

Elementary approach to calculate quantum efficiency of polymer light emitting diodes

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An elementary approach has been suggested to calculate the external quantum efficiency (*EQE*) of polymer light emitting diodes (PLEDs). This approach requires only the electroluminescence (EL) spectrum and illumination versus current characteristics of the devices to calculate the *EQE*. In these calculations the light emission has been considered to be perfectly diffusive from the emission surface. The efficiencies calculated in this way have been compared with the actual values of the *EQEs* for the different PLED structures available in the literature. The calculated values have shown good agreement with the measured values.

Keywords: PLEDs, Quantum efficiency, Organic semiconductors

1 Introduction

Owing to their potential for thin, flexible, large area and cost effective electronic devices, the conducting polymers have emerged as powerful materials for light emitting diodes (LEDs), solar cells, thin film transistors (TFTs) and lasers¹. Since the early demonstration of electroluminescence in organic materials^{2,3} there has been great progress in these materials and the devices with emission spanning the broad spectrum from visible to near infrared radiation have been fabricated and demonstrated⁴⁻⁷. The polymeric light emitting diodes (PLEDs) will give a strong competition to LEDs based on inorganic semiconductors in future. The recent focus is towards the development of polymer white LEDs, which is now considered to be a strong candidate for general illumination purpose⁸.

Efficiency is a key issue for energy-consumption as well as the lifetime of light emitting devices. The ability to operate at a lower input power, at a given luminance, reduces the joule heating and thereby increases the device lifetime. High efficiency and long lifetime are essentially required for commercialization of PLEDs. In recent years, more efficient PLEDs, with low operating voltage and high *EQE* have been developed⁸⁻¹¹. Quantum efficiency is an important parameter for PLEDs. The quantum efficiency is difficult to measure precisely because

one cannot completely collect and detect all the photons emitted from a given EL device. There are very few methods available to measure exact quantum efficiency and in most of these cases an integrating sphere and a monochromator are necessitated¹²⁻¹⁵. Figure 1 shows one of the experimental setups incorporating the integrating sphere and monochromator for determination of *EQE* of EL devices. Often a correction in the emission spectrum is required to be made, where Lambertian's law is not followed¹⁶. The quantum efficiencies determined by such different assessment techniques cannot be inter compared easily as the sufficient details of the procedures adopted are not easily available. Therefore some better alternate method is required for determination of *EQEs* of such devices. In the present study, a method which is reliable and tends itself to calculate the *EQEs* of PLEDs in a cost effective manner has been developed.

2 Theory

The EL in PLEDs is due to the excitonic emission. The electrons and holes, injected respectively from the cathode and anode (usually Al is cathode and indium tin oxide (ITO) is anode), confine in a small region of organic layers and form excitons⁸. The radiative decay of excitons results into the emission of light. The internal quantum efficiency (*IQE*) of a

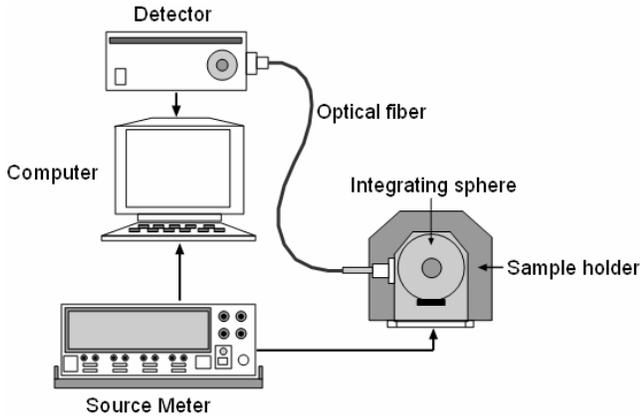


Fig. 1 — Block diagram of experimental set-up possessing integrating sphere for determination of *EQE* of EL devices

PLED is defined as the ratio of the number of photons produced within the device to the number of electrons injected into the device, and is given by:

$$IQE = \gamma \times \eta_s \times \phi_f \quad \dots(1)$$

where γ is a fraction of injected charges that produce excitons and called charge balance factor, η_s is the fraction of singlet excitons called singlet exciton efficiency and ϕ_f is the fraction of energy released from material as light and called quantum efficiency of fluorescence. The *EQE* is related to *IQE* and is given by:

$$EQE = R_e \times IQE \quad \dots(2)$$

where R_e is the extraction or out coupling efficiency representing the number of photons coming out of the device per number of photons generated in the device. In other words the *EQE* is the number of photons emitted externally (P_{ext}) from the device per injected electrons (n_e) and can also be written as:

$$EQE = \frac{P_{ext}}{n_e}, \quad \dots(3)$$

The output optical power (*OP*) (or simply the brightness) of a light source can also be represented in terms of lumens where the corresponding *OP* to 1 lumen is given by:

$$OP(\lambda) = \frac{1}{683 \times K(\lambda)}, \quad \dots(4)$$

where $K(\lambda)$ is the Commission International de l'Eclairage (CIE) standard photopic efficiency

function. Since the energy of a photon is given by $(h \times c)/\lambda$, the number of photons within the 1 lumen of luminous flux will be:

$$P(\lambda) = \frac{\lambda}{683 \times K(\lambda) \times h \times c}, \quad \dots(5)$$

where h is Planck's constant and c is the speed of light. Assuming a perfect diffusive surface for EL emission, the luminous flux $\phi(\lambda)$ of the devices can be written as:

$$\phi(\lambda) = \pi \times L(\lambda). \quad \dots(6)$$

where $L(\lambda)$ is the brightness (luminance) of the device. The number of photons $P_L(\lambda)$ within luminance $L(\lambda)$ can now be given by:

$$P_L(\lambda) = \pi \times \frac{L(\lambda) \times \lambda}{683 \times K(\lambda) \times h \times c}. \quad \dots(7)$$

The total number of photons (P_{total}) emitted in the visible wavelength range, can now be obtained by:

$$P_{total} = \int_{380}^{780} P_L(\lambda) d\lambda \quad \dots(8)$$

or

$$P_{total} = \int_{380}^{780} \frac{\pi \times L(\lambda) \times \lambda}{683 \times K(\lambda) \times h \times c} d\lambda \quad \dots(9)$$

The total luminescence (L_t) of the device can be given by:

$$L_t = \int_{380}^{780} L(\lambda) d\lambda \quad \dots(10)$$

or

$$L_t = \beta \int_{380}^{780} I(\lambda) \times K(\lambda) d\lambda \quad \dots(11)$$

where $I(\lambda)$ is the relative EL intensity and can be obtained from the EL spectrum of the device and β is a constant. Now using Eqs (10) and (11), Eq. (9) can be written as:

$$P_{total} = \pi \times \beta \int_{380}^{780} \frac{I(\lambda) \times \lambda}{683 \times h \times c} d\lambda \quad \dots(12)$$

Experimentally, one can obtain the value of L_t using a luminance meter placed in front of the device, whereas the values of $I(\lambda)$ can be obtained from the EL spectrum. Consequently, P_{total} or P_{ext} can be calculated using Eqs (11) and (12). The number of electrons injected into the device can be obtained by:

$$n_e = \frac{J \times A}{q}, \quad \dots(13)$$

where A is the device area, J is measured current density and q is the charge of an electron. The *EQE* of the devices can now be calculated using Eq. (3). This method enables us to determine the quantum efficiency from the luminance versus current characteristics and the EL spectrum of the devices. A high luminous efficiency can be achieved by increasing and balancing the number of carriers, injected into the emissive layers.

3 Comparison of Theory with Experimental Observations

The external quantum efficiency of a PLED can easily be calculate by recording the EL spectrum and the luminescence versus current characteristics. In order to compare this with already available experimental data¹⁷⁻¹⁹, the EL intensity at different wavelengths from EL spectrum and the luminescence at different current density from the luminescence versus current characteristics of the devices used have been digitized first.

Suzuki *et al.*¹⁷ reported a highly efficient PLED based on the co-polymers consisting of bis(2-phenylpyridine)iridium (acetylacetonate) [Ir(ppy)₂(acac)], *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl) - [1,1'-biphenyl]-4,4'-diamine (TPD) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) as the side groups. The phosphorescent unit was functionalized with a styrene group, and the other units were vinylated by a common acetylation-dehydration procedure. The co-polymers were synthesized with different ratios of Ir(ppy)₂(acac), TPD and PBD units. Figure 2 shows the comparison of *EQE* measured by Suzuki *et al.*¹⁷ for the above mentioned polymer, with the efficiencies calculated by the alternate method given herein. We have used the EL spectrum, current-voltage (*J-V*) and luminescence-voltage (*L-V*) characteristics to calculate the *EQE*. Solid circles correspond to the measured values by Suzuki *et al.* whereas open circles are for the calculated values by new method. A good agreement can clearly be seen between the measured data and the calculated values.

Similarly the comparison of measured data for a PLED based on poly(phenylene-vinylene) (PPV) derivative, reported by Baldo¹⁸ with the calculated values from our procedure is shown in Fig. 3. Solid squares correspond to the values measured by Baldo whereas open squares are for the values calculated by the new method. A good agreement between the calculated values with the measured data can be seen clearly.

Li *et al.*¹⁹ reported efficient and stable green PLED based on a copolymer poly[(9,9-dioctylfluorene)-*co*-(benzodithiazole)] with a cross-linked hole transporting layer of poly[(9,9-dioctylfluorene)-*alt*-(triphenylamine)]. The active layer of green emitting polymer was spin coated on the top of the cross-linked hole transporting layer. The LEDs were

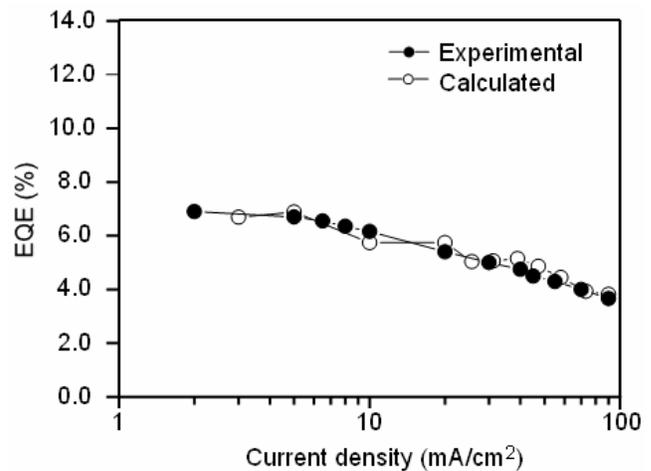


Fig. 2 — Comparison of *EQEs* of a PLED at different current densities measured by Suzuki *et al.*¹⁴ with calculated values

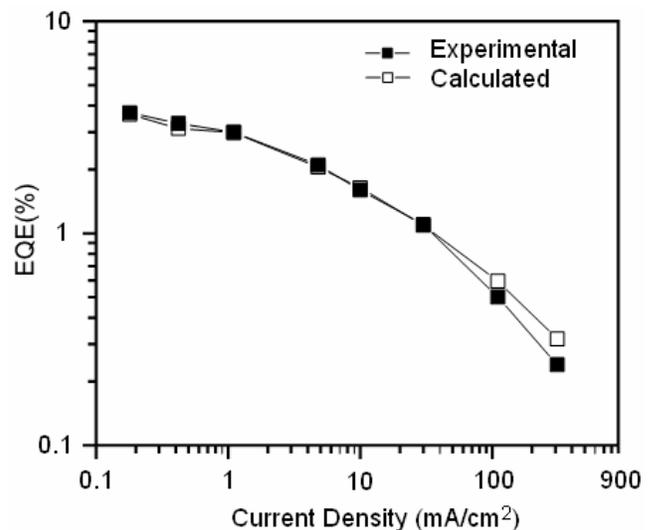


Fig. 3 — Comparison of *EQEs* of a PLED at different current densities measured by Baldo *et al.*¹⁵ with calculated values

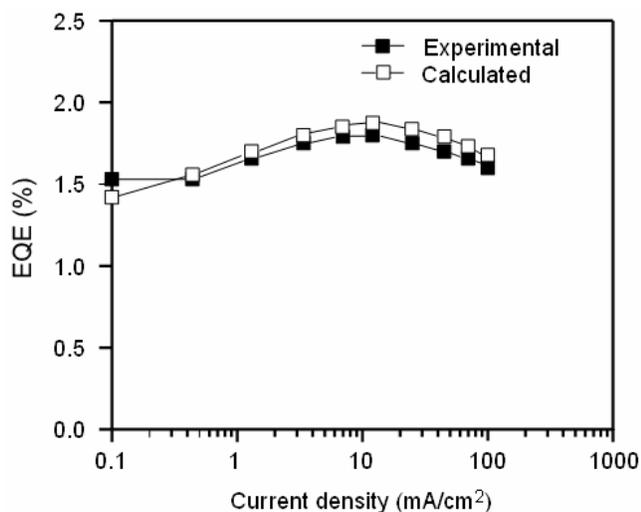


Fig. 4 — Comparison of *EQEs* of a PLED at different current densities measured by Li *et al.*¹⁶ with that of calculated values

prepared in both the single layer and multilayer configurations. The device with cross-linked transport layer exhibited better efficiency compared to that without and was attributed to better carrier injection, reduction in degradation and introduction of impurities in the active layer. We have compared the values calculated by above calculations with the data reported for multilayer LED. We have used the data of EL spectrum, efficiency versus current density characteristics and luminescence versus voltage characteristics to arrive at the *EQE* of the multilayer PLED. Figure 4 compares the analytically calculated values of *EQE* by the new method with the data reported by Li *et al.*¹⁹. It is noted that the calculated values are very near to the experimentally reported values.

The little discrepancy in the earlier reported data and the calculated values by the procedure presented above, can be attributed to the error that occurred during the digitization of the reported data. The alternate method shows a good agreement with the measured values. It is worth mentioning that the proposed method is good enough for calculation of *EQEs* of the small molecular based light emitting diodes as well. As we could not find a report with required detailed characterization of small molecules based LEDs the comparison with our theory could not be presented here.

4 Conclusions

An alternate method to estimate the *EQE* of PLEDs has been presented and the method has been further verified in the light of earlier published data. It is

found that the calculated values are in accord with the reported measurements. During measurement of the luminescence, only the photons emitted from the front side of the devices are detected whereas those emitted from back (if any) and the sides are lost. Therefore this method introduces an error and gives approximate value instead of the actual value of *EQE*. Also if the emission pattern of the PLED does not follow the Lambertian's law, Eq. (6) yields an error. The uncertainty in measurements of the luminescence meter may also introduce an error. However this method is very simple and does not require expensive equipments. It can give an approximate value of efficiency and is useful to calculate efficiencies of devices used for display applications.

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References

- Jain S C, Willander M & Kumar V, *Conducting Organic Materials and Devices* (Academic, San Diego), 2007, p 1.
- Tang C W & Van-Slyke S, *Appl Phys Lett*, 51 (1987) 913.
- Burrouges H, Bardley J, Brown A, *et al.*, *Nature*, 347 (1990) 539.
- Gymer R, *Endevor*, 20 (1996) 115.
- Pei Q, Yu G, Zhang C, Yang Y & Heeger A, *Science*, 269 (1995) 1086.
- Wang E, Li C, Zhuang W, Peng J & Cao Y, *J Mater Chem*, 18 (2008) 797.
- Braun D, Brown A, Slaring E & Meijer E, *Synth Met*, 65 (1994) 85.
- Misra A, Kumar P, Kamalasanan M N & Chandra S, *Semicond Sci Technol*, 21 (2006) R35.
- Mitsui A & Masumo K, *Thin Solid Films*, 442 (2003) 140.
- Chan I M & Hong F C N, *Thin Solid Films*, 444 (2003) 254.
- Kim H, Pique A, Horwitz J S, *et al.*, *Thin Solid Films*, 377-378 (2000) 798.
- Johnson A R, Lee S J, Klein J & Kanicki J, *Rev Sci Instrum*, 78 (2007) 096101.
- http://sales.hamamatsu.com/assets/pdf/catsandguides/e_c992_012.pdf.
- Forrest S R, Bradley D D C & Thompson M E, *Adv Mater*, 15 (2003) 1043.
- Krummacher B C, Nowy S, Frischeisen J, Klein M & Brütting W, *Org Electron*, 10 (2009) 478.
- Buck A, Zeil K, Popp A, *et al.*, *Rev Sci Instrum*, 81 (2010) 033301.
- Suzuki M, Tokito S, Sato F, *et al.*, *Appl Phys Lett*, 86 (2005) 103507.
- Baldo M, *The Electronic and Optical Properties of Amorphous Organic Semiconductors*, Dissertation in Princeton University, 2001, p 70.
- Li J, Sano T, Hirayama Y, Tomita T, Fujii H & Wakisaka K, *J Appl Phys*, 100 (2006). 34506.