

A novel hyperbranched aromatic polyamide containing bithiazole: Synthesis, metal complexation and magnetic properties

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Based on the polycondensation of bifunctional 2,2'-diamino-4, 4'-bithiazole(DABT) and trifunctional 1,3,5-benzenetricarbonyl trichloride (BTC), a novel hyperbranched aromatic polyamide PBD was synthesized with excellent solubility and good thermal stability. The structure of the polymer was confirmed by FT-IR and ^1H NMR spectrum. The calculated degree of branching of our product was 52%. By exploring the influence of several different solvent systems, the yield of the polymer increased in the solvent system of DMAc/LiCl. Two kinds of metal complexes were obtained by chelation of the polyamide with Cu^{2+} and Ni^{2+} , and the metal contents of the complexes were determined by complexometric titration. The magnetic behaviors of the complexes were examined as a function of magnetic field strength at 5 K, and as a function of temperature (5–300 K) at a magnetic field strength of 2.4×10^6 A/m. The results indicated that the complexes were soft ferromagnetic materials with Curie-Weiss temperature at 102 K and 53 K, respectively.

hyperbranched aromatic polyamide, synthesis, magnetic properties

1 Introduction

As early in 1968, Mataga [1] suggested that bonding spin-bearing centers together to create a conjugated polymer could obtain organic ferromagnets.

Years later, numerous researches concerning purely organic magnets were reported. In 1987, Ovchinnikov [2] outlined that such unstable molecules were totally improper 'building blocks' for a ferromagnetic polymer in reality. Various methods had been proposed to overcome the problem but most of them were illustrated at the expense of much reduced exchange interaction. Cao *et al.* [3] successfully repeated the Ovchinnikov's experiment and observed the ferromagnetic hysteresis loop. Itoh and Iwamura *et al.* [4] prepared one of the oligomers as a model for this type of molecular magnet, which achieved a strong exchange inter-

action among the spin bearing centers without high thermal and chemical stability. Allison *et al.* [5] found a possible way to achieve higher thermal stability without losing the essential robust high-spin nature of these systems by 'strain protection'. Busby and Kai *et al.* [6] obtained new high-spin polymers by oxidative doping of networked polyarylamines and showing ferromagnetic coupling in 1996. However, this area is still in its infancy and at present, it is a real challenge to create a molecular ferromagnet with a reasonably high θ . Therefore, extensive studies on organic magnetic materials mostly turn to coordination compounds, which provide a wealth of stable high-spin units. The new compounds that coordinated with transition metals or rare earth metals exhibited better electronic, optical and magnetic properties than the purely organic precursors [7].

In our previous work, a novel polymer (SDP) containing the bithiazole ring was synthesized, and SDP-Prussian blue was prepared from SDP- Fe^{2+} and potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$) by Weng *et al.* [8]. The coordination com-

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pound exhibits a hysteresis cycle at 5 K. In 2003, Tang *et al.* [9] described a new kind of p-conjugated poly(thiazole-2,4-diyl) (PTz) and its complexes incorporating lanthanide ions in the main chain (PTz-Nd³⁺, PTz-Gd³⁺) for the first time. They have Curie – Weiss temperatures of 254 and 28 K, respectively. Two novel fully conjugated polymers containing bithiazole rings were firstly synthesized by Zhou *et al.* [10]. Their lanthanide metal complexes exhibit features of soft ferromagnet. Lin *et al.* [11] obtained two kinds of supramolecular polymeric complexes poly(acrylic acid), and transition metal ions via electrostatic interactions of 2,2'-diamino-4,4'-bithiazole, which showed a special magnetic property.

During the past decade, great attention has been paid to the hyperbranched polymers. Due to their unique chemical and physical properties such as low viscosity, various structures, multifunctional groups and easy processing, they were expected to be potential electronic, optical and magnetic materials in practice [12]. In this work, we tried to explore a novel hyperbranched polymeric magnet with excellent solubility and good thermal stability based on the previous work of our group [10, 13, 14].

2 Experimental section

2.1 Materials

2,2'-diamino-4,4'-bithiazole(DABT) and 1,3,5-benzene tricarbonyl trichloride (BTC) were prepared by ourselves. Anhydrous Lithium chloride was heated with Ammonium chloride at 300 °C under vacuum for 12 h. *N,N'*-dimethylacetamide (DMAc) was shaken with BaO for several days, and refluxed with BaO for 1 h, then fractionally distilled under reduced pressure, and stored over molecular sieves. Dimethyl sulfoxide (DMSO) was refluxed for 4 h over CaO, and dried over CaH₂, then fractionally distilled at low pressure. Triethylamine (TEA) was dried with CaSO₄, and then distilled with P₂O₅ under nitrogen. Methanol was used as purchased.

2.2 Measurements

FT-IR spectra were used to record in the range of 4000–400 cm⁻¹ on a Bruker FT-IR spectrometer using KBr pellets. The content of the metal was determined by complexometry [15]. The viscosity was measured by Ubbelohde viscometer. TGA was performed on a Perkin-Elmer TGA7 instrument in flowing N₂ with a heating rate 10 K/min. Bruker Advance DMX400 obtained ¹H NMR spectrum. UV-vis spectra were collected by UV-1601 UV-vis spectrophotometer. The magnetic measurements were carried out by a magnetometer (PPMS-9T). The magnetization with the applied magnetic field was measured at 5 K, and the temperature dependence of the magnetization was measured from 5 K to 300 K at an

applied magnetic field of 2.4 × 10⁶ A/m.

2.3 Synthesis of hyperbranched aromatic polyamide containing bithiazole (PBD)

A 250 mL three-necked flask equipped with a magnetic stir bar was added 80 mL of freshly distilled DMAc and anhydrous Lithium chloride (1.0 g), then BTC (1.99 g, 0.0075 mol) was dissolved in the mixed solution. The reaction flask cooled in an ice pool for 0.5 h. DABT (1.4175 g, 0.0075 mol) and TEA (1.52 g, 0.015 mol) were added to the three-necked flask, and a heterogeneous solution was obtained. After two hours, the ice pool was moved away, and then let the heterogeneous solution be reacted for another six hours at room temperature. A homogeneous yellow solution was obtained at last. Methanol (20 mL) was subsequently added to quench the residual acid chloride, and the heterogeneous solution was stirred for 30 min, and then filtered. The yellow product was solved in DMAc, then precipitated into methanol, and repeated the operation twice. At last the product was washed twice with basic water, acidic water, and deionized water then precipitated into methanol, filtered and dried at 40 °C in a vacuum oven for 24 h. The route of polymers' synthesis is shown in Figure 1.

2.4 Preparation of polymeric complexes

The PBDs' complexes were prepared by mixing equimolar ratios of CuSO₄ (or NiSO₄) and the polymer in DMSO and stirred at 80 °C for a week under nitrogen atmosphere. The solution was precipitated with water, and then filtered and washed with plenty of deionized water, It was confirmed that there were no rudimental SO₄²⁻ by using the solution of BaCl₂, and dried at 60 °C for 24 h in a vacuum oven. The yields were 64.3% and 68.5% for PBD-4-Cu²⁺ and PBD-4-Ni²⁺, respectively.

3 Results and discussion

3.1 Synthesis of complexes

Polymerization of the monomers A₂ and B₃ generally could result in branching, cross-linking and cyclization reactions. When three-dimensional structure was developed, the product became a gel, which was insoluble in any organic solvents. However, Jikei *et al.* [15] and Lin *et al.* [16] obtained soluble hyperbranched polymers by controlling the polycondensation conditions. According to their studies, we also successfully prepared soluble polymers. During the course of polycondensation, some low molecular weight products or oligomers were obtained, and the yields were no more than 30% by using various organic solvents such as THF, DMAc, and NMP. With the presence of LiCl in the DMAc, the yield was increased more than 98%, and the

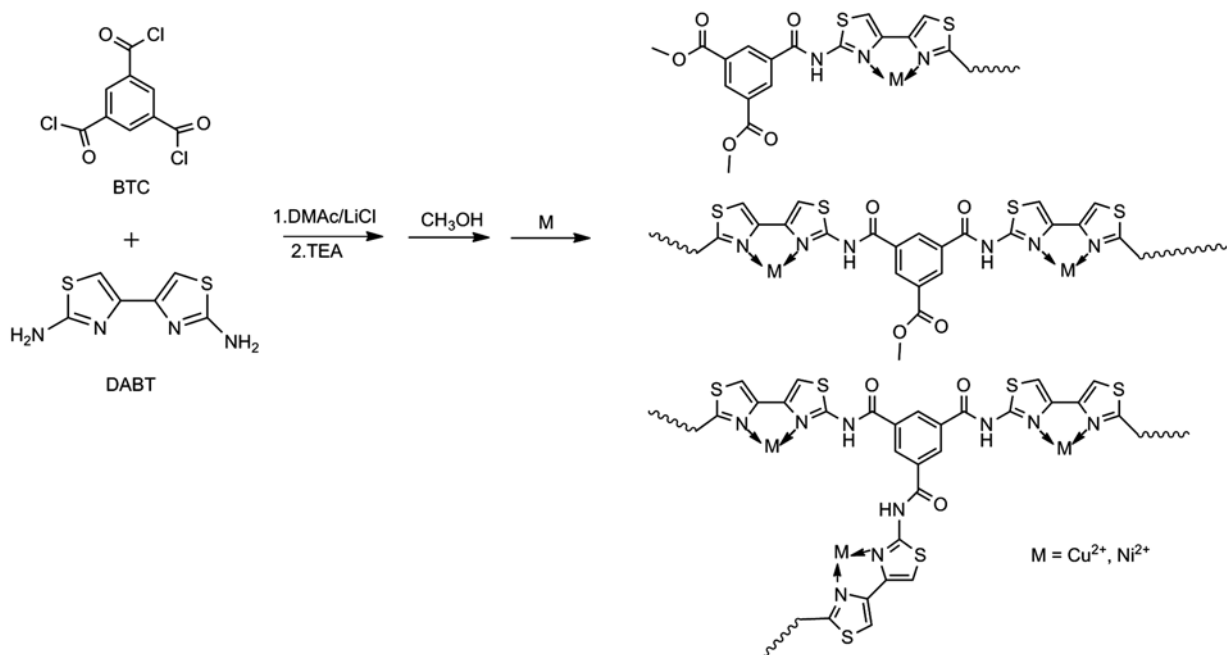


Figure 1 The route of polymers' synthesis and preparation of complexation.

viscosity was reached up to 0.42 (see Table 1). It was obviously the mixed solvent system of DMAc and LiCl that facilitated the polyamide to be easily dissolved in DMAc.

Benefiting from the hyperbranched structure, the complexes could still be dissolved in polar solvents like DMSO, DMAc, NMP and so forth (see Table 2), which was different from previous complexes synthesized in our group. We also tried to investigate the properties of the product in the form of thin film, but failed because of the weakness of the

Table 1 Polycondensation of BTC and DABT in the presence of condensation agents

PBDs	Solvent	Vs (mL)	TEA (mL)	RT (h)	η	Yield (%)
PBD-1	THF	80	1	10	0.08	22
PBD-2	DMAc	80	1	10	0.14	35
PBD-3	NMP	80	1	10	0.17	33
PBD-4	DMAc/LiCl	80	1	8	0.42	98

Table 2 The test of PBDs' solubility in various polar solvents

PBDs	DMF	DMSO	DMAc	NMP
PBD-1	+	+	+	+
PBD-2	±	+	+	+
PBD-3	±	+	+	+
PBD-4	±	+	+	+
PBD-4-M	-	+	+	+

±: Swell; +: soluble; -: not soluble; M = Cu²⁺ or Ni²⁺.

molecular entangle of the polymer. Figure 2 showed the UV–visible absorption spectra of PBD-4 and metal complexes measured in DMSO solution, PBD-4 exhibited two peaks of absorption at 265 and 335 nm, due to the vibration of benzene ring and bithiazole ring, respectively. Compared with PBD-4, the second peak absorption of the PBD-4-Ni²⁺ red shifted to 348 nm, while the one for PBD-4-Cu²⁺, red shifted to 355 nm. One entirely possible explanation is the different coordination structures in the complexes lead to distinct spectra.

The polycondensation of DABT and BTC was characterized by the IR spectra and ¹H NMR spectrum. As shown in Figure 3, the N–H stretching vibration generated the broad absorption at 3403 cm⁻¹, and the corresponding bend vibration produced the peak absorption at 1545 cm⁻¹. The peak at 1667 cm⁻¹ induced by the stretching vibration of the

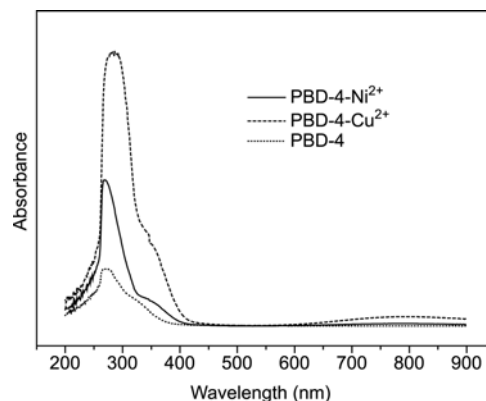


Figure 2 UV-vis absorption spectra of PBD-4 and its complexes.

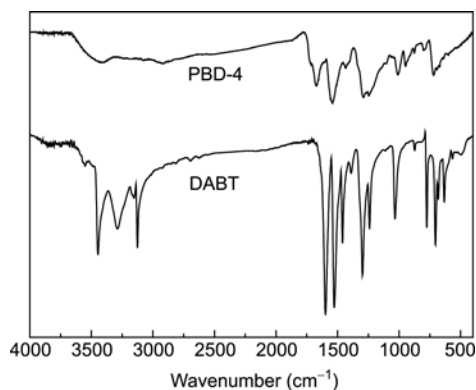


Figure 3 FT-IR spectra of PBD-4 and DABT.

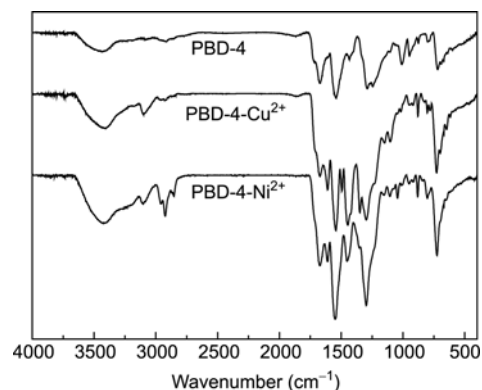


Figure 4 FT-IR spectra of PBD-4, PBD-4-Cu²⁺ and PBD-4-Ni²⁺.

carboxyl C=O indicated the reaction between the group of $-\text{COCl}$ and $-\text{NH}_2$.

With two nitrogen atoms in the bithiazole rings, the polymer presented in this work can chelate with various metal ions by forming steady five-membered ring. The transition metal complexes were prepared as described in Figure 1. In the IR spectra of PBD and its complexes (see Figure 4), the absorption of the imine's nitrogen bond (C=N) of the bithiazole rings was at 1610 cm^{-1} for PBD-4-Cu²⁺ and PBD-4-Ni²⁺, while it didn't appear in the IR spectra of PBD-4. In addition, the stretching vibration peak of the imine's nitrogen bond (C=N) of three compounds was at 1436 , 1440 and 1445 cm^{-1} , respectively. These phenomena showed that the metal ions were coordinated with the two nitrogen atoms of bithiazole rings, which led the bonds of

the rings to require more energy to oscillate. The vibrations absorptions appeared at about 1110 cm^{-1} and 1033 cm^{-1} were belonging to the oscillation of SO_4^{2-} .

The stoichiometric ratio of A groups (amines) to B groups (acid chlorides) was 2:3, and various reagents were used to react with the remaining acid chlorides for the introduction of peripheral functionality. One method to produce peripheral carboxylic acid functionalities (PBD) is quenching the terminal acid chlorides with methanol in the presence of triethylamine, which acted as an acid scavenger. However, ¹H NMR spectrum (Figure 5) revealed a large amount of residual TEA-based ammonium salt still existed even after the polymer was extensively washed by aqueous solutions at various pH values. Methanol was used to consume terminal acid chloride groups in the hyperbranched

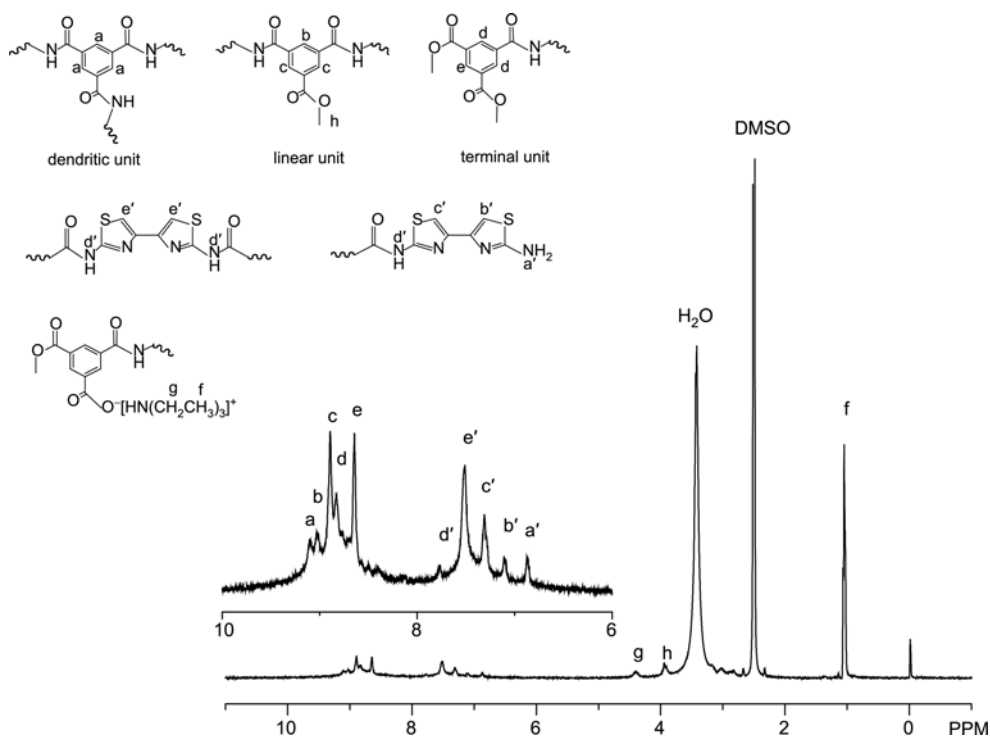


Figure 5 ¹H NMR spectrum of PBD-4.

polyamides. Meanwhile, ^1H NMR spectrum (Figure 5) confirmed the presence of methyl ester terminal groups in addition and minor levels (1 mol%–2 mol%) of residual TEA salts.

The ^1H NMR spectrum of hyperbranched polyamides showed that the resonances from the hydrogens in the *D*, *L* and *T* units had different shifts due to the difference in their chemical environments (Figure 5). To better define the chemical structures of hyperbranched polymers, Fréchet and co-workers quantified the degree of branching (DB) using eq. 1 [17, 18]:

$$\text{DB} = (D+T)/(D+T+L) \quad (1)$$

where *D*, *T*, and *L* refer to the numbers of dendritic, terminal, and linear units in the hyperbranched polymers, respectively. Based on the relative percentages of those units, the calculated DBs ranged between 45% and 55%. According to the equation, the calculated DB of our product was 52%.

However, the hyperbranched polyamide exhibited excellent thermal stability, and 5% weight loss was observed before the onset of polymer degradation (293 °C, Figure 6). The improved thermal stability was ascribed to the lack of the reactive terminal groups (only methyl esters), which excluded the continued polycondensation at high temperatures. As a result, the novel hyperbranched polyamide might be more easily processed than others.

3.2 Magnetic properties

The temperature dependence of the magnetizations for PBD-4- Cu^{2+} and PBD-4- Ni^{2+} at an applied magnetic field of 2.4×10^6 A/m from 5 K to 300 K was shown in Figure 7. As increasing temperature, the magnetizations of PBD-4- Cu^{2+} and PBD-4- Ni^{2+} decreased sharply below 50 K, and then decreased slowly till 300 K. Figures 8 and 9 were the temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PBD-4- Cu^{2+} and PBD-4- Ni^{2+} 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 PBD-4- Cu^{2+} and PBD-4- Ni^{2+} followed the Curie-Weiss relationship, $\chi = C/(T-\theta)$, in the range of 225–300 K, with

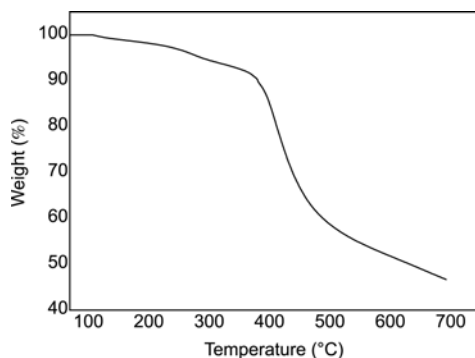


Figure 6 Thermogravimetric analysis of a methyl-terminated PBD-4.

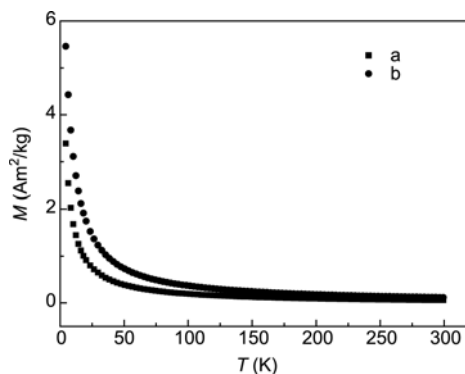


Figure 7 Magnetization as a function of temperature at an applied magnetic field of 2.4×10^6 A/m for PBD-4- Cu^{2+} (a) and PBD-4- Ni^{2+} (b).

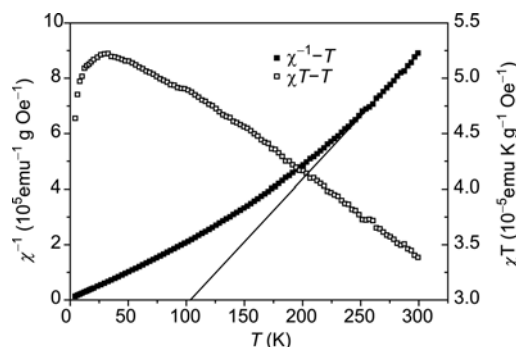


Figure 8 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PBD-4- Cu^{2+} at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 225 K and 300 K.

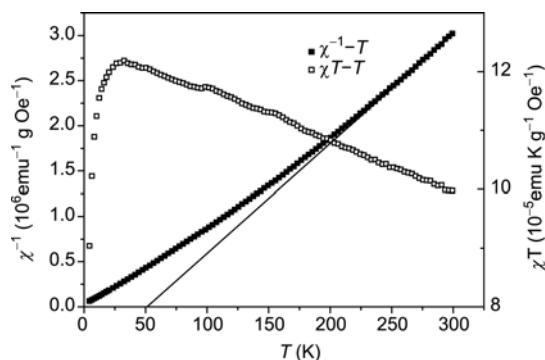


Figure 9 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PBD-4- Ni^{2+} at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 225 K and 300 K.

the Curie-Weiss temperature $\theta = 102$ K and $\theta = 53$ K, respectively. The positive Curie-Weiss temperature indicated that both complexes were ferromagnets.

The magnetic hysteresis loops of PBD-4- Cu^{2+} and PBD-4- Ni^{2+} at 5 K were shown in Figures 10 and 11, and they had the similar shape. From the similar “S” shape and small area of hysteresis loop, it can be deduced that these two complexes are soft magnets. The magnetic properties of PBD-4- Cu^{2+} and PBD-4- Ni^{2+} were summarized in Table 3. Compared with the bithiazole-based complexes in the previous report,

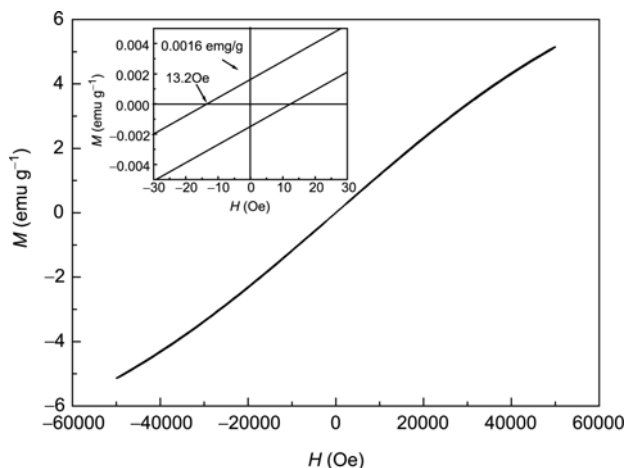


Figure 10 Hysteresis loop (M versus H) at 5 K for the PBD-4- Cu^{2+} complex (Inset: expanded view of the region from -30 to 30).

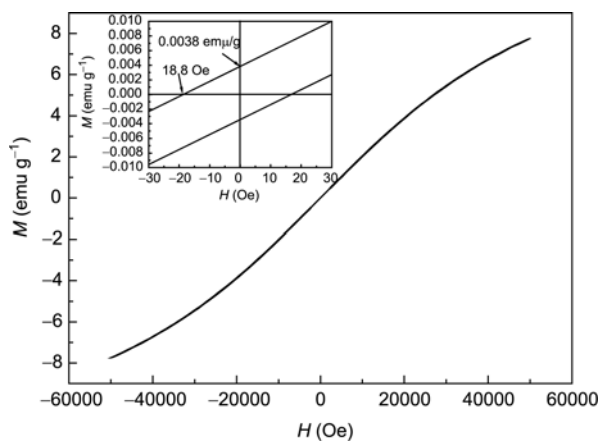


Figure 11 Hysteresis loop (M versus H) at 5 K for the PBD-4- Ni^{2+} complex (Inset: expanded view of the region from -30 to 30).

Table 3 Magnetic properties of PBD-4- Cu^{2+} and PBD-4- Ni^{2+}

PBD-4-M	Metal content (wt%)	T_0 (K)	Coercive field (10^{-4} Oe)	Remnant magnetization (10^{-3} emu/g)
PBD-4- Cu^{2+}	8.6	102	13.2	1.6
PBD-4- Ni^{2+}	5.6	53	18.8	3.8

two complexes have higher relative saturation magnetization and higher metal content. In a word, the hyperbranched polyamide complexes PBD-4- Cu^{2+} and PBD-4- Ni^{2+} are organic soft ferromagnets.

4 Conclusions

In summary, a novel hyper-branched aromatic polyamide containing bithiazole ring was successfully synthesized by the method of polycondensation of bifunctional 2,2'-diamino-4,4'-bithiazole(DABT) and trifunctional 1,3,5-benzenetricarbonyl trichloride (BTC). Furthermore, a premier solution system of this reaction, the mixed solvent of DMAc and anhydrous LiCl, was obtained. The hyperbranched product

could be dissolved in organic polar solvents such as DMAc, DMSO, and NMP. Metal complexes were also prepared by mixing equimolar ratios of CuSO_4 (or NiSO_4) and the polymer in DMSO, and characterized by FT-IR and UV-vis spectra. The metal contents of the two complexes are 8.6% and 5.6% respectively. From the field and temperature dependence of magnetization and hysteresis loop, both of them exhibit the feature of soft ferromagnets. Thanks to the hyperbranched structure, which determined their soluble property, the two complexes are potential magnetic materials, with much more ease of preparation, than other magnets.

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