Development and characterization of an efficient bio-white polymer light-emitting diode with red and green phosphorescent dyes as dopants

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Abstract An efficient white polymer light-emitting diode (WPLED) with stable Commission Internationale de l'éclairage (CIE) coordinates is fabricated. A blue electroluminescence (EL)-emitting conducting polymer [poly(9,9-di-n-hexyl-fluorenyl-2,7-diyl)] is used as a host for red [*Bis*(1-phenyl-isoquinoline)(acetylacetonate)iridium(III)] and green [iridium(III)*tris*(2-(4-tolyl)pyridinato-*N*,C^2)] phosphorescent dyes. Although efficient triplet energy transfer is not possible in the green phosphorescent dye, the self-trapping mechanism is utilized for the emission of EL in the green region while an efficient triplet exciton energy transfer from the host to the red dye is utilized for EL in the red wavelength region. Concentrations of the three constituents are optimized to obtain pure white light of appropriate CIE coordinates. An efficient electron-blocking layer based on a biomaterial (salmon-DNA) is also incorporated in the WPLED to improve the device performance. The WPLED shows three distinguished peaks for the primary colors and achieved a maximum luminance and luminous efficiency of 350 cd/m^2 and 0.86 cd/A, respectively.

Introduction

For the past few years, a large number of workers [1–10] are engaged in the development of white organic light-emitting diodes (WOLEDs). Almost all of them use low-molecular-weight organic materials (LMWOM) such as 1,4,5,8,*N*-pentamethylcarbazole (PMC) for emission of blue electroluminescence (EL) and as a host for red and green phosphorescent dyes. PMC produces singlet excitons (S_1) and triplet excitons (S_3) in the ratio of 1:3 [11]. While S_1 are utilized for blue EL emission, the S_3 are utilized for producing red and green EL from phosphorescent dyes. The internal quantum efficiency of the device is therefore close to 100%. However, LMWOM being insoluble in common organic solvents cannot be spin coated and has to be vacuum evaporated. Not only vacuum evaporation is an expensive, but also it is not possible to deposit large area films by this technique and therefore this method of fabricating WOLED is not commercially viable. White polymer light-emitting diodes (WPLEDs) based on blue EL-emitting conducting polymers using red and green dyes as fluorescent dopants have low efficiencies as compared to WOLEDs because the red and green emitting fluorescent dyes cannot utilize S_3 from the host polymer. The internal quantum efficiency of such a device cannot exceed 25%. In order to utilize S_1 as well as S_3 to produce high efficiency WOLED, one can on principle use three basic color components R, G, and B as phosphorescence dyes. However, blue phosphorescent dyes are unstable and hence such a device has a very low operating life [12].

An ideal solution to be used therefore will be a combination of blue-emitting conducting polymer such as [poly(9,9-di-n-hexyl-fluorenyl-2,7-diyl)] (PFO) as host doped with red and green phosphorescent dyes. In such a system all the S_1 and S_3 can be utilized by the fluorescent PFO and phosphorescent dyes, respectively. Hence, the internal quantum efficiency of such a device can approach 100%. However, the difficulty in this is that all the available green phosphorescent dyes have S_3 energy level

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higher than that of the blue-emitting conducting polymers. As an example S_3 energy level of PFO is 2.15 eV [13] while that of the green phosphorescent dyes is higher (e.g., for Ir(mppy)$_3$, S_3 level is 2.4 eV [14]) and thus S_3 energy cannot flow from former to later. However, the S_3 energy levels of the red dyes (for Ir(piq)$_2$(acac), S_3 level is 2.0 eV [15]) are lower than that of the blue conducting polymer PFO and the S_3 energy transfer from PFO can excite the red dyes easily. In this study, an attempt has been made to fabricate a polymer-based white LED structure. Although the host is still a conducting polymer PFO, the green dye iridium(III)*tris*(2-(4-tolyl)pyridinato-*N*,C^2) (Ir(mppy)$_3$) produces EL in green region, not by the S_3 energy transfer but due to self-trapping mechanism in the green dye itself. This is because the LUMO level of this dye is unusually low 2.4 eV and HOMO level is very high 5.4 eV [14], as shown in Fig. 1. Most of the electrons injected from cathode and holes injected from anode are therefore trapped in the dye molecules and can easily produce singlet and triplet excitons in the dye itself, producing EL in the green region. If the concentration of green dye in the host is appropriate, optimum EL intensity from the green and red dyes can be obtained to produce white light of correct Commission Internationale de l'éclairage (CIE) coordinates. A very significant point to be taken into consideration is that the concentration of the green dye in PFO is very important because not only it produces EL by self-trapping but exciton energy may also be transferred from PFO and green dye to the red dye due to the process of incomplete Forster resonance energy transfer.

Recently, biomaterials are also being used in conducting polymer-based devices to bring into being a new field called bioelectronics [16, 17]. In our previous study, we have successfully improved the device performance of the MEH-PPV and PFO-based polymer light-emitting diodes using salmon-deoxyribonucleic acid (sDNA) [17]. An electron-blocking layer (EBL) based on sDNA–CTMA is also incorporated in the WPLED and the device is now called bio-white polymer light-emitting diode (Bio-WPLED).
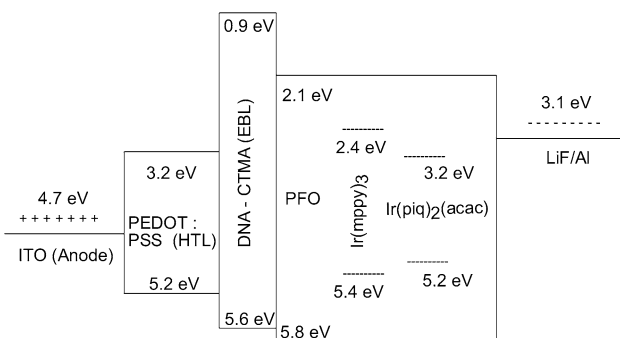
The EBL helps in balancing the charge carriers by blocking electrons due to its very low LUMO level, which enhances the recombination probability of electrons and holes in the emissive layer and hence enhancing the efficiency of the device [17]. The Bio-WPLED shows three primary distinguished color peaks for blue ($\sim$430 nm), green ($\sim$514 nm), and red ($\sim$612 nm). The CIE coordinates become stable at higher voltages and are well within the white region, making the device suitable for the flat panel display technology. The maximum efficiency of this Bio-WPLED is found to be 0.86 cd/A, whereas the blue Bio-PLED fabricated in our previous study showed maximum efficiency of $\sim$0.062 cd/A [17]. The CIE coordinates are found to be (0.30, 0.34) at $\sim$34 V which are closest to the pure white region (0.33, 0.33).

Experimental details

The blue-emitting conducting polymer PFO was procured commercially from Sigma–Aldrich (St. Louis, MO, USA). The green [Ir(mppy)$_3$] and red *Bis*(1-phenyl-isoquinoline)(acetylacetonate)iridium(III) [(Ir(piq)$_2$(acac))] phosphorescent dyes were purchased from American Dye Source (Quebec, Canada). An aliquot of 10 mg/mL PFO was made in chlorobenzene. To this solution red and green dyes were added in the concentrations of 0.2 and 0.8% w/w, respectively. These concentrations were obtained by trial-and-error to obtain best possible EL spectrum. The solution was homogenized using an ultrasonicator and spin coated on a patterned ITO-coated glass (having sheet resistance $\sim$15Ω/$\square$), keeping the spin rate 2000 rpm for 30 s. Before coating the emissive layer, a PEDOT:PSS layer was spin coated on the ITO. This layer acts as a hole transporting layer and also smoothens the uneven surface of the ITO [18].

A thin layer of DNA–CTMA complex was also coated on the PEDOT:PSS layer to be act as an EBL. A buffer layer of LiF 10 nm thick was vacuum evaporated on the active layer, which reduces the potential barrier at the polymer/Al interface [19]. On the buffer layer, aluminum cathode contacts of 100 nm thick were vacuum evaporated at a rate of 0.6 nm/s. A shadow mask was used for the deposition of the cathode resulting in the devices area of 2 mm $\times$ 2 mm. The current voltage characteristics of the device were measured with the help of a Keithley Source Meter (Model: SMU 2400). The luminance intensity of EL was measured using Minolta LS 100 luminance meter. EL spectrum and CIE coordinates were measured by spectral flux measurement system, Labsphere (model: CSLMS 1011). All the measurements were carried out in air at room temperature without any device encapsulation. The schematic for the Bio-WPLED used is shown in Fig. 2.
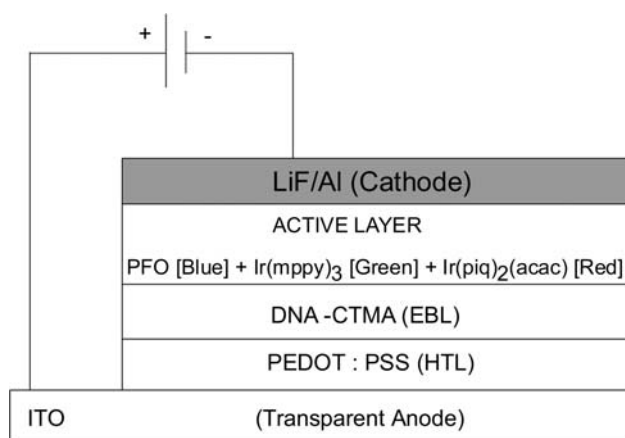

Fig. 1 Energy level diagram for the Bio-WPLED

Fig. 2 Schematic of layers arrangement used for the Bio-WPLED

Fig. 4 EL spectra of the Bio-WPLED for different bias voltages. Inset: CIE coordinates

Results and discussion

The luminance, current density, and bias voltage (L–J–V) characteristics for the WPLED are shown in Fig. 3. The turn on voltage is found to be ∼21 V. Maximum luminance achieved is ∼350 cd/m^2 at a bias voltage of 34 V, above this voltage the device performance starts deteriorating.

The EL spectra for different bias voltages of the fabricated WPLED are shown in Fig. 4. It is found that till 24 V no significant red emission is observed but green emission is still prominent, showing the existence of the charge trapping mechanism in the green dye. As the voltage is increased beyond 25 V, the red emission becomes significant. At ∼32 V, all the three primary color peaks become considerable and remain constant till 34 V. Corresponding CIE coordinates of the WPLED at different bias voltages are also shown in Fig. 4. The CIE coordinates remain stable above 32 V and are well within the white region. At higher voltages charge trapping mechanism in the green dye starts saturating thus saturation in the green peak takes
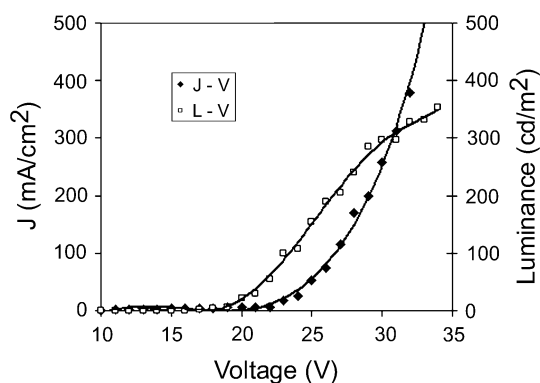

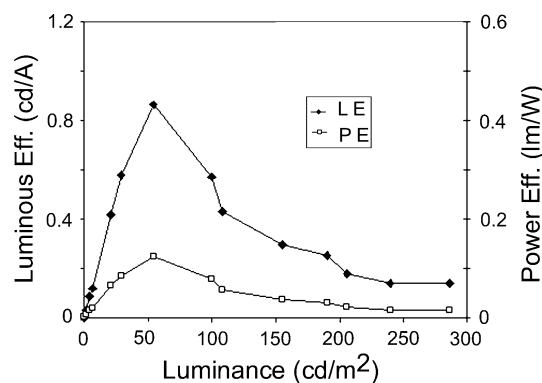Fig. 5 EL efficiency and power efficiency for the Bio-WPLED fabricated

place while blue and red peaks simultaneously increase and grow to be comparable to the green peak. However, increasing the red dye concentration may enhance the efficiency of the device but in that case the spectrum will experience a huge shift toward the red wavelength region. The concentration of the constituents is optimized carefully to get the best-balanced EL spectrum and hence the appropriate CIE coordinates.

Luminous and power efficiencies for the WPLED are shown in Fig. 5. Maximum luminous and power efficiency for the WPLED are achieved to 0.86 cd/A and 0.12 lm/W, respectively, at a typical luminance intensity of 54 cd/m^2.

Conclusions

Self-trapping mechanism in the green phosphorescent dye has been utilized for producing EL by trapping holes and electrons in the dye itself. The concentrations of red and green phosphorescent dopants in the host PFO have been optimized to fabricate a WPLED of appropriate CIE coordinates. An EBL based on bio-material (DNA) was also incorporated in the device structure to enhance the device performance. The device possesses stable CIE

Fig. 3 L–J–V characteristics for the Bio-WPLED fabricated

coordinates at higher voltages with EL spectrum, showing all the three peaks of the primary colors are necessary for the generation of the white light.

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