

Electroluminescence from Exciplex on the Interface Between TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})^*$

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The bilayer organic light-emitting diode (OLED) with a blue fluorescent lanthanum complex, tris(1-phenyl-3-methyl-4-isobutyl-5-pyrazolone)-(2,2'-dipyridyl) lanthanum [$\text{La}(\text{PMIP})_3(\text{Bipy})$], as a light emitting material and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) as a hole transporting material emits bright green light instead of blue light. The data of the absorption, the photoluminescence (PL) and the photoluminescence excitation (PLE) spectra of TPD, $\text{La}(\text{PMIP})_3(\text{Bipy})$ and the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio 1:1) prove that the electroluminescent emission originates from the exciplex on the interface between TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$. By improving device configuration with tris(8-hydroxyquinoline) aluminum (ALQ) as an electron transporting material, a maximum luminance of 800 cd/m^2 was obtained.

Key words: Electroluminescence, Photoluminescence, Lanthanum complex

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Introduction

Since Tang and Van Slyke^[1] reported the first double-layer green thin-film organic electroluminescent device, fluorescent materials, carrier-transporting materials and electrode materials have been widely studied^[2-5]. On the other hand, different kinds of multilayer organic light emitting diodes have been made in order to improve electroluminescence efficiency and other functions^[6-8]. For instance, in order to avoid exciton quenching at metal electrodes, the emitting region can be separated from the electrodes by adding a carrier-transporting layer. The flow of the positive and negative polarons is injected into the emitting region, then a better balance was achieved, so a higher efficiency is obtained^[9,10]. In layered organic light-emitting diodes, the exciplex formation may take place on the interface between the charge-transporting layer and the emitting layer for certain combinations of emitting and charge-transporting materials^[11-15]. The exciplex is a transient donor-acceptor complex that sometimes emits a strong fluorescence at longer wavelengths than the donor or the acceptor.

The recent studies have suggested the possibility of utilizing enhanced exciplex emission in LED devices^[16,17]. Here is reported the electroluminescence from bilayer organic devices in which the green emission peaking at 522 nm originates from an exciplex formed on the interface of a lanthanum complex and TPD. The lanthanum ternary complex, [$\text{La}(\text{PMIP})_3 \cdot (\text{Bipy})$], was synthesized and used as a light emitting material. La^{3+} has no 4f electrons and does not emit visible light^[18]; however, the title complex emits blue photoluminescence (PL) peaking at 460 nm and belongs to the ligand emitting complex, which is just like complex tris(8-hydroxyquinoline) aluminum (ALQ). The devices prepared in this study are listed as follows:

Device 1: ITO/TPD (40 nm)/ $\text{La}(\text{PMIP})_3(\text{Bipy})$ (80 nm)/Mg:Ag(200 nm)/Ag(100 nm).Device 2: ITO/TPD (40 nm)/ $\text{La}(\text{PMIP})_3(\text{Bipy})$ (40 nm)/ALQ (40 nm)/Mg:Ag(200 nm)/Ag(100 nm).

Experimental

Complex $\text{La}(\text{PMIP})_3(\text{Bipy})$ (Fig. 1) was synthesized as described previously^[19]. Elemental anal

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found (%): C 61.37, N 11.02, H 5.16; calcd (%) for $C_{52}H_{53}N_3O_4La$: C 60.94, N 10.93, H 5.21. Organic materials were sequentially deposited by high vacuum (10^{-4} Pa) thermal evaporation onto a precleaned indium tin oxide (ITO) glass substrate with a sheet resistance of $15 \Omega/\square$ supplied by China Shenzhen Wellight Conductive Coating Co., Ltd. A shadow mask with 5 mm diameter openings was used to define the cathode of a layer of Mg and Ag alloy (10:1, the thickness was 200 nm), with a Ag cap of 100 nm. For the PL studies, the mixture of TPD and $La(PMIP)_3(Bipy)$ (molar ratio of 1:1 by using a dichloroethane solution of them) was spin-coated onto a quartz substrate. The ultraviolet-visible (UV-Vis) absorption spectra of the films were measured by using a Shimadzu

UV-3100 UV-Vis spectrometer. The PL and electroluminescence (EL) were measured with a Hitachi F-4500 fluorescence spectrophotometer. The layer thickness was controlled in vacuum with shutters and an L-100 quartz crystal monitor. The brightness was measured by an ST-86LA spot photometer and a close-up lens with a focal spot of 5 mm in diameter. The synchrotron radiation photon-electron spectrum (SRPES) was measured with a photon-electron spectrometer (VSW Scientific Instruments, Ltd.) through synchrotron radiation. Under ultra-high vacuum (3×10^{-8} - 4×10^{-8} Pa), the photon-electron spectrum was recorded at 18.7 eV synchrotron radiation light, from which the first ionization energy (I_p), the HOMO energy level, was derived.

Results and Discussion

$La(PMIP)_3(Bipy)$ film deposited by vacuum sublimation is transparent and homogeneous. Fig. 1(A) shows the absorption spectra of the spin-coated and evaporated $La(PMIP)_3(Bipy)$ films. The spectra of both the films are almost the same, suggesting that the compound can be evaporated without decomposition. It can also be seen that the absorption spectrum of $La(PMIP)_3(Bipy)$ is attributed to the co-absorption of $PMIP^+$ and Bipy. But the PL spectrum of $La(PMIP)_3(Bipy)$ is different from those of $NaPMIP$ and Bipy. Fig. 1(B) shows the PL spectrum peaking at 460 nm for $La(PMIP)_3(Bipy)$ and those for $NaPMIP$ and Bipy peaking at 398 nm and 410 nm, respectively. That means the PL spectra of $PMIP^+$ and Bipy are red-shifted due to the central La^{3+} ion. The measurements of the absorption, PL and photoluminescence excitation (PLE) spectra were made by using the spin-coated films on the quartz substrates. Fig. 2(A) shows the PL spectra of TPD excited at 310 nm, $La(PMIP)_3(Bipy)$ excited at 270 nm, and the mixture of TPD and $La(PMIP)_3(Bipy)$ (molar ratio = 1:1) excited at 280 and 380 nm, respectively. The PL spectra have emission peaks at 406 and 422 nm for TPD, and at 460 nm for $La(PMIP)_3(Bipy)$. Interestingly we found that the mixture of TPD and $La(PMIP)_3(Bipy)$ (molar ratio = 1:1) shows a broad PL band peaking at 522 nm instead of at 406, 422 or 460 nm and that the PL spectra of it excited at 280 and 380 nm are the same except the difference in emission intensity. The disappearance of emissions from the spectra of both TPD and $La(PMIP)_3(Bipy)$ and the appearance of

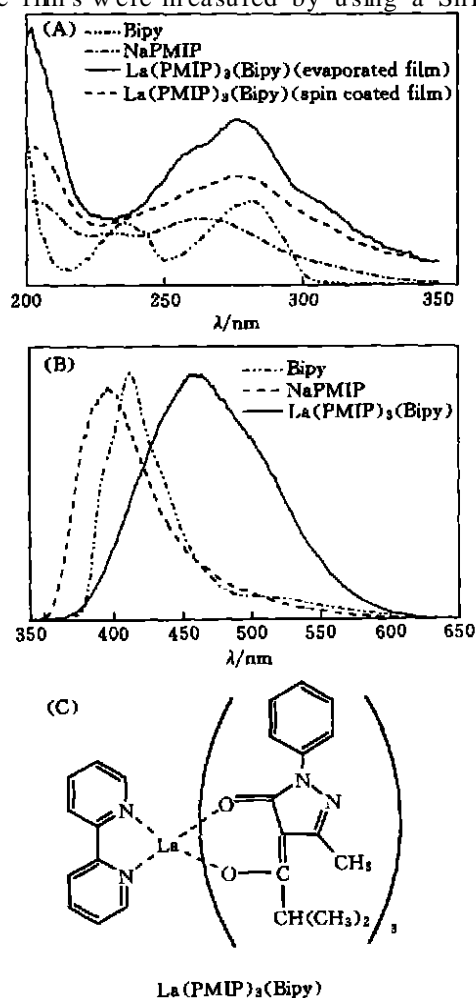


Fig 1 The absorption spectra of $NaPMIP$, $Bipy$ and both spin coated and evaporated $La(PMIP)_3(Bipy)$ in films (about 60 nm) (A), the PL spectra of $La(PMIP)_3(Bipy)$ ($\lambda_{ex} = 270$ nm), $NaPMIP$ ($\lambda_{ex} = 240$ nm) and $Bipy$ ($\lambda_{ex} = 360$ nm) in films (B) and the chemical structural formula of $La(PMIP)_3(Bipy)$ (C).

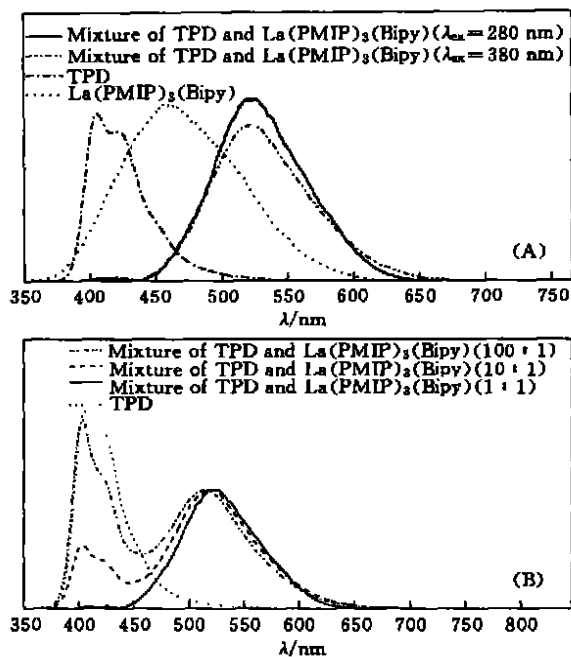


Fig 2 The PL spectra of TPD ($\lambda_{\text{ex}} = 310 \text{ nm}$), $\text{La}(\text{PMIP})_3(\text{Bipy})$ ($\lambda_{\text{ex}} = 270 \text{ nm}$) and the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio = 1 : 1) ($\lambda_{\text{ex}} = 280$ and 380 nm) in the films on quartz substrates (A), the PL spectra of TPD and the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ ($\lambda_{\text{ex}} = 280 \text{ nm}$) in the films with different molar ratios $\{n(\text{TPD}) : n[\text{La}(\text{PMIP})_3(\text{Bipy})] = 100 : 1, 10 : 1, 1 : 1\}$ (B).

the new emission imply that a new species was generated in the mixture. This emission is attributed to the exciplex originating from the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio = 1 : 1). The PL spectra of the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ with different molar ratios (100 : 1, 10 : 1, 1 : 1) in the spin-coated films on the quartz substrates were also measured. As shown in Fig 2(B), when the molar ratio of TPD to $\text{La}(\text{PMIP})_3(\text{Bipy})$ is equal to 100 : 1, two strong emission bands can be found in the PL spectrum, which peak at 406 and 522 nm, respectively; the former is attributed to TPD emission, while the other one originates from the exciplex emission. If the content $\text{La}(\text{PMIP})_3(\text{Bipy})$ was further increased, the relative intensity of the emission from TPD continuously decreases. As the molar ratio reached 1 : 1, the TPD emission totally disappears in the PL spectrum of the mixture. However, no exciplex was found in the CHCl_3 solution of TPD CHCl_3 and $\text{La}(\text{PMIP})_3(\text{Bipy})$ with the molar ratio of 1 : 1 (the concentration is about $1 \times 10^{-4} \text{ mol/L}$). The reason may be that the solvent molecules sur-

round the molecules of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$, which greatly weakens the interaction of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$.

Fig 3(A) shows the absorption spectra of TPD, $\text{La}(\text{PMIP})_3(\text{Bipy})$ and the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio = 1 : 1). When the absorbance of the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio = 1 : 1) is compared with the sum of the TPD layer absorbance and the $\text{La}(\text{PMIP})_3(\text{Bipy})$ layer absorbance, it can be found that there is no new absorption for the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio = 1 : 1), implying that the new species is not directly formed in the ground state, giving support to the existence of an exciplex^[20]. Fig 3(B) shows the excitation spectra of TPD, $\text{La}(\text{PMIP})_3(\text{Bipy})$ and the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio = 1 : 1) recorded at their maximum emission wavelengths 406, 460 and 522 nm, respectively. The PLE intensity of the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio = 1 : 1) is also approximately consistent with the sum of the PLE intensities of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$, further confirming the conclusion made above.

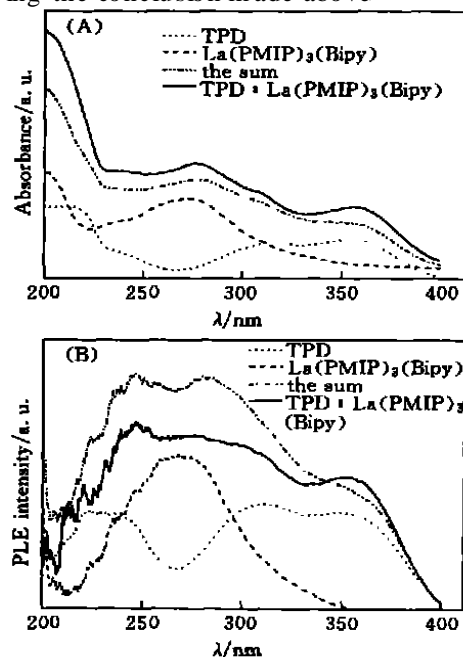


Fig 3 The absorption spectra (A) and the photoluminescence excitation (PLE) spectra of TPD, $\text{La}(\text{PMIP})_3(\text{Bipy})$, the sum of spectra of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$, the mixture of TPD and $\text{La}(\text{PMIP})_3(\text{Bipy})$ (molar ratio 1 : 1) on quartz substrates (B).

The PLEs were recorded at their maximum emission wavelengths 406, 460 and 522 nm, respectively.

By using TPD as a hole transporting layer, device 1 with the structure of ITO/TPD (40 nm)/La(PMIP)₃(Bipy) (80 nm)/Mg Ag (200 nm)/Ag (100 nm) was fabricated without breaking vacuum. As shown in the inset of Fig. 4, the EL spectrum with a peak at 517 nm and a shoulder peak at 420 nm resulted from TPD, is approximately identical to the PL spectrum of the mixture of TPD and La(PMIP)₃(Bipy) (molar ratio = 1:1). It is attributed to the exciplex formed on the interface between TPD and La(PMIP)₃(Bipy). Under a forward bias, a maximum luminance of 30 cd/m² at 20 V was observed. The current density-voltage and luminance-voltage characteristics of device 1 are shown in Fig. 4. The device has a peak power efficiency of 0.01 lm/W with a current density of 0.41 mA/cm² at 7 V and the turn-on voltage of 6 V.

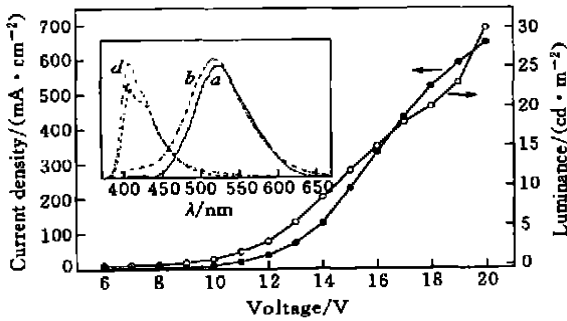


Fig. 4 The current density-voltage and luminance-voltage characteristics of device 1

Inset: a. PL spectra (right axis) of the mixture of TPD and La(PMIP)₃(Bipy) (molar ratio = 1:1) (λ_{ex} = 280 nm); b. EL (left axis) of device 1 at 14 V; c. device A at 10 V; d. device B at 10 V.

In layered organic light emitting devices, exciplex formation often takes place on the interface between the carrier transporting layer and the light emitting layer^[11]. This can be confirmed by designing the following two devices: ITO/TPD (40 nm)/Y(PMIP)₃(TPPO)₂ (80 nm)/Mg Ag (200 nm)/Ag (100 nm) (device A) and ITO/TPD (40 nm)/Y(PMIP)₃(TPPO)₂ (20 nm)/La(PMIP)₃(Bipy) (40 nm)/Mg Ag (200 nm)/Ag (100 nm) (device B). It is known that the peak of the PL spectrum of the complex tris(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone)-bis(triphenyl phosphine oxide) yttrium [Y(PMIP)₃(TPPO)₂] is at 430 nm, and device A shows the peak of the EL spectrum at 425 nm (in the inset of Fig. 4), giving support to the fact that no exciplex was formed under electrical excitation. When a layer of Y(PMIP)₃(TPPO)₂ (20 nm) was inserted between the TPD and La(PMIP)₃(Bipy)

layers in device 1 to form device B, it is found that device B exhibits the EL peak at 425 nm while the peak at 517 nm observed in device 1 disappears (in the inset of Fig. 4). This fact strongly demonstrates that the peak at 517 nm is due to the exciplex formed on the interface between the TPD and La(PMIP)₃(Bipy) layers.

The explanation is based on the relationship of the energy levels of the materials in Fig. 5(A). The I_p of 6.5 eV for La(PMIP)₃(Bipy) was obtained from SRPES. The electron affinity (E_A) for La(PMIP)₃(Bipy), the LUMO energy level, was estimated to be 2.4 eV with reference to the I_p and the UV-Vis optical absorption onset ($\lambda = 300$ nm, 4.1 eV). From the relationship of the energy levels, electrons injected from the cathode may recombine with the holes in the TPD layer or the La(PMIP)₃(Bipy) layer.

By comparison, there is no barrier for electron injection from La(PMIP)₃(Bipy) to TPD, while the barrier for hole injection from TPD to La(PMIP)₃(Bipy) is 1 eV. It was likely that TPD was first excited. This supposition was demonstrated by the following experiment. We selected 380 nm as the excitation wavelength. As shown in Fig. 3(B), by using this excitation light, only TPD can be excited in the two components of the mixture of TPD and La(PMIP)₃(Bipy) (molar ratio = 1:1) since this light can be absorbed by TPD only. As an expected result of excitation, the PL spectrum shows the same curve as that obtained by being excited at 280 nm wavelength light. It means that process 1 is the main one among the three processes, that is, the excited single-state TPD may interact with La(PMIP)₃(Bipy) in the ground state, forming the exciplex.

The formation of exciplexes is easy in the singlet excited state but is difficult in the triplet excited state^[21,22].

With the same ligands as those of La(PMIP)₃(Bipy), the gadolinium ternary complex, tris(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone)-(2,2-dipyridyl) gadolinium [Gd(PMIP)₃(Bipy)] was synthesized. Gd³⁺ has a half-full 4f⁷ electronic configuration and does not emit in visible light range^[18]; however, the above complex emits green PL peaking at 516 nm and belongs to the ligand emitting complex, just like La(PMIP)₃(Bipy). With Gd(PMIP)₃(Bipy) as a light emitting material, the device, ITO/TPD (40 nm)/Gd(PMIP)₃

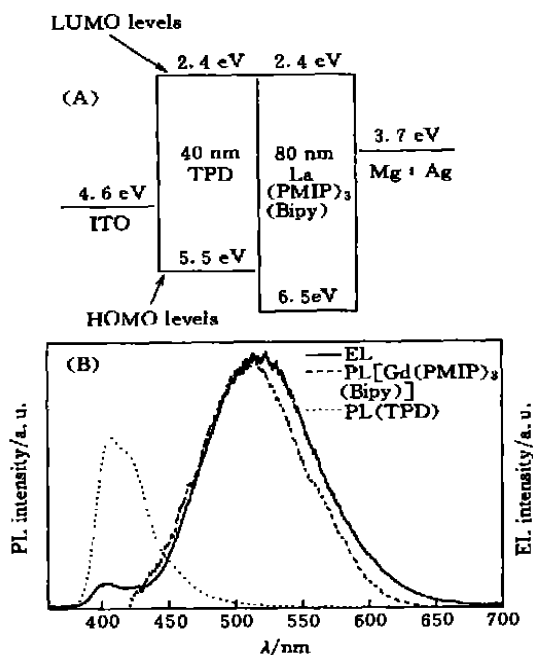


Fig 5 The relative energy levels of materials in device 1 (A) and the PL (Left axis) of TPD and Gd (PMIP)₃(Bipy) ($\lambda_{\text{ex}} = 280 \text{ nm}$) and EL (right axis) of device ITO/TPD (40 nm)/Gd (PMIP)₃(Bipy) (80 nm)/Mg:Ag (200 nm)/Ag (100 nm) at 10 V(B).

(Bipy) (80 nm)/Mg:Ag (200 nm)/Ag (100 nm), was fabricated As shown in Fig 5 (B), the EL spectrum with a peak at 516 nm, and a shoulder peak at 420 nm resulted from TPD is identical to the PL spectrum of Gd(PMIP)₃(Bipy). As was reported^[23], the spin-orbit perturbation of the levels of the ligand electronic states, predominantly induced by the paramagnetic Gd³⁺ ion, causes the longer lifetime of the excited state (ca. 1 μs) of Gd(PMIP)₃(Bipy). But no exciplex was found on the interface between TPD and Gd(PMIP)₃(Bipy). However, TPD and La(PMIP)₃(Bipy) have the shorter lifetime of the excited states (1 ns), and the exciplex at 522 nm can be formed on the interface between TPD and La(PMIP)₃(Bipy).

With ALQ as an electron-transporting layer, device 2 was fabricated Under a forward bias, the device emits green light with a luminance of 800 cd/m^2 at 16 V, resulted from the co-emission of the exciplex and ALQ. This fact supports that La(PMIP)₃(Bipy) is able to transport holes This

was demonstrated by the bilayer device ITO/La(PMIP)₃(Bipy) (40 nm)/ALQ (40 nm)/Mg:Ag (200 nm)/Ag (100 nm), which exhibits a maximum luminance of 380 cd/m^2 at 16 V. Considering the electron conductivity in device 1, we can conclude that the light emitting material La(PMIP)₃(Bipy) can transport both electrons and holes

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