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Electronic structures of organometallic conjugated systems. Possibilities of molecular magnets, magnetic conductors and spin-mediated superconductors composed of metallocene units

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Abstract

Intermolecular CI and ab initio MO studies were carried out for metallocenium-TCNE(TCNQ) complexes to explain the observed magnetic behaviors. The spin polarization and spin delocalization effects in these systems were clarified based on the calculated results. Theoretical possibilities of molecular magnets, magnetic conductors, and spin-mediated superconductors were examined on the basis of the computational results for metallocene conjugated systems, together with various experimental results available. Variations of magnetic properties for the species were clarified from the view point of three phenomenological variables (spin and lattice dimensionalities, and scale factor). From both computational and experimental results, several model Hamiltoians such as Kondo, and RKKY models were derived for elucidation of potential electronic properties of organometallic conjugated systems via π-electron and/or hydrogen bond networks. Possible candidates for organometallic functional materials are proposed on the basis of the computational results, together with various circumstantial experimental results. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Miller and Epstein, and their coworkers [1] have extensively investigated magnetic properties of charge-transfer complexes between ferrocene derivatives and organic acceptors such as TCNE and TCNQ, and have first discovered organometallic bulk CT ferromagnets. They have explained the magnetic behaviors of metalocenium-TCNE(TCNQ) complexes on the basis of the charge-transfer (CT) model (McConnell second model) [2]. However, Hoffman and his coworkers [3] have demonstrated that the ferromagnetic behaviors of decamethylchromocenium-TCNQ and decamethylrnanganocenium-TCNQ complexes cannot be explained by the CT model [1]. Buchachenko [4] has first pointed out an important role of spin polarization (SP) effect (McConnell first model) [5] in metallocenium-TCNE(TCNQ) complexes. Kollmar and Kahn [6] have presented the spin-restricted Hartree-Fock (RHF) plus single excitation CI (SCI) formalism for explanation of the SP effect and have estimated the negative spin densities induced on the cyclopentadienyl (Cp) ring by spins of Cr(III), Mn(III), and Fe(III) ions using semiempirical parametrizations. We have presented the intermolecular CI scheme for emphasizing an important role of the SP effect and other higher-order effects for the metallocenium-TCNE(TCNQ) complexes and have carried out the ab initio unrestricted Hartree-Fock (UHF) calculations of the [Cr(III)Cp_2] and [Ni(III)Cp_2] cores [7]. The ab initio results clearly showed that the SP effect is significant for the [Cr(III)Cp_2] complex, while the spin delocalization (SD) effect is rather pre-

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[1] Dedicated to Professor Nakamura on the occasion of his retirement from Osaka University.

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dominant for the [Ni(III)Cp$_2$] complex. Both RHF-SCI [6] and UHF [7] approaches were consistent with the experiments available [1,3]. However, judging from the experiments available, the transition temperature (T_c) for the magnetic phase transitions are not so high (< 10 K) because of the weak intermolecular (through-space) interactions resulting from the long intermolecular distances [1,3].

Recently many experimental studies [8] have been carrying out to obtain metallocenium CT complexes which may exhibit interesting electronic, magnetic and optical properties. However, intermolecular (through-space) interactions between metallocene and acceptor components were found to be rather weak. On the other hand, synthetic strategies for through-bond magnetic interactions via metallocene groups are still scanty. Experimental studies on radical substituted metallocenes should elucidate the SP and/or SD effects under discussion [1,3]. In the specially promoted research project on organometallic conjugated systems by Nakamura et al. [9], we have conducted theoretical calculations of d-p conjugated systems which are not only important and interesting from the view point of new chemical bondings but also from potential applicability's to electronic, magnetic and optical materials [10]. From the view point of d-p conjugation effects, through-bond couplings between metallocene ligands via π-network and/or hydrogen-bonded network [11] would be very promising. As a continuation of the previous work [9–11], we have extended our basic ideas for molecular design and examined theoretical models for conducting, magnetic and optical phenomena in metallocene conjugated systems. Several theoretical models or hypotheses will be derived for active controls of charge and/or spin-mediated and photo-induced properties of the species. The present paper would summarize recent developments of the intersection area between conducting, magnetic and optical organometallic materials, particularly from our specific interest.

2. Electronic structures of metallocene systems

2.1. Intermolecular CI models

First, let us consider effective exchange interactions for metallocenium-TCNE(TCNQ) complexes [1,3]. They can be approximately described by the Heisenberg model [10] by neglecting an anisotropic term [1]

$$\mathrm{H(HB)} = -\sum 2J_{ab}S_a \cdot S_b \qquad (1)$$

where S_c (c = a,b) denotes the localized spin on site c and J_{ab} is the effective exchange integral between localized spins on metallocene and TCNE(TCNQ) components. The J_{ab} values in Eq. (1) are approximately given by the SOMO–SOMO interactions [12]

$$J_{ab}(\mathrm{SOMO}) = K_{ab} - (cS_{ab})^2 \qquad (2)$$

where K_{ab} and S_{ab} denote, respectively, the potential exchange (PE) via coulombic interaction and overlap integral between magnetic orbitals, and c is a constant. The latter term is often referred to as the kinetic exchange (KE) term. The sign of J_{ab} is usually negative (antiferromagnetc) because of the non-zero orbital overlap [12], while it becomes positive (ferromagnetic) if the overlap integral disappears because of orbital symmetry [13]. The signs of J_{ab} values for metallocenium-TCNE(TCNQ) complexes are, therefore, easily predicted by considering the orbital symmetries of SOMOs. To this end, the spin configurations and their symmetries of metallocenium ions are illustrated in Fig. 1. The PE term is always positive (ferromagnetic) because of the Hund rule. From Fig. 1, the KE-term becomes zero for the V(III) and Fe(III) complexes because of no orbital overlap between SOMO of the metal ion and SOMO of TCNE(TCNQ) anion, and it is negative (antiferromagnetic) for the Cr(III)-, Mn(III)- and Ni(III)-complexes. However, the direct SOMO–SOMO interactions should be weak because of large separation between transitionmetal ion and TCNE(TCNQ) anion. Table 1 sumrnarizes the predicted signs of the J_{ab} (SOMO) values by the orbital symmetry rules [7,12,13].

The effective exchange interactions between metallocenium ions and TCNE(TCNQ) via CT excitations are given by the intermolecular CI (ICI) scheme. Fig. 2 shows the back CT excitation from TCNE(TCNQ) anion to metalocenium ion. The configuration mixings between the ground CT and back CT configurations cause stabilization energies of both low-spin (LS) and high-spin (HS) states, predicting relative stabilities between them. For example, the HS ground state is more stabilized than the LS one for Mn(III) complex because of the stronger mixing with the HS excited configuration, while the situation is reversed in the case of the

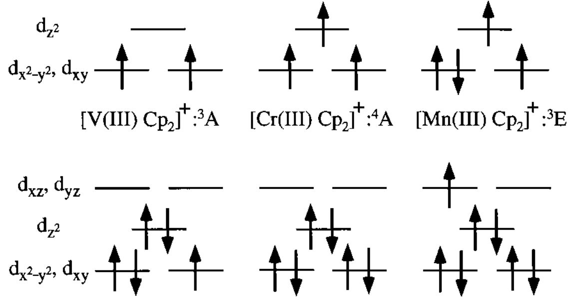


Fig. 1. The orbital configurations of metallocenium ions.

Table 1
Signs of effective exchange integrals for metallocenium-TCNE(TCNQ) complexes estimated by the orbital interaction model

System[a]	SOMO–SOMO interaction			McConnell model (MM)			Jexp[c,d]	
	J(PE)	J(KE)	J(SOMO)	GS[b,c]	Es[b,c]	J(MM)	A1	A2
$[V(L)_2]^+\ A^-$	≥ 0	0	≥ 0	$^{2,4}[^3A \cdot {}^2A]$	$^2[^2E \cdot {}^1A]$	<0		
$[Cr(L)_2]^+\ A^-$	≥ 0	≤ 0	≤ 0	$^{3,5}[^4A \cdot {}^2A]$	$^3[^3A \cdot {}^1A]$	<0	?	>0
$[Mn(L)_2]^+\ A^-$	≥ 0	≤ 0	≤ 0	$^{2,4}[^3E \cdot {}^2A]$	$^4[^4A \cdot {}^1A]$	>0	>0	>0
$[Fe(L)_2]^+\ A^-$	≥ 0	0	≥ 0	$^{1,3}[^2E \cdot {}^2A]$	$^3[^3E \cdot {}^1A]$	>0	>0	>0
$[Ni(L)_2]^+\ A^-$	≥ 0	≤ 0	≤ 0	$^{1,3}[^2E \cdot {}^2A]$	$^1[^1A \cdot {}^1A]$	<0	<0	?

[a] L, C_5Me_5; A^-, $TCNE^-$.

[b] GS, ground state; ES, lowest-excited state.

[c] $^a[^pD^{m+} \cdot {}^qAQ^{n-}]$ (D,M$(L)_2$; A1, TCNE or A2, TCNQ).

[d] Experimental value.

Cr(III) complex. Therefore, the CT model predicts the antiferromagnetic exchange interaction for the chromocenium complex, in contradiction to the experiment, though it works well for the manganocenium complex. Table 1 summarizes the predicted results via the CT interaction mechanism.

In our ICI scheme [7], the spin-polarization (SP) effect is expressed by the configuration mixing of double CT excitations between Cp ring in metallocenium ion and TCNE(TCNQ) anion as illustrated in Table 2. The virtual triplet excitation [7,14] of Cp ring is introduced as a net effect of this SP effect, and the configuration mixing between the ground and SP configurations gives rise to the negative spin densities on the Cp ring. The effective exchange interaction via the SP mechanism is illustrated in Fig. 3. Kollmar and Kahn [6] have applied the SP mechanism for explanation of the ferromagnetic behaviors of the [Cr(III)Cp_2]-TCNE(TCNQ) complex as well as the [Mn(III)Cp_2] and [Fe(III)Cp_2] complexes. We have also concluded that the SP mechanism is predominant for these three species since $|J_{ab}(SP)| > |J_{ab}(CT)|$ at least for the former [7]. However, the CT mechanism [2] employed by Miller and Epstein [1] also works well for the ferromagnetic interactions in the latter two species. Reliable ab initio computations [12] would be indeed necessary for elucidation of relative contributions of the CT and SP mechanisms for the metallocenium complexes.

The superexchange (SE) or spin delocalization (SD) mechanism [12] via Cp anion ring should be operative for the metallocenium-TCNE (TCNQ) complexes. In fact, the SD effect becomes much important for late transition metal ions because of deeper d-energy levels. Fig. 4 illustrates the SD mechanism for the complexes. Instead of the SP mechanism, the positive spin density is induced on the Cp ring via the SD effect as illustrated in Fig. 4. The SD mechanism should be predominant for [Ni(III)Cp_2]-TCNE(TCNQ) complex since the dπ(xz, yz)-orbital of Ni(III) ion interacts strongly with π-MO of CP anion.

In conclusion, several interaction terms (PE, KE, CT, SP, and SD) are thus operative for metallocenium-acceptor complexes. The relative contributions of these terms will be clarified by reliable ab initio computations in the near future. However, we would conclude that the intermolecular CI(ICI) method provides qualitative pictures for effective exchange interactions in general.

2.2. Ab initio calculations of metallocenium units

Ab initio UHF calculations [7,12] were carried out for the $[Cr(III)Cp_2]^+$ (**1**) and $[Ni(III)Cp_2]^+$ (**2**) cores to confirm the above qualitative conclusions by the intermolecular CI model. The former and latter species were predicted to exhibit predominantly the SP and SD effects, respectively. Table 2 summarizes the d-orbital spin densities and electron densities obtained for Cr(III) and Ni(III) in the metallocenium ions by the UHF MINI-1 method [15]. Fig. 5 illustrates the calculated spin-density populations on the cyclopentadienyl rings. Both values of spin densities and electron densities for the Cr(III) ion are almost 1.0 for d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals in accord with the orbital configuration illustrated in Fig. 1. However, the positive spin densities are induced on the d_{zx} and d_{yz} orbitals, showing the SP effect via d-pπ conjugation. The sum of the negative spin densities on the Cp ring via the SP mechanism was calculated to be -0.36 for **1**. This value is consistent with those of the semiempirical RHF-SCI [6] and INDO calculations [16], and also with the present intermolecular CI prediction.

The spin-density and electron-density values for Ni (III) ion are 0.0 and 2.0, respectively, for d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals, showing the closed-shell nature in conformity with the orbital configuration in Fig. 1. The large positive spin density (its sum = 0.80) was induced on the Cp ring of **2**, supporting the SD mechanism. Interestingly, the spin densities for the d_{zx} and d_{yz} orbitals are negative, indicating that the SP mechanism is also operative for **2** though it is not so large. Thus the

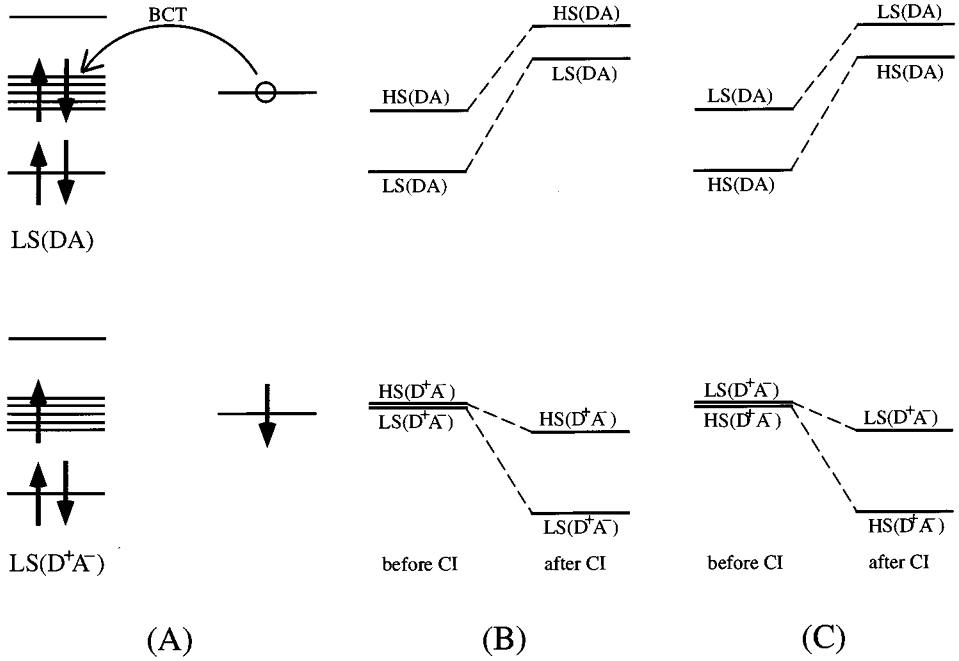


Fig. 2. The CT interaction models for high (HS) and low (LS) states.

ab initio calculations supported the qualitative conclusions based on the intermolecular CI model.

2.3. Molecular design of radical substituted metallocenium units

The above theoretical conclusions enable us to derive several strategies for molecular design of organometallic functional materials [10]. In order to elucidate the SP and SD mechanisms in the metallocenium ions, through-bond interactions via Cp ring would be interesting, leading to molecular design of radical substituted metallocenium compounds (**3**–**6**) as illustrated in [6]. Parallel (**3**–**4**) and perpendicular (**5**–**6**) orbitals interactions are conceivable for effective exchange interactions between the induced spins on the Cp ring and spins of radical substituents ($R^{\bullet}$). Pure organic, organometallic, and inorganic radicals can be used as linkage radicals. The signs of effective exchange interactions are predicted to be positive (ferromagnetic) for **3** and **6** via the SP and SD mechanisms, respectively. On the other hand, the antiferromagnetic exchange interactions are predicted for **4** and **5**. Systematic experimental studies for **3**–**6** are desirable to elucidate the SP and SD mechanisms for metallocenium cores in Fig. 1.

Table 2
d-Orbital spin density (SD) and electron density (ED) of metallocene cations

d-AOs	$[CrL_2]^+$		$[NiL_2]^+$	
	SD	ED	SD	ED
d_{z^2}	0.969	1.025	−0.000	1.992
d_{zx}	0.326	0.781	−0.139	1.429
d_{yz}	0.327	0.781	−0.297	1.340
$d_{x^2-y^2}$	0.966	0.983	−0.004	1.970
d_{xy}	0.966	0.983	−0.004	1.970

3. Variations of electronic properties with three phenomenological variables

3.1. General consideration

Since magnetism and superconductivity are cooperative phenomena [10], we must consider assembled structures of component units in Fig. 6. For phenomenological characterizations of organometallic functional materials, three important variables must be taken into account: (a) dimensionality of model Hamiltonian; (b) lattice dimensionality (1D, 2D and 3D); and (c) scale factor (microscopic, mesoscopic, and macroscopic). For example, Ising [17] and Heisenberg models [18] are one-, two- and three-dimensional spin Hamiltoninas in magnetism and related phenomena. The magnetic properties (M) can be regarded as functionals of the three variables: $M = f(A, B, C)$ as illustrated previously [10]. Therefore, spatial arrangements of the component units in Fig. 6 are of particular importance for active controls of magnetism. Past decades the 3D Heisenberg model has been discussed in relation to molecular ferromagnets, which are usually insulators from electronic conductivity. Recently two different

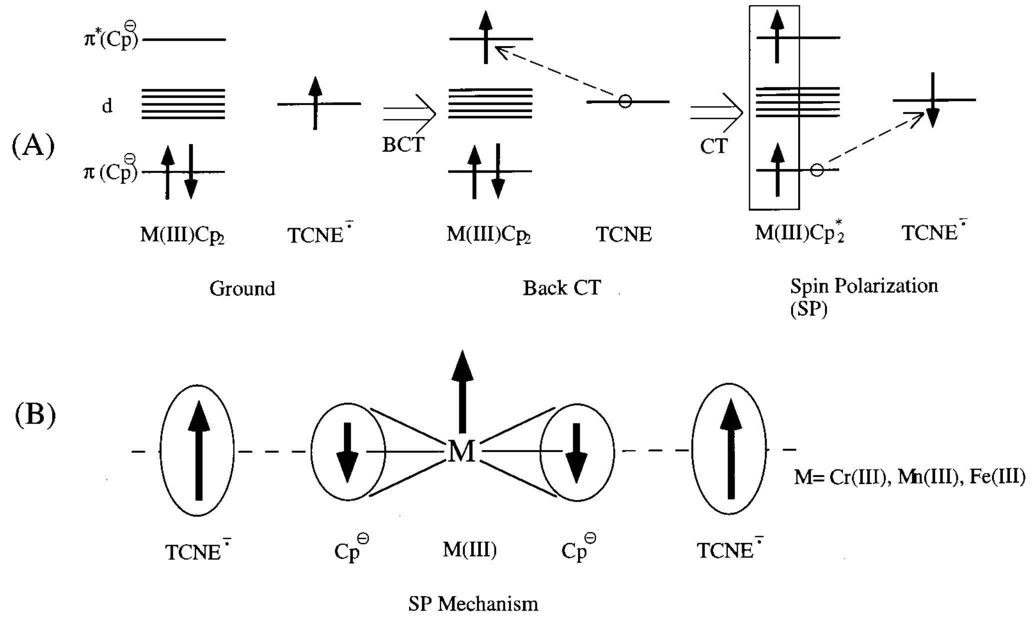


Fig. 3. Schematic illustration of the spin polarization mechanism in metallocenium ions.

attempts have been made in the field of molecular magnetism: one is to synthesize magnetic conductors and the other is to obtain unconventional materials such as spin-mediated superconductors. Therefore it is quite interesting to search these possibilities for metallocenium oligomers and polymers with appropriate linkage groups.

In relation to molecular design of unconventional materials, here let us focus attention to quantum spin phenomena [19] such as spin gap and the spin-mediated high-T_C superconductivity [1], the low dimensional (1D, 2D) [18] magnetic materials with the isotropic Heisenberg model. Recently many theoretical efforts and elaborate calculations were performed in order to elucidate what happens when two, three and many holes are introduced into 2D magnetic planes (intermediate case in the lattice dimentionality) [2]. Various field theoretical models based on the Gauge field [19] have been presented and are solved in both exact and numerical manners. The computational results indicated that the hole or electron doping into low-dimensional lattices may provide exotic phenomena such as magnetic conductivity [20] and spin-mediated superconductivity.

3.2. Previous attempts and available results

Past decade, we considered the single and double chains composed of the organic and inorganic units as possible precursors of the spin-mediated superconductors after doping [10,20,21]. The corresponding single chain (**I**), ladder (**II**), and 2D-sheet (**III**) in copper oxides are shown in Fig. 7. The triangular ladder (**IV**), Kagome ladder (**V**), and their 2D-sheets (**VI**) were also proposed as possible precursors of the spin-mediated superconductors in conformity with the spin frustration model and the resonating valence bond (RVB) model for the high-T_c superconductivity [20,21]. We have also proposed the 2D carbon sheet (**VII**) consisted of the antiaromatic cyclobutadiene and octatetraene skeletons [21], and triangular units (VIII) composed of three cyclopentadienyl radicals as illustrated in Fig. 8.

Very recently, the one dimension chain (SrCu2O) (**Ia**) [22] and two leg ladder compound (**IIa**) [23] in Fig. 7 were indeed synthesized by advanced synthetic technologies using high pressures. Moreover, the superconductivity was discovered in the ladder copper oxide ($Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$) (**IIa**) [24] in Fig. 7. On the other hand, the spin gap (quantum spin) [19] was observed in CaV_4O_9 with the 2D sheet (**IX**) [25], which is isoelectronic to 2D sheet in Fig. 8. Concerning with the spin gap, Haldanes's theory is applicable: spin 1/2 ladders with even and odd columns exhibit finite and zero spin gaps, respectively. Theoretical models for the superconductivity in ladder compounds are also presented by several groups [26], but the conclusions for odd (column number $n > 1$) ladder systems are different depending on the model Hamiltonians employed.

These circumstantial evidence suggest that experimental search for other chain and ladder compounds should be interesting in harmony with the theoretical proposal [20,21]. Thus organometallic conjugated systems with several low dimensional structures in Fig. 7 would be common interesting targets for molecular materials [7]

Mesoscopic linear and ring systems, small magnetic particles so on are also interesting synthetic targets: these are often referred to as zero-dimensional (0D) systems. In this area, quantum tunneling of magnetiza-

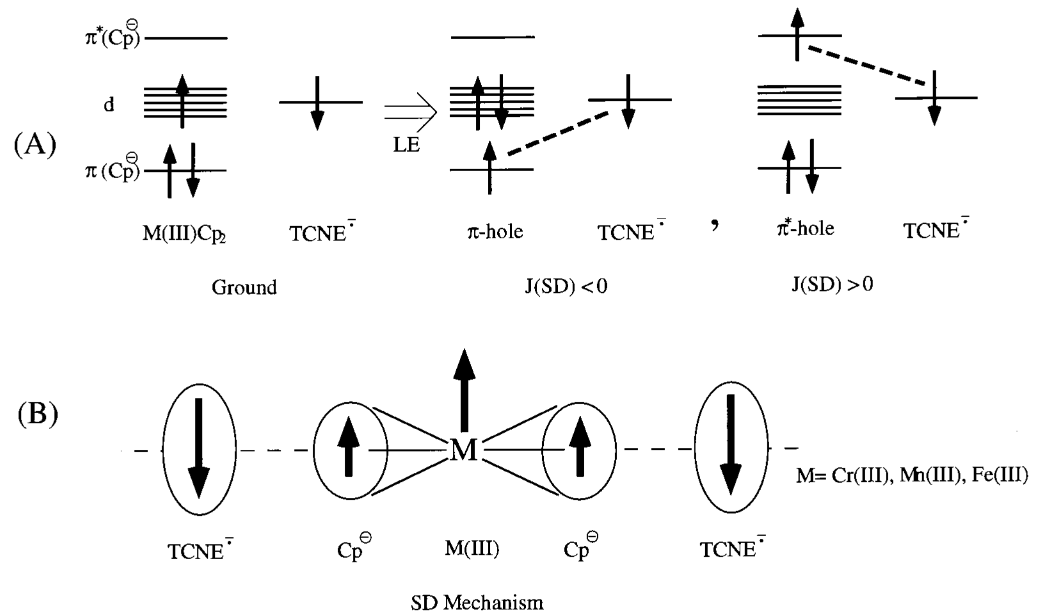


Fig. 4. Schematic illustration of the spin delocalization model in metallocenium ions.

tion, quantum well, quantum devices and single molecular spectroscopy in electron correlation systems are now interesting topics; these phenomena have been well-known in conductors [27]. Both coulomb and spin blockade phenomena may play important roles for controls of electron and spin current. But, these phenomena in the intermediate regime on scale factor are not thoroughly investigated yet in the field of molecular materials, though pioneering work have been performed by several groups [28,29]. We feel that oligomers consisted of the metallocenium units are interesting synthetic targets.

4. Possible strategies for functional materials composed of metallocenium units

4.1. Design of organometallic functional oligomers and polymers

Organometallic functional oligomers and polymers are conceivable on the basis of the guiding principles in Fig. 7 and spin coupling models in Fig. 6. Fig. 9 illustrates several possibilities of metallocenium polymers (**7**–**12**). **7** and **8** are, respectively, possible ferromagnetic and ferrimagnetic (or antiferromagnetic) polymers consisted of metallocene (or metallocenium) and radical (R•) groups. **9** are designed as ferro- or ferri-magnetic ladders. Organometallic magnetic metals or magnetic semi-conductors (**10**) may be possible if acceptor groups can be appropriately designed. Photoinduced ferro- or ferri(antiferro)-magnets are also possible by the photo-induced CT excitations between metallocene and acceptor groups as illustrated by **11**. Similarly photoinduced organometallic magnetic metals or magnetic semiconductors may be realized as shown in **12**.

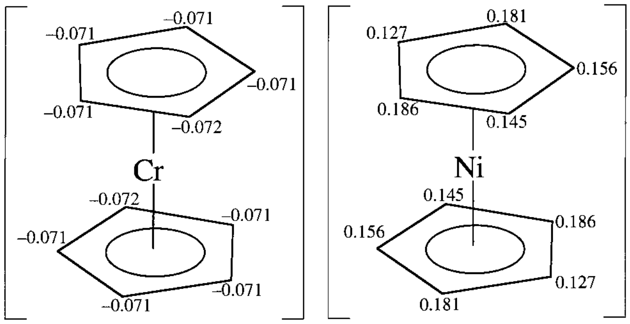
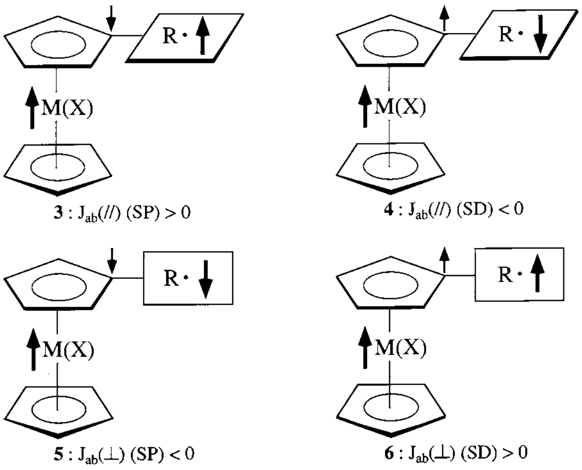


Fig. 5. Spin density populations on the cyclopentadieneyl anion (Cp).



3 : $J_{ab}(//)$ (SP) > 0

4 : $J_{ab}(//)$ (SD) < 0

5 : $J_{ab}(\perp)$ (SP) < 0

6 : $J_{ab}(\perp)$ (SD) > 0

Fig. 6. Metallocene with radical groups as components units.

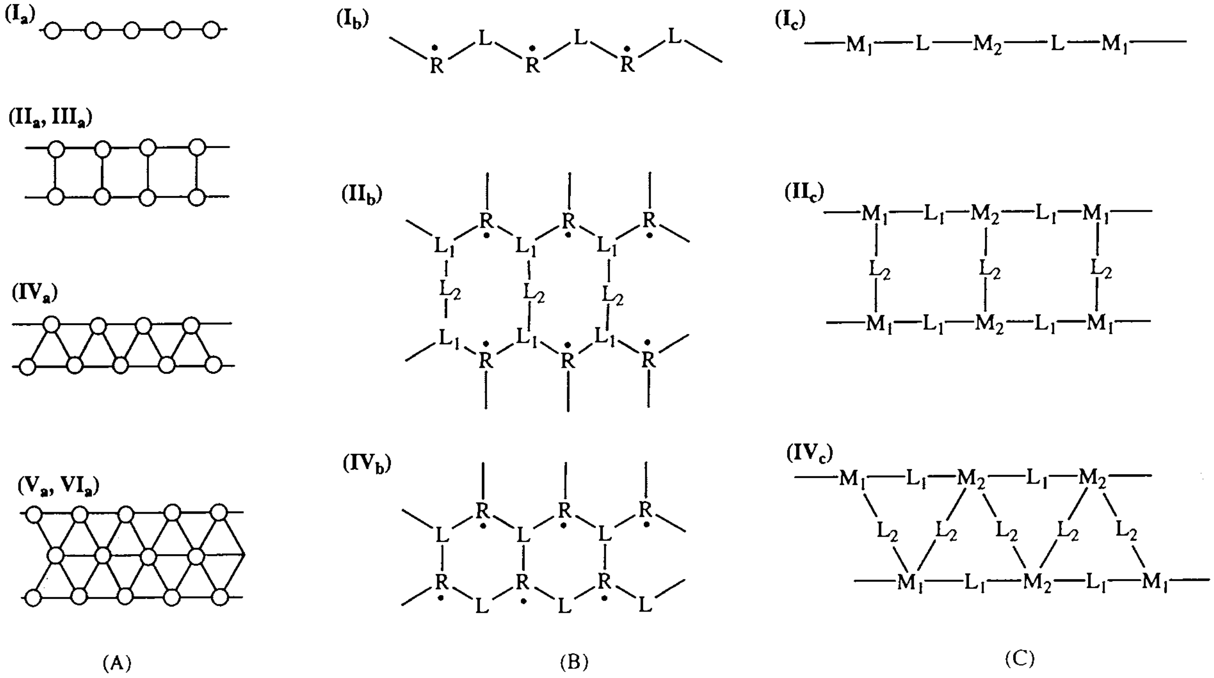


Fig. 7. 1-D, ladder and 2-D spin systems with and without holes (or electrons) which are attractive from magnetism and superconductivity in the copper oxide (A), organic (B), and organometallic (C) systems.

4.2. Magnetic modifications of organic metals

The interactions between conduction electron and spin are often weak in the case of CT complexes between ferrocenium ions and TTF derivatives [20,30]. Previously we have discussed possibilities of magnetic conductors and/or spin-mediated superconductors using radical substituted TTF derivatives. In this situation, the ab initio Hamiltonian can be reduced to Anderson [31] or Kondo Hamiltonian [32] instead of the Heisenberg Hamiltonian

$$\mathrm{H(K)} = -\sum 2J_{\mathrm{ai}} S_{\mathrm{a}} \cdot s_{\mathrm{i}} \tag{3}$$

where S_a and s_i denote the localized spin on site a and spin of conduction electron i, respectively. The conducting polymers coupled with localized spins are interesting from the above itinerant model given by Eq. (3). Since introduction of radical substituent into main chain is not so easy, transition metal complexes can be used to couple with conducting columns. For example, Wu et al. have synthesized the poly(aniline) within a layered magnetic (FeOCl) host [33].

Since the conduction electron is necessary for Kondo model, organic metals constructed of TTF- and BEDT-TTF molecules are possible candidates for magnetic modifications as illustrated in Fig. 10 [10,20,34]. Possibilities of organic Kondo and dense Kondo models by introducing metallocenium groups into TTF, BEDT-TTF and other organic components for organic metals would be interesting as illustrated in Fig. 10. Both segregated and alternated columns are conceivable in relation to several electronic phases in Fig. 10.

4.3. Organometallic RKKY systems and spin-mediated superconductors

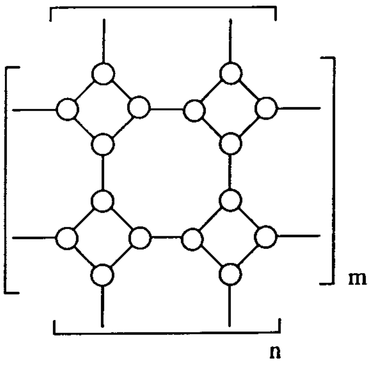
The metallocene groups may interact each other through the conduction electron in doped systems in Fig. 10. In this case, the ab initio Hamiltonian is reduced to the RKKY Hamiltonian [35,36],

$$\mathrm{H(RKKY)} = -\sum 2J_{\mathrm{cd}} S_{\mathrm{c}} \cdot S_{\mathrm{d}} \tag{4}$$

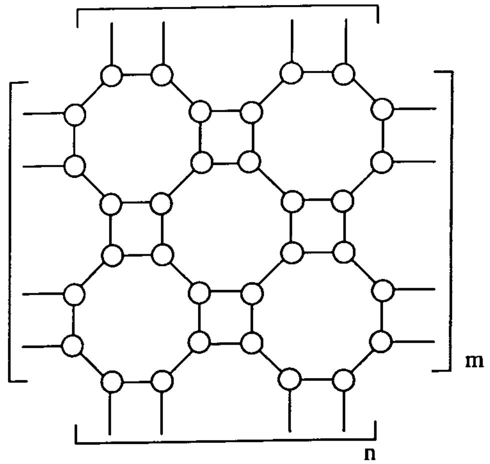
where S_c denotes the localized spin on a site c and J_{cd} is the effective exchange integral caused by the spin polarization of conduction electrons.

$$J_{\mathrm{cd}} = N_{\mathrm{F}}(0)\frac{\sin k_{\mathrm{F}}|r_{\mathrm{i}} - r_{\mathrm{j}}|}{|r_{\mathrm{i}} - r_{\mathrm{j}}|} \tag{5}$$

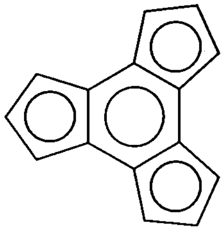
where $N_F(0)$ denotes the density of states at Fermi level, and r_i denotes the position of radical substituent. From Eq. (5), the sign of J_{cd} is variable, depending on the distance between radical sites. CT salts of metallocenes with TTF derivatives would be



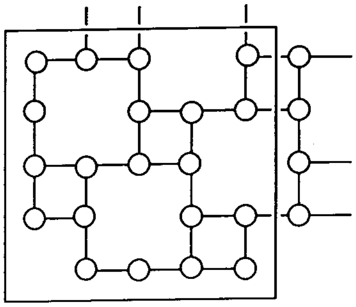
VII$_a$



VII$_b$



VIII



IX

Fig. 8. Networks constructed of cyclobutadiene and cyclooctatetraene units (**VIIa**, **VIIb**) and isoelectronic CaV_4O_9 system (**IX**).

possible candidates for organometallic RKKY systems.

4.4. Organometallic RVB systems

After the discovery of the high-T_c superconductivity [37], triangular spin systems in Fig. 7 have attracted great interest because of the Andersons's resonating valence bond (RVB) theory [38] for magnetism and superconductivity. Many field theoretical models [19] have been presented for the high-T_c superconductivity in conformity with Anderson's proposal. On the other hand, we have considered possible organic [20] and inorganic [39] spin frustration systems such as triangular ladder (**IV**) and Kagome ladder (**V**) in relation to RVB model for copper oxides as illustrated in Figs. 7 and 8. Both through-bond and through-space approaches are possible to construct such spin networks or topology. In both approaches, metallocenium ions would be used as spin sources in organometallic conjugated systems. Such studies have already initiated by Togni et al. [8] We also tried to synthesize low-dimensional systems composed of 4Fe–4S clusters with spin fluctuations, but amorphous oligomers were resulted to prevent further experimental treatments [39].

5. Constructions of networks by hydrogen bondings

From above discussions, active controls of appropriate crystal structures are crucial for accomplishing desired properties of molecular materials. Hydrogen bond has been shown to be one of attractive linkages constructing self-assemblies or supramolecules [40]. Especially, metal–hydrogen bond system is noticeable as strategic crystal engineering leading electronic, magnetic and optical materials [41]. Very recently, Sugawara et al. have reported organics-hydrogen bond system which has revealed the presence of through OH···O hydrogen bond ferromagnetic interactions [42]. Here, we will propose novel organometallics–hydrogen bond systems realizing ferro- or antiferromagnetic organometallic systems proposed in Figs. 6–8. As shown in previous papers [11], the coplanarity between Cp and substituent is very impor-

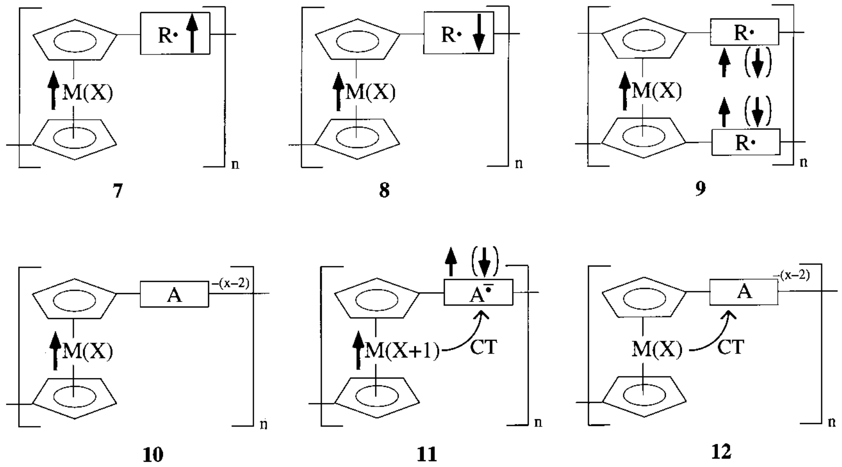


Fig. 9. Possible metallocenium polymers.

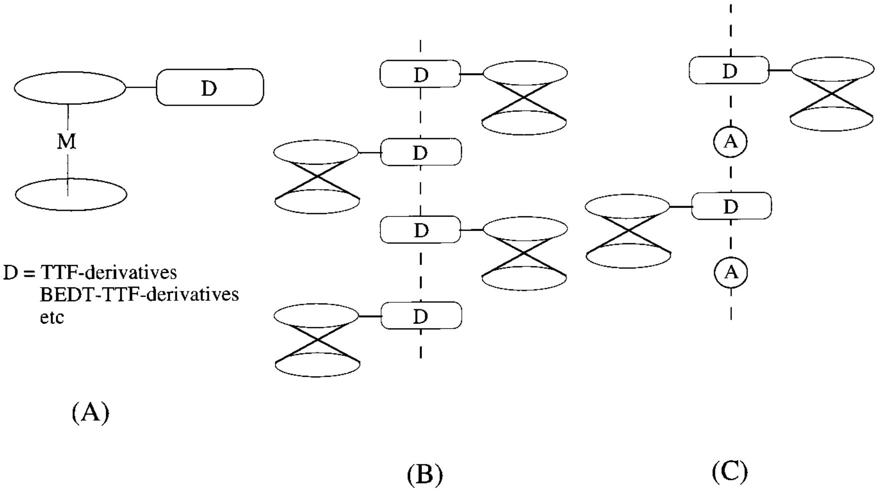


Fig. 10. TTF or BEDT-TTF derivatives with radical groups and organic Kondo model Metallic columns constructed of TTF or BEDT-TTF coupled with transition metal complexes with spins.

tant for ferromagnetic interaction via the SP mechanism. Our presented compounds shown in Fig. 11 satisfy this condition. Amide group (–NHCO–) has been found to prefer a coplanarity with Cp ring because of π-conjugation [11]. In our case, selective ferro- and antiferromagnetic interactions using amide groups and metallocene or metallocenium are shown in Fig. 11(a). The symmetrically substituted metallocene will realize hetero-metal complexes (Fig. 11(b)). On the other hand, unsymmetrical substitutions will give homometallic ferromagnetic interaction. We have already synthesized unsymmetrically disubstituted ferrocene derivatives ([11]b). Synthesis of the other derivatives and the investigations of their magnetic properties are in progress.

6. Concluding remarks

Intermolecular CI and ab initio UHF calculations conclude that the spin polarization (SP) mechanism inducting the negative spin densities on the Cp ring is predominant for the $[Cr(III)Cp_2]^+$ (**1**), while the spin delocalized (SD) mechanism is important for $[Ni(III)Cp_2]^+$ (**2**) core, giving rise to the positive spin densities on the Cp ring. Instead of the metallocenium-TCNE(TCNQ) complexes by Miller and Epstein [1], many d-p conjugated systems [9] via π-networks and hydrogen bonds are conceivable from the theoretical backgrounds discussed in this paper. Big problems are of course how to make possible candidates for metallocene-based magnetic conductors, charge- and/or

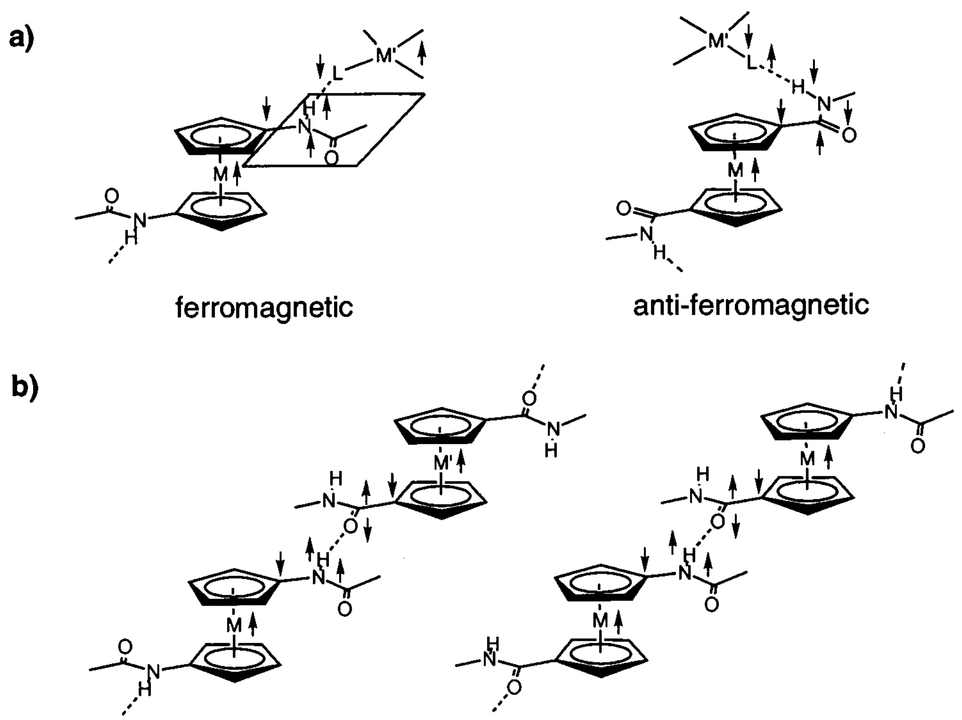


Fig. 11. (a)Ferro- and antiferromagnetic interractions using amide-substituted metallocene or metallocenium cations. (b) Strategic constructions of hetero and homo-metalferromagnetics using symmetrically or unsymmetrically disubstituted metallocenes.

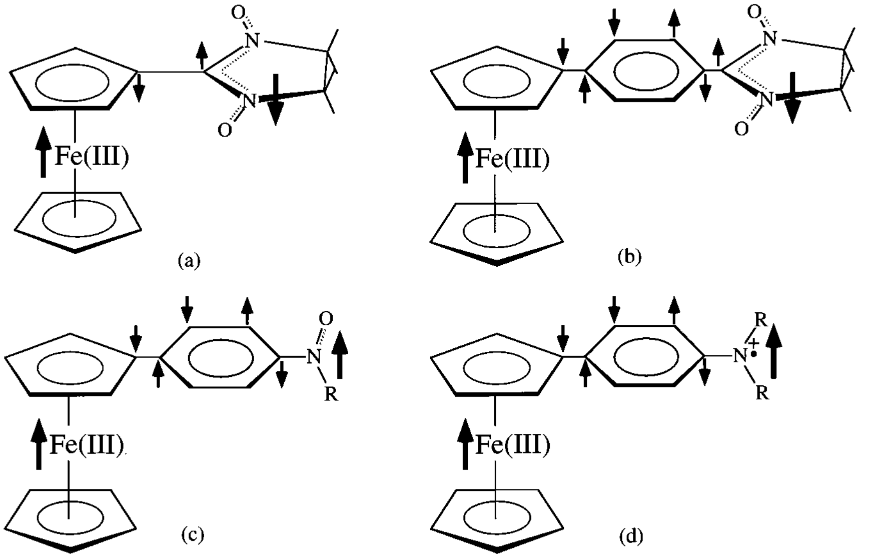


Fig. 12. Ferrocene derivatives with antiferromagnetic couplings, (a) and (b), and ferromagnetic couplings, (c) and (d).

spin-mediated superconductors and photo-induced superconductors.

Synthetic efforts have been carried out by several groups, and Imamura group has synthesized ferrocene derivatives substituted by a nitronyl-nitroxide, which are shown in Fig. 12(a) [43]. The interaction between ferrocene and nitronyl-nitroxide moiety is antiferromagnetic with the effective exchange interaction of ca. -25 cm^{-1} [43], supporting our proposal via the spin polarization (SP) mechanism shown in Figs. 6 and 9. This coincidence encourages our molecular designs of organometallic conjugated systems composed of metallocenium ions. It is also interesting to insert the benzene ring between ferrocene and nitronyl-nitroxide moiety in order to enhance the π-conjugation. As shown in Fig. 12(b), the insertion will lead the antiferromagnetic coupling. Alternatively, the substitution of nitronylnitroxide moiety by nitroxide or amino cation radical group will result in ferromagnetic coupling, as shown in Fig. 12(c, d).

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