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Synthesis and properties of novel fully conjugated polymers containing bithiazole rings

Zhuxian Zhou, Weilin Sun*, Jun Yang, Jiangbin Tang, Zhiquan Shen

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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Abstract

Two novel fully conjugated polymers containing bithiazole rings (PDDBTz and PDABTz) were first synthesized by polycondensation of 2,7-dimethyl-2,4,6-octatriene-1,8-dial with 2,2′-bis(diethylphosphinatyl methyl)-4,4′-bithizole or 2,2′-diamino-4,4′-bithiazole (DABT). The structure of the polymers was determined by IR, ^{1}H NMR and elemental analysis. PDDBTz is soluble in trifluoroacetic acid and DMSO, whereas PDABTz is soluble in common solvent such as THF, DMSO, DMF. Bithiazole rings were introduced to provide bidentate N-donor sites for binding metal ions. Their lanthanide metal complexes were prepared. The magnetic behavior of these polymeric complexes was measured as a function of magnetic field strength (0–60 kOe) at 4 K and as a function of temperature (4–300 K) at magnetic field strength of 30 kOe. The results show that they all exhibit features of soft ferromagnet.

Keywords: Bithiazole; Conjugated polymer; Polymer complexes

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1. Introduction

Conjugated polymers have been interested because of their electrical conductivity and applicability in electro-optical devices [1–5]. More recently, metal-derivitized conjugated systems and new polymer systems have been developed, which are better able to coordinate metal centers [6,7]. The rationale is metalated derivatives could combine the rich electro- and photo-chemical activities of the metal complex with long-range electron transfer. Among the π-conjugated polymers, those with electron-withdrawing imine nitrogen(s) (C=N) are attracting interest, they have the electron-accepting ability and are wonderful reactive for metal-complex, which can modify their optical and electric properties [8,9].

Organic and polymeric magnetic materials have been studied extensively, and a great progress has been achieved during the last decades [10–13]. In 1998, Hoffmann et al. [14] proposed that polymers built from sulfur, carbon, nitrogen-containing five-membered rings would theoretically display magnetic ordering, but none have as yet been proved by experiment. Heteroaromatic rings complexes formed from suitable metals and organic ligands are one kind of the best candidates for organic magnetic materials. Sun et al. [15–17] synthesized bithiazole-containing polymers and found their metal complexes have typically ferromagnetic properties. The crystal structure of metal complexes of the monomer DABT has been characterized by X-ray diffraction [18,19]. The magnetization of these complexes was obviously influenced by the nature of the polymer and the difference of coordinating reactivity among the metal ions.

It has been realized that trivalent lanthanide ions maybe incorporated in supramolecular complexes acting as molecular device [20]. In this paper, we will discuss the synthesis and characterization of two novel fully conjugated polymers PDDBTz and PDABTz. The complexes of the polymers coordinating with lanthanide ions were also prepared. The preliminary magnetic properties of the complexes were also investigated for the first time.

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* Corresponding author. Tel./fax: +86 571 8795 3727.
E-mail address: opl_sunwl@emb.zju.edu.cn (W. Sun).

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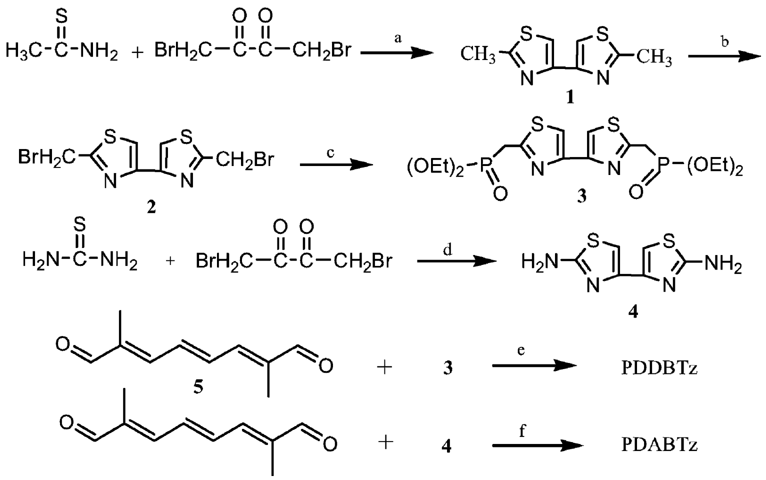


Scheme 1. The synthetic routes of monomers and polymers. Reagents and conditions: a = CH_3CH_2OH, reflux, 6 h; b = NBS, BPO, CCl_4, reflux, 8 h; c = triethyl phosphate, 125 °C, 4 h; d = CH_3CH_2OH, reflux, 1 h; e = anhydrous THF, *t*-BuOK, room temperature, 4 h; f = DMSO, 80 °C, 8 h.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was distilled over CaH_2 before use. 2,3-Butyldione, bromine (liquid), *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), thiourea and thioacetamide were purchased from Shanghai Chemical Reagent Company. 2,7-Dimethyl-2,4,6-octatriene-1,8-dial was synthesized in our laboratory. DABT was prepared according to the literature [21]. $PrCl_3$ and $SmCl_3$ were prepared from HCl and Pr_2O_3, Sm_2O_3, respectively.

2.2. Measurements

^{1}H NMR spectra were recorded on a Bruker Advance AMX-500NMR instrument in CF_3COOD with tetramethyl silane (TMS) as internal standard. A Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer was used to record IR spectra in KBr pellets. The intrinsic viscosity $[\eta]$ was measured in DMSO at 30 °C. Thermo gravimetric analyses (TGA) were carried out with a Pyris-1 thermo gravimetric apparatus. Element analysis was conducted on EA1112 element analyzer. The content of Lanthanide ions was measured by complexometry using EDTA. The conductivity of polymers was measured by four-probe method using Keithley 196 system DMM digital multimeter at room temperature. The magnetic properties of the complex were measured with a physical properties measurement system (PPMS-9T) magnetometer (QUANTUM DESIGN).

2.3. Synthesis of monomers and polymers

The synthetic approach of the polymers (PDDBTz, PDABTz) and the corresponding monomers was outlined in Scheme 1.

2.3.1. 2,2′-Dimethyl-4,4′-bithizole, **1**

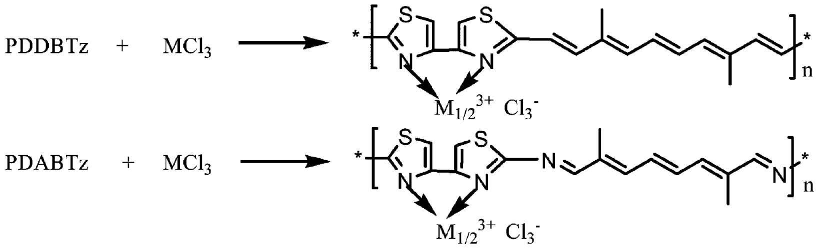
1,4-Dibromobutyldione (19.5 g, 80 mmol) and thioacetamide (14 g, 160 mmol) were mixed in ethanol (400 ml). The mixture was refluxed for 6 h, then mixture was poured into 1600 ml H_2O and the solution was neutralized with aqueous NaOH. The yellow crystal formed and was collected by filtration. The resultant crystal was purified by recrystallization in ethanol and H_2O (1:1) solution. The product was dried in a vacuum at 60 °C for 24 h. The yield was 14 g (89%). Mp = 176–177 °C. IR (KBr, cm^{-1}): 3101 (νCH_3), 1555($\nu C{=}N$), 1495($\nu C{=}C$).

2.3.2. 2,2′-Bis(bromomethyl)-4,4′-bithizole, **2**

2,2′-Dimethyl-4,4′-bithizole (4.7 g, 24 mmol), NBS (10.0 g, 56 mmol) and a catalytic amount of benzoyl peroxide (BPO) were mixed in CCl_4 (250 ml). The mixture was refluxed for 8 h. After the reaction mixture cooled to room temperature, it was extracted with chloroform several times. The extractives were separated by silica gel column chromatography using a mixture of $CHCl_3$ and CCl_4 (1:1) as eluant. A white crude product was obtained. After crystallization in petro-ether (bp 100–120), a white crytal was obtained. The product was dried in a vacuum at 60 °C for 24 h. The yield is 4.7 g (55%). Mp = 159–164 °C. Anal. Calcd for $C_8H_6N_2S_2Br_2$: C, 27.1%; N, 7.9%; H, 1.7%. Found: C, 28.0%; N, 7.9%; H, 1.7%. IR (KBr, cm^{-1}): 2970(νCH_2), 1555($\nu C{=}N$), 1475($\nu C{=}C$), 616($\nu C–Br$). ^{1}H NMR (500 MHz, CD_3Cl): δ 7.8 ppm(s, 2H, bithiazole) 4.7 ppm (s, 4H, $–CH_2Br$).

2.3.3. 2,2′-Bis(diethylphosphinatyl methyl)-4,4′-bithiazole, **3**

The mixture of 2,2′-bis(bromomethyl)-4,4′-bithizole (2.0 g, 5.6 mmol) and triethyl phosphate (2.8 g, 16.8 mmol) was stirred at 125 °C under purified N_2 atmosphere for 4 h. Excess triethyl phosphate was distilled, and the residue was recrystallized from petro-ether (bp 100–120 °C) and dichloromethane (5:1). The



Scheme 2. Preparation of the complexes (M = Pr, Sm).

product was dried in a vacuum at 60 °C for 24 h. The yield is 2.3 g (88%). Mp = 115–118 °C. Anal. Calcd for $C_{16}H_{26}N_2O_6P_2$: C, 41.0%; N, 6.0%; H%, 5.7. Found: C, 41.4%; N, 5.9%; H, 5.7%. IR (KBr, cm^{-1}): 3101(νCH$_3$), 2972(νC–H), 1488(νC=N), 1265(νP=O) 1028(νC–O). ^{1}H NMR (500 MHz, CD$_3$Cl): δ 7.7 ppm (s, 2H, protons of bithizole rings), 4.1 ppm (m, 4H, –OCH$_2$–), 3.5–3.7 ppm(d, 4H, –CH$_2$–P), 1.3 ppm(t, 6H, –CH$_3$).

2.3.4. Synthesis of PDDBTz

A solution of 2,2′-bis(diethylphosphinatyl methyl)-4,4′-bithiazole (0.50 g, 1.07 mmol) and 2,7-dimethyl-2,4,6-octatriene-1,8-dial (0.14 g, 1.07 mmol) in dry THF (50 ml) was magnetically stirred at room temperature under nitrogen atmosphere. Potassium *tert*-butoxide (0.46 g, 4.01 mmol) in 20 ml dry THF was added dropwise using a syringe. The solution was continuously stirred at room temperature under nitrogen atmosphere, about 4 h later it became red and the viscosity increased, indicating the formation of the polymer. Then the solution was precipitated in water (300 ml) with stirring. The precipitate was collected by filtration. The crude polymer was thoroughly washed with water, methanol and acetone. The light red solid was attained after dried under vacuum at 60 °C for 24 h. The yield is 0.27 g (80%). IR (KBr, cm^{-1}): 2917 (νCH$_3$), 1666, 1596 (νC=C), 1459 (νC=N), 1252, 1105, 1050, 1021 (skeletal vibration). ^{1}H NMR (500 MHz, CF$_3$COOD): δ 8.31 ppm(Ar–CH=), 8.06 ppm(2H, =CH–), 7.60 ppm(2H, protons of bithizole rings), 7.05 ppm(2H, –CH=), 6.85 ppm(2H, –CH=), 2.10 ppm(6H, –CH$_3$), 4.27–4.30, 1.35–1.38, 0.39–0.43 ppm (protons of end groups) (Fig. 2). Intrinsic viscosity $[\eta] = 0.09$ dL/g (DMSO, 30 °C).

2.3.5. Synthesis of PDABTz

A mixture of DABT (1.0 g, 5 mmol) and 2,7-dimethyl-2,4,6-octatriene-1,8-dial (0.68 g, 5 mmol) in DMSO (20 ml) was magnetically stirred at 80 °C under nitrogen atmosphere, and red (brown) solution was obtained after 8 h. The solution was precipitated in water (400 ml) with stirring. The precipitate was collected by filtration. The solid was washed by water, methanol and acetone successively. The red solid was attained after dried under vacuum at 60 °C for 24 h. The yield is 1.50 g (92%). IR (KBr, cm^{-1}): 3378 (ν-NH$_2$), 3137 (νC–H), 1661, 1616 (νC=C), 1453, 1525 (νC=N), 1411, 1379, 1277, 1007 (skeletal vibration). ^{1}H NMR (500 MHz, CF$_3$COOD): δ 8.93 ppm(2H, Ar–N=CH–), 6.78 ppm(2H, protons of bithizole rings), 6.71 ppm(4H, –CH=CH–), 1.51 ppm(6H, –CH$_3$) (Fig. 2). Intrinsic viscosity $[\eta] = 0.07$ dL/g (DMSO, 30 °C).

2.4. Preparation of the polymeric complexes

The preparation of the complexes: PDDBTz-Pr^{3+}, PDDBTz-Sm^{3+}, PDABTz-Pr^{3+}, PDABTz-Sm^{3+} is shown in Scheme 2.

$PrCl_3 \cdot 6H_2O$ (0.72 g, 3.0 mmol) and PDDBTz (0.50 g, 1.5 mmol) was dissolved in DMSO and stirred at 80 °C for 4 h under nitrogen atmosphere. The resulting brown solution was deposited in water, and then a brown precipitate of PDDBTz-Pr^{3+} was obtained. The precipitate was filtered, and then washed with water and methanol till adsorbate PrCl$_3$ was removed. The same procedure was applied for the preparation of PDDBTz-Sm^{3+}, PDABTz-Pr^{3+} and PDABTz-Sm^{3+}. According to the data of complexometric titration, the metal contents for complexes were shown in Table 1.

3. Results and discussion

3.1. Synthesis and charaterization

The basic strategies employed for the synthesis of PDDBTz and PDABTz are based on the Witting–Horner reaction [22] and the Schiff reaction, respectively. The structures of the polymers were characterized by IR, ^{1}H NMR and elemental analysis. The structures of the two polymers can be observed in the FT-IR spectra (Fig. 1), which reveals that the two polymers give characteristic peaks in the range of 1400–1550 cm^{-1}, which are due to

Table 1
Metal content of polymer-metal complexes

Polymeric complex	Metal content[a] (wt%)	Suggested formula
PDDBTz-Pr^{3+}	13.6	$[C_{18}H_{16}N_2S_2(PrCl_3)_{0.41}]_n$
PDDBTz-Sm^{3+}	15.5	$[C_{18}H_{16}N_2S_2(SmCl_3)_{0.45}]_n$
PDABTz-Pr^{3+}	13.4	$[C_{16}H_{14}N_4S_2(PrCl_3)_{0.40}]_n$
PDABTz-Sm^{3+}	2.3	$[C_{16}H_{14}N_4S_2(SmCl_3)_{0.05}]_n$

[a] Percentage to the respective dried samples.

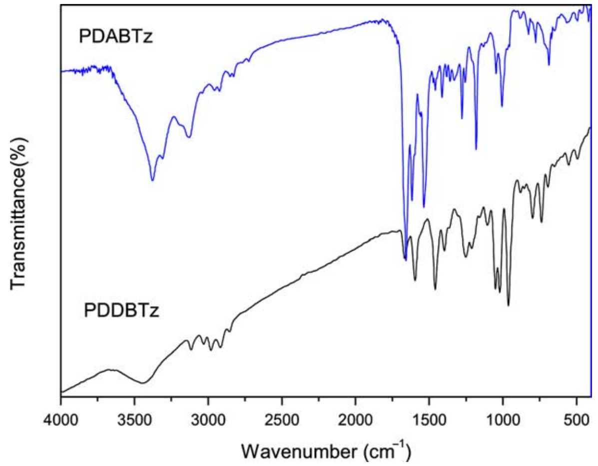


Fig. 1. IR spectra of PDDBTz and PDABTz.

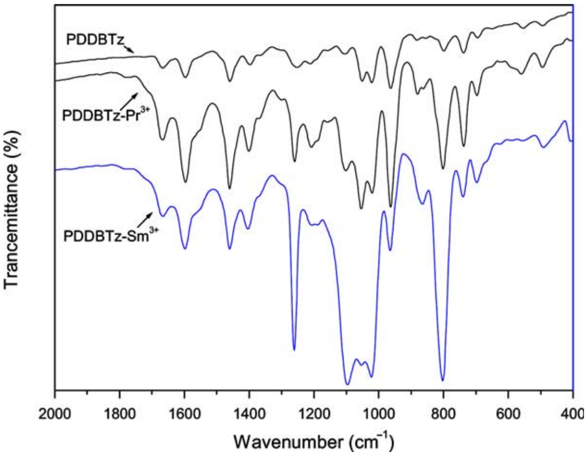


Fig. 3. IR spectra of PDDBTz, PDDBTz-Pr^{3+} and PDDBTz-Sm^{3+}.

from bithiazole rings. The IR spectrum of PDABTz illustrated the stretching oscillation of the new C=N bond appears at about 1617 cm^{-1}. In IR spectrum of PDDBTz, the conjugated C=C bond appears at 1596 cm^{-1} and a sharp absorption peak at 963 cm^{-1}, which corresponds to the out-of-plane bending mode of C–H bond in the *trans*–CH=CH– groups, showing that the generated double bonds are mainly in *trans*-configurations.

The ^{1}H NMR spectra of the polymers are shown in Fig. 2. In the ^{1}H NMR spectrum of PDDBTz, there are five peaks in the filed of 6.85–8.32 ppm, the triple peak in 7.6 ppm belongs to the protons on the bithiazole rings, and the other four are attributed to the alkyl groups. Four peaks were observed in the lower field, the single peak at 2.09 ppm(s) belongs to –CH$_3$, and the other three peaks appearing at 4.27–4.30 ppm(t), 1.35–1.38 ppm(t), 0.39–0.43 ppm(d) belong to the protons of the end group. It is available to estimate the average number of the repeating unit of PDDBTz by computing the ratio of the total resonances of the methyl protons at 2.10 ppm to that of the end group protons, and the average number of the repeating unit is about four. The element analysis confirmed the value. Calcd for $(C_{18}H1_{6}N_2S_2)_4\cdot C_{16}H_{26}N_2S_2O_6P_2$: C, 56.05%; H, 4.78%; N, 7.43%. Found: C, 57.14%; H, 4.92%; N, 7.39%. The yield of low molecular weight product is mainly due to the fact that the high molecular weight polymer is insoluble and by precipitating out of the reaction medium, the effective propagation step is effectively terminated. In the ^{1}H NMR spectrum of PDABTz, The single peak observed at 1.50 ppm belongs to –CH$_3$, and the peak appears at 6.78 belongs to the bithiazole rings, 8.93 ppm belongs to N=CH, and 6.71–6.75 ppm are attributed to the other alkyl groups.

The IR spectra of the complexes and the polymers were shown in Figs. 3 and 4. By comparing the IR spectra of the two polymers and their corresponding Lanthanide ion complexes, it can be found that the absorption remarkably changes between 900 and 1300 cm^{-1}, 1300 and 1660 cm^{-1}, respectively, indicating the formation of the complex. For instance, in comparison with PDDBTz, significant changes were observed in the IR spectrum of PDDBTz-Pr^{3+} (Fig. 3), e.g. the blue-shift of absorption bands at 1459, 1397 and

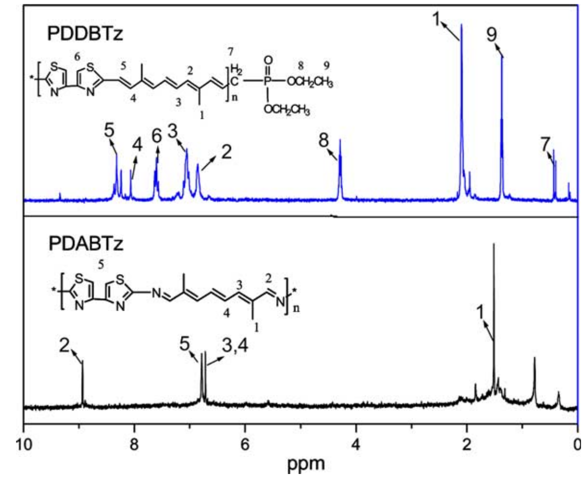


Fig. 2. ^{1}H NMR spectra of PDDBTz and PDABTz in CF$_3$COOD at 500 MHz.

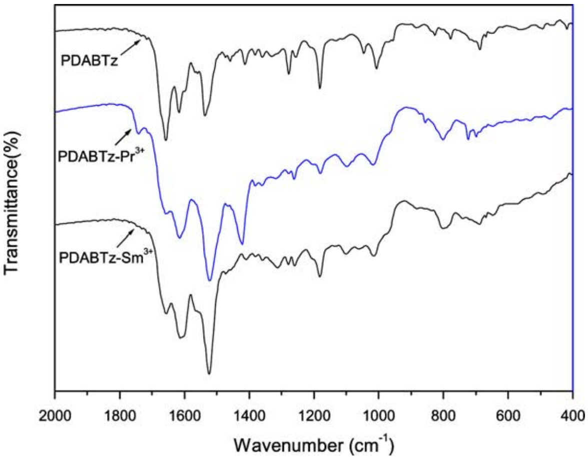


Fig. 4. IR spectra of PDABTz, PDABTz-Pr^{3+} and PDABTz-Sm^{3+}.

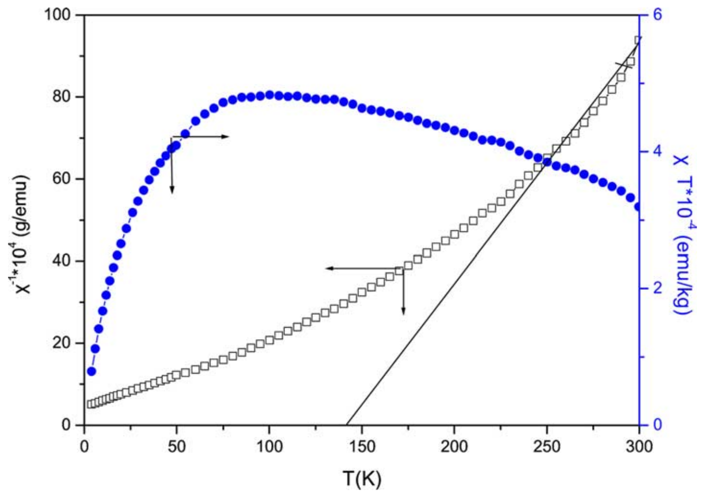


Fig. 5. Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PDDBTz-Pr^{3+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law between 250 and 300 K.

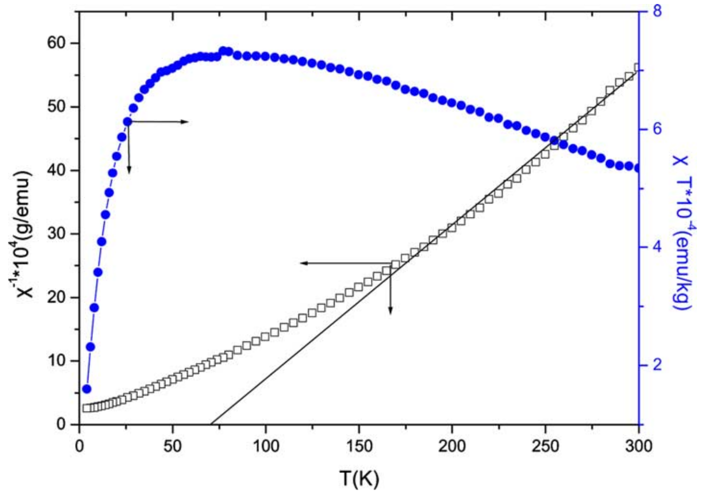


Fig. 6. Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PDABTz-Pr^{3+}at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law between 175 and 300 K.

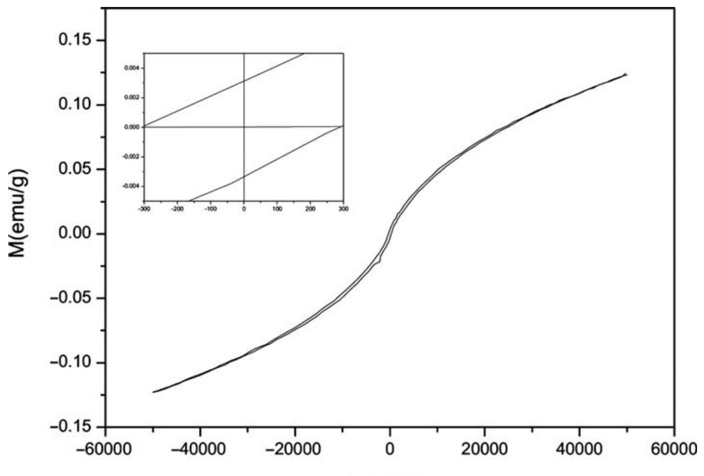


Fig. 7. Magnetic hysteresis loop of PDDBTz-Sm^{3+} at 4 K, (insert) expanded view of the region from −300 to 300 Oe.

1252 cm^{-1} of PDDBTz to 1460, 1403 and 1261 cm^{-1}. This indicates the coordination between the nitrogen atoms of bithiazole rings and the incorporated Pr^{3+}, the skeletal vibrations of the bithiazole rings need higher energy to oscillate because of coordination. Similar changes can be observed within the region of 2000–400 cm^{-1} in IR spectra of the other polymers and their corresponding complexes.

3.2. Properties of the polymers

Thermal stability of the polymers in air or nitrogen atmosphere at heating rates of 10 °C/min was evaluated by thermogravimetric analysis (TGA). It is noticed that the onset temperatures of degradation and the curves of thermal decomposition of the polymers in air was quite similarly to those in nitrogen atmosphere. The decomposition temperatures of the polymers were about 200 °C in both nitrogen and air atmosphere. At 400 °C in air, PDDBTz and PDABTz, respectively, retained about 70 and 74% of their weight, while PDDBTz and PDABTz retained about 65 and 73% of their weight at 400 °C in N_2. The result suggests that two polymers have good thermal stability due to the bithiazole rings. The electrical conductivities (σ) of PDDBTz and PDABTz are 1.1×10^{-9} and 9.3×10^{-10} S cm^{-1}, respectively. Through Iodine doping (saturation doping by using a vacuum line), the electrical conductivity of polymers are, respectively, 1.2×10^{-8} and 9.7×10^{-9} S cm^{-1}, which indicates they are semiconductors.

3.3. Magnetic properties of the polymer complexes

The preliminary magnetic properties of four complexes were investigated. The temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PDDBTz-Pr^{3+} and PDABTz-Pr^{3+} at an applied magnetic field of 30 kOe are shown in Figs. 5 and 6, respectively. It can be seen that the magnetic susceptibility (χ) of these two complex follows the Curie–Weiss relationship, $\chi = C/(T-\theta)$, in the range of 250–300 K and 175–300 K, respectively, with the Curie–Weiss temperature $\theta = 140$ and 70 K, respectively. The positive Curie–Weiss temperature indicates that these two complexes are ferromagnets. The magnetic hysteresis loop of PDDBTz-Sm^{3+} at 4 K is shown in Fig. 7. From the typical S shape and small area of hysteresis loop it can be deduced that PDDBTz-Sm^{3+} is a soft ferromagnet.

4. Conclusions

Two novel fully conjugated polymers containing bithiazole rings were synthesized and characterized. They have good thermal stability. The electrical conductivities of the polymers were measured, which indicates they are semiconductors. The complex of PDDBTz-Pr^{3+}, PDDBTz-Sm^{3+}, PDABTz-Pr^{3+} and PDABTz-Sm^{3+} were prepared and their preliminary magnetic properties were investigated.

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