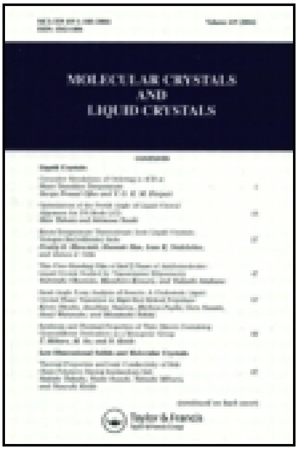

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Storing Spin-Crossover and LC Phase Transitions Information by Hybridizing Spin-Crossover Complexes with a Thermotropic Polymer Matrix - A Novel Case of Multiple Switching

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Storing Spin-Crossover and LC Phase Transitions Information by Hybridizing Spin-Crossover Complexes with a Thermotropic Polymer Matrix – A Novel Case of Multiple Switching

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We have prepared two new spin-crossover (SCO) Fe(II) complexes, [Fe(II)(ODT)$_3$](p-tol)$_2$(I) and [Fe(II)(HET)$_3$](p-tol)$_2$(II). And they were blended with a liquid crystalline (LC) poly(oxetane) (POx). Thermal and spin crossover behavior of the composites then were studied by using a superconducting quantum interference device (SQUID), differential scanning calorimetry (DSC) and extended X-ray absorption fine structure (EXAFS) spectroscopy. When composites carried higher than 20 wt.% of the Fe(II) complexes, they revealed a reversible spin crossover for the low spin (LS) ↔ high spin (HS) transition in addition to the thermal transitions, i.e., glass transition and isotropization, of the LC polymer matrix.

Keywords: Fe(II) complex; hybrid; LC polymer; multiple switching; SCO (spin crossover)

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1. INTRODUCTION

Transition metal complexes with d^4–d^7 electron configurations can adopt two different magnetic states, i.e., low-spin (LS) and high-spin(HS) states, which can crossover thermally or by photo excitation [1]. Spin-crossover phenomenon has been attracting much attention in relation to their potential applications in molecular electronics [2]. The importance of this type magnetic materials is expected to increase in future advanced technologies, especially in the area of the so-called information and display technologies [3–10]. And the recent impetus in the search for few spin-crossover (SCO) materials also stems from the fact that some of them reveal bistability that can be utilized as magnetic molecular switches [11,12]. Recently, Aida and coworkers reported spin-crossover properties of self-assembled Fe(II) complexes with alkyl-tethered triazole ligands [13]. These assemblies exhibited switching behavior between the two spin states triggered by a phase transition of the ligands. Earlier, Gutlich and coworkers synthesized Fe(II) complexes using liquid crystalline ligands [14]. These compounds, however, revealed spin-crossover independent of phase transitions of the ligands. Recently, we reported the SCO properties of hybrids consisting of poly(methyl metacrylate) and Fe(II) complexes, which could be readily solution-cast into films [15].

In this investigation, we studied the feasibility of storing together magnetic and liquid crystalline (LC) phase transition information that would respond to thermal stimulus, i.e., heating or cooling, in the composites prepared by mixing a thermotropic, side-group LC polyoxetane (SCLCP) with two new SCO Fe(II) complexes.

2. EXPERIMENTAL

2.1. Synthesis

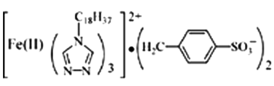
The ligand compounds, 4-octadecyl-1.2.4-triazole(ODT) and 4-(2-hydroxyethyl)-1,2,4-triazole(HET), were prepared following same procedure as reported earlier [14,15]. The LCP matrix, POx, was prepared as described earlier by us [16]. A mixture of the appropriate amount of metal complex and POx was dissolved in dry THF. The whole mixture was stirred for 30 min at 40°C and then THF solvent was removed by vacuum distillation at 60°C.

2.2. Characterization

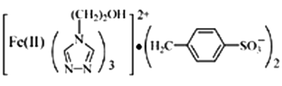
Thermal properties of the metal complexes, POx and Pox/complex composites were studied in a stream of nitrogen on a differential scanning calorimeter (Mettler DSC 821^e, Switzerland) at the heating and cooling rate of 4°C/min. The SQUID magnetometer (MPMS5, Quantum Design, U.S.A.) was used to determine the magnetic properties at temperatures ranging from 150 to 380 K under the magnetic field of 1.0 Tesla. Temperature-dependent Fe K-edge EXAFS spectra of Fe-spin crossover materials have been taken on BL7C1 (Electrochemistry) beamline in a storage ring of 2.5 GeV with a ring current of 130 ~ 185 mA at the Pohang Synchrotron Lab (PSL), Korea. The data reduction of the experimental XAFS spectra was performed by the standard procedure reported previously [17].

3. RESULTS AND DISCUSSION

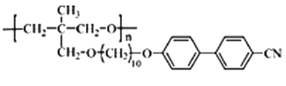
The chemical structures of the two Fe(II) complexes and POx are given bellow:



[Fe(II) (ODT)$_3$] (p-tol)$_2$ (I)



[Fe(II) (HET)$_3$] (p-tol)$_2$ (II)



POx

The complexes I and II are new SCO compounds, both of which could be synthesized via known synthetic routes [18]. The LC polymer, POx, was prepared by cationic ring-opening polymerization [16,19] of the oxetane monomer bearing the cyanobiphenyl pendant. The polymer used in is investigation was found to have the number-average molecular weight ($\overline{Mn}$) of 43,000 and the polydispersity index of 2.8, which were determined by gel-permeation chromatography (GPC, Waters 745, U.S.A.) against polystyrene reference. The degree of polymerization of the polymer, n, in the structural formular shown above, is estimated to be 100.

Thermal properties of the two complexes I and II, the LC polymer POx, and two composites both containing 25 wt.% of I and II were studied by DSC. Complex I reveals the LS → HS transition at 37°C on heating and at 30°C on cooling, whereas complex II exhibits the transition at 24°C on heating and 11°C on cooling. The minimum and maximum points on the thermograms were taken as transition temperatures. The ΔH and ΔS values of the endotherms on the heating thermograms were 14.8 kJ/mol and 48.7 J/mol K for complex I, and 17.7 kJ/mol and 61.3 J/mol K for complex II, respectively. These values are typical of those reported for the LS → HS transitions of Fe(II) complexes [20].

The two composites both exhibit three endothermic transitions on the heating cycles and corresponding three exothermic transitions on the cooling cycle. The lowest temperature transition observed on the cooling DSC thermograms corresponds to the glass transition (T_g) of the POx matrix, whereas the highest temperature transitions correspond to the smectic-to-isotropic phase transition, i.e. isotropization (T_i), of the polymer matrix. And the transitions observed at the temperatures slightly higher than the T_g temperatures are derived from the thermally induced spin-crossover of the two complexes, which is confirmed by a color change: violet color in the LS state and colorless in HS state, and also by superconducting quantum interference device (SQUID) measurements of magnetic susceptibility values ($\chi_M T$). Thus determined data are summarized in Table 1. There are several interesting points to be noted: as just mentioned above, the three distinct thermal transitions are observed reversibly for the composites. Two of the transitions are related to phase transitions of the LC matrix polymer and one to the SCO of the complexes. In other words, the transitions are results of compounding LC properties of the host matrix with magnetic behavior of the organometallic guest.

Secondly, all the transition temperatures, i.e., T_g, $T_{LS\leftrightarrow HS}$, and T_i values, are lowered by mixing the Fe(II) complexes with the LC polymer when compared with the T_g and T_i temperatures of POx itself and the $T_{LS\leftrightarrow HS}$ temperatures of the two Fe(II) complexes.

Especially, the T_i values of the composites depend very strongly on the nature of the complexes or on the structure of the ligands in the complexes. It is clear that [Fe(II)(HET)$_3$(p-tol)$_2$] (complex II) lowers the T_i value (118.0 → 90.3°C) much greater than [Fe(II)(ODT)$_3$(p-tol)$_2$] (complex I) does (118.0 → 116.8°C) when they were mixed with POx. This can be explained by stronger interaction between the hydroxyethyltriazole (HET) ligand and POx than between the octadecyltriazole (ODT) ligand and the matrix polymer, because the hydroxyl groups present in the HET complex are able to form the hydrogen bonds with the oxygens and the C≡N groups in POx. Such strong interactions between the ligand and POx can destabilize the LC phase of the matrix polymer, which would result in a reduction in T_i. The T_g value also lowered due to plasticization of the matrix polymer by the ligands of the complexes. It also is observed that $T_{LS\rightarrow HS}$ values of the complexes are diminished when mixed with POx.

Thirdly, supercooling or hysteresis is observed for all the three transitions; supercooling of glass transition and isotropization is very well known phenomenon in LC polymers [16]. POx exhibits a well-defined fan texture implying the formation of smetic A (S_A) phase, whereas the two composites reveal much disturbed fan textures. The S_A liquid crystalline phase, however, persists in the two composites.

TABLE 1 Comparison of the Transition Temperatures of and Interatomic Distances for the First Nearest Neighbor Fe−N Bond in Pox, Complexes and Composites*

	SQUID measurement			DSC measurement#									
	$T_{LS\leftrightarrow HS}$(°C)			T_g(°C)		$T_{LS\leftrightarrow HS}$(°C)		T_i(°C)					
Sample	Heating ($X_M T$/cm^3 K mol^{-1})	Cooling ($X_M T$/cm^3 K mol^{-1})	ΔT	Heating	Cooling	Heating	Cooling	Heating	Cooling	Spin state	T [K]	R [Å] Fe−N	ΔR [Å]
POx				10.4	8.5			124.2	118.0				
Complex I	37.6	28.2	9.4			36.7	30.0			LS	78	1.97	0.12
	(1.41)	(1.41)								HS	380	2.09	
POx/Complex I	22.2	16.8	5.4	7.8	6.8	23.4	17.3	120.9	116.8	LS	78	1.84	0.33
	(1.33)	(1.40)								HS	380	2.21	
Complex II	25.0 (2.00)	10.6	14.4			24.0	10.8			LS	78	1.99	0.16
		(1.89)								HS	380	2.15	
POx/Complex II	17.9	1.6	16.3	0.3	− 1.1	13.5	2.3	90.7	90.3	LS	78	1.89	0.18
	(1.22)	(1.43)								HS	380	2.07	

*Containing 25 wt.% complex. #Heating and cooling rate:4°C/min.

The two complexes, Fe(II)(ODT)$_3$(p-tol)$_2$ (complex I) and Fe(II)-(HET)$_3$(p-tol)$_2$ (complex II), were colored violet in the LS state, characteristic of d–d electronic transitions of low-spin iron(II) species [13]. Discoloration occurred upon heating to the HS state. On cooling, the white solid returned to its original color. This thermochromism reflects the reversible spin-state transition between the LS-HS states. We also examined the thermally induced LS ↔ HS transitions of the complexes and composites on a SQUID instrument (MPMS5, Quantum Design, U.S.A.) at the magnetic field of 1.0 Tesla. The results are shown in Figure 1 and the analysis results are included in Table 1.

On heating from 150 K on, the molar magnetic susceptibility ($\chi_M T$) value of complex I increased from 0.2 cm^3 Kmol^{-1} at 150 K followed by a jump from 0.6 to 3.2 cm^3 Kmol^{-1} starting from 296 K. This abrupt increase in $\chi_M T$ is a characteristic of LS-to-HS transition. And the complex I exhibits a narrow thermal hysteresis of 9.4°C. On the other hand, complex II, starting from the $\chi_M T$ value of at 0.3 cm^3 Kmol^{-1} at 150 K, reveals a transition from about 270 K ($\chi_M T$ value is 0.74) to

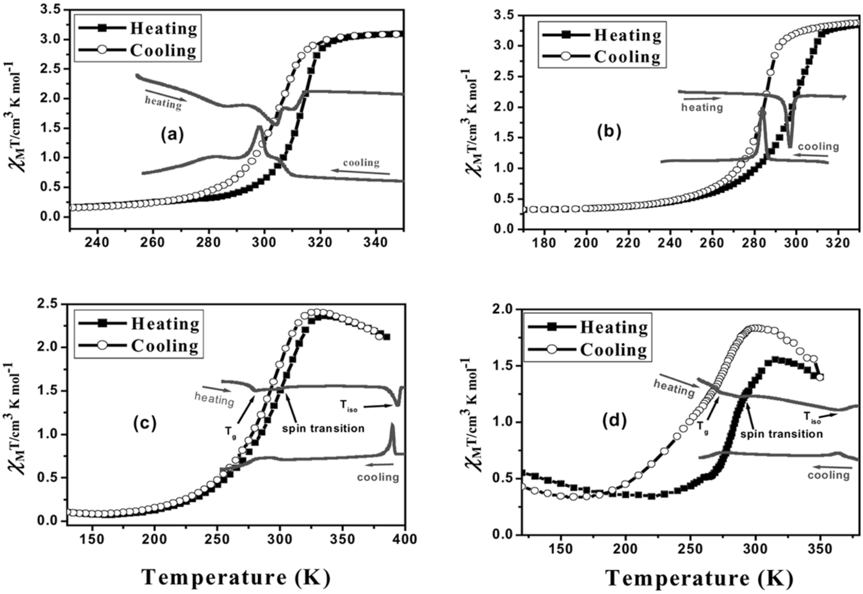


FIGURE 1 Temperature dependence of $\chi_M T$ for (a) Fe(II)(ODT)$_3$(p-tol)$_2$ (Complex I), (b) Fe(II)(HET)$_3$(p-tol)$_2$ (Complex II), (c) Composite I, and (d) Composite II. The corresponding DSC thermograms are shown in solid lines.

350 K reaching the $\chi_M T$ value of about 3.4 $cm^3 Kmol^{-1}$. The complex II exhibits a slightly wider thermal hysteresis (ca. 14.4°C) around room temperature than complex I, see Figure 1 (b).

The transition temperatures determined by DSC and SQUID are somewhat different as shown in Table 1. The differences can be ascribed to the dynamic nature of DSC scanning as compared with the static, temperature equilibriated measurement in the SQUID experiment. We took the midpoints in the SQUID LS $\leftrightarrow$ HS transition curves as transition temperatures. As far as the spin-crossover behavior of the composites is concerned, the SCO temperature of the complexes tends to decrease when mixed with the LC matrix (see Figs. 1 (c) and (d) and Table 1), when compared with their respective SCO temperatures. This phenomenon is commonly observed both in DSC and SQUID experiments.

We performed electronic and local geometric structural analysis of temperature-dependent spin crossover complexes and composites using the Fe K-edge X-ray absorption fine structure (XAFS) spectroscopy. Table 1 summarizes how the bond length of Fe–N obtained by EXAFS spectroscopy changes when the two complexes and their POx composites were heated from 78 K (low spin state) to 380 K (high spin state). It is clearly seen that all the Fe–N bond lengths increase in the HS state when compared to those in LS state. Especially, the increase of bond length for the composites is higher than the increase for the complexes themselves. For an example, the Fe–N distance of $Fe(II)(ODT)_3(p\text{-}tol)_2$ (complex I) is lengthened from 1.97 Å at 78 K (LS) to 2.09 Å at 380 K (HS), whereas the value increases from 1.84 Å to 2.21 Å in composite I.

4. CONCLUSION

Inclusion of information on spin-crossover (SCO) transition together with glass-transition and isotropization in a composite could be achieved by mixing an SCO Fe(II) complex with a liquid crystalline polymer (LCP) matrix. Such composites provide examples of processable materials which are able to exhibit multiple switching or information storage capacity resulted from a combination of SCO complexes and LC transition. Field-induced or mechanical alignment of the LCP matrix should enable us to construct devices that would additionally show an anisotropy in optical properties. Since SCO also can be induced photophysically, devices with photoswitching capacity coupled with thermal induction of phase transitions can be envisaged.

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