

CIE 1931 colour space movement of organic light emitting diode

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2x2 Transfer Matrix modelling is used in order to study the movement of colour point in CIE 1931 colour space. Simulation indicates that increasing the thickness of light emitting layer shifts the CIE 1931 colour space towards the red in a linear fashion until a critical inflexion point. Beyond that point, the colour point reverses in direction. The colour points trace out small circular track by changing the thickness of indium tin oxide and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate). Higher injection cathode is found to red-shift the colour of the OLED. Increasing the concentration of red-emission shifts the CIE coordinate linearly.

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1. Introduction

Efficiency, brightness and lifetime of organic light emitting diode have improved significantly for the past few years [1-2]. It holds great potential for high efficiency lighting application as a part of global effort on reducing carbon footprint. Intensive research and development on cheap manufacturing techniques are spear-headed by start-ups and multinational co-operations in an effort to reduce cost comparable to fluorescent lamp[3]. Polymeric light emitting diode(P-LED) can be fabricated cheaply by rolling method compared with small molecules where layer by layer of organic molecules have to be deposited very carefully[4]. In order to be use as lighting tiles, the colour must be within the Planckian limit and gives a good colour rendering index [5]. We will examine the former in this paper. Colour outside the Planckian limit cannot be considered as white. The movement of colour of a white OLED in CIE1931 colour space is plotted and studied. This will elucidate device and material parameters that are used to tune to the desired white point.

A model is built using 2x2 Transfer Matrix. Details of equations are not shown here as it can be easily found elsewhere [6-7]. The electromagnetic modal field within the organic layer can be obtained from the 2x2 Transfer Matrix. The electric modal field is an important parameter as the spontaneous emission is coupled to the field [7-9]. Such coupling can result in enhancement or suppression of spontaneous emission and hence modifying the colour. The holes and electrons are injected from the anode and cathode respectively. The mobility of electrons and holes are often dissimilar for a given light emitting polymer. For high efficiency devices, the electrons must move faster than holes [9]. Excitons are formed when holes and electrons are columbic attracted to each other. This formed the zone of recombination. The zone of recombination is coupled with the electric modal field to form emission.

In order to produce white light from a polymer, the polymer usually consists of blue host mixed with red dopant [10]. The emission of blue is partially quenched by Förster transfer of energy from the blue host to the red dopant. For high efficiency application, the dopant is often a red phosphorescent material. The thickness and refractive index contrast of the organic light emitting diode (OLED) layers are expected to change the colour of the devices [11].

2. Theory

The structure of the P-LED is ITO/ Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)/ Interlayer Layer (IL)/Light Emitting Polymer (LEP)/Cathode.

The refractive index of the ITO is given by [12]

$$n_{ITO} = 2.525 - 0.001271\lambda \quad (1)$$

where λ is in nm. PEDOT:PSS was known to be anisotropic using variable angle spectroscopic ellisopmetry [13]. However, in this simulation only light emitting normally to the surface is taken into account. Hence, it is reasonable to consider only refractive index perpendicular to the glass plate, n_{\perp} . n_{\perp} is given by

$$n_{\perp} = 0.682e^{\frac{-10^9 \lambda}{176.82}} + 1.5513 \quad (2)$$

where λ is in nm. In order to increase the luminous and power efficiencies of polymeric white light devices, suitable host for the LEP would preferably emit at 450nm and longer as the eyes are insensitive to light at the deep blue. Hence rather than using polyfluorene as a host, a red-shifted polyfluorene such as fluorene substituted pyrenes[14] or flourene substituted thiophene[15] would

be highly preferred. The host would be a greenish blue rather than blue material. The refractive index of the LEP is assumed to have the average refractive index given by lognormal equation which is

$$n = n_o + \frac{A}{\sqrt{2\pi w\lambda}} \exp\left(-\frac{\ln\left(\frac{\lambda_c}{x_c}\right)^2}{2w^2}\right) \quad (3)$$

where n_o is 1.70, $x_c=225$, $w=0.364$, $A=621$ and λ is in nm.

We assume that the recombination profile of the LEP to be far away from the cathode and situated near the IL. The IL serves as a hole transporting layer from the PEDOT-PSS which help to enhance efficiency of polymeric OLED[16]. The interlayer is often consists of deep blue materials or polyfluorene based material. In this simulation, we assumed the refractive index to be similar to the LEP.

System matrix is written from the glass/ITO interface to the polymer/cathode interface. The transmission and reflection of each layer is found and are used to build the wave equation for the whole multilayer. The electric modal field are normalized with respect to the total electric field energy at that wavelength [7]. Zone of emission, F , can be approximated with

$$F = e^{bx} \quad (4)$$

where b is the constant that depends on the dye. In this simulation, we used b as -0.045 and -0.01 for the host and the red dopant. The emission profile for the blue decays sharply from the interlayer while the red dopant tend to decay significantly slower from the IL throughout the LEP as it involves resonance energy transfer and direct excitation of the dye by the blue light. The spectra without cavity effect is modelled using Gaussian equation which is

$$G = \frac{A}{\sqrt{2\pi w}} \exp\left[-2\left(\frac{\lambda - x_c}{2w^2}\right)^2\right] \quad (4)$$

The blue spectra are the sum of G_1 and G_2 and the red spectra are the sum of G_3 and G_4 given by Table 1

The spectra with the cavity effect is given by

$$cavity = \int_{LEP-IL}^{LEP-Cathode} E_N (S_B * R_B + S_R * R_R) dx \quad (5)$$

where the equation is integrated from LEP_IL interface to LEP-Cathode interface, E_N is the normalized electromagnetic modal field within the cavity structure, S_B and S_R are the blue and red spectra respectively, R_B and R_R are the normalized recombination profile for the blue and red dyes respectively. The cavity spectra are then converted into CIE-co-ordinate.

3. Simulation results

The spectrum of white polymer without the cavity effect as given by Table 1 is shown on Fig. 1.

Table 1. Values used to stimulate the white spectrum.

	G_1	G_2	G_3	G_4
x_c	470	500	630	670
W	20	56	25	110
A	1000	2500	700	3500

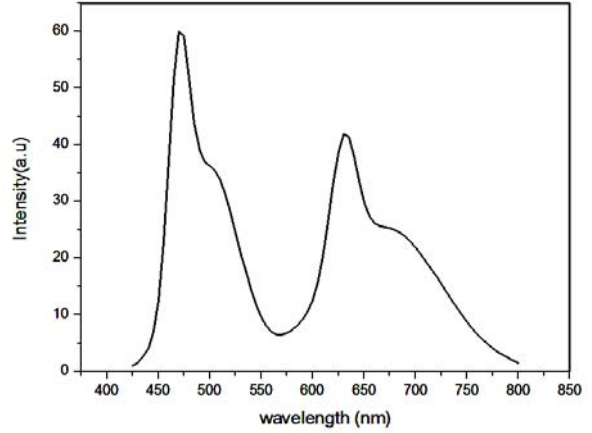


Fig. 1. The spectrum of model polymer without microcavity effect.

For a given white polymer, the thickness of the LEP layer has the most significant impact on colour. The incremental thickness of LEP is 5nm with 50nm as a starting point. The colour becomes redder as the thickness increases moving almost along the Planckian locus as illustrated in Fig. 2.

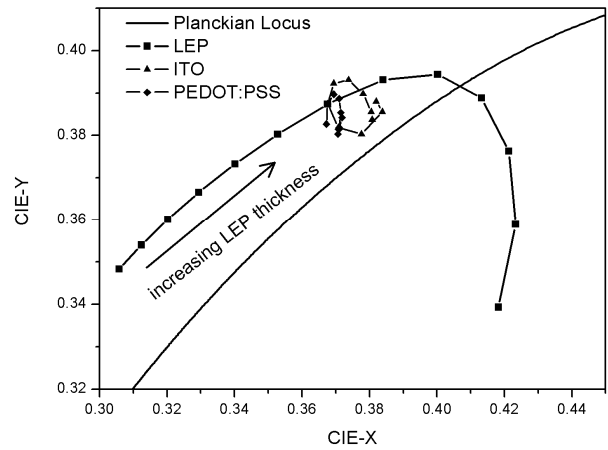


Fig.2. The change of CIE coordinates with respect to Planckian locus when the thickness of LEP, ITO and PEDOT:PSS are changed.

This is the result of coupling of electromagnetic wave at longer wavelength as the emission zone is shifted away from the cathode as the thickness of LEP increases [17]. This is highly advantageous as different colour temperature of white point can be tuned just simply changing the thickness of the light emitting layer. However, at 95nm, there is an inflexion where further increment of LEP thickness resulting in increasingly blue colour. This was not surprising as the length of cavity has increased to the point that it can support second harmonic wave for the blue emission.

In Fig. 2, PEDOT:PSS, and ITO thickness are changed from 40nm and 80nm respectively with 20nm incremental change of thickness. As the refractive index mismatch between glass-ITO and ITO-PEDOT:PSS interfaces are large, the thickness of ITO is expected to influence the colour of the white light devices. However, the change is rather small ~ 0.02 for CIE-x and ~ 0.01 for CIE-y as it moves in a circular motion as shown in Figure 2. Hence, we concluded that ITO thickness can be used to fine-tune the white-light within the Planckian limit. By changing the PEDOT:PSS thickness from 40nm to 200nm, the CIE-y changes ~ 0.01 while CIE-x remains almost constant (~ 0.005) as seen in Fig. 2.

The injection barrier plays a significant role in the location of the zone of recombination. By lowering the cathode injection barrier, the zone of recombination can be shifted away from the cathode. Since the recombination zone is coupled to the electric modal field, this will result in the change of colour. As shown in Fig. 3, the more electrons recombined at near the LEP-IL interface, the redder is the colour where b is defined in equation 4. The low injection barrier can be achieved by using high injection cathode. This would be useful if the LEP layer is very thick. Thinner LEP can be used in junction with higher injection cathode to lower the operating voltage and hence increases power efficiency.

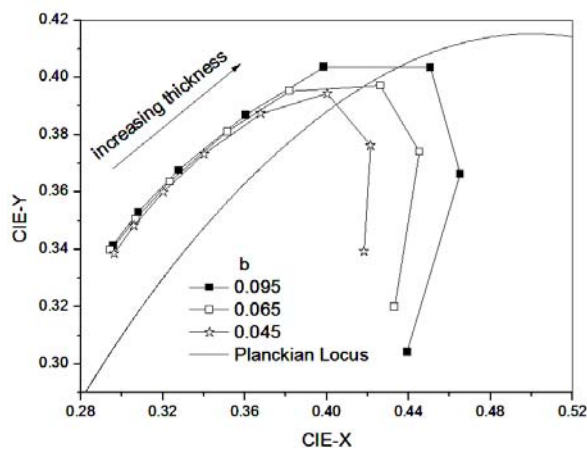


Fig. 3. The change of CIE coordinates with respect to emission profile. Larger b means more confined towards the IL.

From device engineering viewpoint, changing the thickness of LEP and cathode can only result in a large

change of colour. If the colour of the material is far away from the Planckian locus, little can be done to tune the colour to desired Planckian line. One of the strategies to tune the colour into desired white region is by changing the material composites and structures. Here we use a reference P-OLED device structure 120nm ITO/ 60nm PEDOT:PSS/ 20nm IL/ 80nm LEP/cathode to simulate the impact on changing the material composites.

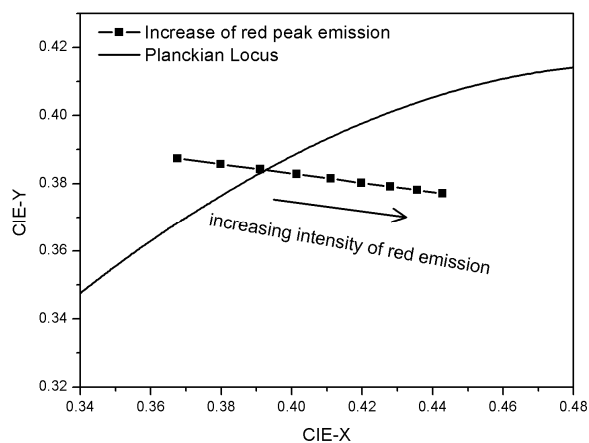


Fig. 4. The movement of colour point when the peak of red emission is incremented by 0.1

One of the strategies to tune the colour is to change the concentration and emission quantum efficiency of the red dopant. By increasing emission from the red spectra for example, the CIE-x would move further into the red as illustrated in Fig. 4. It is highly desirable if warm white is required. In this simulation, the peak of red emission is incremented by 0.1. The next strategy can be done by adding electron withdrawing or donating groups on the materials. The former would result in a blue shifted spectra and the later a red shifted spectra. As shown in Figure 5, the vertical line represents an increment of 5nm shift of blue emission host.

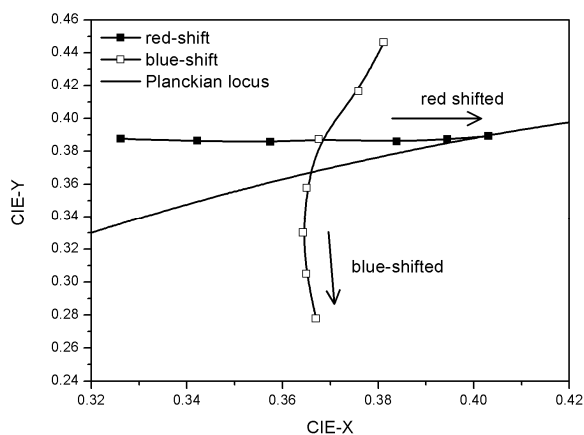


Fig. 5. The movement of white point when the emission is red or blue shifted.

As the host spectra is shifted to bluer region, the CIE-y moves downward with little change of CIE-x. As for the red dopant, an incremental red-shift of 5nm along results in a higher CIE-x. Both lines move almost mutually perpendicular to each other. This strategy provides an excellent way to tune colour [18-19]. However, a larger shift of spectra, lets say more than 10nm might require a complete change of chromophore itself. The peak emission between blue host and red dopant cannot be too near as it would significantly reduce the rate of energy transfer from the host to the red dopant and hence provide further constraint.

4. Conclusions

The colour movement of PLED is studied theoretically with colour movement plotted against CIE co-ordinates. The choice of parameters to tune the colour of white polymer within the stringent limit of Plankian locus is limited for device engineers. Large change of colour can only be achieved by changing the LEP thickness. It is possible to design a material such that different colour temperature of white point can be tuned just simply by changing the thickness of the light emitting layer. Strategies of colour tuning in terms of CIE 1931 are also given.

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