

# Cation size effect on photomagnetism and charge transfer phase transition of iron mixed-valence complexes with spiropyran

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## ABSTRACT

We have investigated the magnetic properties of a photoresponsive organic–inorganic hybrid system, (SP-R)[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] (SP = spiropyran; R = Me, Et, Pr; dto = C<sub>2</sub>O<sub>2</sub>S<sub>2</sub>), under hydrostatic pressures. At ambient pressure, (SP-Et)[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] and (SP-Pr)[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] undergo one and two ferromagnetic phase transitions corresponding to the high-temperature phase with the spin configuration of Fe<sup>II</sup>(S = 2)–Fe<sup>III</sup>(S = 1/2), while (SP-Me)[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] undergoes two ferromagnetic phase transitions corresponding to the coexistence of the high-temperature phase and the low-temperature phase with the spin configuration of Fe<sup>II</sup>(S = 0)–Fe<sup>III</sup>(S = 5/2). Under hydrostatic pressures, (SP-R)[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] (R = Et, Pr) undergo a new ferromagnetic phase transition corresponding to the low-temperature phase caused by the pressure-induced charge transfer phase transition.

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## 1. Introduction

Molecular solids having multifunctionality coupled with transport, optical or magnetic properties have attracted much attention from the viewpoint of the breakthrough of materials science [1–3]. Among various multifunctional materials, molecule-based magnets are one of the leading candidates as photocontrollable multifunctional materials [4]. For instance, the photoinduced magnetism in spin-crossover complexes [5], transition metal cyanides [1,6–8], and organic–inorganic hybrid system [9,10] have been reported. Especially, intercalation magnetic compounds such as honeycomb-layered bimetallic complexes, A[M<sub>1</sub><sup>II</sup>M<sub>2</sub><sup>III</sup>(L)<sub>3</sub>] (A = cation; M<sub>1</sub>, M<sub>2</sub> = transition metal ions; L = oxalato (C<sub>2</sub>O<sub>4</sub>) and related ligands), easily provide a chance to develop photoswitchable magnets [10].

We have investigated dithiooxalato-bridged iron mixed-valence complexes (n-C<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>N[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] (n = 3–6; dto = C<sub>2</sub>O<sub>2</sub>S<sub>2</sub>), which have a two-dimensional honeycomb network structure with an alternating array of Fe<sup>II</sup> and Fe<sup>III</sup> atoms through the dto ligands and the cation layers are intercalated between adjacent [Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>]<sub>∞</sub> layers [11]. Among this system, (n-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] and (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] undergo the thermally induced charge transfer phase transition (CTPT) where the spin configuration reversibly changes between Fe<sup>II</sup>(S = 2)–Fe<sup>III</sup>(S = 1/2) in the high-temperature phase (HTP) and Fe<sup>II</sup>(S = 0)–Fe<sup>III</sup>(S = 5/2) in the low-temperature one (LTP), resulting from minimizing the Gibbs energy in the whole system. The CTPT becomes to be suppressed with increasing the size of intercalated cations [11]. Actually,

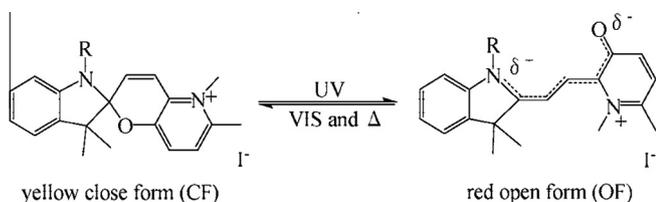
(n-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>N[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] and (n-C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>N[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] show no CTPT. Moreover, all the (n-C<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>N[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] (n = 3–6) show ferromagnetic phase transitions at ~7 K and 13–22 K derived from the LTP and HTP, respectively [11]. The Curie temperature (T<sub>C</sub>) of the LTP is lower than that of the HTP because the Fe<sup>II</sup> site in the LTP is the diamagnetic low-spin state.

As mentioned above, the ferromagnetic transition temperature strongly relates to the occurrence of the CTPT, which can be controlled by changing the intercalated cation. Based on this strategy, we have developed a photoresponsive organic–inorganic hybrid system, (SP-Me)[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] (abbreviated as **1**<sup>Me</sup>; SP-Me = cationic pyrido-spiropyran shown in Scheme 1 [12], in order to control the magnetic properties and the electronic state of the [Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>]<sub>∞</sub> layer (Scheme 2) by means of the photoisomerization of SP-Me. This compound undergoes the CTPT with thermal hysteresis around 75 K and two ferromagnetic phase transitions with T<sub>C</sub> = 5 and 22 K corresponding to the LTP and HTP, respectively. In this system, the photoisomerization of the intercalated spiropyran is induced by UV irradiation, which suppresses the CTPT and leads to the enhancement of T<sub>C</sub> from 5 to 22 K [12].

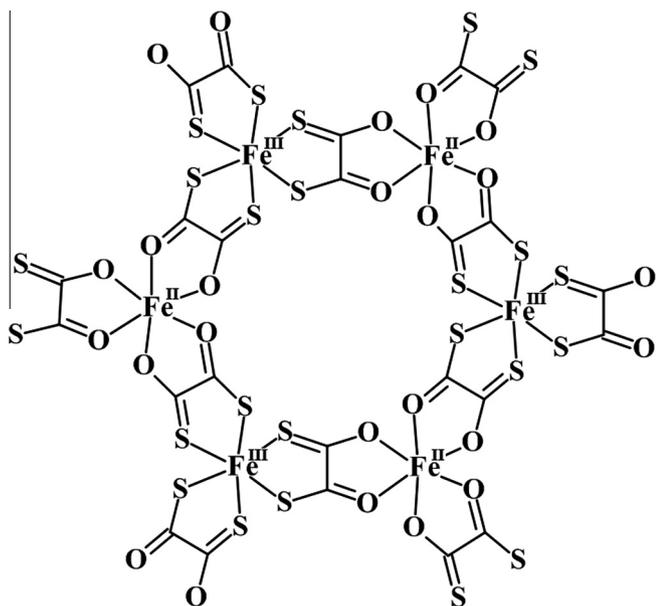
In general, organic–inorganic hybrid systems are easy to perform chemical modification or changing the metal ion. Taking advantage of this feature, we have investigated the magnetic properties of (SP-R)[Fe<sup>II</sup>Fe<sup>III</sup>(dto)<sub>3</sub>] (R = Me (**1**<sup>Me</sup>), Et (**1**<sup>Et</sup>), Pr (**1**<sup>Pr</sup>)), which are chemically modified by the intercalation of spiropyran cations substituted with different alkyl side chains. In this paper, we report the magnetic properties and photoinduced effect on the CTPT and ferromagnetic ordering for **1**<sup>Et</sup> and **1**<sup>Pr</sup> in addition to the previous results of **1**<sup>Me</sup> [12]. Moreover, in order to investigate the pressure effect on the magnetic properties, we also performed magnetic measurements under hydrostatic pressures.

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Scheme 1. Photochromism of cationic spiropyran (SP-R).



Scheme 2. Schematic representation of  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]_{\infty}$ .

## 2. Experimental

### 2.1. Syntheses

#### 2.1.1. Preparation of (SP-R)I (R = Me, Et, Pr)

The precursory SP-Et was prepared according to the literature method [12]. A chlorobenzene solution (50 mL) containing SP-Et of 7.51 g (24.5 mmol) and methyl iodide of 34.8 g (245 mmol) was refluxed overnight. Then the solution was cooled down to room temperature, and the yellow microcrystalline solid was filtered, washed with chlorobenzene, and recrystallized from ethanol. (SP-Et)I was obtained in 78% yield. Similarly, (SP-Me)I and (SP-Pr)I were obtained as yellow microcrystalline solids in 64% and 90% yields, respectively. (SP-Me)I:  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 (s, 3H), 1.35 (s, 3H), 2.80 (s, 3H), 2.93 (s, 3H), 4.53 (s, 3H), 6.52 (d,  $J = 10.8$  Hz, 1H), 6.58 (d,  $J = 8.1$  Hz, 1H), 6.93 (t,  $J = 6.75$  Hz, 1H), 7.10 (d,  $J = 8.1$  Hz, 1H), 7.23 (t,  $J = 6.75$  Hz, 1H), 7.55 (q,  $J = 7.2$  Hz, 2H), 7.87 (d,  $J = 13.5$  Hz, 2H);  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ )  $\delta$  20.18, 22.66, 25.77, 29.56, 42.87, 53.22, 106.53, 107.28, 120.45, 121.47, 122.43, 128.15, 129.04, 130.46, 132.24, 134.67, 135.10, 146.89, 147.19, 152.01. IR (KBr disc) 772(s), 1319(s), 1490(s), 1609(s), 2978(m)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}$ : C, 55.31; H, 5.34; N, 6.45. Found: C, 55.48; H, 5.61; N, 6.23%. (SP-Et)I:  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.20 (t,  $J = 6.75$  Hz, 3H), 1.22 (s, 3H), 1.35 (s, 3H), 2.93 (s, 3H), 3.31 (m, 2H), 4.53 (s, 3H), 6.51 (d,  $J = 10.8$  Hz, 1H), 6.61 (d,  $J = 8.1$  Hz, 1H), 6.90 (t,  $J = 8.1$  Hz, 1H), 7.08 (d,  $J = 8.1$  Hz, 1H), 7.22 (t,  $J = 6.75$  Hz, 1H), 7.51 (q,  $J = 7.2$  Hz, 2H), 7.89 (d,  $J = 8.1$  Hz, 1H);  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ )  $\delta$  14.40, 20.13, 22.62, 25.85, 38.30, 42.90, 53.83, 106.91, 107.02, 119.98, 121.66, 122.26, 128.09, 128.91, 130.44, 132.77,

134.66, 135.02, 145.90, 146.98, 151.93. IR (KBr disc) 767(s), 1316(s), 1487(s), 1607(s) 2976(m)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}$ : C, 56.26; H, 5.62; N, 6.25. Found: C, 56.05; H, 5.72; N, 6.00%. (SP-Pr)I:  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.23 (t,  $J = 6.75$  Hz, 3H), 1.24 (s, 3H), 1.34 (s, 3H), 1.66 (m, 2H), 2.93 (s, 3H), 3.17 (m, 2H), 4.53 (s, 3H), 6.51 (d,  $J = 10.8$  Hz, 1H), 6.60 (d,  $J = 8.1$  Hz, 1H), 6.91 (t,  $J = 6.75$  Hz, 1H), 7.09 (d,  $J = 8.1$  Hz, 1H), 7.21 (t,  $J = 6.75$  Hz, 1H), 7.52 (q,  $J = 7.2$  Hz, 2H), 7.81 (d,  $J = 10.8$  Hz, 1H);  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ )  $\delta$  11.70, 20.15, 22.12, 22.61, 25.71, 42.88, 45.67, 53.89, 106.98, 107.23, 120.03, 121.62, 122.11, 128.06, 128.95, 130.40, 132.86, 134.58, 134.94, 146.50, 147.00, 152.03. IR (KBr disc) 765(s), 1314(s), 1488(s), 1606(s), 2972(m)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}$ : C, 57.15; H, 5.89; N, 6.06. Found: C, 57.43; H, 6.07; N, 5.97%.

#### 2.1.2. Preparation of (SP-R)[ $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3$ ] ( $\mathbf{1}^{\text{Et}}$ , R = Me; $\mathbf{1}^{\text{Et}}$ , R = Et; $\mathbf{1}^{\text{Pr}}$ , R = Pr)

A solution (20 mL) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.15 g, 0.78 mmol) and (SP-Et)I (0.55 g, 1.17 mmol) in a methanol–water mixture of 3:2 ratio was stirred. A solution (30 mL) of  $\text{KBa}[\text{Fe}(\text{dto})_3] \cdot 3\text{H}_2\text{O}$  (0.50 g, 0.78 mmol) in a methanol–water mixture of 3:2 ratio was added to the above solution.  $\mathbf{1}^{\text{Et}}$  was precipitated as black powdered crystals, separated by suction filtration, and washed with methanol and diethyl ether. The yield was 48% as  $\mathbf{1}^{\text{Et}}$ . Similarly,  $\mathbf{1}^{\text{Me}}$  and  $\mathbf{1}^{\text{Pr}}$  were prepared in 30% and 67% yields, respectively.  $\mathbf{1}^{\text{Me}}$ : Anal. Calc. for  $\text{C}_{26}\text{H}_{23}\text{Fe}_2\text{N}_2\text{O}_7\text{S}_6$ : C, 40.06; H, 2.97; N, 3.59. Found: C, 39.77; H, 3.03; N, 3.32%.  $\mathbf{1}^{\text{Et}}$ : Anal. Calc. for  $\text{C}_{27}\text{H}_{25}\text{Fe}_2\text{N}_2\text{O}_7\text{S}_6$ : C, 40.86; H, 3.18; N, 3.53. Found: C, 40.96; H, 3.46; N, 3.40%.  $\mathbf{1}^{\text{Pr}}$ : Anal. Calc. for  $\text{C}_{28}\text{H}_{27}\text{Fe}_2\text{N}_2\text{O}_7\text{S}_6$ : C, 41.64; H, 3.37; N, 3.47. Found: C, 41.92; H, 3.65; N, 3.53%.

### 2.2. Powder X-ray diffraction spectroscopy

The powder X-ray diffraction (PXRD) profiles for  $\mathbf{1}^{\text{Me}}$ ,  $\mathbf{1}^{\text{Et}}$ , and  $\mathbf{1}^{\text{Pr}}$  were obtained with a Bruker New D8 ADVANCE diffractometer equipped with graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature.

### 2.3. Magnetic measurements

The static magnetic susceptibilities were measured by a Quantum Design MPMS-5S SQUID susceptometer under 5000 Oe from 2 to 300 K. The zero-field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) measurements were performed in the temperature range of 2–30 K under an applied field of 30 Oe for the investigation of the ferromagnetic phase. The remnant magnetization (RM) was also obtained in the same temperature region at zero field. The powder sample of ca. 10 mg was wrapped in a polyethylene film and held in a plastic straw. For the magnetic measurement under hydrostatic pressure, we used a Micro Industry pressure cell made of BeCu. The powder sample was wrapped in polyethylene film and was placed in the pressure cell. A mixture of Fluorinert (FC70:FC77 = 1:1) was used as a pressure-transmitting medium. The obtained magnetic susceptibility was corrected for the background and the core diamagnetism estimated from Pascal's constants.

## 3. Results and discussion

### 3.1. Characterization

All the compounds were characterized by IR spectra and PXRD, revealing a honeycomb-layered structure. In the IR spectra, the characteristic antisymmetric C–O stretching modes appeared as single intense bands at 1489, 1491 and 1490  $\text{cm}^{-1}$  for  $\mathbf{1}^{\text{Me}}$ ,  $\mathbf{1}^{\text{Et}}$

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