

White LED based on poly(N-vinylcarbazole) and lanthanide complexes ternary co-doping system

Yanhua Luo^{a,b}, Qing Yan^a, Zhoushun Zhang^a, Xiaowu Yu^a, Wenxuan Wu^a, Wei Su^a, Qijin Zhang^{a,*}

^a CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Key Laboratory of Optoelectronic Science and Technology, Anhui Province, Hefei, Anhui 230026, China

^b School of Electrical Engineering, University of New South Wales, Sydney 2052, NSW, Australia

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ABSTRACT

First, binary and ternary doping system of terbium and/or europium β -diketonate complex doping in poly(N-vinylcarbazole) (PVK) was studied. Energy transfer was analyzed in such complicated doping system. In such a complicated system, inter-molecular energy transfer from PVK to Tb(DBM)₃Phen(TbDP) and Eu(DBM)₃Phen(EuDP), and from TbDP to EuDP exists. The color changed by adjusting the mixing ratio of dopants concentration and excitation wavelength. Further, in the ternary doping system, it is found that white light could be obtained by optimizing the excitation of different wavelength.

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1. Introduction

White organic light-emitting diodes (OLED) are currently considered as low-cost alternatives, large luminance and low weight for applications in flat panel display systems and lighting technology, due to the variety of attainable emission colors, the ease of their production, and the high quantum efficiency [1,2]. In order to obtain white light emission from OLED excitation, more than one molecular species is necessary, since the luminescence of a single organic molecule does not typically span the entire visible spectrum. However, mixing red, green and blue OLEDs in a single system brings forth difficulties in the integration of individual materials [1]. Moreover, the proper selection of red-(Eu³⁺, Pr³⁺, Sm³⁺), green-(Tb³⁺, Er³⁺), and blue-(Tm³⁺, Ce³⁺) emitting lanthanide ions as dopants in a common host material (PVK, for instance) [3–7] could simplify the LED structure and, hence, the fabrication process would reduce the cost and resolving some of the critical integration problem [1].

In particular, a LED device consisting of near-ultraviolet-light chip and red, green and blue luminescent compounds has a large color rendering index [8]. In view of most commercial factors, ultraviolet-light chips have the very significant advantage of employing mercury arc lamps that provide a very bright emission at 366 nm [9]. Under ultraviolet excitation, the very efficient light emission is characteristic of lanthanide β -diketonate complexes

[8,10–12], for β -diketonate ligand sensitize lanthanide emission [13], which absorbs energy, undergoes intersystem crossing into a triplet state, and then transfers its energy to the lanthanide ion [14–16]. Especially, the substitution of the water molecules by other chemical species, such as heterocyclic ligands (e.g., 2,2'-bipyridine and 1,10-phenanthroline (Phen)), substituted sulfoxide and phosphine oxides, and aromatic carboxylic acid, among many others, has been extensively employed in order to improve the light emission. Compounds displaying unusually high emission quantum efficiencies, 70–80%, have resulted from this concept [11].

And one of the strategies adopted in recent years to improve the thermal stability, mechanical properties, and light emission properties of lanthanide β -diketonate chelates simultaneously is their incorporation into polymeric matrices [17] and sol-gel derived organic-inorganic nanostructured hybrids [12]. To incorporate lanthanide ions into conjugated polymers, we synthesized a family of soluble lanthanide complexes with β -diketonate ligands, codissolved the complexes and polymers in a solvent, and cast films. A design rule is imposed by the need for energy transfer from the polymer to the rare earth complex. In order to transfer energy from a conjugated polymer to the ligands of a europium complex by dipole coupling (Förster transfer), the emission spectrum of the polymer and the absorption spectrum of the ligand must overlap [18]. So emissive polymer PVK is often used as a matrix polymer due to its excellent film forming property, into which emitting dyes were dispersed [10,19].

Furthermore, a main problem in these applications is the concentration quenching when the complexes concentration reaches

* Corresponding author. Tel.: +86 551 3601704; fax: +86 551 3601704.

E-mail address: yhluo3@mail.ustc.edu.cn (Q. Zhang).

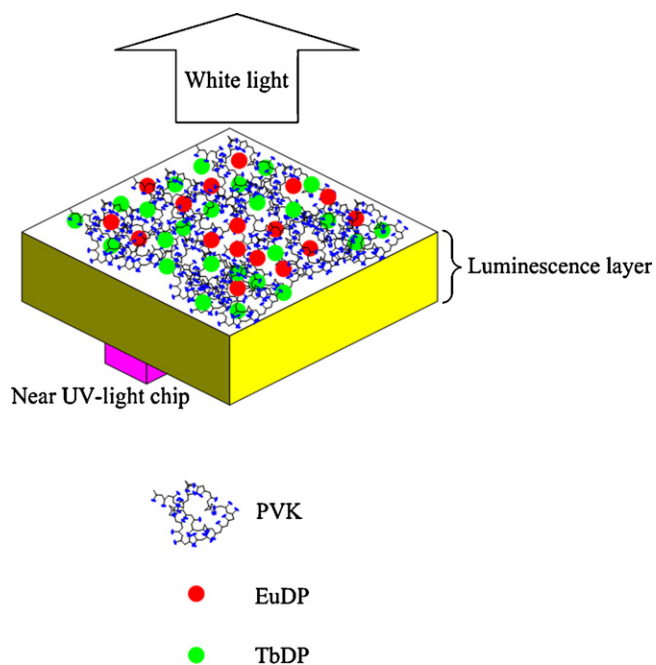


Fig. 1. The model of ultraviolet-excited white LEDs.

a high critical value. One of methods to resolve this problem is co-doping other lanthanide ions that can considerably enhance photoluminescent intensity (co-luminescence effect or sensitization) and have been widely observed in various systems [20–24]. It is believed that there exists an energy transfer among different lanthanide ions in these co-doped materials [25,26]. Energy transfer from Tb^{3+} to Eu^{3+} has been used in various matrices [25–28], in which Eu^{3+} was used as an acceptor and Tb^{3+} as a donor. Ulteriorly, it is an economic way of substitution some of europium complexes with terbium complexes, for the price of europium oxide is about 9 times that of terbium oxide [29].

In this paper, PVK is not only used as the blue emitter but also a matrix dispersing the green and red emitter. Terbium β -diketonate complex is not only used as the green emitter but also a low price energy donor to europium β -diketonate complex which is used as the red emitter. The proposed model for such of ultraviolet-excited white LEDs is shown in Fig. 1. First, binary and ternary doping system of terbium and/or europium β -diketonate complex doping in PVK was studied. Energy transfer was analyzed in such complicated doping system. For the ternary doping system, it is found that white light could be obtained by optimizing the excitation of different wavelength.

2. Experiment

2.1. Materials preparation

Lanthanide complexes ($LnDP$, $Ln^{3+} = Eu^{3+}, Tb^{3+}$) were synthesized according to the procedure reported before [30]; their molecular structure is shown in the inset of Fig. 2. The central ion (Ln^{3+}) is bound to three ligands of dibenzoylmethide (DBM) ions. Phen acts as a synergic shielding ligand, which can reduce the rate of non-radiative decays and enhance the luminescence intensity of the complex strongly [31]. The final products were recrystallized in acetone/petroleum ether (2:1). PVK was synthesized according to Ref. [32] then used as the matrix of the ternary blend and the donor of Förster-type energy transfer.

EuDP, TbDP and PVK were dissolved in chloroform (CHL) with the concentration of 0.010, 0.040, and 0.108 g/mL, respectively. And

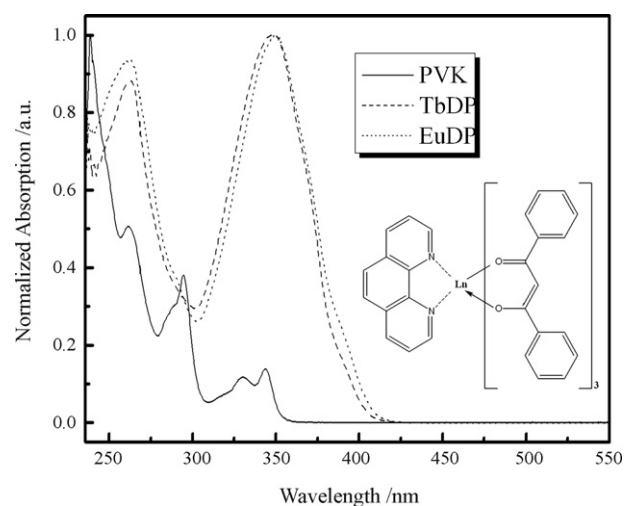


Fig. 2. Absorptions of two complexes and PVK in CHL. Inset is the chemical structure of LnDP.

then different doses of TbDP and EuDP solution, as shown in Table 1, were added to 0.5 mL solution of PVK and then the solution was diluted to 1 mL. Subsequently, the solution was spin-coated on clean glass slides and finally dried at 50 °C under vacuum for 2 days. All the film samples were prepared at the spin speed of 2500 revolution per minute (rpm) and the film thickness is about 20 nm. And the concentration of dopants in all samples is shown in Table 1. Reference samples of TbDP and EuDP doped poly(methyl methacrylate) (PMMA) were the sample $Eu_{0.010}Tb_0$ -PMMA and $Eu_0Tb_{0.010}$ -PMMA as reported in Ref. [16].

2.2. Measurements

Absorption spectra of two complexes and PVK in CHL were obtained on a UV–vis photometer (SHIMADZU UV-2401PC). Photoluminescence (PL) was measured on the RF-5301PC at room temperature and the spectra were measured with UV-39 to filter excess excitation wavelength of UV light, but the measurement of the PL decay curves was performed on FLUOROLOG-3-TAU at room temperature.

3. Results and discussion

3.1. Absorption and fluorescence properties

Absorption spectra of two complexes and PVK in CHL are shown in Fig. 2. The concentrations were all about 20 ppm. The absorption spectrum of PVK in CHL is essentially identical with the spectrum reported by Klopffer for PVK in methylene chloride. Furthermore, the absorption spectrum of PVK and a monomer analog, N-isopropylcarbazole, are largely the same, indicating weak ground state mixing of the chromophores in the polymer [33]. The absorption bands in the spectral ranges 350–300, 300–270, and 270–250 nm were identified with the singlet 1L_b , 1L_a , and 1B_b

Table 1
The dopant concentration of the sample.

Sample number	EuDP (μ L)	TbDP (μ L)	[EuDP] (mol/L)	[TbDP] (mol/L)
No. 1	0	0	0	0
No. 2	20	0	4.4×10^{-3}	0
No. 3	50	0	0.011	0
No. 4	100	0	0.022	0
No. 5	0	100	0	0.082
No. 6	20	100	4.1×10^{-3}	0.082

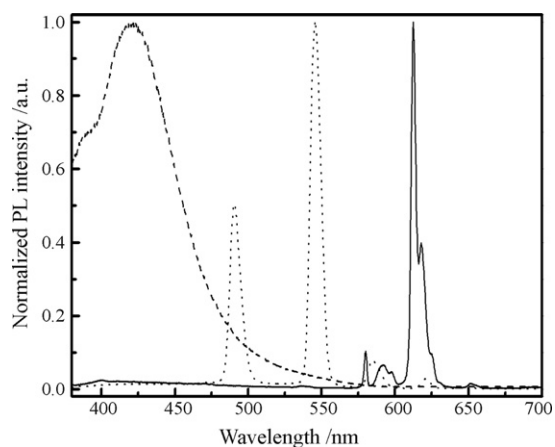


Fig. 3. The emission spectra of PVK film (dash line), EuDP in PMMA (solid line) and TbDP in PMMA (dot line) under the excitation at 350 nm.

transitions, respectively [34]. In the spectra of EuDP and TbDP in CHL, the band of the shortest wavelength appearing at 261 nm may be attributed to $\pi \rightarrow \pi^*$ transition of the benzene ring moiety of DBM, which is strong enough to hide the absorption of Phen [35]. The second band observed at around 350 nm can be assigned to $\pi \rightarrow \pi^*$ transition involving the whole conjugation and delocalization electronic system of the ligand [36–38]. And the band of the longest wavelength shows an obvious bathochromic shift relative to their free ligand, showing the formation of the coordinating bond between ligands and central ions [16,35]. It is worth to note that the absorption of TbDP shows similar absorption band to that of EuDP for their close structures.

In Fig. 3, the emission spectra of PVK, EuDP and TbDP in PMMA under excitation at 350 nm are shown. The emission peak of PVK is 421 nm which mainly originates from the low-energy intrachain excimer [3]. And the emission spectrum of EuDP in PMMA from 380 to 700 nm have four emission peaks centered at 579, 592, 612, 652 nm, which can be assigned to the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, respectively. The presence of only one $^5D_0 \rightarrow ^7F_0$ line indicates that Eu^{3+} ion exists in a single chemical environment [39]. The much stronger intensity of $^5D_0 \rightarrow ^7F_2$ than those of other transitions indicates that Eu^{3+} ion is in a single site without a center of inversion [40]. But for TbDP in PMMA, there are four emission peaks from 380 to 700 nm, which are centered at 489, 546, 584, and 620 nm, and can be attributed to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$, respectively. The strongest peak is located at 546 nm. The CIE chromaticity coordinates of elementary color dopants were calculated from curves shown in Fig. 3 according to Refs. [41–43]. The coordinates of PVK, EuDP and TbDP are (0.1614, 0.0598), (0.5711, 0.3137) and (0.2404, 0.5600), respectively, which could be assigned to blue, red and green color. Therefore, based on these three elements white LED could be made.

3.2. Binary doping system of PVK doped with lanthanide complexes

Fig. 4(a) shows the PL spectra of PVK doped with different amount of EuDP under the excitation at 350 nm. The two distinct emission peaks appear at 421 and 613 nm which are blue emission from the host of PVK and red emission from EuDP, respectively. With increasing of Eu^{3+} concentration the emission at 421 nm decreased and the emission at 613 nm increased gradually, showing inter-molecular energy transfer taken place and resulting in the enhancement of PVK to Eu^{3+} as shown in Fig. 4(b). Seen from Fig. 4, the total tendency of adding the EuDP may quench the luminescence of PVK. But when the concentration of EuDP is so low, the

red emission cannot be detected. Because when the EuDP is low, the luminescence of EuDP is very weak, even though EuDP could quench the luminescence of PVK enhancing itself luminescence, contrarily PVK could quench the luminescence of EuDP. The final result is that the luminescence of PVK becomes weaker, and the luminescence of EuDP is not enhanced enough, lots of the energy may be lost in the transfer process. And it is worth to point out that this result was obtained by exciting at 350 nm that is the maximal absorption peak for EuDP as discussed above concerning intramolecular energy transfer from ligands to central ions. This reveals that Eu^{3+} in the doped system diverts a large portion of the energy absorbed by PVK, which promoted the luminescence quenching of PVK and the luminescence enhancement of Eu^{3+} . Similarly, in the TbDP doping PVK system, the luminescence of PVK could also be quenched by TbDP, which is shown in Fig. 5. And there evidently appears a broad emission band from 400 to 600 nm. Compared Fig. 5 with Fig. 3, the broad band can only be observed in such a system containing both TbDP and PVK. According to Ref. [4], there is a strong phosphorescent band is observed around 500 nm which originates from the radiative transition of the triplet state of the ligand. So it is believed that this broad emission may come from the ligand.

3.3. Ternary doping system of PVK doped with lanthanide complexes

The PL spectra of PVK co-doped with TbDP and EuDP under the excitation at different wavelength are shown in Fig. 6(a). The five distinct emission peaks appear at 490, 545, 580, 591 and 613 nm

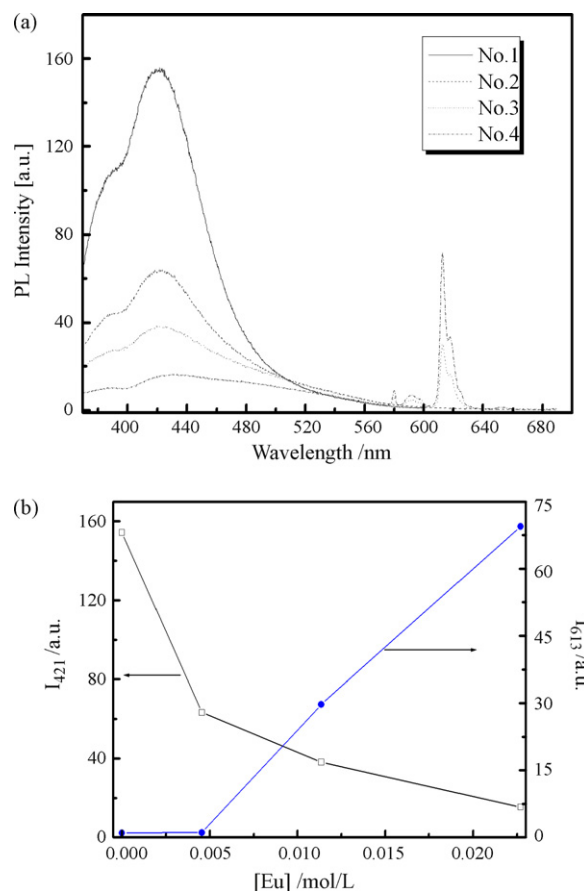


Fig. 4. (a) The PL spectra of PVK films doped with different amount of EuDP under the excitation at 350 nm. Amount of EuDP is increasing from No. 4 to No. 1. (b) The relationship between the corresponding intensity of samples from No. 1 to No. 4 at the 421 and 613 nm and the concentration of EuDP.

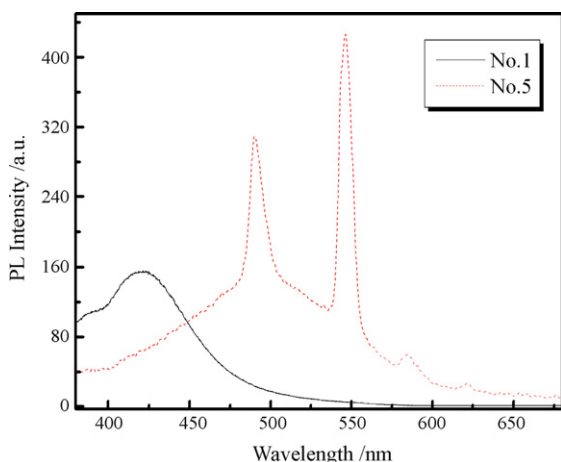


Fig. 5. The PL spectra of No. 1 and No. 5 sample under the excitation at 350 nm.

which are the multiplex emission attributing to TbDP and EuDP. For the excitation wavelength lower than 350 nm, the emission features are similar, and the green TbDP luminescence, the $^5D_4 \rightarrow ^7F_6$ transition (~ 545 nm) dominates. The red $^5D_0 \rightarrow ^7F_2$ EuDP line (~ 613 nm) clearly has a low intensity, a broad emission band from 400 to 600 nm also appears as mentioned above, and no evident PVK emission could be detected. When the excitation wavelength is shorter

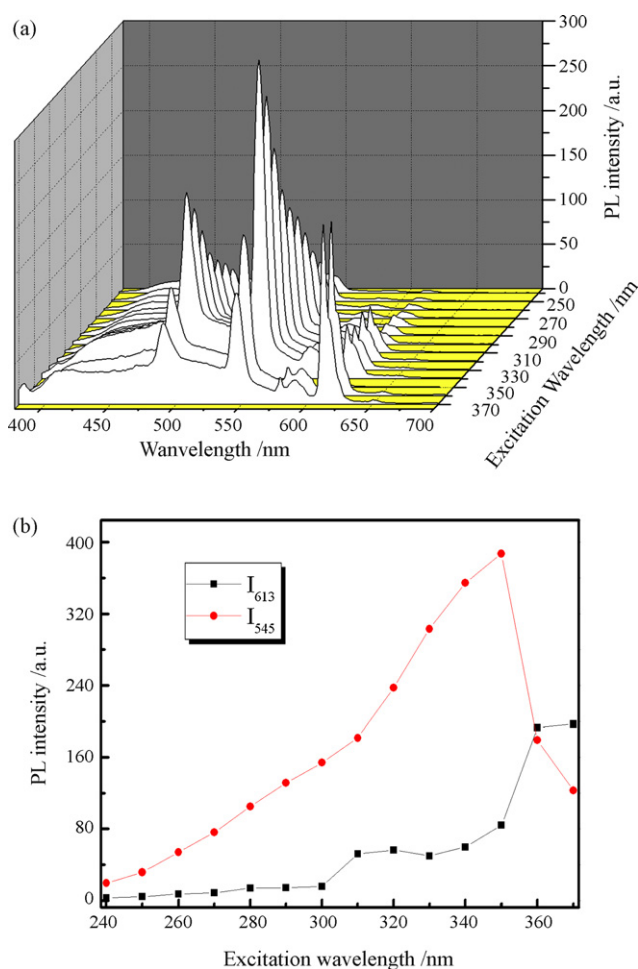


Fig. 6. (a) The PL spectra of No. 6 sample under the excitation at different wavelength. (b) The relationship between the PL intensity at 613 and 545 nm and excitation wavelength.

than 370 nm, the PL intensity at 613 nm increases with the increment of the excitation wavelength and the intensity at 545 nm increases too until the excitation wavelength reach 350 nm, then the intensity may decrease with increasing of the excitation wavelength, which is shown in Fig. 6(b). And it needs to notice that the total luminescent intensity of PVK co-doped with TbDP and EuDP increases until the excitation wavelength is up to 350 nm, and then decreases with the increment of the excitation wavelength shown in Fig. 7, which has similar changing trend with that of TbDP shown in Fig. 6(b).

As it is mentioned above, energy transfer of rare earth ions in PVK exists. Energy transfer in those matrices is considered due to resonant or non-resonant energy transfer of optical energy between center ions in the presence of disorder and non-radiative relaxation processes. Therefore non-exponential decay profiles are considered to be observed in rare earth ions doped solid matrices, which there exists energy transfer between the matrices and doping rare earth ions [44–46]. We have to define the average decay time of lanthanide ion luminescence in singly doped and co-doped PVK. Luminescence intensity $I(t)$ is approximated by the sum of two exponential decay components from

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \quad (1)$$

where τ_1 and τ_2 are short- and long-decay components, respectively. Parameters A_1 and A_2 are fitting constants. Using Eq. (1), the average lifetime (τ) is given by

$$\langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

where weight factors A_1 and A_2 are introduced. As shown in Fig. 8, the decay curve is well fitted using Eq. (1), where complicated decay profiles of rare earth ions and dyes in sol-gel glasses have reasonably been explained by using average lifetimes defined as above [44–46]. And the average lifetime is obtained using Eq. (1), which is listed in Table 2.

Seen from Table 2, the lifetime of 5D_0 of Eu^{3+} in PVK is longer than that in PMMA [47], and the lifetime of 5D_4 of Tb^{3+} in PVK is also longer than that of Tb^{3+} β -diketonate complexes in arachidic acid, showing evidence of energy transfer from PVK to EuDP and TbDP [48]. And in the TbDP and EuDP co-doping PVK system, the lifetime of 5D_0 of Eu^{3+} becomes longer but the lifetime of 5D_4 of Tb^{3+} becomes smaller, which is an obvious evidence that there exists the energy transfer from TbDP to EuDP.

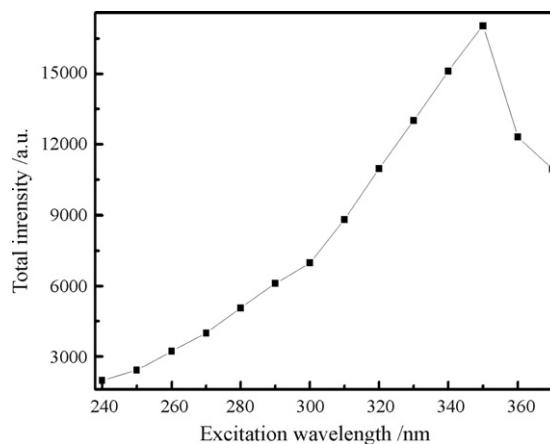


Fig. 7. The total luminescent intensity of PVK co-doped with TbDP and EuDP from 380 to 700 nm under the excitation at different wavelength, which is integrated from 380 to 700 nm in Fig. 6(a).

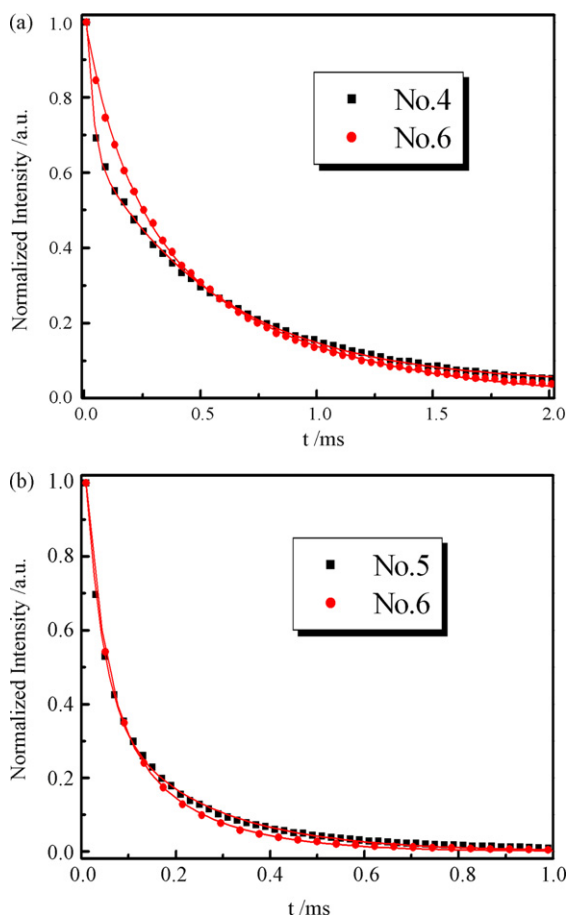


Fig. 8. Decay curves of the transition ($^5D_0 \rightarrow ^7F_2$) of Eu^{3+} (a) in sample No. 4 and No. 6 and the transition ($^5D_4 \rightarrow ^7F_5$) of Tb^{3+} and (b) in sample No. 5 and No. 6, under the excitation at 350 nm.

3.4. Realization of white LED

To obtain an efficient white LED, a mixture of TbDP and EuDP together with luminescent PVK were used. In such a mixture, in principle three emission processes can be envisaged: direct emission from blue, green and red chromophores, and emission solely from TbDP and EuDP due to energy transfer resulting from the overlap between the emission spectrum of PVK and the absorption spectrum of TbDP and EuDP, and emission from EuDP due to energy transfer from TbDP to EuDP, and different emission process corresponds to different color change. And the relative contributions of these two processes will be a function of their ratios in the blend [49]. Fig. 9 shows the 1931 Commission Internationale d'Éclairage (CIE) chart of the light emission shown in Fig. 3, 4(a), 5 and 6(a) [41,42]. As shown in Fig. 9, the coordinates of elementary color dopants, PVK, EuDP and TbDP formed a triangle, which are the elementary color blue, red and green color, respectively. If there is no

Table 2
Fluorescence lifetime of lanthanide complex in solid.

Sample name	$(\tau)_{\text{Eu}^{3+}}$ (ms)	$(\tau)_{\text{Tb}^{3+}}$ (ms)	Reference
No. 4	0.547	NA	NA
EuDP in PMMA	0.486	NA	[47]
No. 5	NA	0.229	NA
Tb(TFA) ₃ Phen/AA (1:1)	NA	0.097	[48]
Tb(HFA) ₃ Phen/AA (1:1)	NA	0.062	[48]
No. 6	0.612	0.134	NA

AA, TFA and HFA are arachidic acid, trifluoroacetylacetone and hexafluoroacetylacetone, respectively.

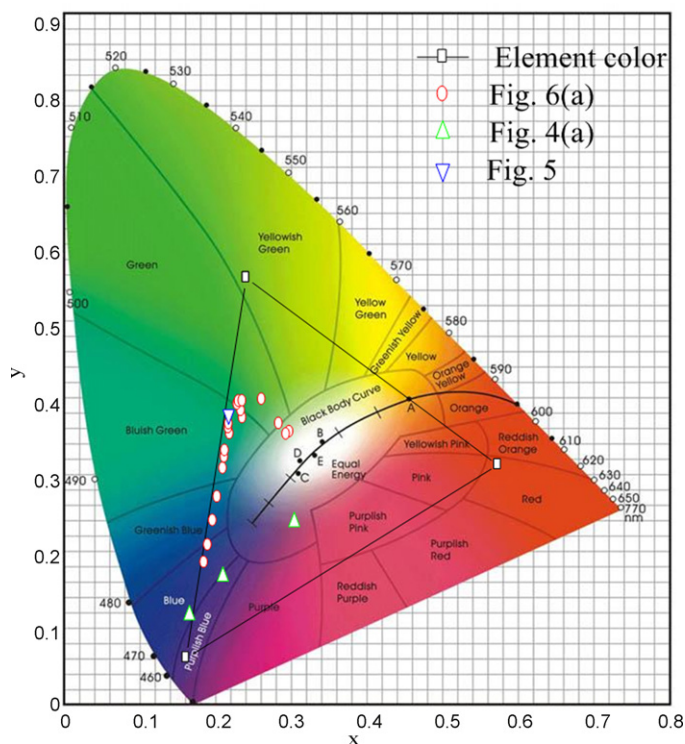


Fig. 9. The CIE chromaticity coordinates of the emission color of element color dopants (PVK, TbDP and EuDP), PVK doped with EuDP shown in Fig. 4(a), PVK doped with TbDP shown in Fig. 5, and PVK co-doped with TbDP and EuDP shown in Fig. 6(a). CIE 1931 chromaticity diagram all possible color coordinates (x, y) are on or inside horseshoe curve pure colors line on the curve, where as the white point has the coordinates (1/3, 1/3). (For interpretation of the references to color in the figure caption, the reader is referred to the web version of the article.)

energy transfer in such a system, any mixture with these dopants may be in the triangle described above.

Dopant EuDP or TbDP and the blue emitting PVK matrix were combined in a blend to obtain efficient red and green PL. It can be observed that the EuDP concentration significantly affects both PL intensity and color. When increasing the concentration of EuDP doped in PVK, the PL intensity of PVK decreases and that of EuDP increases, and accordingly the color changed from purplish blue to red along a deformed arched curve. If there is no energy transfer from PVK to EuDP, in such doping system the color change may have a linear relationship with the increment of EuDP [49]. But due to the energy transfer, the color changed along a deformed arched curve with the increment of EuDP. Especially, sample No. 2 falls outside the triangle, because when the concentration of EuDP is low, adding the EuDP may quench the luminescence of PVK heavily without good red emission, and lots of energy was lost in the transfer process. Similarly, in the TbDP doping PVK system, the color also falls in the triangle, but not at the line connecting with PVK and TbDP, due to energy transfer from PVK to TbDP.

And in such a complicated ternary co-doping system, for different dopant having different excitation spectrum and energy transfer existing, there is an interesting thing that the co-doping system color changed with different excitation wavelength. Furthermore, before the excitation wavelength up to 340 nm, the PL of TbDP is very strong and the color could be changed from purplish blue to bluish green, and the red luminescence of EuDP is too weak to represent, for both the low concentration of red dopant EuDP and unsuitable excitation wavelength, even though some energy could be transferred from PVK and TbDP to it. Further increasing the excitation wavelength, the luminescence of EuDP becomes strong for suitable excitation and strong energy transfer from PVK and TbDP,

and the color becomes closer and closer to the white light. Especially, when the excitation wavelength is longer than 350 nm, the color becomes closer to pure white. Meanwhile, the emissive intensity still does not fall too low as shown in Fig. 6. Ulteriorly, white LEDs can be constructed by simply optimizing the mixing ratio of dopants concentration and excitation, especially for considering using economic mercury arc lamps as pump sources having a very bright emission at 366 nm.

4. Conclusion

TbDP and EuDP were doped into PVK matrix that is amorphous. In such a complicated system, energy transfer from PVK to TbDP and EuDP, and from TbDP to EuDP exists. The color changed by adjusting the mixing ratio of dopants concentration and excitation wavelength. Further, white LEDs can be constructed by simply optimizing the mixing ratio of dopants concentration and excitation light, especially considering using economic mercury arc lamps as pump source and less europium complexes.

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