

**PCBM BASE ACCEPTOR MATERIAL FOR ORGANIC SOLAR CELL
APPLICATION- A DFT STUDY**

*Submitted in partial fulfillment of the requirements for the award of bachelor of science in
chemistry*

by

S. SANTHIYA (Reg.NO.40030031)

G. SIVARAJAN (Reg.No.40030033)



**DEPARTMENT OF CHEMISTRY SCHOOL
OF SCIENCE AND HUMANITIES**

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NAGAR, RAJIV GANDHI SALAI,

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of
SANTHIYA.S (Reg.no.40030031), SIVARAJAN.G(Reg.No. 40030033) who carried out the project entitled "**PCBM BASE ACCEPTOR MATERIAL FOR SOLAR CELL APPLICATION- A DFT STUDY**" under my supervision from
August 2022 to April 2023.

Amirita Paul

GUIDE
Dr. AMIRTA PAUL Ph.D.
ASSITANT PROFESSOR
DEPARTMENT OF CHEMISTRY

J. Karthikeyan
HEAD OF THE DEPARTMENT
HOD CHEMISTRY
SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Jeevan Nagar, Rajiv Gandhi Salai
Chennai - 600 119

Submitted for Viva voce Examination held on

08-05-2023

Ramish

Internal Examiner

V. Indhu

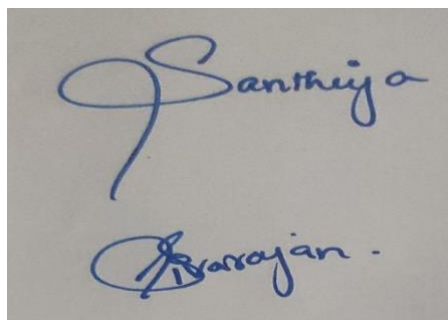
External Examiner

DECLARATION

We ,SANTHIYA.S (Reg.No. 40030031), SIVARAJAN.G (Reg.No. 40030031), hereby declare that the project Report entitled “**PCBM BASE ACCEPTOR MATERIAL FOR SOLAR CELL APPLICATION- A DFT STUDY**” done by us under the guidance of **Dr. AMIRTA PAUL Ph.D.**, Associate Professor, Department of Chemistry, Sathyabama Institute of science and Technology is submitted in partial fulfilment of the requirements for the award of Bachelor of Science degree in Chemistry.

DATE: 08.05.2023

PLACE: CHENNAI

The image shows two handwritten signatures in blue ink on a light-colored background. The top signature is 'Santhiya' and the bottom signature is 'Sivaraajan'.

SIGNATURE OF THE CANDIDATES

**S. SANTHIYA
G. SIVARAJAN**

ACKNOWLEDGMENT

I am pleased to acknowledge by sincere thanks to Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

I convey my thanks to **Dr. Rekha Chakravarthi**, Assistant Professor and Dean, School of Science and Humanities and **Dr.J.KARTHIKEYAN**, Head of the Department, Department of Chemistry for providing me necessary support and details at the right time during the progressive reviews.

I would like to express my sincere and deep sense of gratitude to my project guide to my Project Guide **Dr. AMIRTA PAUL** for his valuable guidance, suggestions and constant encouragement which paved way for the successful completion of my project work.

I wish to express my thanks to all teaching and non-teaching staff members of the Department of Chemistry who were helpful in many ways for the completion of the project.

S.SANTHIYA

G. SIVARAJAN

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LIST OF ABBREVIATION

S.NO	ABBREVIATION	EXPANSION
1.	OSC	Organic solar cell
2.	TiO ₂	Titanium Oxide
3.	DFT	Density Functional Theory
4.	HOMO	Highest Occupied Molecular Orbital
5.	LUMO	Lowest Unoccupied Molecular Orbital
6.	IR	Infra Red
7.	UV-vis	Ultra Violet-visible
8.	JSC	Short Circuit Current
9.	VOC	Open Circuit Voltage
10.	BHJ	Bulk heterojunction
11.	PCE	Power conversion efficiency

CHAPTER 1

INTRODUCTION:

Solar cell is a device which converts the solar radiation into current. Electronic revolutions that happened in the last fifty years led to increase in energy demand which was satisfied by using non-renewable energy resources. This caused depletion of fossil energy resources and increased greenhouse gas emission which induced global warming and sudden natural calamities. To avoid this, we had to switch to an eco-friendlier renewable energy resource, the solar energy. To harvest this energy, we use the solar cell. Thus, solar cell will play a key role in control of environmental deteriorations.

It's said that using a WWS (wind water sun) system ~3,800,000 5 MW wind turbines, ~49,000 300 MW concentrated solar plants, 40,000 300 MW solar PV power plants, ~1.7 billion 3 kW rooftop PV systems, 5350 100 MW geothermal power plants, 270 new 1300 MW hydroelectric power plants, 720,000 0.75 MW wave devices, and ~490,000 1 MW tidal turbines can power a 2030 WWS world that uses electricity and electrolytic hydrogen for all purposes.

The solar cell is in the form of p-n junction. The light that is incident on the solar cell gets absorbed by the solar cell when it has a certain wavelength -the visible light with longer wavelength (those that have less photon energy) are more efficient with photovoltaic cells than ones that have shorter wavelength and is more energetic thus red light produces more electricity than other colors. The absorbed solar energy interacts with the constituents of the semiconducting part of the solar cell. As a result, holes and electrons are formed these are known as minority charge carriers these move to their respective electrodes. The flow of these electrons results in production of electricity

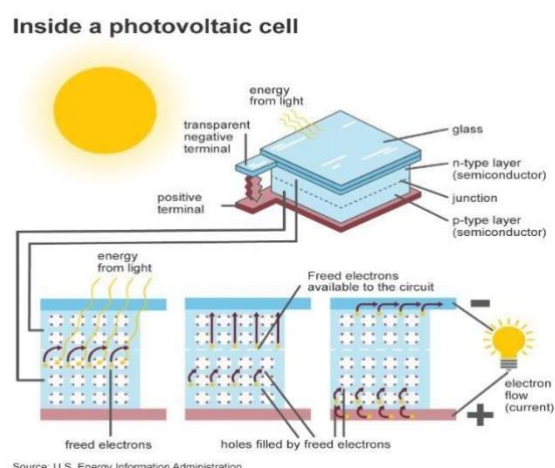


FIG 1

The polymer solar cell has gained a lot of attention in recent days because of the following factors first its active layer is between 150 and 200 nm thick, resulting in a significantly lower use of materials compared with a traditional silicon solar cell. Second the use of cheap, abundant materials like plastics and aluminium and the possibility of processing the active material using existing cost-effective and low-energy printing or coating techniques results in a significantly lower price than silicon-based solar cells and less environmental impact. Thirdly the polymer solar cell has environmental advantages compared with other solar cells. Lastly compared with silicon-based solar cells the production is more energy efficient, and they do not have the problems with heavy metals and chemicals that other (nano) solar thin films have.

The polymer solar cell is a layered structure consisting of three main layers

- i. A transparent front electrode,
- ii. An active layer (which is the actual semiconducting polymer material) and
- iii. A back electrode printed onto a plastic substrate

Polymer solar cells are classified on the basis of the active layer preparation into mono layer, bilayer, BHJ, tandem, and inverted solar cells

For every polymer solar cell except monolayer, we need a donor and an acceptor for the donor layer conjugated polymer or small molecule is most widely used and for acceptor layer polymer, small molecule, perylene diimide, and fullerene derivatives are extensively used.

The ultrafast photo-induced electron transfer from polymer to fullerene, low cost, light weight, large- area application, semitransparency, new market opportunities (e.g., wearable PV) resulted in the flourish of OSCs. Extensive research on the Power conversion efficiency (PCE) has led to development of highly efficient bulk heterojunction (BHJ) single and multijunction organic solar cells with PCEs > 15%. This has been achieved through the development of new photoactive materials, interfacial modification and device architecture design. The limited solubility of pristine C60 showed the lower performance in OSCs, hence, it is compulsory to find soluble fullerene derivative for efficient OSCs. This paves the way for the synthesis of new fullerene derivatives, such as PC61BM, which is highly soluble in aromatic solvents, and efficient electron acceptor than the pristine C60. In OSCs, P3HT polymer and PC61BM are most widely used donor and acceptor respectively.

To commercialize the low cost oscs, PCE should be improved. The PCE can be improved by tailoring the donor and acceptor material with the wide and strong absorption in UV–vis to NIR region, appropriate energy levels, material miscibility, improved charge transporting properties, open circuit voltage (V_{oc}), fill factor (FF) and short circuit current density (J_{sc}). By doing these numerous functionalized fullerene derivatives have been reported with improved efficiency.

In recent past, Chen et al. reported a record high PCE of ~10% for a single junction BHJ OSCs, which was obtained for the PTB7-Th polymer with PC71BM ([6,6]-phenyl-C71-butyric acid methyl ester) acceptor. Similarly small molecule based single-junction BHJ-OSCs with PC71BM reached a record high PCE of ~10%. In the case of tandem solar with PC61BM and PC71BM as acceptor layers reached PCE of ~15%. Similarly, fullerene free bilayer and BHJ solar cell based on small molecule and PCDTBT polymer acceptors showed an improved efficiency of ~8.4% and ~10% respectively. Heliatek achieved the highest certified efficiency of ~12% in December 2013, for a multi-junction solar cell. Though, some highly conjugated n-type polymers, and small molecules performed better than the fullerene derivatives, but PC61/71BM acceptors still the cornerstone of all fullerene derivatives.

In recent years a lot of research has been done to increase the PCE of the BHJ-OSCs but majority of them focuses on the optimization of donors therefore less attention has been given to fullerene-based acceptor materials. Although fullerene derivatives have been widely used, the structural optimization still to be needed to increase the compatibility with the P3HT donors. Bearing in mind the importance of fullerene as an acceptor we have done a systematic study of fullerene modified derivatives that have high PCE and those that have low PCE. The structures of the modified fullerene derivatives that has been taken from [1] was optimized using Gaussian software and the calculations were done. This study will be of use for future researches based on fullerene derivatives as an acceptor for BHJ-OSCs.

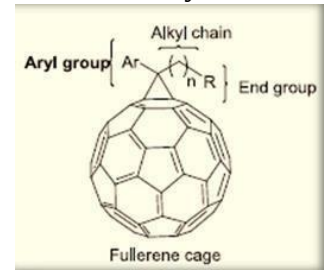
1.2. FULLERENE

Fullerene is the third stable allotrope of carbon it is also called as Buckminster fullerene is any of a series of hollow carbon molecules that form either a closed cage (“buckyballs”) or a cylinder (carbon “nanotubes”). Which was first discovered in 1985 by Sir Harold W. Kroto of the United Kingdom and by Richard E. Smalley and Robert F. Curl, Jr., of the United States. They obtained these cage-like molecules composed of 60 carbon atoms (C_{60}) joined together by single and double bonds to form a hollow sphere with 12 pentagonal and 20 hexagonal faces with 60 bonds out of these 30 conjugated double bonds by vaporising graphite using laser in an atmosphere of helium gas. Higher fullerenes like C_{70} , C_{74} , C_{76} , C_{78} , C_{80} , C_{82} , C_{84} , and etc., are also present in the fullerene family.

2.1. FULLERENE MODIFICATIONS

We have used basic fullerene derivatives that has been modified in three different ways for the study

- i. Modifications on the aryl group
- ii. Modifications on the alkyl chain length and
- iii. Modifications on the end group



SOURCE [1] FIG 2.

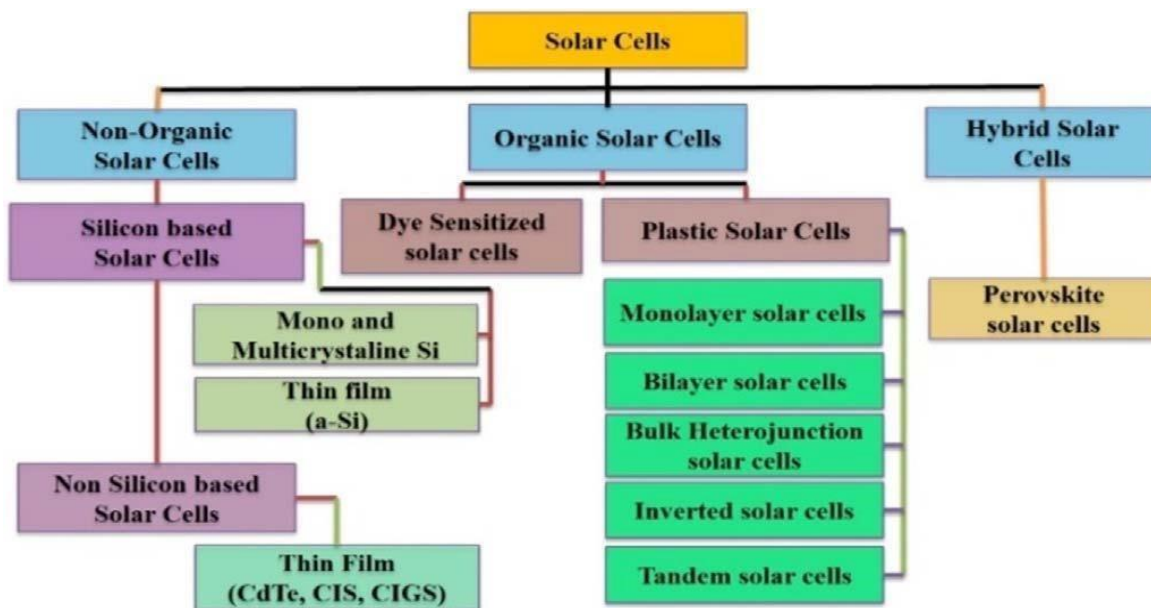
applications

Fullerene based acceptors for efficient bulk heterojunction organic solar cell

Ramasamy Ganesamoorthy, Govindasamy Sathiyam, Pachagounder Sakthivel

1.3. CLASSIFICATION OF SOLAR CELLS

Solar cells are mainly classified into three types non-organic based solar cells, organic based solar cells and hybrid solar cell which is made by a mixture of organic and inorganic materials.



(SOURCE [1]) FIG 3

1.3.1 Non-organic solar cells

These are made by silicon or non-silicon-based materials. Silicon based solar cells are significant due to its higher efficiency and market availability. Pure silicon single crystal or multi crystals are used in the preparation of silicon based solar cells.

1.3.1.1 Single crystal Si solar cells

The single crystal silicon solar cell plays an important role in the solar cell market due to its high PCE than other silicon solar cell. But it was very costly and high energy was needed for the production of good quality single crystals without any imperfections. This was later rectified by the amorphous or thin film inorganic solar cells, but the performance of the device was comparatively very low due to imperfection 1.3.1.2. Thin film solar cells

Even though it is lightweight and cost effective its performance is lower than the crystalline solar cells.

Amorphous silicon solar cells are most often used in scientific calculators, and garden lamps. Cadmium telluride (CdTe), copper indium gallium diselenide (CIGS), amorphous thin-film silicon, and etc., are commercially available thin film solar cells.

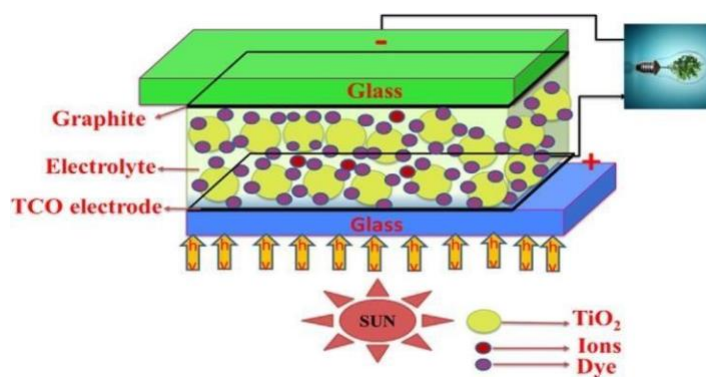
1.3.2 Organic solar cell

Emerging organic solar cells are called as third generation photovoltaic cells because, these materials are the latest entry into the solar cell field. Third generation cells are classified into several types such as, 1.3.2.1.

Dye sensitized solar cell (DSSC)

The working of DSSC is as follows

- i. Light absorption and excitation of an electron.
- ii. Electron transfer (diffusion) from dye to the valence band of the metal electrode TCO/ITO
- iii. Diffusion of electron to the TiO_2
- iv. Electron moves towards the rheostat
- v. The electron reaches the conduction band of iodine
- vi. The redox step here I_3^- is converted into 3I^- or reduction of iodine at the counter electrode
- vii. Diffusion in the electrolyte and regeneration of the oxidized dye.



(Source [1]) DSSC's systematic diagram FIG 4

1.3.2.2. Polymer or plastic solar cells

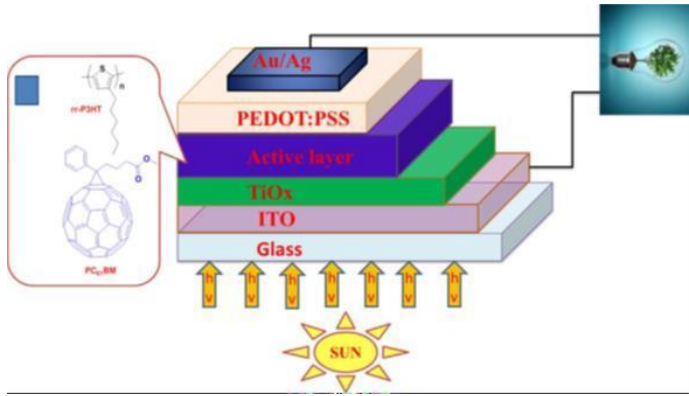
They are classified into five types based on device fabrication methods,

- i. Monolayer solar cells
- ii. Bilayer solar cells
- iii. BHJ solar cells
- iv. Inverted solar cells
- v. Tandem solar cells

1.3.2.2.1 Monolayer solar cell

The Monolayer solar cell is the starting point of the OSCs. Either electron donating or electron accepting material is sandwiched between high and low work function electrodes. When the light strikes on the active layer it emits an electron to the surface of the electrode. Due to lower absorption, it excites a small fraction of the electron hence it reduced the overall performance below 1%. In recent days enormous improvement has come in the single layer solar cells, various single layer materials are used in the solar cells, which showed the PCE less than 2% This difficulty was further rectified by bilayer solar cells.

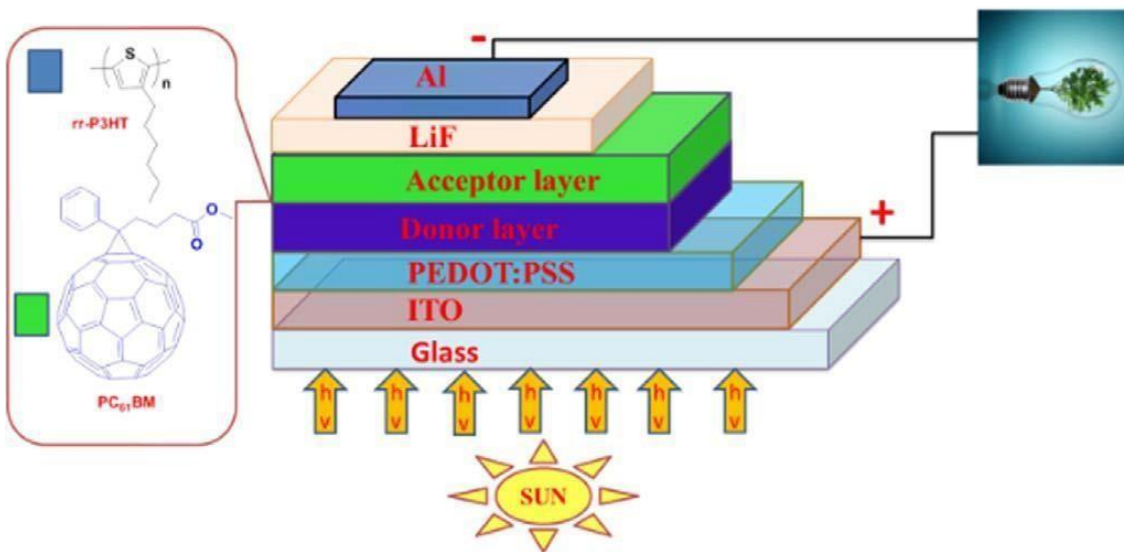
the
glass
and



1.3.2.2.2. Bilayer solar cell

Bilayer solar cells are prepared by coating the electron donating p-type layer and electron accepting n-type layer one after another over PEDOT: PSS (poly-3,4-ethylenedioxythiophene: polystyrene sulfonate) modified ITO (indium tin oxide) electrode. In the bilayer solar cells both, donor acceptor units are present in the active layer, which improved the absorption efficiency of

the OSCs. Though improved absorption and PCE than mono layer, the interfacial area between the donor and acceptor is very low, which limits the generation of exciton this defect was rectified by the BHJOSCs device structure.



(SOURCE [1]) Bilayer OSCs schematic diagram FIG 5

1.3.2.2.3. BHJ solar cell.

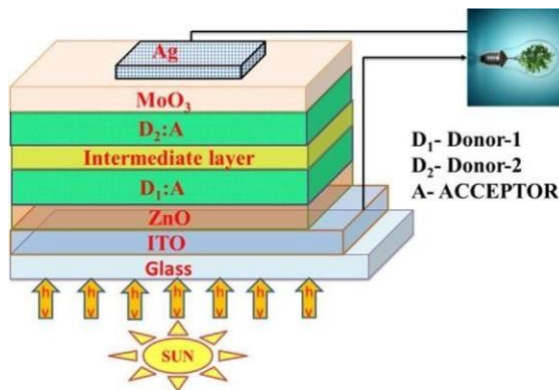
In the BHJ device a blend or mixture of donor and acceptor molecules in same or different solvents were used to form a bi-continual layer. Bicontinuous three-dimensional interpenetrating network yielded an increased D-A interface, which is the necessary criteria for the effective exciton dissociation. Main difference between the traditional bilayer, and BHJ is the wide area of interfacial layer between the active layer materials.

1.3.2.2.4. Inverted solar cell.

The long-time applicability of conventional solar cells is not possible due to the damage caused by the oxygen and moisture in the air to the electrodes which was rectified by the inverted device structure. In the new inverted device structure, high work function metal or metal oxides are used as a cathode which is the top electrode and the low work function metal is used as an anode. The inverted OSCs configuration not only achieved an impressive PCE of ~10.08%, but also exhibited an exceptional device lifetime without any external coating.

1.3.2.2.5. Tandem solar cell

Multijunction or tandem solar cells are two or more solar sub cells connected in series manner. The tandem organic solar cells high theoretical PCE of ~20% which is with the conventional inorganic solar cells, of the tandem solar cell was expensive techniques.



prepared by or parallel showed very comparable main drawback manufacturing

(SOURCE [1]) Tandem OSCs schematic

diagram. FIG 7

1.3.3. Hybrid solar cells

Pure organic solar cell maximum PCE is ~12%, but for the commercial device, it is less than the ~3%, but in the case of inorganic solar cell it is reversible, hence several scientific groups tried in a different way to improve the efficiency of solar cell, so they combined inorganic and organic solar cells and constructed a new device called hybrid solar cells, targeting a better power conversion efficiency in these hybrid systems.

1.3.3.1. Perovskite solar cells

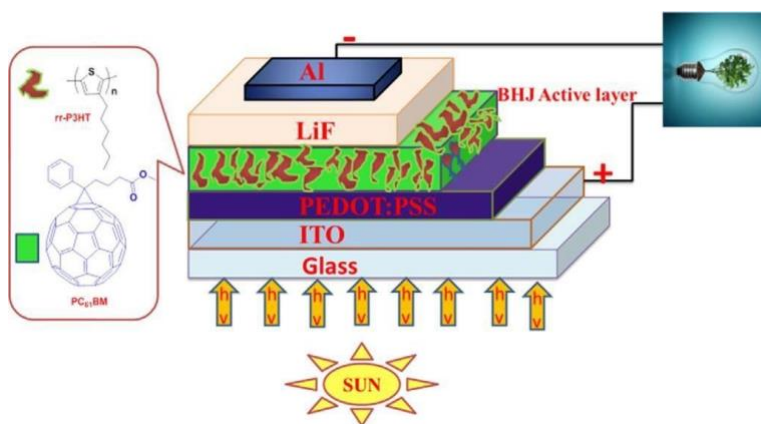
The main competitor to the inorganic solar cell was the Perovskite solar cell due to higher potential to produce comparable PCE with the conventional inorganic solar cells. Solar cell applicable Perovski mineral is a crystal made of calcium titanium oxide. General molecular formula of Perovskite solar cell material is ABX_3 , where A and B are cations coordinate with 12 and 6 'X' anions, which resulted in the formation of cuboctahedral and octahedral geometries respectively with identical crystal structure with calcium titanate.

1.1.4. WORKING OF BHJ-OSCs

The structure consists of a blend of P3HT donor and PC61BM was sandwiched between the PEDOT: PSS coated high work function electrode (anode) and low work function electrode (cathode).

The manner in which is a BHJ-OSC works is as follows

- Absorption of light by the photoactive layer
- Excitation of electrons from HOMO level of either acceptor or donor to LUMO level by sunlight absorption process. This results in the creation of exciton which is electrostatically bond hole and electron pair
- Diffusion of exciton to the D-A interface.
- Disassociation of exciton into electron and hole
- The separated electron and hole will move towards their corresponding electrodes.



(SOURCE [1]) BHJ-OSCs schematic diagram.

1.4 DENSITY FUNCTIONAL THEORY:

Density-functional Theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (or nuclear structure) (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. Using this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function. In the case of DFT, these are functionals of the spatially dependent electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry.

DFT has been very popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. Computational costs are relatively low when compared to traditional methods, such as exchange only Hartree–Fock theory and its descendants that include electron correlation.

Density functional theory (DFT) calculations were applied to estimate the molecular geometry, electronic distribution of frontier molecular orbitals (HOMO and LUMO) and optical specification.

1.4.1 First principle of DFT:

The major advantage of this approach is transition from a wave function, depending on the coordinates of all electrons to a charge density depending on three spatial coordinates only.

1.4.2 What problems does DFT solve?

Atomistic modeling in general, and DFT calculations in particular, provide significant value to researchers and scientists working with chemicals, electronic materials, etc., in two distinct ways:

1. Since it can handle essentially any element in the periodic table in any kind of atomic arrangement, without the need for experimental input parameters, DFT has strong predictive power, even for completely new molecules or materials. In this way, atomistic simulations can reduce development time and cost by down-selection of promising material candidates prior to going into the lab and dealing with expensive and possibly hazardous chemicals with unknown properties and behavior. Using high-performance computer (HPC) clusters, a single person can screen hundreds or even thousands of materials in parallel, vastly outnumbering the number of experiments a human can perform at the same time.

2. Second, DFT calculations are used to help understand how materials and devices behave and operate under different conditions. A trained DFT user can correlate measurement data with simulation results to draw conclusions about the physical origin of certain effects observed in the material or device, but which cannot readily be explained with simple models. Such insight is crucial in order to fully exploit the effects and material in question, and even more so in order to, for instance, scale down device dimensions or optimize material choices or process conditions.

Thus, thanks to its predictive capabilities and atomistic quantum-mechanical nature, DFT is a crucial tool for technology pathfinding, to explore novel materials and exotic physical phenomena, years prior to a first test device being manufactured or even before new material has been fully characterized experimentally!

1.5 ACCURACY CONSIDERATIONS:

A DFT calculation adds an additional step to each major phase of a Hartree-Fock calculation. This step is a numerical integration of the functional (or various derivatives of the functional). Thus in addition to the sources of numerical error in Hartree-Fock calculations (integral accuracy, SCF convergence, CPHF convergence), the accuracy of DFT calculations also depends on the number of points used in the numerical integration.

CHAPTER 2

LITERATURE SURVEY Ethan fullerenes Used as Electron Acceptors in MPolymer Photovoltaic Devices

(Liping Zheng, Qingmei Zhou,Xianyu Deng,Min Yuan,Gang,Yong Cao)

* The results indicates that both interfacial properties of the two phases(donor and acceptor) and mobility of electrons and holes within corresponding phases play an important role in the efficiencies of PV cells.

* This study revealed that methanofullerenes [6,6]-phenyl C₆₁-butyric acid butyl ester,PCBM,possesses better photosensitivity than the PCBM

Material Solubility-Photovotaic Performance Relationship in the Design of Novel Fullerene Derivatives for Bulk Heterojunction Solar cells

(Y Pavel A, Troshin,*Harald Hoppe,Joachim Renz, Martin Egginger,Julia yu,Mayorova,Andrey E.Goryachev,Alexander S,Peregudov, Rimma N. Lyubovskaya, Gerhard Gobsch,N.Serdar Sariciftci,Vladimir F.Razumov)

*It is concluded that the best material combinations are those where donor and acceptor components are of similar and sufficiently high solubility in the solvent used for the deposition of the active layer.

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

To find out the efficiency of solar cell using PCBM base acceptor material for organic solar cell application.

3.2 SCOPE:

Our department has installed a new Gaussian software which is used for the computational chemistry studies. In this regard, our work focuses on finding the efficiency of solar cell using it on the fullerene as an acceptor. In which this solar cell can also be called as the organic Solar Cell .

3.3 OBJECTIVE OF THE STUDY:

1. Selection of fullerene structures and optimizing the corresponding structures in Gaussian software.
2. Finding HOMO–LUMO using Gaussian software
3. The final results are calculated and discussed for finding out the efficiency of solar cell.

CHAPTER 4 METHODS OF COMPUTATION

4.1 GAUSSIAN SOFTWARE:

Gaussian is a computer program used by chemists, chemical engineers, biochemists, physicists and other scientists. It utilizes fundamental laws of quantum mechanics to predict energies, molecular structures, spectroscopic data (NMR, IR, UV) and much more advanced calculations. It is released in 1970 by John Pople and his research group at Carnegie Mellon university as Gaussian70. It has been continuously updated since then and Gaussian16 is the latest version in the Gaussian series of programs. It provides state of the art capabilities for electronic structure modelling. Gaussian16 is licensed for a wide variety of computer system.

4.1.1 *What is new in Gaussian?*

Gaussian6 offers new features and performance enhancements which will enable you to model molecular systems of increasing size, with more accuracy under a broad range of real world conditions. Some of these features include.

- Model reactions of very large system with ONIOM
- Study excited state in the Gas Phase and in solution
- Additional spectra prediction
- New and enhanced methods and algorithm
- Ease of use features
- Performance improvements

4.1.2 *Advanced calculations using Gaussian6*

† Comprehensive Investigations of molecules and reactions:

Predict the structures of transition states and verify that the located stationary points are in fact minima and transition states. You can go on to compute the reaction path following the intrinsic reaction path by following the Intrinsic Reaction Coordinate (IRC) and determine which reactants and products are connected by a given transition structure.

4.1.3 *Explore diverse chemical arenas:*

Gaussian 6 offers a variety of very accurate energy methods for predicting accurate energy methods for predicting thermochemical quantities, photochemistry and other excited states processes and

solvent effects can be taken into account when optimizing structures and predicting most molecular properties.

4.2 Mulliken Population Analysis:

Mulliken atomic charges of the optimized crystal structure were carried out by B3LYP method in gas phase. The Mulliken atomic charges on carbon atoms were exhibited either positive or negative value. All hydrogen atoms were displayed a net positive charge, but H16 was gained maximum positive charge than the other hydrogen atoms, due to the presence of electronegative atom (N13). They act as acceptor atoms. Besides, all oxygen atoms of the optimized compound were shown to have negative charge, which act as donor atoms.

4.3 Frontier Molecular Orbitals:

The highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, of a molecule are called the frontier orbitals. It was Fukui who first noticed the prominent role played by HOMO and LUMO in governing chemical reactions. The positive phase is represented in red colour and the negative phase is represented in green colour.

The energy gap of HOMO–LUMO explains the charge transfer interaction within the molecule. The HOMO–LUMO analysis for fullerene structure. If there is large gap indicates that charge transfer is taking place within the molecule. The energy gap measures the kinetic stability of the molecules. A large gap implies high stability and small gap implies low stability. The high stability in turn indicate slow chemical reactivity and small gap indicates high chemical reactivity. A molecule having higher Soft value is more reactive than a molecule having smaller Soft value. In general, it can be said that the increase in softness increases chemical reactivity and increase in hardness decreases chemical reactivity. The energy gap between HOMO and LUMO has been used to prove the large efficiency of the molecule. More gaps also indicate that the molecule is less polarised and is known as hard molecule and it implies high stability being less chemical reactivity.

CHAPTER 5

RESULTS AND DISCUSSION

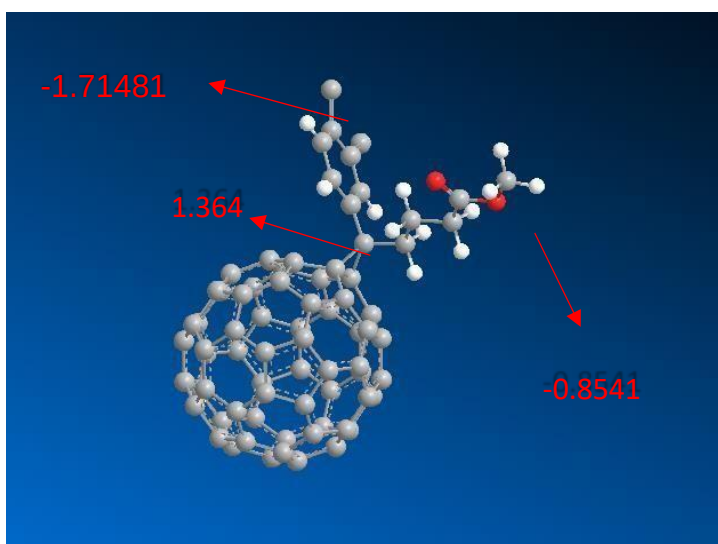
5.1 CHARGE CALCULATION:

The main objective of the work is achieved only by doing the charge calculation, where the fractional charges of the fullerene are considered for calculation.

The charge differences of each molecule are mentioned below.

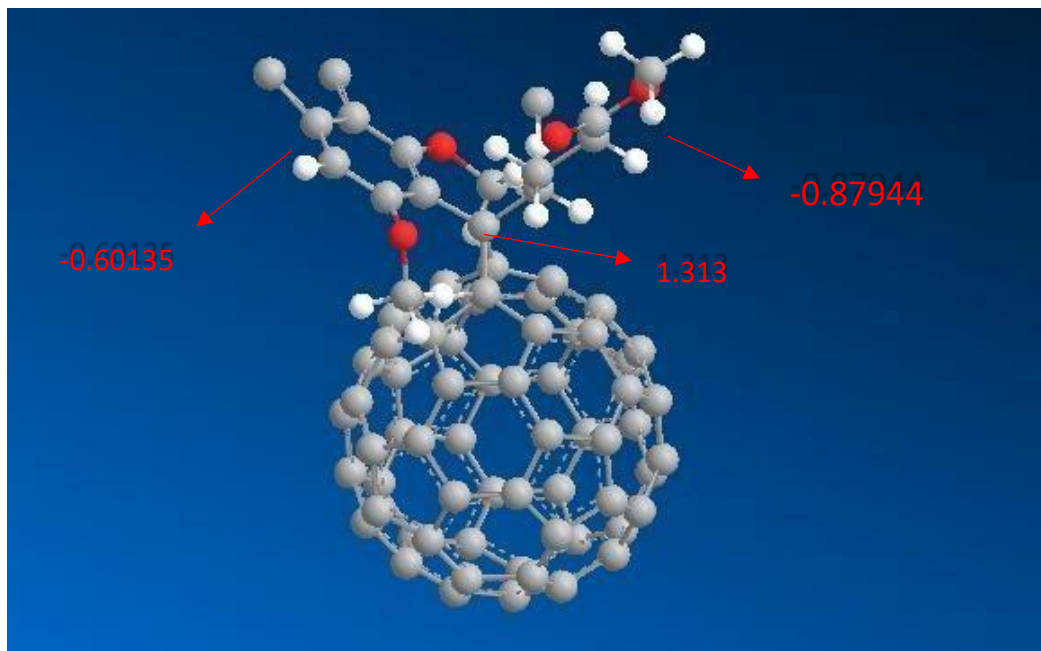
5.1.1 Fraction charge of structure 1

The fraction charge will be different for different ligand. This change is due to the change in electronic environment. The fraction charge value of C61 carbon is 1.364, The fraction value of Aryl group is -1.71481 and The fraction value of End group is -0.8541. End group different from aryl group that has been modified and its result increase in value.



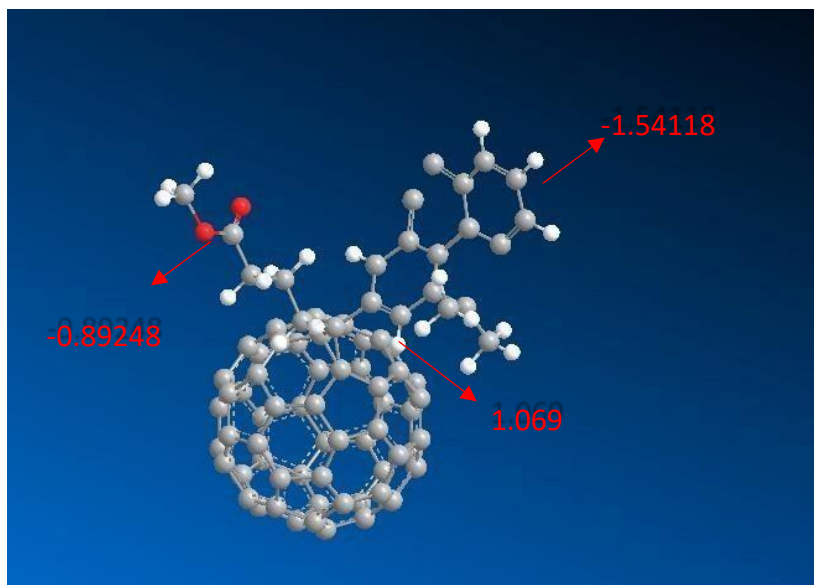
Fraction Charge structure 2:

The fraction charge will be different for different ligand. This change is due to the change in electronic environment. The fraction charge value of C₆₁ carbon is 1.313, The fraction value of Aryl group is -0.60133, and The fraction value of End group is -0.879442. End group different from aryl group that has been modified and its result increase in value.



Fraction Charge structure 3:

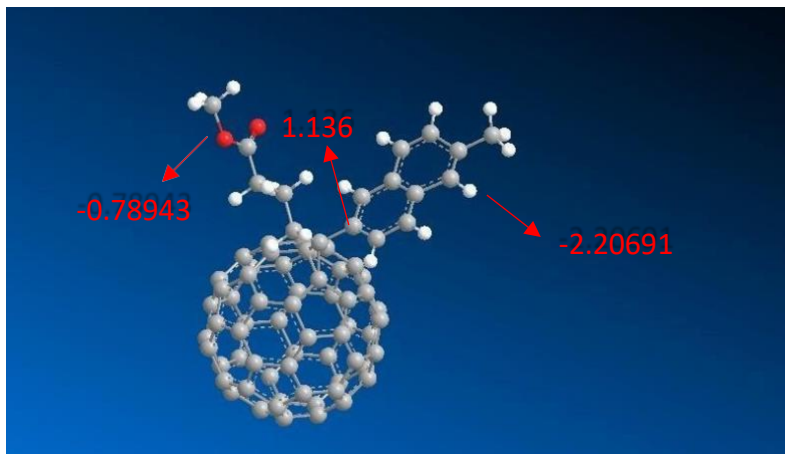
The fraction charge will be different for different ligand. This change is due to the change in electronic environment. The fraction charge value of C61 carbon is 1.069, The fraction value of Aryl group is -1.54118 and The fraction value of end group is -0.89248. End group different from aryl group. that has been modified and it's result increase in value.



Fraction Charge structure4:

The fraction charge will be different for different ligand. This change is due to the change in electronic environment. The fraction charge value of C61 carbon is 1.136, The fraction value of Aryl

group is -2.20691 and The fraction value of End group is -0.78943.Chain group different from aryl group.that has been modified and it's result increase in value.



5.2 Mulliken Charges:

Since only the neutral molecules can opt for the chemical reactions, the molecules which we have taken are analyzed by Mulliken charges which gives the value zero while calculating the overall charges, this also serves as evidence that our molecules are neutral.

Mulliken charges:		
1		
1	C	0.162716
2	C	0.071488
3	C	-0.098790
4	C	0.040407
5	C	-0.161367
6	C	0.069900
7	C	-0.101036
8	C	0.166653
9	C	-0.009849
10	C	-0.017678
11	C	-0.115910
12	C	0.183591
13	C	0.101052
14	C	-0.143982
15	C	-0.009590
16	C	-0.044249
17	C	0.077726
18	C	-0.250604
19	C	0.013321
20	C	0.193549
21	C	-0.251699
22	C	0.243159
23	C	-0.002624
24	C	0.130967
25	C	-0.013799
26	C	-0.158456
27	C	0.149550
28	C	-0.028039
29	C	0.241776
30	C	-0.216380
31	C	0.163206
32	C	0.141367
33	C	-0.024805
34	C	-0.319407
35	C	0.316287
36	C	-0.021488
37	C	0.013910
38	C	0.072601
39	C	-0.148527
40	C	0.072228
41	C	0.121202
42	C	0.131109
43	C	0.160885
44	C	-0.037903

43	C	0.160885
44	C	-0.037903
45	C	-0.063902
46	C	-0.118061
47	C	0.116716
48	C	0.081781
49	C	0.130699
50	C	-0.208570
51	C	0.080753
52	C	-0.166052
53	C	0.334574
54	C	-0.320319
55	C	0.038630
56	C	-0.018704
57	C	-0.138304
58	C	0.029245
59	C	0.023060
60	C	-0.176915
61	C	1.364894
62	C	0.426171
63	C	-0.503821
64	C	-0.466012
65	C	-0.426797
66	C	-0.507759
67	C	-0.088531
68	C	-0.471857
69	C	-0.575283
70	C	-0.816204
71	C	0.127194
72	O	-0.275235
73	O	-0.134694
74	C	-0.191199
75	H	0.125672
76	H	0.139359
77	H	0.128188
78	H	0.141236
79	H	0.151902
80	H	0.182535
81	H	0.179996
82	H	0.177910
83	H	0.179374
84	H	0.152154
85	H	0.159094
86	H	0.159187
87	H	0.128851
88	H	0.126577

Sum of Mulliken charges = -0.00000

Mulliken charges:		
1		
1	C	0.086716
2	C	0.110816
3	C	-0.064504
4	C	0.020135
5	C	-0.123227
6	C	0.068160
7	C	-0.099403
8	C	0.099409
9	C	-0.046456
10	C	0.067827
11	C	-0.176702
12	C	0.099058
13	C	0.083076
14	C	-0.218630
15	C	0.038431
16	C	0.002051
17	C	0.030668
18	C	-0.199043
19	C	-0.031052
20	C	0.206767
21	C	-0.142334
22	C	0.010320
23	C	-0.014383
24	C	0.081688
25	C	0.040821
26	C	-0.185970
27	C	0.083849
28	C	-0.013858
29	C	0.208162
30	C	-0.147451
31	C	0.206204
32	C	-0.047860
33	C	0.354554
34	C	-0.366122
35	C	0.168206
36	C	-0.104000
37	C	0.053786
38	C	-0.004522
39	C	-0.130002
40	C	0.075686
41	C	0.106746
42	C	-0.147621
43	C	0.041642
44	C	-0.188684
45	C	0.293516

50	C	-0.283155
51	C	-0.008418
52	C	-0.123799
53	C	0.155430
54	C	-0.256010
55	C	0.079941
56	C	0.052392
57	C	-0.161732
58	C	0.008303
59	C	0.259824
60	C	0.062266
61	C	1.313439
62	C	-0.141707
63	C	0.027605
64	C	0.105573
65	C	-0.361668
66	C	-0.322798
67	C	-0.529622
68	C	-0.326063
69	C	-0.434529
70	C	-0.859524
71	C	-0.144030
72	O	-0.003891
73	O	-0.062555
74	H	0.122033
75	H	0.131930
76	H	0.152515
77	H	0.147990
78	H	0.146764
79	H	0.139900
80	H	0.141157
81	C	-0.242945
82	H	0.150420
83	H	0.177085
84	H	0.163321
85	C	-0.284621
86	H	0.167492
87	H	0.181687
88	H	0.160130
89	H	0.129564
90	H	0.122334
91	C	-0.051081
92	H	0.137756
93	H	0.134533
94	H	0.133119
95	H	0.134058
96	H	0.135224

Sum of Mulliken charges = -0.00000

(a)

(b)

Mulliken charges:		
1		
1	C	0.100759
2	C	0.084249
3	C	-0.061134
4	C	0.034133
5	C	-0.061957
6	C	0.149852
7	C	0.096417
8	C	0.164660
9	C	-0.211791
10	C	0.043305
11	C	-0.039733
12	C	-0.070147
13	C	-0.101190
14	C	-0.042321
15	C	0.152034
16	C	0.089145
17	C	-0.105222
18	C	-0.195358
19	C	-0.037756
20	C	0.163598
21	C	-0.202837
22	C	-0.011924
23	C	0.042264
24	C	0.076697
25	C	-0.133882
26	C	-0.113812
27	C	0.182603
28	C	0.099162
29	C	-0.062425
30	C	-0.134744
31	C	-0.069415
32	C	0.110087
33	C	-0.259347
34	C	0.756960
35	C	0.006770
36	C	-0.032206
37	C	-0.069358
38	C	0.149495
39	C	0.006109
40	C	0.052435
41	C	0.071979
42	C	-0.020262
43	C	0.128569
44	C	-0.254111

64	C	-0.824365
65	C	0.108338
66	O	-0.243588
67	O	-0.117022
68	C	-0.182790
69	H	0.144160
70	H	0.199108
71	H	0.187292
72	H	0.195646
73	H	0.176294
74	H	0.177293
75	H	0.150881
76	H	0.158837
77	H	0.158198
78	C	1.563728
79	C	0.405949
80	C	-0.511494
81	C	-0.562616
82	C	-0.556407
83	H	0.175579
84	C	-0.336533
85	H	0.164270
86	C	-0.143968
87	H	0.125847
88	H	0.123422
89	H	0.127560
90	C	0.337374
91	C	-0.266569
92	C	-0.338161
93	C	-0.500206
94	H	0.145181
95	C	-0.319379
96	H	0.131217
97	C	-0.186021
98	H	0.121735
99	H	0.125008
100	H	0.126858
101	C	0.166495
102	C	-0.503786
103	C	-0.586883
104	C	-0.522437
105	H	0.171102
106	C	-0.263501
107	H	0.171090
108	C	-0.042863
109	H	0.121499
110	H	0.122414
111	H	0.123033

Sum of Mulliken charges = -0.00000

(c)

Mulliken charges:		
1		
1	C	0.151087
2	C	0.080152
3	C	-0.096088
4	C	0.032532
5	C	-0.176393
6	C	0.046144
7	C	-0.046167
8	C	0.134276
9	C	-0.063707
10	C	-0.027193
11	C	-0.120159
12	C	0.165147
13	C	0.101321
14	C	-0.147812
15	C	0.013733
16	C	-0.041908
17	C	0.079247
18	C	-0.258548
19	C	0.011730
20	C	0.172139
21	C	-0.207937
22	C	0.237274
23	C	0.008884
24	C	0.148797
25	C	0.022356
26	C	-0.135360
27	C	0.130696
28	C	0.000752
29	C	0.259163
30	C	-0.237113
31	C	0.120653
32	C	0.131091
33	C	-0.113483
34	C	-0.285187
35	C	-0.287055
36	C	0.016784
37	C	0.037320
38	C	0.077640
39	C	-0.129412
40	C	0.059011
41	C	0.146245
42	C	0.121311
43	C	0.055555
44	C	0.004316

46	C	-0.107803
47	C	0.085498
48	C	0.097707
49	C	0.164231
50	C	-0.189963
51	C	0.019137
52	C	-0.154606
53	C	0.287989
54	C	-0.278205
55	C	0.025486
56	C	0.005432
57	C	-0.123930
58	C	0.012185
59	C	0.093669
60	C	-0.294814
61	C	1.345808
62	C	0.465218
63	C	-0.534566
64	C	-0.545652
65	C	-0.380420
66	C	-0.409266
67	C	-0.132029
68	C	-0.252996
69	C	-0.590832
70	C	-0.830063
71	C	0.274114
72	C	-0.621640
73	C	-0.560587
74	H	0.125927
75	H	0.130686
76	H	0.126698
77	H	0.126065
78	H	0.128650
79	H	0.140950
80	H	0.149869
81	H	0.163830
82	H	0.138993
83	H	0.139201
84	H	0.149959
85	H	0.136581
86	H	0.138209
87	H	0.134259
88	H	0.137888
89	H	0.135853
90	H	0.140907
91	H	0.127610

Sum of Mulliken charges = -0.00000

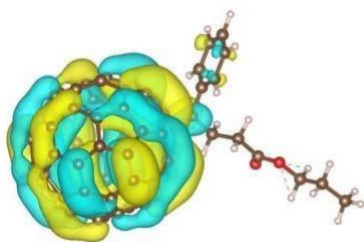
(d)

- a)- Fig.5.2.1- Mulliken charges of structure 1
- (b)- Fig.5.2.2- Mulliken charges of structure 2
- (c)- Fig.5.2.3- Mulliken charges of structure 3
- (d)- Fig.5.2.4- Mulliken charges of structure 4

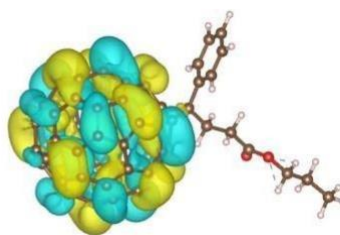
5.3 ANALYSING HOMO AND LUMO

To find the energy gap between the conduction band and valence band it is mandatory to find the HOMO and LUMO orbital present in each molecule.

STRUCTURE 1

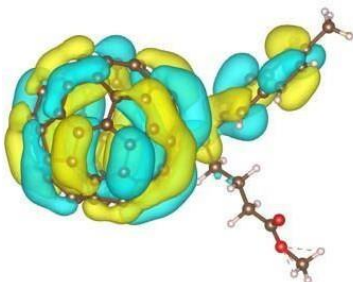


HOMO= 235

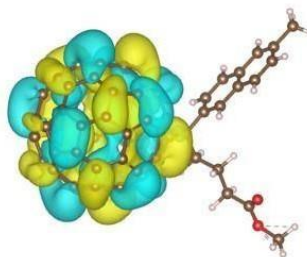


LUMO=236

STRUCTURE 2

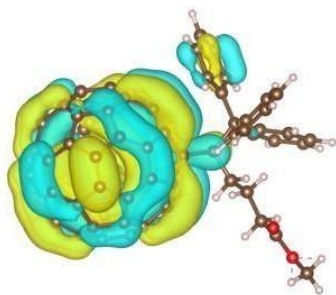


HOMO=248

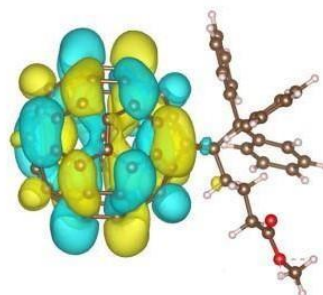


LUMO=249

STRUCTURE 3

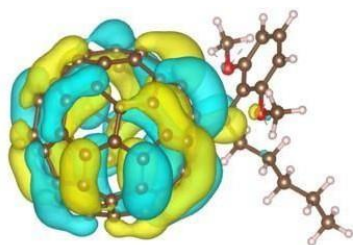


HOMO=275

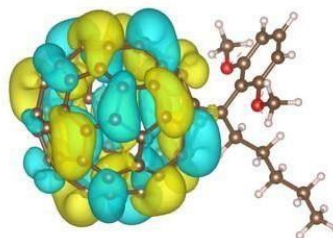


LUMO=276

STRUCTURE 4



HOMO=240



LUMO=241

5.4 ENERGY GAP :

Since we come to know the number of orbitals (HOMO, LUMO) present in the molecules, now it is the mandatory step to find out the energy gap. Once the energy gap for each azo molecule is known, then it is easy to find the amount of energy needed for the molecule. If the energy gap is more then the energy needed for the molecule also increases. Similarly, if the energy gap is less between two orbitals the energy needed for the molecules will also decrease.

The energy gap of the molecule is found by using the formula,

$$\text{ENERGY GAP} = \text{HOMO} - \text{LUMO}$$

The highest value of HOMO and the Lowest value of LUMO are taken into consideration for calculating the energy gap. For example, in a Structure 1 molecule, the highest value of HOMO is said to be -0.22428, and the lowest value of LUMO is said to be -0.13132 the difference between these two values gives the resultant energy gap as -0.09296. Likewise, the energy gap of the rest four molecules is found to be

Structure 2 molecule, the highest value of HOMO is said to be -0.21825, and the lowest value of LUMO is said to be -0.12578 the difference between these two values gives the resultant energy gap as -0.09247.

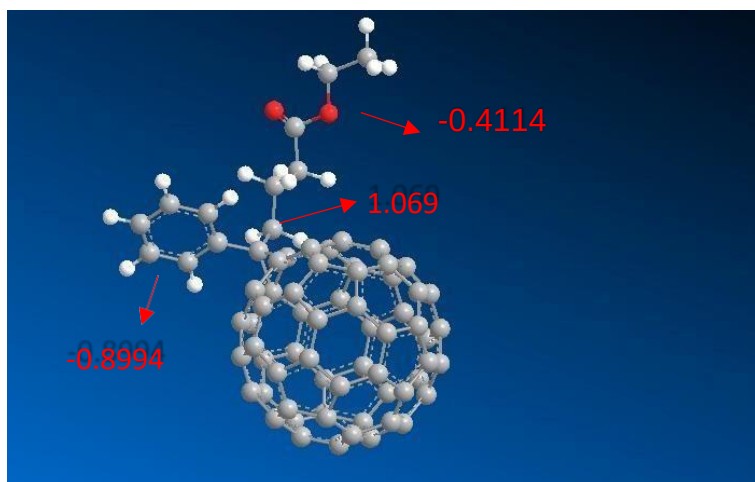
Structure 3 molecule, the highest value of HOMO is said to be -0.22188, and the lowest value of LUMO is said to be -0.12994 the difference between these two values gives the resultant energy gap as -0.09194.

Structure 4 molecule, the highest value of HOMO is said to be -0.22264, and the lowest value of LUMO is said to be -0.13043 the difference between these two values gives the resultant energy gap as -0.09221.

5.2 END GROUP MODIFICATION PCBM:

CHARGE CALCULATION

Fractional charge calculation of Structure 1:



5.2 Mulliken Charges:

Since only the neutral molecules can opt for the chemical reactions, the molecules which we have taken are analyzed by Mulliken charges which gives the value zero while calculating the overall charges, this also serves as evidence that our molecules are neutral.

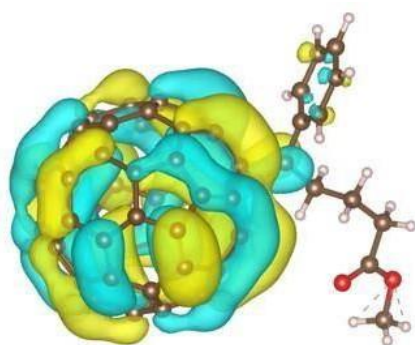
Mulliken charges:					
1			33	C	-0.048599
1	C	0.166317	34	C	-0.285624
2	C	0.088444	35	C	0.280181
3	C	-0.102586	36	C	0.014844
4	C	0.027594	37	C	0.013430
5	C	-0.174622	38	C	0.089592
6	C	0.050810	39	C	-0.092846
7	C	-0.044130	40	C	0.058628
8	C	0.178865	41	C	0.140518
9	C	-0.089545	42	C	0.088980
10	C	-0.031467	43	C	0.170277
11	C	-0.123526	44	C	-0.071575
12	C	0.159655	45	C	-0.088935
13	C	0.092076	46	C	-0.155453
14	C	-0.159619	47	C	0.069288
15	C	0.024713	48	C	0.070130
16	C	-0.043217	49	C	0.145502
17	C	0.088124	50	C	-0.135290
18	C	-0.262759	51	C	0.037662
19	C	-0.028945	52	C	-0.084637
20	C	0.127581	53	C	0.282643
21	C	-0.230496	54	C	-0.273160
22	C	0.233716	55	C	0.061052
23	C	0.025104	56	C	-0.010690
24	C	0.150620	57	C	-0.102614
25	C	0.025728	58	C	0.007862
26	C	-0.110162	59	C	0.010709
27	C	0.116676	60	C	-0.248057
28	C	0.008557	61	C	1.111945
29	C	0.256327	62	C	0.410059
30	C	-0.246272	63	C	-0.478053
31	C	0.141113	64	C	-0.534816
32	C	0.077413	65	C	-0.420099
			66	C	-0.466783
			67	C	-0.101650
			68	C	-0.554772
			59	C	0.0E10709
			60	C	-0.248057
			61	C	1.111945
			62	C	0.410059
			63	C	-0.478053
			64	C	-0.534816
			65	C	-0.420099
			66	C	-0.466783
			67	C	-0.101650
			68	C	-0.554772
			69	C	-0.479488
			70	O	-0.072513
			71	C	-0.188245
			72	O	-0.233026
			73	C	-0.042791
			74	C	-0.123592
			75	C	-0.562680
			76	H	0.128309
			77	H	0.134465
			78	H	0.128111
			79	H	0.127217
			80	H	0.129507
			81	H	0.166675
			82	H	0.174732
			83	H	0.192014
			84	H	0.187140
			85	H	0.160359
			86	H	0.160153
			87	H	0.144026
			88	H	0.144483
			89	H	0.138627
			90	H	0.146808
			91	H	0.137974
			Sum of Mulliken charges = -0.00000		

(A)

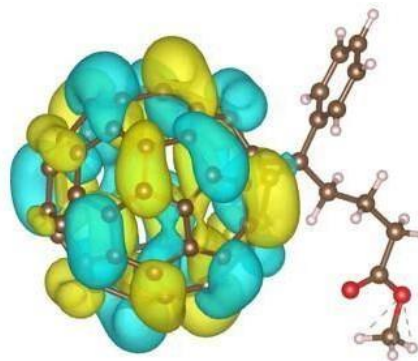
(a)- Fig.5.2.1- Mulliken charges of Structure 1

5.3 ANALYSING HOMO AND LUMO

To find the energy gap between the conduction band and valence band it is mandatory to find the HOMO and LUMO orbital present in each molecule.



HOMO=231



LUMO=232

5.4 ENERGY GAP :

Since we come to know the number of orbitals (HOMO, LUMO) present in the molecules, now it is the mandatory step to find out the energy gap. Once the energy gap for each azo molecule is known, then it is easy to find the amount of energy needed for the molecule. If the energy gap is more then the energy needed for the molecule also increases. Similarly, if the energy gap is less between two orbitals the energy needed for the molecules will also decrease.

The energy gap of the molecule is found by using the formula,

$$\text{ENERGY GAP} = \text{HOMO} - \text{LUMO}$$

The highest value of HOMO and the Lowest value of LUMO are taken into consideration for calculating the energy gap. For example, in a Structure 1 molecule, the highest value of HOMO is said to be -0.22454, and the lowest value of LUMO is said to be -0.13149 the difference between these two values gives the resultant energy gap as -0.09305.

CHAPTER 6

SUMMARY AND CONCLUSION

Organic solar cell (OSC) use an PCBM as an acceptor materials. Based on the ligand nature the nature of fullerene will change. This study shows the change in electron distribution due to the presence of different ligand attached to the C61 carbon with fullerene. Thus, discussed above, the following calculations were done;

- Molecules containing PCBM were selected and optimized using Gaussian software.
- Optimized structures are analyzed using charge calculation Based on the above data, it may be concluded that the nature of the PCBM will influence the fractional charge as well as the nature of Aryl group and End group.

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