Effect of Central Metal Ion, Co\textsuperscript{II} in the Fe\textsuperscript{II} Spin-Crossover Complex in Emulsion Polymerization of Trifluoroethylmethacrylate Using Poly(Vinyl Alcohol)

Atsushi Suzuki\textsuperscript{1+}, Motoi Iguchi\textsuperscript{1}, Takeo Oku\textsuperscript{1} and Motoyasu Fujiwara\textsuperscript{2}

\textsuperscript{1}Department of Materials Science, The University of Shiga Prefecture, Hikone 522-8533, Japan
\textsuperscript{2}Institute for Molecular Science, Okazaki 444-8585, Japan

To apply to magnetic memory device of nanodispersed spin crossover complex, we have studied the magnetic properties of hetero-spin crossover complex of [Fe(Htrz)\textsubscript{3}(4-NHtrz)\textsubscript{3}-x](BF\textsubscript{4})\textsubscript{2} in emulsion polymerization of trifluoroethylmethacrylate using poly (vinyl alcohol) as a protective colloid. Effect of central transition metal ion of Co\textsuperscript{II} ions on the spin crossover complex in the emulsion polymerization was investigated. The experimental results can be explained by theoretical consideration of electron density between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and Fe-N bond lengths, magnetic parameters, g-factor using functional density functional theory. This result was thought to have arisen from ligand field theory with a slight distribution of bond-length based on a slight exchange interaction due to a minor Jahn-Teller effect. [doi:10.2320/matertrans.MB200808]

(Received April 30, 2008; Accepted June 3, 2008; Published July 16, 2008)

Keywords: spin crossover complex, density functional calculations, electro-spin resonance

1. Introduction

Spin crossover phenomenon for 3d elements with electron configurations varying from d\textsuperscript{4} to d\textsuperscript{3} in metal complex at high and low spin state has been known as a thermally induced magnetic bi-stability, and as the light-induced high spin-low spin (HS/LS) phase transition.\textsuperscript{1} The properties of the Fe\textsuperscript{II} spin crossover complex varied with ligand substitution and configurations varying from d\textsuperscript{4} to d\textsuperscript{3} such as Fe\textsuperscript{II}(4-NHtrz)\textsubscript{3}-x.\textsuperscript{2} Güttlich\textsuperscript{3} and Carbonera\textsuperscript{4} have described the spin crossover complex varied with ligand substitution and configurations varying from d\textsuperscript{4} to d\textsuperscript{3} such as Fe\textsuperscript{II}(4-NHtrz)\textsubscript{3}-x.

Recently, switchable magnetic properties such as thermal and photo-induced magnetization switched and photo-induced magnetic properties with the spin transition of spin crossover complex such as [Fe(Htrz)\textsubscript{3}(4-NHtrz)\textsubscript{3}-x](BF\textsubscript{4})\textsubscript{2}.\textsuperscript{5} Moritomo\textsuperscript{5,6} has reported the ligand-induced magnetic switching mechanism of spin crossover complexes such as [Fe(ptz)\textsubscript{3}(BF\textsubscript{4})\textsubscript{2}], which has a short distant of bond between the metal atom and the ligand nitrogen in the complex.

The Fe-Co Prussian blue exhibits thermally induced metal-to-metal charge transfer between the Fe\textsuperscript{II} and Co\textsuperscript{II} ions, which can be expressed as [{Fe\textsuperscript{III}(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})-CN-Co\textsuperscript{III}LS(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})}], [{Fe\textsuperscript{III}(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})-CN-Co\textsuperscript{III}HS(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})}]. The transition temperature depends on the composition, and in general, increases with decreasing mole-ratio of Co/Fe ion. The spin multiplicity of the high-temperature phase with [{Fe\textsuperscript{III}(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})-CN-Co\textsuperscript{III}HS(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})}] structure is larger than that of the [{Fe\textsuperscript{III}(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})-CN-Co\textsuperscript{III}LS(t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0})}] structure. The ligand-cobalt bond is longer than the Co\textsuperscript{II} content in the high temperature phase than in the low-temperature phase. Metal-to-metal charge transfer thought to be caused by an entropy-driven process. This is because the entropy of the Fe\textsuperscript{III}Co\textsuperscript{III}HS state is much larger than that of the Fe\textsuperscript{III}Co\textsuperscript{III}LS state.\textsuperscript{9}

Nanodispersed magnetic semiconductor with the nanometer-sized of hetero spin crossover complex of Prussian blue analogues in many CN-bridged molecular systems have been evaluated for multi-functional applications in electron spin devices, quantum computers, molecular magnetism, and pharmaceutical agents for MRI detection of cancer in medical patients. Kahn\textsuperscript{10} has reported that a certain kind of spin crossover complex such as [Fe(NH\textsubscript{2}trz)\textsubscript{3}-(NO\textsubscript{3})\textsubscript{3}]\textsubscript{0.7}(BF\textsubscript{4})\textsubscript{0.3} could be effectively used for displays and data recording by exploited spin crossover transition. Yamada\textsuperscript{11-13} and Landfester\textsuperscript{14,15} have studied the magnetic properties of nano-dispersed spin crossover complexes such as Fe/Cr-CN-Co Prussian blue derivatives in emulsion polymerization using a common surfactant.

To develop switching electronic devices of nanodispersed spin crossover complex with multiple functions such as a quantum molecular device, we have studied the magnetic properties with the spin transition of spin crossover complex such as [Fe(Htrz)\textsubscript{3}(4-NHtrz)\textsubscript{3}-x](BF\textsubscript{4})\textsubscript{2}H\textsubscript{2}O in the emulsion polymerization of trifluoroethylmethacrylate (TFEMA) using poly (vinyl alcohol) (PVA) as a protective colloid in contrast with sodium laurel sulfate (SLS) as common surfactant.\textsuperscript{16} In the present paper, we will focus on the magnetic properties of nanodispersed hetero-spin crossover complex, with respect of effecting of Co\textsuperscript{II} ion in the Fe\textsuperscript{II}-based spin crossover complex in the emulsion polymerization. Comparison between the magnetic properties of the nanodispersed hetero-spin crossover complex will be described by theoretical consideration with the B3LYP density functional theory (DFT) using the experimental results such as electro-spin resonance (ESR) near the HS/LS phase transition.

2. Experimental

Spin crossover complex, [M(Htrz)\textsubscript{3}(4-NHtrz)\textsubscript{3}-x](BF\textsubscript{4})\textsubscript{2}·nH\textsubscript{2}O varied with central metal ions such as Fe\textsuperscript{II} and Co\textsuperscript{II} at mole ratio of 1/1 was synthesized in methanol as reported in previous papers.\textsuperscript{10} Emulsion polymerizations of TFEMA
using PVA with the spin crossover complex were carried out under argon atmosphere at 50°C for 2 hours. Temperature dependence of ESR spectroscopy (Bruker EMX Plus) of the sample shielded in a quartz tube with He after evacuation with diffusion pump was measured at a constant microwave frequency, 9.4 GHz (X-band). Optimized structure, band distance between Fe and N atom, electron structure, singly occupied molecular orbital (SOMO), spin density distribution, molecular orbital level of d-d transition between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), a splitting of degenerated band level at high spin state and at low spin state, magnetic parameters, principal axial \( g_{xx}, g_{yy}, g_{zz} \), and isotropy g-factor \( g_{\text{iso}} \) (Zeeman splitting factor) and the hyperfine coupling constants (hfc) between the unpaired electron spin and the magnetic nuclei of the spin crossover complex were calculated by DFT using B3LYP, as implemented in the GAUSSIAN03 program (Gaussian Inc.).

### Results and Discussion

Emulsion polymerizations of TFEMA using PVA with the spin crossover complex of \([\text{Fe (Htrz)}_3(4\text{-NHtrz})_3\text{-}_3]^{-} (\text{BF}_4)_2\text{nH}_2\text{O}\) at amino mole ratio \(x = 0.3\) were performed. Figure 1 shows temperature dependence on ESR of the spin crossover complex at bulk state (a), the mono-dispersed complex in emulsion film using PVA (b) and SLS (c) in cooling process. As shown in Fig. 1(a), the ESR behavior at the bulk state represented isotropy magnetic parameter such as \(g = 2.0230\) with a broad width at 295 K and 200 K. These results in anisotropy of g-factor seem to be arisen from a slight molecular distortion of the spin crossover complex near the HS/LS phase transition. At 5 K, we can confirm assignment \(g = 4.02\) as the existed triplet forbidden transition, \(\Delta M_0 = 2\) at \(S = 1\) as the lowest-energy triplet level \(T^1 (S = 1)\) near a half of magnetic field \(\sim 1500 \text{G}\), and \(g = 8.2\) as the quietest forbidden transition, \(\Delta M_0 = 3\) at \(S = 2\) as quintet state. The magnetic parameters in g-factor are thought to be related to the molecular distortion with a slight splitting of molecular orbital at quintet state, and the singlet state.

![Fig. 1](image-url)  \text{Temperature dependence on ESR curves of the Fe}^{II} \text{ spin crossover complex at amine mole ratio } x = 0.3 \text{ in the powder state (a), and those of the emulsion films using PVA (b) and SLS (c) at a constant microwave frequency, 9.4 GHz (X-band).}

Figure 2 shows temperature dependence of ESR spectroscopy in the emulsion films with the spin crossover complex, \([\text{FeCo(Htrz)}_3(4\text{-NHtrz})_3\text{-}_3]^{-} (\text{BF}_4)_2\text{nH}_2\text{O}\) in metal ion of \(\text{Fe}^{II}/\text{Co}^{II}\) at 1/1 of mole ratio (a), and that of powder of the complex at 1/1 (b), and that of the \(\text{Co}^{III}\) complex (c). For this mixed complex in the emulsion, as shown in Fig. 2(a), the single ESR signal peak with a wide magnetic width was observed. This thought to be attributed to a stronger zero magnetic field interaction (D, E) at 273 K. In contrast, for the bulk \(\text{Co}^{III}\) complex at 5 K as shown in Fig. 2(b), the experimental results represented a slight anisotropy of g-factor at the paramagnetic state \((S = 1/2)\), and at multiplet states including quartet state \((S = 3/2)\) and exited triplet state \((S = 1)\). The magnetic behavior in the emulsion film identified that the \(\text{Fe}^{II}\) spin crossover complex existed into the particles in accordance with a strong chemical-affinity of polymerized TFEMA with the \(\text{Fe}^{II}\) complex in the particle. For explaining the magnetic behavior, we theoretically need to discuss the electronic structure such as spin density distribution, band gap between HOMO and LUMO in the \(\text{Co}^{II}\) spin crossover complex near the HS/LS phase transition. The Ising-like model will be extended to the three-center case supported by spin multiplicity of the high-temperature phase at high spin state, the exchange interaction, charge-transfer band of the transition from \(\text{Co}^{III}\) to \(\text{Fe}^{III}\) ion, the metastable \(\text{Fe}^{III}\) \(\text{Co}^{II}\) state, and a slight splitting of energy level in d-d transition near the HS/LS phase transition.

The theoretical consideration of electron structure in the \(\text{Fe}^{II}\) spin crossover complex based on legand field theory would explain the experimental results such as magnetic parameters, g-factor by \textit{ab-initio} calculation using the B3LPZ DFT at the high-spin phase transition. Figure 3 shows singly occupied molecular orbital (SOMO) (MO126e), spin density distribution at \(S = 2\) (a) and HOMO (MO124e) at \(S = 0\) (b) of the \(\text{Fe}^{II}\) spin crossover complex by quantum calculation using the B3LYP DFT. Whereas the SOMO is related to the unpaired electron distribution.
distribution were localized at legand in the spin crossover/0.006 eV in contrast to several splitting of the energy levels
degenerate d-orbital states with a narrow energy level gap at
degenerate d-spin orbital energy level of FeII MOs with a
The optimized electronic structure represented several
density distribution is the difference of (red/green denote the sign of the wave function), the spin
density distribution is the difference of $\alpha$ and $\beta$ spin
density of all electrons showing polarization effect.

HOMO (MO124/C11) delocalized on the FeII central metal atom with N
atoms at ligand in the Fe II spin crossover complex. As shown in
Fig. 3, the optimized structure had a slight molecular
atoms at ligand in the Fe II spin crossover complex. As shown in

The spin density distribution is the difference of $\alpha$ and $\beta$ spin
density of all electrons showing polarization effect.

(red/green denote the sign of the wave function), the spin
density distribution is the difference of $\alpha$ and $\beta$ spin density of all electrons showing polarization effect (excess of $\alpha$ and $\beta$
spin). In the case of SOMO (MO126/C11) at $S = 2$, spin density distribution were localized at legand in the spin crossover
complex. In other case at a low spin state, $S = 0$, HOMO
(MO124/C11) delocalized on the FeII central metal atom with N
atoms at ligand in the spin crossover complex. As shown in
Fig. 3, the optimized structure had a slight molecular
distortion of bond distant between Fe and N atom in the
spin crossover complex at $S = 2$ better than that at $S = 0$.
The optimized electronic structure represented several
degenerated d-spin orbital energy level of FeII MOs with a
slight shift of bond gap between HOMO and LUMO and the
molecular electron density.

Table 1 lists $\alpha$ and $\beta$ electron energy level of FeII MOs at
high state ($S = 2$) and low state ($S = 0$). At the high spin state
($S = 2$), the electronic structure was constructed with four
degenerated d-orbital states with a narrow energy level gap at
0.006 eV in contrast to several splitting of the energy levels
as the restricted orbital states at low spin state ($S = 0$) based
on ligand field theory due to a slight exchange interaction as a
minor Jahn-Teller effect. Environment effect of central metal
ion such as FeIII atom in the spin crossover complex easily
caused a slight splitting in the d-spin orbital energy levels,
which would affect color character, spin multiple, and
magnetic susceptibility near the HS/LS phase transition in
heating process.

The magnetic parameters including principal g-factor, $g_{xx}$,
$g_{yy}$, $g_{zz}$, and isotropy g-factor, $g_{iso}$ in the FeII spin crossover
complex will be explained by the B3LYP DFT. Table 2 lists the theoretical magnetic parameters, g-factor of the FeII
spin crossover complex at the high spin state ($S = 2$). The magnetic parameters in principal g-factor were calculated
as follows: $g_{xx} = 1.9887$, $g_{yy} = 1.9999$, $g_{zz} = 2.0055$ and
$g_{iso} = 1.9981$ as isotropic g-factor, which compared to the
experimental isotropic g-factor, $g_{iso} = 2.0233$ as the bulk
(powder) state. The theoretical g-factor approximately made
agreement with the experimental results. The anisotropic
g-factor in the theoretical results suggests unsymmetrical
molecular-structure. The hfcs ($I_{xx}$, $I_{yy}$, $I_{zz}$) between the
unpaired electron spin and the magnetic nuclei of nitrogen
atom in the FeII spin crossover complex could be calculated
as follows: 0.11 $\times$ 10$^5$, 0.13 $\times$ 10$^5$ and 0.14 $\times$ 10$^5$
(amu-bohr$^2$). Calculated g-factor with slight hfcs was in very
satisfying agreement. Isotropic and anisotropy of magnetic
shield tensor (ppm) at ligand on FeII atom was calculated to be $-16804.32$, $1306.69$, $xx = -16489.88$, $yy =$
$-16524.32$, and $zz = -17398.78$, respectively. The
theoretical results in the magnetic shield tensor with hfcs at
$S = 2$ indicate the anisotropic spin coupling at $B_{aa} =$
$-3.27$ G, $B_{bb} = 1.34$ G, and $B_{cc} = 1.94$ G in principal axis
system. Optimized structure shows 2.10 $\AA$ of bond distant
between Fe and N atom at the high spin state. The bond
distant between Fe and N atom got longer more than 2.15 $\AA$
at a low spin state. Change of anisotropy g-factor with hfcs
related to bond distant between Fe and N atom was explained
by ligand field theory based on a minor Jahn-Teller effect.

<table>
<thead>
<tr>
<th>MO no.</th>
<th>Orbital</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>MO126/C11</td>
<td>-0.279</td>
</tr>
<tr>
<td>$\beta$</td>
<td>MO126/C11</td>
<td>-0.299</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MO no.</th>
<th>Orbital</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>MO125/C11</td>
<td>-0.398</td>
</tr>
<tr>
<td>$\beta$</td>
<td>MO125/C11</td>
<td>-0.296</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MO no.</th>
<th>Orbital</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>MO124/C11</td>
<td>-0.402</td>
</tr>
<tr>
<td>$\beta$</td>
<td>MO124/C11</td>
<td>-0.279</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MO no.</th>
<th>Orbital</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>MO123/C11</td>
<td>-0.430</td>
</tr>
<tr>
<td>$\beta$</td>
<td>MO123/C11</td>
<td>-0.431</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MO no.</th>
<th>Orbital</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>MO122/C11</td>
<td>-0.437</td>
</tr>
<tr>
<td>$\beta$</td>
<td>MO122/C11</td>
<td>-0.435</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MO no.</th>
<th>Orbital</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>MO121/C11</td>
<td>-0.433</td>
</tr>
<tr>
<td>$\beta$</td>
<td>MO121/C11</td>
<td>-0.434</td>
</tr>
</tbody>
</table>

Table 2 Bond distant between Fe and N atom as legand in the FeII based spin crossover complex, [Fe(Htrz)$_3$][(BF$_4$)$_2$]nH$_2$O, theoretical parameters of isotropy g-factor calculated by DFT using B3LYP, in contrast to the experimental results by ESR.

<table>
<thead>
<tr>
<th>$S$</th>
<th>Bond distant in Fe-N ($\AA$)</th>
<th>$g$ (ESR)$^2$</th>
<th>$g$ (DFT)$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.0135, 2.0218, 2.1094</td>
<td>$g = 2.023$, 4.214, 8.358</td>
<td>$g = 1.998$</td>
</tr>
<tr>
<td>0</td>
<td>2.0135, 2.0218, 2.1510</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^1$Calculated by DFT, $^2$As shown in Fig. 1
The theoretical results on the electronic structure of these species are important for clarifying electron transfer rates and thus for understanding the magnetic mechanism near the HS/LS phase transition. In near future, we will report a relationship of charge-transfer from Fe$^{II}$ to Co$^{II}$ ion in the Fe$^{II}$ spin crossover complex at the exited state and the molecular distortion affected with a mixture of Co$^{II}$ ion on the basis of theoretical consideration using experimental results such as UV-vis spectroscopy, and powder X-ray diffraction patterns near the HS/LS phase transition.

4. Conclusion

We have studied the magnetic properties of nanodispersed spin crossover complex in the emulsion polymerization of TFEMA using PVA as a protective colloid. We focus on investigating the magnetic properties, concerning influence of central metal transition ion of Co$^{II}$ ion in the Fe$^{II}$ nanodispersed spin crossover complex in the emulsion by theoretical consideration using DFT and ESR. The experimental results based on the theoretical consideration confirmed multiple spin states including quartet state ($S = 2$), and exited triplet state ($S = 1$) at the high spin state. The phase transition was influenced by central metal transition ion, Co$^{II}$ ion in the Fe$^{II}$ based spin crossover complexes. For the nanosized spin crossover complex integrated into emulsion particles, the HS/LS phase transition clearly involved a gradual shift of g-factor anisotropy in the ESR spectroscopy. This result thought to be attributed with legand field theory regarding a slight exchange interaction between nearest neighbor Fe$^{II}$ atoms caused by molecular distortion with its minor Jahn-Teller effect.

Acknowledgements

We acknowledge Associate Prof. T. Suzuki, Mr. T. Yamanaka and Mr. M. Nagata for optical technique with the financial support of an operating grant from the Institute for Molecular Science (IMS) in Japan. We also thank Mr. E. Miyagawa, Mr. S. Higashiyama for analysis technique in Northeastern Industrial Research Center of Shiga Prefecture.

REFERENCES