CHAPTER – 4
DISCUSSION OF RESULT

Generally conjugated materials exhibit intense and broad absorption, but since the thickness of organic semiconductors has to be tiny, because of short exciton diffusion lengths, the incident light is not captured efficiently. In addition organic semiconductors have well-defined electronic transitions that are typically quite narrow and have a propensity to be very susceptible to the background. Hence the molecular structures and the eventual propensity to aggregate have a considerable influence on the absorption spectrum. We have already mentioned that the low charge mobility\textsuperscript{[1]} (high resistance) of organic semiconductors obliges the device thickness to stay thin. Hence the wavelength of the incident light is longer than film thickness causing optical interference. A standing wave occurs at each interface within the device and the complex refractive indices and the thickness of the different layers govern this wave pattern. The latter interference pattern can be precisely calculated and it corresponds to the exciton generation rate within the whole structure. In MEH-PPV the optical absorption peak is at 2.5 eV. The absorption peak shifts towards lower wavelength region with increasing spin speed\textsuperscript{[2]}. This can be observed from Figures 3.3 to 3.14. The blue shift of the absorption spectra indicates that the conjugation length of MEH PPV was reduced with lesser thickness. It can also be seen from the figures that for a particular species the absorption peaks are blue shifted with respect to thinness, that is thinner the sample lesser the conjugation length of the particular PPV.
Observing the Steady state Photoluminescent (PL) spectra of MEH-PPV, M3EH-PPV and MEH-DOO-PPV from the figures 3.15 to 3.26 we can see that with spin speed (better thinness) the spectra is blue shifted. This phenomena is repeated for all the species of the PPVs. One important phenomena to be noted here is that the energy difference between the absorption peak and the PL peak (also known as Stokes shift) gradually decreases within a species with thinness (spin speed) and again with species$^3$, that is the stoke shift for MEH-PPV(1) is 0.43eV while for MEH-PPV(3) it is 0.41eV similarly for MEH-DOO-PPV(1) it is 0.38eV. This decrease in stokes shift indicates that luminous efficiency of the film increases with increasing spin speed$^4$. The PL spectra of all the species are quite high and it indicates small interchain distances between molecules.

Figures3.27 to 3.36 shows the steady state electroluminescent (EL)$^{5,6}$ spectra of all the polymers under investigation from MEH-PPV(1) to MEH-DOO-PPV(3). It can be observed that EL$^7$ and PL spectra in thin films are very similar, which suggests that the emissions originate from same excited energy levels. Also from the red colored light given out by all the polymers it is difficult to make out by the naked eye to differentiate between the polymers from which the light emanates. Since the spectrograph has a wide range (uv-visible) it is possible from the spectrogram to distinguish the various polymers. MEH-DOO-PPV has the widest spectra of all. The bias voltage for all the single layered device was 6 volts. The device operation of a single layered PLED is determined by three processes, charge injection, charge transport, and recombination. Under forward bias electrons and holes are injected from the cathode and the anode, respectively, into the polymer. Driven by the applied electric field, the charge carriers move through the polymer over a certain distance until recombination takes place. With higher thickness, a higher voltage is needed to operate the diode, but throughout
the study 6V was maintained. In other words, thicker emission layer would consume more energy but the luminance\textsuperscript{[8,9]} did not get higher for a constant applied bias. Consequently, low brightness and current efficiency are obtained for the PLED with a thick light emitting layer thickness. Hence one can observe a slightly better intensities in the thinner layer (higher spin speed) LEDs.

Figures 3.37 to 3.42 are the data recorded for the refractive indices of the polymers. The real parts of the refractive indices were studied for all polymers. In the figure 3.40 they are plotted alongside one another so that one can easily compare the figures. Figures 3.41 and 3.42 are real and imaginary parts of the refractive indices of MEH-PPV. It can be seen that the peak of the real index is not the same as the imaginary refractive index\textsuperscript{[10]} of MEH-PPV. This indicates an amount of optical non linearity in the material; hence one can expect second or third harmonic generation in bulk MEH-PPV. Optical non linearities also support soliton solutions within the material, but since the imaginary refractive index, which is also a measure of loss in the material, is beyond reported values mentioned in other reports. One may also see that as an effect of optical scattering due to some processing problems. Although we had tried to work in the cleanest environment, some amount of moisture might have crept in, which can deteriorate the MEH-PPV layer which is highly sensitive.

Figures 3.43 to 3.45 gives the IV Characteristics of the single layer devices with different PPVs and different thickness\textsuperscript{[11]}. All polymers exhibit almost identical I-V characteristics\textsuperscript{[12]}, yet in the case of MEH-PPVs one can observe that the knee voltage is between 12 and 14 volts, while for M3EH-PPVs this is between 11 and 13 Volts. For MEH-DOO-PPVs it is between 11 and 12 Volts. The knee voltages implies saturation fields or Schottky
barrier\textsuperscript{[13]} fields. For thinner samples the applied voltages are lesser because saturation fields are attained at lower applied voltages. It is also worth noting that the range of saturation voltages are lesser for MEH-DOO-PPVs as compared to MEH-PPVs. The MEH-PPVs also shows higher conductivities after saturation as can be seen from the slope of the IV curve after the saturation point. M3EH-PPVs shows the least conductivity\textsuperscript{[14]}. It implies that heavier the side chain substitution lesser the conductivity, one may also see that in the light of conjugation length of the polymer backbone.

Figure 3.46 to 3.48 indicates the current density vs applied voltage relation (j-V characteristics) under standard illumination 100 mW/cm\(^2\) (AM 1.5 equivalent illumination). The fill factor was calculated for each jV curves and the efficiencies calculated. It was found that M3EH-PPVs gave the maximum efficiency of 0.34\%. This efficiency anyway does not effect the performance of the active layer when used as emissive device, but in photovoltaics this efficiency is of utmost importance.

Figure 3.49 compares the hole mobilities of all the polymer species as a function of electric field\textsuperscript{[15]}. When trying to relate the mobility of carriers to the photovoltaic performance, it is very important to know the slower charge carrier mobility which dominates the total transport in the device. The carrier mobility is strongly dependent on the morphology\textsuperscript{[16]} of the film, therefore it is very essential to know the mobility when the active layer is spin coated. A drop casted film gives lesser mobilities compared to spin coated layer. Lower mobilities may be preferred for very thin polymer LEDs, while in photovoltaics a higher mobility is favoured.
Figure 3.50 to 3.52 reveals Differential Scanning Calorimetry scans of MEH-PPV, M3EH-PPV and MEH-DOO-PPV respectively in Nitrogen atmosphere. It can be observed from the scans that all the three polymers start to soften at around 50°C. The glass transition temperatures range from 50 to 70°C in our case, although there are reports of MEH-PPVs with glass transitions as high as 230°C. This implies the working range of the device prepared cannot exceed certain temperature limits\cite{17} and in extreme conditions the device may start to deteriorate. The thermal stability of the device is therefore measured and recorded. The reason for this low glass transition in the studied polymers may be due to some infiltration of moisture during the sample preparation stage.

The figures 3.53 to 3.55 indicate Dielectric permittivity, since the normalized capacitance was plotted as a function of bias voltage for MEH-PPV, M3EH-PPV and MEH-DOO-PPV respectively. The curves look almost identical with a peak between 2 and 2.5 bias voltage\cite{18}. A drastic fall in normalized capacitance after the peak indicates the onset of carrier injection into the bulk of the material. In the figures 3.56 to 3.59 capacitance is plotted as a function of frequency under constant peak voltage. Since capacitances are circuit elements, one can get an idea of the amount of capacitance that gets to added to that circuit, whose part the device plays a role.

Figures 3.60 to 3.62 is the transient Electroluminescent\cite{19} study to uncover deep levels and traps within the HOMO and LUMO levels of the material. A voltage pulse of 9.5V and 0.4 ms were used for this purpose. The inverse of the relaxation time $\tau$ (the exponential decay\cite{20} that follows the switching off of the pulse) is a measure of trap energies. For MEH-PPV the trap
energies were about 2.6eV while it decreased with M3EH-PPV (2.1 eV) and MEH-DOO-PPV (1.3 eV).

MEH-PPV undergoes a reversible, continuous color change from red to yellow in the practically relevant temperature range of 25 °C - 100 °C. Figures 3.63 to 3.65 show that the absorption of MEH-PPV continuously decreases and blue-shifts as the temperature is increased. This indicates shift in HOMO/LUMO levels responsible for the widening of the bandgap. We find that both the HOMO and LUMO levels increase with heating. Understanding the changes in the energetic structure of this widely used, versatile material at elevated temperatures is important in controlling the operation of such devices as polymer photovoltaics. M3EH-PPV and MEH-DOO-PPV also follows suit with MEH-PPV.

To add a completeness to the study the X-ray diffractogram of the MEH-PPV, M3EH-PPV and MEH-DOO-PPV were also recorded viz. Figures 3.66 to 3.68 along with the Scanning electron micrograph of the samples, figures 3.69 to 3.71. Since the polymers MEH-PPV, M3EH-PPV and MEH-DOO-PPV do not show any crystallinity not much could be concluded from X-ray diffractograms, but the SEM micrographs reveal a smooth morphology, implying good reflectivity. Since good surface finish is the consequence of uniformity and order in the bulk, one can envisage some kind of molecular ordering within the studied material, or in other words the investigated polymers are devoid of any agglomerates and aggregates.
REFERENCES:


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