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# Theoretical investigation on the magnetic interaction of the tetrathiafulvalene–nitronyl nitroxide stacking model: possibility of organic magnetic metals and magnetic superconductors

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## Abstract

The possibility of realizing ferromagnetic conducting crystals was investigated theoretically. Detailed theoretical calculations were carried out for tetrathiafulvalene–nitronyl nitroxide (TTF–NN) and one- and two-hole doped states of its dimer. The result indicated that the sign of effective exchange interactions between TTF–NN is largely dependent on the stacking modes and hole doping states. Well-controlled stacking and hole doping modes of spin-polarized TTF–NN molecule led to positive effective exchange integrals ( $J_{ab}$ ), indicating its possibility as an organic ferromagnetic metal. Thus, charge-transfer (CT) complexes with radical groups will exhibit a ferromagnetic interaction and electronic conductivity may be expected along the donor column, if appropriate columnar stacking and partially hole-doped state were realized. Implications of the calculated results are discussed in relation to the field-induced superconductivity in the field-effect-transistor (FET) and spin FET configurations. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Ferromagnetic conducting crystal; Theoretical calculation; Tetrathiafulvalene–nitronyl nitroxide; Spin-polarized donor; Charge-transfer complexes

## 1. Introduction

For the past decade, we have examined the possibilities of organic magnetic conductors by chemical doping, physical doping, photo-induced charge-transfer (CT) excitation, etc., for molecule-based magnets on theoretical grounds [1–9]. For example, the post Hartree–Fock, CASSCF and CASPT2 calculations have been carried out for hole- [2] or electron-doped [3] polycarbenes and hole-doped polyamines [4] in order to elucidate the spin alignment rule in charged polyradicals. We have theoretically examined possibilities of conversions of CT complexes into organic magnetic conductors by the introduction of a radical substituent into donor (D) or acceptor (A) as spin source [5–8]. Ab initio molecular orbital (MO) calculations have indi-

cated that ferromagnetic intermolecular interactions are feasible in the case of appropriately stacked CT complexes with radical substituent.

Recently, ferro- or antiferromagnetic coupling between conduction electron and localized spin has received great experimental interest in relation to the design and synthesis of new magnetic materials such as organic magnetic metals. Several research groups have indeed synthesized electron donors with stable radical groups (R) as spin sources [10–15]. For example, Sugawara et al performed the oxidation of TTF derivatives with nitronyl nitroxide group (NN) and found that the cation radical of TTF–NN has the ground singlet state, while that of TTF<sup>+</sup> with phenyl nitronyl nitroxide (PNN) is triplet [10,11]. Nakatsuji and Anzai and their group synthesized a lot of donors with nitroxide radicals [12]. They observed the electronic conductivity and magnetic behaviors of both mixed and segregated columns consisted of these compounds and electron acceptors. Their experiments indicated that the CT

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complexes did not exhibit characteristics of magnetic metals, though ferro- or antiferromagnetic semiconductors were realized at low temperatures. Further experimental and theoretical studies are necessary towards the goal.

Very recently, physical doping of organic crystals has been accomplished by using the field-effect-transistor (FET) technique [16,17]. The FET composed of pentacene single crystals indeed works as a ambipolar device. High-purity pentacene single crystals and the pentacene– $\text{Al}_2\text{O}_3$  interface dramatically improves the conductivity of organic semiconductors [16,17], since heavy doping such as one hole (or electron) per one molecule is feasible. Indeed, the field-induced superconductivity is accomplished even in the anthracene and pentacene crystals. We expect rapid development of physical doping of organic crystals by the FET [17] and spin FET [18] techniques. The photo-doping [8,9,19] will be promising for organic systems with low CT excitation energies.

Here, we first perform theoretical calculations of neutral and hole-doped TTF–NN to elucidate the orbital energy level and possible ground spin states. We focus attention on the conformational effect on the effective exchange interaction between doped spin on  $\text{TTF}^+$  and localized spin on NN. Next, theoretical calculations were carried out for the dimer structure with different conformations of  $\text{TTF}^+$ –NN molecules

and we tried to examine variations of the intermolecular effective exchange interactions with stacking modes. Last, DFT (density functional theory) calculations were carried out for the dimer in the different hole-doped states. The implications of the present calculated results are discussed in relation to the organic magnetic metals and magnetic superconductors [20] proposed previously [1–7]. They will be realized by the FET and spin FET techniques.

## 2. Theoretical background

### 2.1. General strategy for organic magnetic metals

Previously, we have theoretically examined the possibilities of conversions of CT complexes into organic magnetic conductors by the introduction of radical substituents into donor or acceptor as spin source [5,6]. We have pointed out possibilities of organic magnetic metals based on the ab initio calculated results. In order to design molecule-based organic metallic ferromagnets, let us first consider the guiding principle and general strategy for the inter-molecular magnetic interaction.

The segregated columns composed of spin-polarized D–R units have been expected to become possible candidates for organic magnetic metals. Here, we considered *syn*- and *anti*-type stackings of D–R molecules **1** and **2** in Fig. 1, respectively. For *syn*-type stacking **1**, antiferromagnetic interactions between R groups may be predominant because of their small spatial distance. While, for *anti*-type stacking **2**, the indirect interaction through the R–D–D–R path is mainly expected. There is a possibility that unpaired electrons on R sites exhibit ferromagnetic spin arrangement.

We have considered two types of *anti*-type dimer units **3** and **4** for the candidate of organic magnetic metals as illustrated in Figs. 2 and 3, respectively. For the two hole-doped *anti*-type dimer unit **3** in Fig. 2, spin alignment in Fig. 2(A) is expected as the ferromagnetic model for organic magnetic metals. Ferromagnetic interaction between D–D is realized due to small overlap integrals and the non-zero potential exchange (PE) term for a specific segregated stacking of donor cation radicals. Since the intramolecular spin arrangement is parallel, ferromagnetic spin order may be realized for this model. Three other models B, C and D in Fig. 2 are not appropriate candidates for organic ferromagnetic metals since B and C exhibit antiferromagnetic interactions on segregated columns, while model D shows anti-ferromagnetic interaction on the whole molecule, though ferromagnetic interaction appears on the segregated donor column. B, C and D are therefore the models for antiferromagnetic metals.

On the other hand, for model **4** in Fig. 3, the donor column is partially hole-doped by one-electron oxida-

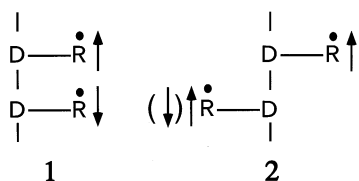


Fig. 1. *Syn* (**1**) and *anti*-type (**2**) stacking models for the electron donor (D) with a radical group (R).

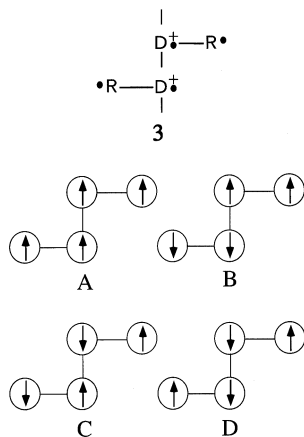


Fig. 2. *Anti*-type stacking model (**3**) for a donor cation radical ( $\text{D}^+$ ) with a radical group (R). (A) shows the highest spin configuration for **3**, while (B), (C) and (D) denote total low-spin configurations.

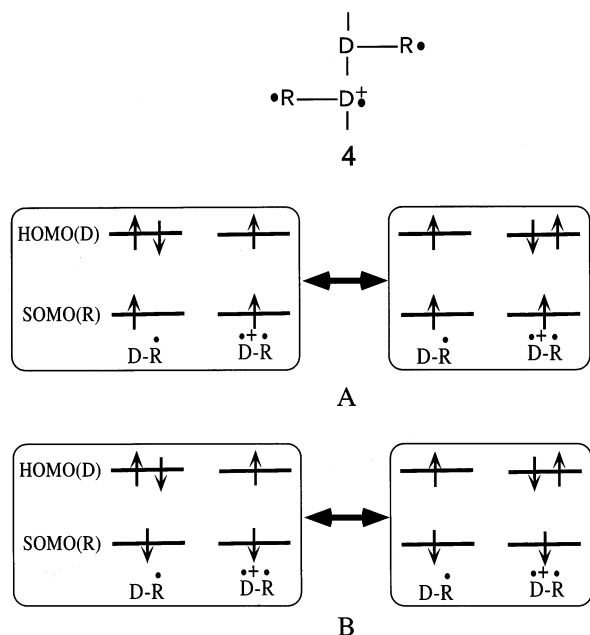


Fig. 3. Anti-type stacking model (4) for the dimer unit with one induced hole. (A) shows the high-spin configuration via the double-exchange mechanism, while (B) denotes the low-spin configuration via the superexchange mechanism.

tion of the dimer unit. Fig. 3(A) illustrates the ferromagnetic spin state based on the double-exchange mechanism. Ferromagnetic interaction is feasible between the unpaired electrons at the radical site and the unpaired electron resides in HOMO of the other D–R molecule when the intramolecular spin arrangement is parallel. From Fig. 3(B), the unpaired electron, which resides in SOMO at the radical site, interacts with the unpaired electron residing in SOMO of the other D–R molecule, via the superexchange interaction between

HOMOs. The ferrimagnetic spin state appears on the partially oxidized dimer in Fig. 3(B), if intramolecular interaction is antiferromagnetic as a result of superexchange.

The possibility of model 3 in Fig. 2 may be low by chemical doping, but it is conceivable by the FET technique [16]. On the other hand, we can expect model 4 even by chemical doping as illustrated in Fig. 3, and model 4 may be metallic because there are delocalized spins on a donor column and those spins itinerate along a segregated donor column. The unpaired electrons residing in radical sites interact ferromagnetically through the conduction electrons via the double-exchange mechanism if an appropriate segregated stacking is accomplished and holes are partially doped. Then, wide band may be formed from the HOMO of D, and the metallic state should be realized.

## 2.2. Design of organic magnetic metals

To realize spin-polarized donor molecule as mentioned above, it is necessary to oxidize not unpaired electrons on the radical sites, but  $\pi$ -electrons on the donor sites. Accordingly, TTF-, (BEDT–TTF)- or BETS-derivatives with radical have been used as strong electron donors. As building blocks of organic magnetic metals, some D–R type molecules are possible candidates as illustrated in Fig. 4. Previously, ab initio UHF calculations were carried out for TTF–R type molecules in Fig. 4 ( $\text{R} = \text{M}$ ;  $-\text{CH}_2$  radical,  $\text{N}$ ;  $-\text{NOH}$  radical). The ground state of cation radicals with the  $\text{CH}_2$  radical group was predicted to be singlet by theoretical calculation [5], while the triplet state was the ground state of  $\text{TTF}^+-\text{M}$  when  $\pi$ -conjugation between HOMO and SOMO was interfered with the internal rotation of the  $\text{CH}_2$  group.

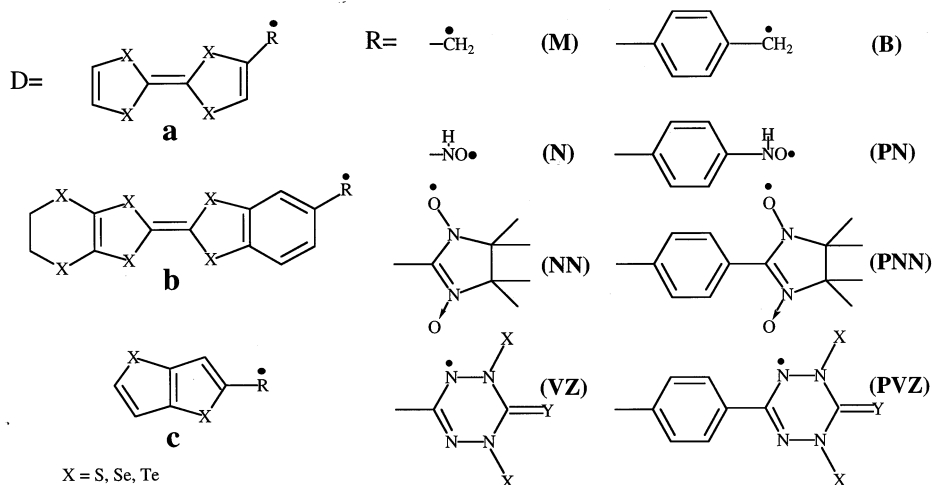


Fig. 4. Electron donors ( $\text{D} = \text{a}$ ,  $\text{b}$  and  $\text{c}$ ) with radical substituents ( $\text{R} = \text{M}$ ,  $\text{N}$ ,  $\text{VZ}$ ,  $\text{B}$ ,  $\text{PNN}$  and  $\text{PVZ}$ ) for building blocks of organic magnetic metals.

Table 1

Valence bond selection rule for TTF derivatives with a radical substituent

R	$\theta = 0^\circ$	$\theta = 90^\circ$	Exp.
M	LS	HS	LS
N	LS	HS	
NN	HS	LS	
VZ	HS	LS	
B	LS	HS	
PN	LS	HS	HS
PNN	HS	LS	
PVZ	HS	LS	

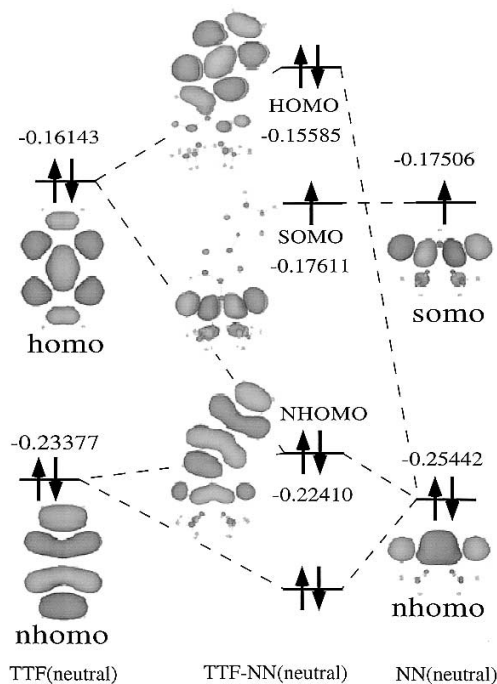


Fig. 5. Shapes of HOMO, SOMO and NHOMO of the TTF–NN molecule, HOMO and NHOMO of the TTF fragment, and SOMO and NHOMO of the NN fragment.

Here, let us consider possible ground spin states of  $\text{TTF}^+$  with radical group (R) as shown in Fig. 4. As in the case of  $\text{TTF}^+-\text{R}$ , we assume that the sign of the induced spin density on the connected carbon atom of R with  $\text{TTF}^+$  plays a crucial role in determining the sign of  $J_{ab}$ . Table 1 summarizes the predicted ground states of  $\text{TTF}^+-\text{R}$  at the planar and perpendicular conformations on the basis of the previous valence bond (VB) or spin polarization (SP) rule [5,6].

The orbital overlap (OO) interaction between SOMO of  $\text{TTF}^+$  and the p-orbital of  $\text{CH}_2$  leads to the singlet ground state of  $\text{TTF}^+-\text{CH}_2$  in the planar conformation, while the orthogonal interaction between them at the perpendicular conformation predicts the triplet ground state, in accord with the ab initio calculations [6]. The nitronyl nitroxide group is probably one of the

most appropriate radicals to examine the selection rule in Table 1. A systematic investigation of the available experiments [10–15] will be performed elsewhere.

### 3. Ab initio calculations of monomer

#### 3.1. Molecular orbital energy levels

It is necessary to examine whether TTF–NN is an appropriate candidate for organic magnetic metals or not. In order to understand electronic structure of neutral TTF–NN molecule, we carried out ab initio MO calculations for planar TTF–NN, TTF and NN.

Full geometry optimization was carried out for these models by means of MOPAC/PM3. Ab initio UHF and DFT calculations were performed to obtain MO energy levels for the optimized planar structures of TTF–NN, TTF and NN models.

From the result of the UB3LYP/6-31G\* calculation, it is found that the HOMO of TTF–NN arising from HOMO of TTF and NHOMO of NN is located above the SOMO of TTF–NN derived from SOMO of NN as illustrated in Fig. 5. The unpaired electron, which resides in SOMO, causes spin-polarization of the  $\pi$ -electrons in HOMO. The orbital energy of an  $\alpha$ -spin in HOMO is stabilized by exchange interaction, while that of a  $\beta$ -spin is relatively unaffected. Consequently, the HOMO electron having a  $\beta$ -spin is removed by one-electron oxidation and a triplet ground state is generated. Under this circumstance, we expect to generate a triplet ground state on one-electron oxidation of the planar TTF–NN molecule [6].

As mentioned above, the reason which ground state is generated by one-electron oxidation, namely triplet or singlet ground state, could be explained by the characteristic orbital energy diagram of the donor radical [6].

#### 3.2. Variation of $J_{ab}$ value with rotational conformations

In contradiction to above prospect, the experimental studies of magnetic measurements by Sugawara et al. [10] indicated that the  $J_{ab}$  value of the cation diradical of TTF–NN molecule is negative, indicating the low-spin singlet with the antiferromagnetic interaction. The reason may be ascribed to the twisted structure between TTF and NN planes due to steric repulsion as illustrated in Fig. 6, though TTF–NN is probably in a glassy state and its crystal structure is not made clear experimentally [10]. Thus, ab initio UHF and DFT calculations were carried out for monomer structures of oxidized TTF–NN molecules. The  $J_{ab}$  values were evaluated for the models according to different dihedral angles between TTF and NN planes in order to investi-

gate structural dependency of the  $J_{ab}$  values as illustrated in Fig. 6(A).

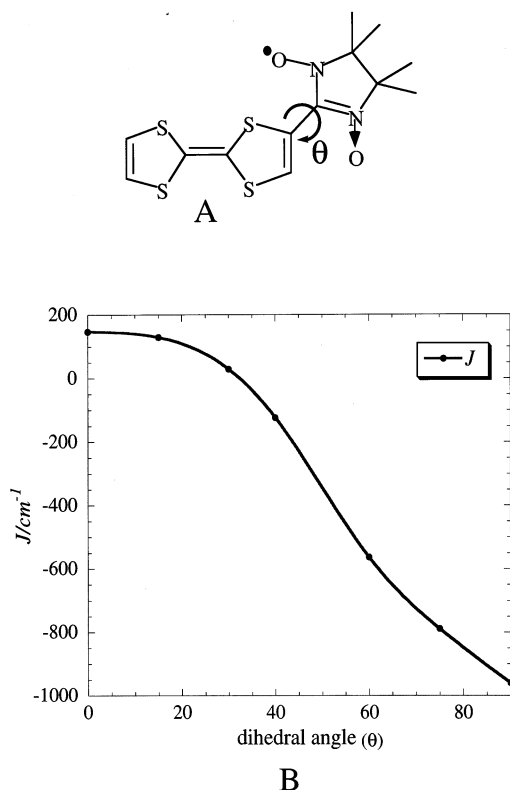


Fig. 6. (A) The internal rotation ( $\theta$ ) of the NN group in TTF–NN and (B) variations of the effective exchange integral ( $J_{ab}$  ( $\text{cm}^{-1}$ )) with the change of  $\theta$  by the UB3LYP/6-31G\* method.

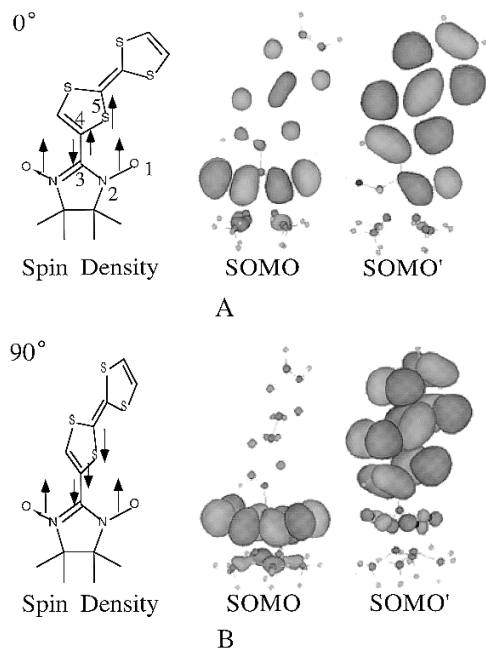


Fig. 7. Schematic illustration of the spin polarization effect and shapes of SOMO and SOMO' for the planar (A) and perpendicular (B) conformations of the cation radical state of TTF–NN (see text).

UB3LYP/6-31G\* calculations were performed to elucidate variations of the  $J_{ab}$  values with change of the dihedral angle of the  $\text{TTF}^+-\text{NN}$  molecule. The calculated results are depicted in Fig. 6(B). When the dihedral angle is  $0^\circ$ , the  $J_{ab}$  value shows the maximum positive value ( $J_{ab} = 147 \text{ cm}^{-1}$ ), indicating the ferromagnetic interaction. While the minimum  $J_{ab}$  value ( $J_{ab} = -960 \text{ cm}^{-1}$ ) was shown at the perpendicular conformation (dihedral angle  $90^\circ$ ). It is found that the  $J_{ab}$  value decreased gradually according to the dihedral angle.

For the planar structure, the spin densities and molecular orbital were calculated and they are illustrated in Fig. 7(A). From the spin density population, it is found that the  $\beta$ -spin on the  $\alpha$ -carbon of the NN site coupled with the  $\alpha$ -spin on the TTF site in conformity with the spin alternation rule. The antiferromagnetic spin coupling indeed appeared between C(3) and C(4) atoms since  $\text{TTF}^+-\text{NN}$  is a planar structure and the overlap integral between p-orbitals on these atoms is not zero. Both SOMO and SOMO' are more or less delocalized on the whole molecule because of this orbital interaction. Thus, the ferromagnetic state is generated for the planar TTF–NN cation radical.

On the other hand, for the perpendicular structure, the SOMOs of  $\text{TTF}^+$  and NN were orthogonal and their orbital overlap is negligibly small. The ferromagnetic interaction between C(3) and C(4) atoms should be induced by the potential exchange (PE) term. As illustrated in Fig. 7(B), both SOMO and SOMO' are localized on the TTF and NN sites, respectively, indicating that the perpendicular structure of molecular orbital causes the localization of two SOMOs. The antiferromagnetic spin state for the perpendicular structure of  $\text{TTF}-\text{NN}^+$  is realized because of the spin polarization of the NN group, in accord with the experimental one [10].

#### 4. Exchange coupling for the dimer unit with two holes

##### 4.1. Intermolecular interaction for sliding conformations

It is necessary to investigate the intermolecular magnetic interaction in stacked planar TTF–NN molecules with the triplet ground state in order to realize the ferromagnetic spin arrangement. The dimer unit is considered as a basic model of an organic ferromagnet, since orbital interaction between radical sites in *anti*-type stacking manner may be expected to be ferromagnetic.

Here, let us examine the intermolecular interaction of model 3. Ab initio UHF/4-31G calculations were carried out for variable parallel stacking of planar triplet molecules. The parameters  $R_1$  and  $R_2$  in Fig. 8 indicate

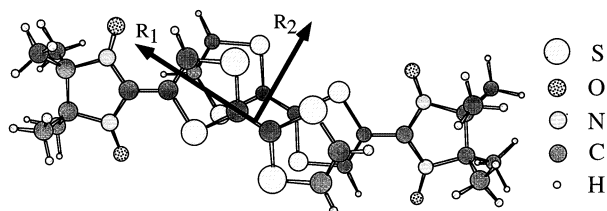


Fig. 8. Stacking mode for the TTF-NN<sup>+</sup> dimer with the fixed interplane distance (4.0 Å).  $R_1$  and  $R_2$  denote parameters responsible for the sliding motion of TTF-NN<sup>+</sup>.

the sliding distance, though the interplane distance is fixed to be 4.0 Å. The intermolecular effective exchange integral ( $J_{ab}$ ) for **3** was calculated by the energy difference between total singlet and quintet configurations.

The evaluated  $J_{ab}$  and energy values for the TTF<sup>+</sup>-NN dimer obtained by the UHF method were illustrated in Fig. 9(A). From this figure, ferromagnetic intermolecular interactions are recognized in some specific sliding conformations of two TTF<sup>+</sup>-NN molecules (for example,  $R_1 = R_2 = -1.0$  Å). In these structures the potential exchange (PE) term is essential to provide positive  $J_{ab}$  values. On the other hand, the negative  $J_{ab}$  values appear in the overlap conformations (for example,  $R_1 = R_2 = 0.0$  Å), showing that the anti-ferromagnetic interaction is dominant. It is concluded that the control of stacking mode is very important for ferro- and anti-ferromagnetic interaction in the segregated columns. The  $J_{ab}$  values largely depend on the orbital overlap between both TTF parts, especially the orbital overlap on sulfur atoms is predominant.

In addition, the potential surface was calculated as shown in Fig. 9(B), indicating that the activation bar-

Table 2

$J_{ab}$  (cm<sup>-1</sup>) value of the TTF-NN dimer ( $R_1 = R_2 = -1.0$ )

Method <sup>a</sup>	Model 3	Model 4
UHF	3.660	3.286
UB3LYP	-4.991	96.08
UB2LYP	-0.5182	131.1
UBLYP	-700.0	-95.37

<sup>a</sup> The 4-31G basis set is used.

rier appears in the conformation, where one TTF molecule is placed above another TTF molecule retaining the large overlap of p-orbital electrons (for example,  $R_1 = -4.0$ ,  $R_2 = 4.0$  Å). Here, strong steric hindrance occurs in these conformations and the stability of the dimer becomes low. These results mean the necessity of total energy consideration for the crystal structure, though the orbital overlap term mainly determines the sign of effective exchange integral in the *anti*-stacking mode.

#### 4.2. DFT calculations of $J_{ab}$ values for the dimer unit

As shown previously [21], the UHF method often overestimates the spin polarization (SP) effect of  $\pi$ -electrons, leading to large ferromagnetic interaction. Therefore, it is desirable to confirm the ferromagnetic interaction concluded for a specific conformation of the dimer unit **3** by the UHF calculation. Here, we have performed both BLYP and hybrid DFT calculations assuming the same geometry. Table 2 summarizes the calculated  $J_{ab}$  values for model **3**. As expected for the calculated results for other radical pairs [22], the BLYP

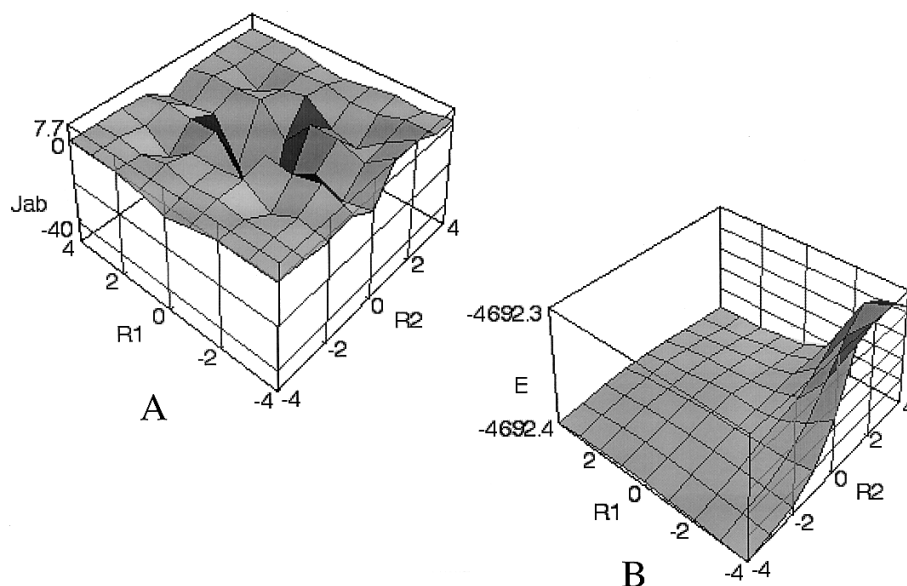


Fig. 9. (A) Variations of the intermolecular effective exchange integrals ( $J_{ab}$ ) with changes of the sliding parameters  $R_1$  and  $R_2$  by UHF/6-31G\* and (B) potential energy surface for the sliding motion of the TTF-NN dimer unit with two induced holes.

method predicted the large negative  $J_{ab}$  value ( $-700 \text{ cm}^{-1}$ ) because of the overestimation of the metallic character. On the other hand, UB2LYP and UB3LYP calculations indicated the small negative  $J_{ab}$  values.

These results, together with the UHF calculation, indicate that the sign of the intermolecular  $J_{ab}$  value for the crystal of one-hole doping state of TTF–NN is subtle and therefore it is highly dependent on crystal structure and other factors. Extensive experimental studies are described in this regard.

## 5. Exchange coupling for the dimer unit with one hole

### 5.1. Importance of the double-exchange mechanism

As discussed in Section 4, the double-exchange mechanism plays a predominant role in the dimer unit **4** with one hole. Here, we carried out both ab initio UHF and DFT calculations of **4** assuming the same stacking mode for **3** with the ferromagnetic interaction predicted by UHF. The total energies of the doublet and quartet states of **4** were used to obtain the  $J_{ab}$  values [6].

Table 2 summarizes the calculated results. From Table 2, the large negative  $J_{ab}$  value for **3** by UBLYP is reduced to about 1/7 because of the strong contribution of the double-exchange interaction. The  $J_{ab}$  values for **4** become positive by UHF, UB2LYP and UB3LYP, supporting the double-exchange mechanism. These results suggest that the same mechanism should be operative even at the strong overlap conformation (for example  $R_1 = R_2 = 0.0 \text{ Å}$ ). In order to confirm this theoretical prediction, we performed both UHF and UB3LYP calculations assuming the conformation. The calculated  $J_{ab}$  values are summarized in Table 3. The calculated  $J_{ab}$  values for **4** are indeed positive because of the double-exchange mechanism in sharp contrast with those of **3**. These results conclude that the 1/2-hole doped segregated column of TTF–NN is a possible candidate for organic ferromagnetic metals since the orbital overlap guarantees the conductivity.

### 5.2. Mixed valence states by FET and photo-induced CT

The present model calculations clearly demonstrated that the double-exchange mechanism providing ferro-

magnetic interaction can be realized by partial oxidation of donors with radical groups. These mixed-valence states can be generated by the FET techniques [16,17], spin FET [18], and photo-induced CT. CT complexes near the neutral-ionic transition would be particularly interesting for the last procedure as pointed out previously [8]. However, the present ab initio calculations suggest that the band gaps remain even in partially oxidized segregated columns. Therefore, ferromagnetic semiconductors may be realized at an ordinary pressure, in accord with the experiments by Nakatsuji et al. [12]. Probably, the high pressure is often required to induce the transition from ferromagnetic semiconductor to the ferromagnetic metal.

## 6. Discussion and concluding remarks

### 6.1. FET and spin FET techniques

Recently, Schon et al. have demonstrated that the FET configuration is remarkably useful for generation of organic metals and organic superconductors by physical doping of hole or electron into organic crystals. For example, the transition temperature ( $T_c$ ) for the field-induced superconductivity of hole-doped  $C_{60}$  is 52 K in the FET configuration. Their finding is consistent with our previous theoretical result on anomalous phases in molecular systems with external field [9].

In this paper, we have theoretically examined the possibility of organic magnetic metals and magnetic superconductors [20] constructed of TTF derivatives with radical groups as spin sources in the FET configurations. The spin FET configuration [18] using ferromagnets as source and drain in Fig. 10(B) may be utilized as a switching device for electron current by ferro- or antiferromagnetic couplings between spins of source and drain, since a lot of precursors can be synthesized by chemical synthesis for appropriate design of orbital energy levels as illustrated in Figs. 4 and 5. The half-metal states are probably interesting for this purpose. Moreover, the high- $T_c$  superconductivity may be expected for magnetic metals because of the cooperative mechanism of electron-phonon and spin fluctuation as shown in our recent paper [23].

Finally, the Josephson junction in Fig. 10(C) could be constructed for active controls of coherence and decoherence phenomena of two small organic superconductors [24]. This configuration might be effective for mesoscopic device of quantum computing in the future [25].

### 6.2. Conclusions

Ab initio UHF and hybrid DFT calculations were performed for the tetrathiafulvalene (TTF) with

Table 3  
 $J_{ab}$  ( $\text{cm}^{-1}$ ) value of the TTF–NN dimer ( $R_1 = R_2 = 0.0$ )

Method <sup>a</sup>	Model 3	Model 4
UHF	−57.95	699.6
UB3LYP	−125.3	187.0

<sup>a</sup> The 4-31G basis set is used.



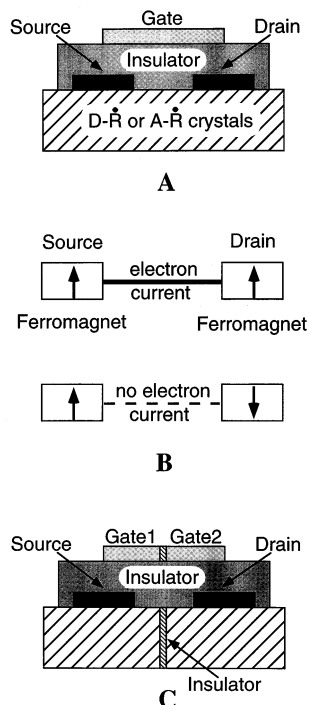


Fig. 10. (A) Schematic illustrations of the FET configuration; (B) spin FET configuration, and (C) the Josephson junction configuration.

nitronyl nitroxide (NN) group in order to elucidate possibilities of generations of organic magnetic metals by hole doping using chemical, physical and other techniques. The following conclusions are obtained from the calculated results:

1. The energy levels of the spin polarized HOMOs are higher than that of SOMO in the cage of TTF–NN, showing a necessary condition for the hole doping into the TTF part.
2. The triplet ground state is predicted for the cation radical state of TTF–NN ( $\text{TTF}^+ \text{--NN}$ ) with the planar conformation, while the spin crossover from the triplet to the singlet state occurs with the internal rotation of the NN group. The calculated result is consistent with the experiment [10].
3. The intermolecular effective exchange integrals ( $J_{ab}$ ) for the dimer unit **3** with two induced holes seem positive at specific stacking modes because of the no SOMO–SOMO orbital overlap. This implies the possibilities of ferromagnetic metal by heavy hole doping into the TTF–NN crystal by the FET [16,17] and spin FET [18] techniques.
4. The high-spin quartet state was calculated to be more stable than the low-spin doublet state for the dimer unit **4** with one induced hole, in conformity with the double-exchange mechanism. The present calculations predict the possibility of an organic

ferromagnetic metal by partial hole doping into the TTF–NN crystal.

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