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Novel ternary copolymer containing both Tb(III) and Eu(III) complexes for white-light electroluminescence

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There has been tremendous interest in the search of rare earth (RE) complexes for use as electroluminescent (EL) materials ever since Kido and his coworkers reported the first light emitting device based on Tb(acetylacetonate)$_3$ (Tb(acac)$_3$) [1]. The significant advantages of rare earth organic materials are the color purity of the generated emission, narrow-band (10–20 nm) emission, long decay times (10^{-2}–10^{-6} s), and high quantum yields. White-light emission based on Tb and Eu complexes small organic molecules have been realized by Kido's and Li's groups independently [2, 3]. However, the use of small organic molecule materials in the fabrication of EL devices is often unsatisfactory because crystallization or melting effects can occur during device operation [4, 5]. Moreover, device fabrication itself is sometimes tedious. The high-quality devices from small organic molecule materials usually require high-vacuum deposition techniques that make processing expensive. Thus, it is obvious that the development of novel polymer materials containing rare earth complex is a fundamental task. In recent years, we have reported that copolymers containing Eu(III) complexes exhibit monochromatic-red-light emission [6–8].

In this paper, copolymers containing both Tb and Eu complexes are synthesized for use in single layer organic light emitting devices (OLEDs), as combination of that with a blue-light emitting N,N′-bis(3-methylphenyl)-N,N′-diphenylbenzidine (TPD) (Fig. 1) dopant, white-light electroluminescence was realized.

Rare earth complex monomers Eu(BA)$_2$(MAA)Phen and Tb(acac)$_2$(MAA)Phen, where MAA = methylacrlic acid, acac = acetyl acetone, BA = benzoylacetone and Phen = 1,10-phenanthrolien, were synthesized as previously reported [7]. The copolymerization of N-vinylcarbazole (NVK), methylmethacrylate (MMA), Eu(BA)$_2$(MAA)Phen and Tb(acac)$_2$(MAA)Phen was carried out with azobisisobutyronitrile (AIBN) as initiator and tetrahydrofuran (THF) as solvent under argon atmosphere at 333 K for 24 h. The chemical structure of NVK-co-MMA-co-Tb(acac)$_2$(MAA)Phen-co-Eu(BA)$_2$(MAA)Phen copolymer (PKMTbEu) is illustrated in Fig. 1.

PKMTbEu's photoluminescence (PL) was investigated both in THF solution and in thin film, and the results are given in Figs 2 and 3 respectively. In Fig. 2, the emission band between 340 and 460 nm is generated from the $^*\Pi \rightarrow \Pi$ transition of carbazole moieties of the copolymer PKMTbEu. The emission peak centered at 350 nm is the normal emission of structured NVK, which is separated by other groups (such as MMA groups). The emission at 370 nm is ascribed to excimer emission from a partial overlap of carbazole chromophores. As it can be seen from Fig. 2, the other four peaks centered at 490, 545, 595 and 615 nm, which originate from transitions between 4f states of RE^{3+} ions in PKMTbEu, may be attributed to $^5D_4$-$^7F_6$ (Tb^{3+}), $^5D_4$-$^7F_5$(Tb^{3+}), $^5D_0$-$^7F_1$ (Eu^{3+}) and $^5D_0$-$^7F_2$ (Eu^{3+}) transition respectively. However, the PL spectrum of PKMTbEu in thin film (Fig. 3) shows that the carbazole emission is red-shifted from 370 to 410 nm and become a broad band compared to that in solution. This can be explained as emission center changes from partial overlap excimer in solution to total overlap excimer in thin film [8]. More over, the RE^{3+} ion emissions at 490, 545, 590 and 615 nm are much stronger in thin film compared to their solution counterparts. This can be ascribed to the more efficient Forster energy transfer from NVK to rare earth complex segments in thin film because of closer distance between these two groups.

The relative PL intensity of luminescence peak at 545 nm in thin film from PKMTbEu synthesized with

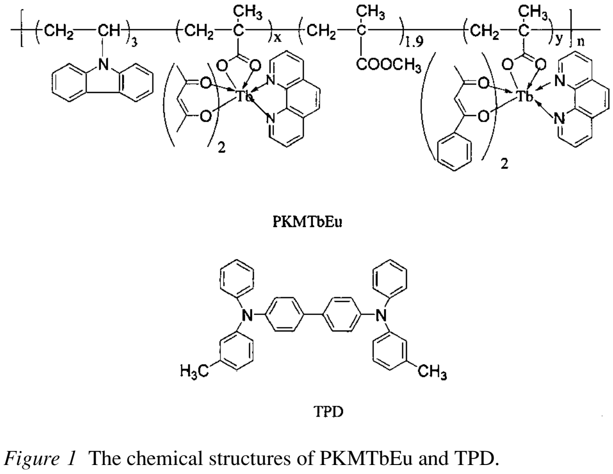

Figure 1 The chemical structures of PKMTbEu and TPD.

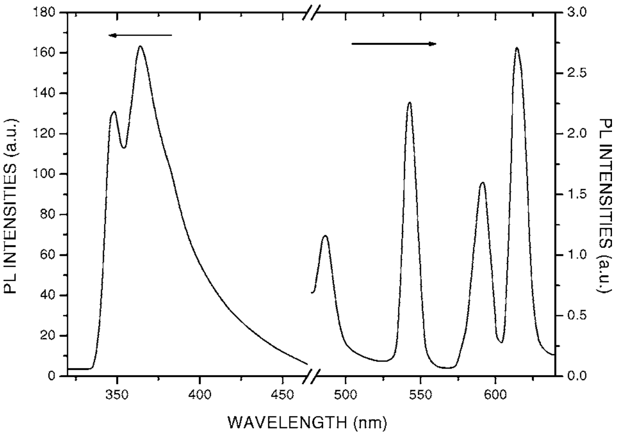

Figure 2 PL spectrum of PKMTbEu ($x = y = 0.05$) in THF solution (2×10^{-6} g/ml), $\lambda_{ex} = 295.4$ nm.

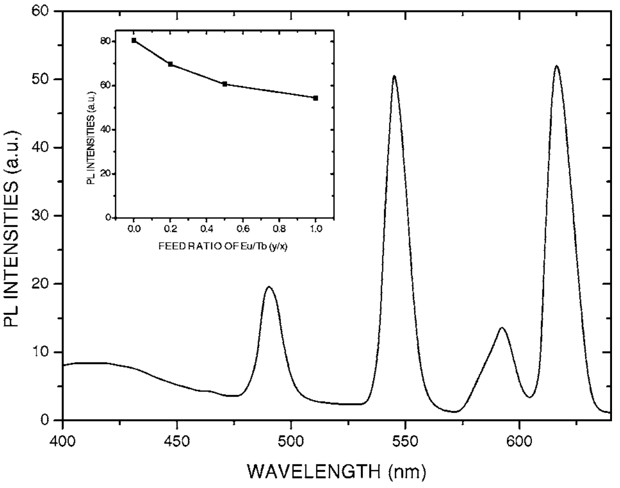

Figure 3 PL spectrum of PKMTbEu ($x = y = 0.05$) in thin film with $\lambda_{ex} = 295.4$ nm. Inset: PL intensities at 545 nm vs. the feed ratio of Eu/Tb complexes (y/x).

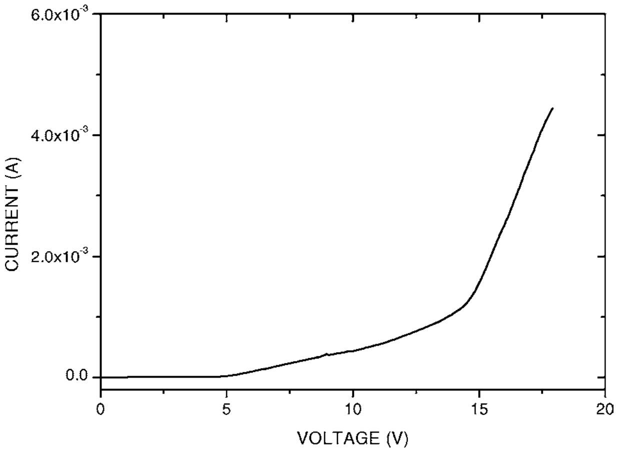

Figure 4 Current-voltage characteristic curve of OLED based on PKMTbEu with $x = y = 0.05$.

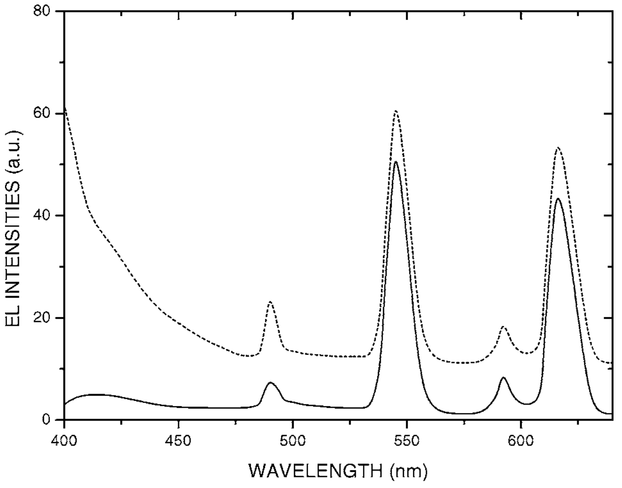

Figure 5 EL spectra of electroluminescent devices under a 15 V forward bias: ITO/PKMTbEu/Al ($x = y = 0.05$) (—); ITO/PKMTbEu:TPD/Al ($x = y = 0.05$, PKMTbEu/TPD = 50/1 w/w) (----).

different Eu/Tb complex monomers feed ratio is also illustrated in Fig. 3 (inset). A little decrease of the PL intensity at 545 nm is observed with the increase of the Eu/Tb complexes feed ratio, which, maybe, results from the decrease of Tb complex monomer units attached to the polymer chain. However, no quenching effect of Tb^{3+} ion emission by Eu^{3+} ion was obviously observed in PKMTbEu, that is, the Forster energy transfer from Tb^{3+} ion to Eu^{3+} ion in PKMTbEu was prohibited, which may be due to that Tb and Eu complex units are well separated from each other by several other segments in polymer chain [9].

In order to investigate the electroluminescent properties of PKMTbEu, a single layer EL device, ITO/PKMTbEu/Al, was fabricated by spin-coating the polymer layer of PKMTbEu from chloroform solution onto the top of indium tin oxide (ITO) glass electrode as anode, and then depositing an Al top electrode as cathode with the active area of 2.5 mm × 2.5 mm by thermal evaporation. The current-voltage (I-V) curve of an ITO/PKMTbEu/Al device is displayed in Fig. 4, showing a typical diode character. With the increase of forward bias, the current increases rapidly after 14.3 V. In this case, in fact, a weak emitting light was observed under dark environment. Moreover, it was found that the color of the emitting light changes from green to yellow as the increase of the Eu/Tb complex feed ratio. It is worth noting that a white emission was observed from the device fabricated with PKMTbEu incorporated with a blue light emitter TPD, ITO/PKMTbEu:TPD/Al.

Fig. 5 shows the EL spectra of both devices: ITO/PKMTbEu/Al and ITO/PKMTbEu:TPD/Al. The electroluminescent process of RE^{3+} ions is presumed as follows. Electrons and holes are injected into the polymer layer from Al and ITO respectively under the driving bias and recombine to produce excitons. The singlet excitons are transferred to the ligand sites of RE complexes, converted into triplet excitons via inter system crossing, and then triplet excitons are transferred to the RE^{3+} ion sites by Dexter mechanism. The energy relaxation from ^5D to ^7F results in sharp emission of RE^{3+} ions [10].

In conclusion, a novel ternary copolymer containing both Tb(III) and Eu(III) complexes (PKMTbEu) was synthesized and its luminescent properties have been investigated. Efficient Forster energy transfer from NVK segments to rare earth metal complex units in the PKMTbEu was observed. The PKMTbEu copolymer would allow fabrication of single layer OLEDs.

The color emitted from the devices can be tuned by variation of Eu/Tb complex feed ratio. The device fabricated with PKMTbEu incorporated with TPD, ITO/PKMTbEu:TPD/Al, exhibits a white emission. Further investigations are in progress.

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