# A study of the dynamics of defect generation in Polyfluorenes and its possible use in the production of stable White Polymer Light Emitting Diodes (WPLEDs)

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**Abstract:** *Polyfluorenes are important class of polymer materials widely used in making polymer light emitting diodes and displays (PLEDs). Defects, called fluorenone, are generated in these polyfluorenes in certain environments. Heat, exposure to ultra violet radiation and reaction with certain metals during processing are some of the effects responsible for such behavior. Due to these defects, blue polyfluorenes red shifts and turn to green and even yellow colors. In this work, effects of Cesium (Cs) and Lithium (Li), two most common cathode material along with Calcium (Ca) has been studied in defect generation and consequent shifting of the electro-luminescent peaks in [9,9-di(ethylhexyl)-fluorenyl-2-7-diyl] (PF2/6), a common polyfluorene emitting in blue region of visible spectrum. It is demonstrated that by doping this material, white polymer light emitting diodes (WPLEDs) can be produced.*

**Keywords:** Polymer Light Emitting Diode (PLEDs); Polyfluorenes; White LEDs (WLEDs); Organic Electronic

## Introduction

There is an urgent need to provide efficient and economical lighting sources for various applications. In recent time, organic light emitting diodes have shown great promise in terms of efficiency, lifetime and reliability. Their use in general lighting and back lighting in LCDs is being seriously contemplated. Many companies like Philips, Osram Sylvania and others have started programs of developing organic light emitting diodes meeting the requirements of luminous efficacy and lifetime for general lighting purpose. The luminous efficacy for white OLED elements up to 25 lm/W with appropriate currents has been achieved in comparison to existing 12 lm/W in general bulbs and 20-26 lm/W in halogen lamps. The luminance level of 800 nits and operation lifetime of 3000 hours is targeted [1]. In liquid crystal displays (LCDs) like laptop computers, different lighting sources, like inorganic LEDs and CFLs along with color filters are used for producing different colors of light. Polymer and small molecules LEDs are perceived to be good replacement of these owing to their thin film form factor. WLEDs have been demonstrated using both small molecules and polymer electro-luminescent materials. Various configurations and technologies have been used in the production of white light. There are three most general configurations for producing WLEDs. In first, stacked layers of three colors using thin transparent electrodes in between has been used mostly with small molecule materials [2]. In second, three colors are placed side by side in pixelated format [3]. This can be optimized for giving colors to produce white light. Third method utilizes the doping of the host material with two other complementary colors in right proportions. This method provides an economical and easy one pot solution for producing white light. Small molecules and polymers, both have been utilized in the above methods. In yet another approach, white light has been produced utilizing the fluoroenone defects in polyfluorene [4]. Polyfluorenes are family of efficient electroluminescent polymer materials. It was earlier thought that EL efficient polyfluorenes having emission peaks throughout the visible spectrum were quite stable and provided the ultimate solution for polymer based LEDs and color displays. However, it has been observed that during storage and processing of the devices, additional peaks crop up in the longer wavelength of the visible spectrum. These peaks have been attributed to certain fluorenone defects. It is argued that these fluorenone defects are responsible of producing exciplexes between two near polymers and production of red emission. WPLEDs have been produced without using any dye or red polymer [5]. In this work, the effect of different cathode materials like Ca, Cs and Li on the emergence of different electro-luminescent peaks due to the generation fluorenone defects have been studied. The effect and stability of these defects with different cathode materials is investigated. It is demonstrated that these defects may be utilized in making white light emitting diodes in single pot solution. WPLEDs have been fabricated using polyfluorenes as host and MEH-PPV as a dopant.

## Experiments

To see the effect of different cathode materials and dopants to produce white light, the device of structures ITO/PEDOT/(PF2/6 with and without MEHPPV)/Ca, Cs or Li/Al as shown in Fig. 1 have been fabricated. Thin layers of Calcium (Ca), Cesium (Cs) and Lithium (Li) of thicknesses of 12 nm, 0.2-0.5 nm and 0.5-1 nm respectively covered with a layer of aluminum of 200 nm thicknesses have been used in these experiments. PEDOT-PSS and polymer thickness were same in devices made with different cathode materials. PEDOT/PSS and polymers have been vacuum annealed. Cathode metals were deposited in 1-2 x $10^{-6}$ mbar vacuum at temperature 70-80$^{o}$C. Subsequently, the

devices were sealed using UV cured epoxy. Coating and sealing processes were done in air.

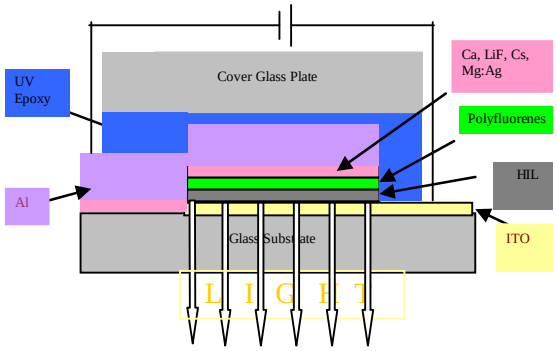
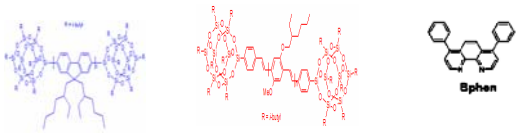



**Figure 1.** Device Structure

The 8 mg/cc solution of PF2/6 end capped with POSS and poly [2- methoxy-5 (2-ethylhexyloxy)-1,4-pheneylene-vinylene] (MEH-PPV) end capped with POSS were prepared in chlorbenzene. An amount of 0.05 ml solution of MEHPPV in 1 ml of PF2/6 solution was used in making WPLEDs.




(a) (b) (c)

**Figure 2.** Structure of (a) PF2/6 (b) MEH-PPV (c) BPhen

In one experiment, a buffer layer of bathophenanthroline (BPhen) was introduced in between the cathode and PF2/6 layer to see the screening the effect of Ca. BPhen is a well known electron transport and hole blocking material used in small molecule OLED devices. The structure of PF2/6 end capped with POSS and MEHPPV end capped with POSS and Bphen are shown in Fig 2 (a), (b) and (c) respectively. The PL has been measured using xenon lamp source with monochromator setup with excitation wavelength of 380 nm. EL spectrum has been measured using Ocean Optics USB 2000 UV/VIS. The luminous intensity ($Cd/m^2$) and (x,y) chromaticity parameters have been measured using Minolta CS-S1w.

### Results & Discussion

The PL spectrum of pure PF2/6 thin film coated on glass substrate and EL spectrum of devices made with Ca/Al as cathode material are shown in Fig.3. The pure PF2/6 gives main peak at 426.79 nm corresponding to band gap of 2.91 eV with a vibronic state at 447.86 nm in blue region of visible spectrum. In devices made of configuration shown in Fig.1, the intensity of main peak 426.79 nm of pure material is almost quenched and an additional broad peak at 519.93nm in the green region of visible spectrum emerges as a dominant peak. It is seems that there is favorable energy transfer from the original material to the material formed due to the reaction of Ca.

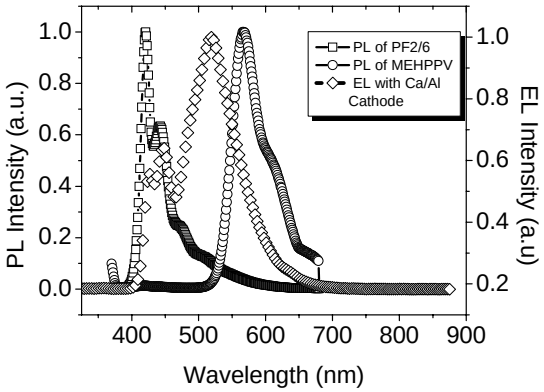



**Figure 3** PL of PF2/6 and MEHPPV and EL of ITO/PEDOT-PSS/(PF2/6)/Ca/Al PLED

It has been shown that this peak is the result of fluorenone defects caused by the catalytic oxidizing behavior of calcium. It has been found through XPS studies [6] that deposited Ca diffuses to the bulk PF2/6 layer and reacts with oxygen present in the environment forming CaO and $CaCO_3$. The (x,y) co-ordinates of this degraded material emerges at x=0.2291 and y=0.3342 in the chromaticity diagram as shown in Fig. 4. The (x, y) co-ordinate of pure white light are desired to be at (0.33, 0.33) in the chromaticity diagram. It is possible to get white light from this material by doping this material appropriately with a polymer or dye to shift the co-ordinates on x axis by introducing red polymer or pigment.

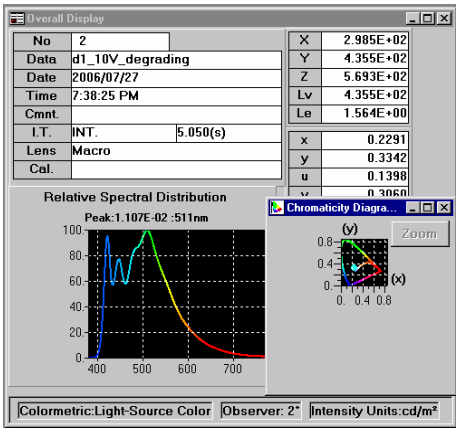



**Figure 4.** EL and Chromaticity diagram of ITO/PEDOT-PSS/(PF2/6)/Ca/Al PLED

Blue Polyfluorenes are important polymer materials for making polymer light emitting diodes and displays. The devices made out of these materials should be stable in

colors. Any reaction and degradation with cathode material is not desirable. Further experiments have been done to see the effect of Li and Cs on the stability of PF2/6 during the fabrication of PLEDs. Cesium and Lithium are important cathode material having low work function with respect of LUMO of polyfluorenes and therefore are favored as cathode metals. The EL spectrum of devices made using different metals along with spectrum of devices with a buffer layer of BPhen of thickness of 12 nm in Ca/Al cathode and PL of pure material are shown in Fig. 5.

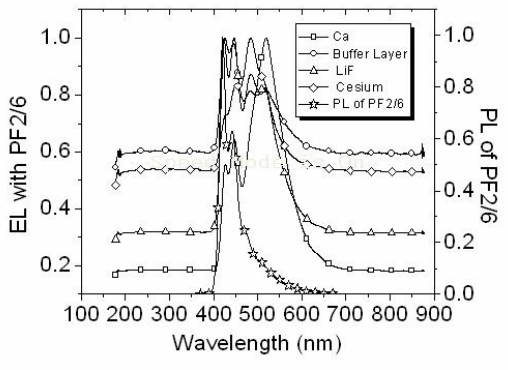



**Figure 5.** EL spectrum of ITO/PEDOT-PSS/(PF2/6) /Ca/ Al PLED with Ca, Buffer layer, LiF, Cs and PL spectrum

In case of devices made of Cs/Al as cathode material, a dominant peak is observed at 483.59nm corresponding to band gap of 2.57 eV. The peak emerged due to the Cs/Al is stronger than that of the peak at 519.93 emerged in devices made with Ca/Al as cathode. In the EL of devices made with Li, two peaks emerge near to 483.59nm and 519.93nm similar to the one seen in the EL spectrum of devices made with Cs and Ca respectively. However, the peaks with Li/Al as cathode material are initially not as strong as seen in EL spectrum of Cs and Ca as cathode materials under the similar processing conditions. These peaks grow in intensity as the bias is applied. It seems that there is an electrically induced effect too causing the defect. These defects give emission peaks around green region of visible spectrum from 483.59nm to 519.93nm and deformed molecules gives bluish green light in place of blue light expected from pure material.

Further experiments were done with doped PF2/6 to produce WPLEDs. The MEH-PPV has been found as favorable dopant polymer. The EL spectrum of devices made with 5 weight percent of MEH-PPV as dopant with different cathode materials are shown in Fig. 6.

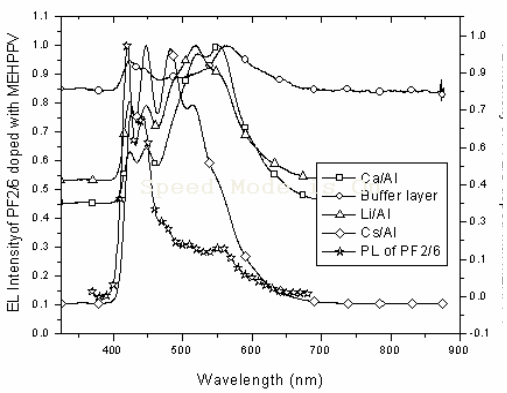



**Figure 6.** EL spectrum of Ca, Buffer layer, LiF, Cs and PL spectrum doped with MEH-PPV

In the PL of PF2/6 doped with 5 weight percent of MEHPPV, a small extra peak at 556nm shows the presence of MEHPPV in the film. The intensity of this peak is quite insignificant in comparison to main peaks due to PF2/6. In the EL of devices made with Ca, Cs and Li, there seems to be favorable energy transfers to peaks generated due to defect formation. Also, the small peak 556nm as seen in the PL of MEHPPV in Fig.6 becomes the EL dominant peak in the presence of Ca. The absorption spectrum of MEHPPV extends from 370nm to 550nm peaking around 480 nm [7] and hence, energy transfer due to host singlet to donor singlet through Dexter process is possible. This is evident as host peak is significantly reduced. The intensification of other peaks due to different metal cathodes is understandable due to the overlap of absorption spectrum of MEHPPV. In the EL spectrum of devices with buffer layer of BPhen no dominant peak other than peaks of PF2/6 and MEHPPV are observed. It seems that buffer layer of BPhen blocks the diffusion of Ca. However, the current and EL intensity is also reduced. The EL and chromaticity diagram of the PLEDs doped with MEHPPV and using Ca/Al as cathode are shown in Fig. 7.

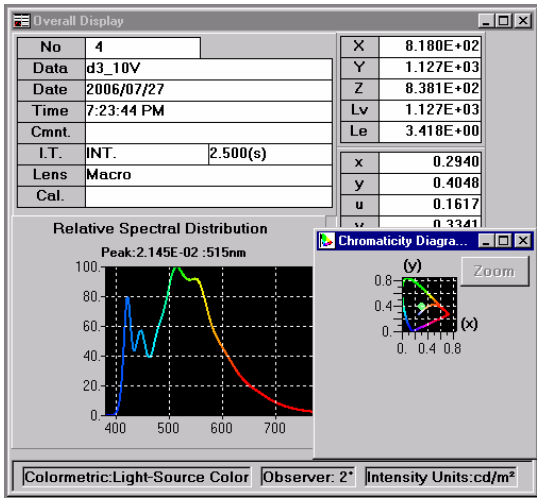
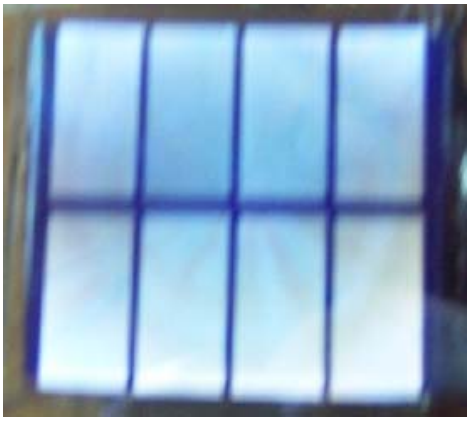



**Figure 7.** EL and Chromaticity diagram of ITO/PEDOT-PSS/(PF2/6) plus 5% MEHPPV/Ca/Al PLED

The (x, y) coordinates have shifted from bluish-white (0.2291, 0.33) in undoped devices to (0.294, 0.404) in MEHPPV doped devices. The co-ordinates are not exactly (0.33, 0.33) as required for pure white light, however, it gives reasonably good bluish tinted white light The definition of 'white light' is rather vague and it can be represented by a sufficiently wide region in the CIE chromaticity diagram covering the coordinate values from 0.28 to 0.48. The white light of a fluorescence tube has x=0.436 and y=0.464 [4]. The electro-luminance of 1127 nits has been obtained in these Whitish LEDs. This figure is close to the required luminance of 800 nits required for general purpose lighting. The devices were found to have the stability problems and degraded in luminance with time. The current was found to decrease. This was expected as all the processing was done in air where oxygen and moisture levels were high.

(a)



(b)

**Figure 8.** (a) Blue light Emitting PLEDs of size 6 x 6 $mm^2$ of structure ITO/PEDOT-PSS/(PF2/6)/Ca/ Al (b) Whitish blue PLEDs of size 20 x 10 $mm^2$ of structure ITO/PEDOT-PSS/(PF2/6 plus 5% MEHPPV)/Ca/ Al

A photograph of blue light BF2/6 polymer LEDs of size 6x6 $mm^2$ and a 2x4 matrix of size 9x20 $mm^2$ of bluish white LEDs made from the doping of MEHPPV in PF2/6 with Ca/Al as cathode are shown in Fig 8 (a) and (b) respectively. There are some patches of non-uniformity in colors seen in Fig 8. These have come mainly due to uneven coating of PEDOT.

## Conclusion

It is shown that not only calcium reacts with PF2/6 and creates fluorenone defects; the presence Cs, Li as cathode materials also cause these defects. The emerged peaks are quite broad and intense in comparison to blue peaks in the pure PF2/6 polymer devices. Further experiments are required to find out the cause of these defects, oxidation or otherwise. One way of avoiding these defects is to introduce buffer layers as to avoid direct contact between polymer and cathode metals. However, as these defects induced peaks emerge near to the same wavelength position characteristics of cathode metals in the green region of visible spectrum, it is possible to make white light emitting diodes by simple one pot solutions.

## Acknowledgement

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