

PREPARATION AND MAGNETIC PROPERTIES OF POLY(SCHIFF BASE) COMPLEXES CONTAINING PHENANTHROLINE UNITS*

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Abstract Two poly(Schiff base)s (PDBT and PDPE) were synthesized by polycondensation of 1,10-phenanthroline-5,6-dione (PD) with 2,2'-diamino-4,4'-bithiazole (DABT) and 4,4'-diaminodiphenyl ether (DAPE), respectively. The structures of the polymers were determined by FTIR and element analysis. The metal (Fe^{2+} , Ni^{2+}) complexes were prepared from the polymers with FeSO_4 or NiSO_4 , and the metal contents of the complexes were measured by complexometric titration. The magnetic behaviors of the complexes were examined as a function of magnetic field strength at 4 K and as a function of temperature (4–300 K) at a magnetic field strength of 2.4×10^6 A/m. The results show that the relative saturation magnetization of the PDBT complexes is higher than that of the corresponding PDPE complexes, and PDBT- Ni^{2+} and PDPE- Ni^{2+} are soft ferromagnets, while PDBT- Fe^{2+} and PDPE- Fe^{2+} exhibit the features of antiferromagnet.

Keywords: Poly(Schiff base); Phenanthroline; Bithiazole; Magnetic properties.

INTRODUCTION

In recent years, there has been great interest in the magnetic properties of organic ferromagnets^[1–4]. As the organic polymeric ferromagnets have unique properties, such as various structures, low density and easy processing, they are used in many fields. For example, the light soft ferromagnetic materials are applied in magnetic-optic materials, novel absorbents of microwave, micromation of electron products, space kinetic systems and universe sail systems^[5–7].

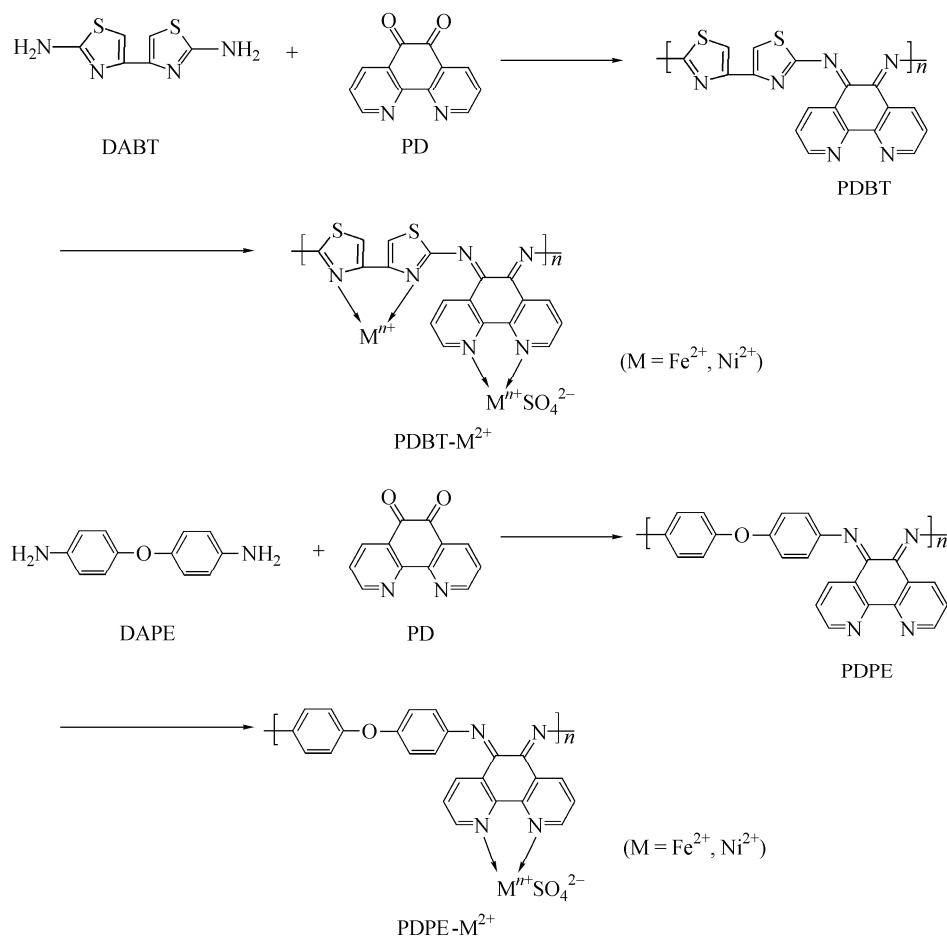
1,10-Phenanthroline and its derivatives are very important ligands in organometallic chemistry, extensively studied for the DNA cleaving activity of their copper compounds and the DNA intercalating properties of the ruthenium compounds, and they play important roles as molecular scaffolding for supramolecular assemblies^[8–11]. 1,10-Phenanthroline-5,6-dione has been widely studied because it carries an ortho-quinonoid system and can provide two diimino nitrogen atoms to form stable complexes with a variety of metal ions, the synthesis and crystal structures of the metal complexes have been extensively studied^[12–14]. It could provide two nitrogen atoms for chelating, just like the 2,2'-diamino-4,4'-bithiazole, which we reported before^[15–20].

Here, on the basis of previous work concerning synthesis and properties of polymeric complexes^[21–23], we attempt to study novel organic materials, which have better properties and multiple functions. In this paper, two poly(Schiff base)s were prepared by 2,2'-diamino-4,4'-bithiazole (DABT) and 4,4'-diaminodiphenyl ether (DAPE) with 1,10-phenanthroline-5,6-dione (PD), respectively (Scheme 1). The structures of the poly(Schiff base) were determined by IR spectroscopy and element analysis. The metal ion complexes (Fe^{2+} , Ni^{2+}) were prepared, and the contents of metal ions were measured by complexometric titration. In the structural units of the polymer, bithiazole rings and phenanthroline rings both have good coordinate ability of the bidentate N-donor sites for binding metal ions. So, they are expected to be used in electronics, optical and magnetic materials.

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Scheme 1 Synthetic routes of PDBT, PDPE and suggested structures for the corresponding metal complexes

EXPERIMENTAL

Materials

1,10-Phenanthroline-5,6-dione (PD) and 2,2'-diamino-4,4'-bithiazole (DABT) were prepared according to the literature^[24, 25], 4,4'-diaminodiphenyl ether (DAPE) was used as purchased. *N,N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) were dealt with as usual.

Synthesis of Poly(Schiff base)s (PDBT, PDPE)

A mixture of aquimolar ratio of PD and DABT (or DAPE) was heated at 90°C in the presence of DMF for 48 h. The precipitate was formed by adding methanol, then filtered, washed successively with water, methanol and acetone and dried at 60°C for 24 h in a vacuum oven. The yield is 60.7% (51.7% for PDPE).

Preparation of Polymeric Complexes

The poly(Schiff base)s' complexes were prepared by mixing aquimolar ratios of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (or $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and polymer in DMSO and stirring at 80°C for 24 h under nitrogen atmosphere. The solution was precipitated with acetone. Then it was filtered and washed with plenty of water and methanol, then dried at 60°C for 24 h in a vacuum oven. (The yields are 72.2% and 62.5% for PDBT- Fe^{2+} and PDBT- Ni^{2+} , respectively).

Measurements

Infrared spectra were taken by using KBr pellets with a Bruker FT-IR spectrometer. The contents of the metal (Fe, Ni) were obtained by complexometry^[26]. The element analysis for C, H and N was performed by using a

Flash EA112 element analyzer. The magnetic measurements were carried out by a magnetometer (PPMS-9T). The magnetization with the applied magnetic field was measured at 4 K, and the temperature dependence of the magnetization was measured from 4 K to 300 K at an applied magnetic field of 2.4×10^6 A/m.

RESULTS AND DISCUSSION

Characterization of the Polymer and Its Complexes

The polycondensation of DABT, DAPE with PD can be observed by comparing their IR spectra. For instance, the IR spectrum of PDPE, compared with that of the monomer PD and DAPE is shown in Fig. 1. As we can see, the reduction of the broad absorption in the range of $3400\text{--}3200\text{ cm}^{-1}$ of N—H stretching vibrations and the disappearance of 1685 cm^{-1} of the stretching vibration of the carboxyl C=O indicate that PDPE was obtained via polycondensation of PD with DAPE. Also, in the spectrum of PDBT (Fig. 2), the C=O bond located at 1685 cm^{-1} disappeared, and two new bonds (C=N) appeared at 1606 and 1641 cm^{-1} , which can be attributed to the C=N of the rings and in the main chain.

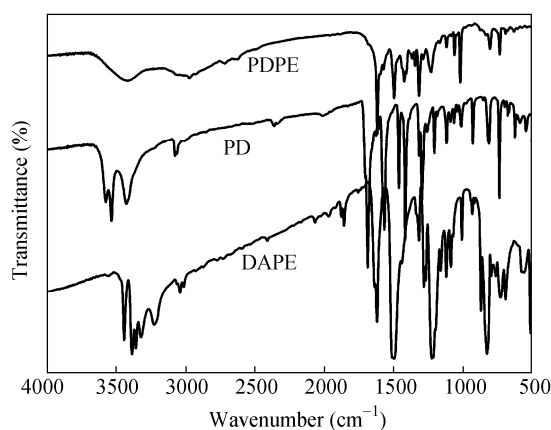


Fig. 1 FT-IR spectra of PD, DAPE and PDPE

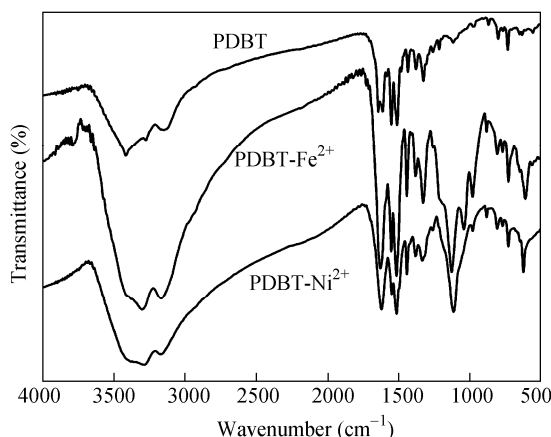


Fig. 2 FT-IR spectra of PDBT, PDBT-Fe²⁺ and PDBT-Ni²⁺

From the results of the element analysis, it is reasonable to hypothesize that the formula for PDBT is $[\text{C}_{18}\text{H}_8\text{N}_6\text{S}_2]_n$ and for PDPE is $[\text{C}_{24}\text{H}_{14}\text{N}_4\text{O}]_n$, because experimental data were well in accordance with the theoretical values (For PDBT, calcd: C 58.06%, H 2.15%, N 22.58%; Found: C 56.16%, H 2.90%, N 20.74%. For PDPE, calcd: C 76.99%, H 3.77%, N 14.96%; Found: C 77.79%, H 3.92%, N 14.81%).

With two nitrogen atoms in the phenanthroline and bithiazole rings, the polymers presented in this work can chelate various metal ions by form steady five-membered rings. The transition metal complexes were prepared as described in Scheme 1 and examined by IR spectroscopy when compared with the corresponding polymers. In the IR spectra of PDBT and its complexes (see Fig. 2), the absorption of the imine nitrogen bond (C=N) of the phenanthroline and bithiazole rings shifts from 1606 cm^{-1} to 1618 cm^{-1} and 1617 cm^{-1} for PDBT-Fe²⁺ and PDBT-Ni²⁺, respectively. While the band for C=N of the main chain moves from 1641 cm^{-1} to 1632 cm^{-1} . These show that the metal ions were coordinated with the two nitrogen atoms of the phenanthroline and bithiazole rings, which causes the bonds of the rings to need more energy to oscillate due to coordination. And as the electron clouds of the C=N bonds of the main chain flow to the phenanthroline rings, making the electron density around the C=N bonds decreased, the stretching vibration of the C=N bond of the polymer shifts to low field. The vibrations which appear at about $1120, 1033, 975\text{ cm}^{-1}$ are belong to the oscillation of SO_4^{2-} . Also for the PDPE complexes (Fig. 3), the stretching oscillation of C=N shifts from 1617 cm^{-1} to 1600 cm^{-1} and 1604 cm^{-1} for PDPE-Fe²⁺ and PDPE-Ni²⁺, respectively. The bands at $1571, 1345, 804\text{ cm}^{-1}$, which are the stretching vibrations of the phenanthroline rings, blueshift to $1585, 1366, 808\text{ cm}^{-1}$ for PDPE-Fe²⁺ and $1586, 1369, 816\text{ cm}^{-1}$ for PDPE-Ni²⁺, respectively.

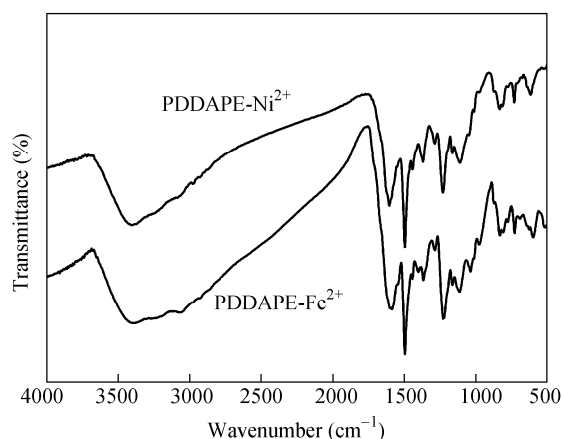


Fig. 3 FT-IR spectra of PDPE-Fe²⁺ and PDPE-Ni²⁺

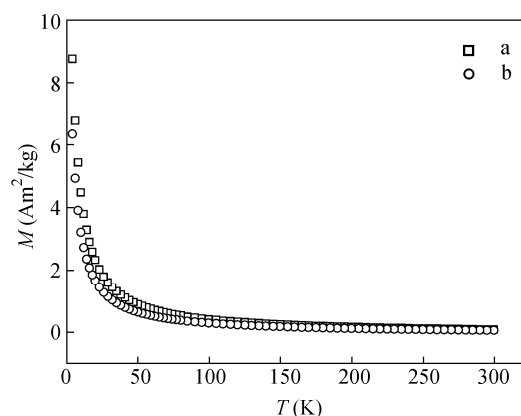


Fig. 4 Magnetization as function of temperature at an applied magnetic field of 2.4×10^6 A/m for PDBT-Ni²⁺ (a) and PDPE-Ni²⁺ (b)

Magnetic Properties

The temperature dependence of the magnetizations for PDBT-Ni²⁺ and PDPE-Ni²⁺ at an applied magnetic field of 2.4×10^6 A/m from 4 K to 300 K is shown in Fig. 4. With increasing temperature, the magnetizations of PDBT-Ni²⁺ and PDPE-Ni²⁺ decrease sharply below 25 K, and then decrease slowly till 300 K.

Figure 5 and Fig. 6 are the temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PDBT-Ni²⁺ and PDPE-Ni²⁺ at an applied magnetic field of 2.4×10^6 A/m, respectively. From these two figures, we could obtain that the magnetic susceptibility of PDBT-Ni²⁺ and PDPE-Ni²⁺ follows the Curie-Weiss relationship, $\chi = C / (T - \theta)$, in the range of 200–300 K, with the Curie-Weiss temperature $\theta = 62$ K and $\theta = 56$ K, respectively. The positive Curie-Weiss temperatures indicate that Ni complexes are ferromagnets. But for PDBT-Fe²⁺ and PDPE-Fe²⁺ (see from Fig. 7 and Fig. 8), the negative Curie-Weiss temperature ($\theta = -81$ K for PDBT-Fe²⁺ and $\theta = -49$ K for PDPE-Fe²⁺) implies the existence of anti-ferromagnetic interaction in these two complexes.

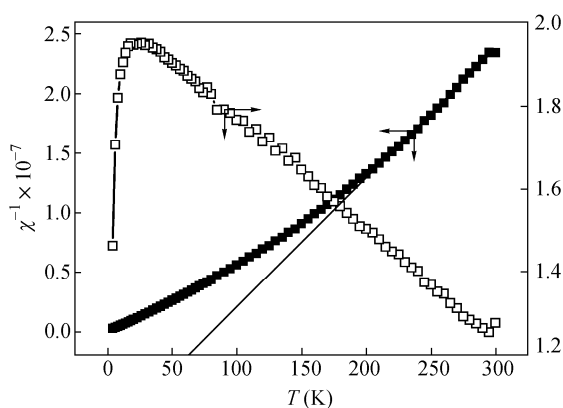


Fig. 5 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PDBT-Ni²⁺ at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 200 K and 300 K.

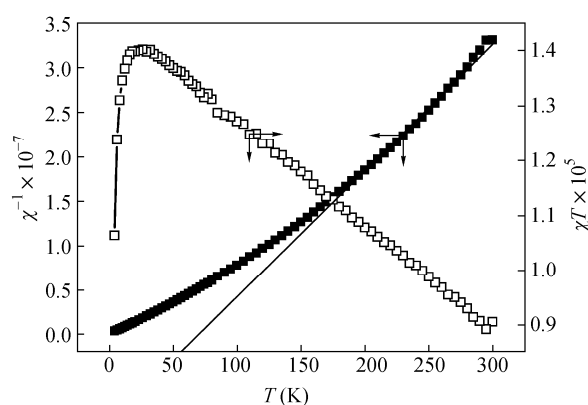


Fig. 6 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PDPE-Ni²⁺ at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 200 K and 300 K.

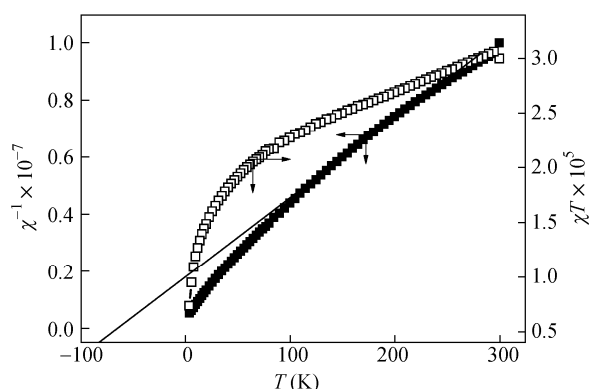


Fig. 7 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PDBT- Fe^{2+} at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 75 K and 300 K.

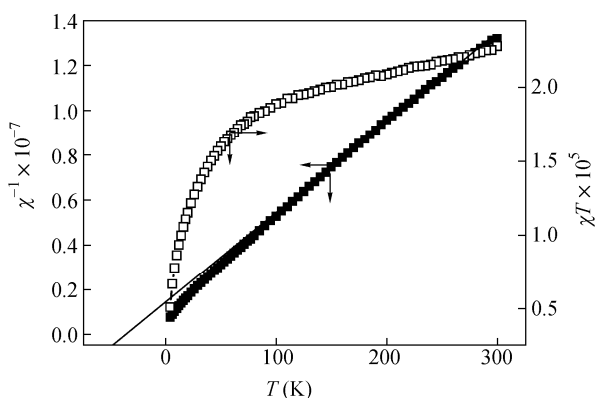


Fig. 8 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PDPE- Fe^{2+} at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 25 K and 300 K.

The magnetic hysteresis loops of PDBT- Ni^{2+} and PDPE- Ni^{2+} at 4 K are shown in Fig. 9 and Fig. 10, and the others have the similar shape. From the typical S shape and small area of hysteresis loop, it can be deduced that these four complexes are soft magnets. The magnetic properties of PDBT- Fe^{2+} , PDBT- Ni^{2+} , PDPE- Fe^{2+} and PDPE- Ni^{2+} were summarized in Table 1. The results indicate that the PDBT complexes have higher relative saturation magnetization than that of the PDPE complexes, though in ferrous complexes, the metal content is lower than that of PDPE complex. It may be attributed to the more regular structure of the conjugated polymer, which made the spin regularly arranged.

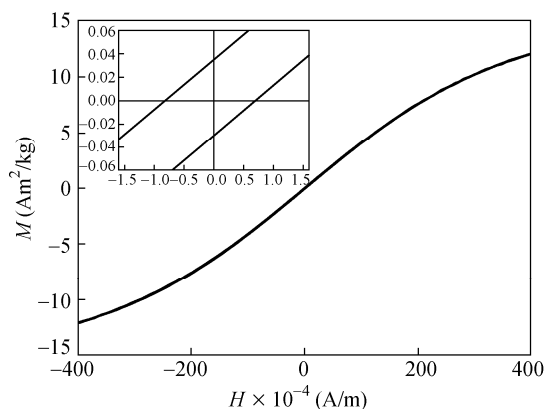


Fig. 9 Hysteresis loop (M versus H) at 4 K for PDBT- Ni^{2+} complex (Inset: expanded view of the region from -1.6×10^4 A/m to 1.6×10^4 A/m)

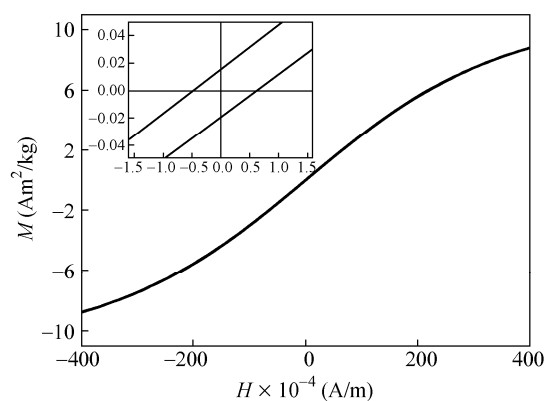


Fig. 10 Hysteresis loop (M versus H) at 4 K for PDPE- Ni^{2+} complex (Inset: expanded view of the region from -1.6×10^4 A/m to 1.6×10^4 A/m)

Table 1. Magnetic properties of PDBT- Fe^{2+} , PDBT- Ni^{2+} , PDPE- Fe^{2+} and PDPE- Ni^{2+}

	Metal content (wt%)	Relative saturation Magnetization (M_s)	θ (K)	Coercive field $\times 10^{-4}$ (A/m)	Remnant magnetization (Am^2/kg)
PDBT- Fe^{2+}	11.6	5.5	-81	2.33	0.069
PDBT- Ni^{2+}	8.7	12.1	62	0.83	0.035
PDPE- Fe^{2+}	12.6	3.8	-49	3.10	0.073
PDPE- Ni^{2+}	6.3	8.8	56	0.48	0.016

CONCLUSIONS

Two poly(Schiff base)s containing phenantroline units, and their transition metal complexes, were synthesized and characterized. The metal contents of the complexes measured by complexometry are 11.6%, 8.7% for PDBT-Fe²⁺, PDBT-Ni²⁺ and 12.6%, 6.3% for PDPE-Fe²⁺, PDPE-Ni²⁺, respectively. The magnetization of nickel complexes is almost twice as that of ferrous complexes, and PDBT-Ni²⁺ has the highest relative saturation magnetization among these complexes. The conjugated polymer PDBT gives rise to metal complexes of higher relative saturation magnetization. From the temperature and field dependence of magnetization and hysteresis loop, it can be concluded that PDBT-Ni²⁺ and PDPE-Ni²⁺ are soft ferromagnets, while PDBT-Fe²⁺ and PDPE-Fe²⁺ exhibit features of antiferromagnet.

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