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Synthetic Metals 91 (1997) 151–154

SYNTHETIC METALS

Energy transfer process from polymer to rare earth complexes

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Abstract

The interaction between poly(*N*-vinylcarbazole) (PVK) and rare earth (RE) complexes, such as Eu(thenoytrifluoacetonato)$_4$-(monopyridinium) (Eu(TTA)$_4$Py), Eu(nitrate)$_3$(monophenanthroline) (Eu(NO$_3$)$_3$phen) and Tb(acetylacetonato)$_3$(monophenanthroline) (Tb(AcA)$_3$phen), was investigated in solution as well as in films using the photoluminescence (PL) spectrum. In chloroform solution, the fluorescent intensity of the Eu(NO$_3$)$_3$phen was enhanced by PVK; however, the fluorescent intensity of the Tb complex was greatly quenched by PVK. Strongly characteristic emissions of Eu^{3+} and Tb^{3+} were observed in Eu and Tb complex-dispersed PVK films, respectively. The excitation spectra of Eu complex-dispersed PVK films and Tb complex-dispersed PVK film are very similar to that of the pure PVK film, indicating that effective energy transfer occurs from PVK to the RE complexes. Based on the above experimental results, three types of organic electroluminescence (EL) devices with structure of ITO/Eu(NO$_3$)$_3$phen:PVK/OXD-7/Al, ITO/Eu(TTA)$_4$Py:PVK/OXD-7/Al and ITO/Tb(AcA)$_3$phen:PVK/OXD-7/Al (ITO = indium–tin oxide) were fabricated. Bright red emission can be observed in the first and second devices while bright green light was emitted from the latter device. © 1997 Elsevier Science S.A.

Keywords: Energy transfer; Electroluminescence; Poly(*N*-vinylcarbazole); Rare earth complexes

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1. Introduction

Organic electroluminescence (OEL) is of great interest because of the novel properties in the applications of flat panel displays [1,2]. It is well known that OEL devices using polymers dispersed with fluorescent dye are important because the devices have better heat stability and simple fabrication processes. Rare earth complexes as fluorescent dyes have been used in OEL devices because the complexes have higher internal quantum efficiencies and sharper band emission properties [3–5]. In this study, the interaction between poly(*N*-vinylcarbazole) (PVK) as the matrix and the rare earth (RE) complexes like Eu(thenoytrifluoacetonato)$_4$(monopyridinium) (Eu(TTA)$_4$Py), Eu(nitrate)$_3$(monophenanthroline) (Eu(NO$_3$)$_3$phen) and Tb(acetylacetonato)$_3$(monophenanthroline) (Tb(AcA)$_3$phen) as dopants are investigated. Finally, organic EL devices based on RE complex-doped PVK films were fabricated.

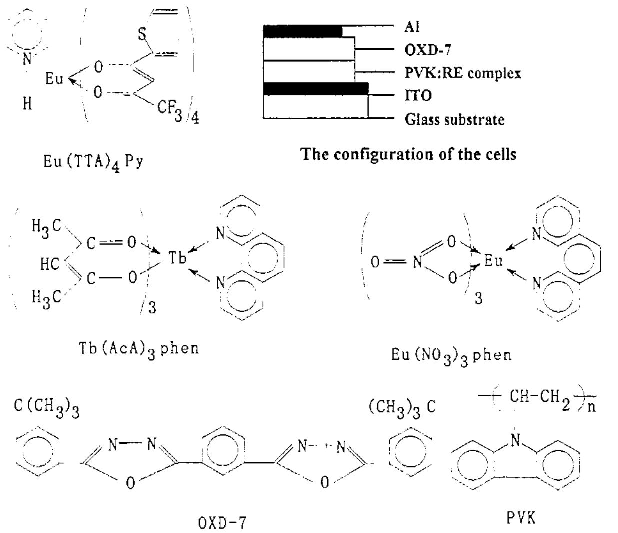

Fig. 1. The molecular structures and cell configuration used.

2. Experimental

In Fig. 1, the molecular structures of materials and the device configuration used in this study are shown. The films of PVK or RE complex-doped PVK are prepared by spin

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PII S0379-6779(97)04000-9

coating the chloroform solution on glass substrate. The photoluminescence (PL) spectra are measured with an F-4000 spectrofluorimeter. As for the fabrication of EL cell, the complex-doped PVK layer is also formed by spin coating on an indium–tin oxide (ITO)-coated glass substrate. Then the OXD-7 layer and Al are respectively deposited onto the PVK:RE complex layer at 3×10^{-5} Torr.

3. Results and discussion

3.1. *PL spectra in solutions*

Fluorescent emission spectra of PVK and PVK:Eu(NO_3)$_3$phen in chloroform solutions are shown in Fig. 2. The emission peak of PVK in chloroform is located at about 388 nm, which is believed to originate mainly from the high-energy intrachain excimer [6]. After adding a small dose of Eu(NO_3)$_3$phen in the solution of PVK chloroform, the emissions of PVK decrease and strong emissions of Eu^{3+} ions are presented in the spectrum. The excitation spectrum (see Fig. 2) shows that there are two excitation bands which are located at 384 and 370 nm, respectively. The 384 nm band corresponds to direct excitation of the ligand of the Eu complex and the 370 nm band is due to the excitation of PVK (the excitation spectrum of PVK is shown in Fig. 4). It indicates that the energy transfer process from PVK to Eu(NO_3)$_3$phen does occur in chloroform solution. This energy transfer process results from a good overlap of the PVK emission spectrum at about 388 nm and the excitation spectrum of Eu(NO_3)$_3$phen at about 384 nm.

Fig. 3 shows emission spectra of Tb(AcA)$_3$phen and PVK:Tb(AcA)$_3$phen in chloroform solutions. Strong sharp emissions of Tb^{3+} ions are observed in the solution of Tb(AcA)$_3$phen in chloroform. The interaction between PVK and Tb(AcA)$_3$phen in chloroform is apparent. From Fig. 3, we see that, as the concentration of PVK is increased, the intensities of Tb^{3+} ion emissions decrease, showing fluorescent quenching effect of PVK to the Tb complex. When the weight ratio of PVK and Tb(AcA)$_3$phen reaches about 4:1, further increase of PVK results in no distinct changes in the emission spectrum. At the ratio of 2:1, on monitoring the emission of Tb^{3+} ions at 546 nm, two peaks (at 310 and 370 nm) appear in the excitation spectrum (see Fig. 4). The 370 nm band corresponds to the excitation band of PVK. The fact that there is a new excitation band at 310 nm but no excitation band of the Tb complexes (at 330 nm) in the spectrum is not clearly understood. A possible reason is that a new structure is formed between the Tb complex and the carbazole group at PVK in this system. We obtained further support on this from Tb complex-dispersed PVK films.

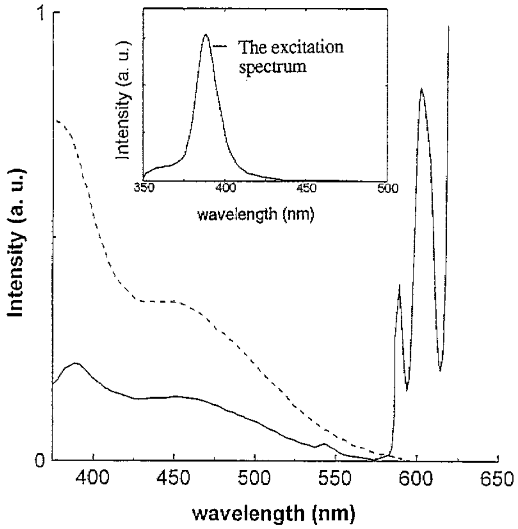

Fig. 2. The emission spectra of PVK (- - -), PVK:Eu(NO_3)$_3$phen (———) and excitation spectrum of PVK:Eu(NO_3)$_3$phen (inset) in chloroform solution.

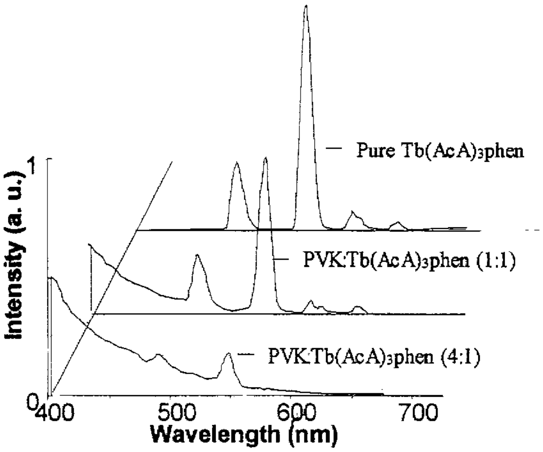

Fig. 3. The emission spectra of Tb(AcA)$_3$phen and PVK:Tb(AcA)$_3$phen in chloroform solution.

3.2. *PL spectra in thin films*

The emission spectra of PVK film and Eu complex-dispersed PVK films are shown in Fig. 5. In film, the emission peak of PVK shifts to 410 nm which mainly originates from the low-energy intrachain excimer [6,7]. Very strong emis-

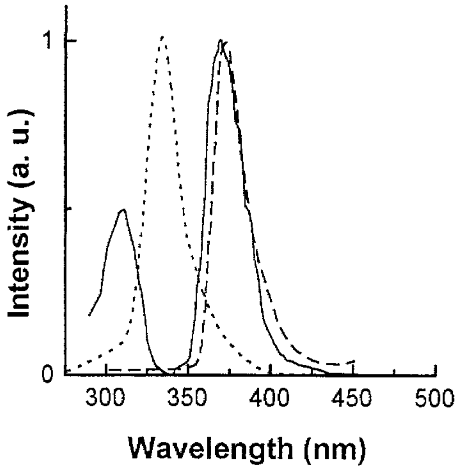

Fig. 4. The excitation spectra of PVK (— —), Tb(AcA)$_3$phen (- - -) and PVK:Tb(AcA)$_3$phen (———) in chloroform solution.

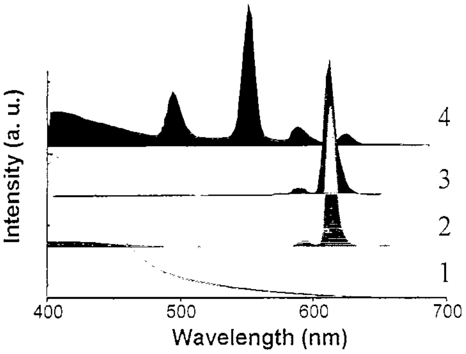

Fig. 5. The emission spectra of PVK, PVK:Eu(TTA)$_4$Py, PVK:Eu(NO$_3$)$_3$phen and PVK:Tb(AcA)$_3$phen as films: 1, PVK; 2, PVK:Eu(TTA)$_4$Py, weight ratio 10:1; 3, PVK:Eu(NO$_3$)$_3$phen, weight ratio 20:1; 4, PVK:Tb(AcA)$_3$phen, weight ratio 7:1.

sions of Eu^{3+} ions dominate the emission spectra of PVK:Eu(TTA)$_4$Py and PVK:Eu(NO$_3$)$_3$phen thin films, and the emission of PVK is hardly visible in the spectra.

The excitation spectra of PVK, PVK:Eu(TTA)$_4$Py and PVK:Eu(NO$_3$)$_3$phen thin films are shown in Fig. 6. The excitation spectrum of PVK becomes a wide-structured band which is dramatically different from that in solution (see Fig. 2) due to enhanced interaction among molecules in the solid state. The excitation spectra of Eu(TTA)$_4$Py and Eu(NO$_3$)$_3$phen in PVK films are very similar to that of PVK, indicating that the emissions of Eu^{3+} ions mainly come from the excitation of PVK.

The emission spectrum of PVK:Tb(AcA)$_3$phen thin film is also shown in Fig. 5. In addition to the strong emission of Tb^{3+} ion, a wide band at 405 nm appears in the spectrum. Monitoring the 546 nm emission of Tb^{3+} ions, an excitation spectrum is plotted in Fig. 6. This spectrum differs greatly from the excitation spectrum of pure Tb(AcA)$_3$phen film, but has the same structure as that of PVK showing that the emissions of Tb^{3+} ions originate from the excitation of PVK.

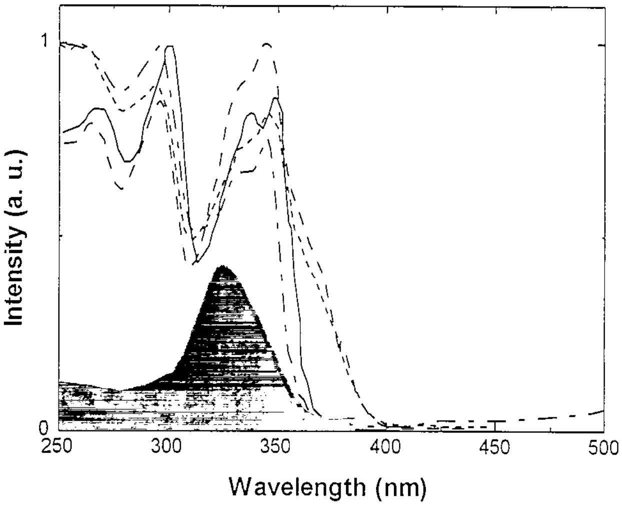

Fig. 6. The excitation spectra of PVK, PVK:Tb(AcA)$_3$phen, PVK:Eu(NO$_3$)$_3$phen and PVK:Eu(TTA)$_4$Py as films: ———, PVK, λ_{ex}=410 nm; - - -, PVK:Eu(NO$_3$)$_3$phen, λ_{ex}=613 nm; —— ——, PVK:Eu(TTA)$_4$py, λ_{ex}=613 nm; – · – PVK:Tb(AcA)$_3$phen, λ_{ex}=546 nm; shaded area, PVK:Tb(AcA)$_3$phen, λ_{ex}=405 nm.

While concentrating on the wide emission band at 405 nm, the excitation spectrum is also shown in Fig. 6. It is surprising that the excitation band is not like that of PVK but a narrow isolated peak at 325 nm, implying that the 405 nm emission band may not come from the intrachain excimer of PVK. This further suggests that a new structure like exciplex may be formed in the Tb complex-doped PVK film.

In other words, an effective energy transfer process from PVK to RE complex occurs in the doped films studied. For the Tb complex-doped PVK system, a new structure such as exciplex may be formed.

The photophysical processes in PVK have been studied extensively in earlier works [6,7]. A basic model can be used to explain the energy transfer mechanism in PVK. Absorption of UV radiation takes place randomly, forming excited singlet states. The lowest excited singlet state forms an exciton that diffuses in the film at a ‘hopping’ mode. The exciton can be trapped either at excimer sites or by guest molecules. Fluorescence emission–absorption processes can be neglected since the thickness of the film is too small.

3.3. EL

Since the excitons in the doped PVK film are trapped by the guest molecules and result in strong emission of RE ions, we expect that EL of RE ions can be observed if a large number of excitons is formed by recombination of electrons and holes in this layer. So we fabricated three types of organic EL devices with structures of ITO/Eu(NO$_3$)$_3$phen:PVK/OXD-7/Al, ITO/Eu(TTA)$_4$Py:PVK/OXD-7/Al and ITO/Tb(AcA)$_3$phen:PVK/OXD-7/Al, respectively. Bright red emissions can be observed in the first and the second devices while bright green light is emitted from the latter device. The question as to whether the energy transfer from PVK to RE complexes also occurs in the EL process is under investigation.

4. Conclusions

In chloroform solution, the energy transfer process from PVK to Eu(NO$_3$)$_3$phen is observed; however, the fluorescent intensity of the Tb complex was greatly quenched by PVK. In films, effective energy transfer occurs from PVK to RE complexes like Eu(TTA)$_4$Py, Eu(NO$_3$)$_3$phen and Tb(AcA)$_3$phen. A new structure like exciplex is possibly formed between Tb(AcA)$_3$phen and PVK. EL of RE ions was obtained in the device which has a Eu complex-doped or Tb complex-doped PVK layer.

Acknowledgements

This research is supported by the National Science Foundation of China and Laboratory of the Excited State Processes, Academia Sinica, China.

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