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Optical and Thermodynamic Analysis of Organic Solar Cells Using Physical and Computational Simulations

WOONG JAE BAEK, RICHARD KYUNG
Choice Research Group

Abstract

Organic solar cell is a type of photovoltaic cell which produces electricity from sunlight by the photovoltaic effect. Conductive organic polymers are used for light absorption and charge the cell. Optical properties and constants of isotropic thin P3HT:PC61BM film systems, such as refractive index, relative permittivity (dielectric constants), and wavelength were considered in the calculations of solar energy. Also the geometrical variations such as thickness and width, and material properties were considered to check those dependencies. Poly(3-hexylthiophene) (P3HT) which is a hydrophobic and well stacking semiconducting polymer was used as an electron donator in the current organic electronics simulations.

As an electron acceptor, PCBM, a fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester, was used in conjunction with the electron donor materials P3HT.

The computational programs such as Avogadro and Chemcraft have been used in an effort to discover the optimal method and to compute the measurements of stability of the solar cell. The Auto Optimize Tool was used for each and every fullerene derivative modeled in this project to determine its optimization energy. The Universal Force Field (UFF) option was selected for all fullerene derivatives modeled.

Introduction

An organic solar cell is a type of photovoltaic cell which produces electricity from sunlight by the photovoltaic effect. Conductive organic polymers are used for light absorption and charge the cell. Numerous studies validating the fullerene's potential to be used in the solar cell have led scientists to assess the safety of fullerene derivatives such as thermodynamical stability. Recently, computational and numerical simulation technology has been used as a means to determine the thermodynamic stability of such molecules. Scientists have modeled nano fullerene complexes, which are believed to be able to virtually attach large quantity of functional groups and donate electrons to polymers.

The current research on organic solar cells has discovered that there are many advantages regarding the use of these solar cells. Organic, polymer-based solar cells, also commonly referred as OSCs, have been found to be new and better alternatives to inorganic cells in several ways. Compared to silicon-based devices, advantageous qualities such as lightweightness, flexibility, semi-transparency, lower manufacturing costs, short energy payback times, and comparatively lower environmentally negative impacts are all advantages that OSCs have been found to have over inorganic cells. This would make OSCs useful for cheap and large scale energy production [1].

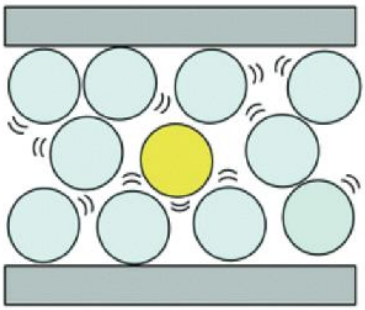


Figure A. Organic polymer molecules are randomly dispersed before they are polarized to electron donors and acceptors in the OSCs

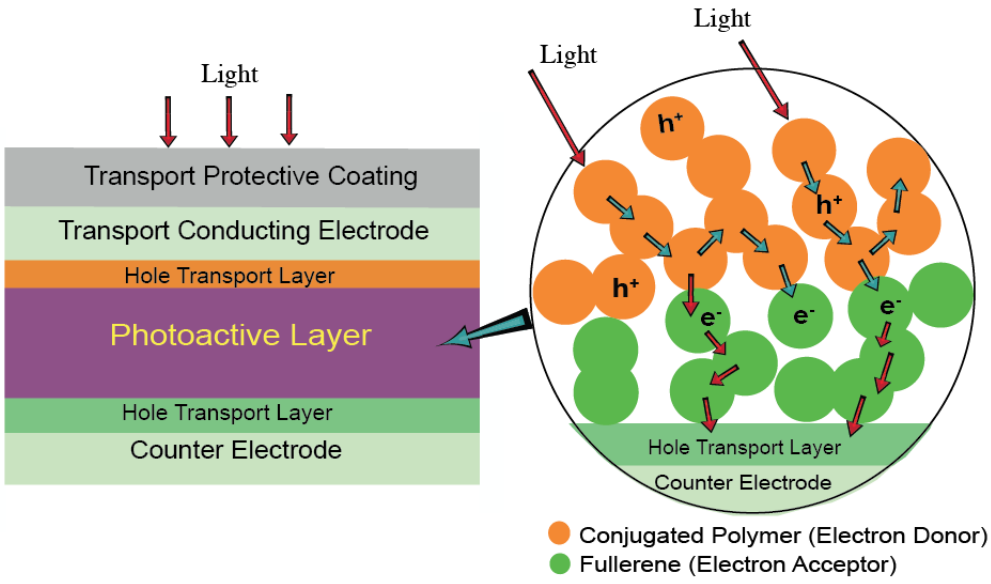


Figure B. Electron donors and acceptors in the OSCs

In this project, we assessed the thermodynamical and stereochemical safety of several types of water-soluble and photovoltaic fullerene derivatives that could be used as electron acceptors. We used the Avogadro software to model, optimize, and compare the resulting molecular optimization energies of the fullerene derivatives. C40, C60, C70, C72, and C80 were used as the fullerene bases for these derivatives.

Materials and Methods

This research uses computational method to study the thermodynamic stability of various fullerene derivatives and optical properties in the photoactive layer in organic solar cell. The research uses computational softwares to further display the optimized geometry energy levels and check electrical energy contour of solar cells. The Avogadro software is an open-source molecular editing program equipped with an auto-optimization feature, which determines the theoretical values of a certain structure's atomic properties. This software allows users to build virtually any molecule and optimize its geometry according to various force field options.

Data and Results

In this project, the following fullerene derivatives were modeled in the Avogadro software:

1. C40, C60, C70, C72, and C80
2. Each doped with the Phenyl-butyric Acid Methyl Ester (PCBM)
3. Phenyl-butyric Acid Cyanate Esters (PCB-Cn Ester)
4. Thienyl-Butyric-Acid-Methyl Ester (THCBM)
5. Indene Monoadduct (ICMA)
6. IPX (http://solennebv.com/product/60ipx/)
7. SAM(C60-Self-Assembled Monolayer) (http://solennebv.com/product/other-derivatives/)

The Auto Optimize Tool was used for each and every fullerene derivative modelled in this project to determine its optimization energy. The Universal Force Field (UFF) option was selected for all fullerene derivatives modelled.

C60, isomers of C40 (C40-C2-2), C70(C70-D5h), C72(C72-D6d), C80(C80-D3-4, C80-D5d-1, C80-D5h-6) with no functional groups attached, were first optimized. The functional groups PCBM, PCB-Cn Ester, and THCBM by themselves were also optimized.

Each isomer chosen for this project (C40-C2-2, C60, C70-D5h, C72-D6d, C80-D3-4, C80-D5d-1, C80-D5h-6) were prepared. The functional groups PCBM, PCB-Cn Ester, THCBM were then added to the fullerenes respectively.

Table 1. Optimized energies of the fullerenes considered

Fullerenes	Energy (kJ/mol)
C40-C2-2	2406.27
C60	4381.08

Table 2. Optimized energies of the C70 fullerenes

Fullerenes	Energy (kJ/mol)
C70-D5h	4290.59
C72-D6d	4909.98

Table 3. Optimized energies of the C80 fullerenes

Fullerenes	Energy (kJ/mol)
C80-D3-4	11588.14
C80-D5d-1	4877.21
C80-D5h-6	11125.57

Because fullerene itself is nonpolar and not active, functional groups are attached to increase its reactivity. As shown in Table 3, the fullerene C80-D3-4 has the highest optimization energy. The optimization energies of the C80-D3-4 were 11588.14 kJ/mol.

Table 4. Optimized Energies of the Functional Groups

Functional Group	Energy (kJ/mol)
PCBM	85.20

PCB-Cn Ester	119.41
THCBM	223.01
ICMA	2642.33
IPX	2756.51
SAM	247.78

As shown in Table 4, the functional group THCBM has the highest optimization energy. The optimization energies of the THCBM were 223.01 kJ/mol.

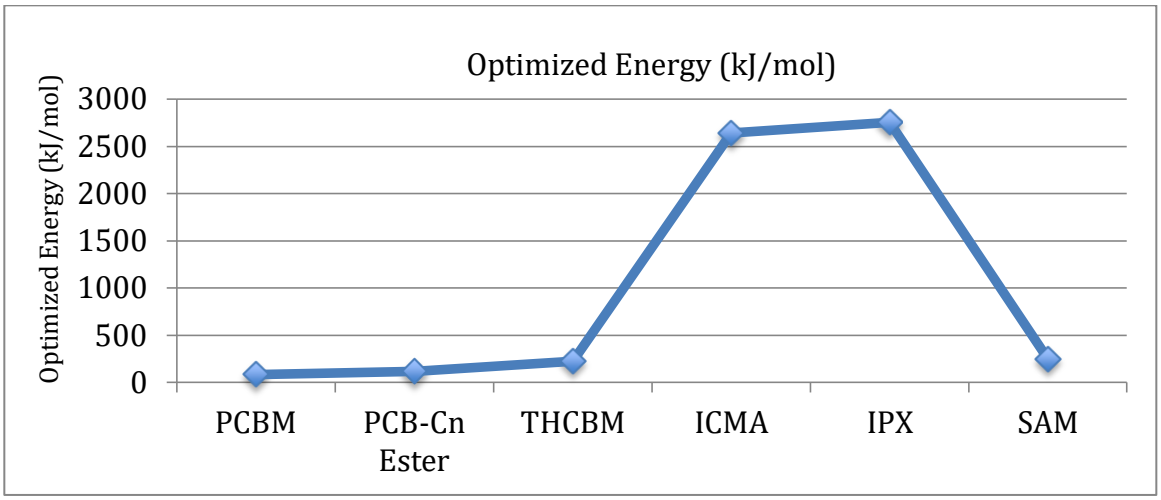


Figure 1A. Optimized Energies of the Functional Groups

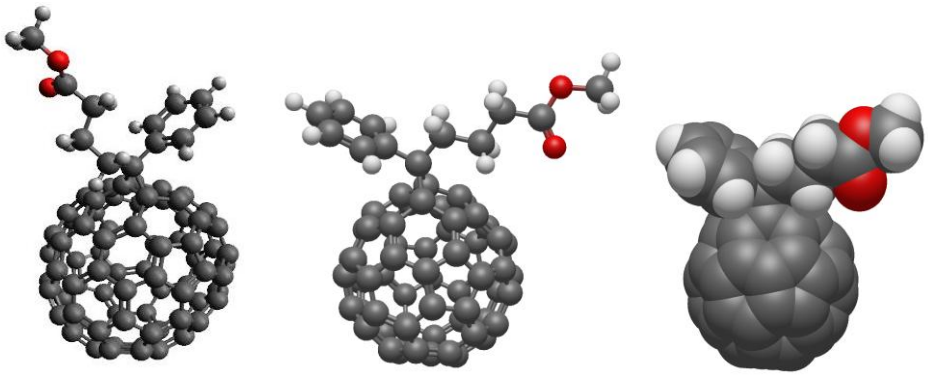
Table 5. Optimized Energies of the Fullerenes with PCBM Attached

Fullerenes with PCBM Attached	Energy (kJ/mol)
C40-C2-2	4009.83
C60	10131.51
C70-D5h	4655.75
C72-D6d	12524.58
C80-D3-4	12355.9
C80-D5d-1	4925.58
C80-D5h-6	11959.42

As shown in Table 5, the C72-D6d fullerene doped with the PCBM functional group has the highest optimization energy, and C80-D3-4 the second highest. Optimized energy plot of the PCBM functional group is found to be as follows:

Figure 1B. Optimized energy plot the PCBM

- C72-D6d



(a) Side view 1 (b) Side view 2 (c) Van deer Waals Sphere
Figure 1C. Optimized energy plot for C72-D6d doped with PCBM

Van deer Waals Sphere in Figure 1C(c) represents a surface through which the molecule might be conceived as interacting with other molecules

- C80-D3-4

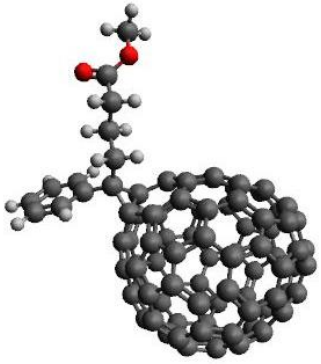


Figure 2. Optimized energy plot for C80-D3-4 doped with PCBM

Table 6. Optimized Energies of the Fullerenes with PCB-Cn Ester Attached

Fullerenes with PCB-Cn Ester Attached	Energy (kJ/mol)
C40-C2-2	4059.80
C60	11011.46
C70-D5h	4636.75
C72-D6d	12309.05
C80-D3-4	3.74e+38
C80-D5d-1	5177.66
C80-D5h-6	12056.42

As shown in Table 6, the C72-D6d fullerene doped with the PCB-Cn Ester functional group has the highest optimization energy, and C80-D5h-6 the second highest. The C80-D3-4 fullerene was not considered here because the optimization energy was too high, and therefore could be considered a theoretically impossible combination of PCB-Cn Ester and C80-D3-4.

- C80-D5h-6

Optimized energy plot of the C80-D5h-6 doped with PCB-Cn Ester is found to be as follows:

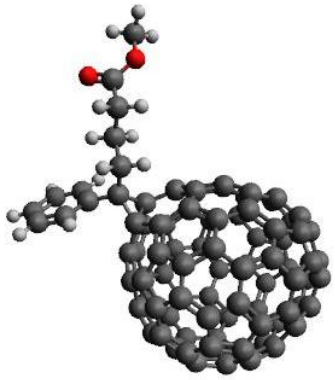


Figure 3. Optimized energy plot of the C80-D5h-6 doped with PCB-Cn Ester

- C72-D6d

Optimized energy plot of the C72-D6d doped with PCB-Cn Ester is found to be as follows:

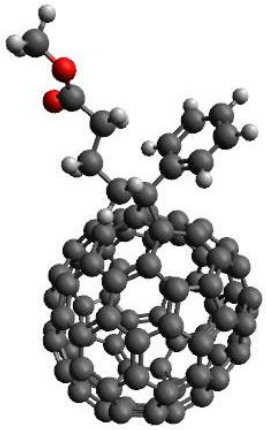


Figure 4. Optimized energy plot for C72-D6d doped with PCB-Cn Ester

Table 7. Optimized Energies of the Fullerenes with THCBM Ester Attached

Fullerenes with THCBM Ester Attached	Energy (kJ/mol)
C40-C2-2	4156.70
C60	11065.21
C70-D5h	4968.41
C72-D6d	3.37e+38
C80-D3-4	19623.61
C80-D5d-1	5180.24
C80-D5h-6	12136.90

As shown in Table 7, the C80-D3-4 fullerene doped with the THCBM functional group has the highest optimization energy, and C80-D5h-6 the second highest. The C72-D6d fullerene was not considered here because the optimization energy was too high, and therefore could be considered a theoretically impossible combination of THCBM and C72-D6d.

- C80-D5h-6

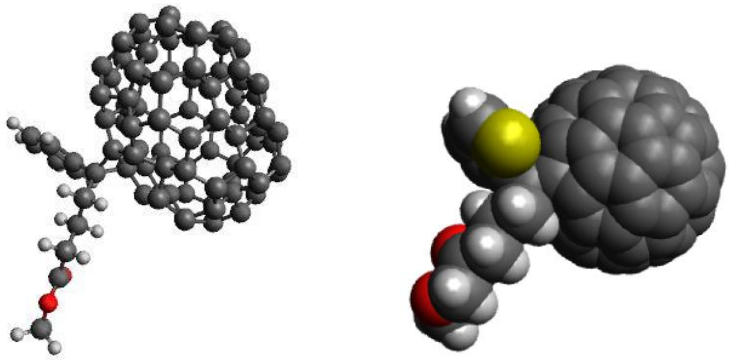


Figure 5. C80-D5h-6 doped with THCBM and itsVan deer Waals Sphere

Van deer Waals Sphere in Figure 5 represents a surface through which the molecule might be conceived as interacting with other molecules.

- C80-D3-4

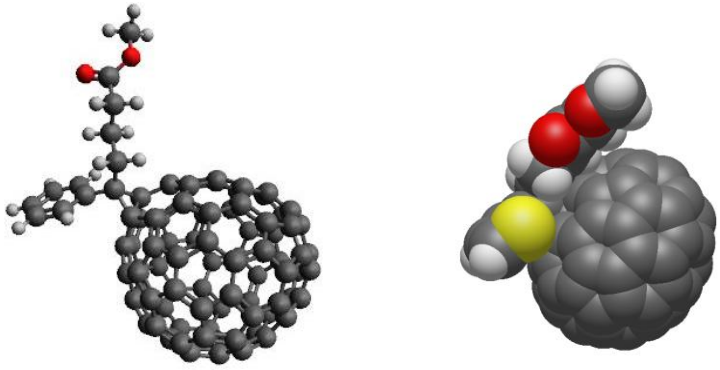


Figure 6. C80-D3-4 doped with THCBM and itsVan deer Waals Sphere

Table 8. Optimized Energies of the Fullerenes with ICMA Attached

Fullerenes with ICMA Attached	Energy (kJ/mol)
C40-C2-2	5934.60
C60	12642.36
C70-D5h	6640.12
C72-D6d	13926.93
C80-D3-4	14269.08
C80-D5d-1	6791.33
C80-D5h-6	13794.77

As shown in Table 8, the C80-D3-4 fullerene doped with the ICMA functional group has the highest optimization energy, and C72-D6d the second highest.

- C72-D6d

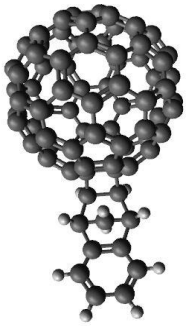


Figure 7. D6d doped with ICMA

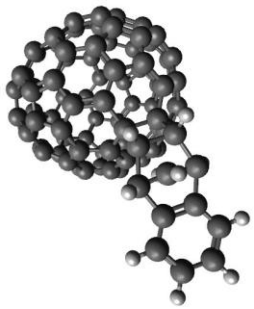


Figure 8. C80-D3-4 doped with ICMA

- C80-D3-4

Table 9. Optimized Energies of the IPX Attached

Fullerenes with IPX Attached	Energy (kJ/mol)
C40-C2-2	5985.09
C60	12764.76
C70-D5h	6798.79
C72-D6d	14073.61
C80-D3-4	14389.32
C80-D5d-1	6824.28
C80-D5h-6	13992.94

As shown in Table 9, the C80-D3-4 fullerene doped with the IPX functional group has the highest optimization energy, and C72-D6d the second highest.

- C72-D6d and C80-D3-4

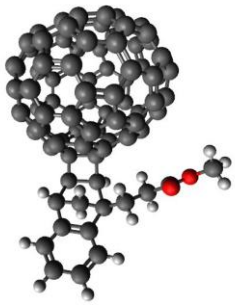


Figure 9. C72-D6d doped with IPX

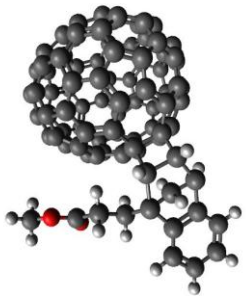


Figure 10. C80-D3-4 doped with IPX

Table 10. Optimized Energies of the Fullerenes with SAM Attached

Fullerenes with SAM Attached	Energy (kJ/mol)
C40-C2-2	3749.50
C60	10554.44
C70-D5h	4087.14
C72-D6d	11789.81
C80-D3-4	12116.99
C80-D5d-1	4413.84
C80-D5h-6	11435.03

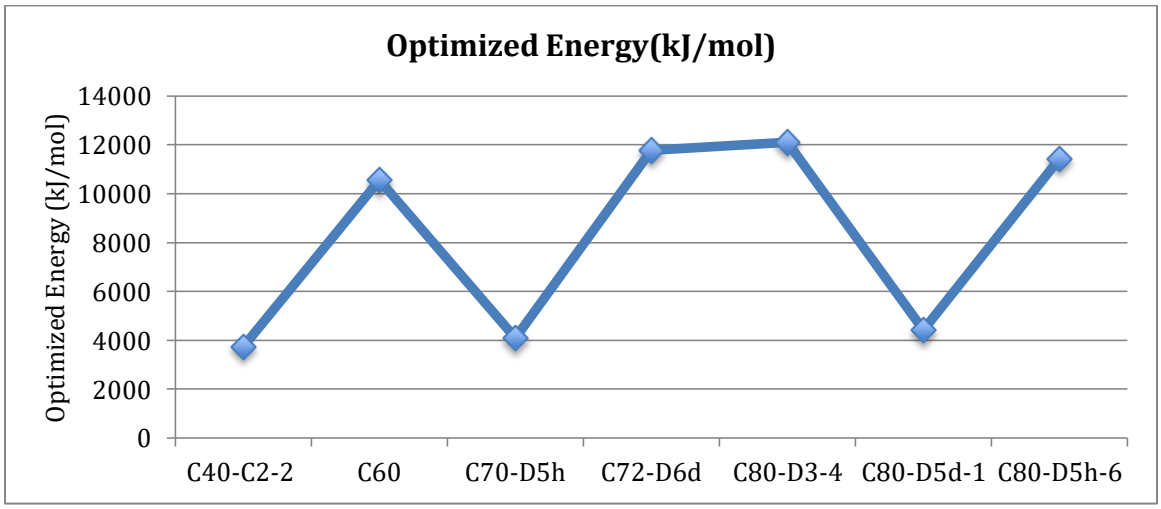


Figure 11. Optimized Energies of the Fullerenes with SAM Attached

As shown in Table 10, the C80-D3-4 fullerene doped with the ICMA functional group has the highest optimization energy, and C72-D6d the second highest.

- C72-D6d

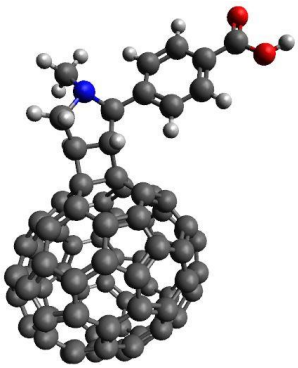


Figure 11. Optimized energy plot of the C72-D6d doped with SAM

- C80-D3-4

Finally, optimized energy plot of the C80-D3-4 doped with SAM is shown as follows:

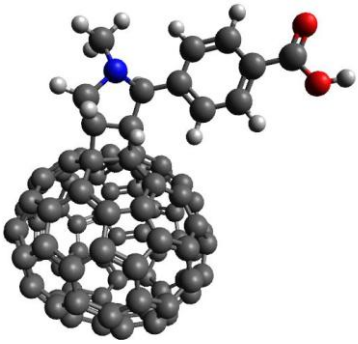


Figure 12. Optimized energy plot of the C80-D3-4 doped with SAM

For all functional groups, the time it took for the fullerene derivative to be optimized increased as the complexity of functional groups increased.

Optical Analysis of Photoactive Layer (P3HT:PC61BM) in the Solar Cell Analysis

Solar cell is a photovoltaic cell which produces electricity in the photoactive layer from sunlight by the photovoltaic effect. Many conductive organic polymers can be used for light absorption and charge the cell. In this paper, optical properties and constants of isotropic thin P3HT:PC61BM film systems were cnsidered for absorption of the lighr. Refractive index, relative permittivity (dielectric constants), wavelength, etc. were considered to check the contour of solar energy in the layer. Also the geometrical properties such as thickness and width, and material properties were considered to check those dependencies.

The computational program, COMSOL has been used in an effort to find the energy contour of the layer in the solar cell.

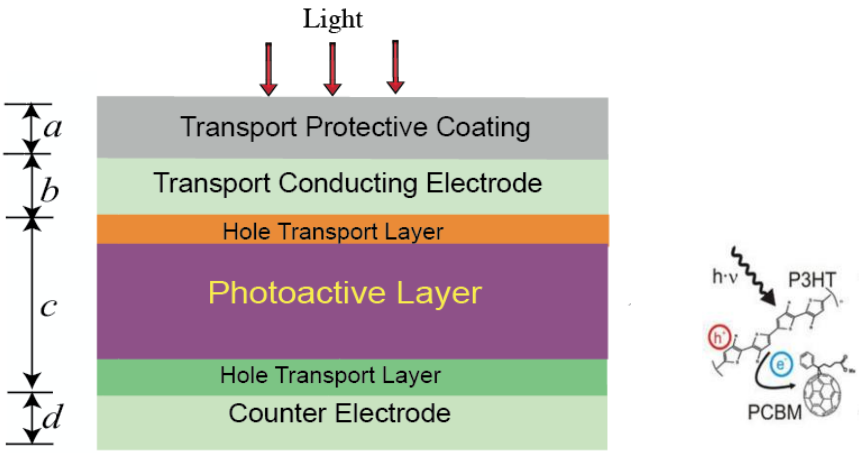
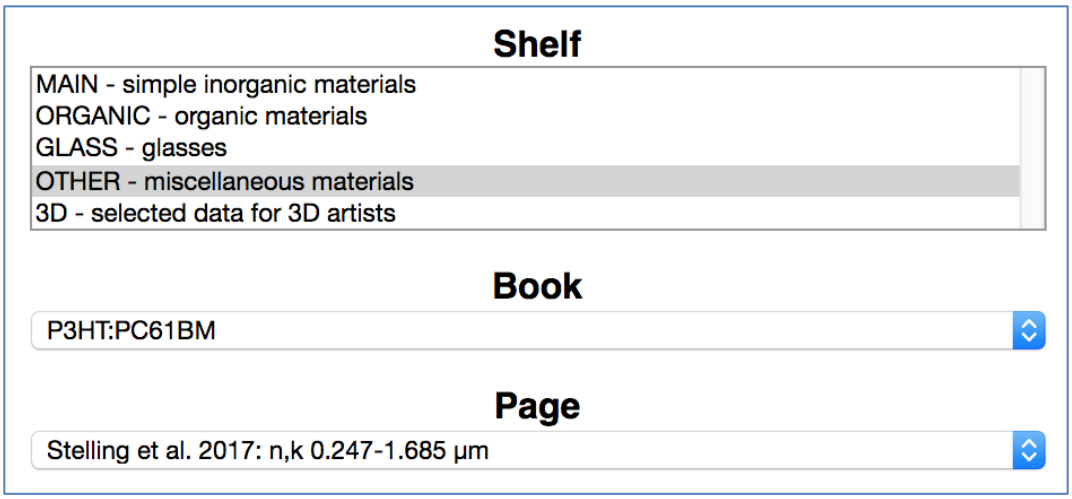


Figure 13. Layers including photoactive layer (P3HT:PC61BM) in the solar cell analysis

Optical constants of P3HT:PC61BM used for Solar Cell Analysis

As an electron acceptor, PCBM, a fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester, was used in conjunction with the electron donor materials P3HT. Poly(3-hexylthiophene) (P3HT) which is a hydrophobic and well stacking semiconducting polymer was used as an electron donator in the current organic electronics simulations. Optical constants of P3HT:PC61BM used for solar cell analysis are shown s follows:



Optical constants of P3HT:PC61BM used for Solar Cell Analysis

Data from: Stelling et al. 2017: n,k 0.247-1.685 µm

Wavelength: 0.68 µm (0.24718 – 1.68492)

Refractive index: n = 1.9

Extinction coefficient: k = 0.0

Relative permittivity (dielectric constants):

$\epsilon 1 = 3.6469$

$\epsilon 2 = 0.000024681$

Incident angle: $\alpha = 45$ deg

Comments:

Isotropic P3HT:PC61BM thin film (thickness 80 nm)

References: C. Stelling, C. R. Singh, M. Karg, T. A. F. König, M. Thelakkat, M. Retsch. Plasmonic nanomeshes: their ambivalent role as transparent electrodes in organic solar cells, Sci. Rep. 7, 42530 (2017) - see Supplementary information (Numerical data kindly provided by Tobias König)

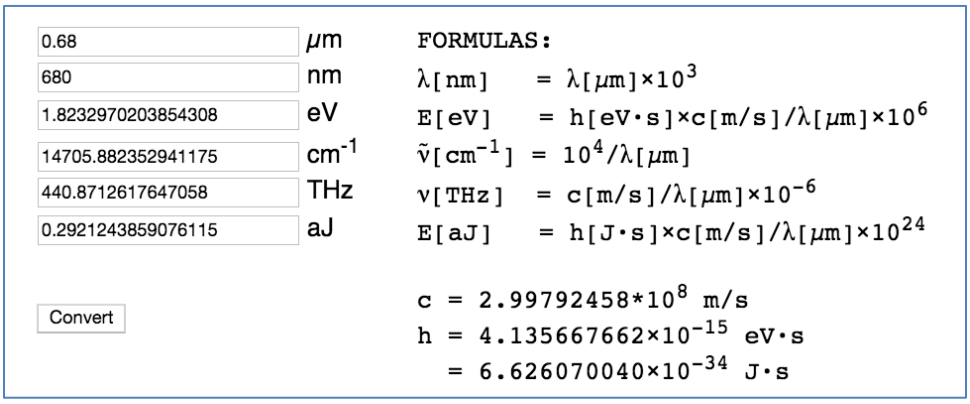
Underneath the Parameter section in the COMSOL, we first had to determine the refractive index for layers, and the thickness of the layers (a, b, c, and d). Then, we set the the wavelength of the light (lam) and number of layers (N_layers), etc.

Optical constants of P3HT:PC61BM used for Solar Cell Analysis

a=300; thickness of coating material (nm)
b=300; thickness electrode 1 (nm)
c=300; thickness of PAL (Photoactive Layer) (nm)
d=300; thicknes of electrode 2 (nm)
width: 1200 (nm)

Transmittance (at 0.68 µm): T = 0.30295
Reflectance (at 0.68 µm): R = 0.097746

Chemical composition
P3HT: (C41H53FO4S4)n PC61BM: C72H14O2
Other names (P3HT): Poly(3-hexylthiophene-2,5-diyl), Plexcore OS 2100
Other names (PC61BM): [6,6]-phenyl-C61-butyric acid methyl ester



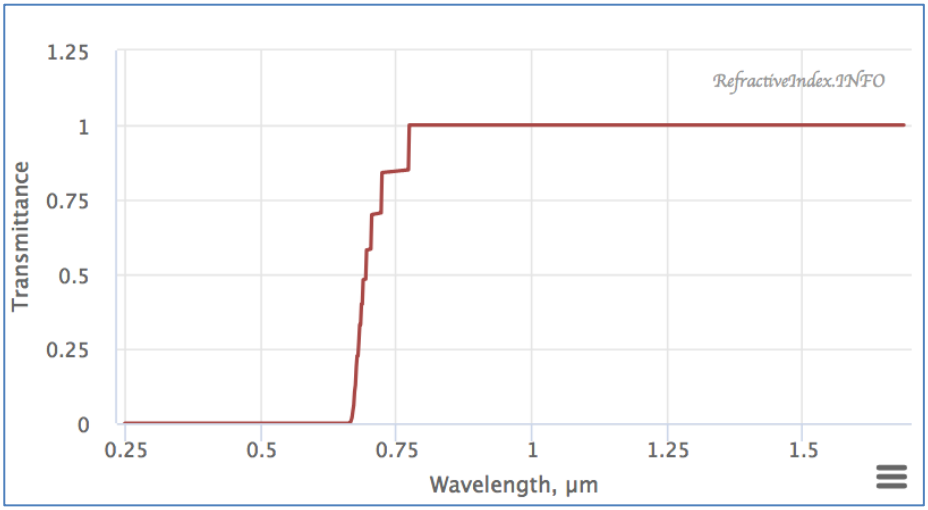


Figure 14. Wavelength-Transmittance, T = 0.30295 at 0.68 µm

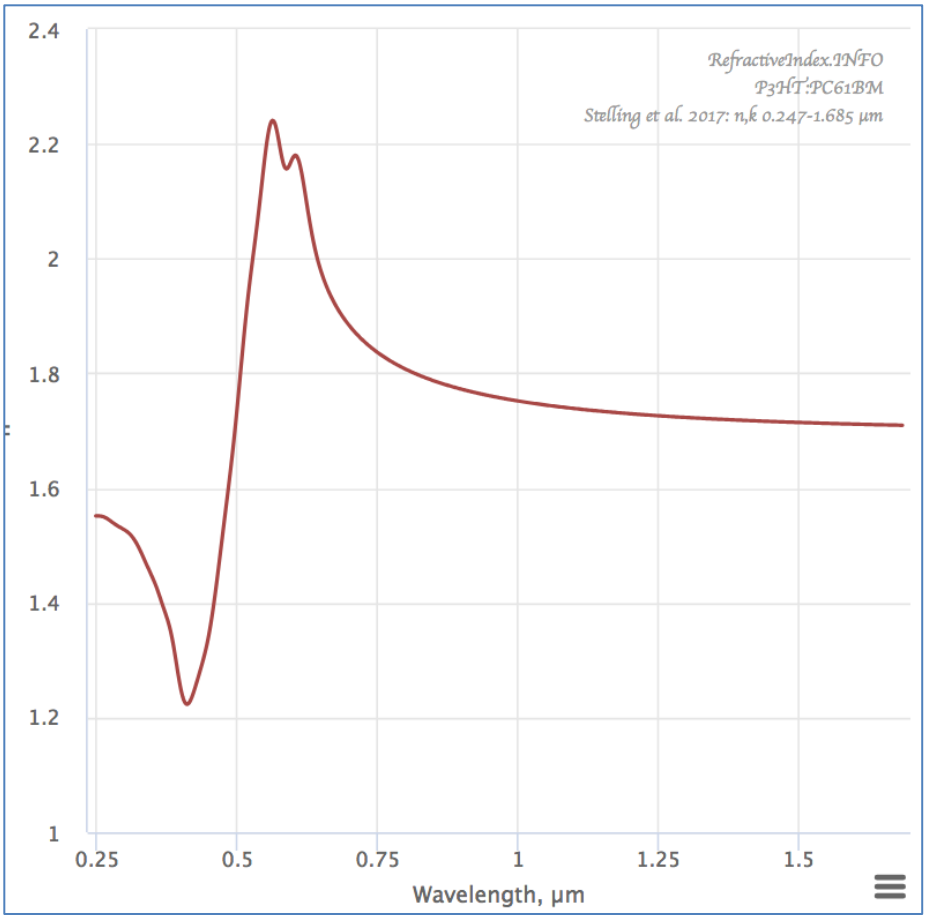


Figure 15. Wavelength-Reflectance, R = 0.097746 at 0.68 µm

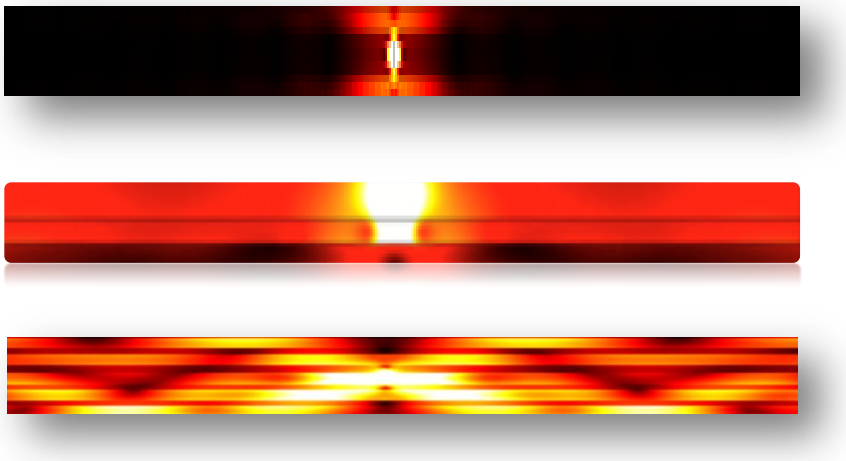


Figure 16. Optical contours of P3HT:PC61BM layer (top to bottom: the layers in the PAL increase. # of layers are 1, 3, 5 respectively)

Discussions and Conclusions

In this project, the thermodynamic stability of fullerene derivatives used in organic solar cells was studied. The Avogadro software was used to measure the optimization energy of each fullerene derivative tested in the experiment. Fullerene complexes with relatively low optimization energies were predicted to be more thermodynamically stable than those with relatively high energies. (Generally, a compound that stabilizes with the least energy is the most stable.) Thus, fullerene derivatives with low molecular energies and short optimization times were predicted to be the safer and more suitable photo acceptors in solar cells.

The development of OSCs will allow for new breakthroughs for solar cells through advantages such as being more lightweight, flexible, semitransparent, having lower manufacturing costs, short energy payback times, and comparatively lower negative impacts.

In this paper, optical properties and constants of isotropic thin P3HT:PC61BM film systems were considered for absorption of the light.

1. We assessed the thermodynamical and stereochemical safety of several types of photovoltaic fullerene derivatives that could be used as electron acceptors.

2. The efficiency of the presented molecules were determined by assessing their thermodynamic stability, and surface functionalization was studied to determine its effects on the the stereochemistry of the molecules.

3. Fullerene complexes that were optimized in a relatively short period of time were also predicted to be more thermodynamically stable, as short optimization times generally equate to spontaneous converging.

4. Fullerene complexes that had greater optimization energies were predicted to react faster and have lower activation energies, due to their higher enthalpies.

5. These results can contribute to future scientists considering using fullerenes as semiconductors in solar cells and in processing methods which could use this information to make judgements on which processes to use for certain fullerenes and functional groups.

6. Refractive index, relative permittivity (dielectric constants), wavelength, etc. were considered to check the contour of solar energy in the layer.

7. Also the geometrical properties such as thickness and width, and material properties were considered to check those dependencies.

8. Solar cell is a photovoltaic cell which produces electricity in the photoactive layer from sunlight by the photovoltaic effect and various conductive organic polymers can be used for light absorption and charge the cell.

There are many ways the P3HT:PC61BM can be used for other optical purposes as well as solar cell analysis. With further research, these layers can be used to create appliances such as micro nano scaled solar cell or bioseonsors. Although, it was once only a theoretical structure that could capture solar energy above the absorption limit through the use of the various refractive index, scientists are now one step closer in producing super solar battery.

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