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Syntheses and magnetic properties of novel complexes of polymer containing bithiazole ring and salicylic acid

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Abstract

A novel polymer (SDP) was first synthesized from 2,2′-diamino-4, 4′-bithiazole (DABT) with salicylic acid and paraformaldehyde (PF). SDP–Fe^{2+} was prepared from SDP and $FeSO_4$ in DMSO. SDP–Prussian blue was prepared from SDP–Fe^{2+} and potassium ferricyanide ($K_3[Fe(CN)_6]$) in DMSO. They were characterized through IR, ^{1}H NMR, XPS and ESR. The magnetic behavior of two polymeric complexes was measured as a function of magnetic field strength (0–60 kOe) at 5 K and as a function of temperature (5–300 K). SDP–Prussian blue exhibits a hysteresis cycle at 5 K, the observed coercive field is $H_c = 40$ Oe, and the remnant magnetization $M_r = 0.035$ emu g^{-1}. The result shows that SDP–Fe^{2+} is an antiferromagnet while SDP–Prussian blue is a ferromagnet. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Synthesis; Magnetic property; Polymer containing bithiazole and salicylic acid

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There has been much interest in the preparation of magnetic polymers. Organic polymers containing paramagnetic species may provide a new kind of magnetic material owing to the magnetically long-range ordering of unpaired electrons through spin–spin interactions [1]. The ability to control the sign and magnitude of the magnetic exchange interaction between adjacent metal ions in a polymeric complex is of fundamental importance for the design and synthesis of new magnetic materials based on polymeric coordination complexes [2]. In 1998, Hoffmann et al. [3] proposed that polymers built from sulfur, carbon, nitrogen-containing five-membered rings would theoretically display magnetic ordering, but none have been synthesized yet. Sun et al. [4] reported the synthesis of poly(Schiff base) containing bithiazole ring (TAPDA) firstly by polycondensation of 2,2′-diamino-4,4′-bithiazole (DABT) with terephthalaldehyde and its properties of permeability, conductivity and metal chelating with noble metal ions. We have reported the synthesis of TAPDA–Fe^{2+} complex and its ferromagnetic properties for the first time [5]. Our interest in the bithiazole-based polymers stems from their potential to bind transition-metal ions. The 4,4′-bithiazole moiety is used to provide dentate N-donor sites for binding metal ions. DABT is incorporated into the polymer main chain, the corresponding resins are expected to form polymeric metal complexes under suitable conditions, and can be employed for potential electrical, magnetic and optical materials by choosing the constituent molecules appropriately.

It is known that hexacyanometalate ions, $[M(CN)_6]^{n-}$, act as good building blocks to provide bimetallic assemblies such as Prussian blue, $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot nH_2O$. Prussian blue and its analogues form a family of magnetic materials, and a high T_C or T_N is reported for some of these assemblies [6–11]. However, as far as we know, no organic magnet from polymeric complex containing bithiazole using hexacyanometalate ions as bridging linkages has been reported. In this paper, we first report the synthesis of organic polymeric Prussian blue analogue and its magnetic properties.

This paper is the first to describe the syntheses of a new polymer (SDP) from DABT condensed with salicylic acid and PF, and its complex with Fe^{2+} (SDP–Fe^{2+}), and the complex (SDP–Prussian blue) from SDP–Fe^{2+} and $K_3[Fe(CN)_6]$. The preliminary magnetic properties of two complexes are also reported for the first time.

DABT was prepared readily from 1,4-dibromobutanedione [12] and thiourea according to literature [13], followed by several times of recrystallizations. The polymer (SDP) was prepared from DABT and salicylic acid and PF as shown in Scheme 1 (Synthetic route of SDP). A mixture of salicylic acid and DABT with PF in the ratio 1:1:2 was

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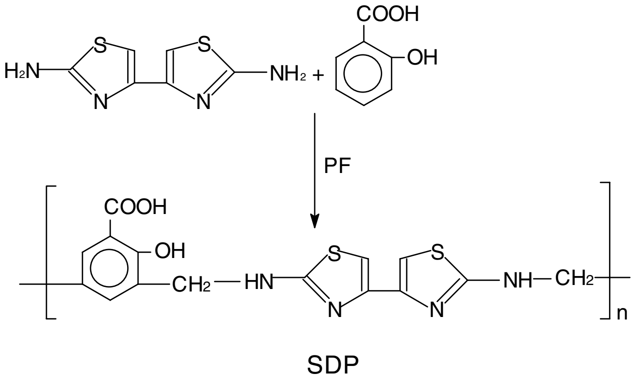

Scheme 1.

heated in the presence of 2 M HCl as a catalyst at 100°C for 3 h. A yellow-green precipitate was formed and filtered, washed successively with water, methanol and ether, and dried under vacuum at 60°C for 24 h.[1]

The polymer–Fe^{2+} complex (SDP–Fe^{2+}) was prepared from SDP and $FeSO_4$ in DMSO at room temperature under purified nitrogen atmosphere for 5 days. A red-brown precipitate was formed and filtered, washed successively with water, methanol and ether, then the precipitated complex was soaked in methanol for 24 h. The complex was isolated by filtration and dried under vacuum at 60°C for 24 h. Thus the polymeric complex (SDP–Fe^{2+}) was obtained.[2]

SDP–Prussian blue was prepared from SDP–Fe^{2+} and $K_3[Fe(CN)_6]$ in DMSO at room temperature for 3 days. The blue-green precipitate was filtered, washed successively with water, methanol and ether, and dried under vacuum at 50°C for 24 h.[3]

The structure of the polymer (SDP) was determined by ^1H NMR and Fourier transform infrared (FTIR). A strong resonance at 6.92 ppm is attributed to the all-equivalent bithiazole ring protons in the ^1H NMR spectrum of SDP. The wide and weak resonance peak at about 11.74 ppm is the COOH peak; at the same time, a broad peak at 8.53–8.55 ppm is present, due to the formation of hydrogen bond by neighboring COOH and OH, and the protons of COOH easily exchange with DMSO-d and H_2O, so the COOH peak at 11.74 ppm is weak. The aromatic ring protons are present at 7.34–7.61 ppm. The CH_2 and NH protons are present at 1.21 and 4.68 ppm. A broad band at 3680–3010 cm^{-1} is observed in the FTIR spectrum of SDP, which is due to the stretching vibration absorption of OH, NH and Ar-H. The other broad band is present at 3000–2500 cm^{-1}, this is a characteristic of COOH group in solid state. The peak at 1590 cm^{-1} is due to phenylene ring stretching vibration (C=C), the peak around 873 cm^{-1} is characteristic of 1,2,3,5-tetrasubstituted aromatic C–H out-of-plane deformations. The bithiazole ring and skeletal stretching vibration absorption are also observed in 1528, 1460, 1390, 1298, 1241 and 1034 cm^{-1} [14]. Thus, overall the solution ^1H NMR and FTIR spectra of SDP are in excellent agreement with the proposed structure.

In the FTIR spectrum of SDP–Fe^{2+}, a significant change observed was that the peak at 1298 cm^{-1} in the spectrum of SDP was blue-shifted to 1349 cm^{-1}. The peak at 1298 cm^{-1} in SDP might be due to the skeletal vibration, which was caused by imino-interchange isomer of 2-amino-thiazole [15]. Due to coordination, imino-interchange isomer no longer existed, and skeletal vibration of bithiazole appeared at 1349 cm^{-1}. This suggested that the coordination has taken place through ring nitrogen atom of thiazole. The peak at 1116, 1054, 990 and 952 cm^{-1} in the spectrum of SDP–Fe^{2+}, which were assigned to ν_{3a}, ν_{3b}, ν_{3c} and ν_1 of SO_4^{2-}, suggested that the SO_4^{2-} is a bidentate ligand via oxygen atoms [16].

The solid state FTIR spectrum of SDP–Prussian blue exhibits two distinct cyano stretching vibrations at 2073 and 2024 cm^{-1}, with the high-frequency band being the most intense. On comparison with $K_3[Fe(CN)_6]$ (ν_{CN} = 2033 cm^{-1}) [10] the low-frequency vibration is assigned to the two equivalent cyano ligands. The high-frequency vibration is then assigned as the axial CN ligand transforming to bridging ligand. This assignment is also consistent with vibrational spectroscopic studies of similar CN-bridged complexes [17].

XPS survey in the range of binding energy from 0 to 1400 eV was conducted to determine the chemical composition of the two complexes. It was found that the complex consists of Fe, N, C, O and S elements, and the atomic concentration of these elements in the two complexes was determined based on the individual XPS spectrum of each element.[2,3] The binding energies of oxygen and nitrogen were changed due to coordination of Fe^{2+}. It was reported that the stoichiometry for metal ions and DABT was in the ratio 1:1 or 1:2. The X-ray crystal structure of the complexes had been determined [14]. According to the analytical data and structure of the complexes, the polymeric complexes were suggested as $[C_{15}H_{12}N_4O_3S_2(FeSO_4)_{0.23}]_n$ and $\{C_{15}H_{12}N_4O_3S_2[FeFe(CN)_6]_{0.2}\}_n$

The ESR spectra of the polymeric complexes, SDP–Fe^{2+} and SDP–Prussian blue, were measured at 77 K and an

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[1] SDP: yield 90%; IR (KBr, cm^{-1}): 3680–3010(broad, s), 3000–2500(broad, s), 1794(s), 1590(s), 1528(s), 1460(s), 1390(m), 1298(s), 1241(m), 1172(s), 1034(s), 873(s), 669(m); ^1H NMR (500 MHz, DMSO-d, ppm): δ 11.74(Ar-COOH, w), 8.53–8.55(broad), 7.78(Ar-OH), 7.34–7.61(aromatic ring, H), 6.92(thiazole ring, H), 4.68(NH), 1.21(CH_2); $[\eta] = 0.231$ dL g^{-1}.

[2] SDP–Fe^{2+}: yield 50%; IR (KBr, cm^{-1}): 3680–3011(broad, m), 3000–2500(broad, m), 1796(m), 1609(s), 1539(s), 1519(s), 1349(s), 1273(m), 1116(s), 1054(s), 990(s), 952(s), 873(s), 668(s), 616(s). SDP–Fe^{2+} is magnetic material and cannot be obtained right NMR resonance. $[C_{15}H_{12}N_4O_3S_2(FeSO_4)_{0.23}]_n$: Calcd C 45.56%, H 3.04%, N 14.17%, O 15.87%, Fe 3.29%; Found C 45.42%, N 14.09%, O 15.93%, S 17.91%, Fe 3.27%.

[3] SDP–Prussian blue: yield 70%; IR (KBr, cm^{-1}): 3307(broad, s), 2909(broad, s), 2073(s), 2024(m), 1794(m), 1610(s), 1540(s), 1521(s), 1349(s), 1076(s), 952(s), 873(s), 669(s). SDP–Fe^{2+}–$Fe(CN)_6$ is magnetic material, and cannot be obtained right NMR resonance. $\{C_{15}H_{12}N_4O_3S_2$-$[FeFe(CN)_6]_{0.2}\}_n$: Calcd C 46.91%, H 2.88%, N 19.44%, O 11.51%, Fe 5.32%; Found C 47.01%, 19.56%, O 11.62%, Fe 5.28%.

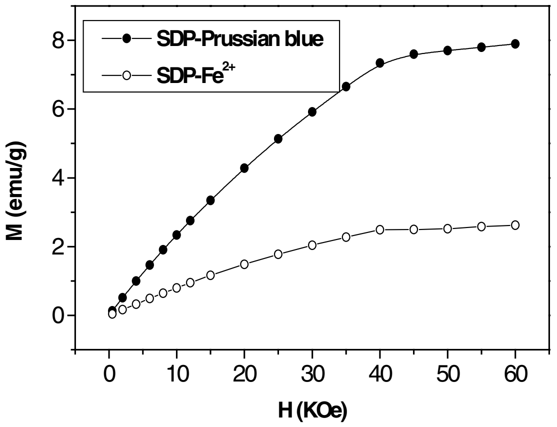

Fig. 1. Magnetization curve (*M*) versus applied field (*H*) at $T = 5$ K for polymeric complexes.

unsymmetrical line of an anisotropy *g* factor was observed. The *g* factors of the two polymeric complexes were 4.1709 and 4.2672 for SDP–Fe^{2+} and SDP–Prussian blue, respectively. All ESR spectra were very broad, implying that the large exchange region is more efficient for the present polymeric complexes. For a bulk ferromagnet, it is necessary that parallel coupling dominates on the scale of the lattice, but the orthogonality conditions are difficult to impose on all the neighbors of a given spin. In other terms, avoiding some bonding interaction between the unpaired electrons represents a big problem. If the spins are different from each other, then the nonorthogonality ions of the magnetic orbitals are not too severe a problem, because an antiparellel alignment of the spins will lead to uncompensated moments and to a weak ferromagnet [18].

A typical relationship between magnetization and applied field for the polymeric complexes at 5 K is shown in Fig. 1. For SDP–Prussian blue, *M* increases sharply until about 40 kOe and the rising trend is slow above 40 kOe. A magnetic saturation effect can be observed for the SDP–Prussian blue, it can be seen that the value of relative saturation magnetization is 7.2 emu g^{-1} for SDP–Prussian blue. This may be a ferromagnet. On the other hand, for SDP–Fe^{2+}, the magnetization increases with increasing applied field in a nearly linear manner. The SDP–Prussian blue has a higher relative saturation magnetization than the other, which might be resulting from the superexchange interaction of ferrous ions and Fe^{3+} in $[Fe(CN)_6]^{3-}$ through cyano (CN) bridging linkage. The magnetization (*M*) normalized with saturated magnetization (M_s) for SDP–Prussian blue is plotted versus the ratio of magnetic field and temperature (*H*/*T*) (Fig. 2). The M/M_s plot of SDP–Prussian blue is compared with the theoretical Brillouin cures for $J = 1/2$–$11/2$. It should be noted here that, for a disperse spin system, an "average" Brillouin function is never followed in a strict manner for monodisperse spin systems. The M/M_s plot is close to the Brillouin curves for $J = 9/2$, which indicates a ferromagnetic coupling.

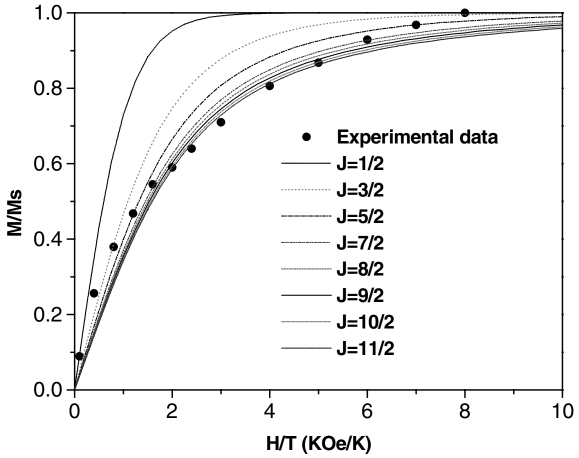

Fig. 2. Normalized plots of magnetization (M/M_s) versus the ratio of magnetic and temperature (*H*/*T*) for SDP–Prussian blue at 5 K, and the theoretical curves corresponding to the $J = 1/2$, 3/2, 5/2, 7/2, 8/2, 9/2, 10/2 and 11/2 Brillouin functions, respectively.

The temperature dependence of χT products of SDP–Prussian blue is shown in Fig. 3. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal constants. For SDP–Prussian blue, the product χT increases with decreasing temperature above 5.1 K, reaching the maximum at 5.1 K, which indicates that the weak ferromagnetic interaction among spins is realized in the solid state between 5.1 and 25 K. The results of the field dependent magnetization (Figs. 1 and 2) also confirmed the above result. The ferromagnetic interaction in SDP–Prussian blue may be due to the superexchange interaction of Fe^{2+} and Fe^{3+} in the $[Fe(CN)_6]^{3-}$ through cyano (CN) bridging linkage. The result indicates weak and short range ferromagnetic ordering for SDP–Prussian blue at low temperatures. For SDP–Fe^{2+}, the product of χT decreases sharply with lowering temperature above 10 K, then decreases gradually with decreasing temperature below 10 K, indicating a strong antiferromagnetic

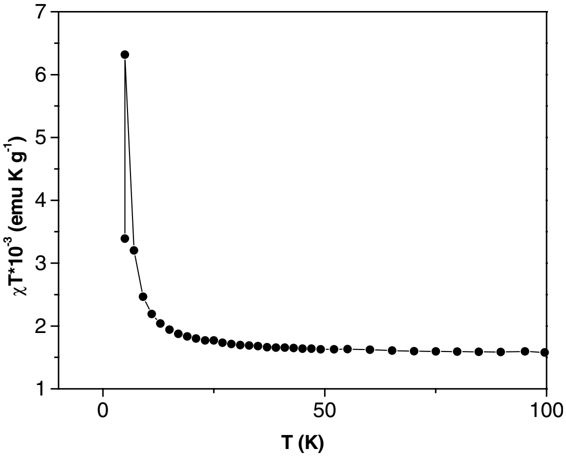

Fig. 3. Magnetic susceptibility data for SDP–Prussian blue at low field $H = 1000$ Oe.

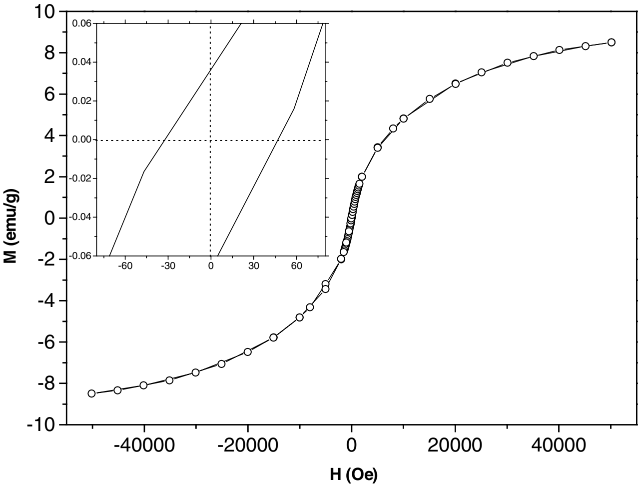

Fig. 4. Field-dependent magnetization showing a hystersis loop of SDP–Prussian blue at 5 K. (Insert) Expanded view of the region from −80 to 80 Oe.

interaction for SDP–Fe^{2+} in the solid state in the range 5–300 K.

To get complementary information on the magnetization of the SDP–Prussian blue, the hystersis curve of SDP–Prussian blue was measured at a low temperature (Fig. 4), which is a characteristic of ferromagnetic interactions. At 5 K, the observed coercive field is $H_c = 40$ Oe, and the remnant magnetization $M_r = 0.01$ *emu* g^{-1}. These data show that the polymeric complex (SDP–Prussian blue) is an organic ferromagnetic polymer. Further investigations by our group are in progress.

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