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Synthesis and properties of two novel poly(Schiff base)s and their rare-earth complexes

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Abstract

Two novel poly(Schiff base)s (PPHBT and PPHPHN) were prepared by polycondensation of 2,2′-diamino-4,4′-bithiazole (DABT), 5,6-diamino-1,10-phenanthroline (DAPH) with bisdecyloxyterephthaldehyde (BDTA), respectively. The structures of the poly(Schiff base)s were determined by IR and ^{1}H NMR spectroscopy. The Nd^{3+} complexes of poly(Schiff base) were prepared and characterized. The contents of Nd for complexes were measured by complexometric titration. The magnetic behavior of the complexes was examined as a function of magnetic field strength at 4 K and as a function of temperature (4–300 K). The results show that both PPHBT-Nd^{3+} and PPHPHN-Nd^{3+} exhibit the characteristic of soft-magnetic materials at low temperature.

Keywords: Poly(Schiff base); Bithiazole; 1,10-Phenanthroline

1. Introduction

Ochinnikov first reported the organic magnets (poly(-BIPO)) in 1987 [1]. From that on, there has been much interest in the preparation of magnetic polymers. Studies of organic and polymeric magnets have made great progress in the last 2 decades due to their advantages compared with traditional magnets, such as the diversity of structures, low density, low magnetic loss, process of preparation without metallurgy at high temperature, etc. Especially the soft ferromagnet tetrabis (dimethylamino) ethylene (TDAE-C_{60}), first discovered by Wudl and his collaborators in 1991 [2], sparked a series of investigations.

Poly(Schiff base), which has many special properties, such as thermal stability, liquid crystalline properties, conductivity, and chelating effect, etc. [3–9], has been drawing the attention of researchers for more than 50 years. A variety of poly(Schiff base)s have been synthesized and characterized [10,11]. They have high thermal stability and high conducting properties due to their great number of aromatic heterocyclic rings and the conjugation over the entire molecules. Now these polymers and their derivatives have been investigated as high-performance polymers for use in ferromagnetic materials, conductors, new composite and photoelectronic materials, potential contrast agents in the magnetic resonance imaging, and so on.

In recent years, Sun et al. carried out a series of studies about the preparation of poly(Schiff base) containing bithiazole rings and their metal complexes [12,13], in which some of these complexes showed soft ferromagnetic behavior. It was found that aromatic heterocyclic polymers containing bithiazole rings are good ligands because the two nitrogen atoms in the bithiazole rings are able to chelate metal ions to form stable five-member rings [14,15]. The crystal structure of metal complexes of the monomer, 2,2′-diamino-4,4′-bithiazole (DABT), has been characterized by X-ray diffraction [16,17]. 1,10-Phenanthroline (phen) and its derivations play important roles for supramolecular assemblies because they can also provide bidentate N-donor sites for chelating with metal ions to form bridge ligands [18–20]. Except that, 5,6-diamino-1,10-phenanthroline can also be condensed with a variety of compounds with carbonyl to form additional derivatives.

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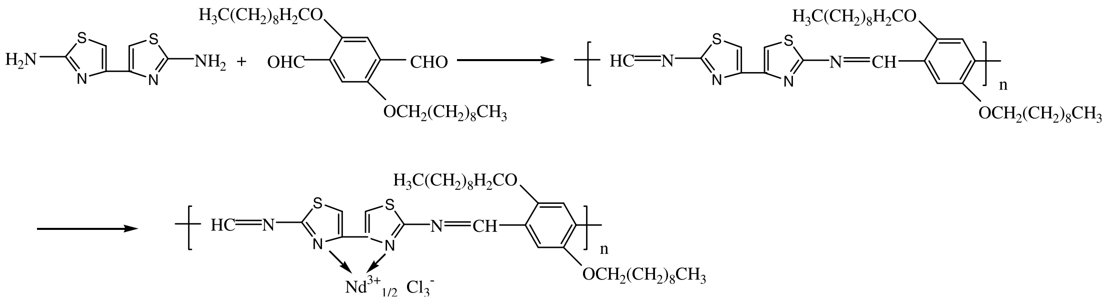


Scheme 1. Preparation of PPHBT and its Nd^{3+} complex PPHBT-Nd^{3+}.

In this paper, we will discuss the synthesis and characterization of two poly(Schiff base)s containing DABT and DAPH and their Nd^{3+} complexes for the first time (Schemes 1 and 2), and compare the magnetic properties of Nd^{3+} complexes of PPHBT and PPHPHN.

2. Experimental section

2.1. Methods

A Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer was used to record IR spectra in KBr pellets. ^1H NMR spectra were recorded on a Bruker Advance AMX-500NMR instrument in CF_3COOD-*d* with tetramethyl silane (TMS) as internal standard. The intrinsic viscosity $[\eta]$ was measured in DMF at 30 °C. The Nd content was measured by complexometric titration, and the magnetic properties of the complexes were measured with a physical properties measurement system (PPMS) magnetometer.

2.2. Materials

2,2′-Diamino-4,4′-bithiazole [21], 5,6-diamino-1,10-phenanthroline [22], and bisdecyloxyterephthaldehyde [23, 24] were prepared according to the literatures. *N*,*N*-dimethyl-formamide (DMF) was dealt with as usual.

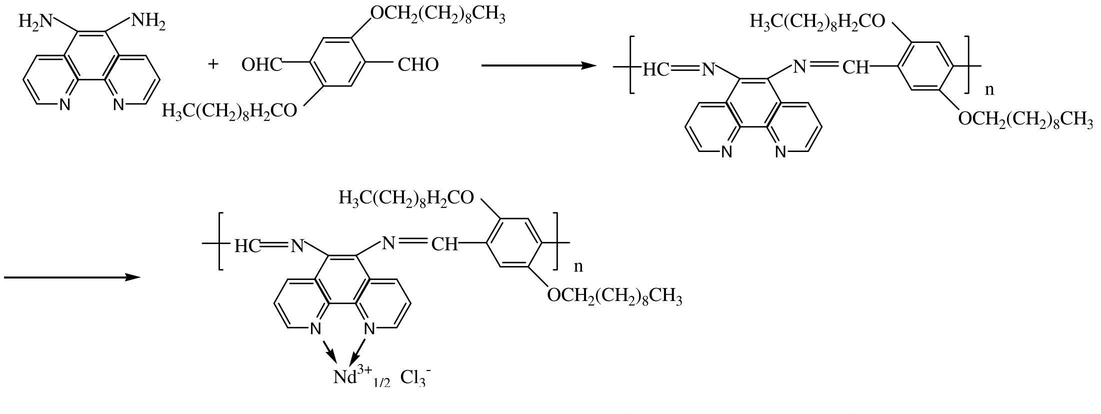
2.3. Synthesis of polymer and the complexes

An equimolar of 2,2′-diamino-4,4′-bithiazole and bisdecyloxyterephthaldehyde was dissolved in DMF to get 5% concentration. The solution was magnetically stirred and kept at 90 °C for 20 h under nitrogen atmosphere, then a black red solution was obtained. After cooling to room temperature, the solution was precipitated in water, and an orange solid was filtered, then washed with water and methanol continuously, dried at 60 °C for 24 h in the vacuum oven. The yield is 78.23%, and the intrinsic viscosity $[\eta]=0.052$ dL/g (DMF, 30 °C). IR (KBr, cm^{-1}): 3365, 2923, 2851, 1606, 1524, 1494, 1465, 1421, 1279, 1202, 1020, 719; ^1H NMR (CF_3COOD-*d*, ppm): 7.59, 7.05–7.15, 4.16, 4.00,1.2–1.9, 0.9.

$NdCl_3\cdot 6H_2O$ and PPHBT (molar ratio 2:1) were dissolved in DMF to get 5% concentration and stirred at 90 °C for 24 h under nitrogen atmosphere. The resulting black red solution was precipitated in water, and then a red–brown solid of PPHBT-Nd^{3+} was obtained. The precipitate was filtered and washed with water till the Nd^{3+} was removed, and then dried at 60 °C for 24 h in the vacuum oven. The yield is 64.34%. IR (KBr, cm^{-1}): 3363, 2923, 2852, 1609, 1524, 1465, 1420, 1306, 1261, 1202, 1021, 801, 720.

PPHPHN and its Nd^{3+} complexes were prepared just as that of PPHBT. The intrinsic viscosity $[\eta]=0.069$ dL/g (DMF, 30 °C) for PPHPHN.

PPHPHN: IR (KBr, cm^{-1}): 3399, 2923, 2852, 1677, 1608, 1562, 1458, 1427, 1393, 1357, 1285, 1207, 1021, 803,



Scheme 2. Preparation of PPHPHN and its Nd^{3+} complex PPHPHN-Nd^{3+}.

740. ^{1}H NMR (CF_3COOD-*d*, ppm): 9.59, 9.40, 8.42, 8.15, 4.99, 4.26, 1.2–2.1, 0.9.

PPHPHN-Nd^{3+}: IR (KBr, cm^{-1}): 3398, 2923, 2852, 1677, 1610, 1562, 1460, 1427, 1395, 1359, 1287, 1261, 1207, 1023, 803, 739.

3. Results and discussions

3.1. Characterization of the poly(Schiff base)s

The structures of poly(Schiff base)s were determined by IR and ^{1}H NMR spectroscopy. Fig. 1 shows the IR spectra of DABT, BDTA and PPHBT. The stretching vibration of the new bond C=N appeared at about 1606 cm^{-1} for PPHBT. Compared with DABT and PPHBT, the very strong absorption at 1597 cm^{-1} of the N–H bending vibration in the IR spectra of DABT was disappeared in the that of PPHBT, and the $-NH_2$ stretching vibrations of DABT in the range of 3127–3447 cm^{-1} and the C=O vibration of BDTA at 1681 cm^{-1} were almost disappeared, too. While the 1202 cm^{-1} for C–O vibrations of aromatic ether and 1020 cm^{-1} for aliphatic ether were appeared. The ^{1}H NMR of the PPHBT was examined in CF_3COOD (Fig. 2), as we can see, the resonance of the bithiazole protons and the aryl protons occur at 7.05–7.15 and 7.59 ppm, respectively. And the resonance of $-OCH_2-$ protons occurs at 4.16 ppm.

The comparison of the IR spectra of DAPH and PPHPHN were shown in Fig. 3.

Also, the strong absorption at 1654 cm^{-1} of the N–H bending vibrations in the IR of DAPH was disappeared in that of PPHPHN, and the alkyl absorption in the BDTA also appeared in the spectra of PPHPHN at 2923 and 2852 cm^{-1}. In the ^{1}H NMR spectrum of PPHPHN (Fig. 4), as expected, the resonance of the bithiazole protons occurs at 8.15 ppm. The peaks at 8.42, 9.40, 9.59 ppm are assigned to the different positional protons of DAPH, and the 4.99 ppm represents the resonance of $-OCH_2-$ protons.

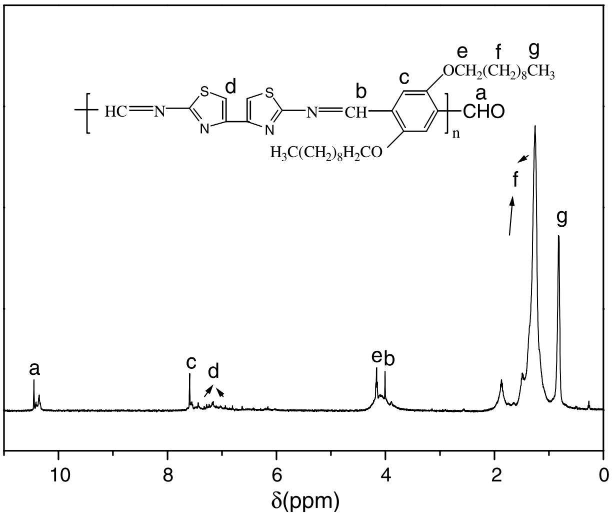


Fig. 2. ^{1}H NMR spectrum of PPHBT.

3.2. Characterization of Nd^{3+} complexes of poly(Schiff base)s

With two nitrogen atoms in both the bithiazole rings and phenanthroline, the polymers studied in this work can chelate various metal ions by forming steady five-member rings. The Nd^{3+} complexes of poly(Schiff base)s were synthesized in Section 2, and Fig. 5 shows the IR spectra of PPHBT-Nd^{3+} and PPHPHN-Nd^{3+}. In comparison with PPHBT, some changes were observed in the IR spectrum of PPHBT-Nd^{3+}, e.g. the blue shift of absorption bands at 1606, 1279 cm^{-1} of PPHBT to 1609, 1306 $cm^{-1}$of PPHBT-Nd^{3+}. This indicates the coordination between the nitrogen atoms of bithiazole rings and the incorporated Nd^{3+}, because the skeletal vibrations of bithiazole rings need higher energy to oscillate due to coordination, and a broad peak at about 3500–3200 cm^{-1} of PPHPHN-Nd^{3+} may also be an evidence of chelation. Similar changes can be observed when compared the IR spectrum of PPHPHN-

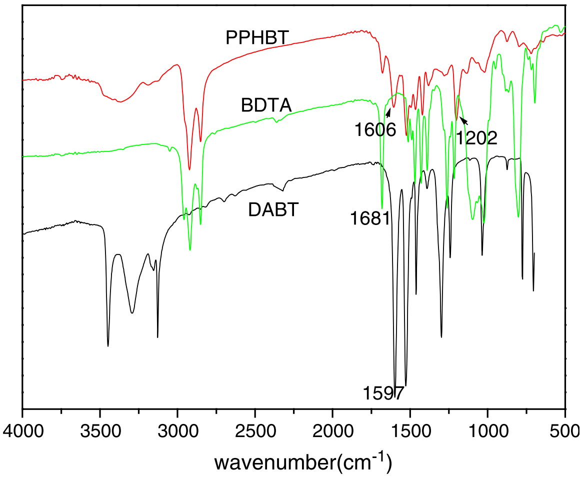


Fig. 1. IR spectra of DABT, BDTA and PPHBT.

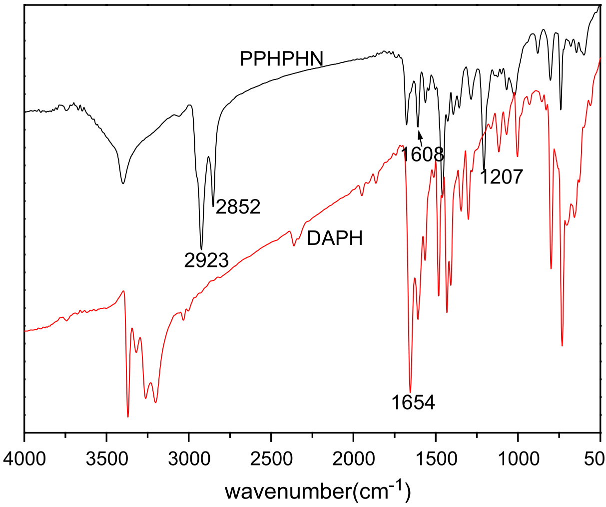


Fig. 3. IR spectra of DAPH and PPHPHN.

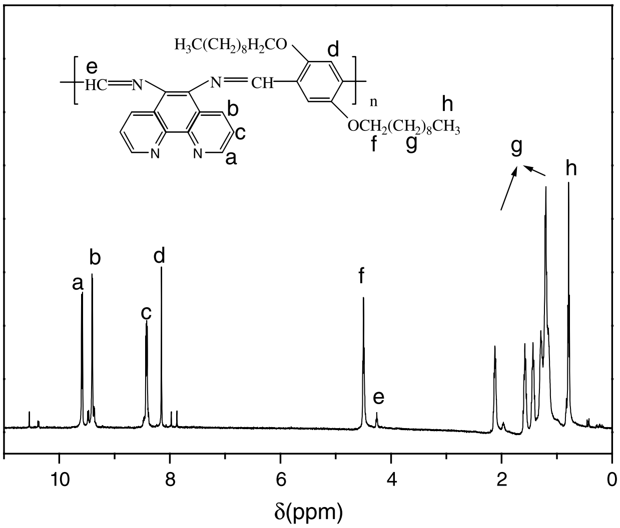


Fig. 4. ^{1}H NMR spectrum of PPHPHN.

Nd^{3+} with that of PPHPHN. The evident changes were the bands at 1608, 1458, 1357 and 1069 cm^{-1} of PPHPHN blue-shifted to 1610, 1460, 1359 and 1098 cm^{-1} of its Nd complex. The Nd contents are measured by complexometry, and are about 3.95, 3.09% for PPHBT-Nd^{3+} and PPHPHN-Nd^{3+}, respectively.

3.3. Magnetic properties of the poly(Schiff base)s complexes

The curves of magnetization (*M*) versus the applied magnetic field (*H*) at 4 K for PPHBT-Nd^{3+} and PPHPHN-Nd^{3+} are shown in Fig. 6. For PPHBT-Nd^{3+}, magnetization increases sharply below 20 kOe. The rising trend slows down above 20 kOe, and then the magnetization nearly approaches saturation at about 40 kOe for PPHBT-Nd^{3+}. This is a typical characteristic of a ferromagnet. The value of relative saturation magnetization is about 0.1 emu/g for PPHBT-Nd^{3+}. For PPHPHN-Nd^{3+}, the magnetization increases sharply below 30 kOe, but rises slowly above 30 kOe. It indicates that PPHPHN-Nd^{3+} is a special ferromagnet, which still exhibits some characteristic of paramagnetism.

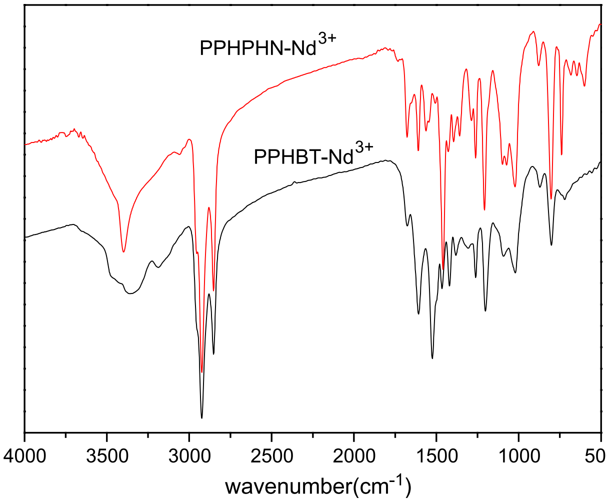


Fig. 5. IR spectra of PPHBT-Nd^{3+} and PPHPHN-Nd^{3+}.

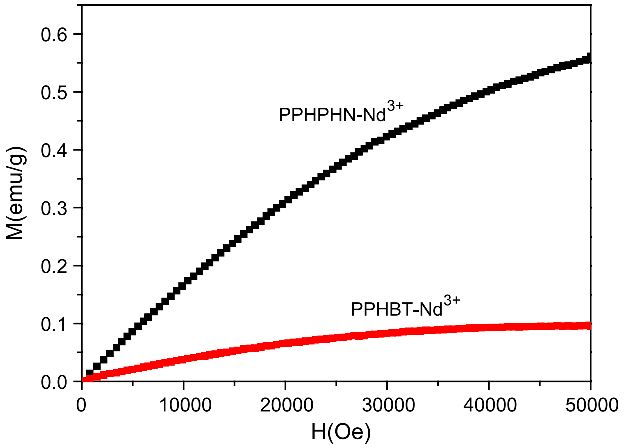


Fig. 6. Magnetization (*M*) versus applied field (*H*) at 4 K for the complexes PPHBT-Nd^{3+} and PPHPHN-Nd^{3+}.

Fig. 7 shows the temperature dependence of the magnetization of PPHBT-Nd^{3+} and PPHPHN-Nd^{3+} at an applied magnetic field of 30 kOe from 4 to 300 K. The magnetization decreased sharply as the temperature increasing when the temperature is below 25 K and then decreased slowly till 300 K.

The temperature dependence of the reciprocal of magnetic susceptibility (χ^{-1}) and χT products of PPHPHN-Nd^{3+} were measured as shown in Fig. 8. The values of χT monotonically increases with a decreasing temperature above 65 K, below 65 K, an abrupt increase in the slope of χT is observed and also a decrease of χT with the same trend of temperature. This suggests that the system approaches a magnetic phase transition at 65 K. The result indicates that the polymeric complex may be three dimensionally at 65 K. It can be seen in Fig. 8 that the

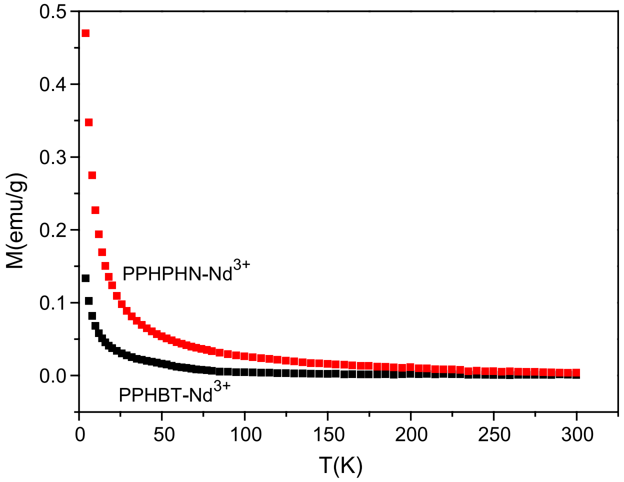


Fig. 7. Temperature dependence of magnetization for PPHBT-Nd^{3+} and PPHPHN-Nd^{3+} at $H=30$ kOe.

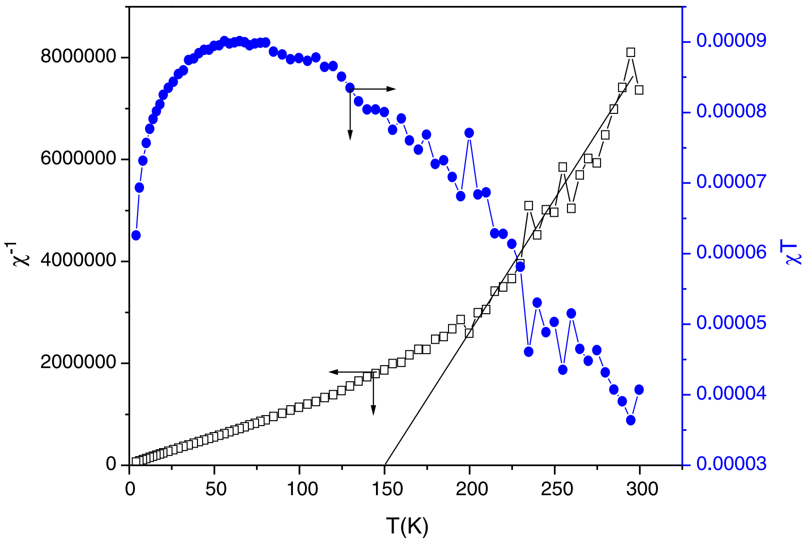


Fig. 8. Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PPHPHN-Nd^{3+} at an applied field magnetic filed of 30 kOe. The straight line is a fit to the Curie–Weiss law between 200 and 300 K.

magnetic susceptibility of PPHPHN-Nd^{3+} follows the Curie–Weiss relationship, $\chi = C/(T-\theta)$, in the range of $200-300$ K, with the Curie–Weiss temperature $\theta = 150$ K. The positive Curie–Weiss temperature indicates that PPHPHN-Nd^{3+} is a ferromagnet. However, in the low temperature stage, the relationship between the temperature and the reciprocal of magnetic susceptibility is not accord with Curie–Weiss relationship, this suggests that there are strong ferromagnetic coupling. The temperature dependence of the reciprocal of magnetic susceptibility (χ^{-1}) and χT products of PPHBT-Nd^{3+} are similar with those of PPHPHN-Nd^{3+}, and the Curie–Weiss temperature $\theta =$ 80 K.

Field dependence hysteresis loops of PPHBT-Nd^{3+} and PPHPHN-Nd^{3+} were generated at 4 K (Figs. 9 and 10), which is a characteristic of ferromagnetic interactions. At 4 K, the observed coercive fields are 100, 83 Oe, and the remnant magnetizations are 0.001, 0.002 emu/g for PPHBT-Nd^{3+} and PPHPHN-Nd^{3+}, respectively. The data show that the polymeric complexes are organic ferromagnetic polymers. Further investigations by our group are in progress.

4. Conclusion

Two poly(Sciff base)s containing bithiazole and phenanthroline and their complexes were synthesized and characterized in this paper. The Nd contents of the two complexes were also measured by complexometry, which are 3.95, 3.09% for PPHBT-Nd^{3+} and PPHPHN-Nd^{3+}, respectively. And the magnetic properties of the polymeric complexes were studied. The magnetization of PPHPHN-Nd^{3+} is almost as six times as that of PPHBT-Nd^{3+} at 4 K. There was a magnetic phrase transition at 65 K in the curve

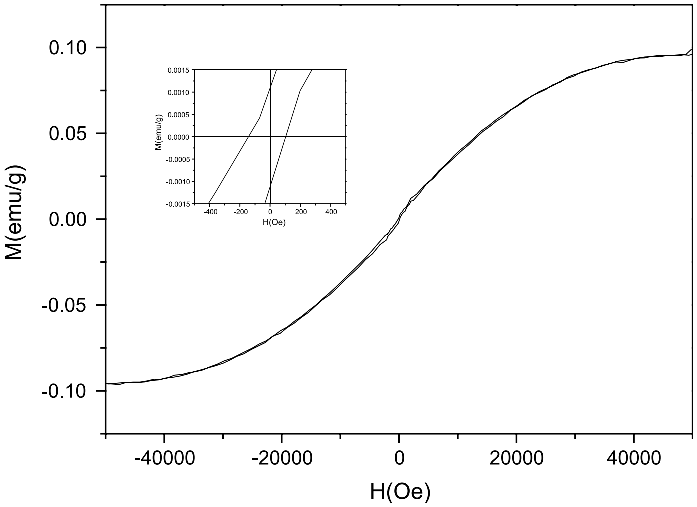


Fig. 9. Hysteresis loop (M versus H) at 4 K for PPHBT-Nd^{3+} complex. (insert) Expanded view of the region from -500 to 500 Oe.

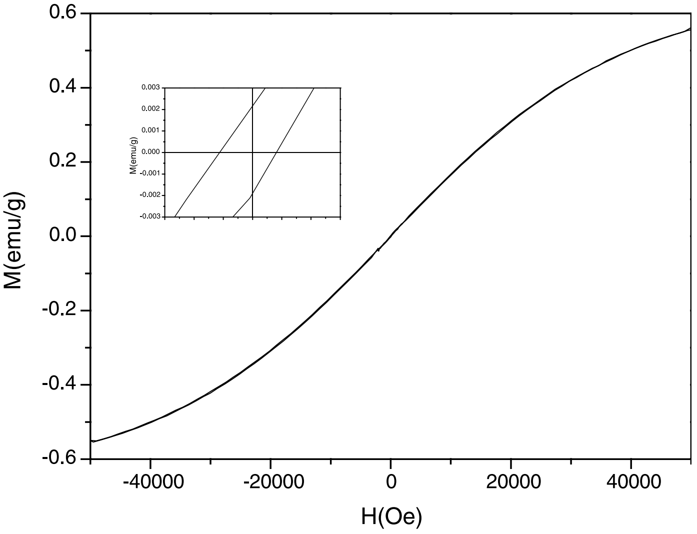


Fig. 10. Hysteresis loop (*M* versus *H*) at 4 K for PPHPHN-Nd^{3+} complex. (insert) Expanded view of the region from −300 to 300 Oe.

of temperature dependence of χT products for PPHPHN-Nd^{3+}, and the Curie–Weiss temperature for PPHPHN-Nd^{3+} is about 150 K. This suggests that when the temperature is below 150 K, PPHPHN-Nd^{3+} complex is a ferromagnet. The same phenomenon was also discovered in the PPHBT-Nd^{3+}, and the Curie–Weiss temperature is about 80 K. Seen from the field dependence hysteresis loops of PPHBT-Nd^{3+} and PPHPHN-Nd^{3+}, both complexes exhibited the characteristic of soft-magnetic materials at low temperature.

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