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Layer-by-layer self-assembly for controlled magnetic multilayer thin film fabrication

Abstract: The copolymer poly[4'-(4-methacryloylphenyl)-2,2':6',2''-terpyridine-co-*N*-(vinylbenzylimino)-diacetic acid] [P(mPhtpy-co-vbda)] was synthesized by the RAFT (reversible addition fragmentation chain transfer) polymerization method and confirmed by Fourier transform infrared spectroscopy and ^1H nuclear magnetic resonance spectroscopy. The bimetallic complexes of the copolymer were prepared by chelating with Nd^{3+} and Co^{2+} . The magnetic multilayer film was fabricated via layer-by-layer (LbL) self-assembly with the copolymer and metal ions (Nd^{3+} and Co^{2+}). Attenuated total reflectance-infrared spectroscopy and UV-Vis spectroscopy were used to characterize the film, indicating that the driving force for fabricating the multilayer film was the coordination interaction. The magnetic behavior of the complexes and the film was measured as a function of the magnetic field strength (0–50 kOe) at 5 K and also of the temperature (5–300 K) at the magnetic field strength (30 kOe). The magnetic hysteresis loops of the complexes and the film showed the typical “S” shape at 5 K, exhibiting the properties of soft ferromagnetic materials.

Keywords: bimetallic complexes; copolymer; layer-by-layer self-assembly; magnetic properties; multilayer film.

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1 Introduction

The layer-by-layer (LbL) assembly technique, which was developed by Decher (1) in the early 1990s, is a very

simple, efficient and inexpensive method for various fabrications of inorganic layer materials, colloid particles, multi-ionic small molecules and even proteins (2). Specifically, this technique can be used for the controlled fabrication of multilayer films based on driving forces such as electrostatic, H-bonding attraction, coordination force, charge-transfer interaction, etc. A well-established LbL multilayer film can be used with various substrates such as gold, quartz, glass, silicon, germanium, platinum and clay (3).

Magnetic polymer-metal complexes have always appealed to polymer scientists. The selected metal ions, the polymer ligand and the interaction between them respectively play important roles on the final magnetic properties. The key to obtaining an ideal magnetic polymer-metal complex is to make a complex gathered and directional arrangement. Thus, the LbL assembly technique is one of the most advanced techniques to fabricate polymer-metal complex layered thin films with precise control of film thickness and composition (4), to make such complex more effective.

2,2':6',2''-Terpyridines, which were firstly synthesized by Morgan and Burstall (5) in the 1930s, have gained much attention due to their strong coordination ability as N-donor ligands capable of coordinating with numerous main-group, transition-metal and lanthanide cations. Their complexes exhibited distinct electrical (6), optical (7), magnetic (8) and catalytic (9) properties, giving them widespread applications in such fields as biomedical sciences (10), light-emitting electrochemical cells (LECs) (11), light-to-electricity conversion (12), etc. Furthermore, they have been used as basic components for fabricating self-assembled functional materials with nanostructures (e.g., based on gold, silver, CdS, TiO_2 , carbon nanotubes) (13–17) as well as surfaces (e.g., glass, gold, graphite) (18–20). With the development of supramolecular chemistry in recent years, the coordinative interaction between metal ions and terpyridinyl ligands has been applied to prepare well-designed supramolecular (co)polymers with various promising properties (21, 22). However, among the great number of 2,2':6',2''-terpyridines and their structural analogs, the magnetic properties of terpyridine-containing LbL multilayer thin films have been seldom reported. In this paper, we report the preparation of a copolymer

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containing a terpyridinyl ring (as an N-donor ligand) and an iminodiacetic acid (as an O-donor ligand) (23, 24) as well as its bimetallic complexes. We also fabricated a multilayer thin film with the copolymer and metal ions (Nd^{3+} and Co^{2+}) via the LbL assembly process and investigated its properties. Such magnetic multilayer thin film shows a great promise in preparing delicate magnetic devices under a complicated environment. Compared with magnetic complexes, e.g., supramolecular complexes, metal complexes containing bithiazole rings, and hyperbranched polymers containing bithiazole (25–28), the film is well organized with magnetic properties, which is significant for the development of organic magnetic applications.

2 Experimental

2.1 Materials

N,N-Dimethylformamide (DMF, laboratory suppliers) was dried using CaH_2 for several days and distilled prior to use. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was purchased from Aladdin Reagent (Shanghai, China). 2,2'-Azobisisobutyronitrile (AIBN, Aladdin Reagent, Shanghai, China) was recrystallized twice with ethanol. The HDPE substrate (29), PE-COOH film (2), cumyl dithiobenzoate (CDB) (30) and neodymium trichloride hexahydrate ($\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$) (31) were synthesized as reported.

2.2 Measurements

A Bruker Vector 22 Fourier transform infrared spectrometer (Bruker, Germany) was used to record the IR spectra in KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance AMX-400NMR instrument (Bruker, Germany) in deuterated reagent with tetramethylsilane (TMS) as an internal standard. Elemental analysis for C, H and N was performed using a Flash EA 1112 element analyzer (Thermo Finnigan, Italy). Attenuated total reflectance infrared spectra were collected using a NicoQt 6700 spectrometer (Thermo Fisher scientific LLC, USA) equipped with an attenuated total reflectance (ATR) accessory. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 1525/2414, Singapore) using THF as the eluent. Polystyrene standards were used to generate a calibration curve. The UV-Vis absorption spectra were obtained on a UV-1601

UV-Visible spectrophotometer (Varian, Co., USA). The metal (Nd, Co) contents were measured by an IRIS Intrepid II XSP inductively coupled plasma emission spectrometer (ICP, Thermo Scientific, USA). The magnetic properties of the complexes and the multilayer film were determined using a physical property measurement system (PMMS) magnetometer (PPMS-9T, Quantum Design, USA).

2.3 Synthesis of 4'-(4-methacryloylphenyl)-2,2':6',2''-terpyridine (mPhtpy)

4'-(4-Methacryloylphenyl)-2,2':6',2''-terpyridine was synthesized according to the literature (32) and presented as a yellow needle crystal. The yield was 0.67 g (85%). m.p. 150–151°C. ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 2.11 (s, 3H, CH_3), 5.84 (s, 1H, CH_2), 6.41 (s, 1H, CH_2), 7.31 (d, 2H, ph-H), 7.38 (t, 2H, py-H), 7.91 (t, 2H, py-H), 7.97 (d, 2H, ph-H), 8.72 (m, 6H, py-H); ^{13}C NMR (100 MHz, CDCl_3 , δ , ppm): 19.09, 119.46, 122.09, 122.82, 124.57, 128.21, 129.11, 136.53, 137.67, 149.71, 150.04, 152.38, 156.61, 166.36; FTIR (KBr): $\nu=2925$ –3061, 1730, 1634, 1605, 1584, 1567, 1512, 1469, 1417, 1386, 1214, 1174, 1128, 1038, 875, 788, 729, 660 and 512 cm^{-1} ; Anal. Calcd. for $\text{C}_{25}\text{H}_{19}\text{N}_3\text{O}_2$ (%): C, 76.34; N, 10.69; H, 4.83; found: C, 75.98; N, 10.42; H, 4.80.

2.4 Synthesis of *N*-(vinylbenzylimino) diacetic acid (vbda)

N-(Vinylbenzylimino) diacetic acid was prepared according to the literature (33) and presented as white clusters of needles. Yield: 20%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 3.49 (s, 4H, CH_2), 3.81 (s, 2H, CH_2), 5.23 (d, 1H, CH_2), 5.81 (d, 1H, CH_2), 6.72 (m, 1H, CH), 7.31 (d, 2H, ph-H), 7.42 (d, 2H, ph-H), 12.33 (s, 2H, COOH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ , ppm): 58.81, 62.03, 119.11, 131.26, 134.15, 141.25, 141.66, 143.73, 177.50; FTIR (KBr): $\nu=3429$, 2969–3053, 1713, 1635, 1512, 1461, 1408, 1346, 1181, 1108, 961, 879, 831, 675 and 533 cm^{-1} ; Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_4$ (%): C, 62.65; N, 5.62; H, 6.02; found: C, 62.88; N, 5.58; H, 6.01.

2.5 Synthesis of copolymer P(mPhtpy-co-vbda)

The copolymer was synthesized by the RAFT (Reversible Addition Fragmentation chain Transfer) polymerization method. CDB (10.9 mg, 0.04 mmol), AIBN (2.2 mg, 0.0133 mmol), mPhtpy (0.786 g, 2.0 mmol), vbda (0.498 g,

2.0 mmol) and DMF (8 ml) were placed in a dry glass ampoule, and the solution was degassed by three freeze-evacuate-thaw cycles. The polymerization was conducted at 70°C for 24 h. After rapid cooling by ice water, the mixture was precipitated in a large excess of ethanol and isolated by filtration. The yield was 88.1%. ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 0.85–2.33 (m, 8H, CH, CH₂, CH₃), 3.36 (s, 4H, CH₂), 3.75 (s, 2H, CH₂), 7.17–9.03 (m, 18H, py-H, ph-H), 12.41 (s, 2H, COOH); FTIR (KBr): ν=3431, 2932–3059, 1745, 1603, 1586, 1568, 1509, 1469, 1443, 1418, 1389, 1209, 1169, 1094, 991, 792, 744, 688 and 518 cm⁻¹. The number average molar mass (*M*_n) and polydispersity (PDI) obtained in THF (1.0 ml/min) of the carbonyl groups were converted to methoxycarbonyl units with dicyclohexylcarbodiimide and 4-dimethylaminopyridine. GPC (THF): *M*_w=12818, *M*_n=11627, PDI=1.10.

2.6 Preparation of the bimetallic complexes P(mPhtpy-co-vbda)-Nd³⁺-Co²⁺

The bimetallic complexes were prepared as follows.

Method 1: The copolymer, NdCl₃·6H₂O and CoCl₂·6H₂O (molar ratio 1:1:1) were dissolved in DMF to a 10% concentration and stirred at 80°C under argon atmosphere for 24 h. The copolymer complex was precipitated by the addition of diethyl ether to the solid-liquid phase mixtures. The precipitate was isolated by filtration and washed with deionized water until the metal ions were removed and then dried at 60°C for 24 h in a vacuum oven. The yield was 61.7%. Co content: 5.84%; Nd content: <0.1%.

Method 2: The copolymer and NdCl₃·6H₂O (molar ratio 1:1) were dissolved in DMF to a 10% concentration and stirred at 80°C under argon atmosphere. After 24 h, the DMF solution of CoCl₂·6H₂O (molar ratio with copolymer 1:1) was injected into the mixture via a syringe and stirred for another 24 h. The precipitate was obtained as above. The yield was 63.4%. Co content: 5.81%; Nd content: 2.47%.

Comparing the two methods, it was found that the higher metal content of method 2 was the better approach to synthesize bimetallic complexes.

2.7 Fabrication of the multilayer film [P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺]_{20x3}

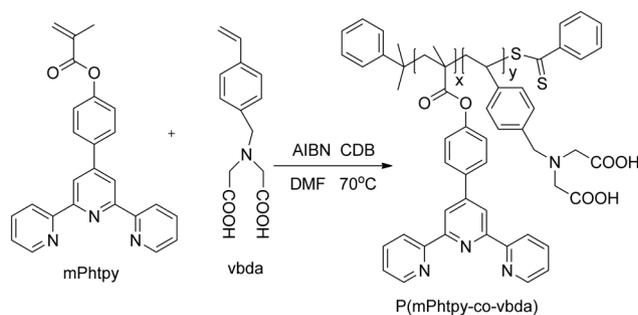
Based on method 2, the multilayer film of P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺ was prepared as follows. NdCl₃·6H₂O

(0.1 g) and CoCl₂·6H₂O (0.1 g) were, respectively, dissolved in H₂O (100 ml) to a concentration of 1 mg/ml. P(mPhtpy-co-vbda) (0.2 g) was prepared in DMF to a concentration of 2 mg/ml. All procedures were carried out at room temperature. Freshly cleaned PE-COOH substrate was first immersed into the DMF solution of P(mPhtpy-co-vbda) for 20 min and then rinsed three times with DMF for 3 min each time and dried by airflow. The P(mPhtpy-co-vbda)-deposited substrate was dipped into the aqueous solution of NdCl₃ for 20 min and rinsed three times with deionized water for 3 min each time and dried by airflow. The substrate was immersed into the aqueous solution of CoCl₂ for 20 min, then rinsed three times with deionized water for 3 min each time and dried by airflow. An alternating [P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺]_{20x3} multilayer film can be obtained by repeating these three steps in a cyclic fashion for 20 times. Co content: 2.75%; Nd content: 19.54%. ATR-IR: ν=3414, 1745, 1647, 1545, 1509, 1469, 1389, 1215, 1169, 1094, 1015, 792 and 744 cm⁻¹.

3 Results and discussion

3.1 Synthesis of mPhtpy and the vbda monomers

The monomers were successfully prepared by the synthetic routes outlined in Scheme 1. ¹H NMR and ¹³C NMR spectra were used to identify the structures of the monomers. As can be seen in the ¹H NMR spectra (Figure 1A), the single peak at 2.06 ppm is attributed to CH₃ and the other two peaks at 5.84 and 6.41 ppm belong to the protons of the vinyl groups (CH₂=C) of mPhtpy. For vbda (Figure 1B), the resonance signal peaks at 5.23, 5.81 and 6.72 ppm belong to the vinyl groups (CH₂=CH), and the characteristic peak at 12.33 ppm is attributed to the carboxyl groups



Scheme 1 Synthetic route of the copolymer.

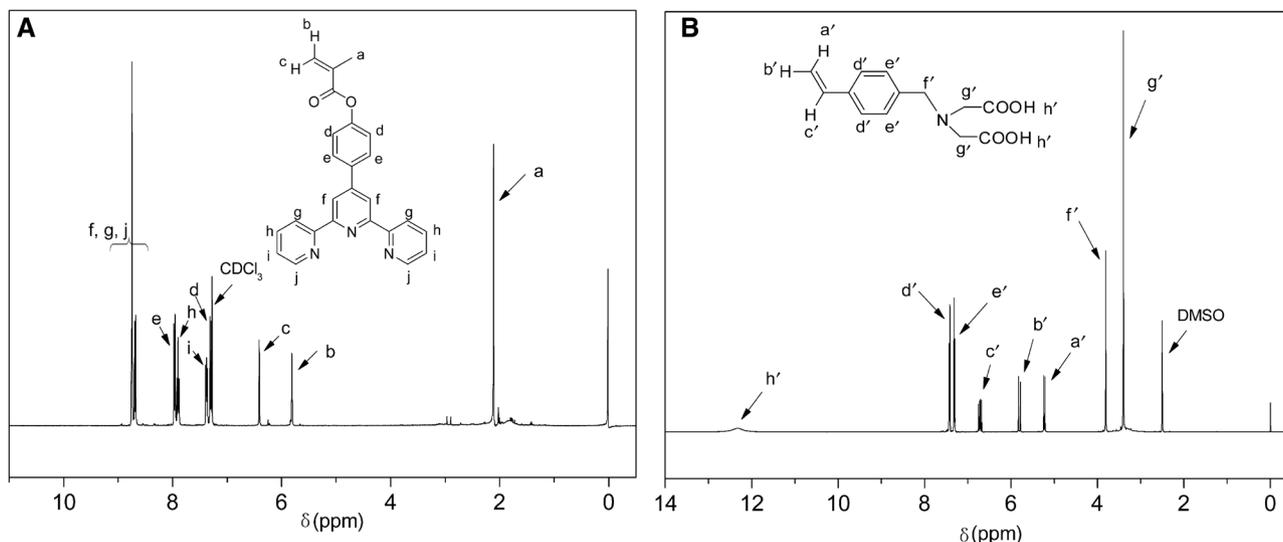


Figure 1 ^1H NMR spectra of mPhtpy (A) and vbda (B).

(COOH). Figure 2 shows the ^{13}C NMR spectra of the monomers mPhtpy and vbda. For mPhtpy (Figure 2A), the peaks at 19.09 ppm (C^{a}) and 128.21 ppm (C^{c}) are attributed to the methyl carbon and methylene carbon of methacrylate, respectively. The peak at 136.53 ppm (C^{b}) belongs to the carbon of the double bond adjacent to the carbonyl group, whereas the peak at 166.36 ppm (C^{d}) is attributed to the carbonyl group. For vbda (Figure 2B), the peaks at 119.11 ppm ($\text{C}^{\text{a}'}$) and 146.66 ppm ($\text{C}^{\text{b}'}$) belong to the methylene carbon and methine carbon of vinyl, respectively. The peak at 177.50 ppm ($\text{C}^{\text{c}'}$) is attributed to the carbonyl groups. These results indicate that the monomers were successfully synthesized.

3.2 Synthesis of the copolymer and polymeric bimetallic complexes

The synthesis of the copolymer is also shown in Scheme 1. The conversion of the monomers to a copolymer was confirmed by the FTIR and ^1H NMR spectra. In the ^1H NMR spectra of the copolymer (Figure 3A), the resonance peaks of the vinyl groups ($\text{CH}_2=\text{C}$ and $\text{CH}_2=\text{CH}$) at the range of 5.81–6.72 ppm disappeared completely. The characteristic peak of the carboxyl groups (COOH) shifted from 12.33 to 12.41 ppm. With the integration of the peaks for terpyridine and benzene rings of mPhtpy ($\text{e}''\text{-j}''$, k'' , l'' , q'' and r'' in Figure 3A) and the peaks for the

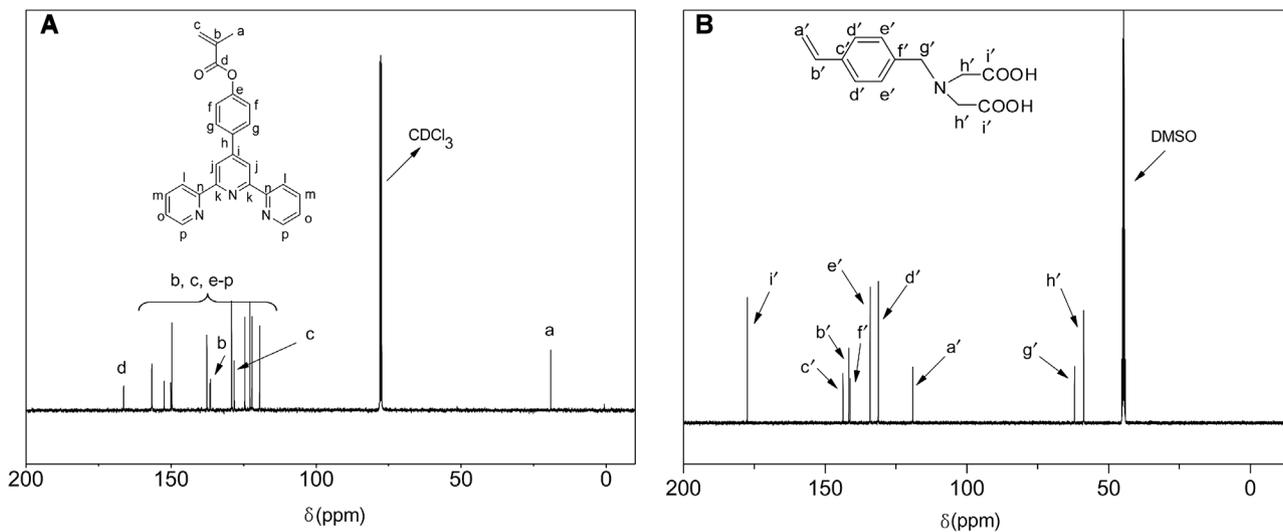


Figure 2 ^{13}C NMR spectra of mPhtpy (A) and vbda (B).

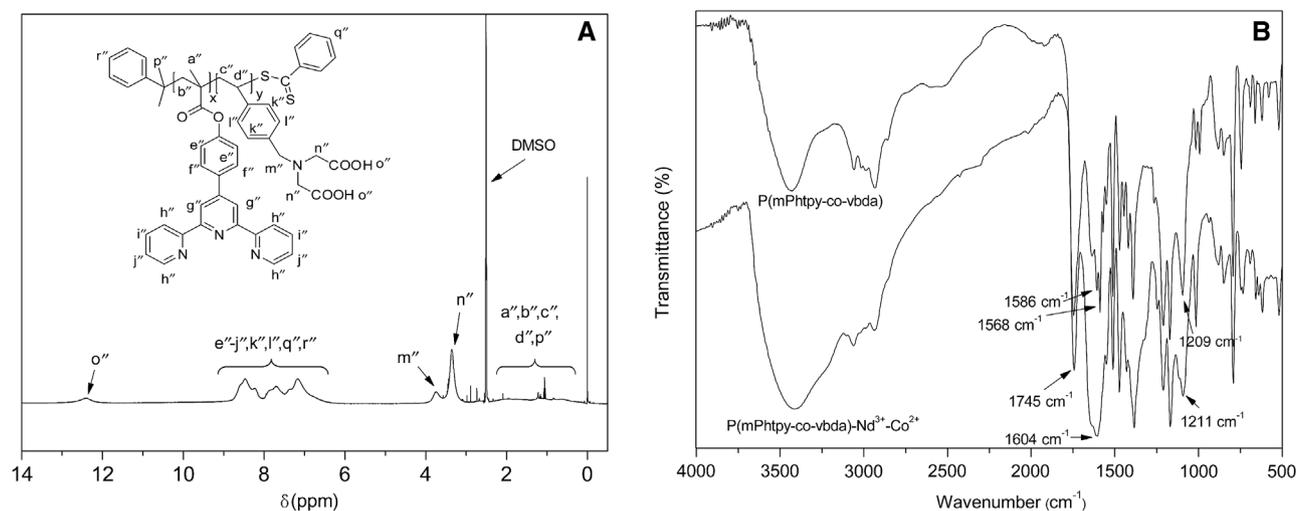
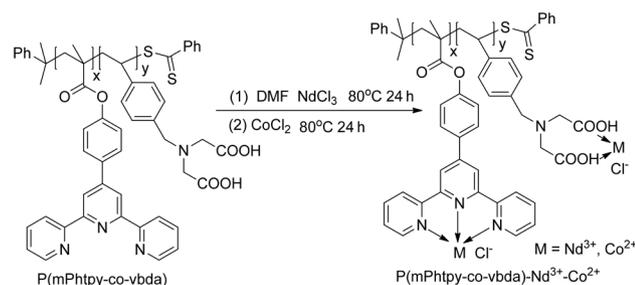


Figure 3 ^1H NMR spectrum of P(mPhtpy-co-vbda) (A). FT-IR spectra of P(mPhtpy-co-vbda) and P(mPhtpy-co-vbda)- Nd^{3+} - Co^{2+} (B).

carboxyl groups (o'' in Figure 3A) of vbda, the molar ratio of the mPhtpy and vbda in the random copolymer was calculated to be 2:1.

Based on the metal contents, the molar ratio of mPhtpy and vbda, as well as the structure of the copolymer, we proposed the possible formula in Scheme 2. The metal ions (Co^{2+} and Nd^{3+}) chelated with the nitrogen of the terpyridine ring to form a stable eight-member structure and also chelated with the carboxyl groups in P(mPhtpy-co-vbda)- Nd^{3+} - Co^{2+} , which is in agreement with the metal contents in the Experimental section. Figure 3B shows the FTIR spectra of the copolymer P(mPhtpy-co-vbda) and the bimetallic complexes P(mPhtpy-co-vbda)- Nd^{3+} - Co^{2+} . The vibration of the C=N bond of the terpyridine ring of the copolymer shifted from 1586 to 1604 cm^{-1} and changed to a broad peak for the complexes (34). The uncoordinated COO stretching band occurred at 1745 cm^{-1} in the copolymer, whereas the coordinated COO stretching band was at 1604 cm^{-1} for the complexes (35).



Scheme 2 Suggested structures of the bimetallic complexes.

3.3 Structural and optical characterization of the film

The multilayer film was characterized by UV-Vis and ATR-IR spectroscopy. The alternating deposition and optical features were monitored by UV-Vis spectroscopy. Figure 4A shows the UV-Vis absorption spectra of the multilayer film consisting of P(mPhtpy-co-vbda) and metal ions (Nd^{3+} and Co^{2+}) with different numbers of layers on a PE-COOH substrate. The optical density of the characteristic multilayer band at 287 nm is a function of layer numbers (linear correlation in Figure 4A, inset), indicating a constant number of layers at each stage. However, the linear correlation was an imperfection of the monolayer and the second layer absorption probably because of the H-bonding attraction of the initial deposition between the copolymer and the PE-COOH substrate (36) and of the instability of the coordination between the copolymer and the metal ions.

The covalent coordination (37) as a driving force for preparing the multilayer film was identified by ATR-IR spectroscopy. Figure 4B shows the ATR-IR spectra of the PE-COOH film and the multilayer films with different layers: $[\text{P(mPhtpy-co-vbda)/Nd}^{3+}/\text{Co}^{2+}]_{4 \times 3}$, $[\text{P(mPhtpy-co-vbda)/Nd}^{3+}/\text{Co}^{2+}]_{8 \times 3}$, $[\text{P(mPhtpy-co-vbda)/Nd}^{3+}/\text{Co}^{2+}]_{12 \times 3}$, $[\text{P(mPhtpy-co-vbda)/Nd}^{3+}/\text{Co}^{2+}]_{16 \times 3}$ and $[\text{P(mPhtpy-co-vbda)/Nd}^{3+}/\text{Co}^{2+}]_{20 \times 3}$. After the PE film was oxidized, the sample with an absorption peak of carboxyl at 1710 cm^{-1} exhibited the hydrophilic surface for assembly. All the ATR-IR spectra had similar peaks at 2917, 2849, 1473 and 731 cm^{-1} , which were attributed to the vibration of C-H of the polyethylene substrate. The peak at 1647 cm^{-1} was

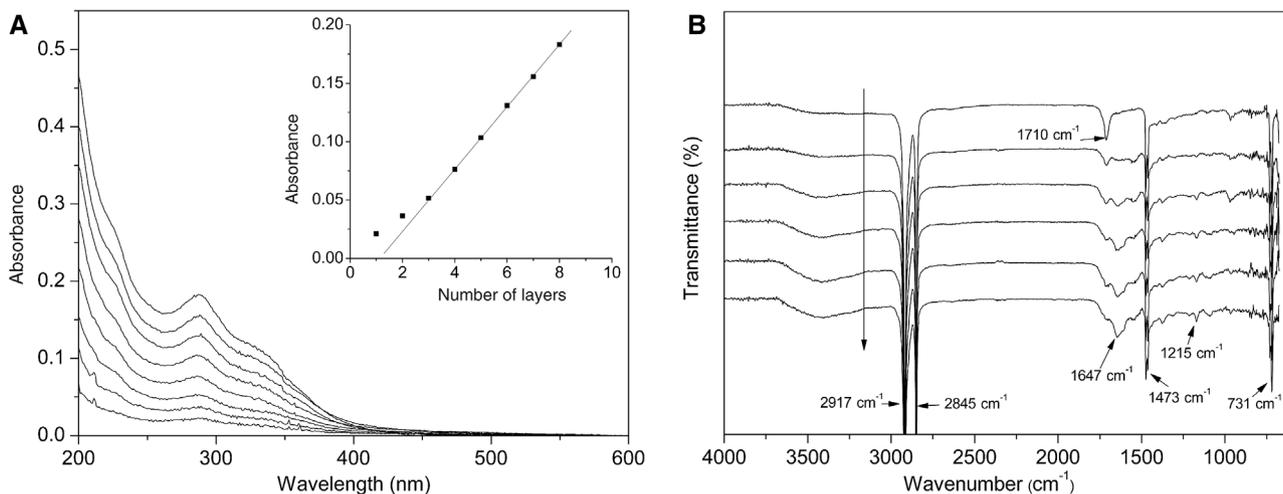


Figure 4 UV-Vis absorption spectra of one to eight layers (from the lower to the upper curves) of the multilayer film P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺. The inset shows the absorbance at 287 nm vs. the number of layers (A). ATR-IR spectra (from the upper to the lower curves) of PE-COOH having a clear carbonyl band at 1710 cm⁻¹ and the multilayer film [P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺]_{n×3} (n=4, 8, 12, 16, 20) being in the region from 700 to 4000 cm⁻¹ (B).

related to the terpyridinyl ring and carboxyl functional groups. The results showed that the peak at 1586 cm⁻¹ for the vibration of the C=N bond of the copolymer shifted to 1647 cm⁻¹ (34), whereas the uncoordinated COO stretching band at 1745 cm⁻¹ obviously shifted to 1647 cm⁻¹ after the coordination (35). Such shifts demonstrated that the ligands, the terpyridinyl and carboxyl groups, formed stable complexes with the metal ions (Nd³⁺ and Co²⁺). Compared with the FTIR spectrum of the complexes P(mPhtpy-co-vbda)-Nd³⁺-Co²⁺ (Figure 3B), the characteristic absorption peak of C=N and COO changed more remarkably because most of the ligands were coupled with Nd³⁺ and the rest were chelated with Co²⁺ in the assembly process. This is also consistent with the measurement of the metal contents.

3.4 Magnetic properties of the copolymer complexes and the thin film

The magnetic behaviors of the copolymer complexes and the thin film were determined by a PPMS magnetometer. Figure 5 shows the temperature dependence of the magnetization (*M*) of the complexes P(mPhtpy-co-vbda)-Nd³⁺-Co²⁺ and the film [P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺]_{20×3} at an applied magnetic field of 30 kOe from 5 to 300 K. For both the complexes and the film, positive magnetization decreased sharply as the temperature increased when it was below 50 K and then decreased slowly.

To obtain a complete information about the magnetization of the complexes P(mPhtpy-co-vbda)-Nd³⁺-Co²⁺ and the film [P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺]_{20×3}, the magnetic hysteresis loops were detected. Figure 6 shows the magnetic hysteresis loops of the copolymer complexes and the thin film at 5 K. The observed coercive field (*H_c*) of the complexes and the film was 1.7 and 0 Oe, respectively (Figure 6A and B inset). The remnant magnetization (*M_r*) of the complexes and the film was 0.03 and 0 emu/g, respectively. The similar “S” shape and such low *H_c* and *M_r* indicate that the complexes P(mPhtpy-co-vbda)-Nd³⁺-Co²⁺ and the film [P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺]_{20×3} were soft ferromagnetic materials.

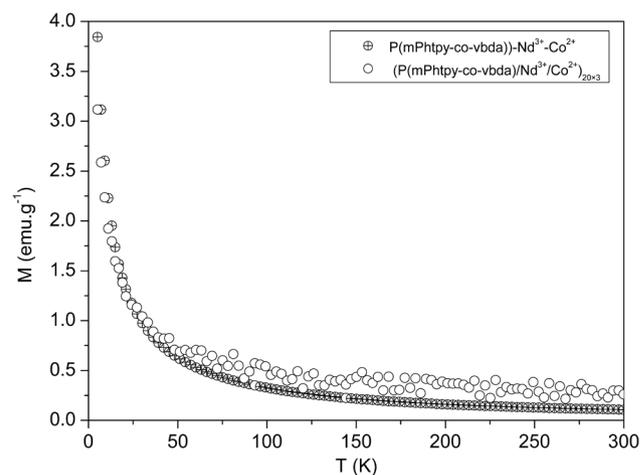


Figure 5 Temperature dependence of magnetization (*M*) for the complexes and the film at *H*=30 kOe.

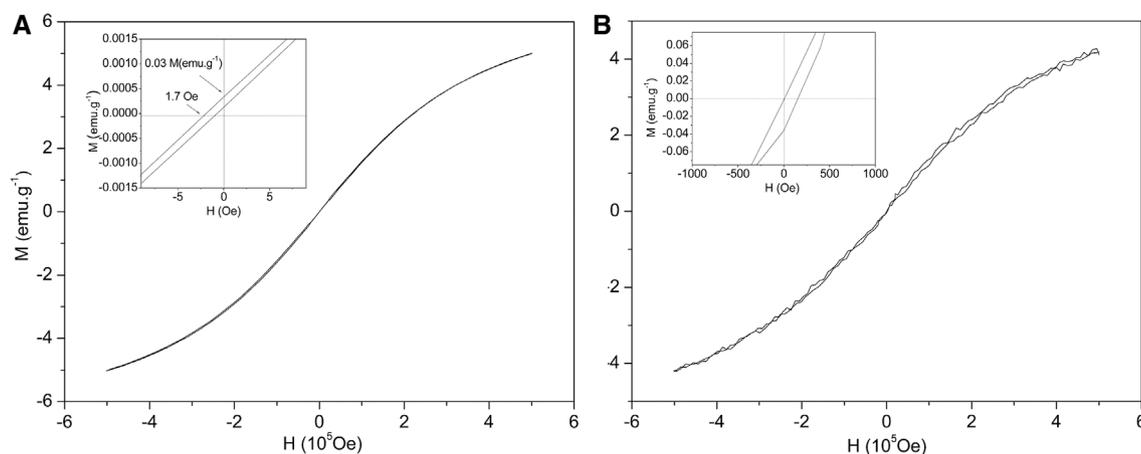


Figure 6 Hysteresis loop (M vs. H) at 5 K for the complexes (inset: expanded view of the region from -10 to 10 Oe) (A). Hysteresis loop (M vs. H) at 5 K for the film (inset: expanded view of the region from -1000 to 1000 Oe) (B).

4 Conclusions

In summary, we synthesized a copolymer P(mPhtpy-co-vbda) and its complexes P(mPhtpy-co-vbda)-Nd³⁺-Co²⁺ as well as prepared a magnetic multilayer thin film [P(mPhtpy-co-vbda)/Nd³⁺/Co²⁺]_{20×3} via the LbL self-assembly approach. The optical properties of the film were first investigated by ATR-IR and UV-Vis spectroscopy. Moreover, the low H_c and M_r and an “S”-shape hysteresis loop of the complexes and the film indicated that both the complexes and the film were soft ferromagnetic materials. It is expected that the magnetic multilayer thin film could be fabricated for delicate magnetic devices under a complicated environment.

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