Preparation and Magnetic Properties of Novel Supramolecular Polymeric Complexes Containing Bithiazole Rings

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ABSTRACT: The preparation and magnetism of two supramolecular polymeric complexes, DABT/PAA-Ni^{2+} and DABT/PAA-Cu^{2+}, which were obtained via electrostatic interactions of 2,2′-diamino-4,4′-bithiazole (DABT), poly(acrylic acid) (PAA), and transition metal ions (Cu^{2+} or Ni^{2+}) were described. FTIR, ^{1}H NMR, and elemental analysis were used to characterize the structures of the obtained supramolecular polymer and the corresponding complexes. The corresponding multilayer films were also constructed on the quartz substrate. UV–vis spectra and AFM images were applied to characterize these films. The result indicates a process of uniform assembling. The magnetic behavior was examined as a function of magnetic field strength at 4 K and as a function of temperature (4–300 K). It was found that DABT/PAA-Ni^{2+} exhibits a ferromagnetic property with a high value of relative saturation magnetization, while DABT/PAA-Cu^{2+} shows a special magnetic property different from the typical magnet. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1714–1722, 2008

Key words: supramolecular structures; bithiazole rings; metal–polymer complexes; thin films; magnetic polymers

INTRODUCTION

For a long time, organic metal complexes have received considerable interest because of their potential applications in the aviation, electronics, chemical engineering, and mechanical engineering areas. The limitations of conventional stepwise covalent construction are recognized, and the utilization of supramolecular methods, for example hydrogen-bonding, metal–ligand interactions, and so forth, has resulted in spectacular supramolecular structures. In recent years, the development of new concepts for the rational design of larger, more complex molecules has led to much progress in supramolecular chemistry.[1] Self-assembly of supramolecular structures is a spontaneous process by which molecules and nanophase entities may materialize into organized aggregates or networks.[2] Through various interactive mechanisms of self-assembly, such as hydrogen bonds, metal–ligand interactions, electrostatic interactions, charge-transfer complexes, van der Waals forces, etc., the technique proves indispensable to recent functional materials and device realizations. The challenges of designing and synthesizing new complexes, the complexity of their structures, and their potential physical properties have continued to attract a great deal of attention.[3,4]

The report of the observation of the first soft ferromagnet below 16 K, a complex of C$_{60}$ with one of the strongest organic donors tetrakis(dimethylamino)ethylene, attracted a great deal of attention.[5] A series of investigations were carried out to elucidate the nature of the unusual magnetic phenomena of such materials,[6–9] but rarely other soft ferromagnets were reported.[7,10] In 1998, Genin and Hoffmann[11] proposed that polymers built from five-membered rings containing sulfur, carbon, and nitrogen would theoretically display magnetic ordering, but none have been synthesized yet. Sun et al.[12] firstly reported the synthesis of poly(Schiff base) containing bithiazole rings (TAPDA) 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. And they have reported the synthesis of TAPDA-Fe^{2+} complex and its ferromagnetic property for the first time.[13] The 4,4′-bithiazole moiety is used to provide donate N-donor sites for binding metal ions. The crystal structure of metal complexes of the monomer DABT has been characterized by X-ray diffraction.[14,15] Subsequently, a series of polymeric

complexes containing bithiazole rings were prepared and exhibited different types of magnetic behaviors.[16–18] The magnetization of these complexes was obviously influenced by the nature of the polymer and the difference of coordinating reactivity among the metal ions. These polymeric metal complexes could be employed for potential electrical, magnetic, and optical materials on appropriately choosing the constituent molecules.

As it is well known, poly(acrylic acid) (PAA) is a weak acidic polyelectrolyte. It can form polyelectrolyte complexes not only by electrostatic interactions with an oppositely charged polyelectrolyte in a specific solution, but also by hydrogen bonds.[19,20] In this article, we report a new approach for the preparation of polymeric magnetic complexes from DABT, PAA, and transition metal ions (Cu^{2+} or Ni^{2+}) on the basis of supramolecular method. The corresponding multilayer films were also constructed on the quartz substrate. The supramolecular polymeric complexes show new magnetic phenomena, which would create great information for the investigating of electrical, magnetic, and optical properties.

EXPERIMENTAL

Materials

All the chemicals used were of AR grade. Tetrahydrofuran (THF) was distilled over CaH_2 before use. Dimethyl sulfoxide (DMSO) was dried using a molecular sieve for several days and distilled prior to use. 2,3-Butyldione, bromine (liquid), benzoyl peroxide (BPO), and thiourea were purchased from Shanghai Chemical Reagent Company (Shanghai, China). Nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) were manufactured by Ningbo Chemical Reagent (Ningbo, People's Republic of China). DABT was prepared according to the literature. The polymerization of acrylic acid was carried out in THF with BPO at 67°C for 1 h. The product was purified by fractional precipitation in chloroform and dried under vacuum. Yield: 80%. $[\eta] = 11.5$ mL/g (1,4-dioxane, 30°C), M_w is 2.3×10^4.[21]

Measurements

A Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer was used to record IR spectra in KBr pellets. ^{1}H NMR spectra were recorded on a Bruker Advance AMX-400 NMR instrument in deuterated reagent with tetramethyl silane as an internal standard. UV–vis spectra were collected by UV-1601 UV–Visible spectrophotometer. The atomic force microscopy (AFM) measurements were performed on a Seiko SPI3800N station (Seiko Instruments, Inc.

Japan) in the tapping mode. The resonance frequency of the Si-cantilever (NSG10, NT-MDT) was about 300 kHz. Typically, the image was obtained with the scan rate of 1 Hz and a resolution of 256 × 256 pixels. The element analysis for C, H, and N was performed by using the Flash EA 112 element analyzer (Thermo Finnigan). The metal ion contents of complexes were analyzed by ethylenediamine-tetra-acetic acid titration using Eriochrome Black T as the indicator.[22] The magnetic measurements were carried out by a Physical Properties Measurement System (PPMS-9T) magnetometer (Quantum Design). The measured temperature ranged from 4 to 300 K and the intensity of magnetic field was measured from −50 to 50 kOe.

Preparation of the supramolecular polymeric complexes and multilayer films

Synthesis of DABT

DABT was prepared from thiourea and 1,4-dibromo-butanedione.[23,24] 1,4-Dibromobutanedione (0.135 mol) and thiourea (0.276 mol) were refluxed at 80°C for 1 h in 300 mL absolute ethanol. The resulting solution was poured into 600 mL hot water and ammonia solution was added until precipitation appeared. The precipitate was filtered, and then recrystallized from H_2O-EtOH (1 : 1 in volume) mixture. Brown needle crystals were obtained, which were filtered and dried at 40°C for 24 h in vacuum. The yield is 95%, decomposition temperature: 240°C. The monomer was characterized by ^{1}H NMR and FTIR spectroscopy. FTIR (KBr, cm^{-1}): ν 3447 (m), 3288 (m), 3127 (w), 1598 (s), 1527 (s), 1460 (m), 1297 (s), 1035 (m). ^{1}H NMR (DMSO-d_6): δ (ppm) 6.9 (4H, NH_2), 6.64 (2H, thiazole H). Anal. Calcd for $C_6H_6N_4S_2$: C, 36.35%; N, 28.26%; H, 3.05%. Found: C, 36.35%; N, 28.18%; H, 3.24%.

Preparation of the supramolecular polymer

Synthesis of supramolecular polymer DABT/PAA: An equimolar ratio of DABT and PAA was dissolved in DMSO to get 10% solid content. The solution was magnetically stirred and kept at room temperature under nitrogen atmosphere. A dark red solution was obtained after reacting for 24 h, and the solution was precipitated in ethyl acetate, and then the deep orange-red solid polymer was collected by filtration. The crude polymer was thoroughly washed with ethyl acetate, methanol, deionized water and acetone, and then dried for 48 h in a vacuum oven. The yield is 75%. FTIR (KBr, cm^{-1}): 3413–2978 (m), 2554 (w), 1943(w), 1712 (m), 1625 (s), 1529 (m), 1450 (m), 1382 (m), 1252–1172 (m), 1044(w), 621–562 (w). ^{1}H NMR (DMSO-d_6): δ (ppm) 1.50–1.74 (CH_3), 2.20 (CH), 7.50 (thiazole H),

7.28 (thiazole H), 12.60 (COOH). Anal. Calcd for $C_{24}H_{30}N_4S_2O_{12}$: C, 45.71%; N, 8.88%; H, 4.80%. Found: C, 41.34%; N, 9.46%; H, 5.00%.

Preparation of the supramolecular polymeric complexes DABT/PAA-Cu^{2+} and DABT/PAA-Ni^{2+}

Synthesis of the complexes DABT/PAA-Cu^{2+}: The DMSO (30 mL) solution of the polymer DABT/PAA (2.71g) was slowly added into a stirred DMSO solution of CuSO$_4$·5H$_2$O (5.00 g) under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 24 h, and then poured into a large amount of ethyl acetate. A light tan powder was filtrated and washed with ethyl acetate, ethanol, deionized water and methanol thoroughly to remove excess physisorption of CuSO$_4$. The washed water was examined with BaCl$_2$ solution. White color precipitate BaSO$_4$ indicated the presence of Cu^{2+}. The precipitate was dried in a vacuum oven for 48 h. FTIR (KBr, cm^{-1}): FTIR (KBr, cm^{-1}): 3296 (broad, m), 2948 (w), 1712 (w), 1630 (broad, s), 1548 (broad, s), 1455 (m), 1417 (m), 1371 (m), 1263 (w), 1200 (w), 1123 (s), 1044 (m), 788 (w), 620 (w), 469 (w). The Cu content is 19.09%.

The DABT/PAA-Ni^{2+} was obtained from DABT/PAA and NiSO$_4$·6H$_2$O following a procedure similar to that described for DABT/PAA-Cu^{2+}. FTIR (KBr, cm^{-1}): 3307 (broad, m), 2925 (w), 1713 (w), 1610 (s), 1544 (s), 1529 (s), 1519 (s), 1452 (w), 1430 (w), 1401 (w), 1361 (m), 1278 (w), 1200 (w), 1144–985 (s), 785 (w), 632 (w). The Ni content is 29.22%.

### Preparation of the multilayer films (DABT/PAA)$_n$-Cu^{2+} and (DABT/PAA)$_n$-Ni^{2+}

The quartz wafer, which was treated at 80°C for 40 min in a mixture of H$_2$O$_2$ (30%)/H$_2$SO$_4$ (V : V = 3 : 7), was used as substrate. It was immersed in DMSO solution of DABT (5 mg/mL) for 60 min, washed with DMSO and deionized water thoroughly, and dried. It was then immersed in the DMSO solution of PAA (2 mg/mL) for 30 min, washed with DMSO and deionized water thoroughly, and dried. In each deposition cycle, a (DABT/PAA)$_1$ bilayer was deposited on both sides of the quartz wafer. The fabrication cycle was repeated for given times to obtain multilayer films (DABT/PAA)$_n$. The (DABT/PAA)$_n$-M^{2+} (M = Ni^{2+} or Cu^{2+}) film was obtained by immersing of a (DABT/PAA)$_n$ multilayer film into a DMSO solution of cuprum sulfate (1 mg/mL, pH ≈ 6) for some time at room temperature, followed by washing with DMSO and deionized water to remove excess physisorbed metal ions (examined by BaCl$_2$ solution). The time was determined by the number of layers. The more the number of layers, the longer the time was needed.

RESULTS AND DISCUSSION

Synthesis and characterization

A schematic synthetic procedures of the supramolecular polymers and the corresponding complexes are demonstrated in Scheme 1. As it is well known, the hydrogen bonding is sensitive to their environment. But Hao and Lian have reported LBL assembly CdSe nanoparticles based on hydrogen bonding in *N,N*-dimethylformamide.[25] However, we find that the hydrogen bonding was disappeared in the process of coordination with metal ions. And the driving force may change into electrostatic interaction between the amino groups and the carboxyl groups in the supramolecular complexes.

The nature of interaction between the polymers was established by IR and ^{1}H NMR spectra. Figure 1 shows the IR spectrum of pure PAA, pure DABT, and DABT/PAA. The broad absorption band around 3300 cm^{-1} and the absorption appearing at 1707 cm^{-1} indicate that the carboxyl group in pure PAA is not in free but in associated state. The absorptions at 1527, 1461, 1390, and 1298 cm^{-1} can be assigned to the ring and skeletal stretching vibration of bithiazole of DABT. The peak at 1298 cm^{-1} might be attributable to the skeletal vibration of imino-interchange isomer of 2-aminothiazole.[26] The absorption peak at 1707 cm^{-1} of the DABT/PAA blueshifted to 1715 cm^{-1} compared with that of the PAA, which shows that carbonyl group is in a less associated state than in pure PAA. Combining the O—H stretching vibration at 2535 and 1949 cm^{-1}, we can infer that hydroxyl group forms stronger hydrogen bonds than in pure PAA.[27] Furthermore, the stretching vibration of N—H takes redshifted from 3447, 3289 to 3413, 3139 cm^{-1} and broadens, while the N—H bending vibrational absorption takes a blueshift from 1598 to 1625 cm^{-1}. And the imino-interchange isomer no longer existed, a skeletal vibration of bithiazole appeared at 1382 cm^{-1}. These changes suggest that hydrogen bonds form between PAA and DABT in adjacent layers.[27–29] In addition, there is almost no other change of positions of the absorption peaks from 1650 cm^{-1} to 1300 cm^{-1}, which implies that the carboxyl group of PAA in the DABT/PAA is not ionized, as well as the amino group of DABT.[30] These results prove that the supramolecular polymer DABT/PAA is not assembled via electrostatic attraction but hydrogen bonding. To obtain more evidence for the formation of supramolecular polymer between DABT and PAA in DMSO, we measured the ^{1}H NMR spectrum of the DABT/PAA in DMSO-d_6. In Figure 2, peaks for the two kinds of amino groups of DABT (6.9 ppm) were found to have shifted to 7.50 ppm. Meanwhile, the broad peak for the carboxyl groups of PAA (12.27 ppm) was noticeably shifted to 12.60 ppm in
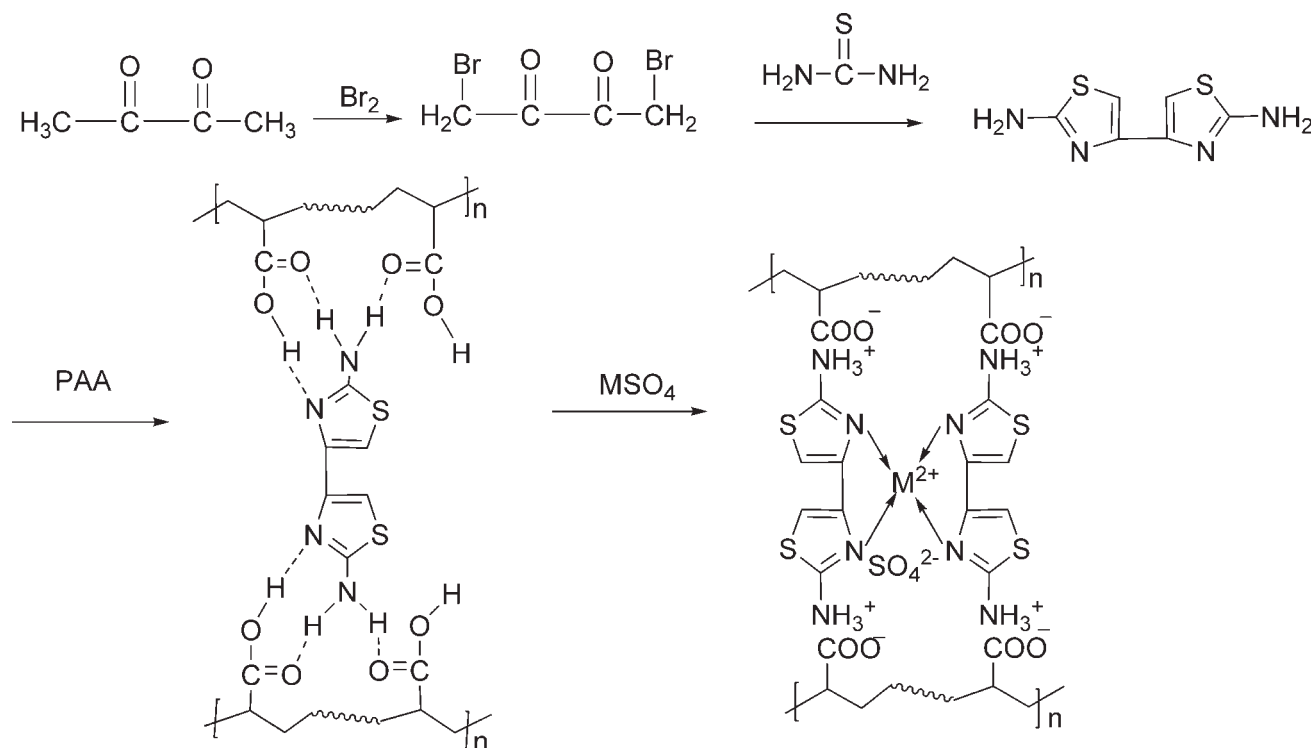
Scheme 1 Preparation routes for the supramolecular polymer and the polymeric complexes ($M = Ni^{2+}$ or Cu^{2+}).

the DABT/PAA. It is known that the peaks of the amino groups and the carboxyl groups shift to the lower magnetic field for the result of the formation of hydrogen bonds with each other. The results of the IR and ^{1}H NMR spectra clearly indicate the successful formation of the hydrogen bonds in the supramolecular polymer DABT/PAA.
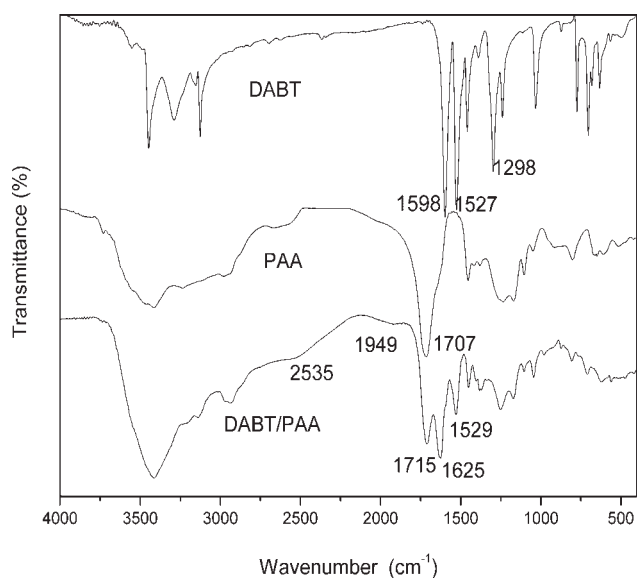

Figure 1 The IR spectra of DABT, PAA, and DABT/PAA.

In comparison with the supramolecular polymer DABT/PAA, significant changes were observed (Fig. 3) for the complexes. Take the DABT/PAA-Ni^{2+} for example, the obvious change is that the disappearance of O—H stretching vibration double peaks at around 2550 and 1940 cm^{−1} and the remarkable reduction of C=O stretching vibration monopeak at 1713 cm^{−1}. The new peaks at 1544 and 1402 cm^{−1} are attributed to the —COO[−] asymmetrical and symmetrical deformation modes, respectively.[31] The absorptions at 1610 and 1519 cm^{−1} can confirm the —NH$_3^+$ formation.[32] All these peaks can prove that the driving force between the amino groups in DABT and the carboxyl groups in PAA is changeable from hydrogen bonding to electrostatic attraction. The skeletal vibration is observed at 1361 cm^{−1} that obviously redshifted compared with the polymer, which indicates the coordination between the nitrogen atoms of bithiazole rings and the incorporated Ni^{2+}, may be attributed to the electron cloud around the C=N bond flow to the complex ions, and the corresponding electron cloud density decrease compared with that in the polymer matrix. Further, the absorption at around 1144–985 cm^{−1} in the spectrum which was assigned to v_{3a}, v_{3b}, v_{3c} and v_1 of SO_4^{2-}, suggested that the SO_4^{2-} is a bidentate ligand via oxygen atoms.[33] From the high metal content and the remarkable reduction of C=O stretching vibration and the high density of the —COO[−] deformation mode, we suggest that the coordination
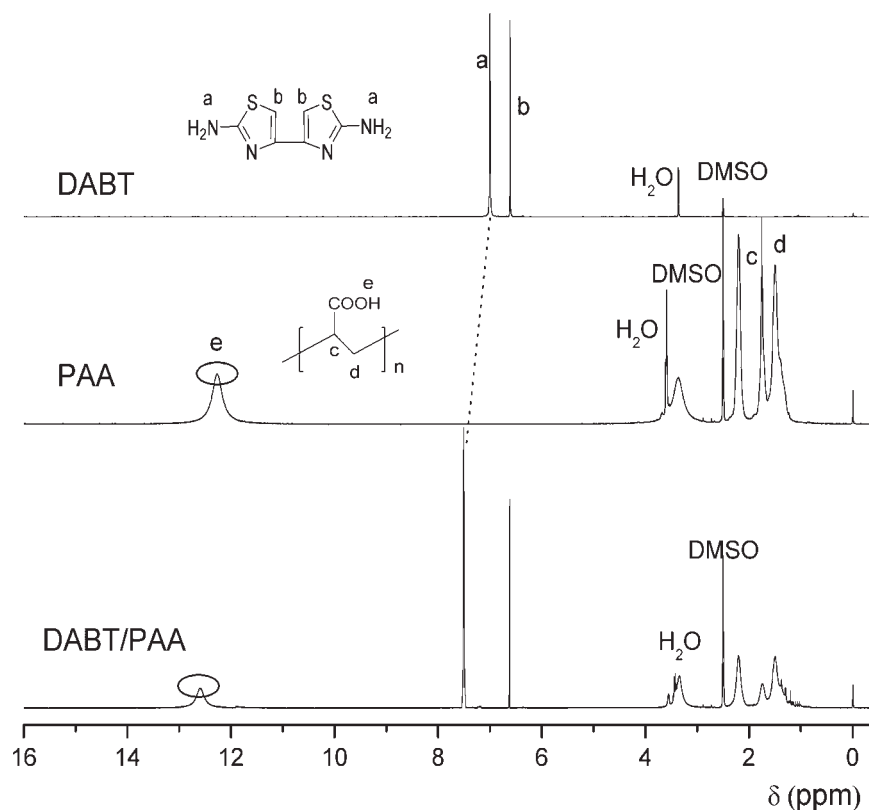
Figure 2 The ^{1}H NMR spectra of DABT, PAA, and DABT/PAA.

has taken place also through the oxygen atom of the residual carboxyl group.

Film properties

UV–visible spectroscopy was used to monitor the assembling process of the supramolecular on the substrate. Figure 4 shows the UV–vis absorption spectra of the multilayer film of PAA and DABT

Figure 3 The IR spectra of DABT/PAA-Cu^{2+} and DABT/PAA-Ni^{2+}.

with different number of bilayers on a quartz slide. The absorbance of the band at 360 nm due to the contribution of bithiazole rings increases linearly with the increasing number of bilayers, thus indicating a uniform assembling process for the multilayer film DABT/PAA [Fig. 4(a), inset]. The DABT/PAA multilayer film was immersed into a solution of metallic sulfate, where the metal ions diffused into the multilayer and chelated to form (DABT/PAA)$_n$-M^{2+} film. Compared with (DABT/PAA)$_6$, the characteristic absorption of bithiazole rings shows a slight redshift ($\sim$ 5 nm) of the (DABT/PAA)$_6$-Cu^{2+} film, and a new absorption appears at about 220 nm. The changes result from the Cu^{2+} chelating not only with the nitrogen atom of bithiazole ring to form stable five-member ring but also the oxygen atom of the residual carboxyl group.[34] The result is in accordance with that of the IR spectra. However, there is an obvious decrease of the absorbance intensity. For the film (DABT/PAA)$_6$-Ni^{2+}, as the same as the (DABT/PAA)$_6$-Cu^{2+} film, the coordination curve not only takes a slight redshift ($\sim$ 6 nm) and a new absorption at 222 nm but also makes obvious decrease of the absorbance intensity [Fig. 4(b)]. Both DABT and PAA are soluble in the solvent DMSO. In the process of coordination with metal ions in DMSO, the (DABT/PAA)$_n$ multilayer film may be subject to a small quantity of loss, which leads to reduced density of the film on the quartz slide. That
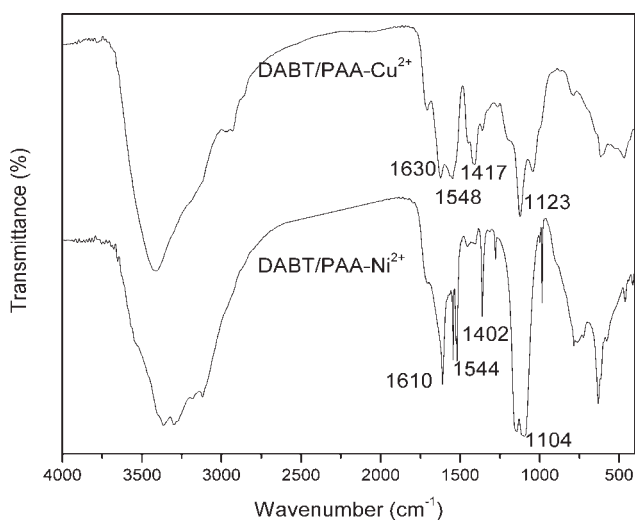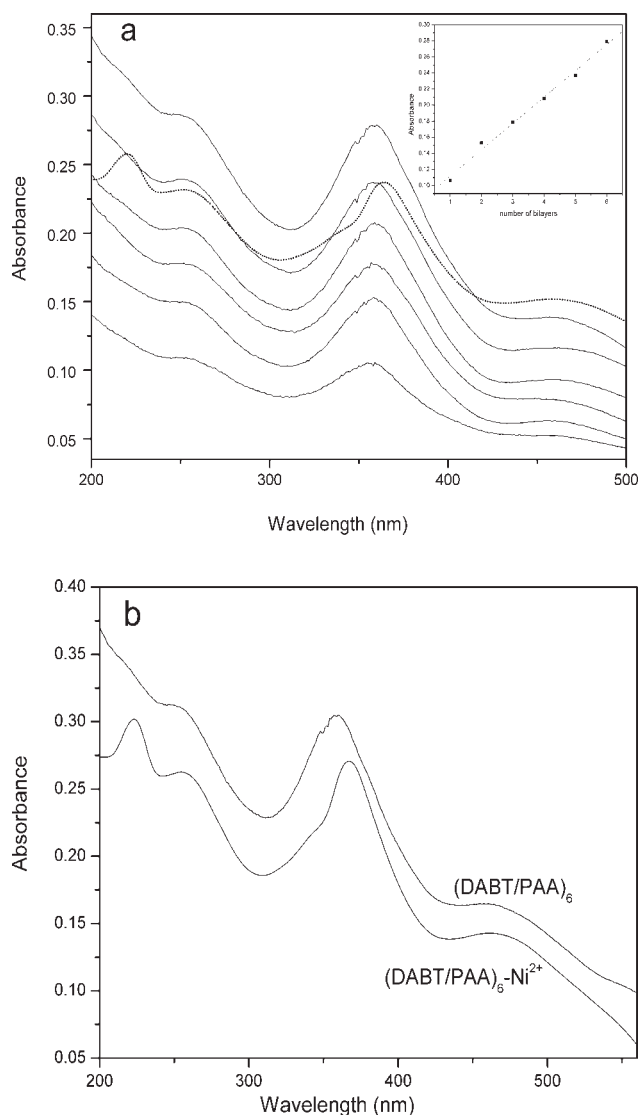
Figure 4 (a) UV–vis absorption spectra of 1–6 bilayer film (from lower to the upper curves) of PAA and DABT on quartz substrate. The dot line is the film (DABT/PAA)$_6$-Cu^{2+}. The inset shows the absorbance at 360 nm versus the number of bilayers. (b) UV–vis absorption spectra of the films (DABT/PAA)$_6$ and (DABT/PAA)$_6$-Ni^{2+} on quartz substrate.

phenomenon may partly result to the decrease of the absorbance intensity. The exact reason remains an interesting challenge. Further studies are in progress.

The morphology of the film was investigated by AFM, as shown in Figure 5. In contrast, it is clear that the surface of the (DABT/PAA)$_6$ film is relatively smoother. The mean roughness (R_a) was calculated to be about 0.67 nm within a given area of $1 \times 1 \ \mu m^2$. This means that the DABT/PAA self-assembling film via hydrogen bonding is of top quality. As shown in Figure 4(b), after coordination with Cu^{2+}, the R_a increases to 1.74 nm, and some aggregates are also visible. That may originate from the

changes of the driving forces. The (DABT/PAA)$_6$-Cu^{2+} film was formed by immersing the uniform (DABT/PAA)$_6$ film into the solution of cuprum sulfate. And in the process of Cu^{2+} diffusing into the film, the access is not homogeneous, which brings on irregular agglomeration of nanogranules. The morphology of the (DABT/PAA)$_6$-Ni^{2+} film is similar to the (DABT/PAA)$_6$-Cu^{2+} film, and some aggregates are visible. The R_a was calculated to be about 1.46 nm within a given area of $1 \times 1 \ \mu m^2$.
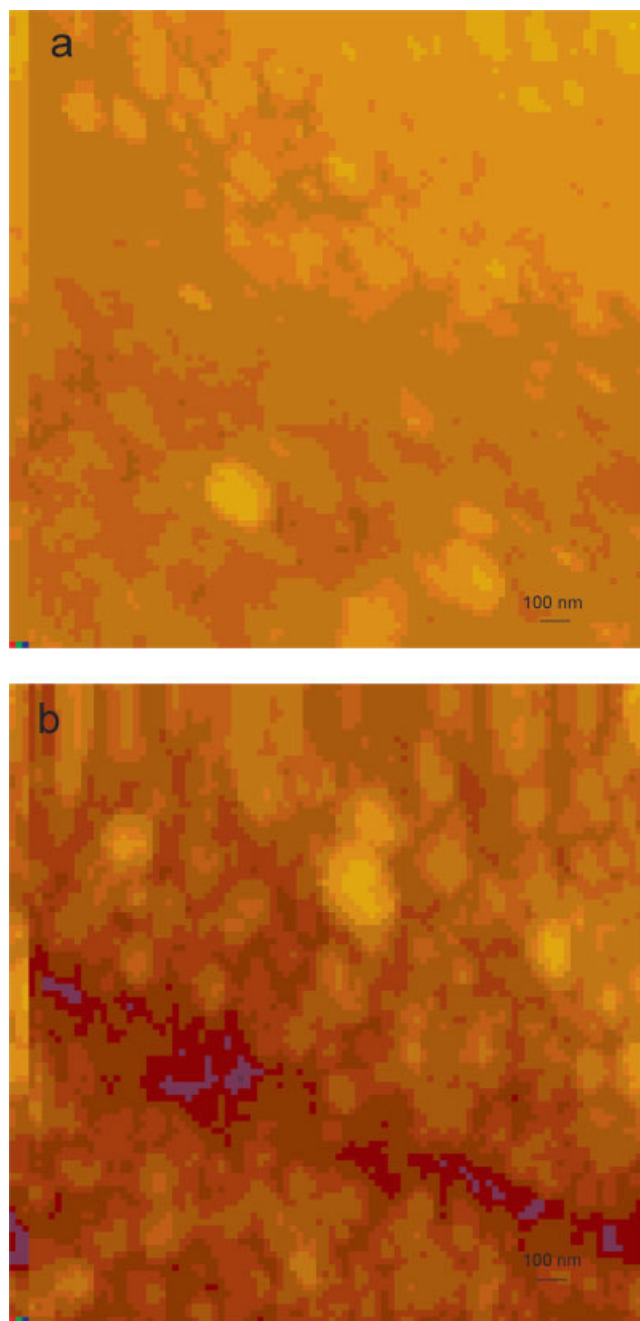

Figure 5 AFM images of the multilayer film (a) (DABT/PAA)$_6$ and (b) (DABT/PAA)$_6$-Cu^{2+}on quartz substrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
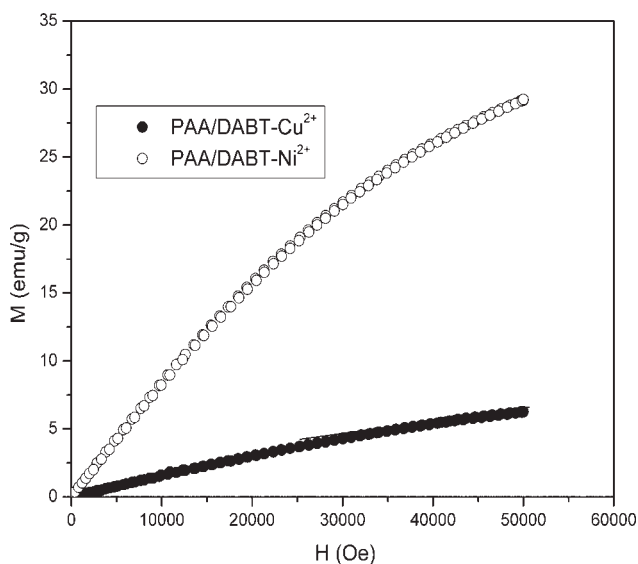
Figure 6 Magnetization as a function of the applied field for DABT/PAA-Cu^{2+} and DABT/PAA-Ni^{2+} performed at $T = 4$ K.

Magnetic characterization

The preliminary magnetic properties of two complexes were investigated. The magnetization of the samples was examined by PPMS magnetometer. The amounts of samples used in magnetic measurement were about 50–100 mg, and were held by the specific tube.

According to expectations, the supramolecular polymer shows diamagnetic property because of the absence of paramagnetic sources just like other pure polymers. The diamagnetic susceptibility is negative even at low temperature. But the magnetic phenomena of the complexes are totally different from the polymer because of the exchange interaction between metal ions and polymer chain. Figure 6 presents a typical ferromagnetic relationship between magnetization and applied field for the complexes at 4 K. For DABT/PAA-Cu^{2+}, the magnetization (M) increases sharply below 30 kOe. The rising trend slows down above 30 kOe and then the magnetization nearly approaches saturation at about 40 kOe for DABT/PAA-Cu^{2+}, for DABT/PAA-Ni^{2+} till about 45 kOe The values of relative saturation magnetization are 6.3 emu/g for DABT/PAA-Cu^{2+} and 29.2 emu/g for DABT/PAA-Ni^{2+}.

The temperature dependence of the magnetization is also studied at an applied magnetic field of 30 kOe from 4 K to 300 K (Fig. 7). For DABT/PAA-Ni^{2+}, the magnetization decreased sharply as the temperature increasing from 4 K to 25 K and then decreased slowly till 300 K. This suggests the system approaches a magnetic phase transition at 25 K. However, for the DABT/PAA-Cu^{2+}, the magnetic phase transition appears at $T = 15$ K.
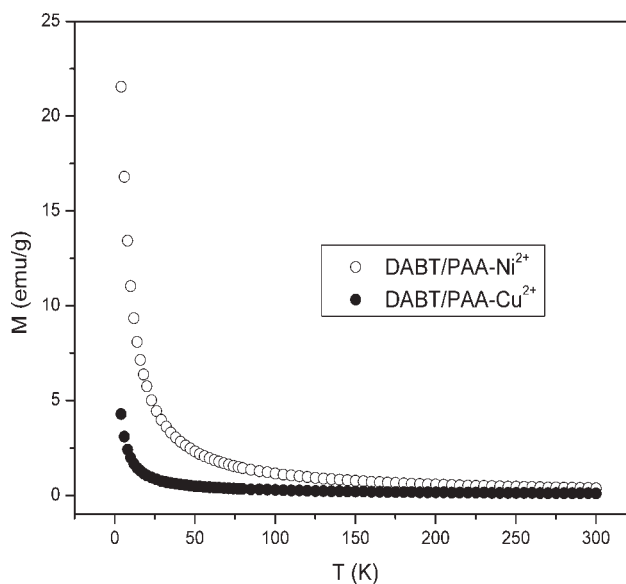

Figure 7 The temperature dependence of magnetization (M) for DABT/PAA-Cu^{2+} and DABT/PAA-Ni^{2+} at $H = 30$ kOe.

Figure 8 reveals that the magnetic susceptibility (χ) of DABT/PAA-Ni^{2+} followed the Curie–Weiss relationship, $\chi = C/(T - \theta)$, in the range of temperature from 100 to 300 K. The positive Curie–Weiss temperature ($\theta = 12.5$ K) implies the existence of ferromagnetic coupling in the complex.[35] It can be deduced that DABT/PAA-Ni^{2+} exhibits ferromagnetic property. The temperature dependence of the reciprocal of magnetic susceptibility (χ^{-1}) and χT products of the complexes were measured as shown in Figure 9. For the DABT/PAA-Cu^{2+} powder, upon cooling down, the product χT decreases gradually
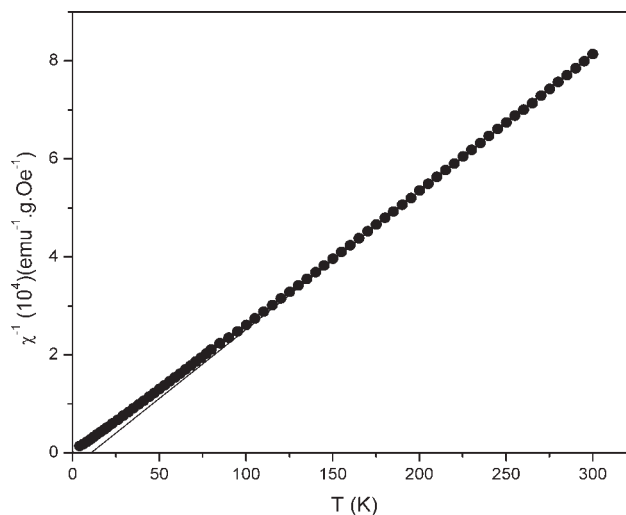

Figure 8 The reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature for DABT/PAA-Ni^{2+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law in the temperature range from 100 to 300 K.
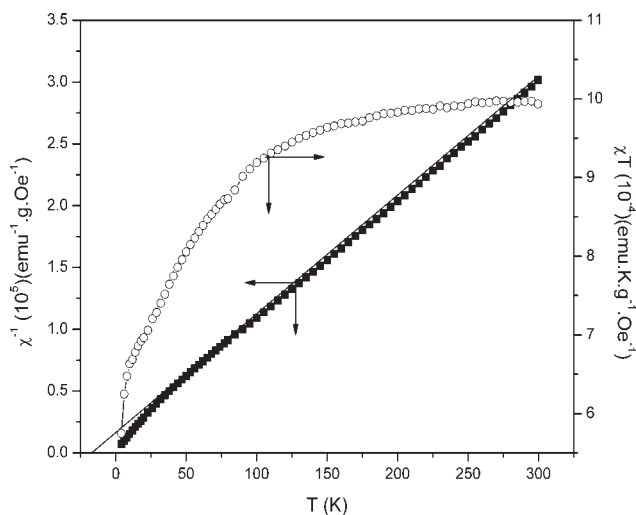
Figure 9 The product of magnetic susceptibility (χ) and temperature (T), and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for DABT/PAA-Cu^{2+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law.

with the decreasing of temperature, indicating the existence of strong antiferromagnetic coupling between the spins of the organic chains. The negative Curie–Weiss temperature ($\theta = -15.8$ K) also indicates the supramolecular powder DABT/PAA-Cu^{2+} is an antiferromagnet. But the curve fashion is different to that of the typical antiferromagnet. It is well known that the reciprocal magnetic susceptibil-

ity (χ^{-1}) of a typical antiferromagnet increases with the temperature decreases under the condition of $T < T_N$ (Neel temperature). On the contrary, the value χ^{-1} for the DABT/PAA-Cu^{2+} powder decreases obviously with temperature decreasing at low temperature range ($T < 50$ K). The phenomenon shows that the supramolecular DABT/PAA-Cu^{2+} powder is a special antiferromagnet, also known as a ferrimagnet.[35] Thus, the same polymeric matrix coordinating with different metal ions could provide different magnetic properties is a very interesting challenge and further investigations are in progress.

At low temperature, the magnetization curve as function of applied field exhibits a hysteresis loop for DABT/PAA-Ni^{2+} complex (Fig. 10), which is characteristic of ferromagnetic interactions. From the typical S shape and small area of hysteresis loop ($H_c = 18.9$ Oe, $M_r = 0.0162$ emu/g) it can be deduced that DABT/PAA-Ni^{2+} is a soft ferromagnet.

CONCLUSIONS

The supramolecular polymer DABT/PAA and the corresponding metal complexes were synthesized and characterized successfully for the first time. The driving force changes from hydrogen bonding to electrostatic interaction for the supramolecular polymer and the metal complexes, respectively. And the metal content of complexes is very high. From the field and temperature dependence of magnetization
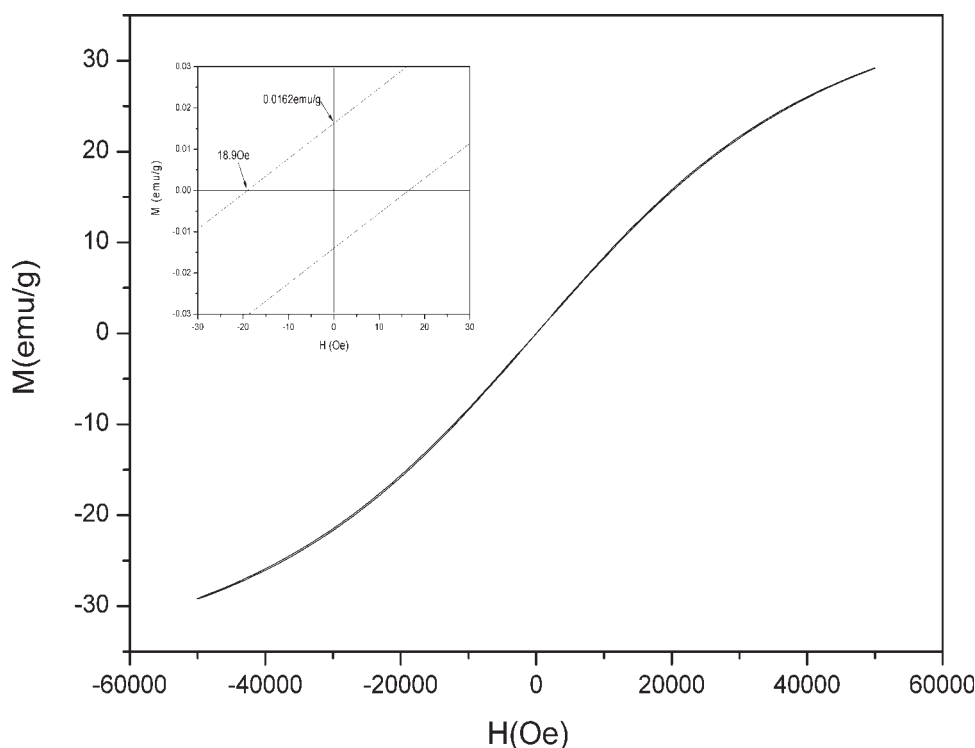

Figure 10 Hysteresis loop (M versus H) at 4 K for DABT/PAA-Ni^{2+}. (inset) Enlarged view of the region from -30 to 30 Oe.

and hysteresis loop, it can be concluded that DABT/PAA-Ni^{2+} is a soft-ferromagnet, whereas DABT/PAA-Cu^{2+} is a soft-ferrimagnet at low temperature. It is noteworthy that a fairly high value of relative saturation magnetization ($M_s = 29.22$ emu/g) was observed for DABT/PAA-Ni^{2+}. The results imply that the different interactions in polymer and the different metal ions can infect the alignment of adjacent paramagnetic spins and then induce different magnetic phenomena. The multilayer thin films assembled on quartz substrate were also prepared and characterized by UV–vis and AFM spectra. The studies of the magnetic properties of these supramolecular polymer complexes will not only contribute to the research concerning the relationship of structure and magnetism, but also provide some useful information for the novel functional materials with electric and magnetic properties.

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