Effect of Alkyl Substitution to the Active Layer Material for Improved Efficiency in Bilayer Organic Solar Cell

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Abstract. Organic based thin film solar cells have achieved considerable power conversion efficiency (PCE). As there is a desire to the benefits of on-demand energy production, future world energy consumption will continue to rise. Bilayer organic solar cell has two active layers in between conductive electrodes. Present report, is a simulation study to compare the PCE of bilayer organic solar cells by varying one of its active layer material using General-Purpose Photovoltaic Device Model or GPVDM software. The materials used for active layer are MEH-M3EH-PPV, MEH-DOO-PPV, MEH-PPV and M3EH-PPV based on the degree of alkyl substitutions. Data of absorption spectrum, refractive index spectrum and photoluminescence spectrum are added as input and obtained the simulation results. Values of power conversion efficiencies, fill factor and other photovoltaic parameter values for each bilayer organic solar cell is obtained. Transmittance spectrum, reflectance spectrum, Current density- Voltage plot, variation of charge density and total charge density with applied voltage are attained from the simulation and compared. The results give out effect of side chain alkyl substitution on efficiency of bilayer organic solar cell. MEH-DOO-PPV with longest alkyl side chain substitution has maximum power conversion efficiency. This intuition helps to design suitable bilayer organic solar cell, which has got its relevant applications in the optoelectronics.

1. Introduction
One of the severe issues with the current world is the increase in energy consumption. So, it’s very important to find new ways to generate energy in which the use of renewable energy generated by solar cell seems to be a solution. But the currentformed by silicon solar cell is at high price. Organic solar cells have gained the interest as they are low cost solar cells and provide the generation of inexpensive renewable energy [1, 2]. The light absorbing layer of organic cells are organic polymer material. In 1995, bulk polymer heterojunction was reported. After 2000, there was a rapid increase in efficiency from 1% to 12%(2013).So the density of photocurrent production by organic solar cell is good enough to be compared with that produced by inorganic solar cell [3]. For Bilayer cells, it has two layers in between the conductive electrodes [4]. The difference between ionization energies and electron affinity generates the electrostatic forces between the interfacesof the two layers. There is a need of exciton production by light in this charged region for efficient collection and charge separation [5]. In comparison with single layer photovoltaic cells, bilayer splits excitons much more efficiently because of the peculiarity of the materials chosen allowing the local electric fields to be strong [6]. The electron accepter layer has a higher ionization potential and electron affinity making the other layer the electron donor [7]. Recently, trial to setup bilayer solar cell is found in different devices but these cannot be compared with the bulk heterojunction equivalents [8]. Bilayer
solar cell have lower heterojunction interfacial area available. In order to overcome this issue, a modulation in the morphology of active layers is required. [9]

Organic Solar Cell consists of two electrodes with a photoactive layer in between. One of the electrodes is transparent and sputtered on a transparent substrate. The other one electrode improves the charge separation and transport in the range of the diffusion length of the excitons [11]. There is a buffer layer between active layer and the electrodes which acts like charge selective conductor by conducting holes and blocking electrons and vice versa. It is in the active layer, where light absorption and charge carrier generation happens. This metallic back electrode either acts as anode or cathode [12, 13]. In this simulation, side chain alkyl substitution effect is studied. This will help the experimental scientists to develop efficient solar cell device thereby saving the time, energy and materials.

2. GPVDM Software

General-Purpose Photovoltaic Device Model (GPVDM) refers to a tool, which is used for the simulation of photovoltaic devices and optoelectronics. The software is also used for the device stability and the clarification of power conversion efficiency (PCE). The software contains an electrical solver, an optical solver, and an easy-to-use graphical interface. The simulation of organic solar cells (OSCs) can be done including transfer matrix models and drift diffusion. The use of our own choice of material and laser spectra allowed both the stimulation and experiment to match [14]

GPVDM simulation software solve: Poisson equation (Equation 1), Bipolar drift–diffusion equations (Equations 2 and 3), Carrier continuity equations (Equations 4 and 5).

\[
\frac{dv}{dx} + \frac{v}{R} = q(n - p) \quad (1)
\]

\[
J_n = q\mu_n \frac{\partial v}{\partial x} + qD_n \frac{\partial n}{\partial x} \quad (2)
\]

\[
J_p = q\mu_p \frac{\partial v}{\partial x} - qD_p \frac{\partial p}{\partial x} \quad (3)
\]

\[
\frac{\partial n}{\partial x} = q(R_n - G + \frac{\partial n}{\partial x}) \quad (4)
\]

\[
\frac{\partial p}{\partial x} = -q(R_p - G + \frac{\partial p}{\partial x}) \quad (5)
\]

3. Materials and Methodology

The device structures used are ITO/PEDOT:PSS/M3EH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-DOO-PPV/PCBM/Al and ITO/PEDOT:PSS/MEH-M3EH-PPV/PCBM/Al, where ITO is the front electrode, Al is used as back electrode, PEDOT:PSS as intermediate layer and M3EH-PPV, PCBM, MEH-PPV, MEH-DOO-PPV, MEH-M3EH-PPV are active layers. Figure 1 depicts the structure of the active layer materials.

![Figure 1. The molecular structure of the active layer material used in this report [15]](image-url)
3.1. Simulation of Bilayer Organic Solar Cell
Aim of this series of work is to understand the PCE of organic bilayer solar cell on varying active layer material. For that the Organic Bilayer Solar cell with two contact electrodes, ITO and Al, the extinction coefficient $k$ values and the refractive index $n$ values are taken from the reported work [16]. There is an intermediate layer of material PEDOT: PSS and the $n$-$k$ values are taken from the doctoral dissertation of Mengfang Li [17]. The simulated devices are having two active layers, one of which is made by the material PCBM, which is fixed in all the simulated devices and the $n$-$k$ values are exported from the reported work [18]. The other active layer is varied and the materials are M3EH-PPV, MEH-PPV, MEH-DOO-PPV and MEH-M3EH-PPV whose molecular structures are shown in figure 1 and the $n$-$k$ values are imported to the simulator from the reported work [15]. Using these data, organic bilayer solar cells with device structure ITO/PEDOT:PSS/M3EH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-PPV/PCBM/Al and ITO/PEDOT:PSS/MEH-DOO-PPV/PCBM/Al, are simulated in GPVDM software. The simulated device structure is shown in figure 2. Absorbance spectrum and refractive index - wavelength plot of ITO, PCBM, PEDOT:PSS, M3EH-PPV, MEH-PPV, MEH-DOO-PPV, MEH-M3EH-PPV and Al is obtained.

![Figure 2. The device structure of simulated bilayer solar cell with active layer MEH-PPV/PCBM](image)

The photoluminescence spectrum of active layer material, PCBM,M3EH-PPV,MEH-PPV, MEH-DOO-PPV and MEH-M3EH-PPV is also obtained. The refractive index spectrum and absorption spectrum of all materials are uploaded in the GPVDM software. Photoluminescence spectra of the active layers are also uploaded. Then the program is allowed to run. Efficiency values for each material, charge density plot, current density plot, photon density, generation rate are obtained as simulation result and it is compared.

4. Results and Discussion

4.1. Power conversion efficiency and electrical parameters of simulated bilayer solar cells
Efficiency of four different bilayer organic solar cells with device structure ITO/PEDOT:PSS/M3EH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-DOO-PPV/PCBM/Al and ITO/PEDOT:PSS/MEH-M3EH-PPV/PCBM/Al are examined using GPVDM software. In case of the materials, the degree of alkyl substitution increases respectively, M3EH-PPV, MEH-M3EH-PPV, MEH-PPV, and MEH-DOO-PPV. From GPVDM simulation results, the
efficiencies of these four bilayer organic solar cells are compared. The photovoltaic parameters of the devices made from M3EH-PPV, MEH-PPV, MEH-M3EH-PPV and MEH-DOO-PPV as active layers are obtained from the simulation. The obtained results are given in Table 1.

| Active layer          | V_{oc} (V) | J_{sc} (mA cm^{-2}) | FF  | V_{max} (V) | J_{max} (mA cm^{-2}) | Max power (Watt m^{-2}) | Efficiency (%) |
|-----------------------|------------|---------------------|-----|-------------|-----------------------|-------------------------|----------------|
| M3EH-PPV              | 0.52       | 4.80                | 0.64| 0.369       | 4.32                  | 15.98                   | 1.59           |
| MEH-M3EH-PPV          | 0.52       | 5.38                | 0.63| 0.368       | 4.78                  | 17.65                   | 1.76           |
| MEH-PPV               | 0.52       | 5.39                | 0.63| 0.368       | 4.82                  | 17.77                   | 1.77           |
| MEH-DOO-PPV           | 0.52       | 5.65                | 0.62| 0.368       | 5.03                  | 18.55                   | 1.85           |

4.2. Variation of Transmitted Light with Wavelength

The absorption and refractive index spectrum of active layer materials is related to its transmittance. Figure 3 shows transmittance versus wavelength for the materials M3EH-PPV, MEH-M3EH-PPV, MEH-PPV and MEH-DOO-PPV. The simulation is carried out for the optical wavelength ranging from 350nm to 625nm and transmittance ranges from 0.0005 a.u to 0.0035 a.u. Initially transmittance of the films are very less, after 500 nm, transmittance is very high which is very useful for a solar cell device.

![Transmittance spectrum of the active layers](image)

It is observed that the first transmission peak is located between 350nm and 450nm. In this range, the highest peak is for MEH-DOO-PPV with transmission of $1.79 \times 10^{-3}$ a.u at 391nm. The transmission is lowest for M3EH-PPV with a peak value of $1.51 \times 10^{-3}$ a.u at 391nm. This finding is in accordance with the efficiency of the used material. That is, the value for transmittance is in the increasing order with increase in efficiency.
4.3. Variation of Reflectance light with Wavelength

The figure 4 shows the reflectance spectrum of MEH-DOO-PPV, MEH-M3EH-PPV, MEH-PPV and M3EH-PPV. There are three peaks, in the region of wavelength range from 350nm to 525nm, next from 525nm to 560nm and third one at 560nm to 600nm.

![Figure 4. Variation of reflected light with wavelength for M3EH-PPV, MEH-PPV, MEH-DOO-PPV and MEH-M3EH-PPV as active layers](image)

The peak in the range, 350nm to 525nm has maximum reflectance value for M3EH-PPV. There is a peak in the range from 400nm to 600nm where the curvature increases, reaches a maximum peak value and then decreases. M3EH-PPV is having maximum peak value in both absorption spectrum and refractive index spectrum and it decreases respectively, M3EH-PPV, MEH-M3EH-PPV, MEH-PPV and MEH-DOO-PPV. Maximum absorption coefficient and refractive index decreases with increase in the degree of alkyl substitution, because increase in number of alkyl substitution leads to reduce in π-electrons per unit volume. In the transmittance spectrum obtained, for the same wavelength range, from 400nm, the transmittance value decreases, reaches a minimum value and then it increases. So, as absorption coefficient and refractive index increases, transmittance decreases. From 400nm, reflectance value increases, reaches minimum and then decreases. M3EH-PPV have maximum reflectance at this range. So, reflectance is directly proportional to absorption coefficient and refractive index.

4.4. Current density- Voltage Curve (J-V Curve)

Characteristics current density v/s applied voltage curve for MEH-M3EH-PPV, MEH-DOO-PPV, MEH-PPV and M3EH-PPV are shown in the figure 5. Short circuit current for the solar cell having the active layer M3EH-PPV is 4.8 mA/cm², 5.38 mA/cm²for MEH-M3EH-PPV, 5.39 mA/cm²for MEH-PPV and for MEH-DOO-PPV is 5.65 mA/cm². But the open circuit voltage (Vₜₒ) remains the same as 0.52 V for all the simulated devices. The fill factor remains nearly same. At the same time, the efficiency of the device increases with the alkyl substitution.
Figure 5. Variation of current density with applied voltage for the solar cells made from M3EH-PPV, MEH-PPV, MEH-DOO-PPV and MEH-M3EH-PPV.

4.5. Basic Electrical Parameters of the Simulated Bilayer Organic Solar Cell

Figure 6. Variation of charge density with applied voltage for the solar cells with active layer as M3EH-PPV, MEH-M3EH-PPV, MEH-PPV and MEH-DOO-PPV.

The plot for charge density as the function of applied voltage is represented in the figure 6. The charge density strongly depends on the applied voltage. It increases rapidly with the increase in the applied voltage. Charge density is almost same for all the solar cells made from M3EH-PPV, MEH-M3EH-PPV, MEH-PPV and MEH-DOO-PPV.
Total charge density v/s applied voltage curve for the solar cells made from M3EH-PPV, MEH-M3EH-PPV, MEH-PPV and MEH-DOO-PPV as active layer is represented in figure 7. The total charge density is almost same for all the devices.

5. Conclusion
This report investigates the PCE of four different bilayer organic solar cell with device structure ITO/PEDOT:PSS/M3EH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-DOO-PPV/PCBM/Al and ITO/PEDOT:PSS/MEH-M3EH-PPV/PCBM/Al. Power Conversion Efficiencies of these four bilayer organic solar cells are obtained using GPVDM software. It is found that the higher efficiency is for ITO/PEDOT:PSS/MEH-DOO-PPV/PCBM/Al where, MEH-DOO-PPV is a PPV derivative which has a greater number of alkyl substitutions among them. From the simulation result, the power conversion efficiency of MEH-DOO-PPV is 1.85% with lowest fill factor of 62%. Transmitted light v/s wavelength plot, reflected light v/s wavelength plot, J-V plot and variation of charge density and total charge density with applied voltage are obtained. From the above simulation results, it is found that for a particular range of wavelength, MEH-DOO-PPV, shows the maximum transmittance and for the same range of wavelength, it shows minimum reflectance. The solar cells with MEH-DOO-PPV has minimum current density when voltage is applied. Beyond a particular voltage, current density of ITO/PEDOT:PSS/M3EH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-PPV/PCBM/Al, ITO/PEDOT:PSS/MEH-DOO-PPV/PCBM/Al and ITO/PEDOT:PSS/MEH-M3EH-PPV/PCBM/Al is almost same. As per the simulation result, power conversion efficiency is directly proportional and fill factor is inversely proportional to the degree of alkyl substitutions. Among the simulated bilayer devices, the device with structure ITO/PEDOT:PSS/MEH-DOO-PPV/PCBM/Al is the most efficient one and is matching with the reported work.

Acknowledgement
The authors thank General Purpose Photovoltaic Device Model Software (GPVDM).
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