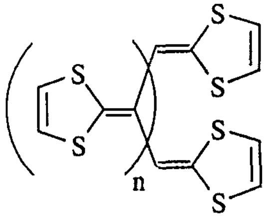


n = 1, 2

8

(**6**),[13] butatrienediylidene-2,2'-bis(1,3-dithiole) (**7**),[13] and 1,3-dithiole [n]dendralenes (n=1,2) (**8**).[14] Except for **6** and **7**, which were extremely unstable in air, the other donors were isolated as stable crystals. Data on redox potentials, especially the first (E_1) and second (E_2) values for the new donors, are very important in designing organic materials with interesting and useful physical properties such as electrical conductivity and ferromagnetism. Table I summarizes the redox potentials of **4**-**8**. All donors have smaller E_1 and E_2 values compared with those for TTF (E_1=+0.34 V and E_2=+0.71 V vs. Ag/AgCl in CH_2Cl_2). This indicates that in the cation radical[15] and dication states of these donors the one-site Coulomb repulsion is greatly reduced as expected from their structures. For **5** the first and second one-electron redox processes occur simultaneously. From consideration of the redox potentials these new donors show great promise for the preparation of organic conductors and furthermore organic superconductors if possible. However, the design of these new donors is lacking in another important respect, i.e. the stacking of the donor molecules. These new donors are supposed to have conformations that are far from planar. It is hoped that the donors can adopt molecular conformations sufficiently planar to allow close stacking in the form of CT complexes and cation radical salts.

The CT complexes and cation radical salts were prepared using these donors and their electrical conducting properties were investigated.[16,17] Comparatively high electrical

TABLE I Redox potentials, E_1 and E_2 of **4**-**8** and TTF as a reference compound.[a]

Donor	E_1	E_2	E_3	E_4
4 (X=Y=S)[b]	+0.20	+0.36		
4 (X=S, Y=Se)[b]	+0.26	+0.40		
4 (X=Y=Se)[b]	+0.33	+0.47		
5[b]	+0.23[e]			
6[c]	(+0.07)[f]	(+0.31)[f]		
7[c]	(-0.12)[f]	(+0.25)[f]		
8 (n=1)[b]	+0.26	+0.40	+1.32[g]	
8 (n=2)[b]	+0.25	+0.37	+0.72[g]	
TTF[d]	+0.34	+0.71		

[a] V vs. Ag/AgCl. [b] Solvent: PhCN. [c] The BF_4 salts of the corresponding dications were used. [d] Solvent: CH_2Cl_2. [e] $E_m=(E_1+E_2)/2$. [f] Irreversible. [g] $E_m=(E_3+E_4)/2$.

conductivities (3×10^{-2} to 8×10^{-1} S/cm) in the form of compressed pellets at room temperature were observed only in the CT complexes with TCNQ. Attempts were made to get their CT complexes as single crystals, but this was successful only for **4**·TCNQ albeit in very small size ($3\times0.05\times0.05$ mm^3) so as to be not suitable for the X-ray structure analysis. Figure 4 shows the dependence of resistance (R, Ω) with respect to 1000/T (K^{-1}) for the **4**·TCNQ single crystal. The electrical conductivity at 300 K was 16 S/cm, and the value gradually increased as the temperature was reduced from 300 to ca. 200 K, reaching a maximum of 23 S/cm. This change of electrical conductivity with respect to temperature implies that the crystal is truely metallic in this temperature range. However, near 200 K a metal-to-insulator phase transition occurred, and below this temperature semiconductor-type behavior was observed. It is not yet clear whether the phase transition is a "Peierls transition" or not. Judging from the results on the electrical conductivities and crystal properties, it appears that the nonplanar conformations of the new donors have an undesirable effect on the stacking of donor molecules in the CT complexes and cation radical salts. This situation was not unexpected from the outset. However, this problem might be overcome by introducing a suitable substituent group so as to give stronger intermolecular interaction.

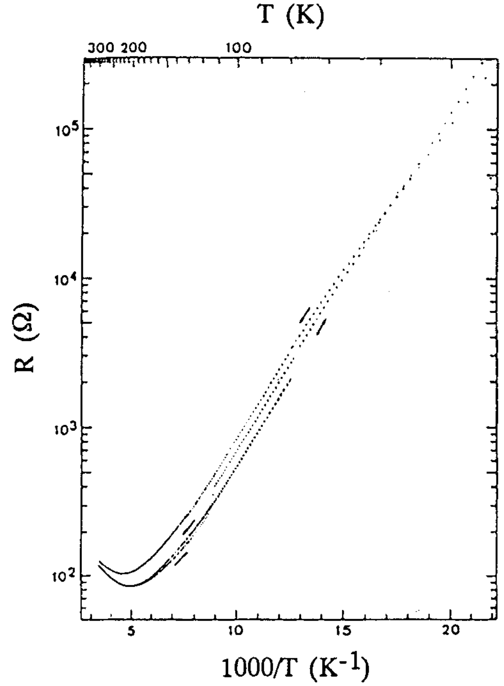
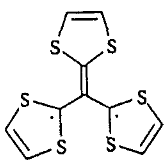


FIGURE 4 The temperature dependence of electrical resistance (R, Ω) for **4**·TCNQ (single crystals).

TWO-DIMENSIONALLY ARRANGED TTF ANALOGUES: TRIMETHYLENEMETHANE AND [n]RADIALENES (n=3,4,5,6)[18] SUBSTITUTED WITH 1,3-DITHIOLE GROUPS

In consideration of several drawbacks on the one-dimensionally arranged TTF analogues, we again attempted to synthesize new donors which have a two-dimensional arrangement of three, four, five and six 1,3-dithiole groups. The target compounds are trimethylenemethane (**9**), and [3]- (**10**), [4]- (**11**), [5]- (**12**) and [6]- (**13**) radialenes substituted with 1,3-dithiole groups. Except for **9** and **10**, the other donors were successfully prepared as a parent system and as a benzo or carbomethoxy derivative. For **9**, a diradical species which is supposed to be very reactive, the benzo derivative of the corresponding dication ($\mathbf{9}^{2+}$) was isolated as a stable salt.[19] Instead of **10** another [3]radialene (**14**) was obtained, which is substituted with a sterically bulky, but still electron-donating, thioxanthenyl group in place of the 1,3-dithiole group.[20] From the crystal structures of the BF_4 salt of the benzo derivative of $\mathbf{9}^{2+}$ and the benzo or carbomethoxy derivatives of [n]radialenes (n=4,5,6) as shown below (Figure 5), their



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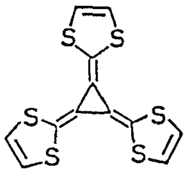

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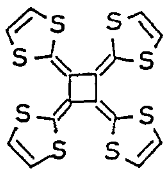

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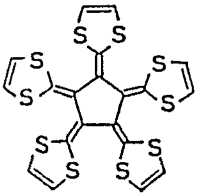
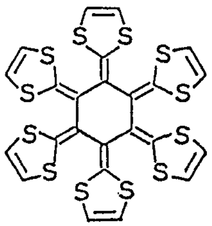
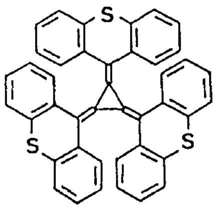


12

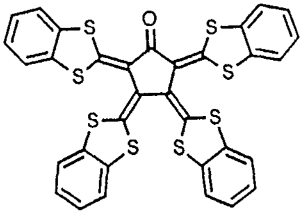


13

molecular skeleton has clearly not a planar structure. A high degree of planarity is expected for **10**, but this compound has not yet been prepared. For the BF$_4$ salt of the benzo derivative of **9**$^{2+}$ one 1,3-benzodithiole group is almost perpendicular (84°) to the remaining bis(1,3-benzodithiole)methylene moiety. The central four-membered ring in the carbomethoxy derivative of **11** adopts a puckered conformation, which has aslo been recognized in the crystal structures of the other [4]radialenes.[21] For **12** the benzo derivative was only prepared, whose X-ray structure analysis is, however, still unsuccessfull. Instead, the crystal structure was obtained for a compound substituted with a carbonyl group in place of one 1,3-dithiole group (**15**).[22] The central five-membered ring adopts a half-chiar conformation with an approximate twofold symmetry passing through the carbonyl bond. The X-ray structure analysis of the benzo derivative of **13** was carried out for the crystals, where the six-membered ring is in a twisted-boat



14



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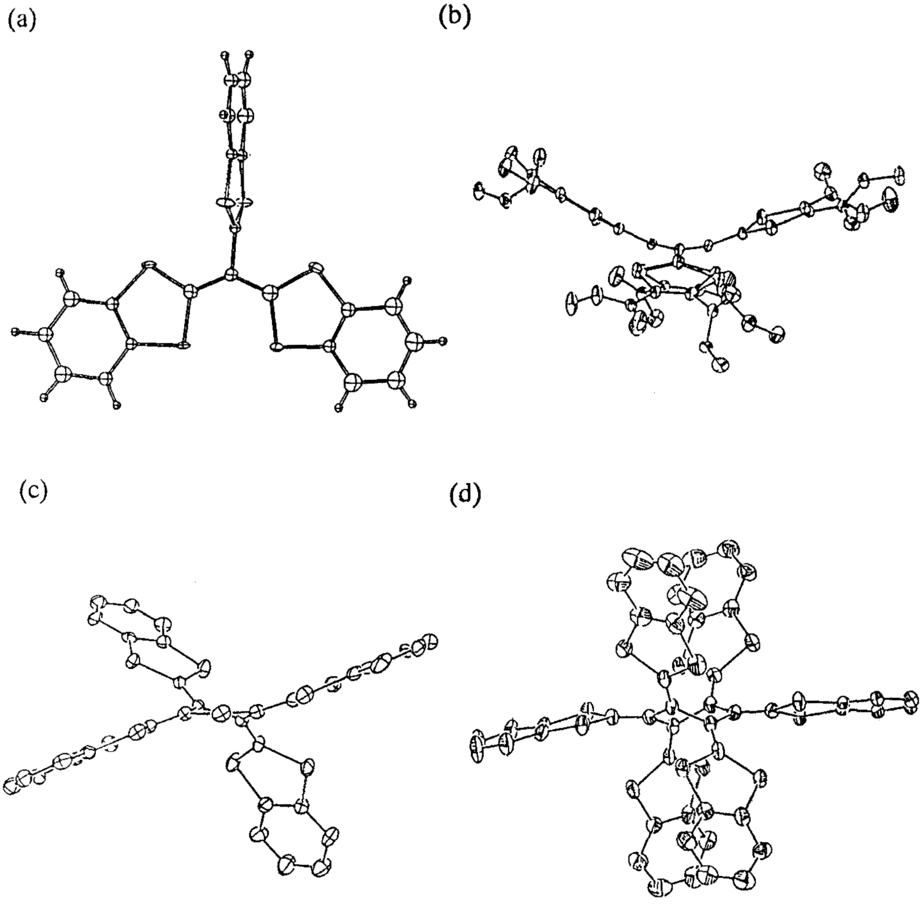


FIGURE 5 ORTEP Drawings of (a) the BF4 salt of the benzo derivative of **9**$^{2+}$ (the two BF_4^- ions are omitted), (b) the carbomethoxy derivative of **11**, (c) **15** and (d) the benzo derivative of **13** with a twisted-boat conformation.

conformation.[23] The conformation is so labile and can be converted to a thermodynamically more stable chair one by heating in solution or more readily by electrochemical redox. It is not yet successful for the X-ray analysis of the crystals in the chair conformation. One should bear in mind that the Ni(0)-catalyzed cyclotrimerization reaction of **6** is utilized for the production of **13**. Assumedly, this reaction involves a crucial intermediate, nickellacycloheptane which is subsequently collapsible to **13** in a thermodyamically less stable twisted-boated conformation accompanying with release of Ni(0).[24] The stereochemistry of reaction in this step must be calrified by characterizing the structure of nickellacycloheptane.

TABLE II Redox potentials, E_1-E_4 of **9**, **14**, **11**, **12**, **15** and **13**.[a]

Donor	E_1	E_2	E_3	E_4
9[b,c]	-0.55	±0.00		
14[d]	+0.67	+0.80		
11[d]	+0.19[j]		(+0.98)[k]	(+1.30)[k]
12[e,f]	+0.36[l]			
15[f]	+0.17[j]		+1.14[m]	
13[f,g,h]	+0.43	(+0.65)[k]		
13[f,g,i]	+0.82[j]			

[a] V vs. Ag/AgCl. [b] The BF_4 salt of the corresponding dication of the benzo derivative was used. [c] Measured in DMF at 0 °C. [d] Solvent: CH_2Cl_2. [e] The benzo derivative was used. [f] Solvent: PhCN. [g] The benzo derivative was used. [h] Twisted boat form. [i] Chair form. [j] $E_m=(E_1+E_2)/2$. [k] Irreversible. [l] $E_m=(E_1+E_2+E_3+E_4)/4$. [m] $E_m=(E_3+E_4)/2$.

For these donors the redox process is composed of either two or four steps up to 2 V vs. Ag/AgCl. The results on the redox potentials are summarized in Table II. In view of very negative E_1 value of the benzo derivative of **9**, supposedly the diradical species is too unstable to be isolated. In fact, this species could be only generated by the electrochemically two-electron reduction of the benzo derivative of $\mathbf{9}^{2+}$ salt in a degassed CH_3CN at -40 °C. However, even in this condition **9** was subjected to gradual decomposition. The smaller E_1 and E_2 redox potentials than those of TTF were obtained for **11**,[21] **12**[5] and **15**,[22] whose first and second one-electron reversible redox processes occurred simultaneously. This gives a great expectation to these donors where there is almost no on-site Coulomb repulsion being responsible for electrical conductivity. The subsequent third and fourth redox waves were observed at the different potentials for **11**, while at the same potential for **12** and **15**, respectively, although the former processes are reversible and the latter ones irreversible. To be noted, for **12** the first and second two-electron transfers possess almost the same redox potentials, so that apparently one-pair of reversible waves is only observed, which involves a net four-electron transfer at the comparatively small potential of +0.390 V vs. SCE (Figure 6). This is the first case of a single-wave four-electron transfer with only one macroscopic redox site in organic redox systems. Based on normal explicit difference digital simulation method assuming Nerstian response the

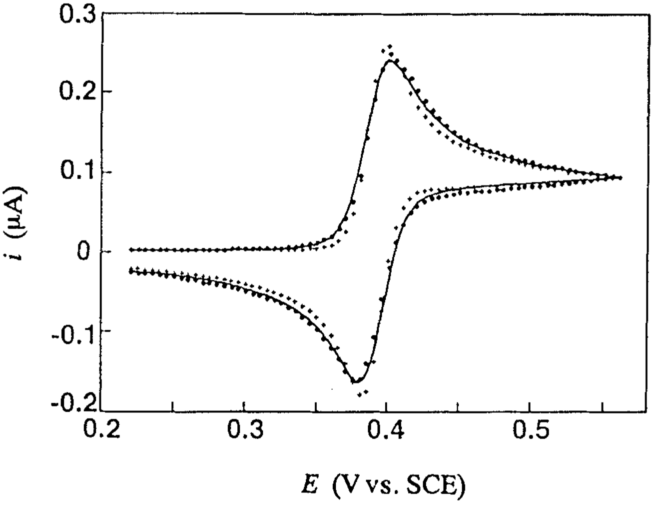
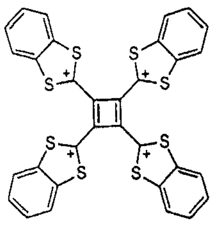


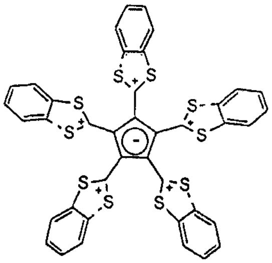
FIGURE 6 Background-corrected cyclic voltammograms of **12** at sweep rate=5 mV/s (•). Solid line and symbol (+) represent the regression curves calculated on the basis of the reversible two-step two-electron and one-step four-electron transfer mechanisms, respectively. The regression curve analyzed based on the four-step one-electron transfer mechanism was practically indistinguishable from the solid line.

detailed redox process of **12** was analyzed.[26] According to the analysis results **12** follows a two-step two-electron transfer and is converted to the tetracation ($\mathbf{12}^{4+}$) via the dication ($\mathbf{12}^{2+}$). The estimated redox potentials for the $\mathbf{12}/\mathbf{12}^{2+}$ and $\mathbf{12}^{2+}/\mathbf{12}^{4+}$ couples are +(0.394±0.003) and +(0.386±0.003) V vs. SCE, respectively. The redox potential of the second two-electron transfer is smaller compared with that of the first one. Thus, three electrons are transferred at virtually no cost in energy after the first electron is tranferred. Two factors play important roles in the unusual multiple electron transfer with enhanced interaction: (1) preferential twist of all five 1,3-benzodithiolyium (1,3-benzodithiole cation) moieties from the central five-membered ring so as to decrease the intramolecular Coulomb repulsion and steric hindrance; (2) the aromatic stabilization arising from the contribution of the cyclopentadienide structure in $\mathbf{12}^{4+}$. In contrast, for the tetracations of **11** and **15** ($\mathbf{11}^{4+}$ and $\mathbf{15}^{4+}$), the cyclobutadiene and cyclopentadienone structures appear in the central rings. Both tetracations are very unstable due to their antiaromatic electronic structures. This is the main cause for the remarkably large E_4 values for **11** and **15**.

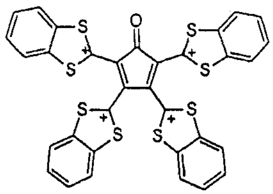
Using the donors with comparatively small E_1 and E_2 redox potentials, i.e. **11** and



11^{4+}



12^{4+}



15^{4+}

15, and the benzo derivatives of **11**, **12** and **15**, were prepared the CT complexes with TCNQ, tetrafluoro-substitutedTCNQ (TCNQF$_4$) and dichlorodicyanobenzoquinone (DDQ). The comparatively high electrical conductivities ((3-8)x10^{-3} S/cm) in the form of compressed pellets at room temperature were observed ony in the CT complexes of **11** with TCNQ and of the benzo derivative of **11** with TCNQF$_4$.[16] The more detailed study on the electrical conducting properties of the CT complexes was prevented, because the single crystals could not be obtained. On the other hand, the cation radical salts were prepared by electrochemical crystallization. The PF$_6$ and ClO$_4$ salts of the cation radical of the benzo derivative of **11** were isolated as single crystals of very small size,[5,27] while the I$_3$ salts of the cation radical of **15** and its benzo derivative as a poweder, respectively.[22] The electrical conductivity of the PF$_6$ salt at room temperature was ca. 1 S/cm, and unfortunately showed a temperature dependence of a semiconductor. For the ClO$_4$ salt the electrical conductivity could not be calculated accurately because the crystal size was too small to be measured. The temperature dependence of electrical conductivity also was like a semiconductor. The activation energies were 0.05 eV and 0.02 eV for the PF$_6$ and ClO$_4$ salts, respectively. The I$_3$ salt of the cation radical of the benzo derivative of **15** showed comparatively high electrical conductivity (2x10^{-2} S/cm) in the form of a compressed pellet at room temperature. In spite of considerable efforts we can not yet get metal-like organic conductors in both CT complexes and cation radical salts of the 1,3-dithiole [n]radialenes.

Among the new donors **9**, **10** and **12** can possess doubly-degenerate highest occupied molecular orbitals (HOMO's), if their molecular symmetry is higher than C$_3$ for **9** and **10**, and than C$_5$ for **12**. Accordingly, the benzo derivative of **9** and the dications of **12** and **14** should all be ground-state triplets, if their molecular symmetry still maintains. Now, the ground spin states of the three triplet species were investigated by ESR spectroscopy and/or SQUID magnetometer. As mentioned above, the benzo derivative of **9** was produced by electrochemical two-electron reduction of the

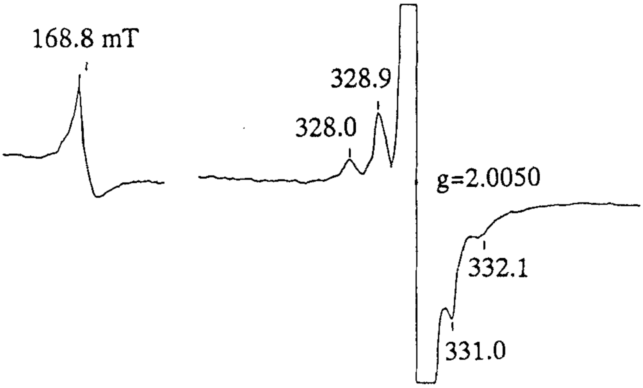


FIGURE 7 The ESR spectrum of the benzo derivative of 9 in a frozen CH_3CN solution measured at -50 °C.

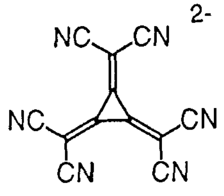
corresponding dication salt in CH_3CN at -40 °C.[25] The solution of the diradical was immediately frozen by cooling to -50 °C and the ESR spectrum was measured. As is obvious from Figure 7, the absorptions on each side of the central line (g=2.0050) are characteristic of randomly oriented triplet species, whose zero-field splitting parameters, $|D'|$ and $|E'|$ are 0.00193 cm^{-1} and ≈ 0 cm^{-1}, respectively. The axial symmetry of the D tensor ($|E'|=0$, also observed in trimethylenemethane: $|D'|=0.025$ cm^{-1} and $|E'|=$ 0 cm^{-1})[28-30] indicates that the two interacting unpaired electrons delocalize with at least C_3 symmetry. The smaller $|D'|$ value observed for this diradical compared with that of trimethylenemethane suggests delocalization of the two unpaired electrons not only over the trimethylenemethane moiety but also over the sulfur atoms. In addition, a half-field resonance ($\Delta m_S=\pm 2$) signal appeared at 168.8 mT. The temperature dependence of the signal intensity obeyed a Curie law in the range of -50 to -196 °C, establishing that the triplet is in the ground state.

By the oxidation of **14** with $Tl(CF_3CO_2)_3$ the CF_3CO_2 salt of the dication (**14**$^{2+}$) was obtained as a dark blue solid.[20,31] The solid exhibited one slightly broad ESR signal with g=2.00353 at 25 °C. In the spectrum at -196 °C the fine structure was observed together with simultaneous appearance of a half-field resonace signal at 164.8 mT. The analysis of the spectrum gave very small $|D'|$ value of ca. 6.5×10^{-4} cm^{-1}, suggesting that the two unpaired electrons are far removed from each other and probably located on the three thioxanthenyl groups. From the temperature dependence of the central broad signal, it was shown that the ground state of **14**$^{2+}$ is centainly a singlet and the triplet state lies by only 0.07 eV higher in energy. The conclusion on a thermally-accesasible triplet of **14**$^{2+}$ was also derived from the experiment in the frozen solution of the **14**$^{2+}$ salt. It is conceivable also for **14**$^{2+}$ that the singlet is favored because the large π electron system decreases electron correlation and the complex structure allows easy symmetry-lowering distorsion. From these reasons a ground-state triplet might be available from the dication of **10**.

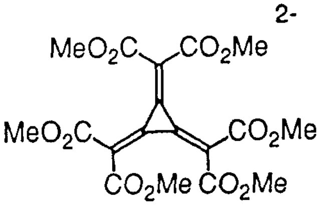
It seemed difficult to produce **12**$^{2+}$ by electrochemical oxidation or by reaction with familiar oxidants such as I_2 and $NOBF_4$, because **12** has very unique redox property of four-electron transfer in one step. Nevertheless, it was overcome utilizing the 1:2 CT complex between **12** and DDQ.[5,27,31] The IR spectrum of the CT complex showed the CN stretching band at 2221 cm^{-1}, which is almost same to that (2220 cm^{-1}) of the anion radical of DDQ ($DDQ^{-\cdot}$). In considering this IR result together with the redox potentials of **12** (see Table II) and DDQ (+0.46 V and -0.42 V vs. Ag/AgCl), the CT complex is actually in the close form to **12**$^{2+}\cdot(DDQ^{-\cdot})_2$. Now, the ground spin state of **12**$^{2+}$ in the CT solid was investigated. In the SQUID measurement the paramagnetic susceptibility (χ_p) of the CT complex was 3.3×10^{-4} emu/mol at 298 K, which is only 6-7 percent of the value (5.0×10^{-3} emu/mol) calculated as a mutually non-interacting spin system composed of **12**$^{2+}$ (S=1, assumed that it is a ground-statet triplet) and two $DDQ^{-\cdot}$ (S=1/2) species. This result can be reasonably interpreted by considering that **12**$^{2+}$ is in the ground-state singlet (S=0) as a result of a Jahn-Teller distortion, and $DDQ^{-\cdot}$'s interact antiferromagnetically with each other. Besides the above situation in the CT solid a small amount of doublet and/or triplet species is still present. The ESR measurement demonstrated that a ground-state triplet species is certainly involved in this contaminate. Thus, a half-field resonance signal of very weak intensity appeared at 163.9 mT at 298 K. The temperature dependence of the signal intensity obeyed a Curie law in the range of 4.5 to 298 K. It is most likely that this ground-state triplet species is **12**$^{2+}$, whose higher molecular symmetry than C_5 accidentally maintains in a specific position of the solid. The fine structure could not be detected at any temperature. It is possible that the fine structure is hidden into the strong central signal because of very small zero-field splitting parameters.

Several theoretical models have so far been proposed for achieving a linear-chain ferromagnetic interaction in organic solids. The most attractive of these are two models proposed by McConnell, based on Heitler-London spin exchange between a positive spin density on one radical and a negative spin density on another radical,[32] and on configurational admixing of a virtual triplet excited state with the ground state for a chain of alternating cation radical donors and anion radical acceptors, respectively.[33] The benzo derivative of **9**$^{2+}$ might become a desirable acceptor in the production of a ferromagnetic CT complex with a dianionic donor, since **9** can participate in the virtual triplet excited state.

The use of hexacyanotrimethylenecyclopropane (HCTMC) and TCNQF4 dianions ($HCTMC^{2-}$ and $TCNQF_4^{2-}$) gave the CT complexes with $\mathbf{9}^{2+}$, but no CT complex was isolated in the use of hexacarbomethoxytrimethylenecyclopropane (HCMTMC) and DDQ dianions ($HCMTMC^{2-}$ and DDQ^{2-}) and instead a coupled product of the cation radical of **9** ($\mathbf{9}^{+\cdot}$) was obtained.[19] In view of the first oxidation potentials of the dianions used ($HCTMC^{2-}$: E_1^{ox}=+0.34 V vs. Ag/AgCl;[34] $TCNQF_4^{2-}$: +0.06 V; $HCMTMC^{2-}$: -0.07 V;[34] DDQ^{2-}: -0.13 V) and of the first reduction potential of $\mathbf{9}^{2+}$ (E_1^{red}=-0.01 V),[19] for the CT complexes obtained the CT from $HCTMC^{2-}$ or $TCNQF_4^{2-}$ to $\mathbf{9}^{2+}$ is unfavorable in energy, resulting in very small CT degree. In fact, the CN stretching frequencies of the CT complexes ($\mathbf{9}^{2+}\cdot HCTMC^{2-}$: 2187 and 2166 cm^{-1}; $\mathbf{9}^{2+}\cdot TCNQF_4^{2-}$: 2162 and 2129 cm^{-1}) are very close to those of $HCTMC^{2-}$ (2181 and 2164 cm^{-1}) and $TCNQF_4^{2-}$ (2162 and 2131 cm^{-1}) rather than of the anion radicals, $HCTMC^{-\cdot}$ (2209 and 2195 cm^{-1}) and $TCNQF_4^{-\cdot}$ (2195 and 2173 cm^{-1}). The accurate CT degree was estimated from the spin amount obtained by ESR measurement. On the other hand, in the use of $HCMTMC^{2-}$ and DDQ^{2-} the CT can be complete, and $\mathbf{9}^{+\cdot}$ is produced together with the corresponding anion radicals. Unexpectedly, $\mathbf{9}^{+\cdot}$ is not so stable as to be susceptible of radical coupling reaction, suggesting that the molecular conformation of $\mathbf{9}^{+\cdot}$ is not like a propeller, but resembles that of $\mathbf{9}^{2+}$ as shown in Figure 5. Assumedly, in this conformation the radical and the positive charge must be separately placed at the bis(1,3-benzodithiole)-methylene and 1,3-benzodithiole moieties.



$HCTMC^{2-}$



$HCMTMC^{2-}$

The spin amounts involved in the CT complexes of $\mathbf{9}^{2+}\cdot HCTMC^{2-}$ and $\mathbf{9}^{2+}\cdot TCNQF_4^{2-}$ as well as the spin interaction between $\mathbf{9}^{+\cdot}$ and $HCTMC^{-\cdot}$ or $TCNQF_4^{-\cdot}$ were investigated by ESR. From the solid ESR spectra of the CT complexes measured at 293 K (Figure 8), for $\mathbf{9}^{2+}\cdot HCTMC^{2-}$ six weak signals due to the fine structure ($|D'|=1.2\times10^{-3}$ cm^{-1} and $|E'|=1.7\times10^{-4}$ cm^{-1}) of a triplet species were observed besides a doublet-like signal, while $\mathbf{9}^{2+}\cdot TCNQF_4^{2-}$ exhibited only a broard and strong doublet signal. The spin amounts of the CT complexes were calculated by comparison with a reference TANOL: 1.64×10^{21} spins/mol and 3.55×10^{22} spins /mol for

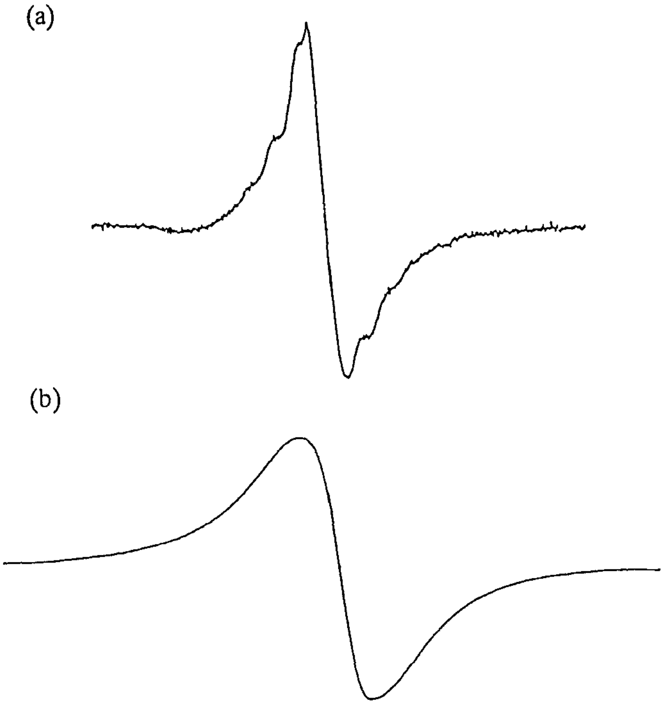


FIGURE 8 The solid ESR spectra of (a) $9^{2+}\cdot HCTMC^{2-}$ and (b) $9^{2+}\cdot TCNQF_4{}^{2-}$ measued at 293 K.

$9^{2+}\cdot HCTMC^{2-}$ and $9^{2+}\cdot TCNQF_4{}^{2-}$, which correspond to the spin contents of 0.27% and 5.89% per formula unit, respectively. Figure 9 shows the temperature dependence of the product of the signal intensity (I) and temperature (I·T) in the range of 15 to 283 K. In both cases the I·T decreased with a lowering temperature in the range of 30-50 to 283 K. However, below 30-50 K the value reversely continued to increase till 15 K, the lowest temperature used in this experiment, suggesting the possibility of ferromagnetic interaction in these CT complexes. This provides a first finding of ferromagnetic interaction in purely organic CT complexes, although it has already been known that in a number of organometallic CT complxes ferromagnetic interaction is not only recognized, but some of them also become ferromagnets with three-diemsional spin ordering.[35] Just about the same time a first CT complex-based purely organic ferromagnet was discovered in the CT complex between C_{60} and tetrakis(dimethylamino)ethylene (TDAE), although the magnetic details still now remain to be not elucidated for insufficient characterization of the crystal structure.[36]

Now that the crystal structure is still unknown, it can't be discussed on the origin of

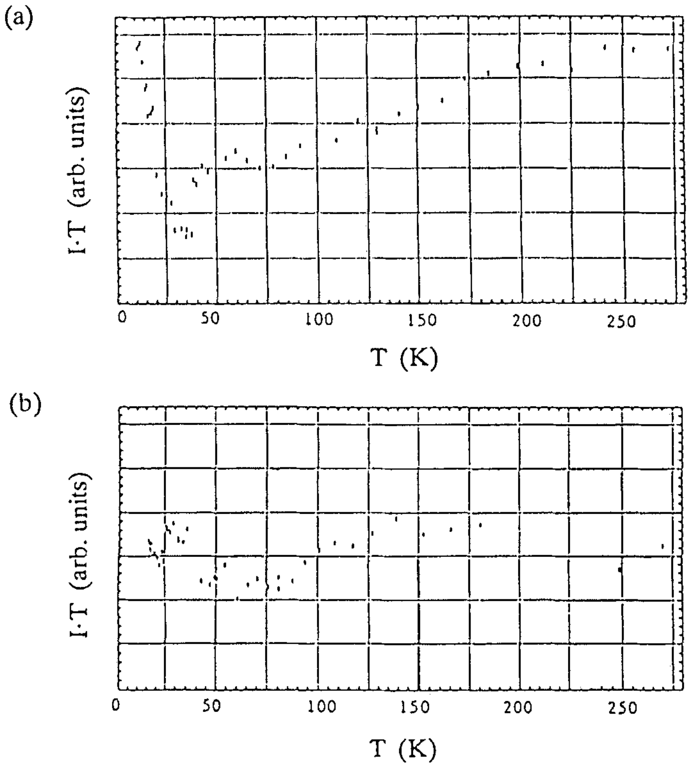
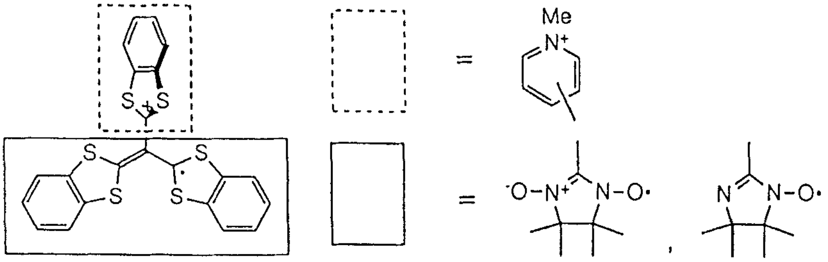


FIGURE 9 The temperature dependence of I·T for (a) $\mathbf{9}^{2+}\cdot$HCTMC^{2-} and (b) $\mathbf{9}^{2+}\cdot$TCNQF$_4{}^{2-}$ in the temperature range of 15 to 283 K.

ferromagnetic interaction in the CT complexes. Nevertheless, it can be claimed that ferromagnetic interaction is not based on the second McConnell model, since the double degeneracy disappears any more by a Jahn-Teller distortion in $\mathbf{9}^{+\cdot}$. The first McConnell model is most conceivable, which has also been proposed for ferromagnetic interaction occurring in the organometallic CT complexes between metallocenes and acceptors such as tetracyanoethylene and TCNQ in opposition to the previous second McConnell model.[37-39] This valuable finding can give a clue to the preparation of new purely organic ferromagnets in the other CT complexes than $C_{60}\cdot$TDAE. As a new cation radical in place of $\mathbf{9}^{+\cdot}$, *p*-(*N*-methylpyridinium)-substituted imidazolin-1,3-dioxyl (**16**) and imidazolin-1-oxyl (**17**) are most promising, which have a structure separating the positive charge and the radical from each other like $\mathbf{9}^{+\cdot}$, but are quite stable compared with $\mathbf{9}^{+\cdot}$.[40] The CT complexes of **16** or **17** with TCNQF$_4{}^{-\cdot}$ or hexacyanobutadienide (HCBD$^{-\cdot}$) were obtained, and the composition of the cation radical and anion radical was 1:1 for each CT complex. In result of magnetic measurements by SQUID magnetometer



the two CT complexes of **17** with $\mathrm{TCNQF_4}^{-\bullet}$ and $\mathrm{HCBD}^{-\bullet}$ (**17**·$\mathrm{TCNQF_4}^{-\bullet}$ and **17**·$\mathrm{HCBD}^{-\bullet}$) exhibited the similar temperature dependence of χ_p·T to that of **9**$^{2+}$·HCTMC^{2-} and **9**$^{2+}$·$\mathrm{TCNQF_4}^{2-}$ (Figure 10). Thus, in the high temperature region χ_p·T decreased with a lowering temperature, but below 10 K the value reversely continued to increase till 2 K. The increase in χ_p·T below 10 K suggests ferromagnetic interaction in the CT complexes. The field dependence of the magnetization gave support

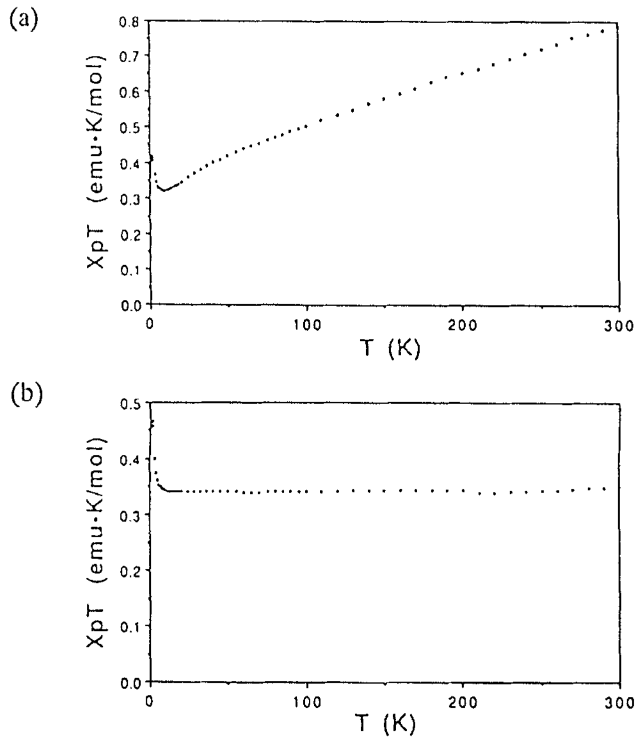
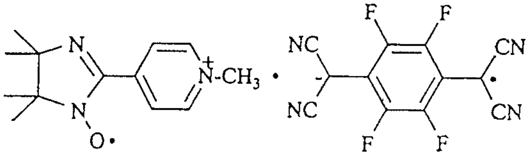
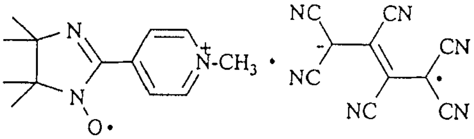


FIGURE 10 The temperature dependences of χ_p·T for (a) **17**·$\mathrm{TCNQF_4}^{-\bullet}$ and (b) **17**·$\mathrm{HCBD}^{-\bullet}$ in the temperature range of 2 to 300 K.



17·TCNQF4$^{-\bullet}$



17·HCBD$^{-\bullet}$

the occurrence. Thus, the magnetization approached to saturation more rapidly with a lowering temperature in the range of 2 to 10 K. Very recently, the magnetic measurement to lower temperature was performed using a ^{3}He-^{4}He dilution refrigerator. The ac susceptibility (χ_{ac}) measurements indicated a ferromagnetic phase transition at about 0.5 K.[41] Furthermore, the magnetization measured at 80 mK showed a characteristic curve of a ferromagnet with a very small hysteresis. Eventually, these CT complexes are actually a first organic ferromagnet based on a stable CT complex with a definite 1:1 composition of the cation radical and the anion radical. The more detailed magnetic properties as well as the origin of ferromagnetic interaction must be elucidated by futher investigation.

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