Fabrication of white organic light-emitting diodes by co-doping of emissive layer

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Efficient white light emission by mixing of red emission from (Ir-BTPA) [bis(2-(2’-benzothienyl) pyridinato-N,C\textsuperscript{3’}) (acetyl-acetonate) iridium(III)] and greenish blue from (FIrPic) [bis(2-(4,6-difluorophenyl)pyridinato-N,C\textsuperscript{2’}) iridium(III)] has been studied. Ir-BTPA and FIrPic are co-doped into a 4, 4’ bis 9 carbozyl (biphenyl) (CPB) host. The device emission colour is controlled by varying dopant concentration. Photoluminescence (PL), electroluminescence (EL) and colour coordinates have been studied as a function of applied voltage. The EL spectra of the devices with the co-doped emissive layer show three emission peaks at 469, 500 and 611 nm. Commission Internationale de l'Eclairage (CIE) coordinates of the devices are 0.27, 0.32 at 18 V and are well within the white region.

Keywords: White OLED, Iridium complexes

1 Introduction
During the last few years, organic electronic devices are being developed for several potentially important applications like organic thin film transistors (OTFTs), organic light emitting diodes (OLEDs) and organic photovoltaic devices (OPVs). The rapid growth of OLEDs is of considerable interest due to their potential application in flexible, cost-efficient and large area flat-panel displays and is considered as a direct replacement for LCD displays. They are also being considered for replacement of incandescent lamps and gas filled tubes for general illumination where good quality white light is of prime importance and hence much effort is being put into the development of novel white light emitters for use in general lighting applications. The efficiency of OLEDs using fluorescent emissive materials is low due to selection rule limitation in which only singlet-singlet transition is allowed and the ratio of the singlet excitons to the triplet in the electron-hole recombination process are only 1:3. This limits the internal quantum efficiency to 25%. By employing the triplet based phosphorescent emitter material, where both singlet and triplet exited states can participate in the radiative process, the internal efficiency of OLEDs can reach as high as 100%\textsuperscript{1,2}. The basic condition to fabricate efficient devices by doping phosphorescent molecules into a host matrix is that the triplet energy of the host matrix must be higher than that of triplet energy of the phosphorescent dopant. This confine the triplet excitons generated in the recombination process on the guest molecule. Most of these phosphorescent dopant molecules are based on heavy metal complexes. Among the many kinds of metal complexes, triplet emitting compounds of trivalent iridium complexes are the most effective and show intense phosphorescence at room temperature\textsuperscript{3}.

Recently, prompted by the availability of highly efficient red, green, and blue phosphorescent emitters\textsuperscript{4,6}, a number of highly efficient phosphorescent small molecules based white OLEDs have been reported\textsuperscript{7,9}. D’Andrade et al.\textsuperscript{10} have reported electro phosphorescent white OLEDs with a triple doped emissive layer. Gao et al.\textsuperscript{11} have obtained white OLEDs by employing a hole-transporting layer of mixed light-emitting organic materials. OLEDs based on multiemissive layers (MEL) show high current density, lower efficiency and shorter life time than single emissive layer (SEL) device\textsuperscript{12}. Very little work has been done on white light emission from single layer devices.

In the present study, white light emitting SEL devices have been fabricated by mixing two phosphorescent materials in a suitable ratio. This white light emission has been achieved by the
addition of the blue light emitted by bis(2-(4,6-difluorophenyl)pyridinato-N,C\(^2\)) iridium(III) (FIrPic) and the red light emitted from bis(2-(2'-benzothenyl)pyridinato-N,C\(^2\)) (acetyl-acetonate) iridium(III) (Ir-BTPA). The energy transfer from the blue emitter to the red emitter has been controlled by careful optimization of the mixing ratio (incomplete energy transfer). 4,4’ bis 9 carboyl (biphenyl) (CBP) which has a large band gap is used as the host matrix.

2 Experimental Details

Device were fabricated on glass substrate coated with 140 nm thick indium tin oxide (ITO) (Vin Karola U.S.A.) having a sheet resistance of 20Ω/□ and optical transmittance of over 85%. These substrates were photo lithographically patterned having 5mm strip and sequentially cleaned in deionized water, acetone, trichloroethylene and isopropyl alcohol for 20 min each in an ultrasonic bath and dried in an oven followed by oxygen plasma treatment foe 5 min to increase its work function. Organic layers were deposited in high-vacuum (10\(^{-6}\) torr) by thermal evaporation of the required organic material onto a cleaned ITO coated glass substrate. Finally a LiF buffer layer and Al cathode were vapour deposited onto organic films. Exposure of the samples to air in between the plasma treatment and the transfer of the substrate in to the evaporation chamber as well as between the deposition process and encapsulation could not be avoided but was kept as short as possible.

The layer thicknesses of the deposited material were measured in situ by a quartz monitor. The structure of the devices is ITO/α-NPD (30 nm)/CBP: FIrPic(5%): Ir-BTPA(\(\times\)%) (25 nm)/BCP (6 nm)/ Alq\(_3\) (28 nm)/LiF (1 nm)/Al (100 nm) where \(x = 0.25\%\), \(0.50\%\). Tris (8-hydroxyquinoline) aluminium (Alq\(_3\)) (Sigma Aldrich) and N,N’-Di-[(1-naphthalenyl)-N,N’-diphenyl]-1,1’-biphenyl)-4,4’-diamine (α-NPD) (sigma Aldrich) were used as the electron and hole transporting layers. 2, 9 dimethyl 4, 7 diphenyl 1, 10 phenanthenrole (BCP) which has a high ionization potential (6.5 eV) has been used as hole blocking layer. Ir-BTPA (ADS) and FIrPic (ADS) co-doped into the wide energy gap CBP (ADS) host were used as emissive layer. The concentration of the Ir-BTPA was 0.5 wt% (Device 1) and 0.25 wt% (Device 2) and that of the FIrPic was 5 wt% in the host matrix of two devices. EL spectra and CIE co-ordinates of the devices were measured by an ocean optics (HR-2000 CG) UV-NIR spectrophotometer and the current–voltage–brightness characteristics were simultaneously measured by a programmable voltage–current source measure unit (Keithley 2400) and luminescence meter (LMT 1009). The photoluminescence spectra were measured on thin film grown in vacuum (\(10^{-6}\)) by thermal evaporation on solvent cleaned glass substrate using a spectrophotometer (Flurolog Jobin Yvon Horiba). All measurements were carried out at room temperature under ambient conditions.

3 Results and Discussion

The molecular structure of host CBP and dopants FIrpic and Ir-BTPA which are used as emissive layer are shown in Fig. 1. The basic OLED device structure and the energy levels of the materials used in this study are shown in Figs 2(a) and 2(b) respectively. The energy levels of these materials were obtained from the earlier studies\(^{13-16}\).

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the host materials are critical for charge balance because the interfacial energy barrier between the charge transport materials and the host materials determines the hole and electron injection in heterojunction devices. In this device, doping concentration of Ir-BTPA is 0.25 wt%, 0.50 wt% and of FIrPic is 5 wt%. The host CBP exhibits efficient energy transfer capability in triggering the emission of various dopants as shown in energy level diagram (Fig. 2(b)).

Energy transfer in phosphorescent OLEDs from singlet to triplet takes place by two mechanisms. One is Forster and the other is Dexter mechanism. Forster transfer describes the energy transfer of singlet and is dependent on the overlap of the host emission spectrum with the absorption of the dopant. Dexter transfer describes the transfer of triplet from host to guest which requires the phosphorescent emission spectrum of the host to overlap with the singlet triplet absorption spectrum of the guest. For the non phosphorescent host, the host triplet must be higher in energy than the guest triplet and there be a significant overlap between the two states\(^{17}\).

The concentration of FIrPic is chosen to be higher than that of Ir-BTPA since a part of the excitons produced at FIrPic molecule is transferred to the lower energy Ir-BTPA by the efficient Dexter transfer mechanism. Further the lower concentration of Ir-BTPA helps in achieving in complete energy
transfer from FlrPic to Ir-BTPA molecules thereby achieving the required colour balance.

Photoluminescence (PL) spectrum of thin film of CBP, FlrPic, Ir-BTPA and their mixture are shown in Fig. 3. The emission peaks are observed at 380 nm for CBP, 472 nm and 498 nm for FlrPic and 620 nm for Ir-BTPA. All the peaks are also observed in the photoluminescence spectrum of the thin films of CBP, FlrPic and Ir-BTPA mixture.

Fig. 4(a) shows the normalized electro-luminescence (EL) spectra of the devices with doping concentrations of 5 wt% FlrPic in CBP (Device 1), 0.5 wt% Ir-BTPA in CBP (Device 2), 5 wt% FlrPic and 0.5 wt% Ir-BTPA in CBP (Device 3) and 5 wt% FlrPic and 0.25 wt% Ir-BTPA in CBP (Device 4) at 11 volt. The EL spectra of the devices with a double-doped emissive layer show three emission peaks at 469 nm, 500 nm and 611 nm (device 3 and device 4). The emission color of OLED device with Ir-BTPA concentration of 0.25 wt% and FlrPic concentration of 5 wt% in CBP host was found to be bluish white light with its EL as shown in Fig. 4(a) (device 4). On
increasing the Ir-BTPA concentration to 0.50 wt%, the emission colour has turned reddish (Fig. 4a, device 3). This shows that by increasing the concentration of Ir-BTPA, more energy is transferred from CBP to dopant, which results in the decrease in the blue emission and an increase in red emission.

The variation of emission spectrum of device (4) was studied as a function of applied voltages is shown in Fig. 4 (b). As the voltage increases, the emission intensity at 500 nm was found to increase sharply relative to the other peaks effecting in a change in emission colour from yellowish white to bluish white. Table 1 shows the change of CIE chromaticity at different voltages (14V to 18 V) for the devices. The CIE coordinates change from (0.279, 0.304) to (0.273, 0.318) as the voltage change from 14V to 18V, which are similar to the reported value\(^{18,19}\). Although the triplet energy state of the FIrPic is higher than that of the CBP\(^{20}\) but the change in CIE coordinate with the current density is relatively small. Since the light emission occurs in a single emissive layer, the recombination zone does not shift as the applied voltage increases and the colour of the emitted light remain in the white region of the CIE diagram.

The luminance-voltage–current characteristics for the white light emitting device are shown in Fig. 5. The slightly higher turn on voltage (~10V) is due to interface resistance between organic layers. The luminance increases linearly with the increasing voltage. The white OLED at 18V has CIE coordinates \(x = 0.27, y = 0.32\) and reaches a maximum luminance 4450 cd/m\(^2\) and the current efficiency 6.97 cd/A at 100 cd/m\(^2\).

**4 Conclusions**

Electro phosphorescent white organic light-emitting devices with a co-doped emissive layer have been fabricated. FIrPic and Ir-BTPA are co-doped into the CBP host. Variation in dopant concentrations controls the color of the device. The maximum
luminance of the device is $4450 \text{ cd/m}^2$. The CIE coordinates of the device are 0.27 and 0.32 which are well within the white region.

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