“OPV Lab” Simulation Tool

Supporting Document

Biswajit Ray, Camila González Williamson, Mohammad Ryyan Khan, and Muhammad A. Alam

1. Introduction

OPV Simulation Tool is an educational resource that predicts the behavior of a bilayer organic solar cell by numerical simulations. By solving the drift-diffusion based transport equations for the flow of excitons, electrons and holes, the OPV Tool calculates the IV curve, the band diagram and the carrier concentration profile, etc. Based on the IV characteristics, the tool also calculates the solar cell performance values such as the efficiency, short circuit current, fill factor, open circuit voltage, etc. In this way, OPV tool is made to find out how the device parameters like carrier mobilities, work function, thickness of layers affects these performance values, mainly, the efficiency. Thus, the tool is a suitable resource for the optimum design of OPV cells.

The structure simulated in the tool consists of bilayer morphology, or a Planar Heterojunction (PHJ) [1], conformed by two organic semiconductors between two electrodes with different work function. One of the organic semiconductors acts as a donor layer (D) and the other as acceptor. Typically the organic materials used in this kind of solar cells are P3HT (for the donor) and PCBM (for the acceptor)[2], thus, some of the default values in the tool correspond to the properties of these materials.

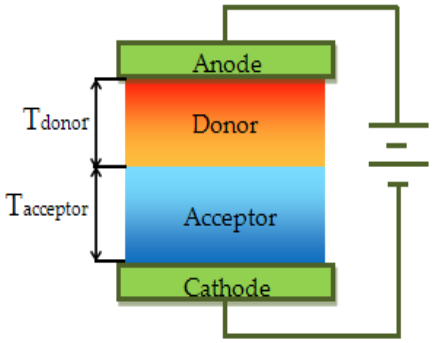

Figure. 1. Bilayer Organic Solar Cell (Planar HeteroJunction)

To calculate the I-V characteristics of the OPV cell the following procedure [3] is adopted in the tool:

1) Optical absorption inside the device is calculated by the transfer matrix method. The absorption profile depends on the complex refractive indices and the thicknesses of various layers in the cell.

2) Exciton diffusion equation is then solved in both donor and acceptor layers. Exciton concentration at the donor-acceptor interface is set to zero with the assumption that exciton dissociation probability is unity and field independent.

3) Charged carrier transport is simulated by the self consistent solution of drift-diffusion and Poisson equation. Generation term in the carrier continuity equation is calculated from the exciton flux at the D-A interface and the recombination of free carriers at the D-A interface is implemented by bi-molecular recombination. We ignore geminate recombination at the interface.

4) The operating temperature is fixed at T_{op} = 300 K. The input irradiance is assumed 1 kW/m^2 for efficiency calculation.

2. Motivation

Organic Photovoltaic Technology (OPV) is a topic of great interest because of its low cost and its capacity for large scale production. Moreover OPV technology offers the possibility of solar cells fabrication in flexible substrates, making them easy to integrate with electrical devices and opening up many more applications like building integrated PV, portable solar cells, etc. On the other hand, the low efficiency and poor operational lifetime [4] of these devices has been limited its commercial usage. Because of this, it is important to achieve a theoretical understanding of OPV operation and a systematic design methodology, so that OPV efficiency can be increased. OPV tool has been created in order to accomplish that objective.

3. Basic operation and device Physics:

OPV operation can be divided in four steps: Photon Absorption, Exciton Diffusion, Charge Separation and Carrier Transport. These steps are shown in Figure 2.

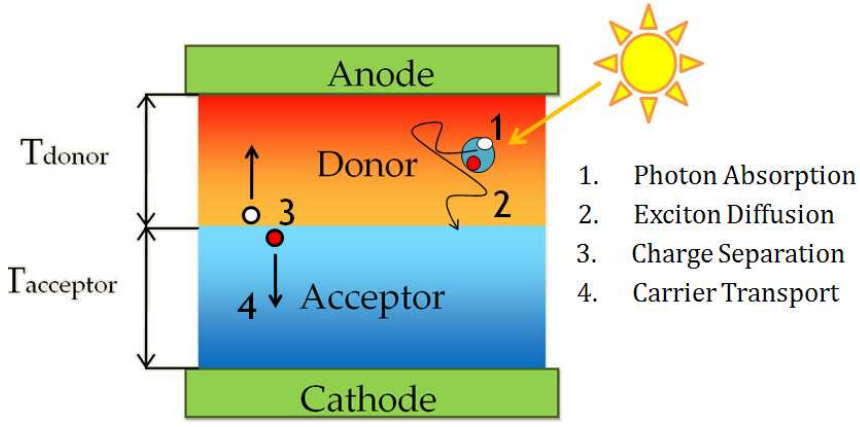

Figure 2. Operation of a bilayer Organic Solar Cell

Following each one of these steps is described:

a. Photon Absorption

Photon absorption process occurs when the incident light is absorbed within the photoactive layer of an organic solar cell. In the tool we assume AM1.5 solar radiation as the incident spectrum. We then use transfer matrix method [5] to calculate the absorption in different layers of the cell. The absorption profile depends on the complex refractive indices and the thickness of the various layers in the cell.

b. Exciton diffusion

Photon absorption creates a tightly bound electron hole pair called exciton in the organic semiconductor. As the exciton is charge neutral, it moves by diffusion in the active layer. In the tool, exciton diffusion is modeled by the following equation:

$$D_{ex}\nabla^2 n_{ex} = G_{ex}(r) - R_{ex}(n_{ex})$$

Where

G_{ex} : Exciton generation
$R_{ex} = n_{ex}/\tau_{ex}$: Exciton recombination
n_{ex} : Exciton concentration
τ_{ex} : Exciton life time
D_{ex}: Exciton diffusion coefficient

The exciton diffusion length, which indicates the distance the exciton can travel without recombining or decaying, can be defined as:

$$L_{ex} = \sqrt{D_{ex}\tau_{ex}}$$

In organic materials, the diffusion lengths are limited to 5-20 nm approximately [5].

c. Charge Separation

Photo-generated excitons are dissociated into electrons and holes at the donor-acceptor heterojunction. We assume the exciton dissociation probability at the heterojunction is high enough that exciton concentration at the donor-acceptor interface is zero. Thus, only the excitons generated within a distance of exciton diffusion length from the heterojunction can contribute to the photo current generation.

d. Carrier Transport

Once the exciton has been dissociated, the holes travel though the donor, and the electrons trough the acceptor. Carrier transport is driven by the electric field across the active layer, which is originated by the work function difference between the two electrodes.

Carrier transport is modeled by the following equations:

Drift-Diffusion Transport Equations:

$$J_e = e\mu_e n(x)E(x) + eD_e\nabla n(x)$$

$$J_h = e\mu_p p(x)E(x) - eD_p\nabla p(x)$$

Electric field, E(x) is calculated by solving Poisson equation self-consistently with the transport equations. In the above equations:

μ_p: Hole Mobility
μ_e: Electron Mobility
D_p: Hole diffusion coefficient
D_e: Electron diffusion coefficient
n(x): Electron concentration
p(x): Hole concentration
E(x): Electric field

Boundary conditions:

$$n(d) = n_{Al} = N_c exp\left(-\frac{\Phi_C - \chi_{acceptor}}{kT}\right)$$

$$p(0) = p_{ITO} = N_V exp\left(-\frac{\Phi_A - \chi_{donor}}{kT}\right)$$

Where
Φ_C, Φ_A : Workfunction of cathode and anode respectively.
$\chi_{acceptor}, \chi_{donor}$: LUMO levels for acceptor and donor.

N_c, N_v: Effective density of states.

Note: Recombination is only effective at the interface. Let us assume, the interface e/h concentrations are:

$$n(d/2) = n_I; \qquad p(d/2) = p_I$$

By taking into account the flux balance, showed in the band diagram of Figure 4, the expression for the current density results in:

$$J_e = J_h = J_{rec} - J_{gen} = q\gamma\left(n_I p_I - n_{i,int}^2\right) - J_{ex}$$

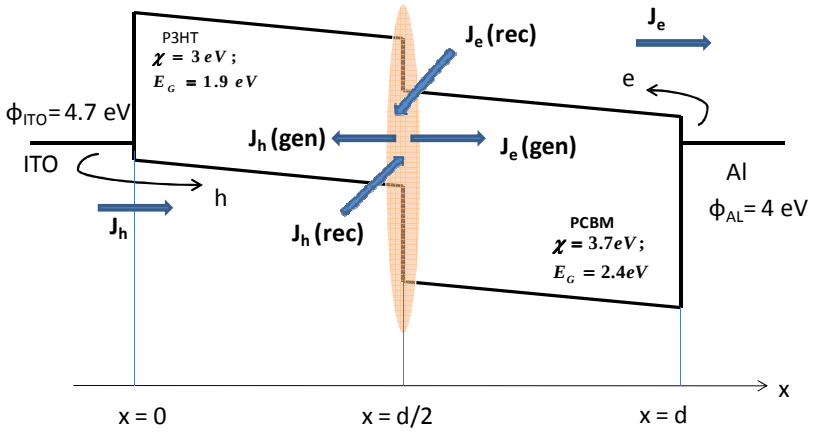

Figure 3. Band diagram of a Bilayer Organic Solar Cell indicating the Flux Balance

From the current density, it is possible to obtain the power density as:

$$P = V * J$$

Also, I_{SC}, V_{OC} can be calculated as well as the Efficiency and Fill Factor:

Fill Factor:

$$FF = \frac{P_{MAX}}{I_{SC} V_{OC}}$$

Efficiency:

$$\eta = \left|\frac{P_{MAX}}{E}\right| * 100\%$$

E: *Irradiance*

4. Input – Output Definition

a. Input Parameters of the tool

The Input Parameters are classified in three main groups: device dimensions, material parameters and simulation conditions. Each one of the input parameters is described below.

Device Dimensions

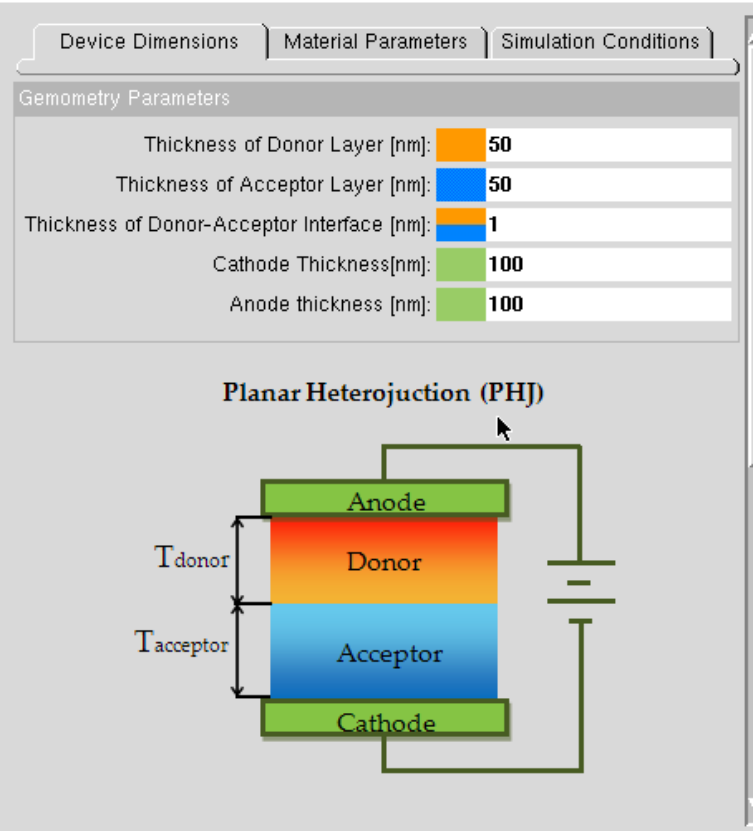

Figure. 4. Device Dimensions tab

TABLE I: Device Dimensions

Input Parameter	Minimum Value	Default Value	Maximum Value	Units
Thickness of donor layer	10	50	200	[nm]
Thickness of acceptor layer	10	50	200	[nm]
Thickness of D-A interface	.5	1	2	[nm]
Cathode Thickness	10	100	200	[nm]
Anode Thickness	10	100	200	[nm]

- Thickness of Donor/Acceptor Layer: Thickness of each one of the polymer layers conforming the Active Layer of the solar cell.

- Thickness of donor-acceptor interface: The interface between the donor and acceptor is diffused in nature with a finite thickness.

- Thickness of Cathode/Anode: Thickness of each one of the metal layers conforming the electrodes of the solar cell.

Material Parameters:

We have assumed following materials for the various layers of the cell. The default values of the material parameters are chosen corresponding to these materials. However, the default values can be changed within a restricted range of values.

TABLE II: Assumed materials for various layers

Cell Layer	**Assumed Materials**
Donor	***P3HT***
Acceptor	***PCBM***
Anode	***ITO***
Cathode	***Al***

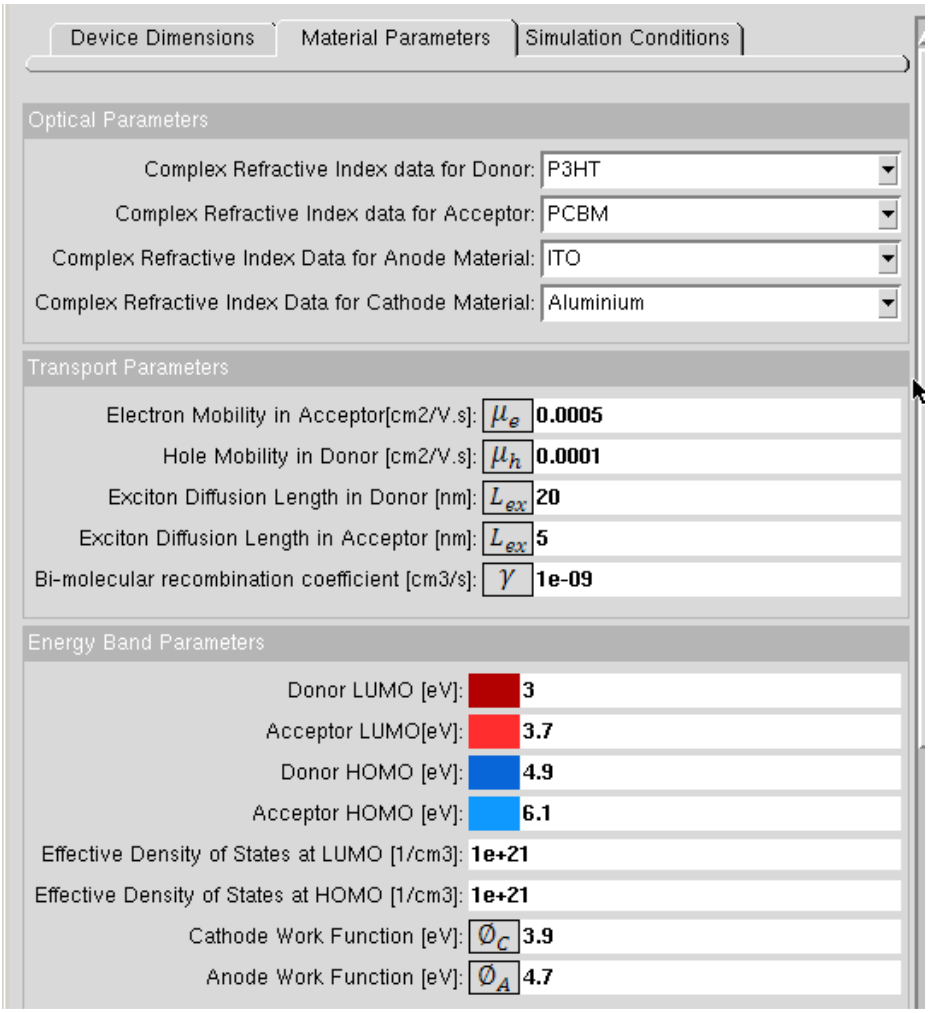

Figure. 5. Material parameters. Default values are for ITO/P3HT/PCBM/Al system

Optical Parameters

Complex refractive indices as a function of wavelength characterize the optical absorption properties of the material. A file is used (for each of the OPV layers) where complex refractive indices are specified as a function of wavelength. Complex refractive index for P3HT, PCBM are obtained from [6]. We obtain data for ITO and Al from [7] and [8] respectively.

Transport Parameters

- Electron mobility in acceptor: Electron current mainly flows in the acceptor. The typical electron mobility in the acceptor is in the range of $(10^{-4} - 10^{-3})Vcm^{-2}s^{-1}$.
- Hole mobility in donor: Hole current mainly flows in the donor. The typical hole mobility in the donor is in the range of $(10^{-5} - 10^{-4})Vcm^{-2}s^{-1}$.
- Exciton Diffusion Length in donor: Excitons are predominantly generated in the donor. Its diffusion length in donor is $\sim (5 - 20)nm$.
- Exciton Diffusion Length in acceptor: Exciton generation in the acceptor is less. Its diffusion length in acceptor is $\sim (1 - 5)nm$

- Bi-molecular recombination coefficient: Charged carrier recombination only occurs at the donor acceptor interface. Bi-molecular recombination coefficient characterizes the strength of recombination at the interface.

Energy Band Parameters

- Donor/ Acceptor LUMO: Energy Level of the Lowest Unoccupied Molecular Orbital in Donor/Acceptor.
- Donor/Acceptor HOMO: Energy Level of the Highest Occupied Molecular Orbital in Donor/Acceptor.
- Effective Density of states: Number of energy states available for electron/holes, at the LUMO/HOMO.
- Cathode/Anode Work Function: Minimum energy necessary to remove an electron from the surface of the Cathode/Anode.

TABLE III: Transport parameters

Input Parameter	**Minimum Value**	**Default Value**	**Maximum Value**	**Units**
Electron mobility in acceptor	1e-6	1.00E-04	100	[$cm^2/(V{\cdot}s)$]
Hole mobility in donor	1e-6	5.00E-04	100	[$cm^2/(V{\cdot}s)$]
Exciton diffusion length in donor	0	20	100	[nm]
Exciton diffusion length in acceptor	0	5	100	[nm]
Bi-molecular recombination coefficient	1e-12	1.00E-9	1e-4	[cm^3/s]

TABLE IV: Energy band parameters

Input Parameter	**Minimum Value**	**Default Value**	**Maximum Value**	**Units**
Donor LUMO ($LUMO_D$)	2.9	3.0	3.1	[eV]
Acceptor LUMO ($LUMO_A$)	3.6	3.7	3.8	[eV]
Donor HOMO ($HOMO_D$)	4.8	4.9	5.0	[eV]
Acceptor HOMO ($HOMO_A$)	6.0	6.1	6.2	[eV]
Density of states in HOMO	10e+20	10e+21	10e+22	[cm^{-3}]
Density of states in LUMO	10e+20	10e+21	10e+22	[cm^{-3}]
Cathode Work Function	3.8	3.9	4.0	[eV]
Anode Work Function	4.6	4.7	4.8	[eV]

Simulation Conditions

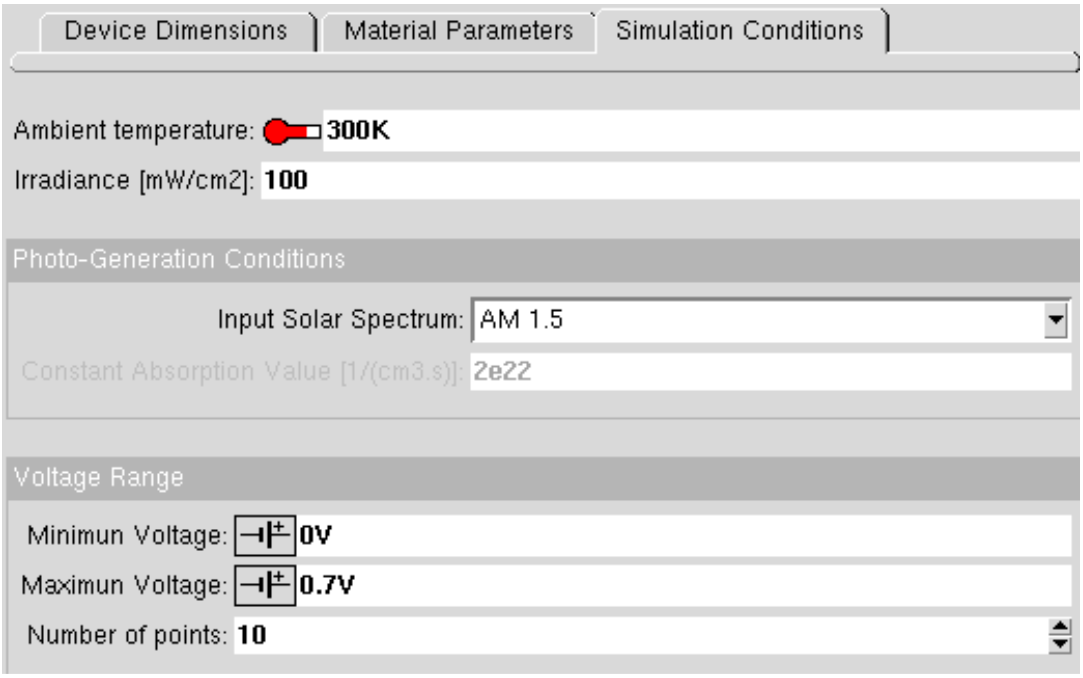

Figure. 6. Simulation conditions tab

TABLE V: Simulation conditions parameters

Input Parameter	**Minimum Value**	**Default Value**	**Maximum Value**	**Units**
Ambient Temperature	300	300	300	[K]
Irradiance	-	1000	-	[W/m^2]
Input solar spectrum	-	AM 1.5	-	[$cm^{-3}s^{-1}$]
Minimum Voltage	-1	0	-	[V]
Maximum Voltage	-	0.7	1	[V]
Number of points	0	50	-	-

- Ambient Temperature: Temperature at which the solar cell will be operated. In the OPV tool it has the fixed value of 300K.

- Irradiance: Irradiance at which the solar cell is exposed. The input irradiance is assumed 1 kW/m2 for efficiency calculation.

Photo-Generation Conditions

- Choice: Photon Absorption Profile: This choice allows the user to decide if the Photon Absorption Profile is going to be constant or not. If the Photon Absorption is non-constant, the tool will calculate its value depending on AM1.5 solar radiation.

- Photon Absorption Profile (constant): Rate at which Photons are absorbed in the active layer of the cell. This input is only available when the user selects Constant Absorption.

Voltage Range

- Minimum Voltage: Lowest voltage to be simulated.

- Maximum Voltage: Highest voltage to be simulated
- Number of points: Number of points of voltage to be simulated.

b. Output results of the tool

Output Plots

TABLE VI: Output Plots

Plot	**X-Axix**	**Units**	**Y-Axis**	**Units**
Light IV curve	Voltage	V	Current density	mA/cm^2
Dark IV curve	Voltage	V	Current density	mA/cm^2
PV Curve	Voltage	V	Power density	mW/cm^2
Carrier Concentration Profile	Position in Active Layer	nm	Carrier concentration	$1/cm^3$
Electric Field	Position in Active Layer	nm	Electric field	V/cm
Band Diagram	Position in Active Layer	nm	Energy	eV
Photon Absorption Profile	Position in Active Layer	nm	Photon Absorption	$1/(cm^3.s)$

The IV curves and the PV curve are plotted using the negative convention for the direction of the current in a solar cell. All the curves of the tool are shown below

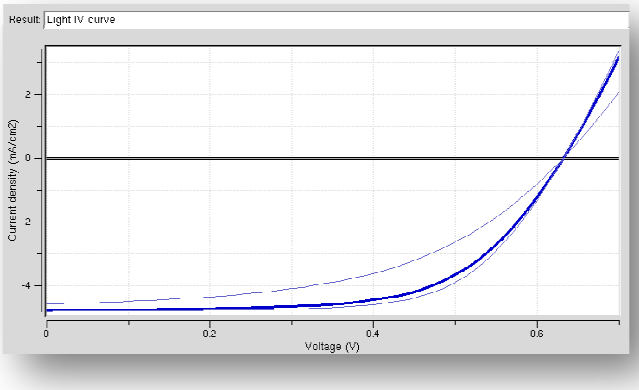

Figure 7. Light IV curve

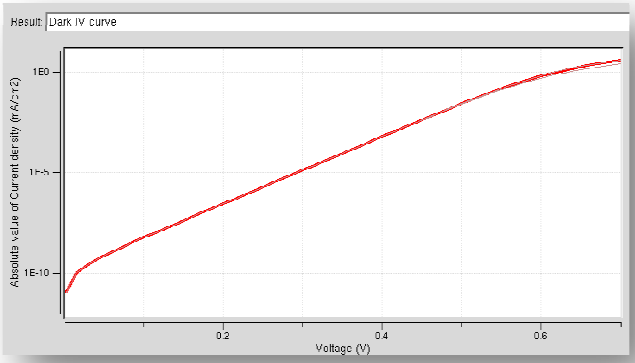

Figure 8. Dark IV curve

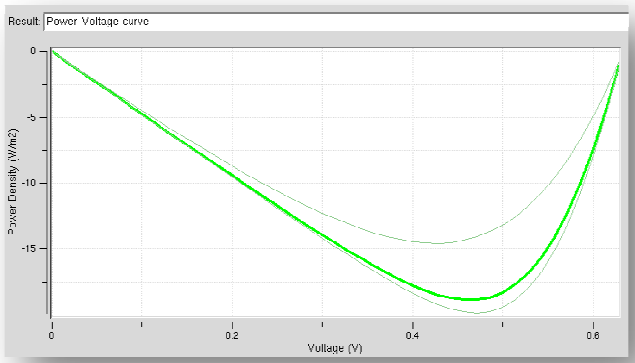

Figure 9. Power-Voltage curve

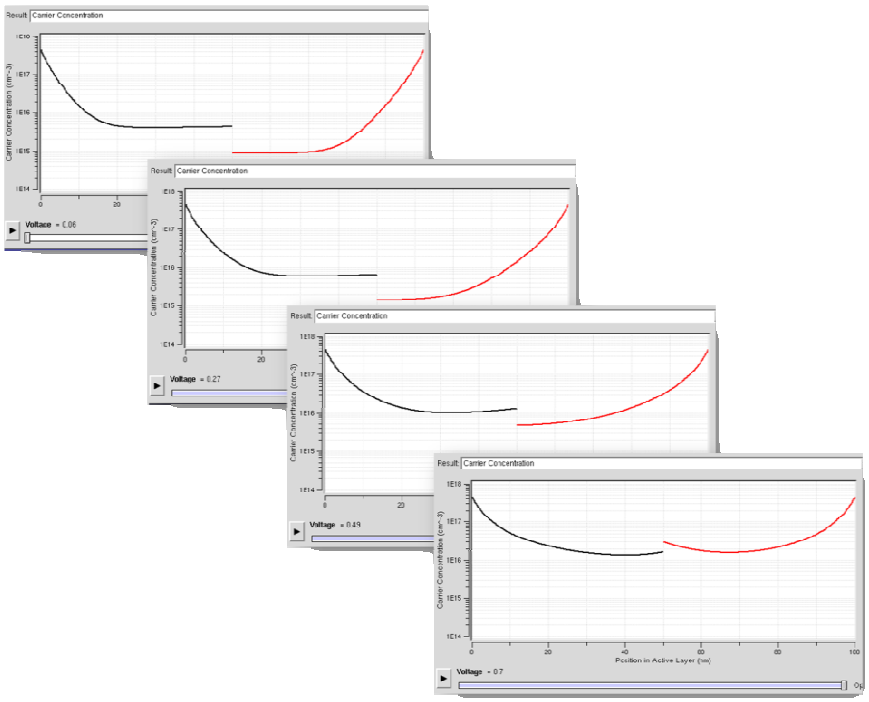

Figure 10. Sequence of the Carrier Concentration Profile for various voltages.

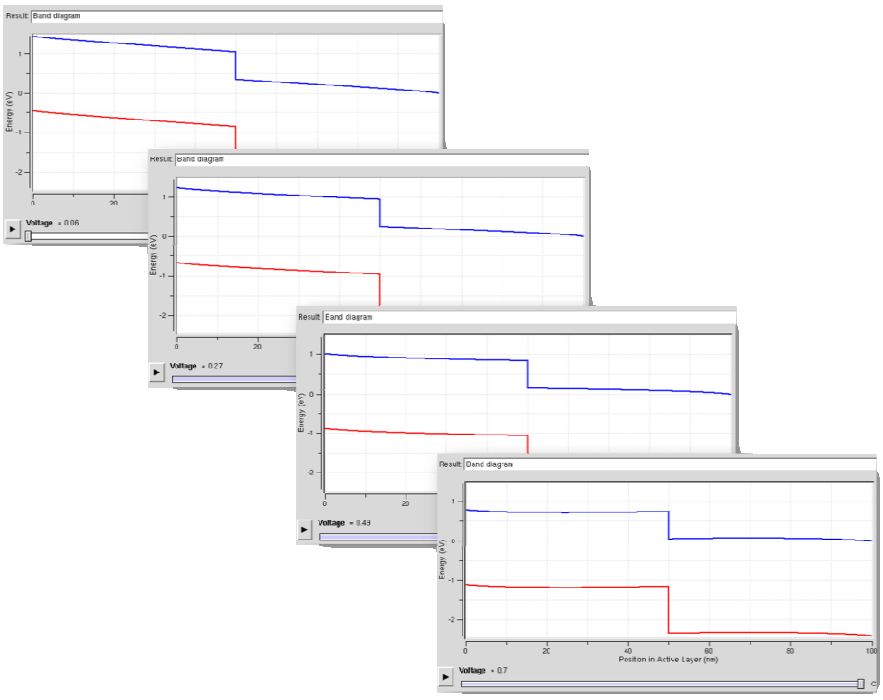

Figure 11. Sequence of the Band Diagram for various voltages

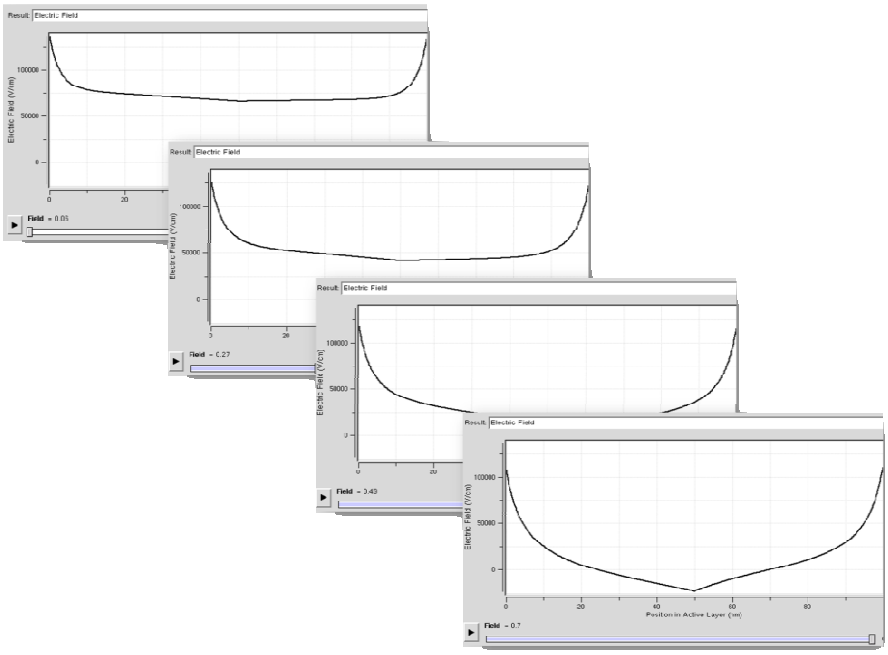

Figure 12. Sequence of the Electric Field across the active layer for various voltages

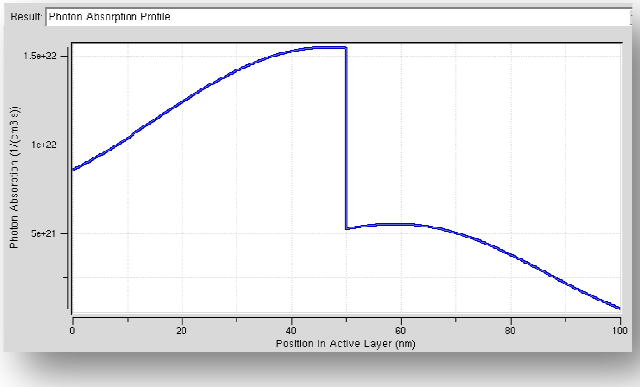

Figure 13. Photon Absorption Profile

OPV Performance Values

The Performance values calculated in the tool are shown below:

- Efficiency [%]
- Fill Factor
- Maximum Power [mW/cm^2]
- Maximum Power Voltage [V/cm^2] (Voltage at the point of maximum power)
- Maximum Power Current [mA/cm^2] (Current at the point of maximum power)
- Open Circuit Voltage [V/cm^2]
- Short Circuit Current [mA/cm^2]

These values are presented as an output text.

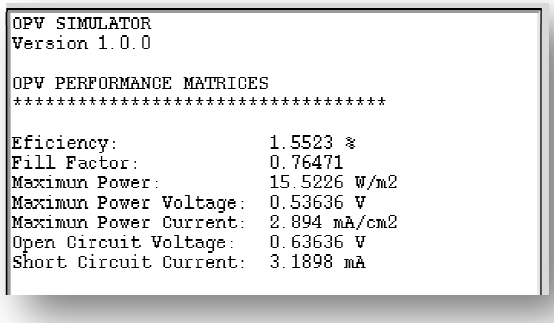

Figure 14. Output text

5. Examples

a. Finding the optimum Donor Thickness for various electron mobilities

In this example, the user is going to obtain the output curves, as well as the performance values, for a given Organic Solar Cell

1. Open the tool. In the Device Dimensions tab, observe the default values Geometry Parameters.

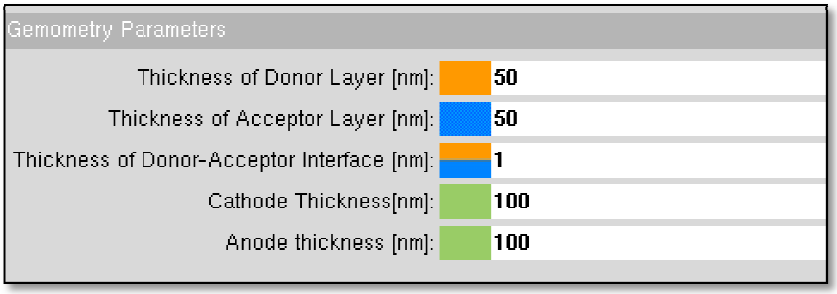

Figure 15

2. Change the default value for the Thickness of Acceptor Layer to 30nm.

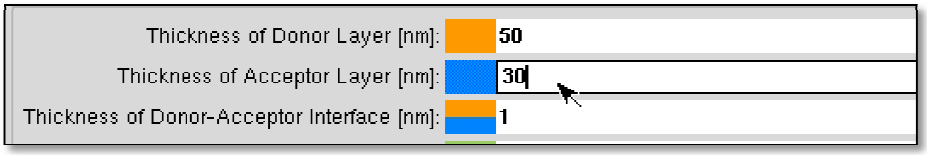

Figure 16

3. Select the Material Parameters Tab. In the Transport Parameters change the value of the Exciton Diffusion Length in Donor to 15nm.

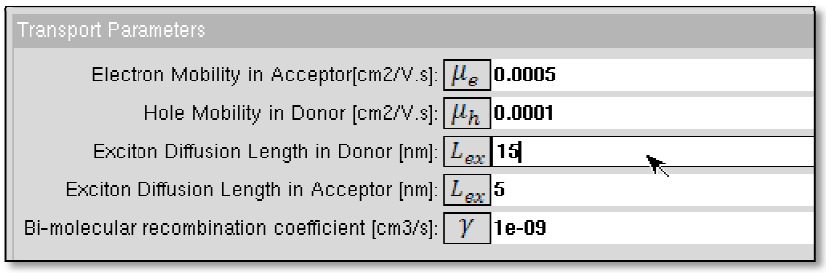

Figure 17

4. Select the Simulation Conditions tab. Observe that the default value for the number of points to be plotted is 100.

Figure 18

5. In the bottom of the tab, press "Simulate"

Figure 19

6. The first result that it is going to be displayed, is the Light IV curve. From this curve it is possible to obtain the values of the short circuit current and open circuit voltage by moving the pointer along the curve. The accuracy of these values depends on the number of points to be plotted.

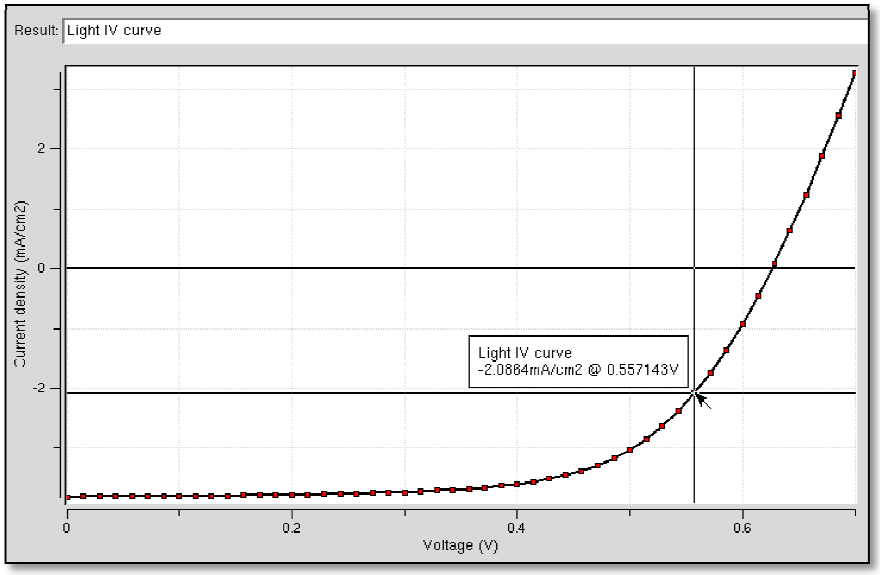

Figure 20

7. By clicking the arrow in the Result part, all the output results are going to be listed.

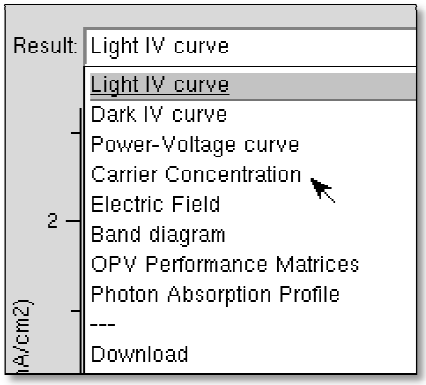

Figure 21

8. Select the "Carrier Concentration" result. This output will show how the carrier concentration varies with voltage.

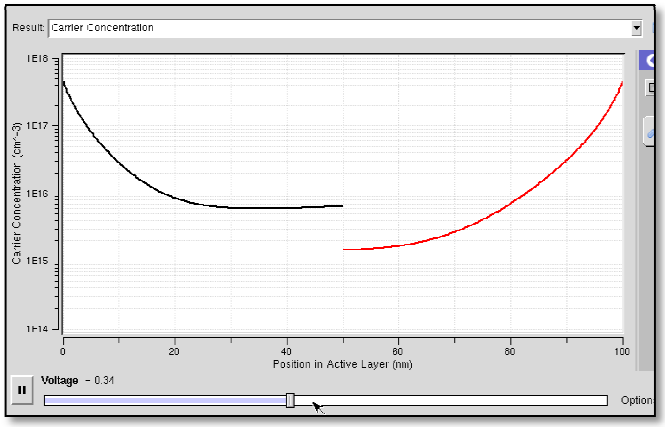

Figure 22

9. By clicking again in the Result list you can select another output. Also, you can download the data from the plot and save it to your computed using the button next to the result list.

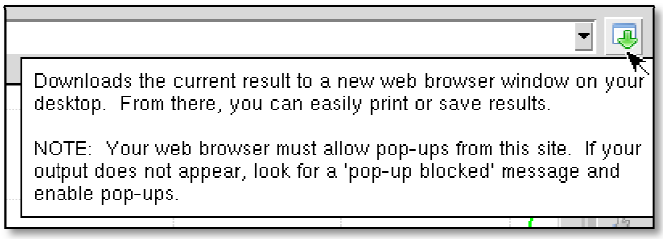

Figure 23

b. S-Shaped IV Curves caused by imbalanced mobilities

In this example, the user is going to be able to plot S-shaped IV curves by varying the mobility mismatch factor defined as:

$$Mobility\ mismatch\ factor = \frac{\mu_e}{\mu_h}$$

According to Wolfgang *et al* [12] the s-shaped curves, can appear when the mobility mismatch factor is larger than 100, for low electron and hole mobilities.

10. Open the tool and set the electron mobility in $1 * 10^{-2}\ \frac{cm^2}{V.s}$ in Device Parameters tab

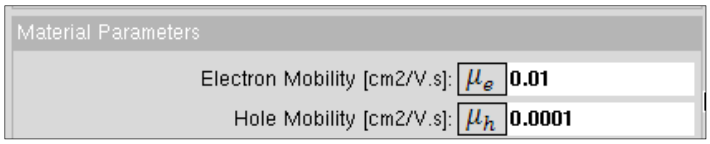

Figure 24

11. In Simulation conditions tab, set the voltage range from 0.2V to 0.75V.

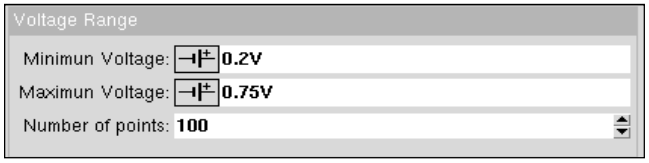

Figure 25

12. Simulate. You will obtain the curve shown in Figure 26.

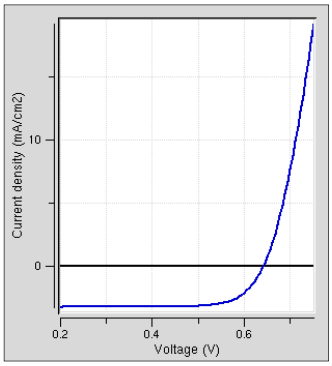

Figure 26

13. In device parameters tab, change hole mobility to $1 * 10^{-5}\ \frac{cm^2}{V.s}$ and simulate again.

14. Repeat the simulation changing hole mobility to $1 * 10^{-6}\ \frac{cm^2}{V.s}$.

15. Click on the 'All' button, located below the plot. You will see the three plots together as it is shown in Figure 27.

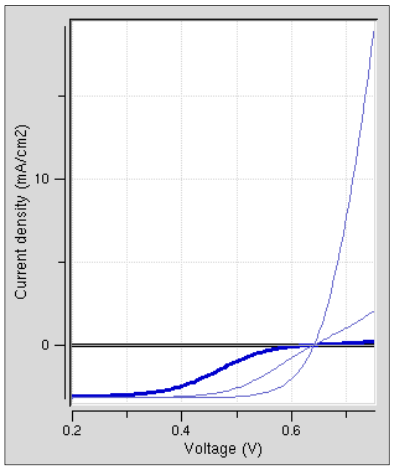

Figure 27

16. You can simulate more posibilities for the electron an hole values. To see them simultaneouly, click on parameters below the plot and then in the 'All' shown in Figure 28.

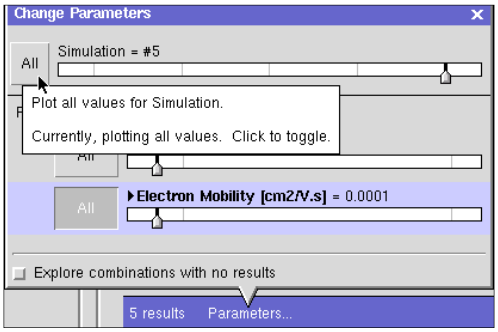

Figure 28

You will obtain the plot shown in Figure 29. You can zoom in the plot by using left-click, and zoom out the plot by using right-click.

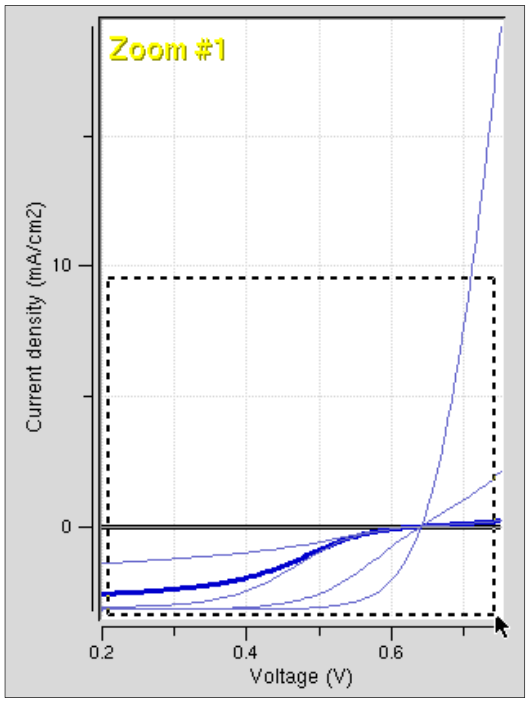

Figure 29

REFERENCES

[1] C.W. Tang, "Two-layer organic photovoltaic cell," *Applied Physics Letters*, vol. 48, Jan. 1986, pp. 183-185.

[2] A.L. Ayzner, C.J. Tassone, S.H. Tolbert, and B.J. Schwartz, "Reappraising the Need for Bulk Heterojunctions in Polymer–Fullerene Photovoltaics: The Role of Carrier Transport in All-Solution-Processed P3HT/PCBM Bilayer Solar Cells," *The Journal of Physical Chemistry C*, vol. 113, Nov. 2009, pp. 20050-20060.

[3] B. Ray, P.R. Nair, and M.A. Alam, "Annealing dependent performance of organic bulk-heterojunction solar cells: A theoretical perspective," *Solar Energy Materials and Solar Cells*, vol. 95, Dec. 2011, pp. 3287-3294.

[4] B. Ray and M.A. Alam, "A compact physical model for morphology induced intrinsic degradation of organic bulk heterojunction solar cell," *Applied Physics Letters*, vol. 99, Jul. 2011, pp. 033303-3.

[5] L.A.A. Pettersson, L.S. Roman, and O. Inganas, "Modeling photocurrent action spectra of photovoltaic devices based on organic thin films," *Journal of Applied Physic*, 1999, pp. 487-496.

[6] V.S. Gevaerts, L.J.A. Koster, M.M. Wienk, and R.A.J. Janssen, "Discriminating between Bilayer and Bulk Heterojunction Polymer:Fullerene Solar Cells Using the External Quantum Efficiency," *ACS Appl. Mater. Interfaces*, vol. 3, Oct. 2011, pp. 3252-3255.

[7] H. Hoppe, N.S. Sariciftci, and D. Meissner, "Optical constants of conjugated polymer/fullerene based bulk-heterojunction organic solar cells," *Molecular Crystals and Liquid Crystals*, vol. 385, Oct. 2011, pp. 113-119.

[8] A.D. Rakic, "Algorithm for the determination of intrinsic optical constants of metal films: application to aluminum," *Applied Optics*, vol. 34, 1995, pp. 4755-4767.