ELSEVIER

Polymer 42 (2001) 4605–4610

polymer

www.elsevier.nl/locate/polymer

A novel high photoluminescence efficiency polymer incorporated with pendant europium complexes

Qidan Ling[a], Mujie Yang[a,*], Zhefu Wu[b], Xianmin Zhang[b], Lianhui Wang[c], Wengong Zhang[c]

[a]*Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*
[b]*Department of Information and Electronic Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*
[c]*Institute of Polymer Science, Fujian Normal University, Fuzhou 350007, People's Republic of China*

Received 22 May 2000; received in revised form 20 October 2000; accepted 24 October 2000

Abstract

A novel copolymer, PVK-*co*-MMA-*co*-Eu(BA)$_2$(MAA)phen (*PKMEu*), was synthesized by free radical copolymeriation of 9-vinylcarbazole, methyl methacrylate with europium-methacrlate complex in THF with AIBN as initiator. The copolymer structure and composition were confirmed by FTIR, UV, ^{13}C NMR and element analysis. The molecular weight was determined by GPC, the number-average molecular weight of *PKMEu* is 10,600 and exhibits a broad weight distribution. *PKMEu* has the glass transition temperature (T_g) of 165°C. TG measurement reveals that the decomposition temperature range of *PKMEu* is 390–600°C. The absolute photoluminescence (PL) quantum efficiency of *PKMEu* was measured using integrating sphere technique. It is about 40.28% with the excitation wavelength of 260 nm. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Europium complex; Copolymer; Photoluminescence efficiency

1. Introduction

Since the first polymer-based light-emitting diode (PLED) was reported [1], there has been extensive research on polymer LEDs and many improvements have been made [2]. Single-color displays fabricated with arrays of polymer LEDs are moving out of the research lab and into the market [3]. Although many conjugated molecules have high photoluminescence (PL) efficiencies (more than 50%), the electroluminescence (EL) efficiencies of the LEDs based on them are incredibly low (less than 5%). One of the reasons is thought to be the formation of triplet excitons. We know that when electrons and holes capture one another to form an exciton, the exciton can either be in a singlet or triplet state. In conjugated molecules only the singlet excitons can generate light, the triplet excitons are lost in nonradiative transitions. On the basis of spin statistics, only 25% of the excitons have singlet character in conjugated molecules. So the quantum efficiency of a conjugated PLED cannot be more than 25%. This drawback of conjugated molecules has triggered efforts to use lanthanide ions, such as Eu^{3+} or Tb^{3+} coordinated to organic ligands, as emitters in organic EL materials [4,5]. In such cases, the energy of singlets and triplets that form on the ligands can be transferred to the f levels of lanthanide ion to generate light. In theory, internal efficiencies of 100% should thus be possible [6].

Another significant advantage of rare earth organic EL materials is the color purity of the generated emission. Full color displays will require pure red, green, and blue emission. Obtaining pure emission colors from conjugated polymers or small organic molecules is difficult because their emission spectra typically have a full width at half maximum (FWHM) of 100–200 nm. In contrast to conjugated molecules, rare earth ions have very sharp emission spectra (FWHM, 10–20 nm). Pure red and pure green light emitting diodes based on low molecular lanthanide complexes have already been reported [7]. In order to obtain high quality film, low molecular weight material usually requires high vacuum deposition techniques (e.g. CVD), which makes processing cost intensive.

Recently the bending of rare earth complexes with polymer matrixes has been reported. EL devices based on these materials were fabricated using spin-coating technique [8,9]. It has been found that the PL efficiency can be enhanced when europium (Eu) complex was blended with polymer [9]. Probably the main disadvantage of this technique is that blending usually does not give a fully

---

* Corresponding author. Tel.: +86-10-6275-1728; fax: +86-10-795-2444.

E-mail address: yangmj@cmsce.zju.edu.cn (M. Yang).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00799-0

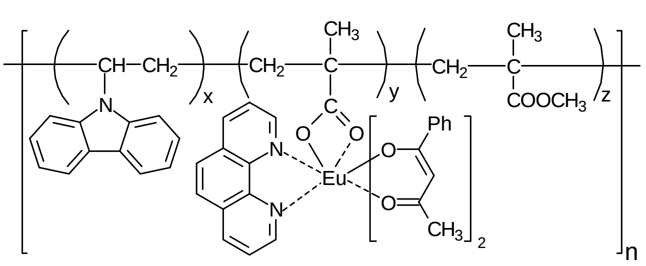

Fig. 1. The structure of PVK-*co*-MMA-*co*-Eu(BA)$_2$(MAA)phen.

dispersed distribution of dopants, and thus would result in the phase separation and ionic aggregation. Polymers in which the lanthanide complexes are covalently bound in the main chain or as side groups would be excellent candidates to overcome the above mentioned difficulties.

In this paper we report an effective synthesis of a novel copolymer containing Eu-complexes and carbazole side groups (Fig. 1). While the carbazole units should enable effective hole transport, electron transport and light emission should be performed by the Eu-complexes [10]. Such a copolymer, act at the same time as charge transport and emissive layer, would allow fabrication of single-layer polymer LEDs. The PL quantum efficiency, usually indicative of EL efficiency, was measured using integrating sphere technique [11,12].

2. Experimental

2.1. Materials

N-vinylcarbazole (NVK) was supplied by Fluka, it was used without further purification. Europium oxide with high purity (>99.99%) was purchased from Shanghai Yuelong Nonferrous Metal Ltd Co., China. The organic ligands, benzoyl acetone (HBA) and 1,10-phenanthroline (phen) were obtained from ACROS and used as received. The initiator, azobisisobutyronitrile (AIBN), was recrystallized from methanol, dried in vacuum and stored under nitrogen. Methacrylic acid (MAA) and methyl methacrylate (MMA) were distilled and stored in refrigerator. All solvents were purchased in analytical grade from Shanghai Chemical Reagent Company and dried before use.

2.2. Preparation of anhydrous europium chloride and europium isopropoxide

$EuCl_3$ (anhydrous) and $Eu(OPr^i)_3$ were prepared according to the procedures described by Taylor and Sinha, respectively, [13,14].

2.3. Preparation of Monomer (Eu(BA)$_2$(MAA)phen), Eu(III)-di(benzoylacetonate)-methacrylate-(1,10-phenanthroline)

To a refluxing solution of europium isopropoxide (4 mmol) in isopropanol (10 ml) and benzene (10 ml), was added dropwise a solution of benzoyl acetone (1.298 g, 8 mmol) in 10 ml of mixed solvent (isopropanol/benzene = 1/1 (v/v)) under the atmosphere of nitrogen. The reaction mixture, containing a precipitate, was refluxed for 1 h on an oil bath. Then another solution of MAA in 10 ml of the mixed solvent was added. The mixture turned clear after a few minutes. Finally, 0.721 g (4 mmol) of 1,10-phenanthroline in 10 ml of the mixed solvent was added, inducing precipitation of the complex. After evaporation of the solvents under reduced pressure, a light yellow powder was obtained. The crude product was purified by reprecipitation from benzene solution into hexane, and dried under vacuum. Yield:1.51 g (51.1%).

FTIR (KBr): 3052 ~ 2947, 1591.3 (s, $\nu_{C=O}$); 1570.7, 1529.8 (s, $\nu_{C=C}$); 1483.2 (m, $\nu_{C=C}$ of phenyl); 1458.5, 1402.4 (s, δ_{CH_3}); 1278.6, 1208.0, 1105.1, 1069.3 (m, β_{CH}); 992.8, 843.8, 773.8 (w, γ_{CH}); 718.3 (m, ν_{Eu-O}) cm^{-1}; Anal. Calcd. ($C_{36}H_{31}N_2O_6Eu$): C, 58.40; H, 4.19; N, 3.79. Found: C, 58.69; H, 4.28; N, 3.20.

2.4. Preparation of copolymer PVK-co-MMA-co-Eu(BA)$_2$(MAA)phen (PKMEu)

The copolymer was synthesized by free radical copolymerization of NVK, MMA and Eu(BA)$_2$(MAA)phen. 0.58 g of NVK, 0.074 g of Eu(BA)$_2$(MAA)phen and 0.004 g of AIBN (initiator) were dissolved in 5 ml of dry THF and 0.20 ml of MMA. The homogeneous solution was purged with nitrogen for 5 min, then sealed and heated in water bath at 60°C for 40 h. The viscous solution was diluted with 5 ml of dry THF, and then was precipitated into 60 ml of methanol under vigorous stirring. The crude product was further purified by three reprecipitations from THF solution into methanol, and dried in vacuum chamber at room temperature for 24 h. Yield: 0.46 g (67.2%).

2.5. Measurements

IR spectra of KBr pellets were recorded on a Bruker Vector 22 IR spectrophotometer. Elemental analyses were performed on an EA 1110 CHNS-O CE Instrument. Molecular weights were determined by GPC using a Waters Model 510 Liquid Chromatograph versus polystyrene standard; THF was used as eluting solvent. Thermogravimetric analysis was carried out on a DuPont Thermal Analyst 2100 System with a TGA 2950 thermogravimetric analyzer under a heating rate of 20°C/min and an air flow rate of 75 cm^3/min. DSC measurement was carried out on the same system with a DSC 2910 Module at a heating rate of 10°C/min in air. ^{1}H NMR and ^{13}C NMR spectra were taken on an Advance DMX500, 500 MHz spectrometer (solvent: $CDCl_3$, internal standard: tetramethylsiliane). Absorption spectrum was determined on a Shimadzu UV-VIS 3101PC Spectrophotometer. The PL spectrum was recorded on a Hitachi 850 Florescence Spectrophotometer. Measurement of the absolute PL

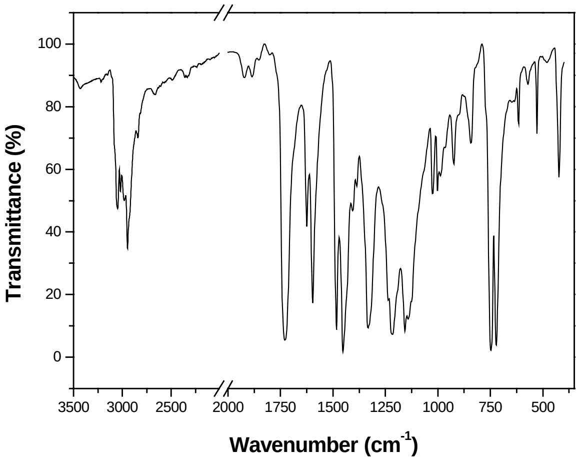

Fig. 2. IR spectrum of *PKMEu* (KBr pellet).

efficiency was performed using an integrating sphere coated on the inside with a diffusely reflecting material MgO. The diameter of the integrating sphere was 200 mm. The polymer film was formed by spin coating from chloroform solution (5 mg/ml) onto a quartz plate. The thickness of the film was about 100 nm.

3. Results and discussion

3.1. Characterization of PKMEu

The Eu-containing copolymer *PKMEu* is highly soluble in $CHCl_3$, THF, CH_2Cl_2, etc., and can form good quality film by spin coating. The molecular weight was determined by gel permetation chromatography (GPC), *PKMEu* has the $\bar{M}_w$ values of 34,900 and exhibits a broad weight distribution (DP = 3.29). The composition of *PKMEu* was determined by element analysis, $x = 0.99$, $y = 0.02$, $z = 1.01$. Anal. Calcd: N, 4.69; C, 76.70; H, 6.38. Found: N, 4.67; C, 77.11; H, 6.37. The content of Eu-complex in copolymer is about 4.82 wt%.

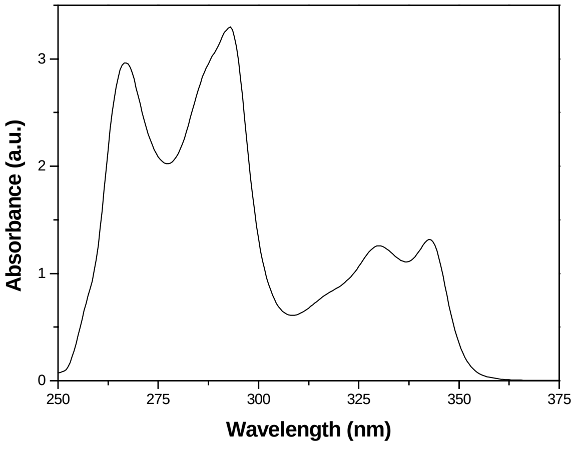

Fig. 3. UV–Vis absorption spectrum of *PKMEu* in THF.

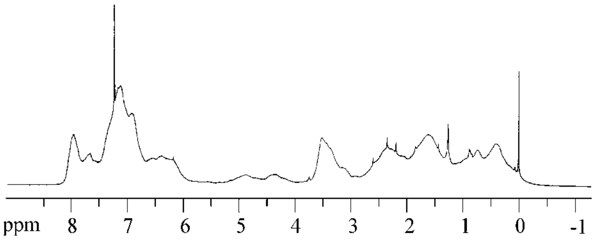

Fig. 4. ^{1}H NMR spectrum (500 MHz) of *PKMEu* in $CDCl_3$.

The IR spectrum of the *PKMEu* is shown in Fig. 2. It shows the characteristic absorption of carbazole moieties [15] at 723.1 and 748.2 cm^{-1}. The strong absorptions of carboxylate groups can be observed at 1729.5 ($\nu_{C=O}$), 1158.5, 1195.0, and 1239.3 cm^{-1} (ν_{C-O-C}). The ring vibration of 1,10-phenanthroline at 1518 cm^{-1} and the absorptions of benzoylacetonate at 1581.4, 1524.6 cm^{-1} cannot be well identified. These bands are buried under the aromatic ring vibrations and C–H bending vibrations of carbazole groups occur at 1625.4, 1597.2, 1483.9, and 1453.4 cm^{-1} owing to the relatively low content of Eu-complexes. However, the stretching vibration of Eu–O [16] can be observed obviously at 412.5 cm^{-1}.

Fig. 3 shows the UV absorption spectrum of *PKMEu* in THF solution. The spectrum exhibits characteristic absorption bands both of carbazole groups (290 and 345 nm), and of carboxylate groups (261 nm). The absorption at 324 nm is attributed to 1,10-phenanthroline. Other absorption bands of the ligands are buried.

Due to the fact that the Eu-complex is paramagnetic, ^{1}H NMR peaks for *PKMEu* are broad and unrecognizable (Fig. 4). Fig. 5 shows the ^{13}C NMR spectrum of *PKMEu* in $CDCl_3$. The signals at 17, 20, 45, 48, 51, and 52 ppm correspond to the aliphatic carbons, while the peaks in the range from 108 to 140 ppm are ascribed to the aromatic carbon atoms. Furthermore, additional peaks are found at 175, 176, and 177 ppm, which represent the carbons of C=O.

The above experimental results suggested the successful formation of copolymer PVK-*co*-MMA-*co*-Eu$(BA)_2$(MAA)-phen.

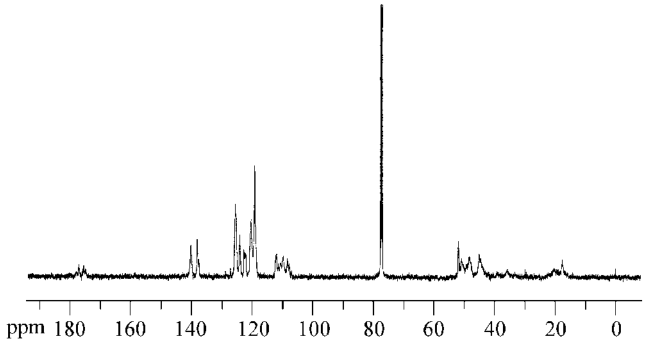

Fig. 5. ^{13}C NMR spectrum (126 MHz) of *PKMEu* in $CDCl_3$.

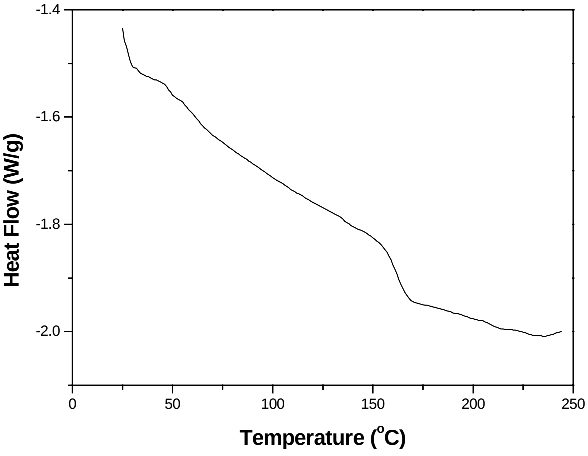

Fig. 6. DSC curve of *PKMEu* under air atmosphere (heating rate: 10°C/min).

3.2. Thermal properties of PKMEu

The thermal property of *PKMEu* was determined by differential scanning calorimetry(DSC) and thermogravimetry (TG). The copolymer has the glass transition temperature (T_g) of 165°C (Fig. 6), which is more than the T_g of PMMA (105°C) and less than the T_g of PVK (190°C). TG measurement shows that *PKMEu* has a good thermal stability, and there is no weight loss up to 390°C (Fig. 7). This is attributed to the introduction of bulky, laterally fixed carbazole side groups to the copolymer. The decomposition temperature (T_d) range of *PKMEu* is 390–600°C.

3.3. PL quantum efficiency of PKMEu

The PL quantum efficiency, Q, is defined as the number of photons emitted in PL per absorbed photon. In this paper, the PL efficiency of *PKMEu* was measured using an integrating sphere. The measurement technique was similar to those reported on previously by Greeham et al. [11].

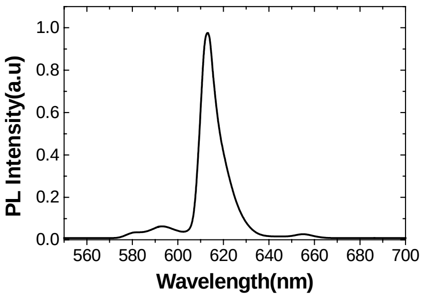

Fig. 8. PL spectrum of *PKMEu* film.

The PL quantum efficiency, neglecting the spectral variation of the system response, is given by

$$x = \frac{X_{\mathrm{sample}} - (R + T)X_{\mathrm{sphere}}}{(1 - R - T)X_{\mathrm{light}}} \tag{1}$$

where R is the reflectance, T is the transmittance, and X_{light} is the signal measured with the laser incident on the sphere with no sample or filter. X_{sample} and X_{sphere} are the signals measured with the sample and filter in place, with the laser incident on the sample and the sphere wall, respectively. The results of measurement are summarized in Table 1. From Eq. (1), it yields, $x = 0.6010$.

The correction factor for the spectral response is given by

$$y = \int \frac{S_{\mathrm{sphere}}(\lambda)L(\lambda)G(\lambda)F(\lambda)}{S_{\mathrm{lamp}}(\lambda)} \times \mathrm{d}\lambda \left(\frac{S_{\mathrm{sphere}}(\lambda_{\mathrm{ex}})G(\lambda_{\mathrm{ex}})}{S_{\mathrm{lamp}}(\lambda_{\mathrm{ex}})} \int L(\lambda)\,\mathrm{d}\lambda \right)^{-1} \tag{2}$$

where $S_{\mathrm{lamp}}(\lambda)$ is the spectrum of the tungsten lamp, $S_{\mathrm{sphere}}(\lambda)$ is the spectral response of the sphere, $L(\lambda)$ is the emission spectrum of sample, $G(\lambda)$ is the quantum efficiency of the detector, $\lambda_{\max}$ is the excitation wavelength (260 nm), and $F(\lambda)$ is the transmission of the filter (Figs. 8 and 9). After integration, y is 1.492.

The PL efficiency is then simply given by $Q = (x/y)100\%$, it is 40.28% (Error, ±2%). The PL efficiency

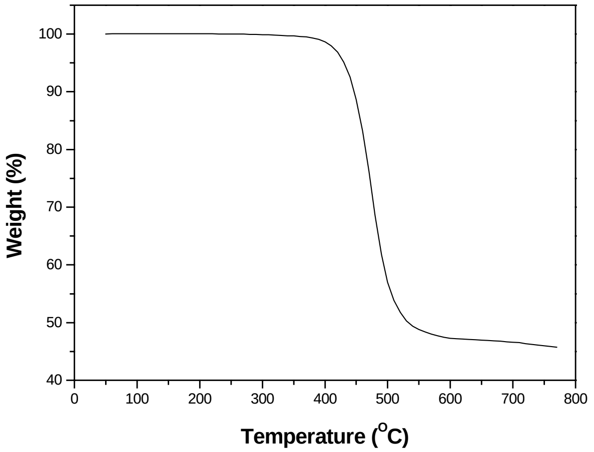

Fig. 7. TG trace of *PKMEu* under air atmosphere (heating rate: 20°C/min).

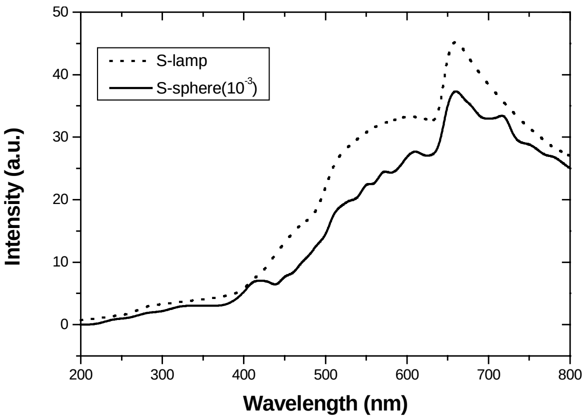

Fig. 9. Spectral response of lamp and sphere.

Table 1
Data of PL efficiency measurement

X_{light}	X_{sample}	X_{sphere}	$R + T$ (%)
1.780	1.024	1.005	67.96
1.750	1.019	0.993	67.96
1.800	1.031	1.021	67.96

of *PKMEu* film is higher than that of both Eu-complex neat film and blending film (Table 2) [9].

The high PL efficiency of *PKMEu* is attributed to the special structure of the copolymer PVK-*co*-MMA-*co*-Eu(BA)$_2$(MAA)phen. Firstly, with one of the coordinate ligand linked to the polymer chain directly, the Eu-complexes are much uniformly dispersed in polymer matrix, thus the concentration quenching, which would reduce the PL efficiency, can be avoided. However, in the Eu-complex neat film and blending film, Eu-complexes often form aggregation, and result in fluorescence concentration quenching. Secondly, energy transfer from carbazole groups to Eu-complexes in the polymeric system can enhance the PL efficiency. The process includes two steps: (1) Foerster energy transfer from carbazole excimer moiety or monomer moiety to the ligands (BA) of Eu-complex; (2) Dexter energy transfer from the triplet states (T_1) of the ligands to the excited states ($^5D_1$, $^5D_0$) of Eu^{3+} by molecular interaction. The second step is similar to the energy transfer mechanism of low molecular Eu-complex. In order to transfer energy by dipole coupling (Foerster transfer, the first step), the emission spectrum of donor (PVK) and the absorption spectrum of acceptor (Eu(BA)$_2$(MAA)phen) must overlap, it is shown in Fig. 10. Foerster energy transfer efficiency is strongly depended on the distance (R) between donor and neighboring acceptor ($\eta_{ET} \propto (R_0/R)^6$). When carbazole groups and Eu(BA)$_2$(MAA)phen are connected to the same polymer chain, the average distance between donor and acceptor is much smaller than that of blending system, so Foerster energy transfer would be more effective in the copolymer system. The additional excitation energy transferred from carbazole groups enhanced the fluorescence efficiency of Eu-complex of the copolymer *PKMEu*.

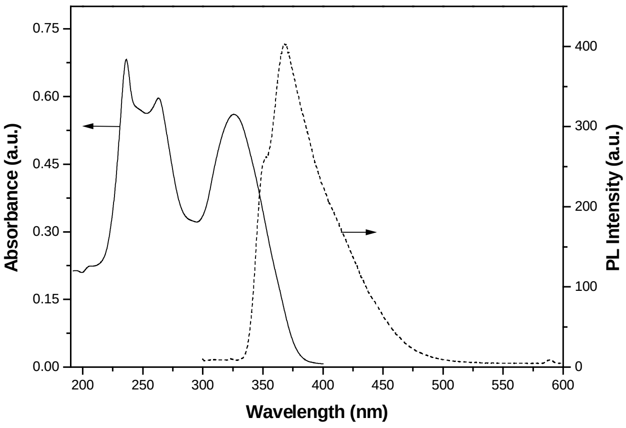

Fig. 10. UV absorption of Eu-containing monomer (solid line) and PL spectrum of PVK (dash line).

Table 2
PL quantum efficiencies of solid films of Eu-complex/polymer blends and Eu-complexes ($\lambda_{ex} = 351$ nm, and a 520 nm high pass filter was used so that only the Eu emission was measured for samples that had blue emission from CN-PPP)

Complex	Efficiency (%)		
	Undiluted Eu complex film	5% (wt) complex blended in CN-PPP	5% (wt) complex blended in polystyrene
Eu(BA)$_3$phen	18	17	18
Eu(DBM)$_3$phen	23	26	29
Eu(dnm)$_3$phen	2.0	27	22

4. Conclusions

- A convenient preparation of rare earth complex containing polymer was developed.
- Compared with the blending system, binding the rare complex directly to the polymer chain, would result in the enhancement of PL quantum efficiency.
- Energy transfer would be more effective with the introduction of carbazole groups to the rare earth complex containing polymer.
- Containing hole-transport, electron transport and rare earth emitter at the same time, the copolymer would allow fabrication of single layer polymer LED.

Acknowledgements

This project was supported by National (29974025) and Zhejiang Provincial (599100) Natural Science Foundation of China, State Key Laboratory of Silicon Materials, Laboratory of Organic Solids, Academia Sinica of China.

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB. Nature 1990;347:539.
[2] Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Bredas JL, Logdlund M, Salaneck WR. Nature 1999;397:21.
[3] Friend RH, Burroughes JH, Shimoda T. Phys World 1999;7:35.
[4] Kido J, Hayase H, Hongawa K, Nai K, Okuyama K. Appl Phys Lett 1994;65:2124.
[5] Kido J, Ikeda W, Kimura M, Nagai K. Jpn J Appl Phys 1996;35:L394.
[6] Justel T, Nikol H, Ronda C. Angew Chem, Int Ed 1998;37:3085.
[7] Kido J, Nagai K, Okamoto Y. J Alloys Comp 1993;192:30.

[8] Liang CJ, Li WL, Yu JQ, Liu XY, Li D, Zhao Y, Peng JB. Chin J Luminesc 1996;17:382.
[9] McGehee MD, Bergstedt T, Zhang C, Saab AP, O'Regan MB, Bazan GC, Srdanov VI, Heeger AJ. Adv Mater 1999;11:1349.
[10] Sun G, Li WL, Zhao Y, Yu Y, Yu JQ, Zhong GZ, Zhao X. Chin J Luminesc 1996;17:91.
[11] Greenham NC, Samuel IDW, Hayes GR, Phillips RT, Kessener YARR, Moratti SC, Holmes AB, Friend RH. Chem Phys Lett 1995;241:89.
[12] De Mello JC, Wittmann HF, Friend RH. Adv Mater 1997;9:230.
[13] Taylor MD, Carter CP. J Inorg Nucl Chem 1962;24:387.
[14] Sinha RPN. Sci Cult 1960;25:494.
[15] Wainwright M, Griffths J, Guthrie JT, Gates AP, Murry DE. J Appl Polym Sci 1992;44:1179.
[16] Gmelin T. Gmelin handbook of inorganic chemistry, vol. 39(D3). 8th ed. New York: Springer, 1981. p. 91–2.