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White Organic Light Emitting Diodes Via Complementary Color Mixing Approach Through Multilayer Device Architecture

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White organic light emitting diodes (WOLEDs) are emerging as potential light emitting technology and have found many applications from back light for liquid crystal displays to next generation displays and solid-state lighting. We report here the fabrication of organic light emitting diodes (OLEDs), which emit white light via multilayer color approach. These WOLEDs incorporated the materials emitting two complementary colors greenish-blue and reddish-orange to make white. The amount of light emitted from each layer was chosen in such a way that the mixture of the two emitted lights gave white light. The amount of light emitted from each layer was controlled by taking optimum thickness of each layer and incorporating a thin hole blocking layer of BCP in between the emissive layers. For greenish-blue light, we used a phosphorescent dopant FIrPic whereas for reddish-orange light we used the phosphorescent dopant $Ir(btp)_2(acac)$ and both of these dopants were doped in the host CBP. We studied the effect of operating voltage on the color of the emitted light of these WOLEDs and found that the color of the emitted light was almost independent of operating voltage. The WOLEDs emitted 1600 cd/m^2 at 15 V with Commission Internationale de I'Eclairage (CIE) coordinates (0.25, 0.32). We also studied the current density vs voltage (*J*-*V*) and voltage vs luminescence (*V*-*L*) characteristics of these devices and calculated their efficiency which was found to be 0.35 cd/A. We also prepared some WOLEDs based numeric displays just of the demonstration purpose.

Keywords: Organic light emitting diodes, WOLEDs, Electroluminescence, Exciton recombination, Charge transport layers, Thin films, Thermal evaporation

1 Introduction

Organic light emitting diodes (OLEDs) were invented by Tang & VanSlyke[1], and gained the global attention as an alternate to conventional light emitting technologies. OLEDs are very thin, light weight, need no backlight like liquid crystal displays and promised to be very cost effective and mechanically flexible as they could be prepared on a flexible substrate like plastic and thin metal foils[2-6]. OLEDs are quite energy efficient and cost effective compared to other display technologies like liquid crystal displays, inorganic light emitting diodes, plasma displays, cathode ray tubes etc. and also have wide viewing angles, high resolution and fast response time. Since the invention of OLEDs enormous efforts have been made to make them commercially viable and thanks to the global research and development work and the excellent features of OLEDs, they are now commercially available[7-12]. OLEDs have revolutionized the area of display technologies and are used in almost every area where displays are used like TVs, Laptops, i-phones, smart mobile phones, digital cameras, music players, wrist watches, video games etc. OLEDs can be processed at low temperatures and have great flexibility in color tunability. It is very easy to make the OLEDs emitting any color of choice by just doing little modification in the device design[12]. Now the global focus is to make white OLEDs (WOLEDs) as they would be highly cost effective, flexible, large area, high resolution with low energy consumption and a perfect choice for full color display and solid-state lighting applications.

Since it is difficult to make a single material, which could emit pure white light with broad spectrum, the white light is achieved either by mixing three primary colors (red, green and blue) or by mixing complementary colors (red & bluish green, blue & orange, green & magenta) to cover the whole visible spectrum from 380 – 780 nm. The WOLEDs could be prepared by incorporating different emitters in a number of ways like following the multilayer approach, single layer approach and down conversion approach[11]. The emission from each component is judiciously controlled in such a way that the color

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mixing gives pure white color. The first WOLED was prepared in 1995 by Kido *et al*., where they incorporated three organic layers emitting red, green and blue in single device[13]. Those WOLEDs had power efficiency < 1 lm/W but enormous research and development work in WOLEDs has now taken the power efficiencies on WOLEDs over 100 lm/W[14,15]. Universal Display Corporation claims that its WOLEDs have potential to achieve >150 lm/W[14]. Research Institute of Organic Electronics, Japan fabricated a 14 x 14 cm^2 prototype of WOLED with power efficiency of 10 lm/W @ 5000 cd/m^2[,16], In 2010, Panasonic reported >30 lm/W and lifetime of >40000 h @1000 cd/m^2. In 2018 OLED works company, prepared bendable WOLED lighting panel on thin glass substrate, which could be bent to 10 cm of bending radius. Though the power conversion efficiency of WOLEDs has been reported over 100 lm/W but the theoretical limit is 248 lm/W[17], and we are still way too far from that value. Therefore, we need to put more efforts to understand and solve the issues associated with WOLEDs. Charge carrier injection into organic semiconductors leads to formation of singlet and triplet excitons. According to the electron spin statistics, 25% excitons are singlet excitons, whereas 75% excitons are triplet excitons. In fluorescent materials only singlet excitons result in light emission whereas triplet excitons decay non-radiatively, therefore the internal quantum efficiency in fluorescent materials is limited to 25% only. The phosphorescent materials can harvest both the singlet and triplet excitons into light emission and their internal quantum efficiency can be 100%. Therefore, to make efficient OLEDs, phosphorescent materials are used as the light emitters[18-20]. For the efficient harvesting of triplet excitons, the phosphorescent emitters are doped in a wide band gap host material, so that the electrons and holes injected into host material could be easily transferred to phosphorescent dopant (also called guest material) and recombine there to emit the light from the dopant. The selection of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the host material plays very important role in efficiency harvesting of both the singlet and triplet excitons. To achieve high efficiencies, host needs to have wide energy band gap than dopant to allow the efficient energy transfer from the host to the triplet energy of the dopant and it is possible only when the triplet energy of the dopant is lower that the triplet energy of the host. Iridium and platinum complexes show intense phosphorescent emission properties and are very efficient materials for OLEDs applications[18, 21-23]. These phosphorescent complexes can be incorporated into a single layer or distributed in multiple layers depending upon the strategies of making OLED to approach white emission. Efforts have also been made to harvest the triplet excitons in fluorescent materials by thermally activated delayed fluorescence and by some other approaches as well[21, 24].

In the present article we report the fabrication of WOLEDs following a very simple device design. We have used two phosphorescent materials emitting two complementary colors greenish blue and reddish orange and incorporated them in the OLEDs in multilayer device designs to make pure white emission. For greenish blue emission we used phosphorescent bis[(4,6-difluorophenyl)-pyridinato-N,C2']c(picolinate)iridium(III) (FIrPic) whereas for reddish orange emission we used phosphorescent bis(2-(2'-benzothienyl)pyridinato-N,C3')iridium (acetylacetonate) (btp$_2$Ir(acac)). Both of these phosphorescent emitters were doped in 4,4’-bis(9-carbazolyl)-biphenyl (CBP), which is a very commonly used host material for phosphorescent emitters. The amount of the dopants in the host material was precisely controlled to achieve white light from the devices. The devices have shown to emit very stable white light and the purity of the emitted light was checked by varying the applied voltage across the devices. Where the WOLED exhibited CIE coordinates (0.28, 0.33) at 10 V, the CIE coordinates showed a minute shift to (0.25, 0.32) when a 15 V was applied across the device. We have also studied the *J*-*V* and *V*-*L* characteristics and calculated the power efficiency of the WOLEDs.

2 Experimental

The WOLEDs were fabricated on indium tin oxide (ITO) coated glass substrates in the structure ITO/α-NPD:F$_4$TCNQ (30 nm)/CBP:FIrpic (25nm)/BCP (5 nm)/CBP:Ir(btp)$_2$(acac)(10 nm)/Alq$_3$ (10 nm)/LiF(0.5 nm)/Al (150 nm). Here N-[3-methyl-4-[2-methyl-4-(N-naphthalen-1-ylanilino)phenyl]phenyl]-N-phenylnaphthalen-1-amine (α-NPD) worked as hole transport layer (HTL), bathocuproine (BCP) works as hole blocking layer (HBL), Alq$_3$ works as electron transport layer (ETL) whereas LiF works as electron injecting buffer layer. CBP:FIrPic is the greenish blue emitter whereas CBP:Ir(btp)$_2$(acac) is the reddish orange emitter. Here ITO works as anode whereas Al works as cathode. Fig. 1 (a) shows the schematic

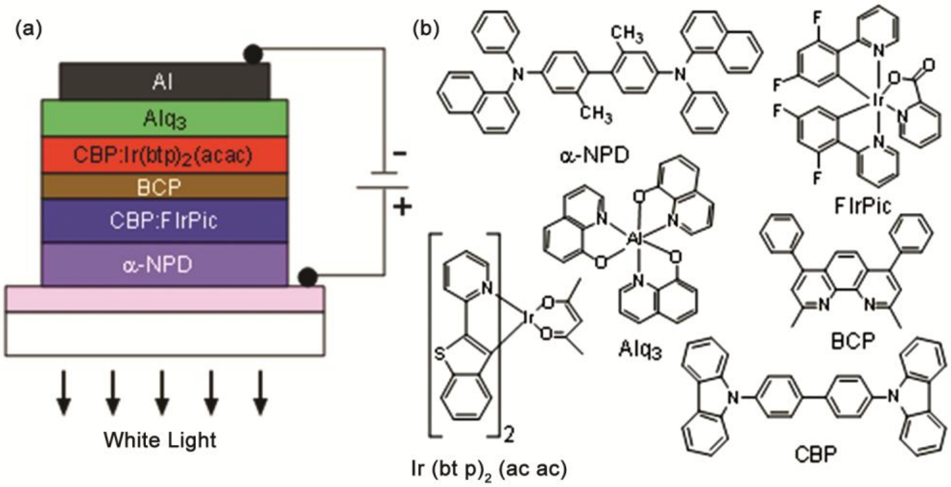

Fig. 1(a) — Schematic structure of the fabricated WOLEDs and (b) molecular structures of the materials used therein.

structure on the fabricated WOLEDs whereas Fig. 1(b) shows the molecular structures of different materials used in WOLEDs. Prior to any deposition on the ITO coated glass substrates, the ITO layer was etched in the stripe form via wet chemical method. The etched substrates were properly cleaned via standard cleaning procedure. In brief the substrates were first cleaned with soap solution and the washed with distilled water. The substrates were then sequentially cleaned with acetone, trichloroethylene and iso-proponol and finally dried at 100 °C in vacuum oven for 20 min. The cleaned ITO substrates were coated with 30 nm of αNPD:F_4TCNQ. α-NPD is frequently used as HTL in OLEDs and F_4TCNQ has been observed to improve hole injection into α-NPD[25], therefore to improve the hole injection into α-NPD we doped it with 0.5wt % of F_4TCNQ. For the greenish blue emission FIrPic was 10wt % doped in CBP and 25 nm of FIrPic doped CBP layer was deposited on F_4TCNQ doped α-NPD. BCP is an important material and used for electron transport and hole blocking applications in OLEDs. We deposited a very thin layer of 5 nm of BCP on FIrPic doped CBP. After that for reddish orange emission 10 nm of 5wt % Ir(btp)$_2$(acac) doped CBP layer was deposited on BCP. On the Ir(btp)$_2$(acac) doped CBP layer 10 nm of Alq$_3$ was deposited which was followed by deposition of 0.5 nm of LiF and 150 nm of Al. All the depositions from HTL to top metal electrode were carried out via thermal evaporation in a vacuum chamber with the base pressure less than 1×10^{-5} Torr. Al electrodes were deposited in the cross geometry to the ITO electrodes through shadow masks, which resulted in the device active area of 0.9 cm^2. The film thickness and the rate of depositions of different layers were measured using a digital quartz crystal thickness monitor. The performance of these WOLEDs was measured using different characterization tools. The electroluminescence (EL) spectra of the devices were measured using UV-VIS-NIR spectrometer from Ocean Optics (HR-2000 CG). Along with the EL spectrum, the Ocean Optics spectrometer also gave us the corresponding CIE coordinates of the emitted light. Keithley 2400 source meter was interfaced with Minolta (LS-110) luminescence meter and connected with the computer to get the current density-voltage (*J*-*V*) and voltage-luminescence (*V*-*L*) characteristics of WOLEDs.

3 Results and discussion

For white light emission it is very important that the constituent lights, whether three primary colors or the complementary colors, are mixed in the right amount otherwise one will dominate over other and we will not get white emission. For the WOLEDs we chose to mix two complementary colors greenish blue and reddish orange and the corresponding materials used to emit these colors were phosphorescent FIrPic and Ir(btp)$_2$(acac) respectively. The phosphorescent materials were doped in large band-gap CBP host. Fig. 2 shows the schematic energy level diagram of the WOLEDs prepared here. The energy levels of each material have been mentioned in the energy level diagram. The energy levels of FIrPic and Ir(btp)$_2$(acac) have been represented by dashed lines in between the energy band of CBP. The band-gaps of the FIrPic and Ir(btp)$_2$(acac) fell quite well within the band-gap of CBP. Application of a forward bias (+ve voltage to ITO with respect to Al) on the devices led to the hole injection from ITO to F_4TCNQ doped α-NPD and electron injection from Al to Alq_3. F_4TCNQ doping in α-NPD assists the hole into α-NPD whereas LiF assists electron injection into Alq_3. The injected holes transport through α-NPD and reach CBP:FIrPic interface, whereas injected electrons transport through Alq_3 and reach CBP:$Ir(btp)_2(acac)$ interface. Holes are further injected into CBP:FIrPic layer whereas electrons are further injected into CBP:$Ir(btp)_2(acac)$ layer. Some of the injected holes transport through inject into CBP:$Ir(btp)_2(acac)$ whereas some of the injected electrons transport through the inject into CBP:FIrPic. The electrons and holes in the CBP:FIrPic layer are initially in CBP but are immediately transferred to FIrPic energy levels and recombine in FIrPic to give greenish blue light. The electrons in LUMO of CBP are transferred to LUMO of FIrPic and holes in HOMO of CBP are transferred to HOMO of FIrPic. Similarly the electrons and holes in the CBP:$Ir(btp)_2(acac)$ layer are initially in CBP but are immediately transferred to $Ir(btp)_2(acac)$ energy levels and recombine in $Ir(btp)_2(acac)$ to give reddish orange light. The electrons in LUMO of CBP are transferred to LUMO of $Ir(btp)_2(acac)$ and holes in HOMO of CBP are transferred to HOMO of $Ir(btp)_2(acac)$. The energy transfer from CBP host to the phosphorescent guest happens via Dexter energy transfer mechanism[11]. Dexter energy transfer allows both the singlet to singlet and triplet to triplet energy transfers. If there was no BCP layer in between the two emissive layers, the electrons and holes could easily distribute throughout CBP and recombine to emit light from both the emissive layers in an uncontrolled way as both the emissive layers had the same host material CBP. In this situation, it would have been quite difficult to control the emission from each layer and the color of emitted light would not have been white. Therefore, for complete control on the emitted color it was very important to control the electron-hole recombination in each layer. To control the amount of electrons and holes recombining in each layer we introduced a thin layer of BCP in between the two emissive layers.

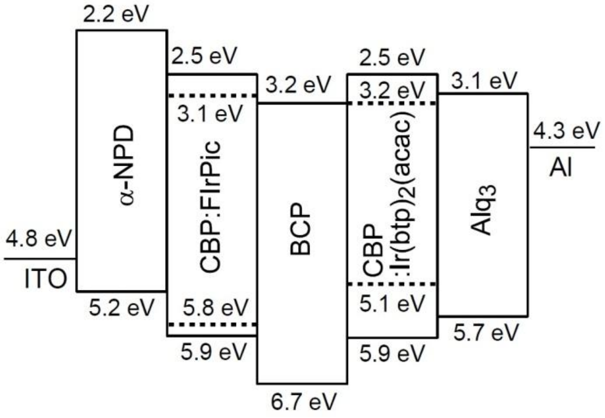

Fig. 2 — Schematic energy level diagram of the fabricated WOLEDs.

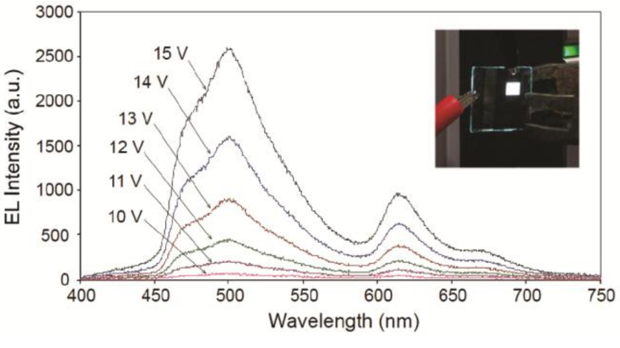

Fig. 3 — EL spectra of WOLED measured at different applied voltages. Inset shows the photograph of the WOLED operating at 10 V.

BCP has quite high HOMO energy compared to CBP and had an interface barrier of 0.6 eV for hole injection from CBP to BCP, therefore BCP works as a hole blocking layer. Due to high interface barrier the holes try to tunnel through BCP and reach on the other side of the BCP layer. However, the amount of holes flux tunneling through BCP is controlled by varying its thickness. Thicker the BCP layer, lesser the tunneling of holes through it. However, for a given thickness of BCP layer the amount of hole flux tunneling through it can also be controlled by varying the applied electric field. In the present OLEDs, BCP controls the migration of the holes from greenish blue emitter to reddish orange emitter or in other words BCP controls the distribution of holes and electrons in the two emissive layers. We found that 5 nm of BCP was optimum thickness of BCP to give optimum electron-hole recombination in both the emissive layers and the mixture of the emitted light from the two emissive layers resulted in the white light. Fig. 3 shows the EL spectra of the WOLED measure at different applied voltages and inset shows the photograph of the WOLED at 10 V. The EL spectrum of the WOLED was quite broad and spanned from around 420 nm to 720 nm covering the entire visible range. Though the EL spectrum of WOLED at any voltage exhibited two peaks, one at 500 nm and the other at 624 nm, the EL peak at 500 nm comes from the emission from FIrPic and the EL peak at 624 nm comes from the emission from $Ir(btp)_2(acac)$. It is worth mentioning here that the EL spectrum of the individual

CBP:FIrPic emissive layer spans from around 420 nm to 600 nm and the EL spectrum of CBP:Ir(btp)$_2$(acac) spans from around 520 nm to 720 nm. The Spectrum of the WOLED was the overlap of the emission from the two layers emitting two complementary colors. The CIE coordinates of the emitted light at 10 V were (0.28, 0.33), which were very close to those of the ideally pure white light (0.33, 0.33). It can be clearly seen from EL spectra that in the white light the contribution of the emission from FIrPic was more than that form Ir(btp)$_2$(acac), it was because we needed more bluish contribution than reddish to make a white. Therefore the amount of emitted light from Ir(btp)$_2$(acac) was kept lower by keeping its doping amount and the film thickness lesser than that of FIrPic.

We studied the effect of applied voltage on the shift in the color of the emitted light from WOLED. The EL spectra were measured at different voltages from 10-15 V and the measured EL spectra are shown in Fig. 3. The increment in applied voltage resulted in the increment in the intensity of the emitted light. The increment in the EL intensity with applied voltage can be understood from the enhanced electron-hole injection and as a result the enhanced electron-hole recombination in each emissive layer. But interestingly the increment in the applied voltage did not have any significant effect on the color of the emitted light. We also measured the CIE coordinates of the emitted light at different voltages and are given in Table 1. The CIE coordinates of the WOLED changed from (0.28, 0.33) to only (0.25, 0.32). We usually expect that the emission of a device coming from different emissive layers could shift due to imbalanced electrons-holes injection. The variation in applied voltage was also expected to result in imbalanced tunneling of the electrons and hole through BCP. But in the present structure there was only a minute change in the CIE coordinates with the applied voltage and the color of the emitted light was still reasonably good white color of the CIE diagram. The variation in the applied voltage did not change the recombination zones. Though it increased the number of injected electrons and holes but the adopted device design did not let to change the ratio of the emitted lights and the output light remained the same with increased intensity.

Table 1 — CIE coordinates of WOLED at different applied voltages.

Applied Voltage	CIE Coordinates
10 V	(0.28, 0.33)
11 V	(0.27, 0.33)
12 V	(0.26, 0.32)
13 V	(0.26, 0.32)
14 V	(0.25, 0.32)
15 V	(0.25, 0.32)

To calculate the power efficiency of the WOLED we measured its *J-V* and *V-L* characteristics. Fig. 4 shows the *J-V* and *V-L* characteristics of the WOLED. Both the current and luminescence varied non-linearly with increment in the applied voltage. The WOLED exhibited brightness of 1580 cd/m^2 at 15 V. The *J-V* and *V-L* characteristics led us to calculate the power efficiency of 0.35 cd/A at 14 V. For the public demonstration we fabricated a WOLED numeric display. The display was fabricated exactly in the same device design on ITO coated glass substrates, following exactly the same procedure as mentioned in experimental section. The display worked very well and was operated through the electronic circuit of a digital counter from 000 to 999. Fig. 5 shows the

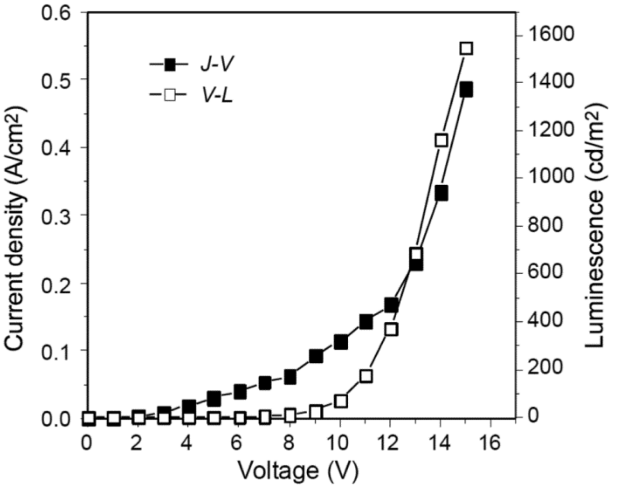

Fig. 4 — *J-V* and *V-L* characteristics of the WOLED. The *J-V* and *V-L* characteristics led us to calculate the power efficiency of WOLED.

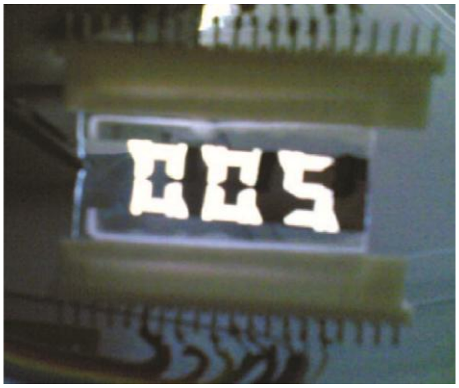

Fig. 5 — Photograph of the WOLED numeric display prepared in the similar device design and in similar conditions as those of small area WOLED shown in Fig. 1.

photograph of the WOLED display captured at the digital count of 005.

4 Conclusion

We have presented here a very simple method to fabricate WOLEDs. The WOLEDs have been fabricated following the complementary color mixing approach. We used two phosphorescent emitters, one emitting greenish blue light (FIrPic) whereas the other emitting reddish orange light (Ir(btp)$_2$(acac)), in multilayer device design. The two emitters were doped in CBP and the emission from each layer was precisely controlled by introducing an optimum thickness of a hole blocking layer in between the two emissive layers. The ratio of the two emitted lights to get pure white was also controlled by varying the dopant concentrations and film thicknesses of the two emissive layers. The WOLED exhibited the CIE coordinates (0.28, 0.33) at 10 V. The proposed WOLED structure exhibited quite stable white emission, with optimized recombination of electrons and holes in the two emissive layers and did not shift upon changing the applied voltages from 10 to 15 V. The studies presented here would help the researchers to develop WOLEDs emitting pure white light, with the emitted color independent of applied bias voltage.

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