Optical characterization of MEH–PPV/Alq$_3$ composite films

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Conjugated polymers are best-suited materials for opto-electronic applications because unlike inorganic semiconductors they can be processed from environment friendly non-toxic techniques at low cost. Devices made from these materials are flexible and mechanically strong. Their band gap can be easily tuned by changing the molecular structure such as chain functionalization, doping and effective π-conjugation length. Recently high purity polymers have become available at reasonable cost. This has provided impetus to the application of these materials to many electronic devices such as transistors [1–2], photodiodes [3–4], solar cells [5–6], light emitting diodes (LEDs) [7–8]. The discovery of efficient electroluminescence in PPV by Burroughes *et al.* [7] has triggered a lot of interest in this material and its derivatives. However many aspects of optical and electrical properties of this compound are still under investigation. For further improvements of these devices, there are few problems, which have to be taken care of.

Polymer LED operates by the injection of holes from positive electrode (e.g. ITO for MEH–PPV) and electrons from the negative electrode (e.g. Ca for MEH–PPV). The injected electrons and holes are trapped in the polymer chains and form positive and negative polarons. These polarons capture one another within the polymer chain and form a neutral exciton either a singlet (total spin quantum number $s = 0$) or a triplet ($s = 1$), which are strongly localized due to their confinement in polymer chains. The exchange energy between the singlet and triplet exciton is quite large ($\sim$1 eV) due to their confinement [9], therefore the crossover of triplets to singlets is very unlikely. The radiative emission (EL) is only due to the decay of a singlet from excited state to ground and triplet excitons do not play any role in EL [9]. Using measurements of EL detected electron spin resonance, it has been shown by Swanson *et al.* [10] that typically the ratio of singlet to triplet exciton is 1:3. It is therefore essential that all polarons must be captured within the thickness of the polymer material to form excitons. For this to happen the thickness of films must be large as compared to the collision capture radius of charged polarons. This has made necessary to use a hetrostructure composite of two different layers, one having a higher mobility for holes (e.g. MEH–PPV) and the other having higher mobility for electrons (e.g. CN–PPV and Alq$_3$). This structure will not only allow a proper balance between the concentration of electrons and holes at the interface but will also slow down the polarons at the interface due to the potential barrier experienced by injected electrons to arrive at LUMO of MEH–PPV and injected holes to arrive at HOMO of Alq$_3$. As a result of this the capture cross-section for positive and negative polarons will increase near the interface.

In the present work optical characterization of MEH–PPV/Alq$_3$ composite has been made by studying its absorption and photoluminescence spectra. The MEH–PPV films were grown over glass substrate using spin cast technique. MEH–PPV powder, obtained from Aldrich Sigma (Japan), was dissolved in p-xylene at a concentration 10 mg/ml to obtain thicker films of thickness $\sim$400 nm. The solution was repeatedly filtered to obtain a homogeneous solution. The speed of the spinner was kept at 2000 rpm. Since MEH–PPV is a poor electron transporting material, Alq$_3$, which is

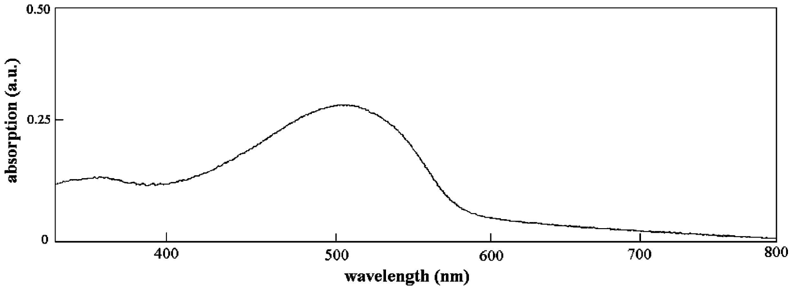

Figure 1 UV/visible absorption spectrum of spin coated MEH–PPV film on glass substrate.

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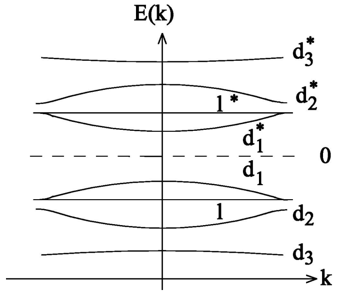

Figure 2 Band structure of PPV.

good electron transporting material, was deposited using vacuum evaporation technique on MEH–PPV films. The thickness of Alq$_3$ layer was kept ∼1000 Å.

The absorption spectrum of a typical MEH–PPV film, obtained using Hitachi model 3410, is shown in Fig. 1. It is observed that there is a broad absorption peak at 500 nm and a narrow low intensity peak at 334 nm. The band structure of PPV as proposed by Chandross *et al.* [11] is shown in Fig. 2. The first peak is due to $d_1 \rightarrow d_1^*$ transition, while second peak is due to next higher transition *i.e.* degenerate $d_1 \rightarrow 1^*$. We have not been able to observe the higher order transitions $l_1 \rightarrow d_1^*$ and $l \rightarrow 1^*$ due to the fact that these transitions overlap with glass absorption spectra. The observed spectrum is rather broad because the chain length of MEH–PPV is distributed over a wide range. The absorption edge is found to be at 2.1 eV.

The absorption spectrum for a typical MEH–PPV/Alq$_3$ composite film is shown in Fig. 3. It is found that absorption peak in MEH–PPV has shifted from 500 nm wavelength to 400 nm in the composite. The absorption peak in the composite is much stronger as compared to that of MEH–PPV film. This is due to the fact that the Alq$_3$ film also contributes to the absorption. The peak in composite films is at a lower wavelength, which is due to higher HOMO–LUMO gap of Alq$_3$ (2.8 eV) as compared to that for MEH-PPV (2.4 eV). The PL spectrum for composite film is shown in Fig. 4 along with the PL spectrum for the MEH–PPV film. This PL spectrum is obtained in wavelength range 400–700 nm using a Hitachi F-2500 Fluorescence spectrophotometer. The excitation wavelength was 450 nm, which is obtained from Ar$^+$-laser. It is found that PL intensity of MEH–PPV/Alq$_3$ composite films is higher by a factor of ∼3 as compared to MEH–PPV film. This shows that the recombination of photogenerated electrons and holes in the composite films is more efficient. This is due to high mobility of electrons in Alq$_3$ as compared to that in MEH–PPV. A proper balance between electron and hole concentration is thus maintained in composite films, which does not exist, in single MEH–PPV film. Further, there is a shift of PL peak towards smaller wavelength side (from 590 nm in MEH–PPV to 500 nm in the composite structure). This is due to the higher band gap of Alq$_3$ as compared to that of MEH–PPV. The PL spectrum is narrower as compared to absorption spectra in both the cases and the PL spectra are red shifted with respect to absorption spectra. The absorption spectrum is broad because they examine all the polymer chains. For PL emission spectrum, the photogenerated charge carriers give their excess energy to the lattice and relax to the ground state, emitting a PL.

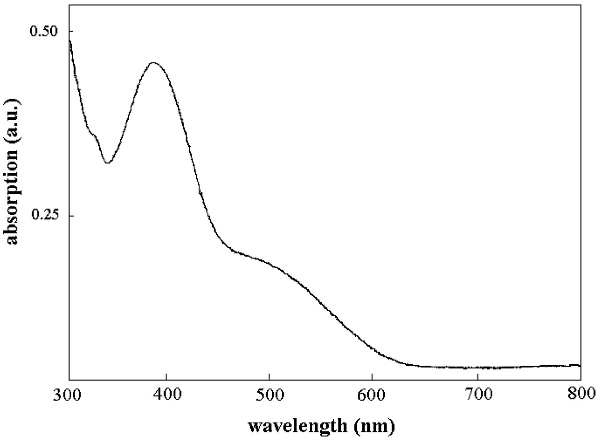

Figure 3 UV/visible absorption spectrum of MEH–PPV/Alq$_3$ composite film on glass substrate.

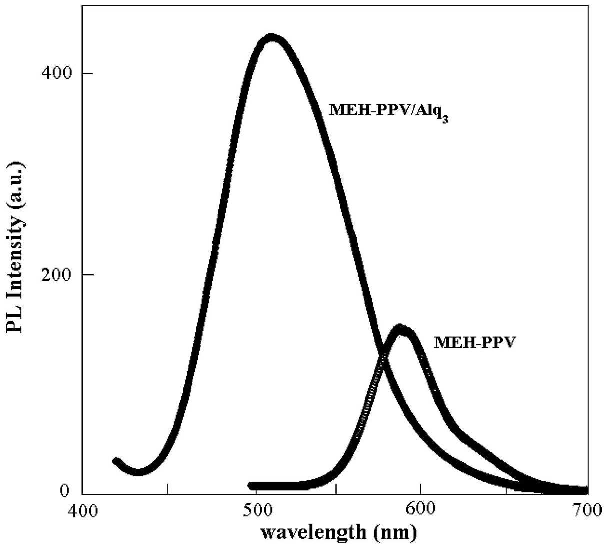

Figure 4 Photoluminescence spectra of MEH–PPV and MEH–PPV/Alq$_3$ composite films on glass substrates ($\lambda_{ex} = 450$ nm).

It is therefore concluded that optical properties of MEH–PPV films is greatly improved by using a bilayer hetrostructure with Alq$_3$.

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