

# Synthesis and Luminescence Studies of Poly(Vinyl Acetate)–Eu (III) Coordination Compound

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**ABSTRACT:** In this research, the polymeric coordination compound of PVAc–Eu (III) was synthesized, and the formation of coordination bonding between Eu (III) and the carbonyl oxygen in PVAc was investigated by Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy (RS), and X-ray photoelectron spectroscopy (XPS). The luminescent characteristics/properties of the prepared PVAc–Eu (III) were studied using fluorescence spectroscopy (FS). The results indicated that (1) the interaction/association between PVAc and Eu (III) in the prepared PVAc–Eu (III) was coordination bonding instead of weak physical

adsorption, and (2) the photoluminescence intensity of PVAc–Eu (III) was approximately three times that of EuCl<sub>3</sub>. This research provided a theoretical foundation for the potential use of PVAc–Eu (III) as an innovative polymeric luminescent material, particularly for the applications in areas such as adhesives, coatings, textiles and others, the areas in which PVAc is an important raw material. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3617–3622, 2007

**Key words:** luminescence; fluorescence; Eu (III); poly(vinyl acetate); polymeric coordination compound

## INTRODUCTION

Research on polymeric coordination compounds can be both fundamental and applied, and has attracted increased attention. Polymeric coordination compounds, of which the desired properties may be inherited from both the coordinated metal ions and the polymeric ligands, have potential applications in many areas including, but not limited to, electromagnetics,<sup>1</sup> smart optoelectronics,<sup>2</sup> nonlinear optical devices,<sup>3</sup> and catalysis.<sup>4</sup>

The lanthanide metal ions are among the most interesting metal ions, because they usually exist as trivalent ions, in which their electron configurations are (Xe) 4f<sup>*n*</sup> with *n* varying from 1 (Ce<sup>3+</sup>) to 14 (Lu<sup>3+</sup>). The transitions of the f-electrons in different energy levels are responsible for the observed photoluminescent properties, which are favorable for sev-

eral kinds of applications. For example, the images of conventional televisions and computer screens have resulted from the luminescence of lanthanide metal ions. However, it is difficult to generate luminescence by direct photoexcitation of free lanthanide metal ions, because the ions are inefficient at absorbing and emitting light. In contrast, many lanthanide coordination compounds (complexes), which contain organic ligands, are capable of emitting strong and characteristic luminescence.<sup>5–7</sup> In the lanthanide complexes, the organic ligands with lone-pair and/or  $\pi$ -electrons can serve as the light absorbing chromophores. If the excited state of the attached organic ligand is energetically high enough and the collected energy can be transferred through the coordination bond to the lanthanide metal ion held nearby, the characteristic luminescence would be emitted. Compared with other luminescent materials, the lanthanide coordination compounds possess the following desired properties:

1. *Long luminescent lifetime:* Lanthanide complexes display luminescent lifetimes of several hundred microseconds, while the lifetimes of many other luminescent materials are typically on the order of nanoseconds.
2. *Visible luminescence:* Unlike other luminescent materials, most lanthanide complexes emit light in the visible region with a wavelength of > 500 nm.

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3. *Sharp luminescent peak*: Lanthanide complexes typically exhibit sharp luminescent peaks with half-widths within the range of 10–20 nm, which are much narrower than those of most other luminescent materials (usually > 50 nm).

In this research, Europium trivalent ion (Eu (III)) was selected to synthesize the coordination compound, because Eu (III) is well known for being able to emit strong and characteristic luminescence in the visible region.

Poly(vinyl acetate) (PVAc), widely used in adhesives, paints, textile sizing, and nonwoven binders, is one of the industrial polymers that can form polymeric coordination compounds. This is because the lone-pair electrons on the carbonyl oxygen in each repeating unit of PVAc can coordinate with lanthanide metal ions.<sup>8</sup> Compared with other organic ligands, PVAc is inexpensive and less toxic. Furthermore, PVAc is a synthetic thermoplastic that can be readily processed into different forms and shapes, such as emulsions, films, and fibers. Thus, the coordination compounds made from PVAc and lanthanide metal ions may be particularly useful for the applications in which both luminescent and other physical/mechanical properties are required, e.g., (1) special adhesives and/or paints with unique luminescent properties, and (2) the next generation of military apparel with specially designed light detectable/recognizable functions.

In the present research, the polymeric coordination compound of PVAc–Eu (III) was synthesized. The formation of coordination bonding between Eu (III) and the carbonyl oxygen in PVAc was investigated by Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy (RS), and X-ray photoelectron spectroscopy (XPS); and the luminescent characteristics/properties of the prepared PVAc–Eu (III) was studied by fluorescence spectroscopy (FS). The objective of this research was to study the synthesis and luminescent characteristics/properties of PVAc–Eu (III), and to provide a theoretical foundation for the potential applications of PVAc–Eu (III), particularly in the areas in which PVAc is an important raw material.

## EXPERIMENTAL

### Materials

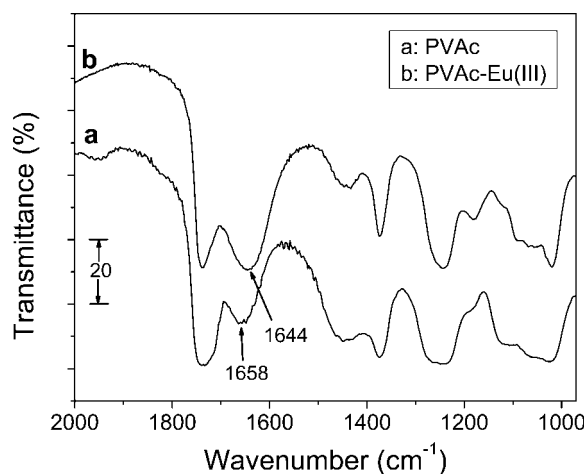
PVAc homopolymer with a number average molecular weight ( $M_n$ ) of approximately 170,000 g mol<sup>-1</sup> was obtained from WanWei Corporation (Chaohu, China). Reagent-grade Europium oxide (Eu<sub>2</sub>O<sub>3</sub>) with a purity of 99.99%, and other chemicals, including absolute ethanol and HCl, were purchased from Yue Long Chemical Company (Shanghai, China). The materials were used without further purification.

### Synthesis of PVAc–Eu (III)

To synthesize PVAc–Eu (III), 0.4 g Eu<sub>2</sub>O<sub>3</sub> was first converted to EuCl<sub>3</sub> by reacting with 10 mL HCl (3.0M) in a three-neck flask at the room temperature (~ 25°C). The flask was subsequently placed in an oil-bath to evaporate/remove the excess amount of hydrochloride and water. Then, 0.585 g PVAc and 100 mL absolute ethanol were added in the three-neck flask, and the flask was fitted with an overhead stirrer and a water-cooled condenser. After refluxing the mixture at 80°C for 4 h, it was poured into a glass Petri dish. After the solvent (absolute ethanol) evaporated, the film sample of PVAc–Eu (III) was obtained. In the prepared sample, the feed molar ratio of Eu (III) to the repeating unit of PVAc was 1 : 6. The sample had been kept in a vacuum oven (pressure: ~ 1 mm Hg, temperature: ~ 75°C) for ≥ 24 h before it was characterized/analyzed.

### Characterization of PVAc–Eu (III)

The samples of PVAc–Eu (III), as well as PVAc and EuCl<sub>3</sub> (for comparative purposes), were characterized/analyzed using the instrumentation of FTIR, RS, XPS, and FS. IR measurements were performed on a WQF-300 Fourier transform infrared spectrometer (Beijing Ruili Analytical Instruments, Beijing, China). The FTIR specimens were prepared by casting dilute PVAc–Eu (III) and PVAc solutions (with concentrations lower than 0.1 wt %) on KBr plates, using absolute ethanol as the solvent. The FTIR spectra were acquired by scanning the specimens with a resolution of 4 cm<sup>-1</sup> for 64 times in the wavenumber range of 400–4,000 cm<sup>-1</sup>. Raman spectra were recorded on a Renishaw Raman spectrometer (Renishaw Apply Innovation, Gloucestershire, UK) with a laser excitation wavelength of 514 nm. The same specimens used for FTIR were also used for RS. XPS analysis was performed on an ESCALab Mark II Electron Spectrometer (VG Scientific, East Grinstead, UK) with a magnesium and aluminum dual anode X-ray source. The binding energy of the aliphatic C 1s was set at 285 eV, and the spectra were offset accordingly to compensate for the shift as a result of the charging effect. The XPS specimens were made by simply cutting PVAc–Eu (III) and PVAc film samples into small pieces suitable for XPS characterization. Luminescence spectra were obtained from a Hitachi model F-4500 Fluorescence Spectrophotometer (Hitachi High-Technologies, Tokyo, Japan). In the luminescent characterization, 0.1M solutions of PVAc–Eu (III), PVAc and EuCl<sub>3</sub> in absolute ethanol were used as the specimens.



**Figure 1** FT-IR spectra of (a) PVAc and (b) PVAc-Eu (III). Spectra were offset for clarity.

## RESULTS AND DISCUSSION

### Formation of PVAc-Eu (III) coordination compound

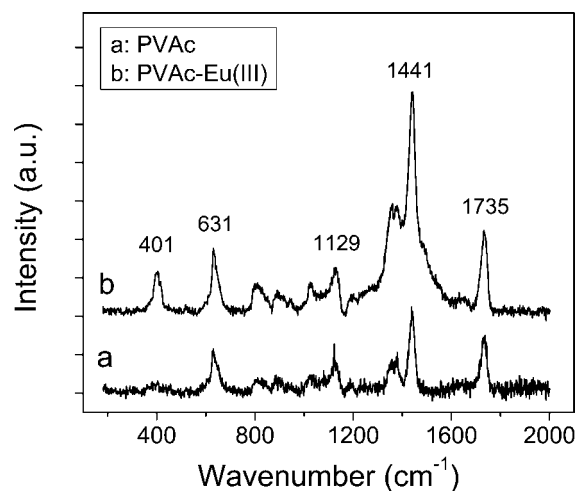
Coordination theory suggests that PVAc, with an electron-rich ester group in each repeating unit, could form coordination bonds with lanthanide metal ions. Nevertheless, little publication has been found in this area. In this research, the coordination compound of PVAc-Eu (III) was synthesized using the method described in the Experimental section; three types of instrumentation (i.e., FTIR, RS, and XPS) were employed to test the hypothesis that the interaction/association between PVAc and Eu (III) in the prepared PVAc-Eu (III) was actually coordination bonding instead of physical adsorption.

Figure 1 shows the acquired FTIR spectra of (a) PVAc and (b) PVAc-Eu (III). The most interesting difference between the two spectra occurred in the region of carboxylate asymmetric stretch [ $\nu_{as}(\text{O}=\text{C}-\text{O})$ ]. The  $\nu_{as}(\text{O}=\text{C}-\text{O})$  of PVAc was at approximately  $1658 \text{ cm}^{-1}$ , whereas the  $\nu_{as}(\text{O}=\text{C}-\text{O})$  of PVAc-Eu (III) was at approximately  $1644 \text{ cm}^{-1}$ . The absorption band of  $\nu_{as}(\text{O}=\text{C}-\text{O})$  shifted to lower wavenumbers for 14 wavenumbers, which indicated that coordination bonding between PVAc and Eu (III) was formed, as reported in the previous publication.<sup>9</sup> The reason for the shift was that the lone-pair electrons on the carbonyl oxygen in PVAc were donated to form the coordination bond. This reduced the electron density at  $\text{O}=\text{C}-\text{O}$  moiety and caused the absorption band of the  $\text{O}=\text{C}-\text{O}$  structure to shift toward a lower wavenumber. Additionally, Figure 1 also indicated that the intensity of the  $\nu_{as}(\text{O}=\text{C}-\text{O})$  band in PVAc-Eu (III) was almost the same as the intensity of the carbonyl stretching band

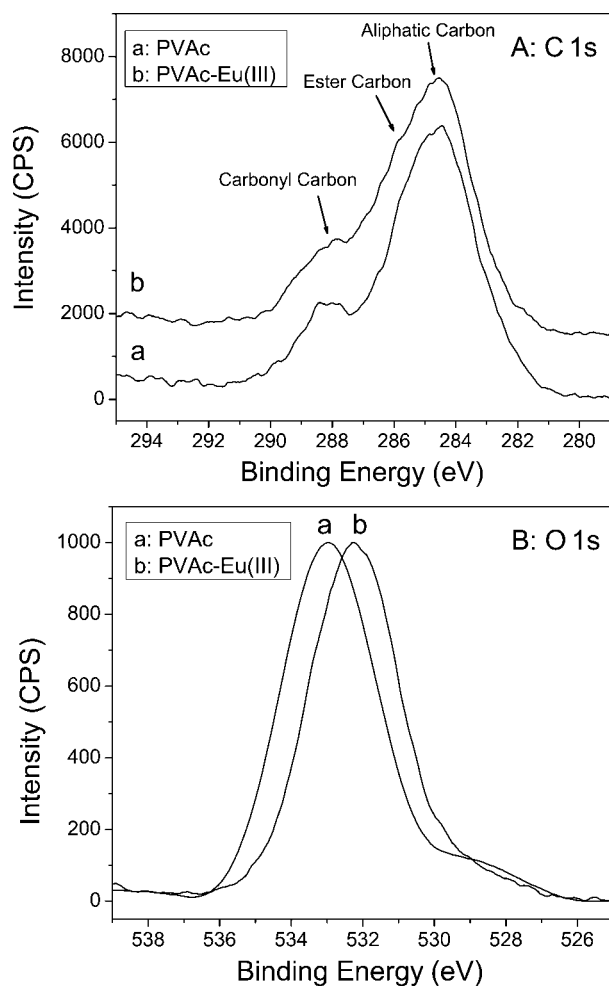
(approximately  $1737 \text{ cm}^{-1}$ ). However, the intensity of the  $\nu_{as}(\text{O}=\text{C}-\text{O})$  band in PVAc was much weaker than that of the carbonyl stretching band. Presumably, this was because the carbon-oxygen double bond structure was partially disrupted following the formation of coordination bonding, and this caused the absorption band of the carbonyl stretching to become weaker. Taken together, FTIR results suggested that the interaction/association between PVAc and Eu (III) in the synthesized PVAc-Eu (III) was coordination bonding instead of physical adsorption.

More convincing evidence for the formation of coordination bonding was obtained from the Raman spectra of (a) PVAc and (b) PVAc-Eu (III). As shown in Figure 2, peaks around  $631$ ,  $1129$ ,  $1440$  and  $1733 \text{ cm}^{-1}$  were characteristic Raman absorption bands of PVAc. The peak around  $401 \text{ cm}^{-1}$ , however, originated from the Eu (III)-O coordination bond. As reported previously,<sup>10,11</sup> the symmetric stretching of the Eu (III)-O coordination bond accounted for this notable Raman absorption at  $401 \text{ cm}^{-1}$ .

Further evidence for the formation of the Eu (III)-O coordination bond can be acquired from XPS spectra. Figure 3(A,B) show high-resolution XPS regions of C 1s and O 1s, respectively. In Figure 3(A), the C 1s regions of both (a) PVAc and (b) PVAc-Eu (III) consist of three components corresponding to three types of carbon atoms: the aliphatic carbon ( $\sim 285 \text{ eV}$ ), the ester carbon ( $\sim 286.5 \text{ eV}$ ), and the carbonyl carbon ( $\sim 288.5 \text{ eV}$ ). Compared with PVAc spectrum (curve a), the slight difference of the PVAc-Eu (III) spectrum (curve b) in the carbonyl region was due to the coordination of Eu (III) ions with the carbonyl groups. The formation of Eu (III)-O coordination bond affected the environment



**Figure 2** Raman spectra of (a) PVAc and (b) PVAc-Eu (III). Spectra were offset for clarity.



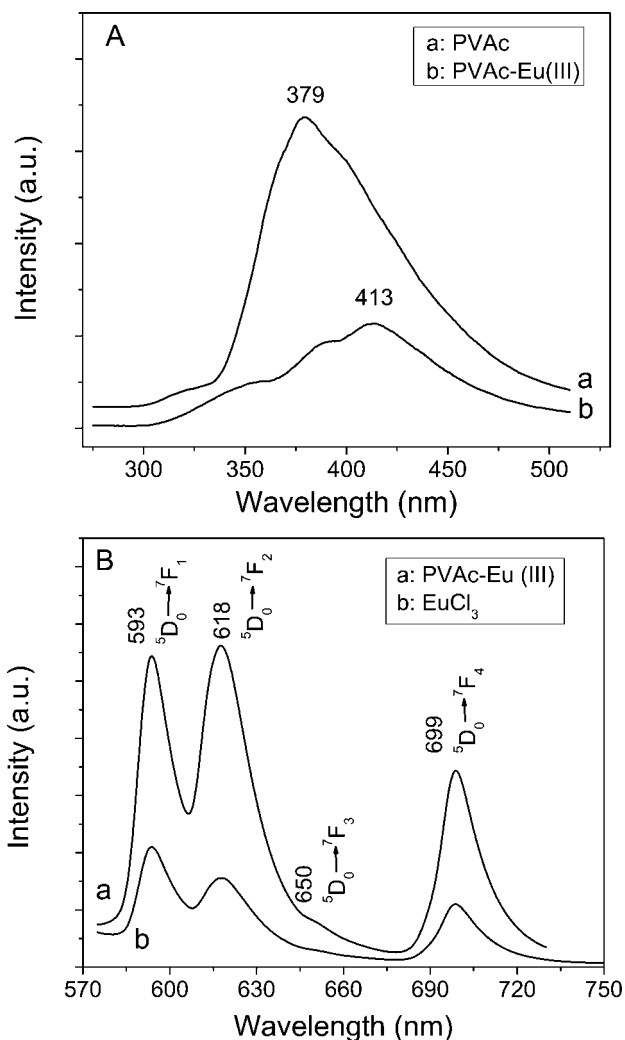
**Figure 3** XPS spectra of (a) PVAc and (b) PVAc-Eu (III) in (A) C 1s and (B) O 1s regions. The binding energy of the aliphatic C 1s was set to be 285 eV; the spectra were offset accordingly to compensate for the shift as a result of the charging effect.

of carbonyl structure, with the following results: (1) the binding energy of carbonyl C 1s shifted a little lower; and (2) the relative intensity of carbonyl C 1s became weaker in PVAc-Eu (III) than those in PVAc. Additionally, the formation of Eu (III)—O coordination bond caused the O 1s binding energy of PVAc-Eu (III) to shift  $\sim 0.8$  eV lower than that of PVAc, as shown in Figure 3(B). Taken together, the XPS results also indicated that the interaction/association between PVAc and Eu (III) in the synthesized PVAc-Eu (III) was coordination bonding instead of physical adsorption, and the prepared PVAc-Eu (III) was indeed a coordination compound. The formation of polymeric coordination compound containing of Eu (III) was reported before by Xu et al.,<sup>12</sup> and their results also indicated that the interaction/association between polymer (polydimethylsiloxane in their research) and Eu (III) was actually coordination bonding.

### Luminescence studies of PVAc-Eu (III) coordination compound

Fluorescence spectroscopy (FS) was employed to study the luminescent characteristics/properties of the synthesized PVAc-Eu (III) coordination compound; FS of PVAc and EuCl<sub>3</sub> were also conducted for comparison purpose. In the FS studies, the specimens were 0.1M solutions of PVAc-Eu (III), PVAc, and EuCl<sub>3</sub>, using absolute ethanol as the solvent.

Figure 4(A) compares the fluorescent emissions between (a) PVAc and (b) PVAc-Eu (III) upon photoexcitation at 264 nm. The fluorescent emission band of PVAc was  $\sim 379$  nm, while the band of PVAc-Eu (III) was  $\sim 413$  nm. This finding suggested that the PVAc component in PVAc-Eu (III) had



**Figure 4** Luminescent spectra of PVAc, EuCl<sub>3</sub>, and PVAc-Eu (III): (A) Fluorescent emissions of (a) PVAc and (b) PVAc-Eu (III) upon photoexcitation at 264 nm. For comparison, the PVAc concentrations were kept the same (0.1M) in both solutions. (B) Fluorescent emissions of (a) PVAc-Eu (III) and (b) EuCl<sub>3</sub> upon photoexcitation at 370 nm. Spectra were offset for clarity.

different chemical environment/molecular structure as compared with the neat PVAc. Additionally, the fluorescent intensity of PVAc was  $\sim 3.5$  times as strong as that of PVAc–Eu (III). This indicated an efficient energy transfer from the PVAc ligands to the coordinated Eu (III) ions in the PVAc–Eu (III) coordination compound. Such result was desired because the large amount of energy transfer could significantly enhance the luminescence of Eu (III). The above two results could also be used to further prove the interaction/association between PVAc and Eu (III) in PVAc–Eu (III) was coordination bonding, because typical physical adsorption could result in neither the large shift in fluorescence nor the efficient energy transfer.

Figure 4(B) shows the luminescent spectra of (a) PVAc–Eu (III) and (b)  $\text{EuCl}_3$  upon photoexcitation at 370 nm. Both spectra displayed characteristic fluorescent emissions of Eu (III) at approximately 593, 618, 650, and 699 nm, which corresponded to the electron transitions from the excited state of  $^5\text{D}_0$  to the ground states of  $^7\text{F}_1$ ,  $^7\text{F}_2$ ,  $^7\text{F}_3$ , and  $^7\text{F}_4$ , respectively.<sup>11</sup> The effect of different PVAc/Eu(III) ratios on the luminescence characteristics/properties was also tested. No significant difference of luminescence intensity was observed when the feed ratio changed from 5 : 1 to 8 : 1. This suggested that the feed ratio of 6:1 was suitable for the sample preparation.

Unlike many Eu (III)-containing solid-state materials and/or chelate complexes in which the luminescent emission bands are split by the field generated by the tightly held neighboring atoms and/or ligands, PVAc–Eu (III) coordination compound had luminescent emission bands that were not split. This might imply that the Eu (III) ions were probably not tightly held in a rigid matrix, and that the PVAc chain segments (i.e., ligands) might be somewhat mobile. Nevertheless, the intensities of the luminescent emission bands of the PVAc–Eu (III) coordination compound were approximately 3 times as strong as that of  $\text{EuCl}_3$ , indicating that the luminescent efficiency of PVAc–Eu (III) was much higher than that of  $\text{EuCl}_3$ . Therefore, the prepared PVAc–Eu (III) coordination compound could be a useful polymeric luminescent material.

## SUMMARY

PVAc, one of the synthetic polymers that can form coordination compounds with metal ions, was studied to synthesize the coordination compound with Eu (III). The formation of Eu (III)—O coordination bond was confirmed by the results acquired from FTIR, RS, and XPS. FTIR results indicated that (1) the absorption band of the carboxylate asymmetric stretch shifted lower from  $1658\text{ cm}^{-1}$  in PVAc to

$1644\text{ cm}^{-1}$  in PVAc–Eu (III), and (2) the intensity ratio of the carboxylated asymmetric stretching band over the carbonyl stretching band (around  $1737\text{ cm}^{-1}$ ) in PVAc was higher than that in PVAc–Eu (III). Both results suggested that Eu (III)—O coordination bond was formed. In Raman spectra, the characteristic band around  $401\text{ cm}^{-1}$  was originated from the symmetric stretching of the Eu (III)—O coordination bond. The XPS spectra also showed that (1) the binding energy of carbonyl C 1s was shifted a little lower, and (2) the relative intensity of carbonyl C 1s was weaker in PVAc–Eu (III) than those in PVAc, and (3) the binding energy of O 1s in PVAc–Eu (III) was  $\sim 0.8\text{ eV}$  lower than that in PVAc. All these results suggested that the interaction/association between PVAc and Eu (III) was indeed coordination bonding instead of physical adsorption.

The luminescent characteristics/properties of the synthesized PVAc–Eu (III) coordination compound were studied using FS. The research revealed that (1) the luminescent properties of PVAc–Eu (III) resulted from both the coordinated Eu (III) ions and the PVAc ligands; (2) PVAc, after absorbing energy upon photoexcitation, could effectively transfer the energy to Eu (III) through the Eu (III)—O coordination bond by nonradiative pathways, and resulted Eu (III) to transit from the ground state to the excited state of  $^5\text{D}_0$ ; and (3) when the excited electrons in  $^5\text{D}_0$  transitioned back to the ground states of  $^7\text{F}_1$ ,  $^7\text{F}_2$ ,  $^7\text{F}_3$ ,  $^7\text{F}_4$ , the characteristic fluorescence was emitted at the wavenumbers of 593, 618, 650, and 699 nm, respectively. As compared with the fluorescence generated by 0.1M  $\text{EuCl}_3$  absolute ethanol solution, the fluorescence of 0.1M PVAc–Eu (III) absolute ethanol solution was approximately 3 times as strong. This suggested that the PVAc ligands could effectively serve as the light-absorbing chromophores, and PVAc–Eu (III) could be a useful polymeric luminescent material; particularly for the applications in the areas such as adhesives, coatings, and textiles, the areas in which PVAc is an important raw material.

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