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A novel bithiazole-containing polymeric complex with soft ferromagnetism

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A novel polymer resulting from the polycondensation of 2,2′-diamino-4,4′-bithiazole (DABT) with 5,5′-methylene-bis-salicylaldehyde (MBSA) and its ferric complex are described. Analyses of Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) revealed that both bithiazole residue and Schiff-base moiety acted as coordination sites for Fe^{3+} ions in the polymeric matrix. The magnetic behavior of the complex was studied as a function of magnetic field strength (0–60 kOe) at 25 K and as a function of temperature (5–300 K) at a magnetic field strength of 30 kOe. The hysteretic loop was measured at 5 K for the complex showing coercivity (H_c) of 20 Oe and remnant magnetization (M_r) of 0.002 emu/g, which is much lower than those of bithiazole-based polymeric complexes previously reported. The results indicated that the present complex is of the typical characteristics of a soft ferromagnet. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: bithiazole; soft ferromagnetism; synthesis; FT-IR; X-ray

INTRODUCTION

Organic magnetism is a rapidly developing field that combines the skills of experimental and theoretical scientists in many areas of chemistry and physics.[1–7] The design and preparation of organic soft ferromagnets remain one of the greatest challenges in these fields.[8,9] In 1991, Allemand and coworkers discovered an organic ferromagnet based on fullerene, tetrakis(dimethylamino)ethylene-C_{60} ($C_{60}TDAE_{0.86}$).[8] This compound was thought to be a very interesting material in view of its higher transition temperature (~16 K) and coercive field of 0 Oe, although it was unstable and very sensitive to air.

With a view to searching for potential materials for electrical, magnetic, and optical application, in recent years the authors' research group has been working on the synthesis and property of bithiazole-based polymers and their metal complexes. As a result, some novel polymeric complexes containing bithiazole moieties have been prepared and their magnetic behavior has also been examined systematically.[10–14] Recent progress demonstrated that the bithiazole-polymer comprised of Prussian blue exhibits relatively low coercivity ($H_c = 40$ Oe).[11] In the present work the synthesis of a novel bithiazole-containing polymer having a Schiff-base structure has been reported and its ferric complex. The obtained products have been characterized by ^{1}H-NMR, FT-IR spectroscopy, elemental analysis, and X-ray photoelectron spectroscopy (XPS), and their magnetic properties have been examined.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were dried and purified by the usual reported method. 2,2′-Diamino-4,4′-bithiazole (DABT)[15] and 5,5′-methylene-bis-salicylaldehyde (MBSA)[16] were prepared according to the literatures, followed by recrystallization.

Synthesis of polymer and polymeric complex

The polymer and corresponding iron(III) complex were prepared by following the similar procedure described previously.[10] A glacial acetic acid solution of DABT (2.5 mmol) was added to a solution of MBSA in THF/glacial acetic acid (volumetric ratio 1:1) and then the mixture was stirred for 30 min at 60°C. The resulting precipitate was filtered, then washed with water, methanol and ether, and dried under vacuum (yield 85%). The intrinsic viscosity $[\eta] = 0.287$ dl/g (DMSO, 30°C). IR (KBr, cm^{-1}): 3352 (w), 2919 (w), 1631 (vs), 1349 (s), 1124 (m), 873 (m), 669 (m); ^{1}H-NMR (500 MHz, DMSO-*d*): δ 10.3 (ArOH), 7.35–7.64 (aromatic protons), 7.03 (bithiazole ring), 6.81 (–CH=N–), 3.92 and 2.57 ppm (–CH_2–). In a nitrogen atmosphere, the bright orange polymer (referred to as PMD hereafter) reacted with $FeCl_3$ at 80°C for 24 hr in OMSO solution. The brown-red polymeric complex precipitated from the reaction mixture was filtered and washed successively with DMSO, water and methanol. For further purification, the ferric complex (referred to as PMD-Fe^{3+}) was soaked in a large amount of methanol and stirred for 24 hr. The complex was isolated in a 90% yield and dried under vacuum at 60°C for 24 hr.

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Measurements

FT-IR spectra were recorded on a Bruker Vector 22 using KBr pellets. The elemental analysis for PMD-Fe^{3+} complex was carried out using atomic absorption spectrometry (HITACHI 180-50 spectrometer). XPS was performed with an ESCACA-BII X-ray photoelectron spectrometer. Excitation was produced by monochromatized 1485.6 eV Al-K_α radiation. The spectrometer was calibrated with respect to the C_{1s} 284.5 eV line. The magnetic measurements were carried out on a MPMS-7 magnetometer. The magnetization of the applied magnetic field (i.e. hysteretic loop) was measured at 200 K, and the temperature dependence of the magnetization was obtained in a temperature range varying from 5 to 300 K.

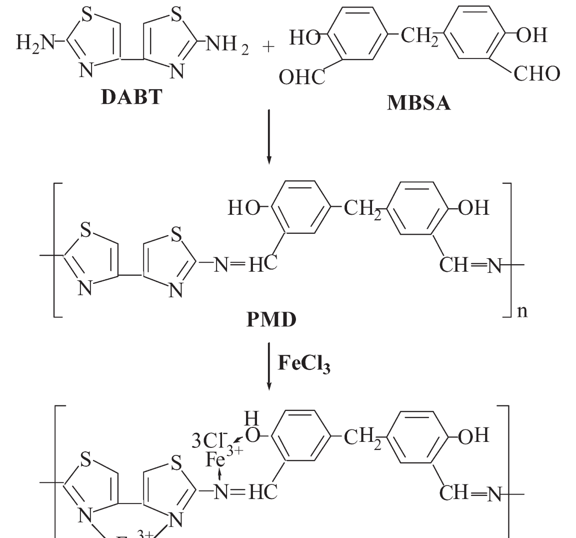
RESULTS AND DISCUSSION

Characterization for polymer PMD and its iron(III) complex

As shown in Scheme 1, polymer PMD is a poly(Schiff base) derived from DABT and MBSA via a condensation reaction. The polymer was obtained as a bright orange solid being insoluble in common organic solvents except in DMSO and acetic acid. The corresponding polymeric complex PMD-Fe^{3+} was even insoluble in DMSO and dimethyl formamide (DMF), which makes it difficult to characterize these materials. However, the structure of PMD was determined by ^1H-NMR and IR spectroscopy (see Experimental section). In the ^1H-NMR spectrum, the resonance absorption at 7.03 ppm is assigned to the protons of the bithiazole ring, while the multi peaks at 7.35–7.64 ppm are attributed to the aromatic protons of salicylaldehyde residue. The signals of $-CH_2-$ and $-CH{=}N-$ appeared at 2.57 and 6.81 ppm, respectively.

IR spectra of the as-prepared samples are shown in Fig. 1. It can be observed that the spectrum of PMD-Fe^{3+} complex is different from that of the original polymer. The skeletal vibration of thiazole moiety which appears at 1298 cm^{-1} in the polymer shifted to 1273 cm^{-1} in the spectrum of the polymer complex. Furthermore, the spectrum of the complex has a new sharp peak at 1520 cm^{-1}, but does not contain the absorption at 1349 cm^{-1} that is characteristic of the polymer. These observation may be attributable to the coordination interactions between Fe^{3+} ion and nitrogen of bithiazole moiety as well as to the formed six-membered ring structure containing CH=N group.[17] The formation of bithiazole-based polymer complexes with iron(II) has been studied before.[10] In that case, the formation of the complex was also accompanied by a similar change in the IR spectra.

Further evidence in support of the coordination has been obtained from XPS spectra of PMD-Fe^{3+} complex (Fig. 2 and Table 1). Fe 2*p* core level photoelectron spectrum has been



Scheme 1. Synthetic route and expected structure of PMD-Fe^{3+} complex.

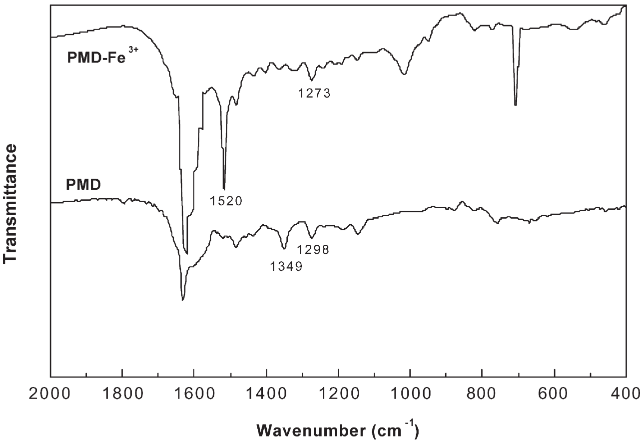


Figure 1. The FT-IR spectra of polymer (PMD) and corresponding iron(III) complex.

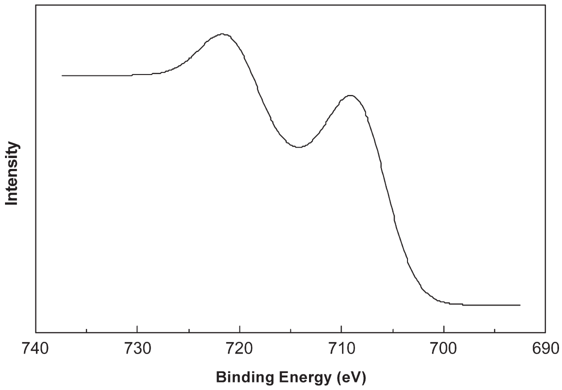


Figure 2. Fe 2*p* XPS spectrum of PMD-Fe^{3+}complex.

Table 1. Binding energies of Fe 2*p* core levels in PMD-Fe^{3+} complex and other Fe-containing materials

	Binding energy (eV)		
Materials	Fe $2p_{3/2}$	Fe $2p_{1/2}$	Ref.
PMD-Fe^{3+}	709.5	722.6	This work
Fe	707.3	720.3	16
Fe_3O_4	710.8	724.7	16, 17
Fe_2O_3	711.6	725.1	16, 18

inspected in an effort to understand the chemical structure of the iron species in the polymeric matrix. It is generally considered that the peaks near 709.5 and 722.6 eV in the Fe 2p XPS spectrum may be respectively related to the binding energies of Fe 2$p_{3/2}$ and Fe 2$p_{1/2}$. It can be seen from Table 1 that the binding energies are not in conformity with those for typical Fe, Fe_3O_4, or Fe_2O_3 reported in the past.[18–20] At the same time, in comparison with PMD the binding energies for oxygen and nitrogen in the Fe^{3+}-complex changed from 532.5 to 533.7 eV and from 399.8 to 401.1 eV, respectively. These phenomena indicated that both bithiazole and Schiff-base moieties may act as bidentate ligands for ferric ions in the complex.

Based on the results of the elemental analysis, it is reasonable to hypothesize that the formula for PMD-Fe^{3+} complex is $[C_{21}H_{14}N_4O_2S_2(FeCl_3)_2]_n$ because experimental data were well in accordance with theoretical values (analytical calculation: C 33.95%, H 1.90%, N 7.54%; Found: C 34.51%, H 2.04%, N 8.35%, Fe 15.86%). This formula means that the number of coordinated Fe^{3+} ions per the repeat structural unit is about 2. As shown in Scheme 1, a probable coordination structure is suggested for the complex, in which bidentate ligands come from the same polymer chain and the metal ion takes a planar geometry. However, it should be pointed out that the complex may be constructed by different polymeric ligands with a coordination number of 4 as proposed in a previous report.[21]

Magnetic measurements

Measurements of the magnetic susceptibility at an external field of 30 kOe were carried out over the temperature range 5–300 K and a typical plot is represented in Fig. 3. It can be observed that the magnetic susceptibility (χ) of PMD-Fe^{3+} complex follows the Curie–Weiss relation [$\chi = C/(T-\theta)$][22] in the temperature range 300–175 K, indicating its paramagnetic behavior at a higher temperature. However, in the temperature region below 175 K, the experimental curve deviated from the Curie–Weiss relation. This suggests the presence of exchange interaction at lower temperature scope. The positive Curie–Weiss temperature ($\theta = 75$ K) implies the existence of ferromagnetic coupling below 75 K. The plot also shows a dependence of the χT product on temperature. That is, the χT increases with decreasing temperature up to a maximum value at ~25 K and then drops down. It must be noted that the maximum χT of about 5.6×10^{-3} emu K/mol is extremely low compared with the expected value for the structure unit with spin quantum number $S = 1/2$. This may be associated with the antiferromagnetic interaction among spins of Fe^{3+} ions. However, the exact reason why χT is so low and decreases sharply below 25 K remains to be elucidated.

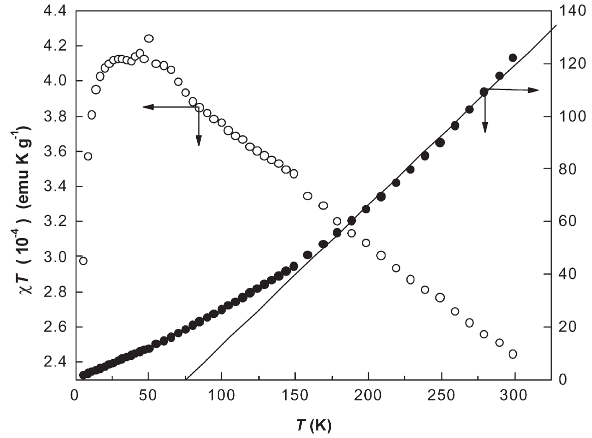


Figure 3. Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PMD-Fe^{3+} complex at an applied magnetic field of 30 kOe. The solid line is a fit to the Curie–Weiss relation.

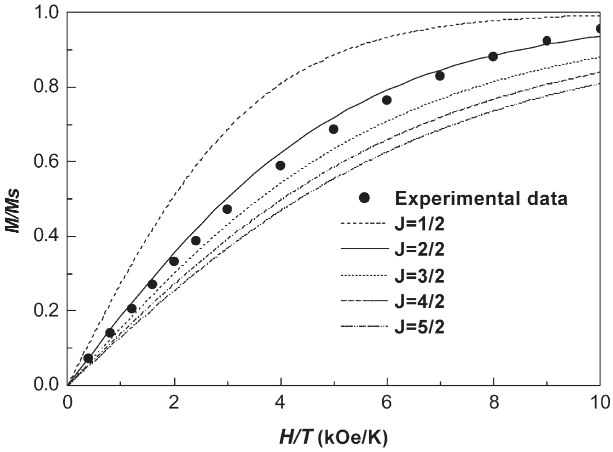


Figure 4. Normalized plots of magnetization (M/M_s) versus the ratio of magnetic field and temperature (H/T) for PMD-Fe^{3+} complex at 5 K, and the theoretical curves corresponding respectively to $J = 1/2$, 2/2, 3/2, 4/2, and 5/2 Brillouin functions.

The magnetization (M) normalized with saturation magnetization (M_s) for PMD-Fe^{3+} complex is plotted versus the ratio of magnetic field and temperature, as shown in Fig. 4. In comparison with the Brillouin curves, the experimental M/M_s plot was close to the theoretical curve for $J = 2/2$. Figure 5 shows the plot of magnetization (M) versus the applied field (H) for the complex at 5 K. With the enlargement of the applied field, the magnetization increased rapidly at first and then levels off slowly, and the estimated saturation magnetization is found to be 2.3 emu g for this sample.

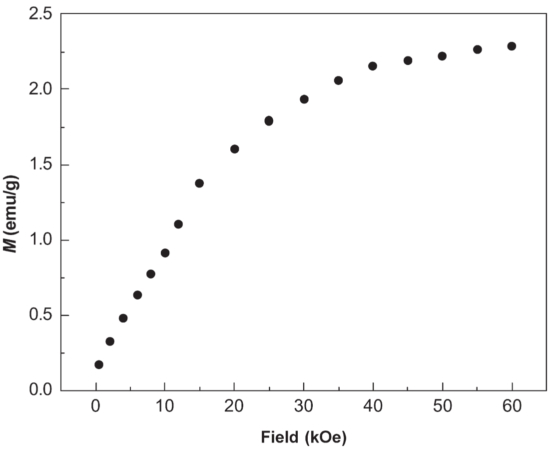


Figure 5. Magnetization (M) versus applied field (H) at 5 K for PMD-Fe^{3+}complex.

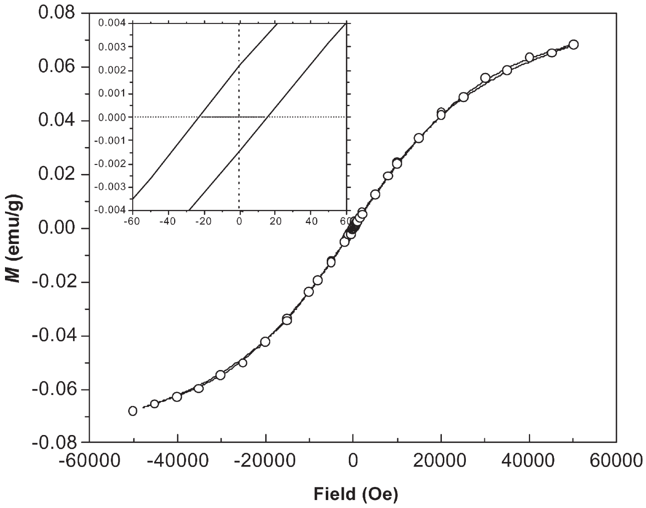


Figure 6. Field-dependent magnetization showing a hysteretic loop for PMD-Fe^{3+} complex at 25 K. Insert: expanded view of the region from -60 Oe to 60 Oe.

It is well known that the magnetic property of polymeric complexes arises from the magnetic exchange interactions between metal ions in the polymer matrix. As shown in Fig. 6, the magnetization of PMD-Fe^{3+} complex as function of an applied field exhibited an hysteretic loop at a temperature of 25 K, which is characteristic of ferromagnetic interactions. The observed coercive field (H_c) and the remnant magnetization (M_r) were respectively 20 Oe and 0.002 emu g, which was much lower compared with that of the bithiazole-Prussian system previously reported.[11] From the observation it may be concluded that the as-synthesized complex is a very soft ferromagnetic material. The decrease of both H_c and M_r values might be related to the strong magnetic interaction in the Schiff base π−conjugation system.[23]

CONCLUSION

A novel bithiazole-containing polymer with Schiff-base unit and its iron(III) complex were prepared. It was demonstrated that the ferric irons were incorporated into the polymer matrix via a coordination interaction. An interesting observation on the magnetic measurements was that the polymeric complex exhibited a typically soft magnetic behavior in terms of the coercive field and remnant magnetization.

Acknowledgments

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