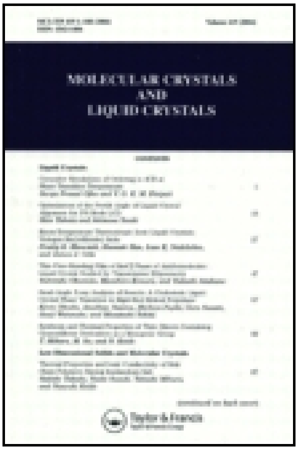

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: N. Shimamoto, S. Ohkoshi, O. Sato & K. Hashimoto (2000): Photochromic Behavior Based on Spin Transition on a Cobalt-Iron Polycyanide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 344:1, 95-100

To link to this article: http://dx.doi.org/10.1080/10587250008023820

*Mol. Cryst. Liq. Cryst.*, 2000, Vol. 344, pp. 95-100
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Printed in Malaysia

# Photochromic Behavior Based on Spin Transition on a Cobalt-Iron Polycyanide

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Magnetic and photochromic behaviors of cobalt-iron polycyanide ($Na_{0.34}Co_{1.33}Fe(CN)_6 \cdot 4.5H_2O$) were investigated. This compound changes its spin state via photo-induced charge transfer between a low spin state of $Fe^{II}$($S$ = 0)-CN-$Co^{III}$($S$ = 0) and a high spin state of $Fe^{III}$ ($S$ = 1/2)-CN-$Co^{II}$($S$ = 3/2). The spin transition is accompanied by a color change, indicating a potential application for novel photochromic material.

*Keywords:* cobalt-iron cyanide; spin transition; photochromism; Prussian blue analogues

## INTRODUCTION

Prussian blue analogs with either ferro or ferri magnetic properties are classified into so-called molecule-based magnets, which consist of molecular building blocks. One of the interesting aspects of molecule-based compounds is that a design of various functionalizations is easier compared to the bulk materials.[1]

We have previously found that one of the Prussian blue analogs, cobalt-iron polycyanide changes its spin state between the $Fe^{II}$($S$ = 0)-CN-$Co^{III}$ ($S$ = 0) low spin (LS) state and the $Fe^{III}$($S$ = 1/2)-CN-$Co^{II}$($S$ = 3/2) high spin (HS) state by the intermolecular electron transfer.[2] The spin transition can be controlled by a concentration of interstitial alkali cations, $Na^+$ and $K^+$, at room temperature[2], and by a photo irradiation at low temperature below 26K, causing an increase of spontaneous magnetization.[3-5]

In the present work, we have studied a thermal and a photo-induced spin transitions in a paramagnetic region, which is accompanid by a color change from purple to red.

## EXPERIMENTAL SSECTION

**Sample Preparation.** An aqueous solution of $CoCl_2$ (2 mM) and NaCl (1 M) was slowly added to a vigorously stirred aqueous solution of $Na_3Fe(CN)_6$ (2 mM) and NaCl (1 M), yielding a cobalt iron polycyanide microcrystalline powder sample.

**Characterization.** Elemental anaysis yields the formula $Na_{0.34}Co_{1.33}Fe(CN)_6 \cdot 4.5H_2O$ [Anal. Calcd: Na, 2.06 %; Co, 20.7 %; Fe, 14.7 %;C, 18.9 %; N, 22.1 %; H, 2.39 %; O, 18.9 %. Found: Na, 2.15 %; Co, 21.7 %; Fe, 15.4 %; C, 18.4 %; N, 20.9 %; H, 2.39 %; O, 18.9 % ( Na : Co : Fe = 0.13 : 1.41 : 1 and H : O = 2 : 1 )]. The powder X-ray diffraction measurement of the $Na_{0.34}Co_{1.33}Fe(CN)_6 \cdot 4.5H_2O$ indicated a typical face-centered cubic (fcc) pattern. The scaning electron microscope observation revealed that the powder samples consisted of cubic crystalline grains, about 500 nm side length.

Magnetic properties were investigated with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). A light from Hg-Xe lamp was guided via optical fiber into the SQUID magnetometer. The UV-Vis spectra were recorded on a UV-3100 (Shimazu) at controlled temperature by a closed-cycle helium refrigerator (Iwatani Co.,Ltd).

## RESULTS AND DISCUSSION

The product of the molar magnetic susceptibility ( $\chi_M$ ) and temperature ( $T$ ) is shown as a function of temperature in Figure 1. By decreasing the temperature with a rate of 1 K/min, the $\chi_M T$ value radually decreased slightly in the range from 300 K to 200 K, but dropped abruptly from 4.3

cm$^3$ mol$^{-1}$ K at 190 K to 1.5 cm$^3$ mol$^{-1}$ K at 170 K, and then decreased slowly again below 170 K. This result indicates that the spin transition from Fe$^{III}$-CN-Co$^{II}$ to Fe$^{II}$-CN-Co$^{III}$ took place in the temperature between 190 K and 170 K, due to the electron transfer from Co$^{II}$ to Fe$^{III}$. During the warming process, however, the $\chi_M T$ value rose abruptly from 1.6 cm$^3$ mol$^{-1}$ K at 210 K to 4.5 cm$^3$ mol$^{-1}$ K at 230 K, showing that the reverse spin transition took place at a higher temperature region. These spin transitions with a hysteresis of about 40 K width occurred repeatedly.

The changes of the spin state are accompanied with a color change. Figure 2 are shown the UV-Vis spectra of this sample at 290 K (broken line) and 50 K (solid line). The low spin state has a broad absorption around 550 nm which is due to the charge-transfer (CT) band from Fe$^{II}$ to Co$^{III}$.[5]

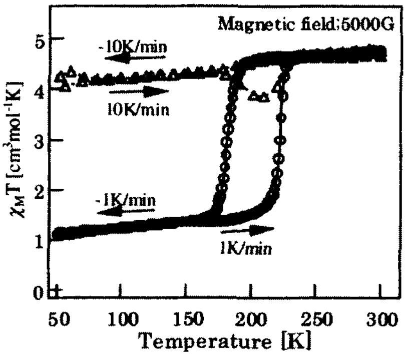

FIGURE 1. $\chi_M$T vs. temperature plots for $Na_{0.34}Co_{1.33}Fe(CN)_6 \cdot 4.5H_2O$.

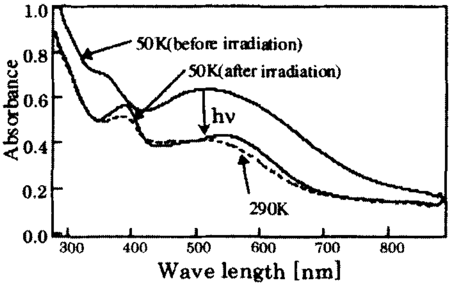

FIGURE 2. UV-vis spectra for $Na_{0.34}Co_{1.33}Fe(CN)_6 \cdot 4.5H_2O$ at 290K (broken line), and at 50K before and after light irradiation(solid line).

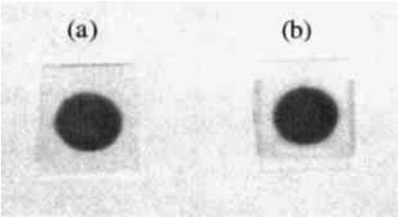

FIGURE 3. Color change of $Na_{0.34}Co_{1.33}Fe(CN)_6 \cdot 4.5H_2O$.
(a)the HS state of Fe$^{III}$-CN-Co$^{II}$.
(b)the LS state of Fe$^{II}$-CN-Co$^{III}$
See Color Plate I at the back of this issue.

$1.19\times10^{20}$ and $0.87\times10^{20}$ molecules.cm$^{-3}$ for the A and B isomers prior to UV and green photo-orientation, respectively), the UV and green irradiation intensity range imposes about 0.14 to 1.42 and 0.26 to 1.79 incident photons per isomer per second, respectively. The probe was the red light ($\lambda$ = 633 nm) of a He-Ne laser (power ~ 2.4 mW, and ~ 1 mm-diameter spot), so as photo-orientation processes of the isomer B are probed independently from those of the isomer A. Dark conditions were employed to avoid the influence of the room light on the isomerization reaction.

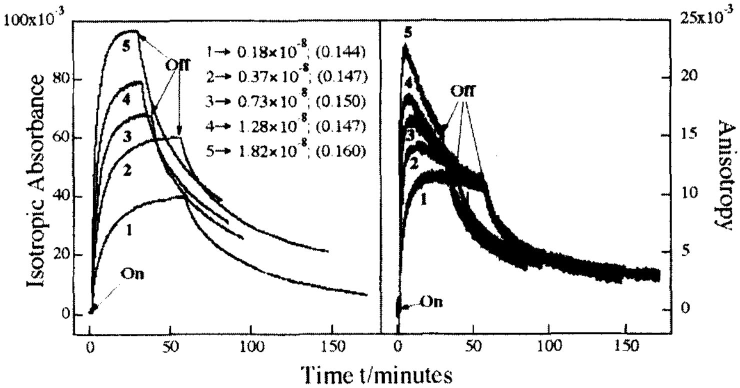

FIGURE 1 Real time evolution of the isotropic absorbance (left) and the anisotropy (right) of SP in PMMA upon linearly polarized UV irradiation for several irradiation intensities. The numbers from 1 to 5 indicate the value of the irradiation intensity in units of Einstein.s$^{-1}$.cm$^{-2}$ with the corresponding sample absorbance at the irradiation wavelength, e.g. 365 nm (value between brackets). The moments of turning the irradiation light on and off are indicated.

Absorbance of light polarized parallel and perpendicular to the irradiating light polarization was measured and the isotropic absorbance, the anisotropy, and the order parameter were deduced. The latter was other words, the color of the compound changed from red to purple by the irradiation below 190 K.

This change can be monitored by measuring magnetic properties. The $\chi_M T$ value versus time plot at 50 K with $H$ = 5000 G is shown in Figure 5. The $\chi_M T$ value of LS state increased gradually with the light irradiation time, and was saturated at the same value of that of the HS state obtained by the rapid cooling.

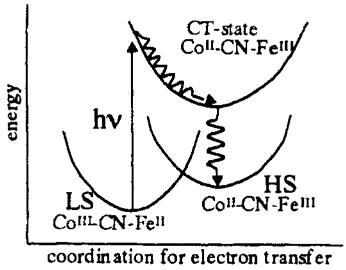

FIGURE 5. Schematic representation of the potential energy curves for the LS state and the HS state,and the light induced spin transition process at 50K.

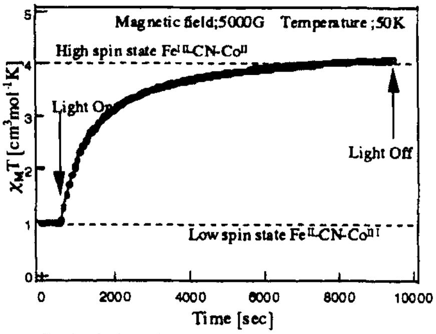

FIGURE 6. Light induced spin transition from a low spin state to a high spin state.

The present photo-induced color change, photochromic behavior, of $Na_{0.3}Co_{1.33}Fe(CN)_6 \cdot 4.5H_2O$ is different from the conventional photochromic processes[6], because the former process is induced without either reactions with other reactant, rearrangements, dissolution or photopolymerization. Therefore, a superior in repeatability is expected in the present system as compared with the conventional photochromic reactions.

Moreover the large hysteresis suggests that existence of strong cooperative interaction among metal ions.[7] In other words, light intensity threshold may exist in the photo-induced process. The present process resembles the LIESST ( light induced exited spin state trapping ) phenomenon reported with Fe$^{II}$ spin crossover complexes such as

$[Fe(pic)_3]X_2\cdot sol\cdot EtOH$ (pic = 2-(aminomethyl)pyridine; X = Cl, Br; sol = MeOH ), $[Fe(phen)_2(NCS)_2]$ (phen = phenanthroline), and so on[8,9] in the point that both processes are based on spin transitions. The spin transition on the LIESST, however, is based on the interatomic $Fe^{II}$ metal,. not between the interatomic ones.

From the viewpoints of practical applications, both the LIESST and the present spin transition process should be proceeded around room temperature. This is, in general, very difficult because the hight of the potential barrier between a ground state and a metastable state cannot be controlled easily. However, the thermal spin transition of the present system has a large hysteresis in the room temperature region, where the HS state may form the ground state, while the LS state is the metastable state. This suggests that the photochromic reaction can be induced around room temperature with the present compound. The study along this line is being under investigation.

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