

Designed Magnetic Multilayer Thin Films Fabricated via the Layer-by-Layer Assembly of Polycyanofullerenes

Jin Luo, Yanhua Wang, Rong Ren, Weilin Sun, Zhiquan Shen

Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Correspondence to: W. Sun (E-mail: opl_sunwl@zju.edu.cn)

ABSTRACT: The layer-by-layer self-assembly technique was used to fabricate a series of multilayer thin films with poly[4'-(4-methacryloylphenyl)-2,2':6',2''-terpyridine] (PmPhtpy), polycyanofullerenes, and transition metals (Ni^{2+} and Co^{2+}). The polymer PmPhtpy was prepared by free-radical polymerization, and this was confirmed by Fourier transform infrared (FTIR) and ^1H -NMR spectroscopy. The polycyanofullerenes, which were characterized by FTIR, ultraviolet–visible (UV–vis), and ^{13}C -NMR spectroscopy, was synthesized via the bromination of fullerene and then substitution with a nucleophilic reagent [potassium cyanide (KCN)]. The optical properties of the films were measured by attenuated total reflection infrared and UV–vis spectroscopy, and the results indicate that the driving force of the fabrication of the multilayer film was the coordination interaction. The magnetic behavior was examined as a function of the magnetic field strength at 5 K and the temperature (5–300 K). The magnetic hysteresis loops of the films showed a typical S shape at 5 K; this suggested soft ferromagnetic properties. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40681.

KEYWORDS: films; magnetism and magnetic properties; self-assembly

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INTRODUCTION

Fullerenes, which were first discovered in 1985 as a family of high-symmetric carbon cages,¹ have been widely used in the fields of electronics, magnetics, superconducting materials, medicine, biochemistry, electrochemistry, and photophysics because of their unique structure and conjugated electronic characteristics.^{2–8} To create such applications, extensive studies have been carried out to obtain fullerene thin films with two- and three-dimensionally ordered structures. Distinct methodologies have been used to form epitaxial films, such as Langmuir–Blodgett films,^{9–12} chemically self-assembled films,^{13,14} and sol–gel films.¹⁵ The layer-by-layer (LbL) assembly technique, which was originally reported by Iler¹⁶ in the 1960s, has been improved to be a versatile and powerful technique for fabricating layered thin films with precise control of the film thickness and composition.^{17,18} Since the first report of a uniform fullerene multilayer film prepared by the LbL assembly technique, some fullerene-containing films have been fabricated,^{19–24} but magnetic properties in fullerene-containing LbL multilayer thin films have seldom been reported. Up to this point, fullerene derivatives functionalized as magnetic materials are still organic small molecules.^{3,25,26}

In our previous work, Sun and coworkers^{27,28} fabricated several magnetic thin films containing transition-metal ions and polymers via an LbL assembly process. We found that the LbL assembly technique was an effective approach for preparing flexible magnetic thin films. In this article, we synthesized polycyanofullerenes containing cyan chelating groups with nice solubility in many polar solvents. Furthermore, we also fabricated three kinds of multilayer thin films with polycyanofullerenes, the polymer poly[4'-(4-methacryloylphenyl)-2,2':6',2''-terpyridine] (PmPhtpy) containing terpyridine chelating groups,²⁹ and different transition metals (Ni^{2+} and Co^{2+}) via the LbL assembly process and examined their magnetic properties. Compared with magnetic polymeric complexes,^{30–33} these films were well-ordered, flexible, and stable with different magnetic properties. This should promote the development of organic magnetic applications.

EXPERIMENTAL

Materials

N,N'-Dimethylformamide (DMF) was dried with CaH_2 for several days and distilled before use. Tetrahydrofuran (THF) was freshly distilled over sodium with benzophenone as an indicator. Fullerene (C_{60} , 99.5%), methacryloyl chloride (95%), and

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cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were purchased from Aladdin Reagent (China). Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was manufactured by Ningbo Chemical Reagent (China). 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice with ethanol. The high-density polyethylene (HDPE) sample, having a density of 0.962 g/cm^3 , was used as the substrate. Pellets were pressed into 0.02-mm-thick films at 170°C . The HDPE substrate,³⁴ polyethylene (PE)-COOH film,²⁷ and 4'-(4-hydroxyphenyl)-2,2':6',2''-terpyridine (HOPhtpy)³⁵ were prepared according to the literature.

Instrumentation

A Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer was used to record IR spectra in KBr pellets. Attenuated total reflection (ATR)-IR spectra were collected with a NicoQt 6700 spectrometer equipped with an ATR accessory. The molecular weights and molecular weight distributions were determined by gel permeation chromatography (Waters 1525/2414) with THF as the eluent. Polystyrene standards were used to generate a calibration curve. Ultraviolet-visible (UV-vis) absorption spectroscopy was conducted on a UV-1601 UV-vis spectrophotometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker Advance AMX-400 NMR instrument in a deuterated reagent with tetramethylsilane as the internal standard. The element analysis for C, H, and N was performed with a Flash EA 1112 element analyzer (Thermo Finnigan). The magnetic measurements were carried out by a physical properties measurement system (PPMS; PPMS-9T) magnetometer (Quantum Design). The measured amount of films used in the magnetic measurements was about 100 mg, and the curled films were held by a specific tube. The measured temperature ranged from 5 to 300 K, and the intensity of the magnetic field was measured from -50 to 50 kOe .

Synthesis of the Monomer 4'-(4-Methacryloylphenyl)-2,2':6',2''-terpyridine (mPhtpy)

HOPhtpy (0.65 g, 2.0 mmol) and triethylamine (0.20 mL, 2.2 mmol) were dissolved in DMF (10 mL), and methacryloylchloride (0.14 mL, 2.2 mmol) was added dropwise at 0°C to the solution. After the addition was complete, the mixture was stirred for another 12 h. Then, saturated NaHCO_3 (100 mL) was added to the mixture. The precipitate was isolated by filtration under washing with water (100 mL) and recrystallized from methanol. A yellow crystal needle crystal (mPhtpy) was obtained.

Yield: 0.67 g (85%), mp = $150\text{--}151^\circ\text{C}$. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 2.11 (s, 3H, CH_3), 5.81 (s, 1H, CH_2), 6.41 (s, 1H, CH_2), 7.30 (dd, J -couplings (J) = 6.9, 5.2 Hz, 2H, phenyl-H (ph-H)), 7.38 (t, 2H, py-H), 7.90 (t, 2H, pyridyl-H (py-H)), 7.96 (d, J = 8.5 Hz, 2H, ph-H), 8.71 (m, 6H, py-H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ): 19.09 (CH_3), 119.46, 122.09, 122.82, 124.57, 128.21 (CH_2), 129.11, 136.53, 137.67, 149.71, 150.04, 152.38, 156.61, 166.36 ($\text{C}=\text{O}$). FTIR (KBr): ν = 2925–3061 (m), 1730 (s), 1634 (w), 1605 (m), 1584 (s), 1567 (s), 1512 (s), 1469 (s), 1417 (m), 1386 (s), 1214 (m), 1174 (s), 1128 (s), 1038 (m), 875 (s), 788 (s), 729 (m), 660 (s), 512 cm^{-1} (m). 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%.

Synthesis of the Polymer PmPhtpy by Free-Radical Polymerization

Polymerization reactions were carried out in THF solution at 60°C with AIBN as a free-radical initiator. In a dried and degassed ampule, mPhtpy (1.572 g, 4 mmol) and AIBN (6.56 mg) were placed, degassed, flushed with nitrogen three times, and then sealed tightly. A volume of 5 mL of newly distilled THF was injected into with a syringe. The mixture was polymerized at 60°C for 24 h. The polymer PmPhtpy was precipitated in a large excess of diethyl ether and isolated by filtration. The resulting product was dried *in vacuo* at 50°C for 48 h.

Yield = 82.7%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 1.27–1.96 (m, 2H, CH_2), 2.51 (s, 3H, CH_3), 7.01–8.36 (m, 14H, py-H, ph-H). FTIR (KBr, ν): 2931–3504 (m), 1750 (s), 1645 (m), 1606 (m), 1585 (s), 1568 (m), 1509 (s), 1468 (m), 1416 (m), 1388 (m), 1206 (m), 1169 (s), 1110 (m), 1016 (m), 880 (w), 792 (s), 741 (m), 660 (w), 518 cm^{-1} (w). Gel permeation chromatography (THF): weight-average molecular weight = 19,144, number-average molecular weight = 14,107, and molecular weight distribution = 1.36.

Synthesis of the Polycyanofullerenes [$\text{C}_{60}(\text{CN})_x$ ($x \leq 24$)]

The $\text{C}_{60}\text{Br}_{24}$ was synthesized according to the literature³⁶ as a yellowish orange solid.

Yield: 0.34 g (86%). FTIR (KBr, ν): 1649 (w), 1245 (m), 1182 (w), 1086 (w), 1045 (m), 945 (m), 911 (m), 847 (s), 776 (s), 751 (w), 719 (w), 602 (w), 546 cm^{-1} (m). ANAL. Found: C, 25%; Br, 75% (on the basis of the $\text{C}_{60}\text{Br}_{27}$ composition).

$\text{C}_{60}\text{Br}_{24}$ (0.288 g, 1.0 mmol) and potassium cyanide (0.195 g, 30 mmol) were added to 20 mL of dried DMF. The mixture was stirred for 72 h and evaporated. The resulting sample was separated on a silica-gel column (DMF). The product of polycyanofullerenes was dried in a vacuum-dried box at 50°C for 48 h.

Yield = 0.121 g (90%). FTIR (KBr, ν): 2203 (s), 1656 (m), 1555 (m), 1491 (w), 1390 (w), 1096 (m), 803 (w), 545 cm^{-1} (m). $^{13}\text{C-NMR}$ (100 MHz, hexadeuterated dimethyl sulfoxide, δ): 55–68 (broad peak), 110–120 (broad peak), 130–160 (broad peak). UV-vis [$\text{CH}_3\text{CH}_2\text{OH}$ maximum wavelength (ϵ): 204 nm].

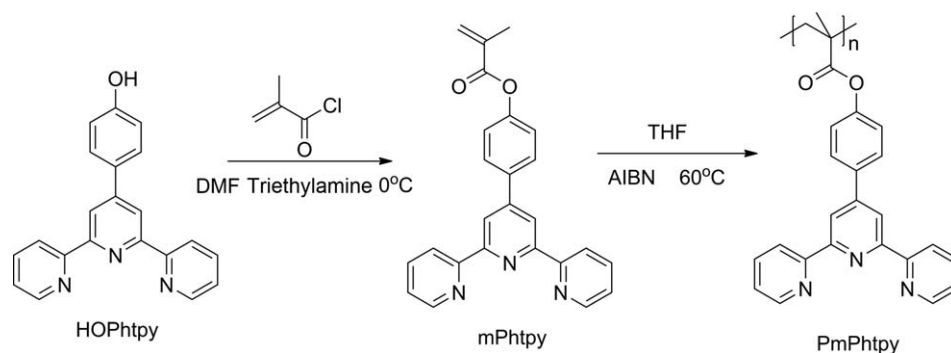
Preparation of the Multilayer PmPhtpy/ Ni^{2+} / $\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}$, PmPhtpy/ Co^{2+} / $\text{C}_{60}(\text{CN})_x/\text{Co}^{2+}$, and PmPhtpy/ Co^{2+} / $\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}$ Films

The experimental details for the preparation of the multilayer films are listed in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomer and the Polymer

The schematic synthetic procedures of the monomer and the polymer are demonstrated in Scheme 1. The monomer and the polymer were characterized by $^1\text{H-NMR}$ and FTIR spectroscopy, and the chemical shifts of the protons and the absorption peaks of the functional groups are displayed in the Supporting Information (Figures S1 and S2). For mPhtpy (Figure S1a), the single peak at 2.06 ppm belonged to CH_3 , and the other two peaks at 5.84 and 6.41 ppm belonged to the protons of the vinyl



Scheme 1. Synthetic route of the monomer and the polymer.

groups ($\text{CH}_2=\text{C}$). The FTIR spectra of the mPhtpy monomer showed two bands corresponding to the $\text{C}=\text{C}$ (1635 cm^{-1}) and $\text{C}=\text{O}$ (1730 cm^{-1} ; Figure S2). After polymerization, the characteristic peaks at 5.84 and 6.41 ppm of the vinyl groups ($\text{CH}_2=\text{C}$) disappeared completely (Figure S1b). The resonance signal peak at 1.27–1.96 ppm was attributed to the alkyl group (CH_2-C). The peak of the methyl protons shifted from 2.06 to 2.51 ppm. The absorption peaks at 1645 cm^{-1} could be assigned to the stretching vibrations of the $\text{C}=\text{N}$ bond (Figure S2). The absorption peak at 1635 cm^{-1} , which corresponded to the $\text{CH}_2=\text{C}$ groups, disappeared in PmPhtpy. The skeletal vibration of the carbonyl group ($\text{C}=\text{O}$) redshifted to 1750 cm^{-1} .

Figure 1 shows the ^{13}C -NMR spectrum of mPhtpy. The peaks at 19.09 ppm (C^a) and 128.21 ppm (C^c) were attributed to the methyl carbon and the methylene carbon of methacrylate, respectively. The peak at 136.53 ppm (C^b) was attributed to the carbon of the double bond adjacent to the carbonyl group, whereas the peak at 166.36 ppm (C^d) was attributed to the carbonyl group.

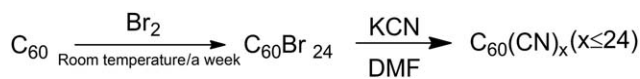
Synthesis and Characterization of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$)

The synthetic route of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$) is demonstrated in Scheme 2. Tebbe et al.³⁶ synthesized a highly symmetrical $\text{C}_{60}\text{Br}_{24}$ and characterized bromofullerenes by IR, Raman, and

single-crystal X-ray analysis. According to the method, we treated C_{60} with excess neat bromide and characterized the product using FTIR spectroscopy. As shown in Figure 2, the peaks at 1245, 1182, 1086, 1045, 847, 776, 546, and 527 cm^{-1} appeared in the curve; this was basically in accordance with the peaks reported in a previous article.³⁶

On the basis of the nucleophilic substitution reaction, $\text{C}_{60}\text{Br}_{24}$ reacted with the nucleophilic reagent potassium cyanide (KCN). The peak at 2170 cm^{-1} in the curve (Figure 2) was the characteristic absorption peak of the cyano groups. $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$) had an outstanding solubility in polar solvents (e.g., ethanol, acetone, THF, DMF, N, N'-dimethylacetamide, dimethyl sulfoxide) because of the introduction of polar groups ($-\text{CN}$) into the structure of C_{60} .

The ^{13}C -NMR spectrum of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$) is shown in Figure 3. Two broad peaks in the ranges 130–160 and 55–68 ppm belonged to sp^2 and sp^3 carbons, respectively, of C_{60} .³⁷ A broad peak at 110–130 ppm was attributed to the absorption of $-\text{CN}$ groups.^{38,39} Figure 4 shows the UV-vis spectrum of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$) recorded in ethanol. The strong absorption peak of the



Scheme 2. Synthetic route of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$).

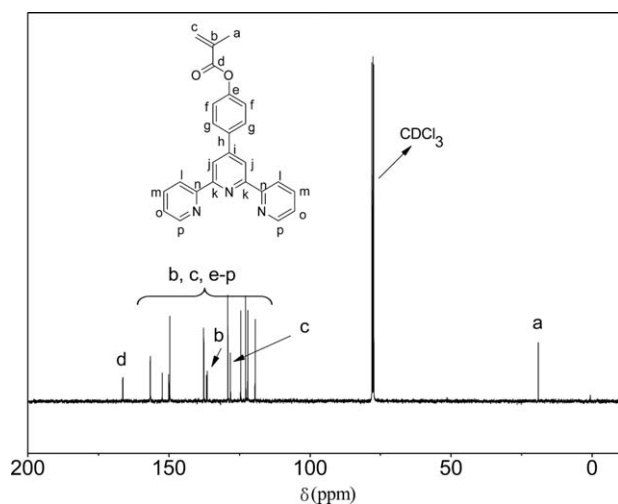


Figure 1. ^{13}C -NMR spectrum of mPhtpy.

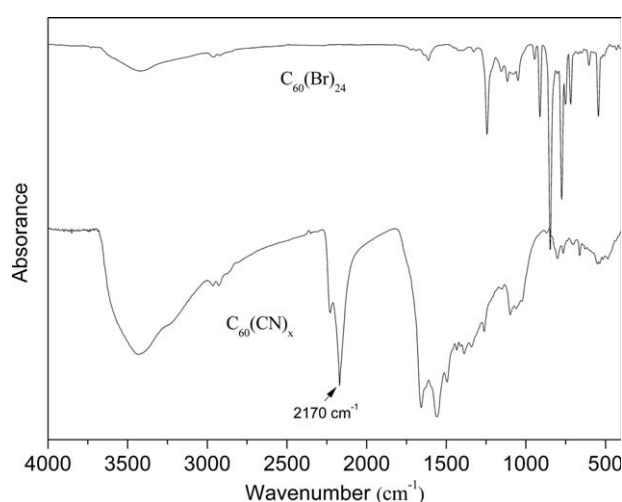


Figure 2. FTIR spectra of $\text{C}_{60}\text{Br}_{24}$ and $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$).

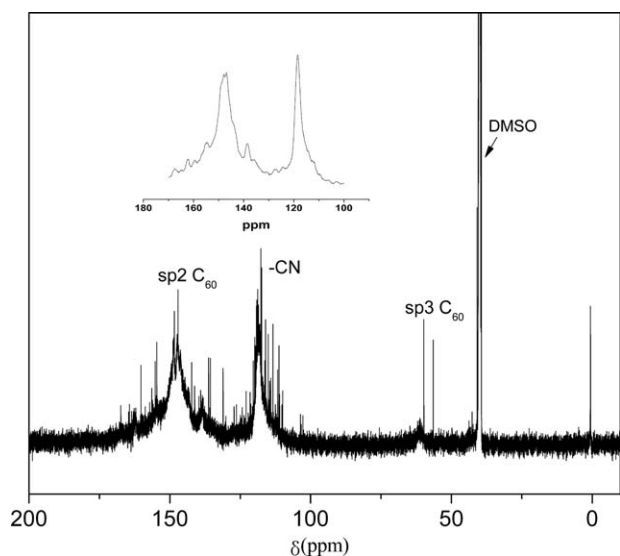


Figure 3. ^{13}C -NMR spectrum of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$). The inset shows an expanded and smoothed view of the region from 100 to 160 ppm.

compound was close to 204 nm with extended tailing in the visible region. The UV-vis spectrum of the compound containing fullerene had similar characteristic absorptions to those in the literature.⁴⁰

Structural and Optical Characterization of the Films

In the deposition process, the color of the film turned deeper as the number of layers increased. Figure 5 shows that the colorless oxidized polyethylene (PE-COOH) film gradually changed into a yellow multilayer film ($\text{PmPhtpy}/\text{Ni}^{2+}/\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}$) $_{n \times 4}$ (from left to right, $n = 6, 10$). The multilayer films were characterized by ATR-IR and UV-vis spectroscopy.

The driving force for the fabrication of the multilayer films, which was based on covalent coordination,⁴¹ was identified by ATR-IR spectroscopy. Figure 6 shows the ATR-IR spectra of the film PE-COOH and the multilayer films with different layers [$\text{PmPhtpy}/\text{Ni}^{2+}/\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}$] $_{n \times 4}$ ($n = 2, 4, 6, 8, \text{ and } 10$). The results illustrate that the intensity of the characteristic peaks

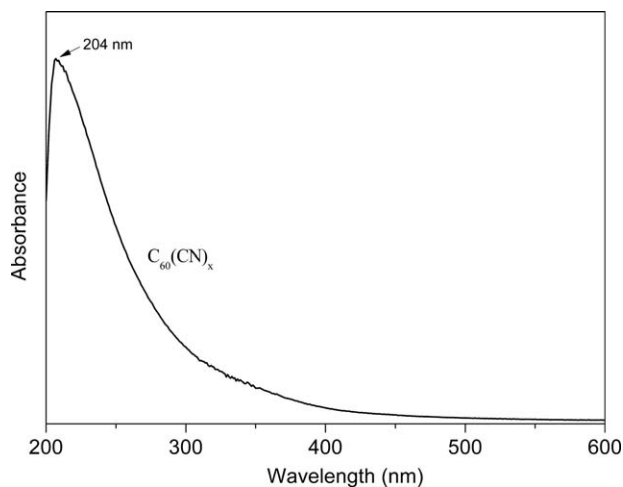


Figure 4. UV-vis spectrum of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$) recorded in ethanol.

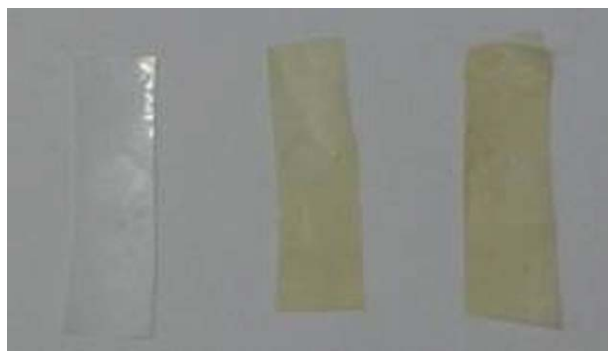


Figure 5. Photograph of the HDPE film and [$\text{PmPhtpy}/\text{Ni}^{2+}/\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}$] $_{n \times 4}$ ($n = 6$ and 10) magnetic multilayer films (from left to right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gradually increased with increasing layers and became more and more obvious. After the PE film was oxidized, the sample with an absorption peak of carboxyl at 1710 cm^{-1} provided a hydrophilic surface for assembly (Figure 6). Compared with the FTIR spectrum of the polymer PmPhtpy (Supporting Information, Figure S2), the vibration of the C=N bond of the terpyridine ring redshifted from 1645 to 1654 cm^{-1} , and the characteristic absorption of the carbonyl group (C=O) peak at 1750 cm^{-1} was unchanged. In addition, the characteristic absorption peak of the cyano group of the polycyanofullerenes also redshifted from 2170 to 2231 cm^{-1} . The phenomenon demonstrated that the ligands (terpyridine and cyano groups) formed stable complexes with the transition-metal ions. Similar changes were observed in the ATR-IR spectra of the ($\text{PmPhtpy}/\text{Co}^{2+}/\text{C}_{60}(\text{CN})_x/\text{Co}^{2+}$) $_{10 \times 4}$ and ($\text{PmPhtpy}/\text{Co}^{2+}/\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}$) $_{10 \times 4}$ films; the driving force was also the coordination interaction between the transition metals (Co^{2+} and Ni^{2+}) and the ligands (terpyridine and cyano groups) in the polymer PmPhtpy and $\text{C}_{60}(\text{CN})_x$.

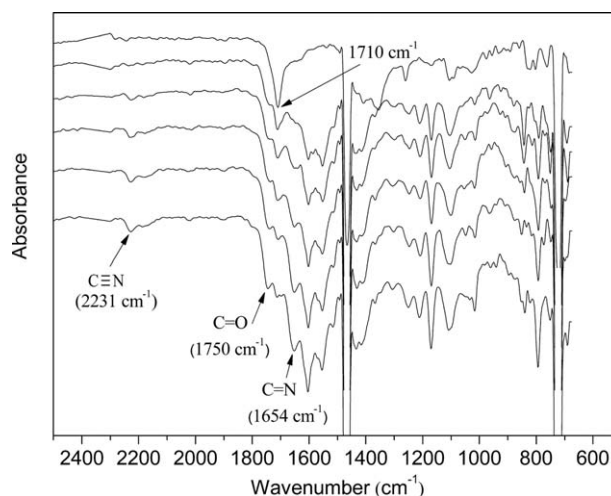


Figure 6. ATR-IR spectra of PE-COOH with a clear carbonyl band at 1710 cm^{-1} and [$\text{PmPhtpy}/\text{Ni}^{2+}/\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}$] $_{n \times 4}$ ($n = 2, 4, 6, 8, \text{ and } 10$) multilayer films in the region from 500 to 2500 cm^{-1} (from upper curves to lower curves).

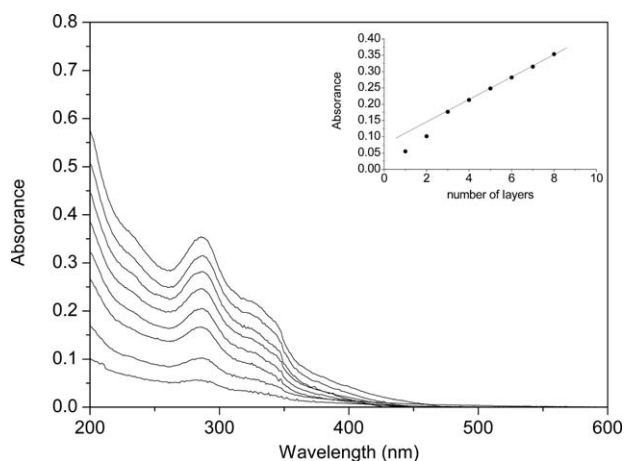


Figure 7. PmPhtpy/Ni²⁺/C₆₀(CN)_x/Ni²⁺ multilayer films with one to eight layers (from lower curves to upper curves) The inset shows the absorbance at 286 nm versus the number of layers.

UV-vis spectroscopy was used to monitor the assembly process of the eight-layer (PmPhtpy/Ni²⁺/C₆₀(CN)_x/Ni²⁺)_{10×4} multilayer thin films (Figure 7). The linear increase of the absorbance at 286 nm with increasing number of layers implied a relatively uniform assembly process of the multilayer film (Figure 7 inset). However, the linear correlation was incomplete with the monolayer and second layer absorption, probably because the interactions of the initial deposition (polymer and PE-COOH substrate) were H-bonding attraction⁴² and the instability of the coordination between the polymer, C₆₀(CN)_x, and metal ions. [PmPhtpy/Co²⁺/C₆₀(CN)_x/Co²⁺]_{10×4} and [PmPhtpy/Co²⁺/C₆₀(CN)_x/Ni²⁺]_{10×4} showed a similar trend to that of the multilayer film [PmPhtpy/Ni²⁺/C₆₀(CN)_x/Ni²⁺]_{10×4}. All of the results of these measurements verify that well-organized close-packed multilayer films were formed on the substrate PE film.

Magnetic Properties of the Multilayer Films

The magnetization of the films was examined by a PPMS magnetometer. The amount of each film used in the magnetic mea-

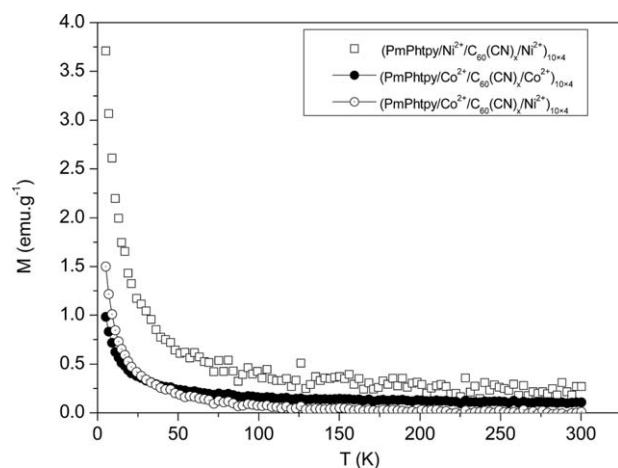


Figure 8. Temperature (T) dependence of magnetization (M) for the [PmPhtpy/Ni²⁺/C₆₀(CN)_x/Ni²⁺]_{10×4}, [PmPhtpy/Co²⁺/C₆₀(CN)_x/Co²⁺]_{10×4}, and [PmPhtpy/Co²⁺/C₆₀(CN)_x/Ni²⁺]_{10×4} films at magnetic field strength (H) = 30 kOe.

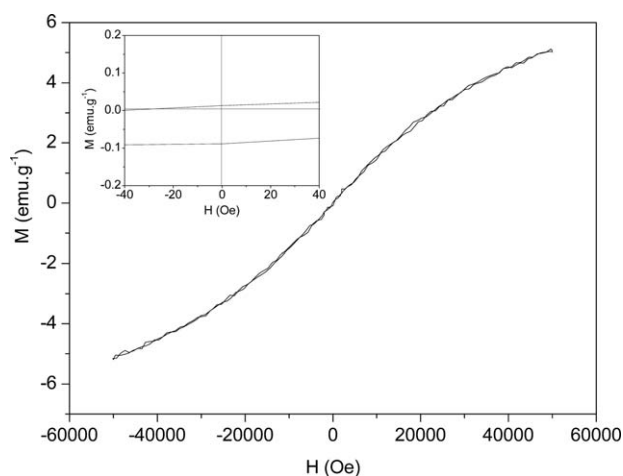


Figure 9. Hysteresis loop [magnetization (M) vs magnetic field strength (H)] at 5 K for the [PmPhtpy/Ni²⁺/C₆₀(CN)_x/Ni²⁺]_{10×4} multilayer thin film. The inset shows an expanded view of the region from -40 to 40 Oe.

surement was about 200 mg, and the films were held by a specific tube. From the previous experiments, we observed that the PE film showed diamagnetic properties because of the absence of paramagnetic sources.²⁷ Therefore, the diamagnetic PE substrate was deducted in the processing data. Figure 8 shows the temperature dependence of the magnetization of the films [PmPhtpy/Ni²⁺/C₆₀(CN)_x/Ni²⁺]_{10×4}, [PmPhtpy/Co²⁺/C₆₀(CN)_x/Co²⁺]_{10×4}, and [PmPhtpy/Co²⁺/C₆₀(CN)_x/Ni²⁺]_{10×4} at an applied magnetic field of 30 kOe from 5 to 300 K. The magnetization increased sharply as the temperature decreased below 50 K.

To obtain complementary information on the magnetization of the three multilayer thin films, the magnetic hysteresis loops showed their characteristics of ferromagnetic interactions at 5 K (Figures 9–11) and exhibited similar S shapes. The coercive field (H_c) and the remnant magnetization (M_r) of the three kinds of multilayer thin films were almost equal to zero. From the typical S shape and such low H_c and M_r values, we concluded that

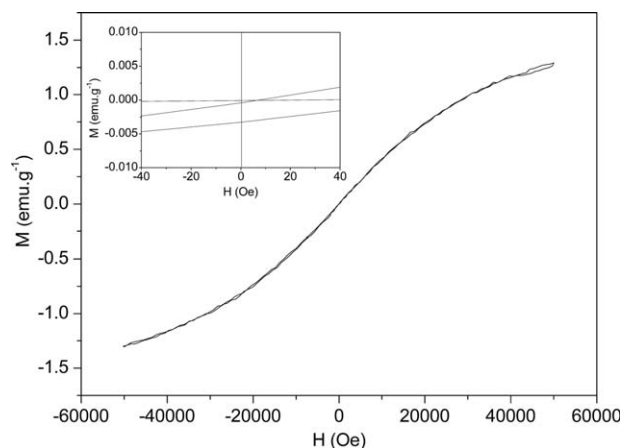


Figure 10. Hysteresis loop [magnetization (M) vs magnetic field strength (H)] at 5 K for the [PmPhtpy/Co²⁺/C₆₀(CN)_x/Co²⁺]_{10×4} multilayer thin film. The inset shows an expanded view of the region from -40 to 40 Oe.

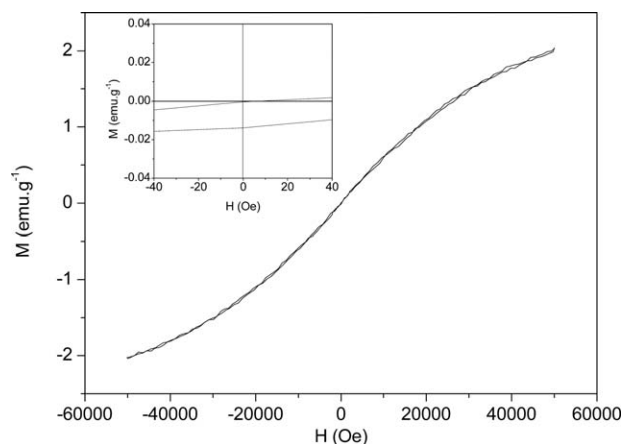


Figure 11. Hysteresis loop [magnetization (M) vs magnetic field strength (H)] at 5 K for the $[\text{PmPhtpy}/\text{Co}^{2+}/\text{C}_{60}(\text{CN})_x/\text{Ni}^{2+}]_{10 \times 4}$ multilayer thin film. The inset shows an expanded view of the region from -40 to 40 Oe.

the three kinds of multilayer thin films were soft ferromagnetic materials.^{27,28}

CONCLUSIONS

In summary, we prepared three kinds of magnetic multilayer thin films consisting of $\text{C}_{60}(\text{CN})_x$ ($x \leq 24$), the polymer PmPhtpy, and transition metals (Ni^{2+} and Co^{2+}) via LbL self-assembly and characterized them by UV-vis and ATR-IR spectroscopy for the first time. The magnetic properties of the films were studied. From the low H_c and M_r values and the S-shaped hysteresis loop of the films, we concluded that the films showed soft ferromagnetic properties. We not only studied the fabrication and magnetism of these multilayer thin films but also gleaned some useful information for the C_{60} -containing functional materials produced via the LbL assembly approach. This study demonstrated an effective and promising way to fabricate different C_{60} -containing functional films with various attractive properties. Furthermore, it is very promising for the fabrication of delicate magnetic devices under a sophisticated environment.

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