



Efficient Green Phosphorescent Organic Light Emitting Diode using Iridium Complex

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We report here the fabrication and characterization of an efficient green phosphorescent organic light emitting diodes (PhOLED) using phosphorescent iridium complex, tris(2-phenylpyridine) iridium (III) ($\text{Ir}(\text{ppy})_3$). $\text{Ir}(\text{ppy})_3$ is an organic phosphorescent material, which emits green light via both the singlet as well as triplet exciton relaxation. To avoid triplet-triplet annihilation and for efficient light emission, the phosphorescent emitters should be doped in a suitable host material which has band-gap larger than the doped guest material and the band gap of the guest should lie within the band-gap of the host. We optimally doped phosphorescent $\text{Ir}(\text{ppy})_3$ into a fluorescent 4,4'-bis(9-carbazolyl) biphenyl (CBP) host and used it as the emitter to prepare PhOLEDs. The PhOLED exhibited green electroluminescence (EL) in the range ~ 480-650 nm with EL peak at 550 nm along with a shoulder at 510 nm. The Commission Internationale de l'éclairage (CIE) colour coordinate of the device was measured to be (0.25, 0.60). The current density vs voltage vs luminescence (J - V - L) characteristics of the device led us to calculate its current efficiency, which was found to be 28.9 cd/A at 7V. The efficiency of PhOLED decreased with increment in the applied voltage beyond 7 V and has been attributed to the triplet-triplet annihilation due to high injected current densities.

Keywords: Organic light emitting diodes; Electroluminescence; Phosphorescent Iridium complex; Dexter energy transfer; Host-Guest system

1 Introduction

The first breakthrough in the field of organic electroluminescence took place in 1987, when Tang and VanSlyke prepared first organic light emitting diode (OLED) using well studied tris(8-hydroxyquinoline) aluminium (Alq_3) organic semiconductor¹. Though the efficiency of first OLED was not very high but this invention attracted global attention as OLEDs could lead to the development of advanced electronic devices and revolutionize the areas of lighting and display technologies. The beauty of organic semiconductors is that they have lots of benefits over the conventional semiconductors like the organic semiconductor devices are thin, light weight and mechanically flexible²⁻⁴. They are processed at relatively lower temperatures and the devices can be prepared in large areas quite easily. They can be prepared on flexible substrates like plastic or metal foils to make flexible OLEDs with wide viewing angle, fast response and high resolution. On the top of that, OLEDs are highly cost effective compared to conventional lighting technologies. Since

the discovery of OLEDs, intense efforts have been made globally to improve their performance and thanks to global research & development work, the OLEDs are now available in the market⁵⁻⁷. OLEDs have revolutionized the area of display technologies and are available as displays for various electronic devices ranging from small applications like music players, wrist watches, digital cameras, mobile phones and toys to bigger applications like laptops and televisions. It is very easy to achieve OLEDs emitting any colour of choice by just doing little modification in the device design⁶. Intense efforts are now being made to develop white OLEDs for general lighting purposes and make them commercially available⁸⁻¹¹.

OLEDs are two electrode systems, where light emitting layer is sandwiched between two electrodes along with charge transport layer. One of the electrodes works as anode whereas other electrode works as cathode. Under the applied forward bias, anode injects holes whereas cathode injects electrons into the emissive layer. The injected electrons and holes form excitons in the emissive layer and the excitons decay either radiatively or non-radiatively. In the radiative exciton decay, the exciton energy is

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released in the form of light whereas in the non-radiative exciton decay the exciton energy is released in the form of heat. According to the electron spin statistics, the injected charge carriers form 25% singlet excitons and 75% triplet excitons. The organic light emitting materials can be classified into fluorescent and phosphorescent emitters. In the fluorescent materials, only singlet excitons could lead to radiative recombination and the triplet excitons are non-radiative as direct transition from triplet excited state to singlet ground state is prohibited. Therefore, the internal quantum efficiency in fluorescent materials is limited to maximum 25%. Tremendous efforts have been focused on improving the efficiency of OLEDs and the efficiency barrier in OLEDs could be overcome if one could harvest the triplet transitions also, and that has been possible by employing the phosphorescent materials in OLEDs. In case of phosphorescent materials both the singlet and triplet exciton can decay radiatively and the internal quantum efficiency in phosphorescent materials can be 100%. As the phosphorescent materials are highly efficient compared to fluorescent materials, the most efficient OLEDs incorporate phosphorescent materials as light emitters and such OLEDs are known as phosphorescent OLEDs (PhOLEDs)¹²⁻¹⁸. Though the fluorescent materials could be used in OLEDs without doping but the phosphorescent materials are always doped in a suitable wide band-gap material in little wt% concentration. In such a system the wide band gap material is called host material whereas the dopant is called guest material. If the phosphorescent guest is not doped in wide band-gap host, triplet-triplet annihilation will take place in phosphorescent material and the OLEDs will not be very efficient. The host material is chosen to be of wider band-gap because both the electrons and holes injected into lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the host need to be transferred to LUMO and HOMO of the phosphorescent guest and recombine there to give the characteristic light of the phosphorescent material. In a way the excitons formed in the host are transferred to the guest via Dexter energy transfer mechanism. In the Dexter energy transfer mechanism, the exciton energy in one material is transferred to the other material via electron-hole exchange which is favoured by their energy levels. In this way the exciton in one material is transferred to other material. The selection of

HOMO and LUMO of the host material plays very important role in efficiency harvesting of both the singlet and triplet excitons in the guest material. The singlet and triplet energies of the guest should be lower than those of the host materials for efficient exciton transfer. Iridium and platinum complexes have shown intense phosphorescent emission properties and are very efficient materials for OLEDs applications¹²⁻¹⁵. The light emission from PhOLEDs is generally called electro-phosphorescence. The advent of electro-phosphorescent devices has greatly improved the outlook for applications of OLEDs by raising the internal quantum efficiency from 25% to near 100%^{13,14}.

Green OLEDs have found relatively more applications than other single colour OLEDs. Some of the examples for green OLEDs applications are traffic light signal, EXIT and other signages at various locations, digital electronic displays, building decorations, full colour OLED displays, white OLEDs via three primary colour approach etc. In this paper we report the fabrication of efficient green PhOLED using Ir(ppy)₃ as the light emitting material. For the doping of Ir(ppy)₃ in a wide band-gap host, we used 4,4'-N, N'-dicarbazole-biphenyl (CBP) as the host. CBP has shown perfect LUMO and HOMO energy levels for efficient exciton transfer from CBP to Ir(ppy)₃. For efficient light emission the doping of Ir(ppy)₃ in CBP was precisely controlled and the optimum doping concentration was found to be 10 wt%. The PhOLED exhibited green emission with EL peak at 550 nm and the CIE coordinates to be (0.25, 0.60). The PhOLED was subjected to current density-voltage (*J-V*) and voltage-luminescence (*V-L*) characteristics which led us to calculate the current efficiency to be 28.9 cd/A at 7V.

2 Experimental details

The PhOLEDs were prepared on indium tin oxide (ITO) coated glass substrates. The ITO coated glass substrates (Sheet Resistance 15 Ω/sq) were patterned in the stripe design by wet chemical etching method. In brief, for wet chemical etching the ITO substrates were coated with a photoresist and exposed to UV light through a photographic negative. The UV light exposure cured the photoresist through the transparent area of the negative and made it hard to scratch. The unexposed area of the photoresist was removed with the help of developer and then the substrates were dipped in dilute HCl solution and a little amount of

Zn dust was sprinkled over the substrate to remove the ITO from the places where there was no photoresist. After the ITO was completely etched out from the places where there was no photoresist, the substrates were washed with water. Finally, the hard section of the photoresist was removed by acetone. The ITO under the hard photoresist was not etched out by the acid as it could not reach there. After etching, the ITO substrates were cleaned through standard cleaning procedure. In brief the ITO coated substrates were sequentially cleaned with soap solution, distilled water, acetone, trichloroethylene and iso-propanol and finally dried at 100 °C for 20 min. in a vacuum oven. The cleaned ITO substrate were treated to oxygen plasma under reduces pressure for 15 min to increase their work function. Oxygen plasma was created by applying a very high AC voltage between two electrodes under low pressure of oxygen environment. The PhOLEDs were prepared in ITO/ α -NPD: F₄TCNQ (30 nm)/CBP:Ir(ppy)₃ (10 wt%) (25 nm)/BCP (5 nm)/Alq₃ (10 nm)/LiF(0.5 nm)/Al (150 nm)

structure on glass substrates. Here ITO works as anode and Al works as cathode. 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), CBP:Ir(ppy)₃ works as the green emitter, bathocuproine (BCP) works as hole blocking layer (HBL), Alq₃ works as electron transport layer (ETL) and LiF works as electron injecting buffer layer. All these layers were deposited by thermal evaporation material in a vacuum chamber. Fig. 1 (a) shows schematically the deposition of different materials on ITO coated glass substrate to fabricate PhOLEDs. Fig. 1(b) shows the molecular structures of different materials used in the PhOLEDs fabricated here. First of all the cleaned ITO substrates were coated with 30 nm of α -NPD:F₄TCNQ. α -NPD is frequently used as HTL in OLEDs and F₄TCNQ has been observed to improve hole injection into α -NPD¹⁹, therefore to improve the hole injection into α -NPD we doped it with 0.5wt% of F₄TCNQ. After deposition of α -NPD:F₄TCNQ, a 25 nm of Ir(ppy)₃ doped CBP layer

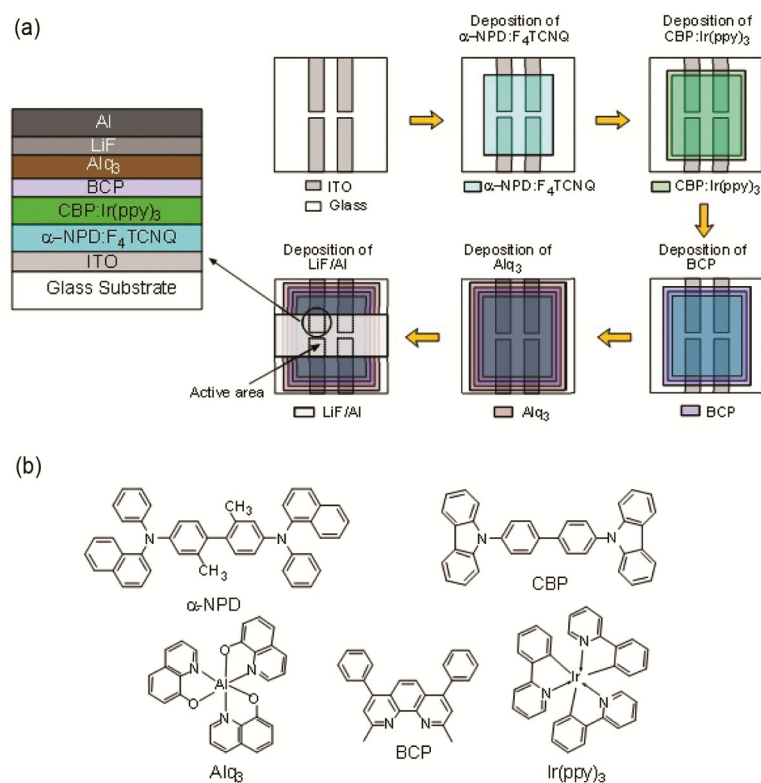


Fig. 1 — (a) Schematic representation of the deposition of different layers on ITO coated glass substrate to make efficient green emitting PhOLEDs. The layer-by-layer structure of the PhOLED has also been shown schematically. (b) Molecular structures of the materials used to fabricate green emitting PhOLED. Here α -NPD works as HTL, Alq₃ works as ETL, BCP works as hole blocking layer and CBP works as host for the green emitting Ir(ppy)₃ guest.

was deposited on it. Ir(ppy)₃ was doped 10 wt% in CBP. After that a very thin layer of 5 nm of BCP was deposited on CBP:Ir(ppy)₃ emissive layer. BCP is an important material and used for electron transport and hole blocking applications in OLEDs. On the BCP layer, a 10 nm of Alq₃ 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 0.12 cm². The HTL, emissive layer, BCP and Alq₃ layer were deposited at 1 Å/s, LiF was deposited at 0.2 Å/s and Al electrode was deposited at 10 Å/s. The film thicknesses and rates of depositions of different materials were determined from a digital quartz crystal thickness monitor. After fabrication the PhOLEDs were subjected to different characterizations like EL spectrum, *J-V* and *V-L* characteristics. The 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 unit 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 PhOLEDs.

3 Results and Discussion

In the present studies, for green emitting PhOLEDs, the phosphorescent Ir(ppy)₃ has been doped 10 wt% in CBP. α -NPD and Alq₃ have been used as HTL and ETL respectively. Here BCP works as hole blocking layer and confines the injected electrons and hole in the emissive layer. Fig. 2(a) shows schematically the energy level diagram of Ir(ppy)₃ based PhOLEDs fabricated here. The energy levels of Ir(ppy)₃ have been represented by dashed lines in between the energy band of CBP. The values of HOMO and LUMO levels for different materials have been taken from literature. F₄TCNQ doping in α -NPD assists the holes transportation into α -NPD whereas LiF assists electrons injection into Alq₃. Application of a forward bias (+ve voltage to ITO anode with respect to Al cathode) results in injection of electrons from Al into LUMO of Alq₃ through electron injection buffer layer of LiF and injection of

holes from ITO into HOMO of α -NPD. Under the applied electric field, the injected electrons transport through LUMO of Alq₃ and BCP and inject into LUMO of CBP in the emissive layer on the other hand the injected holes transport through HOMO of α -NPD and inject into HOMO of CBP. The energy offsets in the LUMOs of α -NPD and CBP and HOMOs of CBP and BCP provide enough barriers for electrons not to transfer into α -NPD and holes not to transfer into BCP respectively. BCP has quite high HOMO energy compared to CBP (~ 0.8 eV), therefore BCP works as a hole blocking layer. We found that

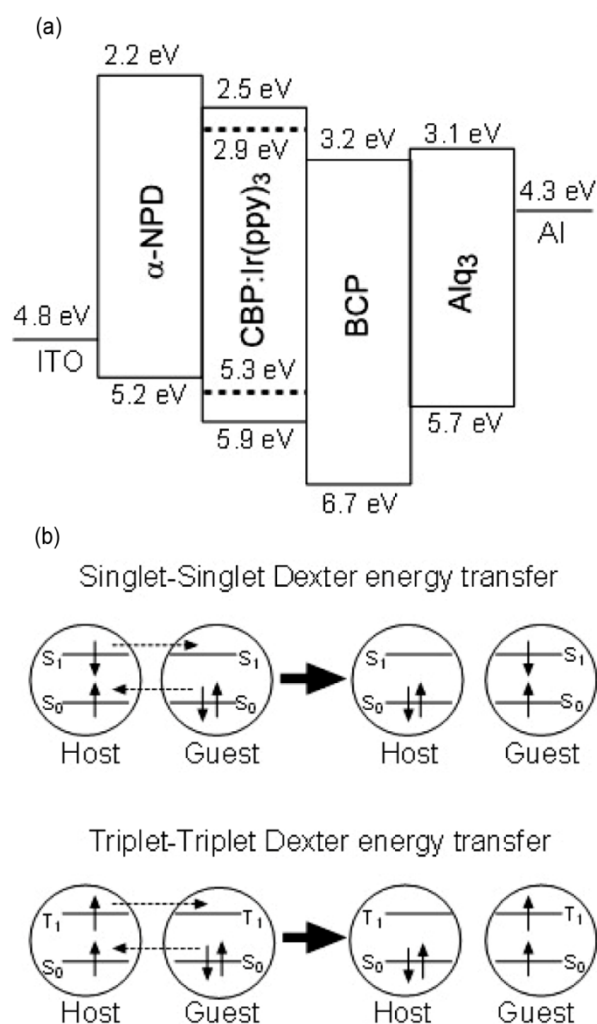


Fig. 2 — (a) Schematic energy level diagram of the PhOLED. The energy levels of Ir(ppy)₃ are shown by dashed lines within the band gap of CBP. All the values of the energy levels have been taken from the literature. (b) Schematic representation of the singlet-singlet Dexter energy transfer and triplet-triplet Dexter energy transfer between host and guest molecules. In a way, Dexter energy transfer is the diffusion of the excitons from host to guest.

5 nm of BCP was optimum thickness of BCP to give optimum electron-hole recombination in the emissive layer to achieve highest efficiency. The injected electrons and holes are confined within the CBP:Ir(ppy)₃ emissive layer. Now both the singlet and triplet excitons formed in CBP are immediately transferred to Ir(ppy)₃ via Dexter energy transfer mechanism and recombine in Ir(ppy)₃ to give green light. Fig. 2(b) shows schematically the Dexter energy transfer mechanism between host and guest molecules. Dexter energy transfer allows both the singlet to singlet and triplet to triplet energy transfers. For the Dexter energy transfer the electron from LUMO of the host is transferred to LUMO of the guest whereas one electron from HOMO of the guest occupies the hole in the HOMO of the host leaving one hole behind in the HOMO of the guest. In this way we get one electron and one hole in the LUMO and HOMO of the guest that form one exciton in the guest molecule. Basically, this energy transfer is the diffusion of excitons from host to guest. Dexter energy transfer is a non-radiative process. The Dexter energy transfer is favoured by the relative energy levels of the HOMOs and LUMOs of the host and guest molecules. As the HOMO and LUMO energy levels of Ir(ppy)₃ exist in between the band-gap of CBP, the Dexter energy transfer becomes very easy from CBP to Ir(ppy)₃. The singlet and triplet excitons generated in CBP host are transferred to the singlet and triplet energy states of Ir(ppy)₃ guest and form the singlet and triplet excitons there, and both types of these excitons decay radiatively in Ir(ppy)₃. Or in other way, in the singlet and triplet energy transfer the electrons in LUMO of CBP are transferred to LUMO of Ir(ppy)₃ and holes in HOMO of CBP are transferred to HOMO of Ir(ppy)₃.

For the efficient Dexter energy transfer between host and guest molecules, the inter-molecular distance between them plays very important role. For Dexter energy transfer the inter-molecular distance should be a short range separation of 5~20 Å^{8,20}. This range of molecular separation is usually achieved with ~ 5 to 15 wt% doping of the guest molecule in the host. If the inter-molecular distance between host and guest molecules is more than this range then Dexter energy transfer does not take place and the excitons recombine within the host itself and we get light emission from the host. If the inter-molecular distance between host and guest molecules is less than this range then the triplet-triplet annihilation takes place and some of the triplet excitons recombine without

emitting the light and energy of those excitons is wasted as heat. In the PhOLEDs prepared here the optimum concentration of Ir(ppy)₃ has been found to be 10 wt% in CBP, therefore we report here the properties of the PhOLED prepared with 10 wt% doping of Ir(ppy)₃ in CBP only. Also, the electron and hole transporting layers and electron and hole injection layers play a very important role to get the higher probability of electron-hole recombination within the emissive region.

Fig. 3 shows the EL spectrum of the green PhOLED at 7 V. The EL spectrum ranged from ~ 480-650 nm with EL peak at 550 nm along with a shoulder at 510 nm. The EL occurs due to electronic transitions between LUMO and HOMO energy levels. The energy and amount of the emitted photons of particular energy depend upon the distribution of energy difference between LUMO and HOMO energy levels as well as their density of states²¹. Therefore, the shoulder at 510 nm in the EL spectrum can be attributed to characteristics distribution and density of states of HOMO and LUMO levels in the HOMO and LUMO bands of Ir(ppy)₃ respectively. The CIE coordinates of the PhOLED were measured to be (0.25, 0.60). The inset of Fig. 3 shows the photograph of the PhOLED operated at 7 V. To calculate the power conversion efficiency of the PhOLED we measure its *J-V* and the corresponding *V-L* characteristics. Fig. 4 shows the *J-V* and *V-L* characteristics of the PhOLED. Both the current and luminescence varied non-linearly with increment in the applied voltage. The PhOLED generated brightness of 25,500 cd/m² at 14 V. The inset of

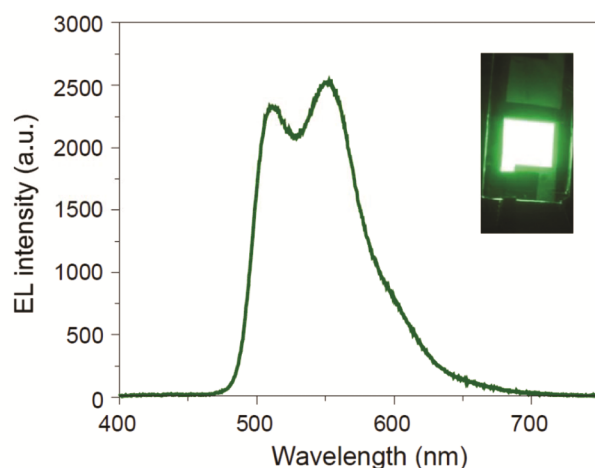


Fig. 3 — EL spectrum of the green emitting PhOLED. The inset shows the photograph of the PhOLED operated at 7 V.

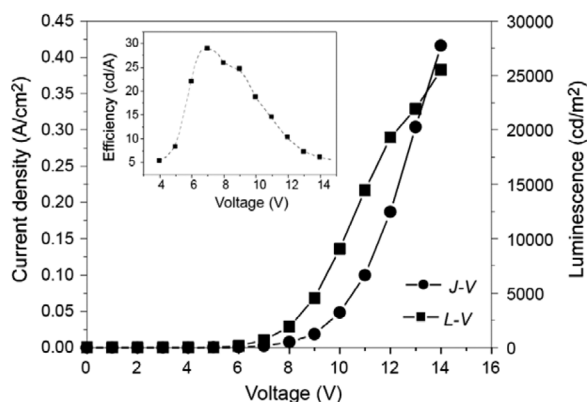


Fig. 4 — J - V and V - L characteristics of the PhOLED. The graph with filled circle symbols represents the J - V characteristics whereas the graph with filled square symbols represents the V - L characteristics. Inset shows the plot of efficiency of PhOLED as a function of the applied voltage. The PhOLED exhibited maximum efficiency of 28.9 cd/A at 7 V.

Fig. 4 shows the plot of current efficiency of the PhOLED as a function of applied voltage from 4 to 14 V. The efficiency of PhOLED increased with the applied voltage first up to 28.9 cd/A at 7 V and then decreases with increment in applied voltage. The increment in the efficiency with applied voltage can be understood from the fact that as the applied voltage increases, the number of injected electrons and holes also increases. The increased injection of electrons and holes increases the current through the device. Increased injection of charge carriers results in increased recombination of electrons and holes in the emissive layer and as a result the brightness of the emitted light also increases with applied voltage. The efficiency of the PhOLED was found to be maximum 28.9 cd/A at 7 V, which suggests that the PhOLED exhibited quiet efficient injection and recombination of charge carriers at 7 V. At 7V the luminescence of the emitted light was 709 cd/m². As the applied voltage increased further the efficiency of the PhOLED decreased. At 10 V the efficiency of the PhOLED was found to be 18.7 cd/A and it reduced to 6.1 at 14 V. The reduction in efficiency of the PhOLED after 7V can be understood from the fact that high current densities in PhOLEDs results in triplet-triplet annihilation. The triplet-triplet annihilation increases as the current density through the device increases beyond the optimum current. This observation is in quite good agreement with the investigations made by other groups as well²².

As green OLEDs have numerous applications in display area, we prepared a green light emitting seven



Fig. 5 — Photograph of the green emitting seven segment display prepared in the same device design as that of the green PhOLED reported here. The seven segment display was connected to a digital counter circuit and the photograph was captured at the digital count of 9.

segment display using Ir(ppy)₃ based PhOLED just for the public demonstration. 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 it was operated through an electronic circuit of a digital counter from 0 to 9. Fig. 5 shows the photograph of the green PhOLED seven segment display, captured at the digital count of 9.

4 Conclusions

We have reported here the fabrication and characterization of green light emitting PhOLED using Ir(ppy)₃ as the phosphorescent emitter. For efficient light generation Ir(ppy)₃ was doped into wide band-gap CBP host. The injected electrons and holes form singlet and triplet excitons in the CBP host that are transferred to Ir(ppy)₃ guest via Dexter energy transfer and recombine there to give green light emission. The EL spectrum of the PhOLED spanned from 480 nm to 650 nm and exhibited emission peak at 550 nm with a shoulder at 510 nm. The shoulder in the EL spectrum has been attributed to the characteristics distribution of density of states in the HOMO and LUMO bands of Ir(ppy)₃. The CIE coordinates of the emitted light were measured to be (0.25, 0.60). The optimized device structure resulted in the efficiency of 28.9 cd/A at 7 V with brightness of 709 cd/m². The PhOLED exhibited brightness of 25,500 cd/m² at 14V. The efficiency of the PhOLED first increased with increment in the applied voltage

up to 7 V and then decreased with further increment in the applied voltage. The reduction in the efficiency of the PhOLED beyond 7V has been attributed to the triplet-triplet annihilation due to high injection current densities. Overall, the PhOLED reported here exhibited efficient green light emission with efficiency of 28.9 cd/A at low operating voltage of 7 V with brightness of 709 cd/m², and is a noticeable contribution, which will help the researchers to make efficient green OLEDs for a variety of applications.

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References

- 1 Tang C W & Van S SA, *Appl Phys Lett*, 51 (1987) 913.
- 2 Choi S, Kang C, Byun C W, Cho H, Kwon B H, Han J H, Yang J H, Shin J W, Hwang C S, Cho N S, Lee K M, Kim H O, Kim E, Yoo S & Lee H, *Nat Commun*, 11 (2020) 2732.
- 3 Jang H J, Lee J Y, Kwak J, Lee D, Park J H, Lee B & Noh Y Y, *J Inform Disp*, 20 (2019) 1.
- 4 Cho H, Byun C W, Kang C M, Shin J W, Kwon B H, Choi S, Cho N S, Lee J I, Kim H, Lee J H, Kim M & Lee H, *J Inform Disp*, 20 (2019) 249.
- 5 Wu Z & Ma D, *Mater Sci Eng Rep*, 107 (2016) 1.
- 6 Zou S J, Shen Y, Xie F M, Chen J D, Li Y Q & Tang J X, *Mater Chem Front*, 4 (2020) 788.
- 7 <https://www.oled-info.com/lg-oled>.
- 8 Misra A, Kumar P, Kamalasanan M N & Chandra S, *Semicond Sci Technol*, 21 (2006) R35.
- 9 Misra A, Kumar P, *Indian J Pure Appl Phys*, (2022) (accepted).
- 10 <https://oled.com/oleds/white-oleds-woleds/>.
- 11 Wu S F, Li S H, Wang Y K, Huang C C, Sun Q, Liang J J, Liao L S & Fung M K, *Adv Funct Mater*, 27 (2017) 1701314.
- 12 Zhang Q, Tsang D, Kuwabara H, Hatae Y, Li B, Takahashi T, Lee S Y, Yasuda T & Adachi C, *Adv Mater*, 27 (2015) 2096.
- 13 Zhang G, Xing G, Lang J, Li C, Wang X & Wang D, *Opt Commun*, 459 (2020) 124921.
- 14 Dai X & Cao J, *Org Electron*, 78, (2020) 105563.
- 15 Xia D, Wang B, Chen B, Wang S, Zhang B, Ding J, Wang L & Jing X, *Angew Chem*, 53 (2014) 1048.
- 16 Friend R H, Gymer R W, Holmes A B, Burroughes J H, Marks R N, Taliani C, Bradley D D C, Santos D A D, Bredas J L, Logdlund M & Salaneck W R, *Nature*, 397 (1999) 121.
- 17 Baldo M A, O'Brien D F, Thompson M E & Forrest S R, *Phys Rev B*, 60 (1999) 14422.
- 18 Adachi C, Baldo M A, Thompson M E & Forrest S R, *J Appl Phys*, 90 (2001) 5048.
- 19 Kumar R, Khare N, Bhalla G L & Kamalasanan M N, *Thin Solid Films*, 518 (2010) 61.
- 20 Tokito S & Tanaka I, *Electrochemistry*, 76 (2008) 1.
- 21 Kumar P, *Organic Solar Cells: Device Physics, Processing, Degradation and Prevention*, CRS Press, Taylor & Francis Group, 2006.
- 22 D'Andrade B W & Forrest S R, *Adv Mater*, 16 (2004) 1585.