Charge Transfer Assisted Ferromagnetic Coupling Observed in an Ion-Radical Salt of a Cross-Cyclophane TTF-Based Donor

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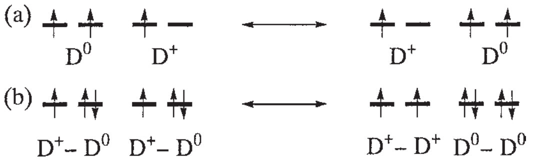
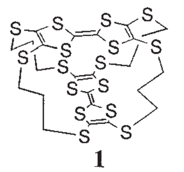
The ferromagnetic interaction was observed in a conducting ion-radical salt of a TTF-based cross-cyclophane type dimeric donor.

For designing molecular conducting ferromagnets,[1] Wudl et al. proposed a unique electronic structure, which was constructed by the stacking of a ground state triplet diradical donor (D^0) with degenerate HOMOs in a mixed-valence state ($\cdots D^0D^+D^0D^+D^0D^+\cdots$) as shown in Scheme 1a.[2] A similar electronic structure may be realized if two singly oxidized dimeric donors (D^+–D^0) are in resonance with a doubly oxidized state (D^+–D^+) of a ground state triplet and a neutral one (D^0–D^0) as a charge-tansferred state (Scheme 1b).



Scheme 1. Spin alignments (a) in a Wudl model and (b) in a cation radical salt of a dimeric donor with degenerate HOMOs.

From the above viewpoint, it is interesting to prepare a dimeric donor which exhibit a ferromagnetic intramolecular coupling in the doubly oxidized state by virtue of the charge-transfer interacton. As a model compound which satisfies the above requirment, here we propose a novel TTF-based dimeric donor (**1**) in which two equivalent donor units are constrained in a cross-cyclophane type geometry with four trimethylenedithio chains.[3] Generally speaking, unpaired electrons in the dication-diradical of a dimeric donor are likely to be coupled antiferromagneitcally. In the dication-diradical of **1**, however, the through-space interaction between singly oxidized donor units should be negligibly small, because two donor units are fixed in an orthogonal orientation by trimethylene chains. Therefore, there is a chance for the dimeric donor to manifest a ferromagnetic coupling if the through-bond[4] interaction (vide infra) operates efficiently.



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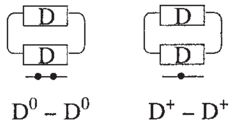
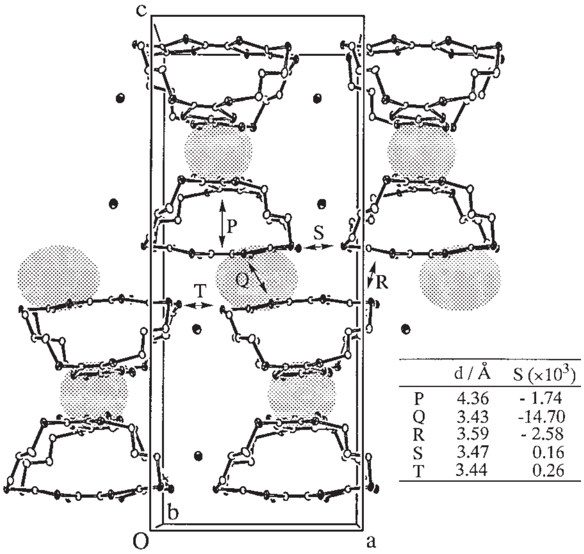


The cross-cyclophane type TTF donor (**1**) afforded ion-radical salts, **1**·Br·TCE$_2$ (TCE = 1,1,2-trichloroethane), by electrocrystallization in the presence of tetra-*n*-butyl ammonium bromide.[3d] An X-ray crystallographic analysis of the salt (space group: $P4_1$) reveals that cation radicals of **1** are stacked nearly parallel to the *c* axis and they are arranged in an array along the *a* and *b* axes, which are equivalent to each other (Figure 1). The intramolecular S···S distances between the TTF units are rather remote and they are in a range of 4.36–4.56 Å (along P in Figure 1), while the intermolecular S···S distances between the facing donor planes and those of the corner-to-corner contacts are 3.43 Å (along Q), and 3.47 Å (along S, T), respectively. Inside the cavity created by surrounding donors, a bromide ion and two solvent molecules of 1,1,2-trichloroethane are incorporated per one donor molecule.



	d / Å	S (×10^3)
P	4.36	- 1.74
Q	3.43	-14.70
R	3.59	- 2.58
S	3.47	0.16
T	3.44	0.26

Figure 1. Molecular arrangement in **1**·Br·TCE$_2$ salt: Hatched regions correspond to the strongly interacting sites between donor units. Shortest intermolecular S···S distances (d) and the sum of overlap integrals (S) along the directions indicated by P–T are also shown in the table.

Magnetic property of the polycrystalline sample was also measured by a SQUID magnetometer with increasing temperatures from 2 K to 300 K (Figure 2).[5] The $\chi_P T$ value was evaluated to be 0.370 emu·K·mol^{-1} at room temperature, indicating that each donor molecule carries one unpaired electron taking the molecular weight estimated from the elemental analysis into account. The temperature dependence of the $\chi_P T$ value was analyzed in terms of a one-dimensional ferromagnetic Heisenberg chain ($J/k_B = +1.6$ K) with antiferromagnetic couplings ($J/k_B = -0.1$ K)[6] with adjacent chains ($Z = 4$).[7] Judging from the calculated overlap integrals (Figure 1), the unpaired electrons are mainly distributed in a region where HOMO and SOMO interact intermolecularly (along Q). Since these regions are located above and below the cyclophane donor **1**, the ferromag-

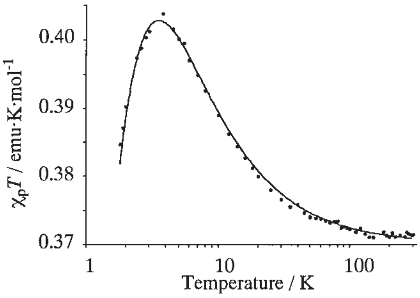


Figure 2. Temperature dependence of the procuct of paramagnetic susceptibility and temperature ($\chi_P T$) of **1**·Br·TCE$_2$. The solid curve denotes the theoretical fitting for the one-dimensional ferromagnetic Heisenberg chain with antiferromagnetic couplings between adjacent chains.

netic interaction detected here may be ascibed to the intramolecular origin (vide infra).

In order to obtain information on the spin-correlation in the doubly oxidized state of **1**, the PM3 calculation was carried out on the dication-diradical species (D^+–D^+).[8] There are nearly degenerated SOMOs and most of the coefficients of SOMO are localized on each donor unit, respectively. This means that the intramolecular electronic interaction between SOMOs should not be significantly large. However, it is to be noted that there are small coefficients at the middle carbon atom of the trimethylene chains (Figure 3a). Therefore the ferromagnetic coupling between unpaired electrons derived from the CT state (D^+–D^+) because SOMOs of D^+–D^+ have a space-sharing nature.[9] The spin-polarization mechanism[10] along the trimethylenedithio chains is also considered to be operating (Figure 3b). Although the salt could be regarded as a Mott insulator at low temperatures where the magnetic interaction became predominant, the conductivity of the single crystal of the ion radical salt exhibited semiconducting behavior at elevated temperatures.[11]

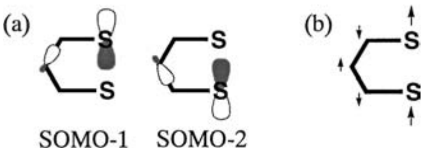


Figure 3. Ferromagnetic coupling mechanisms of 1^{2+} based on the through-bond interaction: (a) two degenerate SOMOs sharing coefficients on the middle carbon of the chain, (b) a long-range ferromagnetic coupling through π–σ and σ–σ spin polarization.

In summary, the cation radical salts of **1** turned out to exhibit the ferromagnetic interaction even when the dimeric donors are singly oxidized. The ferromagnetic one-dimensional interaction may be achieved on the basis of the ferromagnetic through-bond coupling and the intermolecular HOMO-SOMO interaction between the facing donor units (Figure 4). Namely the ferromagnetic coupling in **1**·Br·TCE$_2$ may be originated from the contribution of the charge-transfer state. The present result may be the first experimental evidence for the appearance of the ferromagnetic coupling assisted by the intermolecular CT interaction. Although a suitable chemical modification is needed, this cyclophane donor **1** can be classified as a new class of compounds in the research for conducting magnetic materials.

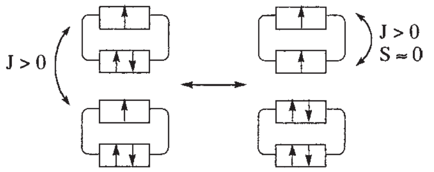


Figure 4. Schematic drawing of the electronic structure of the ion-radical sals of the dimeric donor, exhibiting the charge transfer assisted ferromagnetic coupling.

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6 The interchain antiferromagentic interaction may be originated from the superexchange mechanism on the basis of the SOMO-HOMO-SOMO interaction along the Q, R, and Q directions.

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8 A cyclic voltammogram of **1** shows redox peaks at 0.64 and 0.77 V (vs Ag/Ag$^+$). The small splitting of 0.13 V between the first and the second oxidation potentials of **1** suggests that the diradical dication (D^+–D^+) state contributes to the electronic structure of $1^{+\bullet}$ in the solid state.

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11 The conductivity of the single crystal of the salt was measured to be 1×10^{-3} S·cm^{-1} along the *a* (or *b*) axis and 6×10^{-4} S·cm^{-1} along the *c*-axis at room temperature. The temperature dependence of the conductivity of the salt exhibited a semiconducting behavior ($E_a = 0.090$ and 0.28 eV along *a* (*b*) axis and *c* axis, respectively, in the temperature range of 180–280 K).