



# Green exciplex emission from a bilayer light-emitting diode containing a rare earth ternary complex

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## Abstract

A bilayer organic light-emitting diode using a blue-fluorescent yttrium complex, tris(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone)-(2,2'-dipyridyl) yttrium [Y(PMIP)<sub>3</sub>(Bipy)] (YPB) as an emitting material and poly(*N*-vinylcarbazole) (PVK) as a hole-transporting material emitted bright green light instead of blue light. It was attributed to the exciplex formation at the solid interface between the PVK and YPB layers, which was demonstrated by the measurement of the absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the mixture of PVK and YPB (molar ratio 1:1). The device exhibited a maximum luminance of 177 cd/m<sup>2</sup> and a peak power efficiency of 0.02 lm/W. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Generally, multilayer organic light-emitting devices (OLEDs) consisting of charge-transporting and emitting layers exhibit higher performance than single-layer devices because in the multilayer devices more balanced charge carriers are confined within the emitting layers [1]. At the interfaces of these multilayer devices, important photochemical phenomenon such as exciplex or electroplex formation may occur [2–6], especially when poly(*N*-vinylcarbazole) (PVK) acts as a hole-transporting layer.

Rare earth complexes are of interest because they show sharp emission bands and some are very suitable for multicolor display. Generally speaking, Y<sup>3+</sup> is a non-fluorescent ion and does not emit visible light [7]; however the titled yttrium ternary complex, tris(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone)-(2,2'-dipyridyl) yttrium [Y(PMIP)<sub>3</sub>(Bipy)] (YPB) can emit blue photoluminescence (PL) emission of 452 nm and belongs to ligand emitting complex, just like complex tris(8-hydroxyquinoline) aluminum (ALQ). We fabricated a bilayer device with the electroluminescence (EL) emission of 502 nm, originating from the exciplex formed at the interface between the PVK and YPB layers. The devices prepared in this Letter are listed as below:

Device 1: ITO/PVK (40 nm)/YPB (80 nm)/Mg:Ag (200 nm)/Ag (100 nm),

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Device 2: ITO/PVK (40 nm)/YPB (40 nm)/ALQ (40 nm)/Mg:Ag (200 nm)/Ag (100 nm),

Device 3: ITO/YPB (40 nm)/ALQ (40 nm)/Mg:Ag (200 nm)/Ag (100 nm).

## 2. Experimental

The complex YPB (Fig. 1) was synthesized as the method similar to that reported previously [8]. Found (%): C, 63.74; N, 11.85; H, 5.50. Calc (%) for  $C_{52}H_{53}N_8O_6Y$ : C, 64.06; N, 11.49; H, 5.48. As shown in Fig. 1, the absorption spectrum of YPB is attributed to the co-absorption of  $PMIP^-$  and Bipy.

PVK (Acros Organics) was spin coated from a dichloroethane solution onto a pre-cleaned indium tin oxide (ITO) glass substrate with a sheet resistance of  $15 \Omega/\square$  supplied by China Southern Glass Holding. Organic materials were sequentially deposited by high vacuum ( $10^{-6}$  Torr) thermal evaporation onto the PVK film. A shadow mask with 5 mm diam openings was used to define the cathode of a 200 nm thick layer of Mg:Ag (10:1)

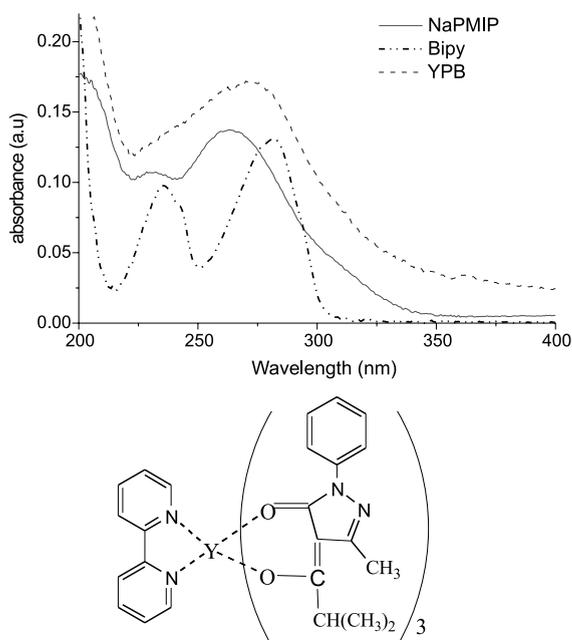


Fig. 1. The absorption spectra of YPB, NaPMIP and Bipy in films (about 60 nm). The inset shows the chemical structural formula of YPB.

alloy, with a 100 nm thick Ag cap. For PL studies, the mixture of PVK and YPB (molar ratio 1:1) was spin coated from a dichloroethane solution onto a quartz substrate. The PL and EL were measured with an F-4500 fluorescence spectrophotometer. The layer thickness was measured by a Dektak surface profile measuring system and an IL-1000 quartz crystal monitor. The brightness was measured by a ST-86LA spot photometer and a close-up lens with a focal spot of 5 mm in diam. The ionization potential ( $I_p$ ) and the electron affinity ( $E_A$ ) for YPB were measured with ultraviolet photoelectron spectroscopy (UPS) and UV-Vis optical absorption spectroscopy.

## 3. Results and discussion

As indicated in Fig. 2, the PL for the single PVK layer has peak emissions of 392 and 408 nm, similar to those reported [6], and the PL for the single YPB layer shows an emission of 452 nm. It is interesting to find that the mixture of PVK and YPB (molar ratio 1:1) shows broad PL emission of 497 nm instead of 392, 408 or 452 nm. The disappearance of the emissions from both PVK and YPB and appearance of the new emission imply that a new species of chromophore is generated in the mixture. We attributed this to the exciplex formation originating from the mixture of PVK and YPB (molar ratio 1:1).

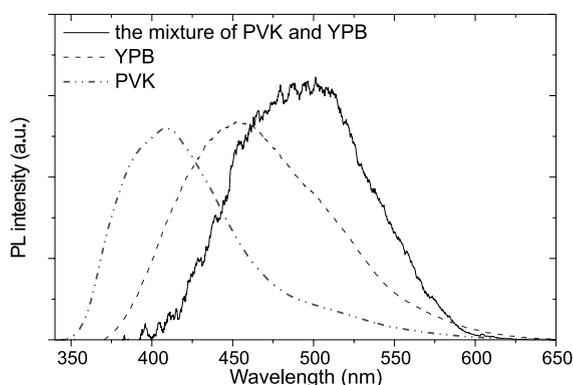


Fig. 2. The PL spectra of PVK ( $\lambda_{ex} = 240$  nm), YPB ( $\lambda_{ex} = 270$  nm) and the mixture of PVK and YPB (molar ratio 1:1) ( $\lambda_{ex} = 245$  nm) on quartz substrates.

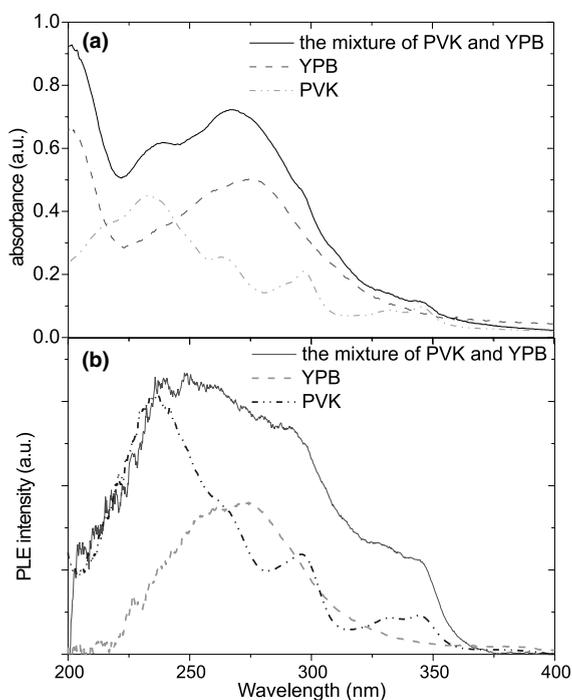


Fig. 3. (a) Absorption spectra and (b) photoluminescence excitation (PLE) spectra of PVK, YPB and the mixture of PVK and YPB (molar ratio 1:1) on quartz substrates. The PLEs were recorded at their maximum emission wavelength 410, 452 and 497 nm, respectively.

Fig. 3a clearly shows that the absorption of the mixture of PVK and YPB (molar ratio 1:1) coincides with the sum of the single PVK layer absorption and the single YPB layer absorption. The absence of any new absorption in the mixture of PVK and YPB (molar ratio 1:1) means that the new species is not directly formed in the ground state, giving support to the existence of the exciplex. Fig. 3b shows the excitation spectra of PVK, YPB and the mixture of PVK and YPB (molar ratio 1:1) recorded at their maximum emission wavelength 410, 452 and 497 nm, respectively. Again, the same phenomenon was observed, confirming the conclusion made above.

As shown in the inset of Fig. 4, the EL emission at 502 nm of device 1, with a shoulder peak at 392 nm resulting from PVK, is identical to the PL emission of the mixture of PVK and YPB (molar ratio 1:1), although slightly red-shifted. This fact indicates that the exciplex is responsible for the EL emission. Upon a forward bias, a maximum luminance of 177 cd/m<sup>2</sup> 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 0.02 lm/w with a current density of 0.68 mA/cm<sup>2</sup> at 10 V and a turn-on voltage of 5 V.

In layered OLEDs, exciplex formation often takes place at the interface between the charge-

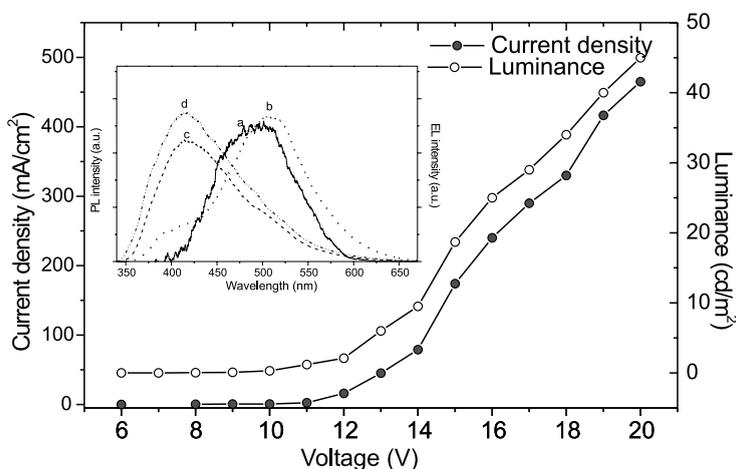
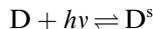


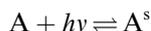
Fig. 4. The current density–voltage and luminance–voltage characteristics of device 1. Inset: (a) PL (left axis) of the mixture of PVK and YPB (molar ratio 1:1) ( $\lambda_{\text{ex}} = 245$  nm) and EL (right axis) of (b) device 1 at 10 V, (c) device A at 10 V and (d) device B at 14 V.

transporting layer and the emitting layer [3]. This can be confirmed by designing the following two devices: ITO/PVK (40 nm)/Y(PMIP)<sub>3</sub>(TPPO)<sub>2</sub> (80 nm)/Mg:Ag (200 nm)/Ag (100 nm) (device A) and ITO/PVK (40 nm)/Y(PMIP)<sub>3</sub>(TPPO)<sub>2</sub> (20 nm)/YPB (60 nm)/Mg:Ag (200 nm)/Ag (100 nm) (device B). It is known that the PL emission of the complex tris(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone)-bis(triphenyl phosphine oxide) yttrium [Y(PMIP)<sub>3</sub>(TPPO)<sub>2</sub>] is at 430 nm, and device A showed the EL emission of 415 nm (in the inset of Fig. 4), giving support that no exciplex was formed under electrical excitation. Inserting a layer of Y(PMIP)<sub>3</sub>(TPPO)<sub>2</sub> (20 nm) between the PVK and YPB layers in device 1 to form device B, it is found that device B exhibited the EL emission of 415 nm and the peak of 502 nm observed in device 1 disappeared (in the inset of Fig. 4). This fact strongly demonstrates that the peak of 502 nm is the exciplex formed at the interface of the PVK and YPB layers.

In photochemistry, an exciplex is formed according to the following mechanism [9,10]:



or



where 's' denotes the singlet state of the donor (D) or acceptor (A), respectively. An exciplex is formed when the excited state of a very polarizable species participates in charge-transfer interaction with other polarizable species. As a result, the metastable species, termed as an exciplex, is a new electronically excited species. Exciplex emission is usually observed as broad structureless band to the red of the monomer emission and different from neither emission of the donor nor emission of the acceptor. Our experimental result is the case.

It can be explained from the relationship of the energy levels of the materials. The  $I_p$  of 6.56 eV for YPB was obtained from UPS. The  $E_A$  for YPB

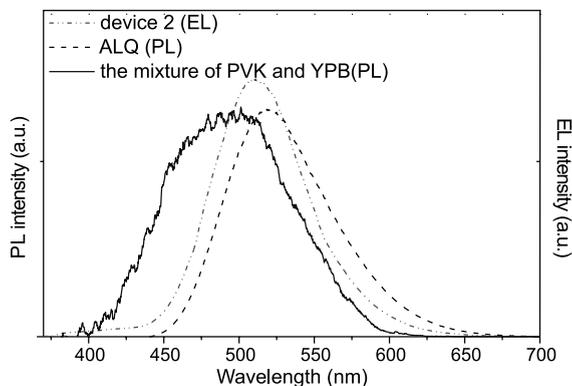


Fig. 5. PL (left axis) of the mixture of PVK and YPB (molar ratio 1:1) ( $\lambda_{\text{ex}} = 245$  nm) and ALQ ( $\lambda_{\text{ex}} = 245$  nm) on quartz substrates and EL (right axis) of device 2 at 12 V.

was estimated to be 1.99 eV on the basis of the  $I_p$  and the optical absorption maximum ( $\lambda_{\text{max}} = 271.6$  nm, 4.57 eV). The  $I_p$  and  $E_A$  for PVK are 6.1 and 1.2 eV, respectively [11]. A barrier of 0.79 eV for the electron injection from the YPB layer into the PVK layer is higher than that of 0.46 eV for the hole injection from the PVK layer into the YPB layer. Therefore, it is suggested that the exciplex be formed by the interaction between the excited singlet state YPB, generated by recombination of holes and electrons within the YPB layer, and PVK in the ground state.

Using ALQ as the electron-transporting layer, device 2 exhibited a luminance of 1750 cd/m<sup>2</sup> at 15 V. As shown in Fig. 5, the EL emission of 510 nm, is attributed to the co-emission of the exciplex and ALQ. This fact shows that YPB is able to transport holes, which was demonstrated by device 3. In the absence of the hole-transporting layer PVK, it exhibited a luminance of 147 cd/m<sup>2</sup> at 16 V. Considering the electron conductivity of YPB shown in device 1, we can conclude that YPB has an ability of transporting both electrons and holes.

#### 4. Conclusion

In summary, an yttrium complex YPB was synthesized and used as a charge-transporting and

emitting material in OLEDs. The device ITO/PVK (40 nm)/YPB (80 nm)/Mg:Ag (200 nm)/Ag (100 nm) exhibited the EL emission of 502 nm, which was attributed to exciplex formation at the solid interface between PVK and YPB. It was further demonstrated by device B. Inserting a layer of Y(PMIP)<sub>3</sub>(TPPO)<sub>2</sub> between the PVK and YPB layers, the exciplex emission of 502 nm disappeared.

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