Fluorescent Copolymers of N-Vinylcarb-Azole and Eu-Complexed Acrylic Acid as Anti-Falsification Packaging Materials

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Abstract: Europium complexes were excellent chromophores that exhibited intense fluorescence with a narrow spectral bandwidth (5-10 nm). But non-uniform blending or dispersion of complex resulted in phase separation, decomposition and inefficient energy transfer to reduce emission efficiency. The complexes were covalently attached to the main chain of polymers, which improved film quality, thermal stability and solubility. $Eu(TTA)_2(AA)phen$ as europium complex monomer (ECM) was prepared by Eu^{3+} coordinating with 1,10-phenanthroline (phen), acrylic acid (AA) and 2-thenoyltrifluoroacetone (TTA). Fluorescent Polymer 1 (P_1, molar ratio for ECM/N-vinylcarbazole, NVK, 1/60) and Polymer 2 (P_2, 1/30) were synthesized. The emission wavelength of ECM in tetrahydrofuran (THF) was at 614nm. With the increasing of molar ratio of Eu in polymers, the emission peak of P_2 in the 350-500 nm region in either film or THF was lower and one of P_2 at about 614 nm was higher compared to P_1. Collective states of polymers in both film and THF had less effect on emission wavelength at 614 nm. Glass transition temperatures and thermal decomposition temperatures of ECM, P_2 and P_1 were observed at 118, 174, 178 °C and 269, 250, 227°C, respectively, which showed that they were high thermal stabilities. From the differential scanning calorimetry (DSC) curves of P_2 and P_1, no noticeable crystallization took place. The atomic force microscope (AFM) images of copolymers film revealed good film quality to avoid phase separation. The big overlap between emission spectra of carbazole and absorption spectra of Eu complex moieties raised effectively intramolecular energy transfer from carbazole unit to europium ions and improved emission efficiency. It was desirable to prepare fluorescent inks containing P_1 and P_2 for anti-falsification packaging.

Keywords: Europium complex; Acrylic acid; N-vinylcarbozole; Energy transfer; Fluorescent copolymer.

1. Introduction

Among red emission organic materials, europium (Eu) complexes were one of the most important rare earth complexes. Eu complexes had high theoretical fluorescent quantum efficiency (up to 100 %), exhibited photoluminescence with narrow spectral bandwidth (full width at half maximum, FWHM<10 nm) at ca. 614nm and a relatively decay life (10^{-2}-10^{-6} s) [1-3]. Copolymer complexes were polymers with the complexes bonded to the main chain or as pendant groups. These copolymers were highly soluble in common organic solvents, cast into high quality of film, to avoid phrase separation and ionic aggregation as dopant, which showed excellent thermal stability. Transport of electrons and holes was balanced through blending together or copolymerizing and fluorescent quantum efficiency was improved [4-5]. These had spurred considerable interest in the application of anti-falsification printing ink and electroluminescence (EL) for display technology [6-8].

To improve the stability and luminescent efficiency of compounds, a tetrabasic complex of europium with 1-phenyl-1, 3-butanedione (BA), acrylic acid (AA) and 1, 10-phenanthroline (Phen) was incorporated into silica matrix [9]. The carbazole derivatives were one of the most widely employed hole-transporting materials and donors. The terpolymers of N-vinylcarbazole (NVK), methyl methacrylate (MMA) and europium-methylacrylic acid (MAA) complex, such as, poly(NVK-*co*-MMA-*co*-$Eu(BA)_2(MAA)phen$), poly(NVK-*co*-MMA-*co*-$Eu(BA)_2(AA)$ phen) and poly(NVK-*co*-MMA-*co*-$Eu(TTA)_2$ (MAA)phen) were prepared [10] and electrochemical and electroluminescent properties were investigated [11]. Poly(NVK-*co*-$Eu(TTA)_2$(4- vinylbenzozate)phen) was synthesized and the single layer copolymer light-emitting diode was fabricated and studied [5]. The terbium-complexed acrylic acid as light-emitting unit (guest) and N-vinylcarbazole as hole transporting unit (host) were attached to the same main chain, efficient energy transfer [12] occurred possibly from donor to acceptor due to the large overlap of emission band of carbazole unit and the absorption band of terbium-complex. It was desirable to synthesize multifunctional materials and simplified fabrication for device. Undoubtedly, it was focus to synthesize polymers linked light-emitting unit, hole-transporting unit or electron-transporting unit through chemical bonds.

In this paper, $Eu(TTA)_2(AA)phen$ (ECM) was synthe-

sized by Eu^{3+} coordinating with 1,10-phenanthroline (phen), acrylic acid (AA) and 2-thenoyltrifluoroacetone (TTA). Two copolymers (P_1 and P_2 consisting of molar ratio 1/60 and 1/30 for ECM/NVK, respectively) of poly(NVK-*co*-Eu(TTA)$_2$(AA)phen) were obtained, the absorption and emission spectra of ECM, P_1 and P_2 in diluted THF and film were investigated. Glass transition temperatures (Tg), thermal decomposition temperatures (Td) were analyzed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in detail. The surface topography of copolymer film was analyzed by atomic force microscope (AFM). Intramolecular energy transfer from carbazole unit to europium complex was discussed.

2. Experimental

2.1. Instruments

The synthesized compounds were characterized by element analysis, FT-IR spectra and ^{1}NMR, recorded on Carlo Erba 1106, Shimadzu FT-IR 8400 spectrometers and Bruker DMX-300 respectively. The UV-vis absorption and fluorescent spectra were measured by using GBC Cintra 303 UV-vis Spectrophotometer and Perkin Elmer LS-55 Luminescence Spectrometer. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and AFM images were performed on Netzsch DSC-200PC, Netzsch TG-209 and Veeco DI Innova.

2.2 Synthetic procedures

2.2.1 Preparation of europium complexed monomer (ECM)

A concentrated solution of $EuCl_3$ was obtained by mixing 0.71 g (2.00 mmol) Eu_2O_3 with HCl (6.0 mol/l), PH value of the mixture was adjusted to ca. 6 by adding aqueous sodium hydroxide (weight ratio, 10 %). 1.77 g (8.02 mmol) TTA dissolved in 18 ml ethanol was added into 15 ml of an aqueous ethanol containing $EuCl_3$, which was stirred 30 min. at 60 °C. 0.72 g (4.01 mmol) phen in 9 ml ethanol was added and refluxed for 1 h. 0.29 g (4.01 mmol) AA in 9 ml ethanol was adjusted to 6 (PH value) and added dropwise into the reactor at 50 °C and stirred for 24 h. The above mixture of solution was cooled to room temperature. A precipitate was filtered out and washed with aqueous ethanol, ECM was obtained and dried, yielding 80.1 %.

^{1}HNMR ($CDCl_3$, 300MHz) δ(ppm): 9.51(phen-H), 8.49(phen-H), 7.61, 6.96(Ar-H), 6.50(Th-H), 6.20(Ar-H), 3.15(=CH). FT-IR (KBrpellet, cm^{-1}): 1691, 1625, 1600, 1577, 1541, 1508, 1464, 1413, 1357, 1309, 1247, 1230, 1186, 1062, 933, 844, 788, 723, 682, 642, 582. Anal. Calcd. for $C_{31}H_{19}EuF_6N_2O_6S_2$ C:44.02, H:2.25, N:3.31, S:7.57; Found: C:43.53, H:2.16, N:3.82, S:7.86.

2.2.2 Preparation of the copolymer complexes

A mixture of NVK, a calculated amount of ECM and AIBN initiator was dissolved in 3 ml of dry THF in a three-neck flask equipped with a magnetic stirring bar. The solution was purged with nitrogen and was continuously stirred at 60 °C for 72 h. The viscous solution was diluted with 2 ml of THF and precipitated into 30 ml of methanol under vigorous stirring, product solid was collected by filtration and dried. The feed molar or weight ratios of the monomers in the polymerization reaction were showed in Table 1.

Table 1 The feed ratios of the monomers and initiator

Polymers (molar ratio)	Feed ratio			Yield %
	ECM (g)	*NVK (g)*	*AIBN (g)*	
P_1 (1:60)	0.042 (0.05 mmol)	0.58 (3.00 mmol)	0.004	70.2
P_2 (1:30)	0.169 (0.20 mmol)	1.16 (6.00 mmol)	0.008	60.2

FT-IR (KBrpellet, cm^{-1}): 3049, 2970, 2932, 1626, 1601, 1487, 1453, 1406, 1330, 1223, 1156, 1123, 1093, 1026, 1000, 924, 840, 746, 719, 615, 576, 527, 419. ^{1}HNMR ($CDCl_3$, 300MHz): δ(ppm): 1.05-1.27 (CH_2, AA), 1.96 (CH, AA), 3.16-3.23 (CH, NVK), 4.89 (H, carbazole), 6.37-6.90 (H, carbazole), 7.15 (H, carbazole), 7.50-7.83 (H, carbazole).

3. Results and discussions

3.1 Synthesis and characterization

The synthetic routes to europium monomer and copolymers were showed Scheme 1. When feed ratio of ECM/NVK increased from P_1 to P_2 the yield of copolymers decreased due to the lower reactivity of ECM compared to the reactivity of NVK. The antisymmetric and symmetric stretching vibrations of carboxylate groups showed at 1600 and 1463 cm^{-1}. The C=O and C=C stretching vibrations of coordinated TTA ligand in the complex appeared at 1626 and 1541 cm^{-1}, The ring vibration of 1, 10-phenanthroline (phen) was at 1508, 1413 cm^{-1}. These absorption bands were not found owing to relatively low content. The C=C stretching vibrations of NVK at 1639 cm^{-1} was absent in copolymer, this indicated that copolymerization were complete. The two strong sharp peaks were at 723, 750 cm^{-1} in NVK and at 719, 746 cm^{-1} in P_1 or P_2, respectively, which belonged to the characteristic absorption of the carbazole moieties.

3.2 Photophysical properties

The UV-vis absorption (a) and emission spectra (b) of ECM, P_1 and P_2 in diluted THF were showed in Fig. 1.

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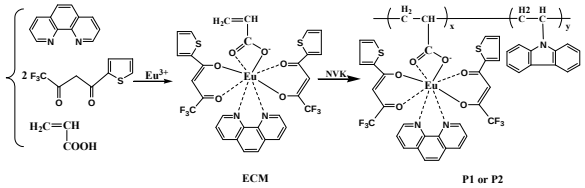
One located at 306-393 nm was mainly contributed by the ligand TTA, the other was at 241-306 nm mainly due to phenanthroline absorption. The absorption band of acrylic acid (AA) was a medium intensity at 202-240 nm, very weak absorption of Eu^{3+} appeared at 200-300 nm, so the absorption of complex mainly originated from the TTAs and phen. When ligands TTAs, AA and phen were coordinated to the center Eu^{3+}, complex monomer with larger conjugated system had strong and broad absorption peaks at 265, 341 nm [9]. The UV absorption spectra of P_1 and P_2 in diluted THF appeared main peaks at 238, 260, 294, 330, 343 nm. The shape of the absorption spectra for P_1 and P_2 were similar.



Scheme 1 The synthetic routes to europium complexed monomer and copolymers

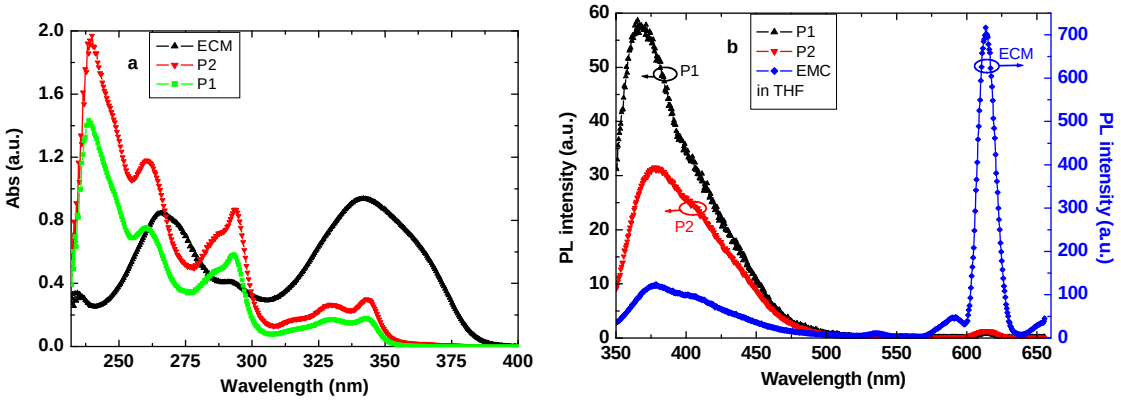


Fig. 1 UV-vis absorption (a) and emission spectra (b) of ECM, P_1 and P_2 in diluted THF

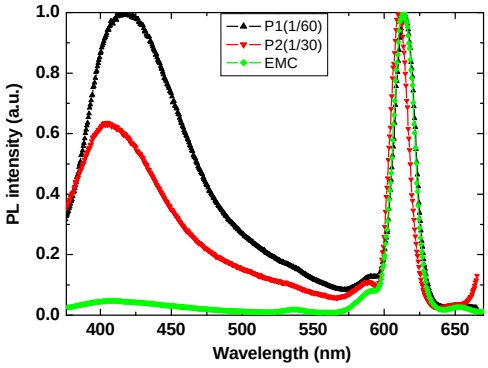
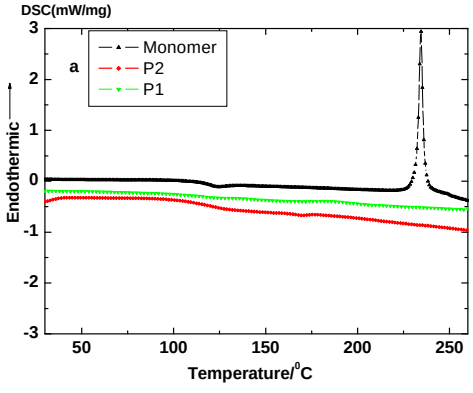


Fig. 2 Emission spectra of P_1, P_2 and EMC in solid film



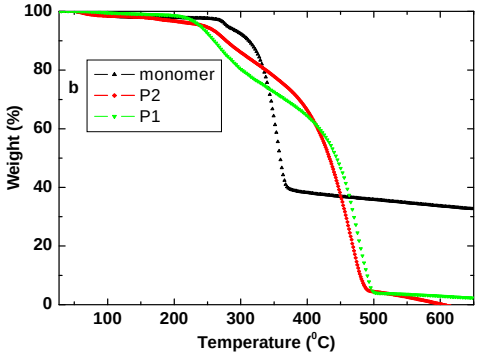


Fig. 3 DSC (a) and TGA (b) curves of ECM, P_1 and P_2

The emission spectra of P_1 and P_2 in diluted THF consisted of two parts of emission peaks. The first ranged from 350 to 500 nm, this broad band was associated with the $\pi \rightarrow \pi^*$ transition of the carbazole moieties. The emission peaks at 591, 614 and 652 nm from ECM, P_1 and P_2 in diluted THF in the red region were attributed to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ transitions of Eu^{3+} ions, respectively, which remained unchanged, but PL intensity rose from P_1 to P_2. In the copolymers (P_1 and P_2), carbazole was the dominant component.

Emission spectra of solid film preparing by spin-coating from a solution of P_1 or P_2 in toluene were observed in Fig. 2. Emission peak of P_1 between 375-550 nm in the blue region was higher than one of P_2, this indicated that feed ratio of carbazole in P_1 was more

than that in P_2. While emission peak of P_1 at 614 nm was lower than one of P_2, this mainly resulted from less feed ratio of Eu in P_1. In a word, collective states of polymers (P_1 or P_2) in solid film or diluted THF had less effect on emission peak at 614 nm.

3.3 Thermal properties

The thermal properties of ECM, P_1 and P_2 were determined by differential scanning calorimetry (DSC) (Fig. a) and thermogravimetric analysis (TGA) (Fig. b) under nitrogen atmosphere seen in Fig. 3.

Samples using DSC were heated from 25 to 70 °C at a rate of 10 °C /min, then cooled to 10 °C and reheated at the same heating rate to 260 °C. Samples using TGA were heated at a rate of 10 °C/min under N_2 flow from 25 to 650 °C. Melting point (Mp), glass transition temperature (Tg, mid-point), thermal decomposition temperature (Td, onset), rate of weight loss (Rl) and rate of remaining weight (Rr) were showed in Table 2. A glass transition temperature (Tg) of ECM was observed at 118 °C and a melting point was detected at 234 °C. Tgs of P_2 and P_1 were 174, 178 °C and no noticeable crystallization in the temperature range took place, while the Tg of the PVK (NVK homopolymer) was at about 210 °C. Thermaldecomposition temperature s of ECM, P_2 and P_1 were observed at 269, 250, 227 °C, rates of weight loss of ECM, P_2 and P_1 were 58 % (371 °C), 91 % (491 °C), 94 % (499 °C), respectively, which showed that they were high thermal stabilities. At 650 °C the white powders residues were identified as europium oxide. The rates of remaining weight (1.8 %, 2.3 %) of the Eu_2O_3 residues were in better agreement with the Eu content of P_2 and P_1.

Table 2. The thermal properties of ECM, P_1 and P_2

Comp.	Tg/°C	Mp/°C	Td/°C	Rl/(%,°C)	Rr/(%,°C)
ECM	118	234	269	58 (371)	32.6 (650)
P_2 (1/30)	174	no	250	91 (491)	1.8 (650)
P_1 (1/60)	178	no	227	94 (499)	2.3 (650)

3.4 Copolymers film

The atomic force microscope (AFM) images of P_1 copolymer film (top figure) and PVK film doped with EMC (bottom figure) were given in Fig. 4.

The film cast from P_1 at the concentration of about 20mg/ml in toluene was completely homogeneous, which revealed good film quality to avoid phase separation. In contrast, segregated particles of sizes in the range of 18-78 nm were observed in the composite film of PVK doped with EMC (EMC/PVK molar ratio, 1/60). The particles were probably the molecular aggregates of Eu complex part separated in composite film. Phase separation and aggregation of Eu complex wound result in the non-radioactive relaxation and the triplet-triplet annihilation. So the possibility of preparing thin films containing P_1 and P_2 was very desirable for application in OLEDs and printing packaging ink.

3.5 Energy transfer

The peak from P_2 in the range of 350-500 nm should be mainly attributed to emission of the carbazole group. Fig. 5 showed that their bigger overlap area existed between the emission spectra of P_1 solid film and absorption spectra of EMC solid film. Eu^{3+} ion's emission in copolymer wound be enhanced by Förster energy transferred from carbazole groups to europium complex. The Förster energy transfer rate (r) was decided by spectra overlap integral (J) and donor-acceptor distance (R): $r \propto J/R^6$, we expected possibility of energy transfer from carbazole to Eu complex moieties. The singlet excitons from the ligands were converted into the triplet excitons by intersystem crossing. The triplet excitons were then transferred to the Eu^{3+} ions to give the characteristic emissions.

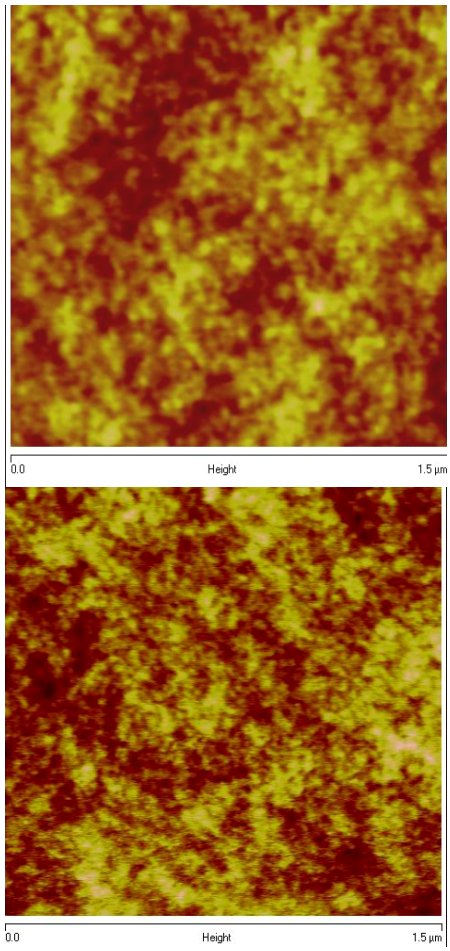


Fig. 4 AFM images of P_1 copolymer film (top figure) and PVK film doped with EMC (bottom figure)

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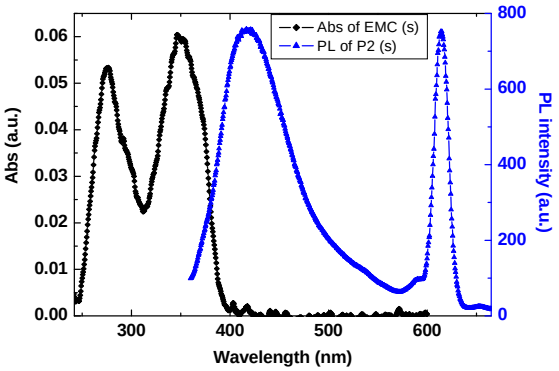

Fig. 5 Absorption spectrum of ECM (left) and emission spectrum of P_2 (right) in solid films

It was known that singlet and triplet state energy levels [13] of TTA and phen. Energy transfers from the S_1 excited state of phen or TTA to T_1 of TTA. Finally energy transferred from T_1 excited state of TTA to $^5D_0$ of Eu^{3+}.

4. Conclusions

Europium-complexed monomer (ECM) and two copolymers of poly(NVK-*co*-Eu(TTA)$_2$(AA)phen) (P_1 and P_2 including 1/60 and 1/30 for ECM/NVK, respectively) were synthesized. The absorption and emission main peaks of ECM were at 341 nm and 614 nm. Feed molar ratio of Eu in polymers increasing, the emission peak of P_2 in the 350-500 nm region in either film or diluted THF was lower, while the one of P_2 at about 614 nm was higher compared to P_1. Collective states of polymers (P_1 or P_2) in both solid film and diluted THF had less effect on emission peak at 614 nm. Intramolecular energy transfer from carbazole unit to europium complex occurred. P_1 and P_2 showed high thermal stabilities and highly soluble and no noticeable crystallization. AFM images of copolymers film revealed good film quality to avoid phase separation. It was desirable to prepare fluorescent inks containing P_1 and P_2 for anti-falsification packaging.

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