

**High-Throughput Screening to Enhance D- π -A
Interaction in Functional Materials: Exploring the
Synergistic Effects and Applications**

BY

MUHAMMAD HAROON

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This thesis, written by **Muhammad Haroon** under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMISTRY**.

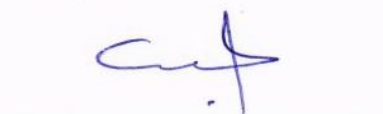


Prof. Khalid R. Alhooshani

Department Chairman



Prof. Tawfik A. Saleh
(Advisor)



Prof. Abdulaziz A. Al-Saadi
(Member)



Prof. Suliman Saleh Al-Homidan
Dean of Graduate Studies



Prof. Nisar Ullah
(Member)

Nov 30, 2022

Date



Prof. Bashir Chanbasha
(Member)



Dr. Abdulraman Al-Betar
(Member)

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Dedicated

To My Parents, Family Members, My Wife, My Daughter, My Son, and All Those Who
Supported Me at Any Stage of My Life and All Well Wishers

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LIST OF ABBREVIATIONS

OSC	:	Organic Solar Cell
LED	:	Light Emitting Diode
OPV	:	Organic Photo Voltaic
DFT	:	Density Functional Theory
TD-DFT	:	Time Dependent Density Functional Theory
NLO	:	Nonlinear Optical
CT	:	Charge Transfer
D-π-A	:	Donor- π -Acceptor
NFA	:	Non-Fullerene Acceptors
NFSMA	:	Non-Fullerene Small Molecular Acceptors
PSCs	:	Perovskite Solar Cells
A-D-A	:	Acceptor-Donor-Acceptor
FMO	:	Frontier Molecular orbital
TDM	:	Transition Density Matrix
DOS	:	Density of State
NBO	:	Natural Bond Orbital
RE	:	Reorganizational Energy

ABSTRACT

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Functional materials refer to those materials that have specific functions through the effects of light, electricity, magnetism, heat, chemistry, and biochemistry. They are not only recognized for their mechanical but also for physical, chemical, or physicochemical properties. Small external stimuli like temperature, electric and magnetic field can update their properties. Due to this reason, they are widely used in display, memory, and telecommunications. Among several types of functional materials, nonlinear optical (NLO) materials and photovoltaic materials for organic solar cells are of our interest. NLO functional materials are the materials of intense radiation and can exhibit exponential behavior of light. Solar cell functional materials are kind of photoelectric semiconductors that use sunlight to directly generate electricity and are good source of green energy.

In the present research, the influence of several donor/acceptor and π -bridging conjugated organic segments on the energy differences between local excitations and singlet as well as triplet charge-transfer (CT) states have been examined to fine tune the properties of materials by employing virtual high-throughput techniques with the help of quantum chemical calculations on variety of D- π -A molecules. All the studied compounds are excellent functional materials with efficient photovoltaic and nonlinear optical properties.

There is a significant effect on the photophysical and charge transport properties by applying strong electron acceptor or electron withdrawing group whether on the terminal acceptor moiety or by doing bridging modifications. Among five projects, first one (chapter 2) is studied for nonlinear optical response and four projects (chapter 3 to 6) are designed for photovoltaic and light absorption applications. We are hopeful that our theoretically designed compounds will be helpful for experimental scientists to synthesize the compounds with high conversion efficiency and significant light harvesting properties.

ملخص الرسالة

[الاسم الكامل: محمد هارون]

في المواد الوظيفية: استكشاف التأثيرات والتطبيقات D-π-A عنوان الرسالة: [فحص عالي الإنتاجية لتعزيز تفاعل التآزرية]

مجال التخصص: [الكيمياء]

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تشير المواد الوظيفية إلى تلك المواد التي لها وظائف محددة من خلال تأثيرات الضوء والكهرباء والمغناطيسية والحرارة والكيمياء والكيمياء الحيوية. لا يتم التعرف عليها فقط بسبب خصائصها الميكانيكية ولكن أيضاً لخصائصها الفيزيائية أو الكيميائية أو الفيزيائية الكيميائية. يمكن للمنبهات الخارجية الصغيرة مثل درجة الحرارة والمجال الكهربائي والمغناطيسي تحديث خصائصها. لهذا السبب ، يتم استخدامها على نطاق واسع في العرض والذاكرة والمواد (NLO) والاتصالات. من بين عدة أنواع من المواد الوظيفية ، تعتبر المواد البصرية غير الخطية هي مواد للإشعاع الشديد ويمكن أن NLO كهروضوئية للخلايا الشمسية العضوية موضع اهتمامنا. المواد الوظيفية تظهر سلوكاً أسياً للضوء. المواد الوظيفية للخلايا الشمسية هي نوع من أشباه الموصلات الكهروضوئية التي تستخدم ضوء الشمس لتوليد الكهرباء مباشرة وهي مصدر جيد للطاقة الخضراء

على فروق الطاقة بين الإثارات - π في هذا البحث ، تم فحص تأثير العديد من المقاطع العضوية المانحة / المتوافقة و لضبط خصائص المواد عن طريق توظيف تقنيات (CT) المحلية وحالات القميص وكذلك حالات نقل الشحنة الثلاثية جميع D-π - A. افتراضية عالية الإنتاجية بمساعدة الحسابات الكيميائية الكمومية على مجموعة متنوعة من جزيئات المركبات المدروسة عبارة عن مواد وظيفية ممتازة ذات خصائص ضوئية ضوئية غير خطية فعالة. هناك تأثير كبير على الخصائص الفيزيائية الضوئية وخصائص نقل الشحنة من خلال تطبيق متقبل إلكترون قوي أو إلكترون مع ، مجموعة رسم سواء على مجموعة متقبل الطرفية أو عن طريق إجراء تعديلات التجسير. من بين خمسة مشاريع تمت دراسة الأول (الفصل 2) للاستجابة الضوئية غير الخطية وأربعة مشاريع (الفصل 3 إلى 6) مصممة لتطبيقات الطاقة الكهروضوئية وتطبيقات امتصاص الضوء. نأمل أن تكون مركباتنا المصممة نظرياً مفيدة للعلماء التجريبيين لتجميع المركبات بكفاءة تحويل عالية وخصائص كبيرة لحصاد الضوء

CHAPTER 1

INTRODUCTION

Donor (D) - acceptor (A) based compounds with large NLO properties and high photoelectric response have remained the attention of sizeable research exertions because of their applications in the fields such as optical memory, frequency doubling, optical modulation, and energy storage [1-5]. Even though organic compounds are not as efficient as inorganic materials, they have been recognized well in the field of nonlinear optical materials because they show a number of advantages over the traditional inorganic crystals or compounds: (A) organic compounds show high molecular hyperpolarizabilities (β) and efficient NLO response; (B) these are economical to synthesize and (C) their fabrication is relatively easy; (D) and also compatible with present technology based on semiconductor devices; and last but not least (E) their molecular structures can be altered in many ways allowing to tune optical and electronic properties exceptionally for highly in-demand and challenging applications [1, 3-5].

1.1 Background

In one of the classes of D- π -A configured compounds, organoimido containing organic segments are taken as excellent tunable composite materials for charge transfer properties. The organoimido derivatives are greatly studied, and their synergistic effects have been explored in recent times [6-30].

On the other hand, during the last decade, one of the most dangerous issues is pollution and energy crises in our globe. Non-renewable energy sources are not only diminishing constantly but also causing unfavourable impacts on the environment [31]. Recently, many alternative renewable energy sources for example biomass, hydro power, wind power and solar cells have appeared as essential substitutes to compensate these problems. Due to the easy and abundance availability of sunlight, solar cells have got a huge attention from the researchers. In solar cells the electricity is generated by the photoelectric effect from direct conversion of sunlight [32, 33].

Bulk hetero-junction (BHJ) organic solar cells (OSCs) have gained much consideration because of ease of fabrication to get high power conversion efficiency (PCE). BHJ was synthesized by Yu and co-workers [34]. A good efficiency about 18% had already been achieved BHJ-OSCs [35, 36]. Fullerene acceptors PC61BM and PC71BM also provide great efficiency [37-41]. Moreover, non-fullerene acceptor molecules with different donor and acceptor configuration have been reported [42-45]. Some non-fullerene acceptors (NFAs) show robust absorption in visible and infrared range [46-49]. In short, these donor-acceptor based compounds exhibit good power conversion efficiency and can be considered for electro optics.

NLO materials and OSCs owing to their low-cost roll-to-roll processing and viewpoint in manufacturing photovoltaic modules of large scale are the focus of ongoing research [50]. The OSCs based multi and single junction devices offer very high power conversion efficiencies (PCEs) [35, 51]. These well-known accomplishments have been significantly contributed by fullerene free or non-fullerene small molecular acceptors (NFSMAs)

because of their solid state structures, facile tunability in energy levels and strong LHE (light harvesting efficiency) values [52, 53]. Until now, A–DA'D–A and A–DD'D–A are the most common NFSMAs molecules that are present in literature. In these molecules DA'D and DD'D act as central fused-ring core units. For instance, Zhan et al. developed a milestone molecule ITIC having A–DD'D–A framework [54]. The COi8DFIC or O6T4F is another famous NFSMA molecule developed by Ding et al. [46, 55] exhibited record breaking PCE of 17.4% and efficiently contributed to tandem OSCs. Famous A–DA'D–A type molecule Y6 with 15-17 % PCEs in OSCs of single junction type is reported by Zou et al [47]. However, tedious synthesis of these fused-ring NFAs make them inappropriate candidates for OSCs commercial applications and also, they are not cost-effective materials. For example, initiating from diethyl 2,5- dibromoterephthalate, thienothiophene, and 2-bromothiophene combining with benzothiadiazole, ITIC, O6T4F and Y6 molecules synthesis require 8, 11 and 10 steps respectively [46, 47, 54-56]. Furthermore, fused-ring NFAs are used for the tunability of chemical structures, For example, conjugated materials properties can be generally optimized by changing alkyl chain [57]. Since alkyl chain can be changed at initial steps of the synthesis, therefore, it is difficult in fused-ring NFAs to change alkyl chain [58]. Thus, low-cost NFAs with higher performance and new design are the need of hour.

1.2 Literature Review

It is vital to design and synthesize such non-fused NFAs that offer synthetic ease and diversified building blocks. In an attempt to construct such materials, few non-fused electron acceptors of A–D–D'–D–A type are reported by researchers [59]. By tuning the

device fabrication conditions and optimizing the chemical structures, resulting non-fused NFAs based OSCs achieved a record breaking 13% PCE [60]. This PCE approaches the 15.1% champion efficiency achieved by fused-ring NFAs of A-DD'D-A type [61-64]. A-D-A'-D-A type new non-fused NFAs is generated by altering middle D' motif to A' unit. A-D-A'-D-A framework containing non-fused NFAs showed broader absorption and offer manifold FMOs to accept electrons from excited donors. This architecture is discussed only in a few pioneering works. So, the potential of non-fused NFAs containing A-D-A'-D-A has not been fully explored yet. Therefore, we have made structural tailoring at end-capped terminal acceptor unit of non-fused non-fullerene acceptor molecule BTCIC-4Cl with A-D-A'-D-A framework and new molecules with computational investigations.

Furthermore, the nature of the donor moiety and acceptor molecule, role of the π -conjugated linkers or spacers have significant contribution on the nonlinear properties of the molecules and materials. The electron acceptor and electron donor moieties can significantly fine-tune the photophysical and nonlinear optical properties of the materials. For example, POM-based organic-inorganic hybrid composite materials with D- π -A formation have great ability to alter the charge transfer and thus leading to an eye-catching NLO response as shown in Figure 1.1 and 1.2.

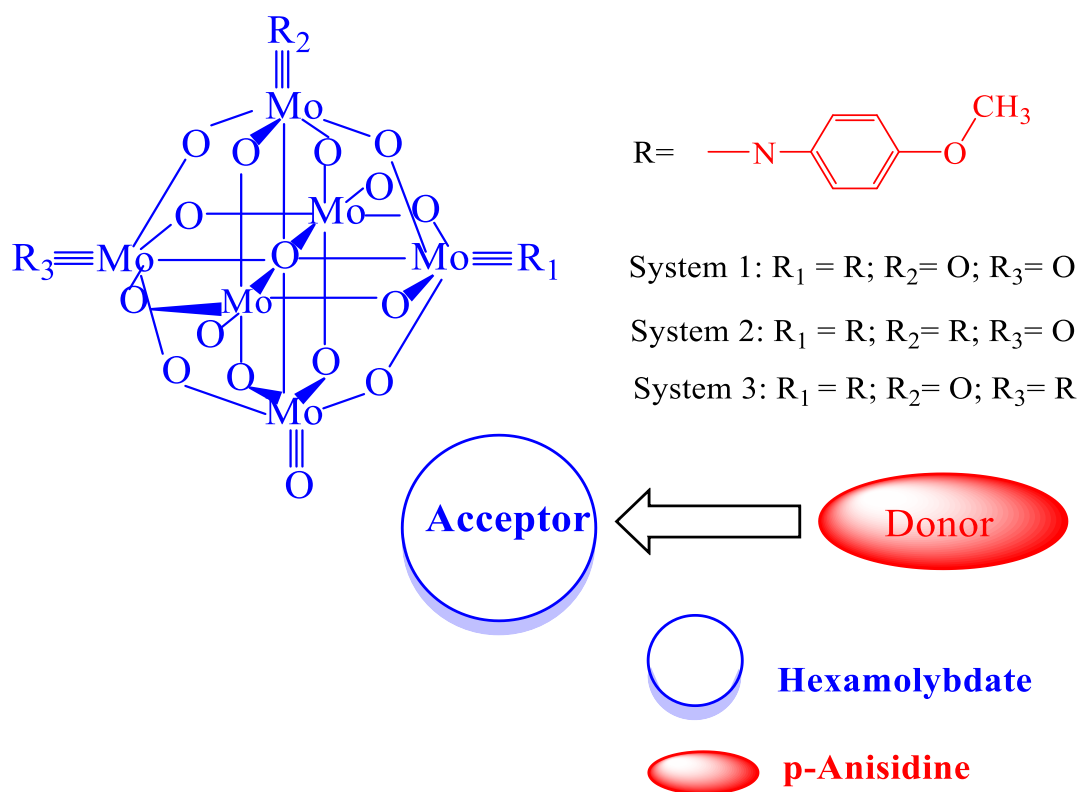


Figure 1. 1. Cluster based calculation models of D- π -A configuration.

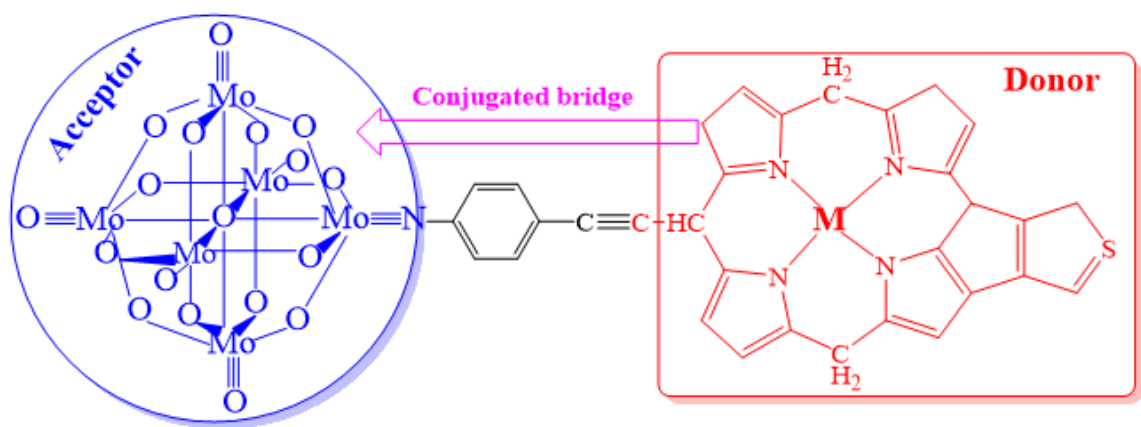


Figure 1. 2. D- π -A calculation model where M = Zn and Fe

However, the well-known traditional electron donating groups; oxido ($-O^-$), amino ($-NH_2, -NHR, -NR_2$), hydroxy, alkoxy acylamido ($-NHCOR$), acyloxy ($-OCOR$), (di) alkylphosphino, alkylthio, phenyl, vinyl, alkyl, fluoro and electron acceptor groups; nitro, cyano, sulfonyl, haloformyl ($-COX$), formyl ($-CHO, -COR$) nitroso ($-N=O$) are extensively used to explore the charge transfer properties of D- π -A systems. Along with the above-mentioned groups, some other electron donor and acceptor groups can also be employed to enhance the NLO and light harvesting properties of the materials by employing cutting-edge computational techniques, mostly DFT calculations. Some examples of the donor and acceptor compounds are given below in Figure 1.3.

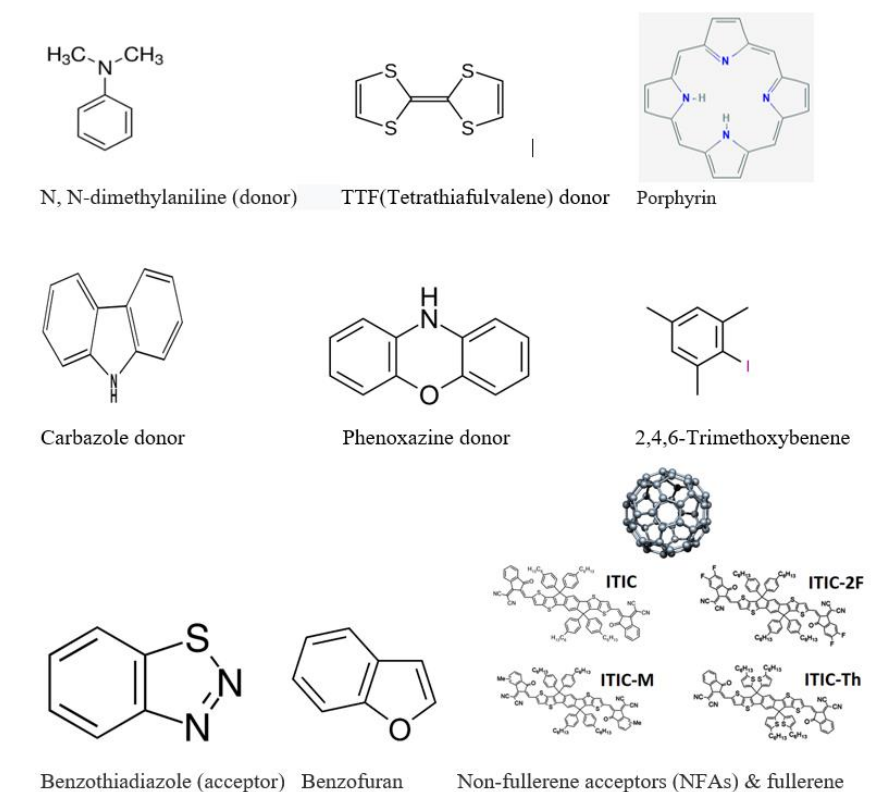


Figure 1. 3 Some important donors and acceptors for our designed D- π -A molecules

In the past few years, the photovoltaic materials from contemporary technological point of view are functioning as fully integrated gears in numerous optoelectronic applications.

Therefore, various experimental and computational researchers around the globe have pursued novel materials to increase their nonlinearity, photovoltaic characteristics and applications in contemporary technological fields. Here, our idea is that under high-throughput screening, only DFT calculations by using B3LYP, CAM-B3LYP, LC-BLYP, HF, M06, M062X methods are performed on hundreds of compounds and simply highly efficient molecules are taken for further studies (NLO and Solar Cells as Functional Materials).

1.3 Objectives of Research

This project covers the following goals/objectives:

- (1) To design different non-fullerene or fullerene-based molecules in various D- π -A or D-A systems which are expected to be used as functional materials. For example, thiazoline derivatives might be used for NLO study.
- (2) Through different modifications, the resulting molecules have efficient charge transfer, low HOM-LUMO gap and high electron and hole mobility which is the main concern of nonlinear optics, solar cells, open circuit voltage and stability of organic solar cells.
- (3) Some other features like polarizabilities, hyperpolarizabilities, oscillation, reorganization energy for electron and hole, dipole moment and charge transfer analysis.
- (4) A wide range of theoretical systems development to explore the relationships between the structures and the optical, electronic and NLO properties and organic solar cells.

1.4 Computational Methodology

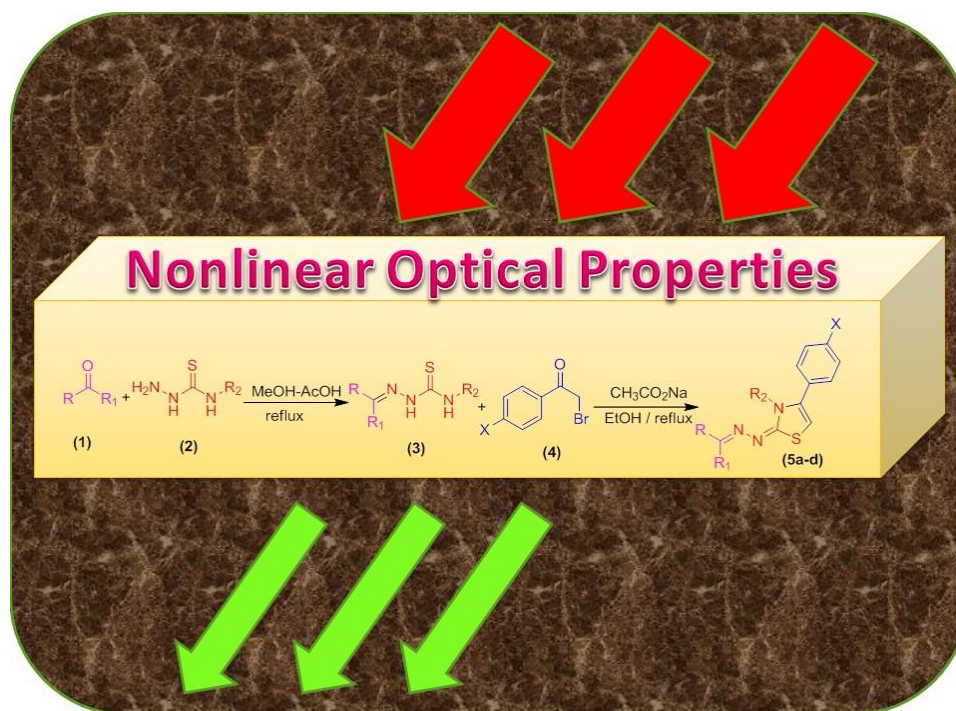
In this research work, mostly Gaussian 09W [65] was implemented to perform all computations and their results were interpreted through GaussView 6.0 program [66]. Entire computational work was performed at KFUPM. Initially, reference compounds selected from literature were optimized using B3LYP, M06-2X, M06, LC-BLYP, CAM-B3LYP, ω B97XD, MPW1PW91 with different basis sets such as 6-31G(d,p), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311+G(2d,p) and 6-311++G(2d,2p). Frequency analysis was carried out using above mentioned functionals to confirm the presence of optimized structure at true minima in potential energy surface. The optimized geometry of reference molecules were subjected to photophysical analysis to obtain the maximum absorption value of reference molecule. The conductor-like polarizable continuum model (CPCM) [67] was used to examine the effect of solvent in different computations. Photophysical analysis was carried out employing time dependent DFT (TDDFT) at above mentioned levels of theory and basis set combinations and results obtained at these functionals were compared with experimental reported maximum absorption value of reference molecule. Those functional were selected for performing further computational jobs at which good concurrence with experimental value was found. The density of states (DOS), transition density matrix (TDM), frontier molecular orbital (FMOs), binding energy, charge transfer analysis and reorganization energy values were calculated at similar level of DFT. Reorganization energy was calculated with the help of equations present in the literature [68]. (E_0) for neutral molecule, (E_0^+) and (E_0^-) for cation and anion through optimization were also calculated. Furthermore, different software were used to plot different graphical representations, like origin 9.2 for plotting graphs. DOS calculations

were carried out with PyMOlyze 2.0 [69]. The ChemBio 3D was used to generate initial 2D to 3D structure conversion. MultiWFN was used for drawing transition density plots. In addition, different other software's like, Avogadro, Chemcraft, and Swizard programs were also used for plotting different graphs and pictorial purposes.

CHAPTER 2

Development of potent thiazoline based functional materials:

Synthetic and computational approaches



2.1 Introduction

Thiazolines or dihydrothiazoles are important five-membered heterocyclic compounds which have been widely studied in medicinal chemistry due to their pharmacological importance and attracted the attention of chemists since these derivatives exist in many biochemical reactions in living organisms [70]. A number of these analogues have been synthesized in the last decades and evaluated for many interesting biological activities such as antitumor, anti-inflammatory, antiviral, anti-microbial and antioxidant properties [71]. Many researchers studied the thiazolines as enzyme inhibitors, for instance, urease, butyrylcholinesterase and carboxylesterase inhibitory potential of these analogues have been reported [72]. Also in natural products, the thiazoline moiety is the structural part of numerous fascinating biologically active scaffolds such as thiagazole, mirabazole and curacin A [73].

The progression of new synthetic methodologies provides efficient substitutes to traditional protocols [74]. Owing to their biological worth, thiazoline containing molecules have gained great attraction as synthetic targets [75]. A few routes for the synthesis of thiazolidin-2-imines have been reported in the literature [76]. Amongst them, thiourea and halocarbonyl are commonly applied functionalities in various methods for synthesis of thiazolidine derivatives [77]. An efficient, one-pot, three-component route was described for the preparation of thiazolidin-4-ol derivatives and glycothiazolines from glycals [78]. Enantiospecific synthesis of thiazolidine scaffolds has been reported by exploiting inactivated chiral aziridines and isothiocyanates [79]. While intramolecular CS bond formation methodology was adopted to furnish

thiazolines and thiazines [80]. Methylhydrazines are known to be an ambident substrate, giving possible reaction products with various electrophiles [81]. A radical path-way was used to synthesize 2-aminothiazoles from thiourea and active methylenes by means of TBHP/AIBN [82]. Currently, electrosynthesis of thiazolidine derivatives has been reported via oxysulfurization of thiourea molecules [83]. The conservative methodology comprises of the reaction of isocyanates and imine but the shortcoming relates to toxic nature of isocyanates. In this study, we therefore describe metal free and benign methodology for an easy and efficient access to biologically significant thiazoline scaffolds by cyclization of thiosemicarbazones and phenacyl bromides under catalysis of sodium acetate in ethanol. Carbonyl compounds were reacted with N⁴-substituted thiosemicarbazides to give the respective thiosemicarbazones. Substitution at N⁴ position not only increase the yield of the products but also provides stability to the thiazoline ring. The absence of free NH due to substitution at N⁴ position might also be important for attaining the appropriate geometries for studying the gap between transitions which provided excellent correlation.

Nonlinear optical (NLO) materials due to their easy structural tailoring, facile synthesis, low cost, fine tuning of absorption wavelength and large number of applications ranging from healthcare to telecommunication and information technology are getting immense attention currently. The scientists from experimental as well as computational groups are focusing these NLO compounds for their versatile and unique applications in optical communication, optical computing, dynamic image processing, nuclear science, biophysics, surface interface and solid physics [84]. The literature survey shows that organic compounds are the noticeable chemical

architectures that have significant nonlinear optical response [85]. Due to the higher structural complexity and supramolecular nature owing a number of π -electrons, organic compounds can offer a more suitable skeleton as compared to the transition metal organo-metallic framework. For the better understanding of NLO behavior of a compound, detailed knowledge of its composition is extremely important as optical response depends on the electronic architecture of entire organic compounds [86]. The linear and nonlinear responses are of extreme significance for the proper estimation of NLO properties of a compound. So, herein we are reporting the synthesis, characterization (UV, FT-IR, ^1H -NMR, ^{13}C -NMR) of novel thiazoline derivatives (**5a-d**). Computational chemistry has been used additionally to compute the UV-Vis, IR, electronic and detailed nonlinear (NLO) properties of investigated molecules **5a-d**. The DFT-based theoretical calculation reveals the NLO response efficiency of the newly synthesized thiazoline derivatives that may have substantial applications at the advanced level. We are optimistic that this synergistic experimental-computational insight will offer these compounds as proficient NLO compounds for future technological applications.

2.2 Experimental Section

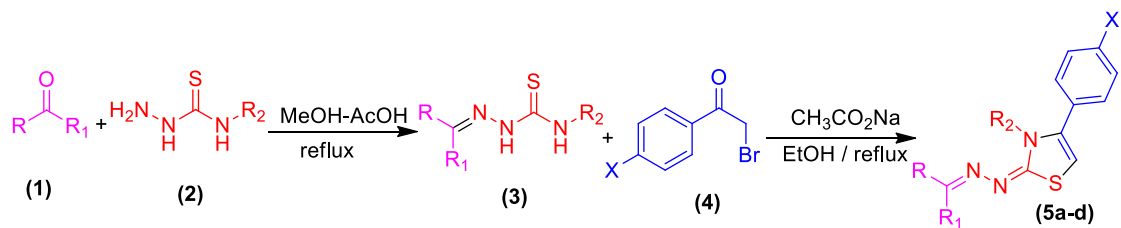
2.2.1 Chemistry of Molecules

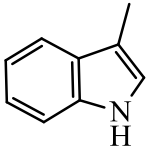
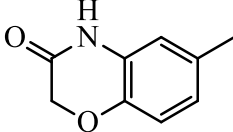
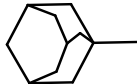
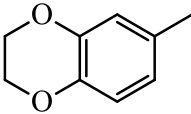
The novel thiazoline derivatives (**5a-d**) bearing benzoxazinone, adamantyl, benzodioxane and indole nuclei were synthesized in two steps and this is outlined in Scheme 1. In the first step, thiosemicarbazone intermediates (**3**) were synthesized by condensation of equimolar quantities of various carbonyl compounds (**1**) with

appropriate N⁴-substituted thiosemicarbazides (**2**) employing methanol solvent and glacial acetic acid in catalytic amount (1-2 drops). In the second step, the respective thiosemicarbazones (**3**) were cyclized with 4-substituted (chloro, nitro) phenacyl bromides (**4**) in absolute ethanol/anhydrous sodium acetate to afford the target five-membered heterocyclic thiazoline derivatives (**5**).

The structures of target thiazolines were established by using spectral and elemental analysis. The IR spectrum of indole-based thiazoline **5a** showed a band due to N-H stretching at 3413 cm⁻¹ whereas C=N at 1609 cm⁻¹. In IR spectrum of **5b**, a strong band was appeared at 3315 cm⁻¹ resulting from N-H stretching while characteristic bands due to lactam C=O and azomethine C=N bonds were observed at 1687 cm⁻¹ and 1587 cm⁻¹ respectively. In the compounds **5c** and **5d**, azomethine C=N band in IR was appeared at 1617 cm⁻¹ and 1604 cm⁻¹ respectively. The ¹H-NMR spectra of all the four products **5a-d** did not display any downfield signals due to N⁴-H and N²-H of corresponding thiosemicarbazones. Nevertheless, a singlet peak due to indole N-H in **5a** and lactam N-H in **5b** and was detected at 11.52 and 10.78 ppm correspondingly. In all the compounds, CH-S protons of thiazoline ring were seen to resonate at 6.12-6.99 ppm as singlet peak. Furthermore, the spectral data of other protons (aliphatic and aromatic) were in good accordance with the anticipated structures of target products. The ¹³C-NMR (carbon nuclear magnetic resonance) spectra of synthesised molecules also favoured the proposed structures. In ¹³C-NMR spectra of **5a-d**, methyl carbons were observed at δ_c 12.37-18.23 ppm whereas methylene carbons of **5b** and **5d** were resonated at 67.25 ppm and 59.80 ppm respectively. Carbons of S-CH= moiety of thiazoline ring in all the derivatives were appeared in the region

of 96.18-102.43 ppm. In the ^{13}C -NMR, the compounds displayed signal at δ_{C} 151.54-166.12 ppm owing to azomethine $\text{C}=\text{N}$ functionality. The downfield lactam $\text{C}=\text{O}$ signal in **5b** was found at 166.80 ppm. The resonance for other aliphatic and aromatic carbons was in accordance with the reported ranges for the similar carbons



Compound	R	R ₁	R ₂	X
5a		H	2,6-(CH ₃) ₂ C ₆ H ₃	NO ₂
5b		CH ₃	2,6-(CH ₃) ₂ C ₆ H ₃	Cl
5c		CH ₃	2-CH ₃ C ₆ H ₄	Cl
5d		CH ₃	2,6-(CH ₃) ₂ C ₆ H ₃	Cl

Scheme 1: Synthesis of novel Thiazoline derivatives **5a-d**

Yield 84 %; m.p. 294-296 °C; IR $\nu_{\max}$ (cm⁻¹): 3413 (NH), 3117 (Ar-H), 1609 (N=C), 1542, 1508 (C=C, aromatic); ¹H-NMR (DMSO-*d*₆, 400 MHz) δ ppm: 2.13 (s, 6H, (CH₃)₂-aromatic), 6.99 (s, 1H, SCH=C), 7.13-7.24 (m, 5H, Ar-H), 7.35-7.38 (m, 2H, Ar-H, CH=N), 7.43-7.45 (m, 1H, Ar-H), 7.67 (d, 1H, *J* = 2.8 Hz, Ar-H), 8.05-8.08 (m, 2H, Ar-H), 8.26-8.28 (m, 1H, Ar-H), 8.33 (s, 1H, indole CH), 11.52 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ ppm: 18.25 ((CH₃)₂-aromatic), 99.73 (S-CH=), 105.18 (Ar-C), 112.35 (aromatic), 112.86 (aromatic), 120.93 (aromatic), 122.45 (aromatic), 122.97 (aromatic), 124.05 (aromatic), 124.88 (aromatic), 128.56 (aromatic), 129.16 (aromatic), 129.41 (aromatic), 130.82 (aromatic), 136.37 (aromatic), 137.05 (aromatic), 137.57 (aromatic), 137.92 (aromatic), 147.33 (N-C=), 149.49 (N-N=C), 165.11 (N=C-N); Anal calcd for C₂₆H₂₁N₅O₂S (467.54): C, 66.79; H, 4.53; N, 14.98; Found: C, 66.85; H, 4.50; N, 14.92.

Yield 84 %; m.p. 260-262 °C; IR $\nu_{\max}$ (cm⁻¹): 3315 (N-H), 3115 (Ar-H), 2910 (CH₃), 1687 (C=O), 1587 (N=C), 1519, 1489 (Ar-C=C); ¹H-NMR (DMSO-*d*₆, 400 MHz) δ ppm: 2.05 (s, 3H, C=N-CH₃), 2.10 (s, 6H, (CH₃)₂-aromatic), 4.59 (s, 2H, CO-CH₂-O), 6.77 (s, 1H, S-CH=), 6.96 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.11-7.13 (m, 4H, Ar-H), 7.17-7.20 (m, 1H, Ar-H), 7.29-7.34 (m, 3H, Ar-H), 7.42 (d, 1H, *J* = 2.0 Hz, Ar-H), 10.78 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ ppm: 14.61 (CH₃), 18.22 (CH₃)₂-aromatic), 67.25 (CH₂-O), 102.43 (CHS), 113.75 (aromatic), 116.28 (aromatic), 121.52 (aromatic), 127.51 (aromatic), 128.90 (aromatic), 129.28 (aromatic), 129.36 (aromatic), 129.43 (aromatic), 129.73 (aromatic), 133.21 (aromatic), 133.80

(aromatic), 136.40 (aromatic), 136.49 (aromatic), 138.68 (aromatic), 144.50 (N-C=), 155.23 (N-N=C), 165.11 (NCN), 166.80 (HNCO); Anal calcd for $C_{27}H_{23}ClN_4O_2S$ (503.02): C, 64.47; H, 4.61; N, 11.14; Found: C, 64.41; H, 4.64; N, 11.18.

Yield 83 %; m.p. 168-170 °C; IR $\nu_{\max}$ (cm^{-1}): 3103 (aromatic), 2898 (CH_3), 1617 (C=N), 1544, 1486 (C=C, aromatic); 1H -NMR ($CDCl_3$, 400MHz) δ ppm: 1.69-1.78 (m, 6H, $-CH_2$, adamantyl), 1.81 (s, 3H, CH_3CN), 1.83 (bs, 6H, $-CH_2$, adamantyl), 2.05 (bs, 3H, $-CH_2$, adamantyl), 2.27 (s, 3H, CH_3 -Ar), 6.12 (s, 1H, CHS), 7.01-7.05 (m, 3H, Ar-H), 7.13-7.16 (m, 3H, Ar-H), 7.21-7.23 (m, 2H, Ar-H); ^{13}C NMR ($DMSO-d_6$, 100 MHz) δ ppm: 12.37 (CH_3), 18.23 (CH_3 -aromatic), 28.46 (adamantyl), 36.99 (adamantyl), 39.89 (adamantyl), 40.32 (adamantyl), 100.88 (S-CH=), 126.61 (aromatic), 128.34 (aromatic), 128.43 (aromatic), 128.95 (aromatic), 129.14 (aromatic), 129.96 (aromatic), 130.95 (aromatic), 134.07 (aromatic), 136.69 (aromatic), 137.23 (aromatic), 139.12 (N-C=), 166.12 (N-N=C), 169.00 (N-C=N); Anal calcd for $C_{28}H_{30}ClN_3S$ (476.08): C, 70.64; H, 6.35; N, 8.83; Found: C, 70.69; H, 6.33; N, 8.87.

Yield 85 %; m.p. 184-186 °C; IR $\nu_{\max}$ (cm^{-1}): 3110 (aromatic-CH), 2916 (CH_3), 1604 (N=C), 1569, 1487 (C=C, aromatic); 1H -NMR ($CDCl_3$, 400 MHz) δ ppm: 2.13 (s, 3H, CH_3 -CN), 2.14 (s, 6H, $(CH_3)_2$ -aromatic), 4.25 (s, 4H, $-O(CH_2)_2O-$), 6.17 (s, 1H, SCH), 6.82 (d, 1H, $J = 8.8$ Hz, Ar-H), 6.98-7.03 (m, 4H, Ar-H), 7.10-7.13 (m, 3H, Ar-H), 7.34-7.37 (m, 2H, Ar-H); ^{13}C NMR ($DMSO-d_6$, 100 MHz) δ ppm: 9.77 (CH_3), 13.54 ($((CH_3)_2$ -aromatic), 59.57 (CH_2 -O), 59.80 (O- CH_2), 96.18 (S-CH=), 110.48 (aromatic),

112.09 (aromatic), 114.99 (aromatic), 123.70 (aromatic), 123.73 (aromatic), 123.84 (aromatic), 123.86 (aromatic), 124.82 (aromatic), 128.04 (aromatic), 131.87 (aromatic), 134.24 (aromatic), 138.38 (aromatic), 139.61 (N-C=), 151.54 (NN=C), 161.45 (NCN); Anal calcd for C₂₇H₂₄ClN₃O₂S (490.02): C, 66.18; H, 4.94; N, 8.58; Found: C, 66.24; H, 4.90; N, 8.65.

2.3 Computational procedure

Employing density functional theory (DFT) [87], GaussView 5.0 [88] in combination with Gaussian 09 program package [89] was used accordingly for making input files and running computational calculations of investigated compounds **5a-d**. Initially, investigated compounds were optimized at 6-311+G(d,p) basis set and M06 functional to acquire their lowest potential energy structures. To confirm the stability of **5a-d**, the optimized structures were subjected to vibrational analysis using DFT/M06/6-311+G(d,p) method. Resulting vibrational values reflected the absences of any imaginary frequency and confirmed the presence of optimized structures at potential energy surfaces with true minimum. The electronic properties including molecular electrostatic potential surfaces (MEP), natural bond orbital (NBO) and frontier molecular orbital (FMO) analysis of **5a-d** were estimated using same 6-311+G(d,p) basis set and M06 functional. NLO properties of investigated compounds **5a-d** were calculated with HF method, exchange correlation functional B3LYP, range-corrected methods LC-BLYP, CAM-B3LYP and meta-hybrid GGA methods M06, M062X in coupling with 6-311+G(d,p) basis set. Different computational chemistry programs

like Chemcraft [90], Avogadro [91] and GaussView 5.0 [88] were employed for fetching out the output data and deducing the output files.

2.4 Molecular geometrical parameters

Computational optimization of investigated compounds **5a-d** has been performed to study molecular geometric parameters. The geometrical parameters obtained have been optimized through estimation by M06/6-311g+(d,p) method. Comparison of structural parameters of entitled molecules those obtained through XRD and optimized through DFT studies have been listed in Tables S1-S4 (supplementary information). The tabulated statistics shown that X-ray determined bond length, angles and DFT calculated structural parameters are in satisfactorily agreement. The infinitesimal difference is usually foreseen due to phase difference among DFT and XRD calculations which were performed in gas and solid phase respectively.

Indistinguishable measured DFT and SC-XRD values of bond lengths are found to be 1.214 Å for O3-N8 in **5a**. For C13-C14 and C33-C34 of **5b**, it is found about 1.387 and 1.495 Å. The bond length for C11-C24 and C16-C17 is measured as 1.745 and 1.498 Å in **5c**. For N3-C13, C24-C25 and C32-C34 in **5d**, these values are marked as 1.288, 1.396 and 1.414 Å respectively. The maximum deviation in bond length value compared in DFT and single crystal analysis was examined as 0.036 Å for N5-N6 in **5a**, 0.021 Å for N4-C15 in **5b**, 0.071 Å for C27-C28 in **5c** and 0.096 Å for N5-C15 in **5d**. The minimum bond length deviation was calculated to be -0.032 for C23-C24, -0.025 for S2-C20, -0.092 for C30-C31 and -0.045 for C18-C19 in **5a-d** respectively (Tables S1-S4).

While considering about bond angle, the identical values as determined by XRD and DFT were found to be 122.3°, 129.3° and 122.5° for N5-C17-C10, C11-C10-C17 and C11-C12-C13 in **5a** respectively, and 121.8 and 119.1° for C22-C23-C24 and C27-C32-C33 in **5c** respectively. The highest deviation in bond angle value by comparing DFT and SC-XRD was seen to be 1.9° for C10-C11-C16, 2.8° for N5-C15-C16, 3.7° for C29-C30-C31 and 3.6° for N4-N3-C13 in **5a**, **5b**, **5c** and **5d** respectively. Nevertheless, the least deviation value in bond angle was calculated to be -2.7° for N5-N6-C18 in **5a**, -5.6° in **5b** for N6-N7-C19, -3.2° for N3-N4-C18 in **5c** and -13.8° in **5d** for C17-N5-C24 through comparing SC-XRD and DFT investigations. Overall for aforesaid compounds, the deviation in bond lengths and bond angles exists in the span of -0.092 to 0.096 Å and -13.8 to 3.6° respectively (Tables S1-S4).

For impartial comparison between DFT and experimental investigation in regard to optimization, error was also calculated by using equation1.

$$\text{Mean Absolute Deviation (MAD)} = \frac{\sum_{t=1}^n |\text{EXP} - \text{DFT}|}{n} \quad (1)$$

Here in above equation 1, t shows numeral of bond angles and length values, n represented the total numeral of bond angles or lengths values, DFT described the computationally calculated values of bond angles or bond lengths values and EXP experimentally determined values of bond angles or bond lengths. Where by taking absolute sum of difference between the computational and the experimental values that was divided by total number of bond angles or bond lengths values, mean absolute deviation (MAD) can be calculated.

Error metric is generally employed for Mean square error. Because of squaring bigger numbers comprising of a biggest impact when compared with smaller number square, it penalizes large errors.

$$\text{Mean Square Error (MSE)} = \frac{\sum_{t=1}^n (\text{EXP} - \text{DFT})^2}{n} \quad (2)$$

By proceeding the MSE square, root mean square error (RMSE) is calculated. It's the foremost utilized error metric and especially contemplated for the crystals under examined.

$$\text{Root Mean Square Error (RMSE)} = \sqrt{\frac{\sum_{t=1}^n (\text{EXP} - \text{DFT})^2}{n}} \quad (3)$$

By dividing the average value of absolute errors with experimental value, Mean Absolute Percentage Error (MAPE) is calculated. The discussed errors are determined by using equation 4 and results are tabulated in Table 2.1

$$\text{Mean Absolute Percentage Error (MAPE)} = \frac{\sum_{t=1}^n \left| \frac{\text{EXP} - \text{DFT}}{\text{EXP}} \right|}{n} \times 100 \quad (4)$$

Table 2. 1: Calculated error values for investigated molecules 5a-d

Compound	Parameter	MAD	MSE	RMSE	MAPE
ds	r				
5a	Bond	0.009	0.0002	0.013	0.6895
	Length	8			
	Bond	0.568	0.6369	0.798	0.4804
	Angle	5			
5b	Bond	0.009	0.0002	0.0123	0.6645
	Length	4			
	Bond	0.873	1.5948	1.2629	0.7402
	Angle	2			
5c	Bond	0.029	0.0015	0.0383	2.0407
	Length	3			
	Bond	0.991	1.723	1.3126	0.866
	Angle	2			
5d	Bond	0.028	0.0014	0.0381	1.9906
	Length	9			
	Bond	2.316	13.213	3.6349	2.024
	Angle	4			

MAD=Mean Absolute Deviation, MSE=Mean Square Error, RMSE=Root Mean Square Error, MAPE=Mean Absolute Percentage Error

For the structural calculations, usually used method is RMSE approach, that's way we used this approach to analyze our molecules. It was examined that the RMSE values of

entitled molecules for bond length are in smaller magnitude. However, the calculated values for bond angles of RMSE were in larger magnitude. In **5v** and **5d**, RMSE values of angles are found higher as greater deviations occur.

2.5 Natural bond orbital (NBO) analysis

NBO analysis is a marvelous technique that not only gives useful evidences about charge transfer in both filled and virtual orbital but also provide useful insight about the intra-molecular and inter-molecular interactions among bonds [92]. NBO analysis is also used to explore donor to acceptor shifting of charge densities and intermolecular delocalization. Stabilization energy offered to studied molecules by different types of transition of can be estimated by Equation 5 using second-order perturbation theory.

$$E^{(2)} = q_i \frac{(F_{i,j})^2}{\varepsilon_j - \varepsilon_i} \quad (5)$$

NBO examination has been enforced on **5a-d** molecules and some important values are shown in Table 2.2.

Table 2. 2: Representative values of natural bond orbital analysis for 5a-d compounds.

Compounds	Donor(i)	Type	Acceptor(j)	Type	E(2)	E(J)E(i) ^b (a.u)	F(I,j) ^c (a.u)
5a	C39-C47	π	C43-C45	π^*	104.5	0.16	0.115
	C35-C37	π	O3-N9	π^*	0.52	0.06	0.005
	N9-C34	∂	C29-C30	∂^*	6078	0.05	0.474
	C48-H51	∂	C47-C48	∂^*	0.50	0.97	0.02
	O2	LP(1)	C29-C30	∂^*	2708	0.2	0.663
	S1	LP(1)	N6-N7	∂^*	0.50	0.95	0.019
5b	C29-C31	π	O4-C19	π^*	252.62	0.48	0.325
	C38-C40	π	C48-C50	π^*	0.58	0.32	0.012
	C55-H57	∂	C48-H49	∂^*	2896.34	0.04	0.292
	N9-C42	∂	C43-C44	∂^*	0.50	1.33	0.023
	N5	LP(1)	O4-C19	π^*	296.85	0.06	0.122
	N9	LP(1)	C29-C31	∂^*	0.55	0.89	0.021
5c	C52-C54	π	C49-C50	π^*	23.93	0.29	0.075
	C49-C50	π	C39-C40	π^*	0.55	0.3	0.012
	C20-H63	∂	C59-H61	∂^*	53.17	5.68	0.492
	C7-C10	∂	C7-H8	∂^*	0.50	1.01	0.02
	N5	LP(1)	N4-C35	π^*	49.76	0.3	0.111
	N4	LP(1)	N5-C49	∂^*	0.58	0.77	0.019
5d	C25-C26	π	C28-C30	π^*	25.08	0.26	0.073
	N4-C21	π	N4-C21	π^*	1.59	0.35	0.023
	C52-H58	∂	C52-H58	∂^*	60.96	6.07	0.545
	C36-C48	∂	N5-C35	∂^*	0.50	1.05	0.021
	N5	LP(1)	N4-C21	π^*	49.63	0.3	0.11
	N5	LP(1)	C22-C24	∂^*	0.50	0.89	0.021

Among commonly found four types of electronic transitions $\sigma \rightarrow \sigma^*$ transitions are found slightest dominant while $\pi \rightarrow \pi^*$ were observed most prominent, while $LP \rightarrow \pi^*$ and $LP \rightarrow \sigma^*$ were slightly dominant transitions found in investigated molecules **5a-d**. Through $\pi \rightarrow \pi^*$ transitions, charge transfer and the presence of conjugation among studied molecules can be examined. The most reasonable transitions having giant stabilization energy value are; $\pi(C39-C47) \rightarrow \pi^*(C43-C45)$, $\pi(C29-C31) \rightarrow \pi^*(O4-C19)$, $\pi(C52-C54) \rightarrow \pi^*(C49-C50)$ and $\pi(C25-C26) \rightarrow \pi^*(C28-C30)$ with stabilization energy values 104.5, 252.62, 23.93 and 25.08 kcal/mol respectively for **5a-d**. While transitions having least stabilization energies 0.52, 0.58, 0.55 and 1.59 kcal/mol are $\pi(C35-C37) \rightarrow \pi^*(O3-N9)$, $\pi(C38-C40) \rightarrow \pi^*(C48-C50)$, $\pi(C49-C50) \rightarrow \pi^*(C39-C40)$ and $\pi(N4-C21) \rightarrow \pi^*(N4-C21)$ for **5a**, **5b**, **5c**, and **5d** respectively (Table 2.2).

In agreement to resonance, similar type of interactions were observed such as $LP1(O2) \rightarrow \sigma^*(C29-C30)$, $LP1(N5) \rightarrow \pi^*(O4-C19)$, $LP1(N5) \rightarrow \pi^*(N4-C35)$ and $LP1(N5) \rightarrow \pi^*(N4-C21)$ created 2708, 296.85, 49.76 and 49.63 kcal/mol stabilization energy in **5a**, **5b**, **5c**, and **5d** respectively. These were the highest values of stabilization energies for LP transitions. Contrarily, $LP1(S1) \rightarrow \sigma^*(N6-N7)$, $LP1(N9) \rightarrow \sigma^*(C29-C31)$, $LP1(N4) \rightarrow \sigma^*(N5-C49)$ and $LP1(N5) \rightarrow \sigma^*(C22-C24)$ produced 0.50, 0.55, 0.58 and 0.50 kcal/mol stabilization energy and these were the least values of stabilization energies of entitled species (Table 2.2).

The $\sigma \rightarrow \sigma^*$ transitions are usually based on weak donor (σ)-acceptor (σ^*) interactions opposite to $\pi \rightarrow \pi^*$ interactions. The transitions; $\sigma(N9-C34) \rightarrow \sigma^*(C29-C30)$, $\sigma(C55-H57) \rightarrow \sigma^*(C48-H49)$, $\sigma(C20-H63) \rightarrow \sigma^*(C59-H61)$ and $\sigma(C52-H58) \rightarrow \sigma^*(C52-H58)$, having 6078, 2896.34, 53.17 and 60.96 kcal/mol energy demonstrating highest

stabilization energy amongst all the $\sigma \rightarrow \sigma^*$ interactions in all studied compounds **5a**, **5b**, **5c**, and **5d** respectively. On the other hand, $\sigma(\text{C48-H51}) \rightarrow \sigma^*(\text{C47-C48})$, $\sigma(\text{N9-C42}) \rightarrow \sigma^*(\text{C43-C44})$, $\sigma(\text{C7-C10}) \rightarrow \sigma^*(\text{C7-H8})$ and $\sigma(\text{C36-C48}) \rightarrow \sigma^*(\text{N5-C35})$ with stabilization energy 0.50 kcal/mol was the least values among all $\sigma \rightarrow \sigma^*$ transitions in **5a**, **5b**, **5c**, and **5d** respectively (Table 2.2). These results prove the successful transfer of electrons (charge transfer), so, all studied molecule would be with astonishing NLO properties..

2.6 Vibrational Analysis

By applying DFT based vibrational analysis, a clear understanding of the vibrational modes existed in investigated compounds **5a**, **5b**, **5c**, and **5d** were explored in gas phase at M06/6-311+G(d,p) functional. The experimental and calculated vibrational bands for **5a-d** are given in Tables S5-S8 (Supplementary information) while experimental absorption spectra of **5a**, **5b**, **5c**, and **5d** are displayed in Figures S1-S4 (Supplementary information) respectively.

2.6.1 C-H vibrations

In 3100-3000 cm^{-1} range, stretching vibrational frequencies of C-H bond present in hetero aromatic and aromatic rings were calculated [93]. In the studied compounds, DFT based stimulated C-H stretching vibrational bands in benzene ring were located in the range of 3214-3165, 3198-3161, 3184-3135 and 3191-3161 cm^{-1} in **5a**, **5b**, **5c**, and **5d** respectively (Tables S5-S8). These values are in line with vibrational bands of **5a**, **5b**, **5c**, and **5d** measured experimentally at 3117 cm^{-1} , 3115 cm^{-1} , 3103 cm^{-1} and

3110 cm^{-1} respectively and also with the reported range 3100-3000 cm^{-1} ²⁴. Similarly, the stimulated symmetrical and asymmetrical stretching vibrational absorption bands in C-H bond of methyl group were analyzed by DFT in the range of 3116-3016 cm^{-1} for **5a**, 3115-3018 cm^{-1} for **5b**, 3135-3117 cm^{-1} for **5c** and 3114-3016 cm^{-1} for **5d**. Moreover, in **5a**, **5b**, **5c**, and **5d** scissoring and twisting DFT based absorption band of C-H in methyl group were located at 1505-1449, 1504-1466, 1467-1449 and 1505-1444 cm^{-1} respectively, which are in nice harmony with experimental vibrational bands at 1508, 1489, 1486 and 1487 cm^{-1} respectively. However, the rocking vibrational modes of DFT based were found to be 1515-1475 cm^{-1} in **5a**, 1659-1631 cm^{-1} in **5b**, 1622-1512 in **5c** and 1662-1505 cm^{-1} in **5d** and experimentally observed spectra shows these absorption bands at 1609, 1587, 1583 and 1569 cm^{-1} ((Tables S5-S8 and Figures S1-S4 (Supplementary Information))).

2.6.2 C-N vibrations

The experimental IR spectrum of indole-based thiazoline **5a** showed a band due to C-N stretching at 1609 cm^{-1} which are in reasonable agreement with DFT calculated C-N vibrational band found at 1621 cm^{-1} . In IR spectrum of **5b**, a single band resulting azomethine C-N bonds were observed at 1587 cm^{-1} experimentally and at 1603 cm^{-1} through DFT computations respectively which are in good harmony with each other. In the compounds **5c** and **5d**, azomethine C-N band in IR was appeared at 1617 and 1604 cm^{-1} which are in excellent connection with DFT computed C-N bands at 1622 and 1603 cm^{-1} respectively (Tables S5-S8 and Figures S1-S4 (Supplementary Information)).

2.6.3 C-C vibrations

The vibrational bands for the C-C stretching have been usually located in the span of 1650-1400 cm^{-1} [94]. The stimulated DFT based C-C vibrations for benzene ring were investigated in the span of 1675-1626 cm^{-1} in **5a**, 1659-1504 cm^{-1} in **5b**, 1644-1512 cm^{-1} in **5c** and 1673-1505 cm^{-1} **5d** (Tables S5-S8 (Supplementary Information)).

2.6.4 N-H absorption bands

The N-H stimulated stretching modes were noticed at 3661 cm^{-1} for pyrrole in **5a**. Similar stretching absorption band was observed at 3591 cm^{-1} for morpholine ring in **5b**.

2.7 UV–Vis Spectral Analysis

To investigate the different phenomena of entitled molecules **5a**, **5b**, **5c**, and **5d** such as charge transfers, molecular orbital excitations and absorption process UV–Vis Spectral study was executed. DFT calculation has been performed by using M06/6-311+G(d,p) level in gaseous phase, while experimental investigations were obtained in chloroform and n-hexane and some of the important results are tabulated in Table 2.3, while their experimental pictographs are shown in Figures S5-S8 (Supplementary Information).

Table 2. 3: UV-Visible spectral analysis of investigated molecules 5a, 5b, 5c, and 5d

Compounds	λ (nm)	Exp λ (nm)	E (eV)	f_{os}	MO contributions
		≈ 345			
5a	341.047	(Chloroform) ≈ 350 (n-hexane)	3.6354	0.4178	H $\rightarrow$ L+1 (92%)
		≈ 350			
5b	354.109	(Chloroform) ≈ 355 (n-hexane)	3.5013	0.5024	H $\rightarrow$ L+1 (93%), H $\rightarrow$ L (4%)
		≈ 320			
5c	308.21	(Chloroform) ≈ 315 (n-hexane)	4.0227	0.0817	H $\rightarrow$ L+1 (39%), H $\rightarrow$ L+3 (31%)
		≈ 350			
5d	351.210	(Chloroform) ≈ 355 (n-hexane)	3.5302	0.8578	H $\rightarrow$ L+1 (95%)

MO=molecular orbital, H=HOMO, L=LUMO, f = oscillator strength

The above Table 2.3 described that higher value of maximum absorption of wave length that matches satisfactorily with experimentally determined λ_{max} values at ≈ 345 in chloroform and ≈ 350 in n-hexane with higher oscillation strength 0.5024 was 354.109 nm in **5b** with 3.5013eV excitation energy and H $\rightarrow$ L+1 (93%), H $\rightarrow$ L (4%)

molecular orbital contribution. This value becomes narrow in **5d** to 351.210 nm as examined at higher oscillation strength 0.8578, excitation energy of 3.5302 eV showing H→L+1 (95%) molecular orbital contribution quite matches with experimental absorption λ_{max} values at ≈ 350 in chloroform and ≈ 355 in n-hexane respectively. Furthermore, this value of maximum absorption wave length decreased to 341.047 nm in **5a** having 3.6354 eV excitation energy with H→L+1 (92%) molecular orbital contribution, 0.4178 oscillation strength exhibit excellent correlation with experimental λ_{max} values ≈ 345 in chloroform and ≈ 350 in n-hexane respectively. Similarly, least DFT calculated λ_{max} value 308.21 nm with 4.0227, 0.0817 and H→L+1 (39%), H→L+3 (31%) transition energy, oscillation strength, molecular orbital contribution respectively was found in **5c** which exhibit excellent concurrence with experimental λ_{max} values ≈ 320 in chloroform and ≈ 315 in n-hexane respectively. Overall results indicate that both DFT computed and experimental determined λ_{max} values are in excellent agreement with each other. This investigation also shows that **5b** is red shifted among all studied molecules.

2.8 Frontier molecular orbital (FMO) analysis

To reveal the electronic as well as optical properties, chemical stability and light absorption ability of studied compounds, frontier molecular orbital (FMOs) investigation is an admirable descriptor. The lowest unoccupied molecular orbital and highest occupied molecular orbitals which are abbreviated as LUMO and HOMO respectively are the substantial quantum/orbitals of FMOs. Mostly, LUMO showed the electron accepting nature while HOMO exhibited electron donating features. The

energy gap or band gap ($E_{\text{gap}}=E_{\text{LUMO}}-E_{\text{HOMO}}$) of FMOs orbitals is an important parameter for describing the chemical reactivity and dynamic stability of the entitled compounds. Moreover, the bonding frame work is also described by the surface of these molecular orbitals. So, the energies and band gaps of three significant pairs of molecular orbitals HOMO are examined by using M06 functional and results are displayed in Table 2.4 while their molecular orbitals are pictographically portrayed in Figure 2.1.

Table 2. 4: The E_{HOMO} , E_{LUMO} and energy band gap of investigated compounds 5a, 5b, 5c, and 5d

Compounds	H	L	ΔE	H-1	L+1	ΔE	H-2	L+2	ΔE
5a	-	-	2.825	-	-	5.326	-	-	5.592
	5.552	2.727		6.532	1.206		6.758	1.166	
5b	-	-	4.114	-	-	5.237	-	-	5.608
	5.605	1.491		6.573	1.336		6.725	1.117	
5c	-	-	4.332	-	-	5.425	-	-	6.156
	5.590	1.258		6.480	1.055		7.062	0.906	
5d	-	-	4.081	-	-	5.236	-	-	5.519
	5.403	1.322		6.326	1.090		6.530	1.011	

H=HOMO; L= LUMO; HOMO=highest occupied molecular orbital; LUMO=lowest unoccupied molecular orbital, $\Delta E = E_{\text{LUMO}}-E_{\text{HOMO}}$; Energy is in eV.

It is elucidated from the above Table 2.4 that higher value of band difference of LUMO/HOMO was 4.332 eV as observed in **5c** with -5.590 and -1.258 eV HOMO and LUMO values respectively. This band gap decreased to 4.114 eV in **5b** having -5.605/-1.491 eV of HOMO/LIMO energies. This decrease in energy difference may be due to the 3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one group that is electron with drawing

group as compare to cyclo alkyl group hence, increase the resonance and made it more stable by lowering the band gap as compared to **5c**. This band gap further becomes narrowed to 4.081 eV in **5d** showing the -5.403 and -1.322 eV of HOMO and LUMO respectively. The presence of 2,3-dihydrobenzo[b][1,4]dioxine that is more electron with drawing group increase the resonance which in turn decreased the band gap and stable the crystal. The lowest band gap is found to be 2.285eV in **5a** molecule with -5.552 and -2.727 eV energies of HOMO and LUMO respectively which might be due to the presence of indole and more electron with drawing NO₂ group that lowers the energy between orbitals. The decreasing order of band gap is found **5c > 5b > 5d > 5a**. Similar decreasing ΔE phenomenon was observed for the HOMO-1, LUMO+1, HOMO-1 and LUMO+1 orbitals (see Table 2

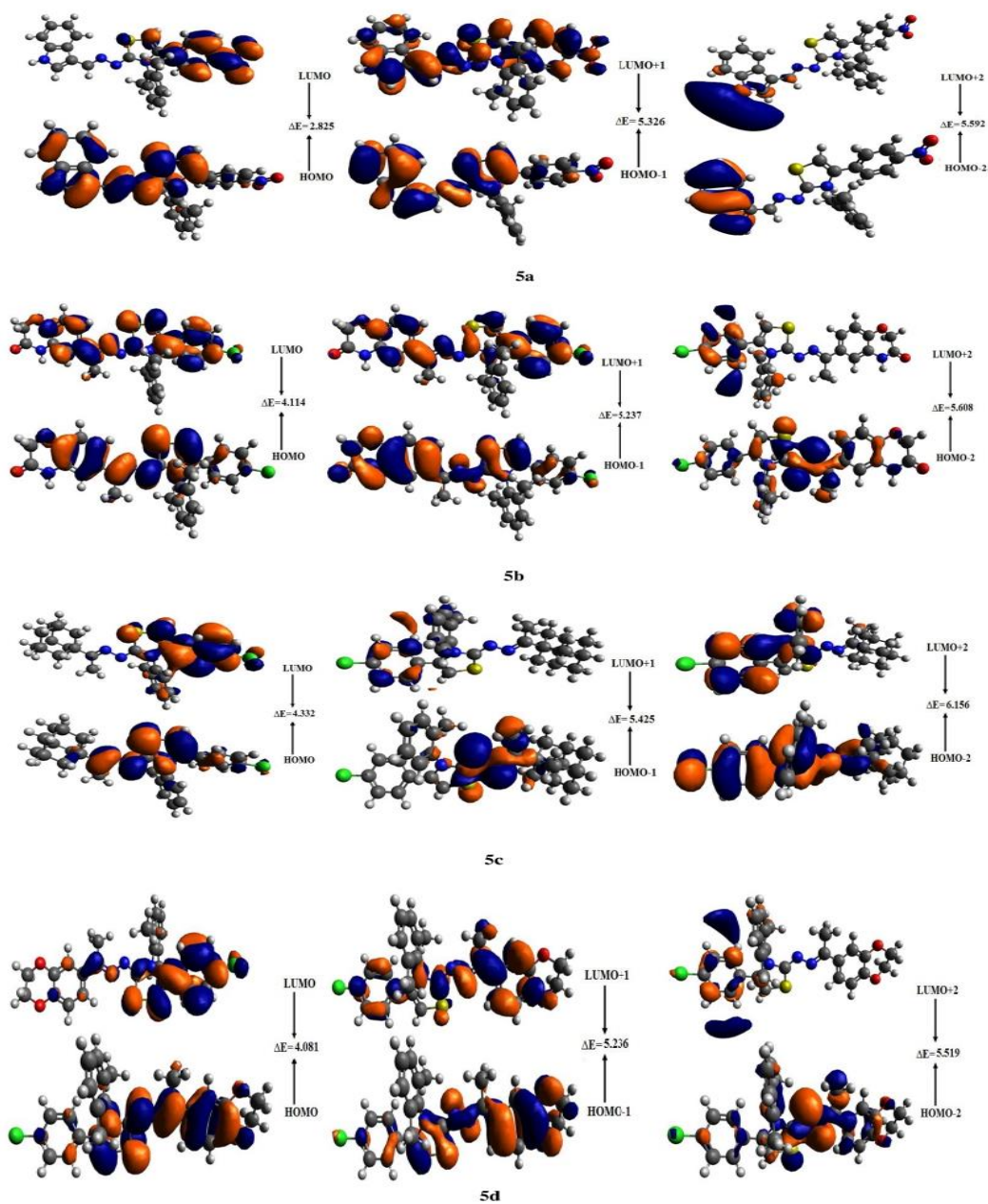


Figure 2. 1: Frontier molecular orbitals of entitled compounds 5a-d.

In **5a**, HOMO charge density is located at (Z)-2-((E)-((1H-indol-3-yl)methylene)hydrazono)-4-phenyl-2,3-dihydrothiazole portion while LUMO it is concentrated on 4-phenyl-2,3-dihydrothiazole part of the molecule. In **5b** at 6-((Z)-1-((Z)-(4-(4-

chlorophenyl)thiazol-2(3H)-ylidene)hydrazono)ethyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one portion, both HOMO and LUMO both are concentrated. The charge density in **5c** for HOMO is located at (Z)-ethylidenehydrazono)-3-phenyl-2,3-dihydrothiazole moiety while for LUMO, it is concentrated over 4-(4-chlorophenyl)-3-(o-tolyl)-2,3-dihydrothiazole part. Similarly in **5d**, both HOMO and LUMO charge density is present at (Z)-4-(4-chlorophenyl)-2-((E)-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethylidene)hydrazono)-2,3-dihydrothiazole part of the entire molecule and (see Figure 2.1).

The charge density for both HOMO-1 and LUMO+1 is concentrated at (Z)-2-((E)-((1H-indol-3-yl)methylene)hydrazono)-4-(4-nitrophenyl)-2,3-dihydrothiazole part in **5a**. At 6-((Z)-((Z)-(4-(4-chlorophenyl)thiazol-2(3H)-ylidene)hydrazono)methyl)-3,4-dihydro-2H-benzo[b][1,4] oxazin-2-one part, HOMO-1 is populated in **5b** while LUMO+1 exists all over the molecule. For HOMO-1, the charge density in **5c** is present at (Z)-2-(propan-2-ylidenehydrazono)-3-(o-tolyl)-2,3-dihydrothiazole moiety and small charge density of LUMO+1 at N-(1-(4-chlorophenyl)vinyl)-N,2-dimethylaniline respectively. In **5d** at (Z)-4-(4-chlorophenyl)-2-((E)-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethylidene)hydrazono)-2,3-dihydrothiazole HOMO is concentrated and for LUMO too (see Figure 2.1).

Moreover, for the HOMO-2 and LUMO+2 orbitals charge density in **5c** is concentrated at (Z)-4-(4-chlorophenyl)-2-((Z)-ethylidenehydrazono)-3-(o-tolyl)-2,3-dihydrothiazole portion and at 4-(4-chlorophenyl)-3-(o-tolyl)-2,3-dihydrothiazole moiety respectively. In **5b** crystal, HOMO-2 charge density is located all over the molecule, while for LUMO+2, it is observed at 4-(4-chlorophenyl)-3-(2,6-

dimethylphenyl)-2,3-dihydrothiazole part. In **5d** charge density for HOMO-2 is concentrated all over the molecule while for LUMO+2 is located at 4-(4-chlorophenyl)-3-(2,6-dimethylphenyl)-2,3-dihydrothiazole moiety. In **5a** for LUMO+2 orbital charge density is present at (1H-indol-3-yl)methanimine while for HOMO-2 is concentrated at indole moiety (see Figure 2.1).

2.9 Global reactivity parameters

HOMO-LUMO energies are further utilized to evaluate the promising global indices of reactivity [95] which provide information regarding stability, chemical reactivity and internal charge transfer among **5a-d**. The values of ionization potential, electronic affinity, chemical hardness, electronegativity, electrophilicity and global softness are calculated by utilizing equations mentioned in supplementary information and results are collected in Table 2.5.

Table 2. 5: Global reactivity descriptors of investigated molecules **5a**, **5b**, **5c**, and **5d**.

Compounds	I	A	X	η	μ	ω	σ
5a	5.55	2.727	4.1395	1.4125	-4.1395	6.06565	0.353982
5b	5.60	1.491	3.548	2.057	-3.548	3.05987	0.243072
5c	5.59	1.258	3.424	2.166	-3.424	2.706319	0.23084
5d	5.40	1.322	3.362	2.040	-3.362	2.770499	0.245038

In the above table I is the ionization potential, A is the electron affinity, X is the electronegativity, η is the global hardness, μ is the chemical potential ω is the global electrophilicity, and σ is the hardness of the molecule. The capability of electron donating is actually the electron affinity which is used to pull an electron from HOMO. Electronegativity is also another important factor that describes the ability to attract electron towards itself. It is shown by the negative values of the chemical potential that molecules are stables. It is indicated from Table 2.5 that the higher value of I is calculated as 5.60 eV. Almost similar I value 5.59 eV is noted in **5c** with the lowest value of 1.258 eV is electron affinity among all the investigated compounds. Least value of ionization energy is 5.403 eV with A value of 1.322 eV as determined in **5d**. The order for A is **5c** < **5d** < **5b** < **5a**. Among all the molecules, the greater value of harness is found in **5c** which is 2.166 eV. While **5a** shows the least value 1.4125 eV as has smaller band gap. The order for hardness is **5c** > **5b** > **5d** > **5a**. However, the species with smaller energy difference are considered as soft molecules hence, more reactive. Among the analyzed molecules **5a** represent the maximum value of softness 0.353982 eV, so more reactive compound (see Table 2.5). The order for softness is **5a** > **5d** > **5b** < **5c**. This order is exactly inverste to the hardenss value order and similar to the HOMO-LUMO energy gaps order. Ddiscussion concludes that **5a** is the most reactive, soft and least stable molecule due to least HOMO-LUMO energy gap amongst all investigated compounds. Contrarily, **5c** is the molecule having largest energy gap, greater hardness, least softness and more stability among all studied molecules. Overall, all investigated molecule is soft enough to utilize in biological as well as NLO properties.

2.10 Nonlinear optical (NLO) analysis

The synthesis of NLO organic material has gained significant attention in research area due to a number of uses in different fields such as photonics, electro-optic modulation, in optical communication technologies and harmonic generation [96]. Now a days, scientists and researchers prefer organic NLO materials instead of their inorganic counterparts because of their large number of design possibilities, short response time, low cut-off wavelengths and large optical nonlinearity [3]. The NLO properties of investigated compounds **5a**, **5b**, **5c**, and **5d** are e tabulated in Tables 6-8

Following equations 6, 7 is used to calculate average polarizability and first hyperpolarizability values.

$$\langle a \rangle = 1/3(a_{xx} + a_{yy} + a_{zz}) \quad (6)$$

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyx})^2]^{1/2} \quad (7)$$

The dynamic frequency dependent second hyperpolarizability γ is calculated by using following equation 7.

$$\langle \Upsilon \rangle = \frac{1}{5} (\Upsilon_{xxxx} + \Upsilon_{yyyy} + \Upsilon_{zzzz} + 2[\Upsilon_{xxyy} + \Upsilon_{yyzz} + \Upsilon_{xxzz}]) \quad (8)$$

The total results computed for dipole moments (D), dipole polarizabilities (α_{total}) and first hyperpolarizabilities (β_{tot}) of investigated compounds **5a**, **5b**, **5c**, and **5d** at B3LYP, LC-BLYP, CAM-B3LYP and M06, M062X in coupling with 6-311+G(d,p) basis set are collected in Table 2.6. While results exhibited by individual components like μ_x , μ_y , μ_z in case of dipole moment,

major contributing tensors α_{xx} , α_{yy} , α_{zz} in case of dipole polarizabilities (α_{total}) and contributing tensors β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{yyz} , β_{xzz} , β_{yzz} , β_{zzz} for first hyperpolarizabilities (β_{tot}) are mentioned in Tables S9-S11 (Supplementary Information) respectively.

Table 2. 6: Computed dipole moments (**D**), dipole polarizabilities (α_{total}) and first hyperpolarizabilities (β_{tot}) of investigated compounds 5a, 5b, 5c, and 5d

Property	Compound	B3LYP	CAM-B3LYP	LC-BLYP	HF	M06	M062X
μ_{total} (D)	5a	2.5696	2.4279	2.3811	2.5183	2.5720	2.4292
	5b	1.7636	1.7623	1.7660	1.7983	1.7660	1.7669
	5c	0.3926	0.3914	0.3928	0.4044	0.3928	0.3830
	5d	0.5178	0.5046	0.5067	0.5042	0.5067	0.4724
α_{total} (a.u)	5a	427.52	401.72	381.56	374.49	424.07	400.39
	5b	441.53	419.81	388.03	388.03	399.38	419.30
	5c	395.43	381.99	367.73	360.69	367.73	382.44
	5d	428.47	408.37	389.25	379.67	389.25	407.71
β_{tot} (a.u)	5a	14068.40	4934.04	2848.91	2275.52	10747.84	4986.80
	5b	1974.91	1359.80	896.12	287.42	896.12	1476.27
	5c	675.42	146.83	105.63	62.80	105.63	188.71
	5d	635.94	502.65	359.36	211.67	359.36	563.20

The dipole moment results computed at B3LYP, CAM-B3LYP, LC-BLYP, HF, M06 and M062X methods are presented in Table 2.6. The results indicate that highest electric dipole moment (μ_{total}) is computed as 2.5720 D for compound **5a** computed from M06 method, while lowest dipole moment value 0.3830 D is noticed for compound **5c** computed from M062X method among all investigated compounds. Among all studied functionals, meta-hybrid GGA method M06 shows highest electric dipole moment 2.5720 D in **5a**. The HF method exhibit highest electric dipole moment values 1.7983 D and 0.4044 D in case of **5b** and **5c** respectively. Similarly, exchange correlation functional B3LYP exhibit the highest value 0.5178 D of electric dipole moment for **5d**. On the other hand, LC-BLYP with 2.3811 D, CAM-B3LYP with 1.7623 D, M062X with 0.3830, 0.4724 D are the lowest values of electric dipole moment (μ_{total}) than other investigated methods found in **5a**, **5b**, **5c**, and **5d** respectively. Overall, decreasing order of μ_{total} is **5a** > **5b** > **5d** > **5c**. Total dipole moment of urea molecule is 1.3732 D [97] which is considered as standard molecule for comparing dipole moment and β_{tot} results. The dipole moments of **5a**, **5b** are calculated greater than urea molecule.

The exchange correlation functional B3LYP and HF method among all investigated functionals exhibited the highest (427.52, 441.53, 395.43, 428.47 a.u) and lowest (374.49, 388.03, 360.69, 388.03 a.u) average polarizability values in investigated compounds **5a**, **5b**, **5c**, and **5d** respectively (Table 2.6). Compound **5b** among all investigated compounds exhibited the highest $\langle\alpha_{tot}\rangle$ values with all investigated methods. In contrast, Compound **5c** demonstrated the lowest average polarizability value calculated from all methods and amongst all studied molecules. The order of

average polarizability values with all opted methods is found to be B3LYP> M06> CAM-B3LYP> M062X> LC-BLYP> HF in **5a**, B3LYP> CAM-B3LYP> M062X> LC-BLYP> M06> HF in **5b**, B3LYP> M062X> CAM-B3LYP> LC-BLYP> M06> HF in **5c** and B3LYP> CAM-B3LYP> M062X> LC-BLYP> M06> HF in **5d**.

Results of β_{tot} mentioned in Table 2.6 indicate that among computed methods, B3LYP shows the highest computed β_{tot} values 14068.40, 1974.91, 675.42 and 635.94 (a.u) in **5a**, **5b**, **5c** and **5d** respectively. Contrariwise, lowest computed β_{tot} values 2275.52, 287.42, 62.80 and 211.67 (a.u) in **5a**, **5b**, **5c** and **5d** respectively are exhibited by HF method. Compound **5a** due to their highest charge separation (dipole moment) value and reasonably high dipole polarizability displayed the highest β_{tot} value among all studied compounds. Similarly, lowest β_{tot} values at all methods are exhibited by **5c**. The urea molecule comparative analysis consequently proved that β_{tot} magnitudes of **5a-d** are observed higher than urea molecule. In a nutshell, exceptional NLO characteristic of investigated compounds is evident from the above mentioned comparative data. The major contributing tensors and computed second hyperpolarizability (γ) findings for **5a**, **5b**, **5c**, and **5d** obtained from different computational methods including B3LYP, CAM-B3LYP, LC-BLYP, HF, M06 and M062X methods are collected in Table 2.7.

Table 2. 7: The computed second hyperpolarizability γ and major contributing tensors (a.u) for 5a, 5b, 5c, and 5d

Compounds	Methods	γ_x	γ_y	γ_z	Average< γ >	Magnitude of γ
5a	B3LYP	1.192 x10 ⁶	4.179 x10 ⁴	1.933 x10 ⁴	1.253 x10 ⁶	1.193 x10 ⁶
	CAM-B3LYP	3.300 x10 ⁵	2.738 x10 ⁴	1.607 x10 ⁴	3.734 x10 ⁵	3.314 x10 ⁵
	LC-BLYP	1.742 x10 ⁵	2.051 x10 ⁴	1.291 x10 ⁴	2.077 x10 ⁵	1.759 x10 ⁵
	HF	1.158 x10 ⁵	1.905 x10 ⁴	1.365 x10 ⁴	1.485 x10 ⁵	1.181 x10 ⁵
	M06	8.347x10 ⁵	3.500 x10 ⁴	1.741 x10 ⁴	8.871x10 ⁵	8.356 x10 ⁵
	M062X	3.393 x10 ⁵	2.635 x10 ⁴	1.507 x10 ⁴	3.808 x10 ⁵	3.407 x10 ⁵
5b	B3LYP	4.226 x10 ⁵	3.483 x10 ⁴	2.021 x10 ⁴	4.776 x10 ⁵	4.245 x10 ⁵
	CAM-B3LYP	2.526 x10 ⁵	2.525 x10 ⁴	1.610 x10 ⁴	2.939 x10 ⁵	2.543 x10 ⁵
	LC-BLYP	1.637 x10 ⁵	1.875 x10 ⁴	1.269 x10 ⁴	1.951 x10 ⁵	1.652 x10 ⁵
	HF	1.032 x10 ⁵	1.611 x10 ⁴	1.241 x10 ⁴	1.317 x10 ⁵	1.052 x10 ⁵
	M06	1.637 x10 ⁵	1.875 x10 ⁴	1.269 x10 ⁴	1.951 x10 ⁵	1.652 x10 ⁵
	M062X	2.609 x10 ⁵	2.450 x10 ⁴	1.532 x10 ⁴	3.007 x10 ⁵	2.625 x10 ⁵
5c	B3LYP	1.553 x10 ⁵	3.401 x10 ⁴	2.088 x10 ⁴	2.102 x10 ⁵	1.604 x10 ⁵
	CAM-B3LYP	9.603 x10 ⁴	2.469 x10 ⁴	1.666 x10 ⁴	1.374 x10 ⁵	1.005 x10 ⁵
	LC-BLYP	6.499 x10 ⁴	1.831 x10 ⁴	1.303 x10 ⁴	9.634 x10 ⁴	6.877 x10 ⁴
	HF	4.562 x10 ⁴	1.568 x10 ⁴	1.226 x10 ⁴	7.356 x10 ⁴	4.977 x10 ⁴
	M06	6.499 x10 ⁴	1.831 x10 ⁴	1.303 x10 ⁴	9.634 x10 ⁴	6.877 x10 ⁴
	M062X	9.994 x10 ⁴	2.501 x10 ⁴	1.673 x10 ⁴	1.417 x10 ⁵	1.044 x10 ⁵
5d	B3LYP	3.804 x10 ⁵	3.387 x10 ⁴	1.992 x10 ⁴	4.342 x10 ⁵	3.824 x10 ⁵
	CAM-B3LYP	2.280 x10 ⁵	2.454x10 ⁴	1.602 x10 ⁴	2.685 x10 ⁵	2.299 x10 ⁵
	LC-BLYP	1.489 x10 ⁵	1.824 x10 ⁴	1.265 x10 ⁴	1.798 x10 ⁵	1.505 x10 ⁵
	HF	9.504 x10 ⁴	1.576 x10 ⁴	1.239 x10 ⁴	1.232 x10 ⁵	9.713 x10 ⁴
	M06	1.489 x10 ⁵	1.824 x10 ⁴	1.265 x10 ⁴	1.798 x10 ⁵	1.505 x10 ⁵
	M062X	2.358 x10 ⁵	1.668 x10 ⁴	1.536 x10 ⁴	2.679 x10 ⁵	2.369 x10 ⁵

It is evident from Table 2.7 that $\langle\gamma\rangle$ values are contributed minutely by z-direction tensor γ_z and largely by tensor along x-direction (γ_x). The HF method among all investigated methods shows lower $\langle\gamma\rangle$ values for all investigated compounds. These lowest $\langle\gamma\rangle$ values are 1.485×10^5 , 1.317×10^5 , 7.356×10^4 and 1.232×10^5 (a.u) for investigated molecules **5a**, **5b**, **5c**, and **5d** respectively. On the other hand, highest second hyperpolarizability values 1.253×10^6 , 4.776×10^5 , 2.102×10^5 and 4.342×10^5 (a.u) are exhibited by exchange correlation functional B3LYP among all investigated methods in studied compounds **5a**, **5b**, **5c**, and **5d** respectively. The decreasing order of $\langle\gamma\rangle$ values among **5a-d** is: **5a** > **5b** > **5d** > **5c**. Since compound **5a** contains the lowest energy gap and greater softness values, so it exhibits more distortion in terms of higher charge separation (induced electric dipole moment values) which makes it more polarizable, hence, highest NLO value is exhibited by this molecule among all investigated molecules. In a nutshell, exceptional NLO characteristic of investigated compounds is evident from the above mentioned comparative data. At 0 and 0.02389 nm, the $\gamma(-\omega, \omega, 0, 0)$ and $\gamma(-2\omega, \omega, \omega, 0)$ were estimated and results are collected in Table 2.8.

Table 2. 8: Frequency dependent second hyperpolarizability (*a.u.*) of investigated compounds 5a, 5b, 5c, and 5d

Parameters	Frequency ω	B3LYP		CAM-B3LYP		LC-BLYP	
Compound		5a	5b	5a	5b	5a	5b
$\gamma(-\omega, \omega, 0, 0)$	0.000	1.253×10^6	4.776×10^5	3.734×10^5	2.939×10^5	2.077×10^5	1.951×10^5
	0.02389 nm	1.624×10^6	5.168×10^5	4.056×10^5	3.108×10^5	2.178×10^5	2.033×10^5
$\gamma(-2\omega, \omega, \omega, 0)$	0.000	1.253×10^6	4.776×10^5	3.734×10^5	2.939×10^5	2.077×10^5	1.951×10^5
	0.02389 nm	3.250×10^6	6.094×10^5	4.849×10^5	3.484×10^5	2.408×10^5	2.217×10^5
		HF		M06		M062X	
		5a	5b	5a	5b	5a	5b
$\gamma(-\omega, \omega, 0, 0)$	0.000	1.485×10^5	1.317×10^5	8.871×10^5	1.951×10^5	3.808×10^5	3.007×10^5
	0.02389 nm	1.541×10^5	1.360×10^5	1.068×10^6	2.033×10^5	4.123×10^5	3.163×10^5
$\gamma(-2\omega, \omega, \omega, 0)$	0.000	1.485×10^5	1.317×10^5	8.871×10^5	1.951×10^5	3.808×10^5	3.007×10^5
	0.02389 nm	1.666×10^5	1.454×10^5	1.719×10^6	2.217×10^5	4.976×10^5	3.560×10^5

Parameters	Frequency ω	B3LYP		CAM-B3LYP		LC-BLYP	
Compound		5c	5d	5c	5d	5c	5d
$\gamma(-\omega, \omega, 0, 0)$	0.000	2.102 x10 ⁵	4.342 ×10 ⁵	1.374 x10 ⁵	1.835 ×10 ⁵	9.634 x10 ⁴	1.798 ×10 ⁵
	0.02389 nm	2.223 x10 ⁵	4.685 ×10 ⁵	1.426 x10 ⁵	2.833 ×10 ⁵	9.879 x10 ⁴	1.870 ×10 ⁵
$\gamma(-2\omega, \omega, \omega, 0)$	0.000	2.102 x10 ⁵	4.342 ×10 ⁵	1.374 x10 ⁵	3.159 ×10 ⁵	9.634 x10 ⁴	1.798 ×10 ⁵
	0.02389 nm	2.471 x10 ⁵	5.482 ×10 ⁵	1.529 x10 ⁵	2.110 ×10 ⁵	1.042x10 ⁵	2.031 ×10 ⁵
		HF		M06		M062X	
		5c	5d	5c	5d	5c	5d
$\gamma(-\omega, \omega, 0, 0)$	0.000	7.356 x10 ⁴	1.232 ×10 ⁵	9.634 ×10 ⁴	1.798 ×10 ⁵	1.417 ×10 ⁵	2.679 ×10 ⁵
	0.02389 nm	7.513 x10 ⁴	1.271 ×10 ⁵	9.879 ×10 ⁴	1.870 ×10 ⁵	1.416 ×10 ⁵	2.883 ×10 ⁵
$\gamma(-2\omega, \omega, \omega, 0)$	0.000	7.356 x10 ⁴	1.232 ×10 ⁵	9.634 ×10 ⁴	1.798 ×10 ⁵	1.417 ×10 ⁵	2.679 ×10 ⁵
	0.02389 nm	7.846 x10 ⁴	1.355 ×10 ⁵	1.042 ×10 ⁵	2.031 ×10 ⁵	1.524 ×10 ⁵	3.226 ×10 ⁵

In **5a**, highest and lowest $\gamma(-\omega,\omega,0,0)$ values computed at 0 nm are found to be with B3LYP functional 1.253×10^6 (a.u) and HF functional 1.485×10^5 (a.u.) respectively. Similar effect is observed in **5b**, **5c** and **5d**, where B3LYP and HF functionals exhibited highest and lowest $\gamma(-\omega,\omega,0,0)$ values at 0 nm respectively. With increase in wavelength from 0 to 0.02389 nm, an augmented response in $\gamma(-\omega,\omega,0,0)$ values is noted at all invested functionals and studied compounds.

Results of $\gamma(-2\omega,\omega,\omega,0)$ mentioned in Table 2.8 indicate that highest value in **5a** at 0 nm is measured as 1.253×10^6 (a.u) from B3LYP functional which becomes more promising 3.250×10^6 (a.u) with increasing the wavelength to 0.02389 nm. In **5b**, highest and lowest $\gamma(-2\omega,\omega,\omega,0)$ values are found to be with B3LYP and HF functionals at both 0 and 0.02389 nm. The highest $\gamma(-2\omega,\omega,\omega,0)$ values at 0 and 0.02389 nm in case of **5c** are marked as 2.102×10^5 (a.u), 2.471×10^5 (a.u) respectively from B3LYP functional. HF functionals both at 0 and 0.02389 nm exhibit least $\gamma(-2\omega,\omega,\omega,0)$ values for **5c**. Similarly in **5d**, highest and lowest $\gamma(-2\omega,\omega,\omega,0)$ values are found from B3LYP and HF functionals at both 0 and 0.02389 nm.

Studied thiazoline based compounds exhibit better dipole moment, $\langle\alpha_{tot}\rangle$ and β_{tot} results as compared to reported pyrimidine substituted diaryl ethers [98] dipole moment, $\langle\alpha_{tot}\rangle$ and β_{tot} results computed at different functionals (CAM-B3LYP, LC-BLYP, HF, M062X, M06).

Overall NLO findings conclude that studied molecules **5a-d** contain reasonable dipole moment values and polarizable character. Furthermore, second hyperpolarizability, (SHG) form $\gamma(-2\omega,\omega,\omega,0)$ and EOKO (Electro-optic Kerr effect) form $\gamma(-\omega,\omega,0,0)$

results noticeably point out that **5a-d** are satisfactory NLO aspirants for next generation optoelectronic devices.

2.11 Molecular Electrostatic Potential

Electron density of a compound is investigated through molecular electrostatic potential analysis. The color in MEP analysis actually defines the sites for electrophilic and nucleophilic attack [99]. Electrostatic potential magnitude is increasing in following order; red<orange<yellow<green <blue [100]. From Figure 2.2, it can be seen that negative potential (red color) is shown by oxygen atoms, while blue area shows positive potential exhibited mostly by hydrogen and carbon atoms. Green is mostly exhibited by chlorine atom. From red, blue and green colors, it is cleared that different reaction sites are presents in all molecules.

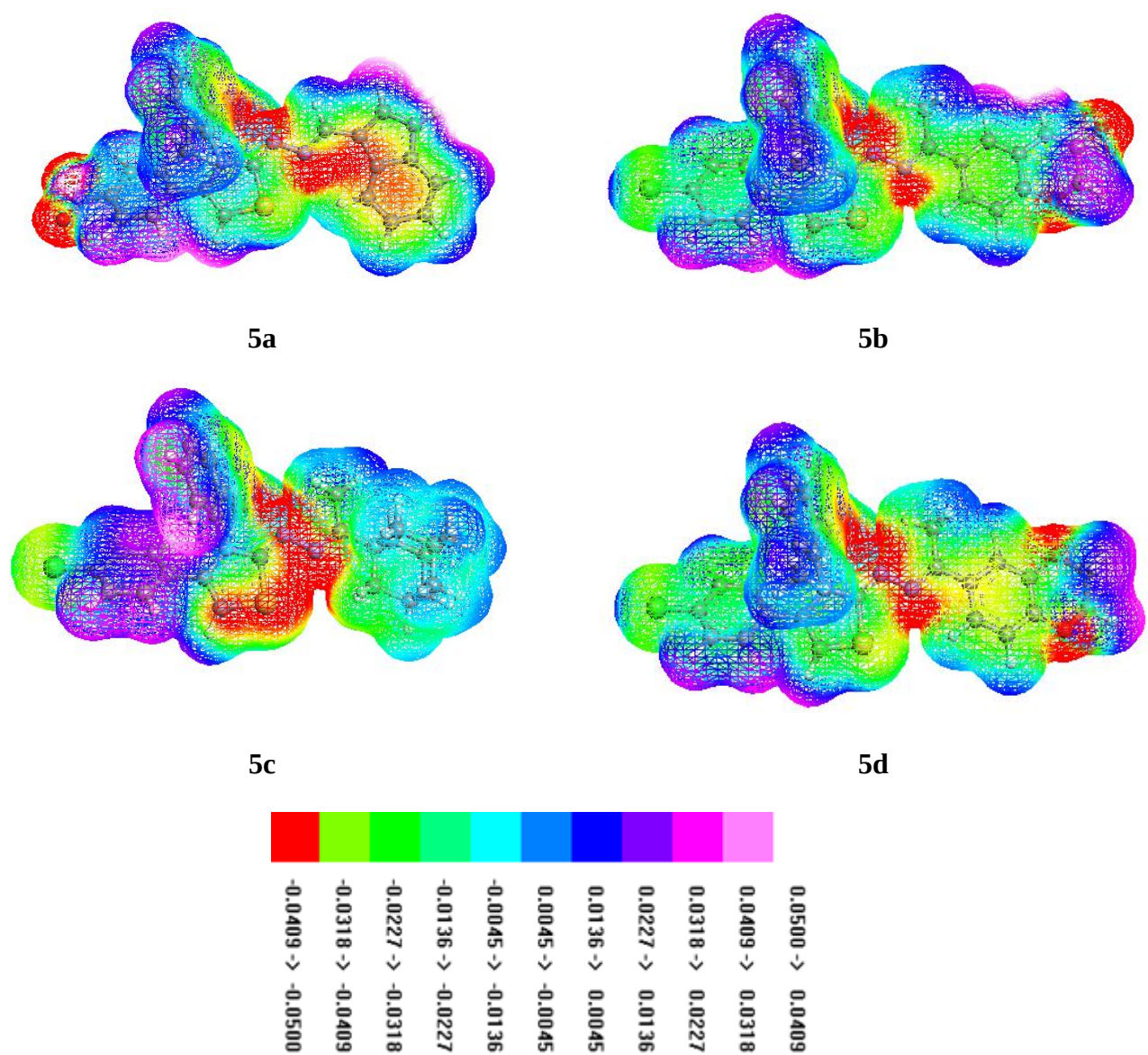


Figure 2. 2: MEPs and color scheme of the studied compounds 5a-d

2.12 Outcomes

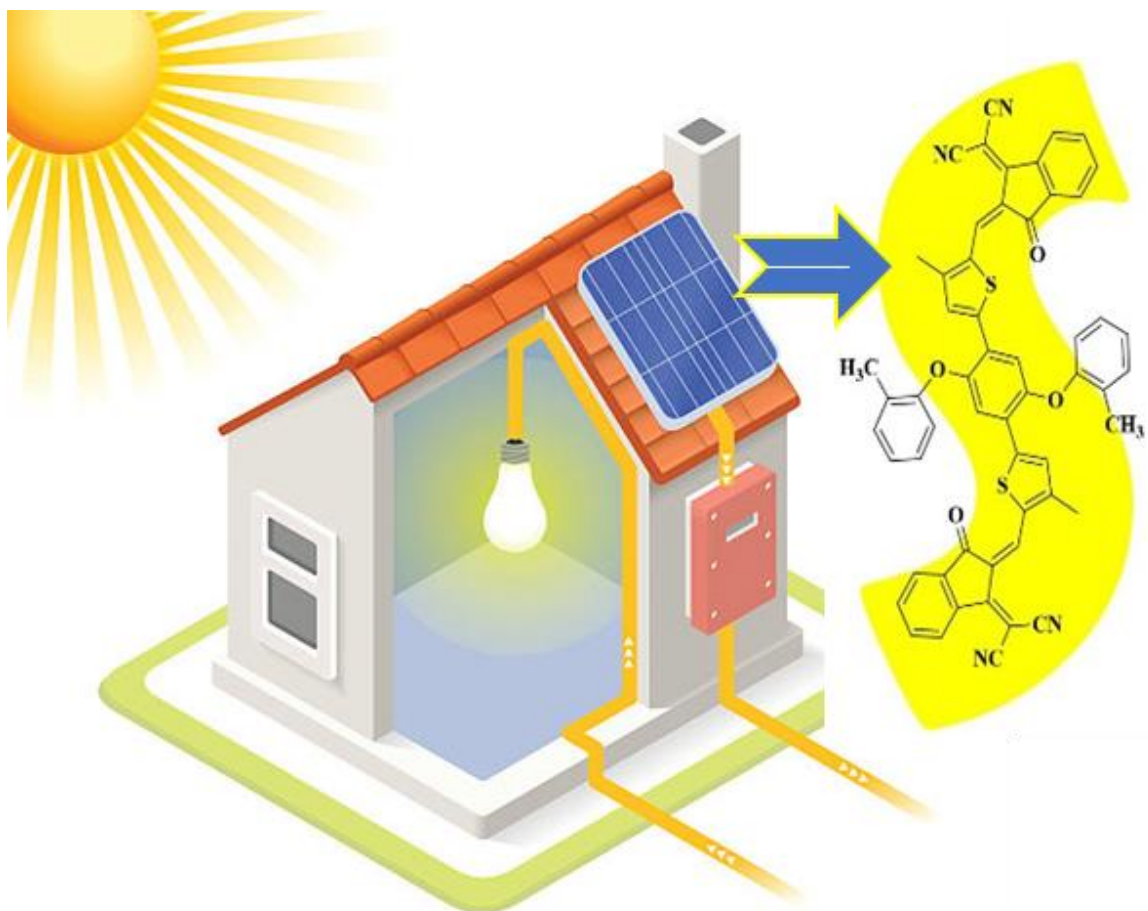
Four novel thiazoline derivatives were synergistically explored for their experimental (synthesis, UV–Visible, EIMS, elemental analysis) as well as computational (FT-IR, UV-

Visible, FMO, NBO, MEP, NLO) insights. The synthesis of novel thiazolidines (5a-d) was achieved through convenient cyclization of thiosemicarbazones with phenacyl bromides. Excellent concurrence among overall experimental (FT-IR, UV-Visible) and DFT computed (FT-IR, UV-Visible) results confirmed the purity of investigated molecules 5a, 5b, 5c and 5d. Compound 5b is found red shifted among all studied molecules. The lowest band gap is found to be 2.285eV in 5a due to the presence of indole and more electron with drawing NO₂ group that lowers the energy between orbitals. The order of energy gap is found as 5c > 5b > 5d > 5a. Global reactivity results confirmed that 5a is the most reactive, soft and least stable molecule due to least HOMO-LUMO energy gap, while 5c is the molecule having largest energy gap, greater hardness, least softness and more stability amongst all investigated compounds. All the investigated functionals exhibited the highest (427.52, 441.53, 395.43, 428.47 a.u) and lowest (374.49, 388.03, 360.69, 388.03 a.u) average polarizability values in 5a-d respectively. The HF method showed the lowest $\langle\gamma\rangle$ values which are 1.485×10^5 , 1.317×10^5 , 7.356×10^4 and 1.232×10^5 (a.u) for investigated molecules 5a, 5b, 5c, and 5d respectively. While, highest second hyperpolarizability values 1.253×10^6 , 4.776×10^5 , 2.102×10^5 and 4.342×10^5 (a.u) are exhibited by B3LYP functional among all investigated methods in studied compounds 5a, 5b, 5c, and 5d respectively. Overall NLO findings concluded that studied molecules 5a-d contain reasonable dipole moment values and polarizable character.

CHAPTER 3

S-shaped fullerene-free acceptor molecule for optoelectronic

properties: Computational study for organic solar cells



3.1 Introduction

Bulk-heterojunction polymer solar cells are commonly known as super solar cells because of their flexibility, low weight and effective fabrication [101,102]. These solar cells contain an active layer which is made up of a donor polymer with a unique derivative of fullerene-free acceptor material. But these derivatives of fullerene-free materials expressed certain draw backs like very instability with weak light absorption capability in the visible region [47, 103, 104].

Next era challenge is belonged to term fullerene-free derivatives with high absorption intensities with high light harvesting capacity [105]. Although some unique and extraordinary effective non-fullerene derivatives like Y6 and ITIC were synthesized and used in perovskite solar cells (PSCs) but certain things are needed to be improved like symmetry and configuration [106, 107].

In acceptor molecules, the twisted backbone has out of plane rings and long chains that behave as donor unit and the end-capped units mainly contain malononitriles as acceptor units [108–111]. This makes a perfect A-D-A symmetry and this allows a perfect transportation of charges from one end to other end with low voltage loss [112-115]. The presence of out of plane rings on the backbone offered certain delights for PSCs such as low aggregation in the blend film or active layer and high solubility in the solvent [116-122].

Recently, improving the efficiencies and to overcome the limitations of the fullerene-free acceptors, new series of acceptor have been synthesized. Wang and his collaborates, synthesized three unique systems named as SM1, SM2 and SM3 for possible utilization in

the OSCs [123]. Among these systems, SM1 was super molecule in active layer due to high absorption, reduces voltage loss and high fill factor with light harvesting capability.

Following this line, we decided to design new fullerene-free acceptor materials by alteration in the end-capped of SM1 molecule [123] . And in this way new five molecules are designed and examined through DFT and TD-DFT. The backbone in these molecules have twisted backbone with fused rings out-of-plane fashion. The main backbone is donor in nature and end-capped units are acceptor in nature. Certain geometric characteristics with photovoltaic potential of modelled molecules are examined through frontier MOs, light absorption ability, energies of excitation and binding, hole and electron reorganization, and open circuit voltage analysis. Further, transition density matrix analysis also performed to locate the charge density and oscillating strength of the modelled molecules. The examined results have recommended that the modelled molecules are effective contributors for highly stable and impeccable organic solar cells.

3.2 Computation methodology

Gaussian and GaussView programs are utilized for computation of different parameters and screening of results. Cam-B3LYP, PEBPEB, MPW1PW91, HSEH1PEB, and B3LYP with 6-31G(d,p) in dilute solvent (chloroform) are used with the help of TD-DFT for computation of light absorption capability of reference molecule. After careful examination, it was found that MPW1PW91 is the most appropriate functional for further analysis.

Reorganization of charges have two types of energies, i.e. internal and external reorganization energy. The internal energy showing the internal morphology of active layer

and external reorganization energy shows the external solvent effects. In this report, the study of active layer ignores the external reorganization energy as its contribution is very small or minimum. Equations given in literature are used for computations of hole and electron reorganization energy at MPW1PW91/6-31G(d,p) [118, 124-126]

3.2.1 Selection of computational methods at 6-31G(d,p) basis set

In foregoing report, five different and frequently used methods, i.e., Cam-B3LYP, PEBPEB, MPW1PW91, HSEH1PEB, and B3LYP with 6-31G(d,p) in dilute solvent (chloroform) are used with the help of TD-DFT for computation. The computed values are 633, 611, 596, 609, and 618 nm for Cam-B3LYP, PEBPEB, MPW1PW91, HSEH1PEB, and B3LYP, accordingly. Light absorption value of reference solvent was 584 nm [123] (calculated experimentally). From values and Figure 3.1, it is suggested that the method MPW1PW91 with 6-31G(d,p) is the reliable methodology for next analyses.

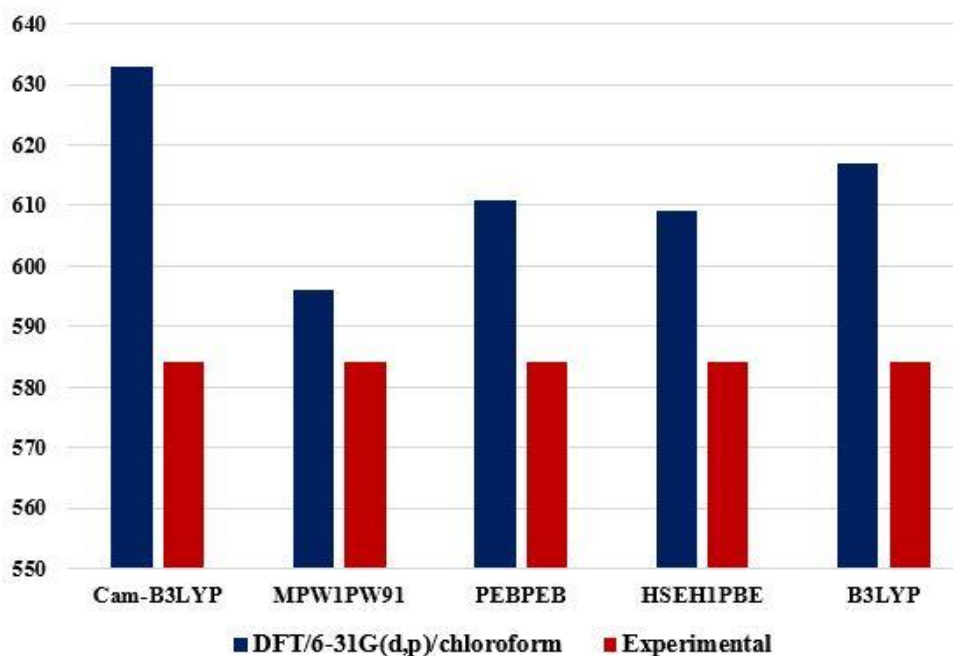
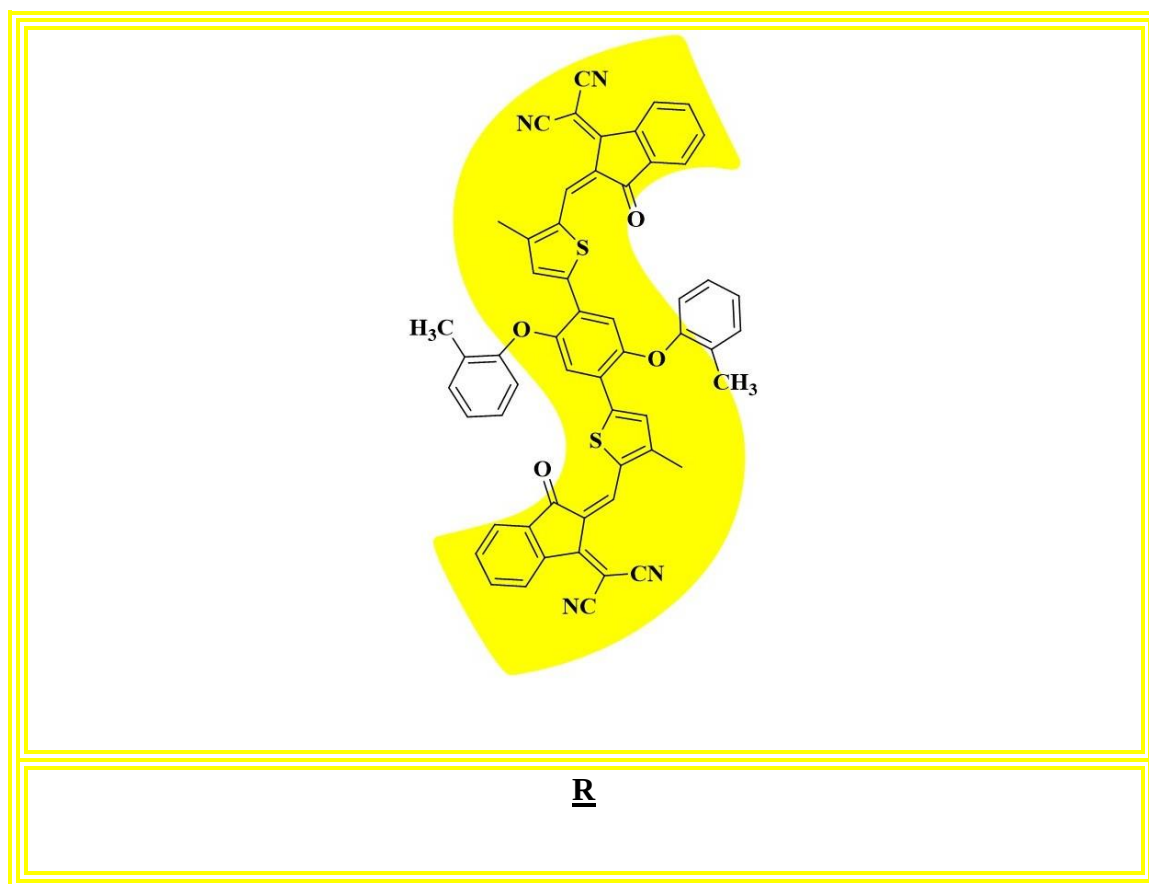


Figure 3. 1. TD-DFT based computed absorption values of reference molecule

End-capped alteration as mentioned earlier is a successful strategy for designing new and efficient molecules for active layer [127]. In this report, end-capped alteration of reference was done with different halogens, cyano, acetates, and thiophene rings for obtaining efficient molecules with reduced band gap and high charge mobility as shown in Figure 3.2.



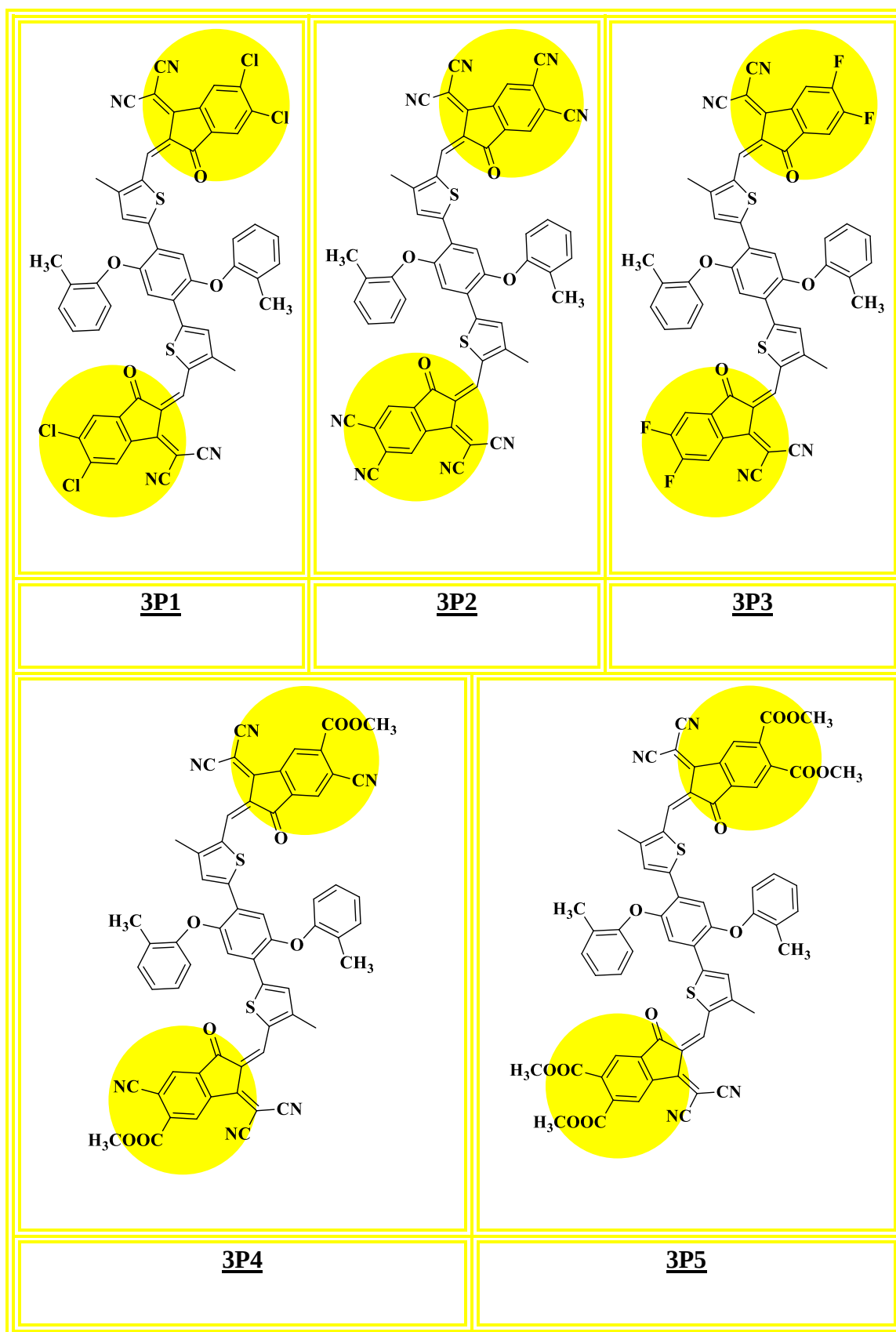
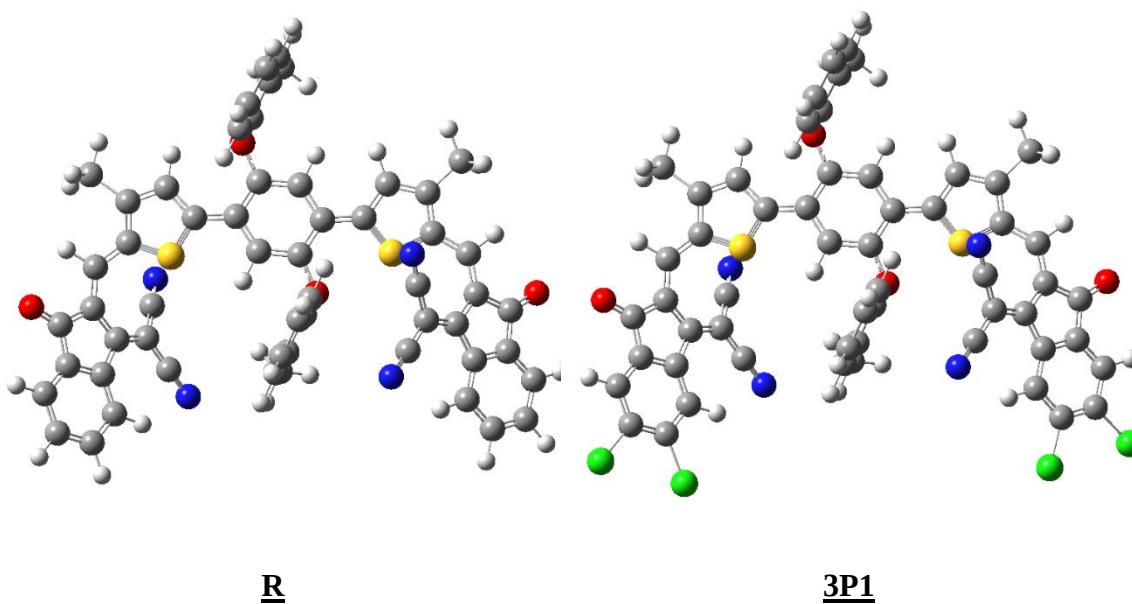


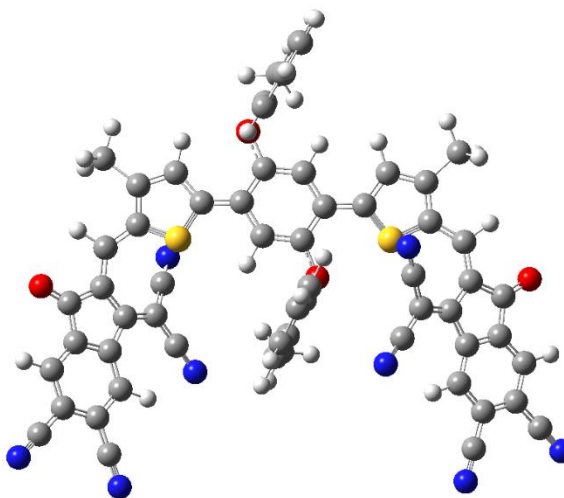
Figure 3. 2. Molecular designing of R and 3P1 to 3P5 by end-capped alterations

3.3 Study of frontier MOs

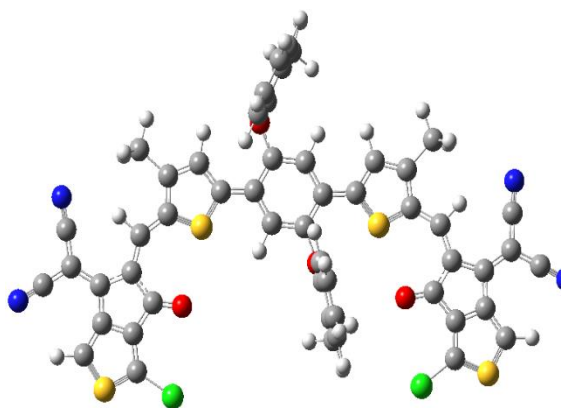
Opto-electric, and electronic nature of the active layer molecules are estimated with the aid of study of frontier molecular orbitals [2, 117,128] . The location and position of charge density is also examined through the presence of FMOs. Optimized/relaxed structures of R and 3P1 to 3P5 are expressed in Figure 3.3. The spreading of the FMO, i.e., HOMO and LUMO on the reference and modelled molecules are expressed in Figure 3.4.

The energy of orbitals with the band gap values are tabulated in Table 3.1. Small values of band gap cause the narrowing of band gap which allow easy flow of charge density from lower energy level to higher one. The DFT based computed HOMO energy values are -5.852, -6.122, -6.397, -6.432, -6.191, and -6.210 eV, for R and 3P1 to 3P5, accordingly. LUMO energy values are -3.353, -3.772, -4.027, -4.402, -3.782, -3.796 eV for R and 3P1-3P5.

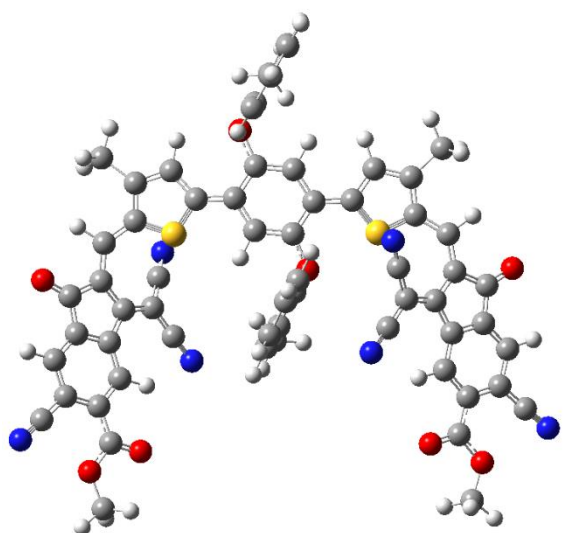




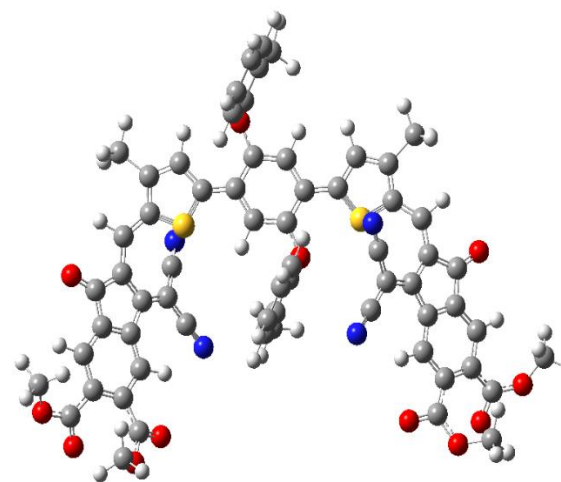
3P2



3P3



3P4



3P5

Figure 3. 3. Optimized/relaxed structures of R and 3P1 to 3P5 at MPW1PW91 with 6-31G(d,p)

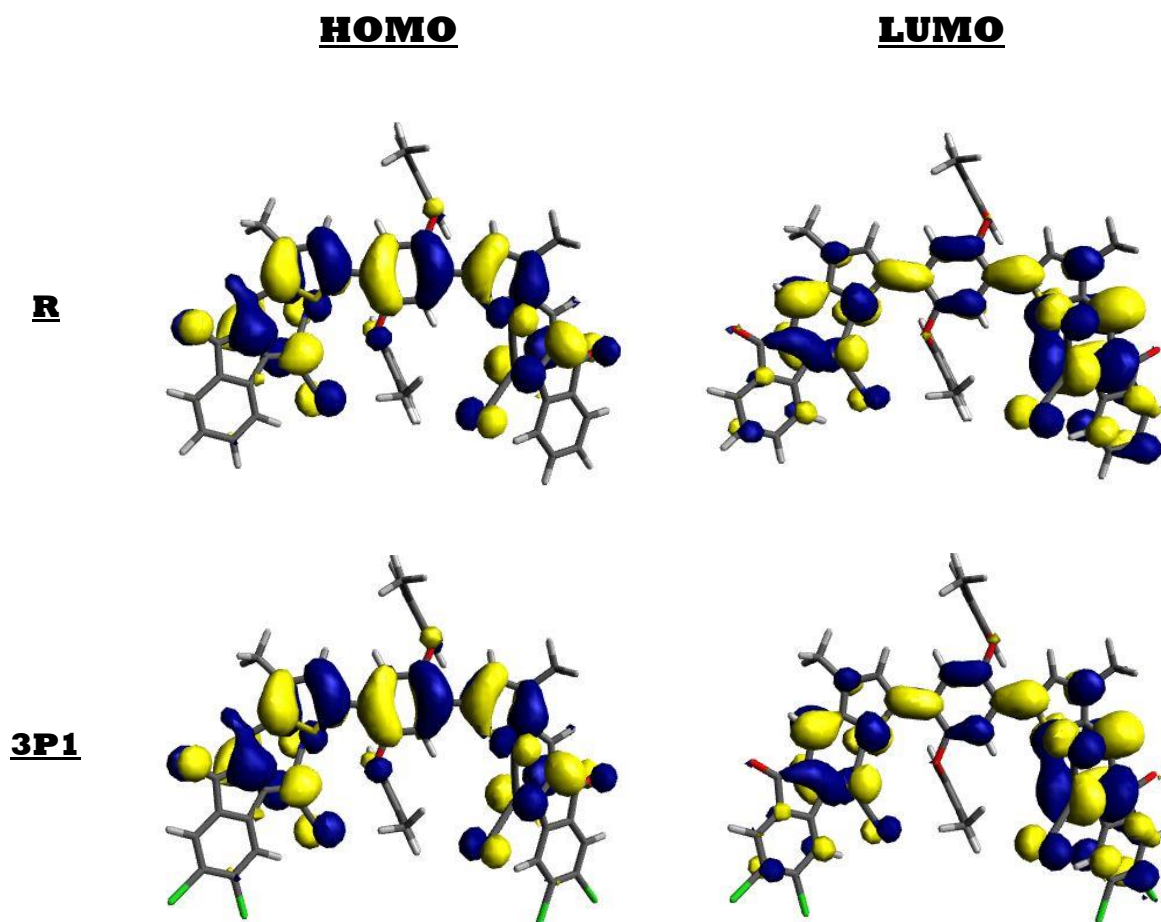
The calculated band gap of reference is 2.499 eV. The 3P1 to 3P5 has band gap values as 2.350, 2.370, 2.030, 2.409, and 2.414 eV, accordingly. Modelled molecules (3P1 to 3P5) expressed small values of band gap than the reference molecule (R). The order of energy band gap is: **R > 3P5 > 3P4 > 3P2 > 3P1 > 3P3**. From this order, lower values of band gap of modelled molecules are also confirmed. These small values cause reduction in the gap between two FMOs. These narrow band gaps in modelled molecules are because of efficient end-capped units. Least value is found in 3P3 that is because of fluorine units present in end-capped moiety of the 3P3.

Table 3. 1: Orbitals energies along with band gap of reference and modelled molecules

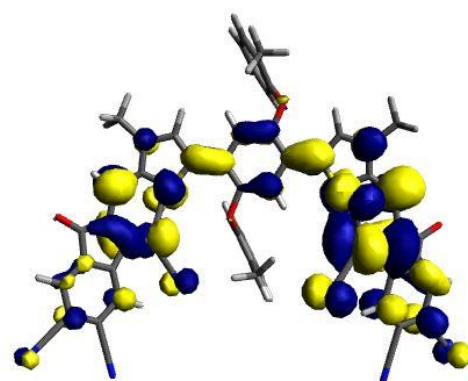
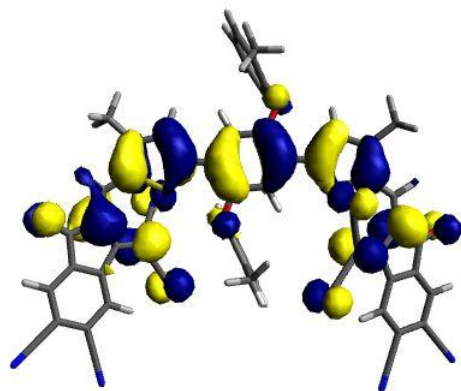
Systems	HOMO	LUMO	Band gap
R	-5.852	-3.353	2.499
3P1	-6.122	-3.772	2.350
3P2	-6.397	-4.027	2.370
3P3	-6.432	-4.402	2.030
3P4	-6.191	-3.782	2.409
3P5	-6.210	-3.796	2.414

From above discussion and values, it is clear that the modelled molecules are effective contributors for high performance organic solar cells. The spreading of MOs also

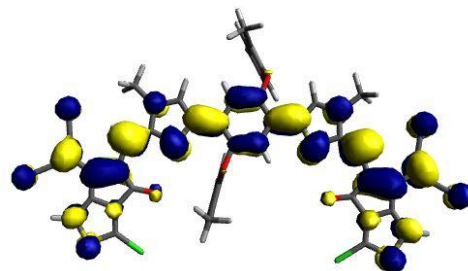
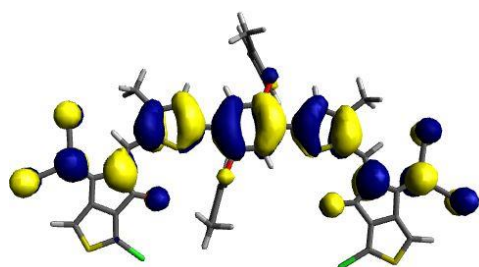
supported these lines as HOMO is spread on donor and LUMO greatly present on end-capped acceptors.



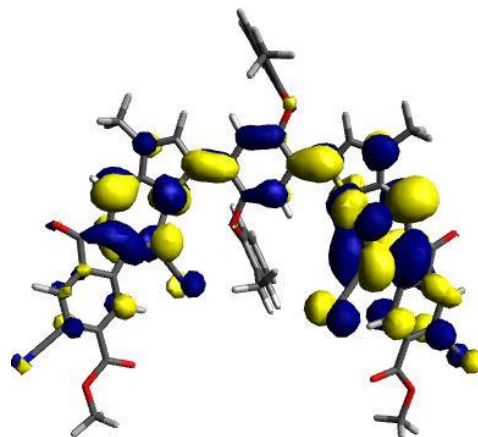
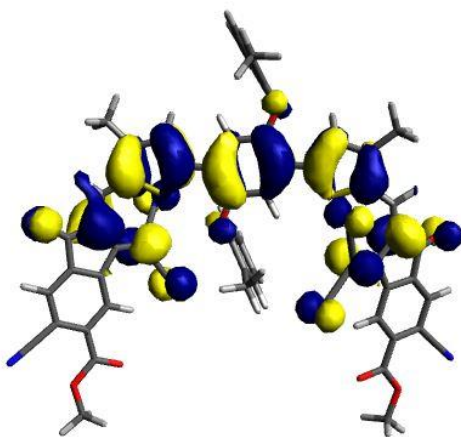
3P2



3P3



3P4



3P5

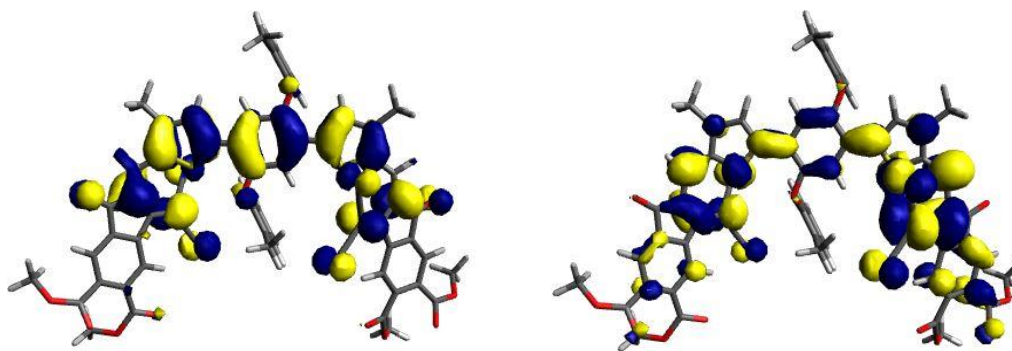


Figure 3. 4. HOMO and LUMO distribution on R and 3P1 to 3P5

3.4 Study of photovoltaic potential

Oscillating strength, light absorption range, energy of exciton, with contribution of molecular orbitals are known as photovoltaic characteristics of the active layer molecules. The high absorption values with good oscillating strength allow better photovoltaic potential.

Reference (R) has light absorption value as 596 nm (DFT) and 584 nm (experimental). Modelled molecules 3P1 to 3P5 have light absorption values as 633, 611, 609, and 618 nm for Cam-B3LYP, PEBPEB, HSEH1PEB, and B3LYP respectively. All modelled molecules expressed red-shift in the absorption spectrum which is because of effective super halogens, cyano, and acetates atoms. Red-shift in light absorption offers high photovoltaic potential of respective molecule. Among the modelled molecules, again 3P3 has high light absorption value which is because of efficient fluorine atoms. 3P1 also has high light absorption which is because of again super halogen, i.e., chlorine. The order of oscillating strength of R and 3P1 to 3P5 is: **3P3** (2.99 eV) > **3P1** (2.91 eV) = **3P4** (2.91 eV) > **3P2** (2.90 eV) > **3P5** (2.89 eV) > **R** (2.87 eV). The values advocated that the modelled

molecules have high oscillating strength and are highly recommended for efficient photovoltaic devices.

Table 3. 2: Photovoltaic components of reference and 3P1 to 3P5 at MPW1PW91/6-31G(d,p)

Systems	Light absorption	Energy of excitation	f_{os}	Contributions
R	596	1.932	2.87	HOMO→LUMO(97%)
3P1	611	1.745	2.91	HOMO→LUMO(98%)
3P2	606	1.882	2.90	HOMO→LUMO(98%)
3P3	622	1.603	2.99	HOMO→LUMO(99%)
3P4	610	1.872	2.91	HOMO→LUMO(98%)
3P5	609	1.891	2.89	HOMO→LUMO(99%)

Excitation of the charges is important when a photon of certain wavelength falls on them [129-133]. Low or small values of excitation energy represents the easy and high excitation of the charges upon falling of low energy photon. The active layer molecules are highly depended on the wavelength of the falling of the photon. Similarly, the active layer molecules are also depended on the values of excitation of the charges. The TD-DFT based computed or estimated values of excitation energy are tabulated in Table 3.2. The reference molecule has excitation energy as 1.932 eV and modelled molecules 3P1 to 3P5 have excitation values as 1.745, 1.882, 1.603, 1.872, and 1.891 eV, accordingly.

All the modelled molecules have less values of excitation which mean that these molecules have good potential of excitation of charges upon falling of less energetic photon [134-138]. Among the modelled molecules, 3P3 has small value of excitation that is because of red-shifting and high oscillating strength. Results of photovoltaic properties evidently suggested that these modelled molecules are effective contributors for highly stable organic solar cells.

3.4.1 Hole and electron reorganization energy

Upon hitting of photon with active layer molecules, the reorganization of hole and electron is very important as it is deciding factor for transportation of hole and electron towards respective electrodes. Least/small values of hole and electron reorganization energies allow high mobility of hole and electron towards the respective electrodes.

Reorganization of charges have two types of energies, i.e. internal and external reorganization energy. The internal energy showing the internal morphology of active layer and external reorganization energy shows the external solvent effects. In this report, the study of active layer ignores the external reorganization energy as its contribution is very small or minimum.

The computed value of hole reorganization of reference is 2.098 and modelled molecules 3P1 to 3P5 have hole reorganization as 2.091, 2.089, 2.093, 2.092, 2.091, accordingly as shown in Table 3.3. Modelled molecules have comparable values of hole reorganization with the reference. Among the modelled molecules, 3P2 has low value of hole reorganization and high hole transfer rate which is because of cyano units in the end-capped acceptor.

Table 3. 3: Hole and electron reorganization energies (RE) of R and modelled molecules

Systems	Hole RE	Electron RE
R	2.098	1.399
3P1	2.091	1.398
3P2	2.089	1.392
3P3	2.093	1.366
3P4	2.092	1.380
3P5	2.091	1.396

The electron reorganization of computed molecules also estimated and the results are expressed in Figure 3.5. Reference molecule has electron reorganization as 1.399 and modelled molecules 3P1 to 3P5 as 1.398, 1.392, 1.366, 1.380, 1.396, accordingly. The modelled molecules have small values of reorganization of electron and high electron transport rates. Among the modelled molecules, 3P3 molecule has high electron transport which is because of fluorine end-capped units. Results of both reorganization energies indicate that modelled molecules are effective contributors for high performance OSCs.

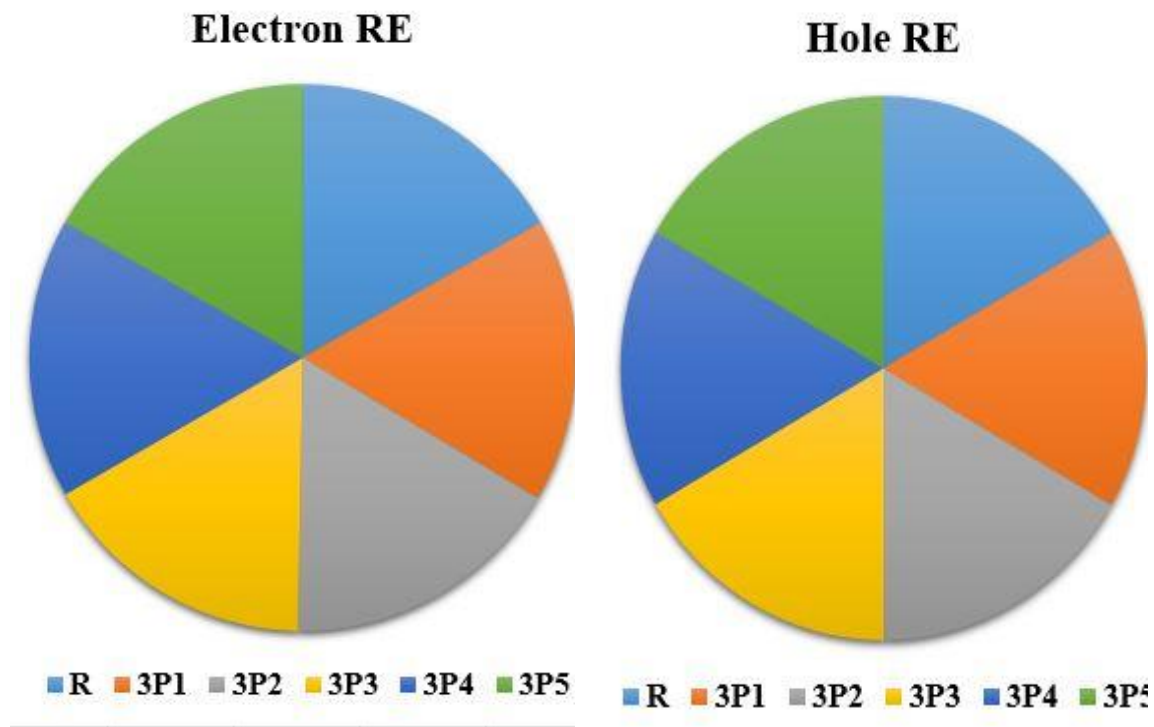


Figure 3. 5. Hole and electron reorganization of R and modelled molecules

3.4.2 Open circuit voltage

Fill factor, with open circuit voltage and J_{sc} decide the light harvesting ability of a solar cells. Among these, open circuit voltage can be computed theoretically by using donor polymer with fullerene free acceptors. Moreover, the photo-generated and light-saturated currents are contributed for computations of open circuit voltage. Open circuit voltage is the current drawn from any photovoltaic device at null voltage. Theoretical estimation of open circuit voltage is done by using a donor polymer with acceptor molecule. In foregoing report, a well-known and frequently used donor polymer PTB7-Th is used with reference and modelled molecules.

The calculated values of V_{oc} after proper matching of energy levels of donor and acceptor molecules is expressed in Figure 3.6. Reference molecule has V_{oc} as 1.55 V and modelled molecules 3P1 to 3P5 have V_{oc} as 1.13, 0.87, 0.50, 1.12, and 1.10 V. All modelled molecules have comparable values of open circuit voltage with reference molecule. Among 3P1 to 3P5, high values of V_{oc} is seen for 3P1 which is because of super halogen present in the end-capped of the 3P1 molecules. From results of V_{oc} , it is comparatively estimated that the modelled molecules are effective contributors for solar cell's active layer.

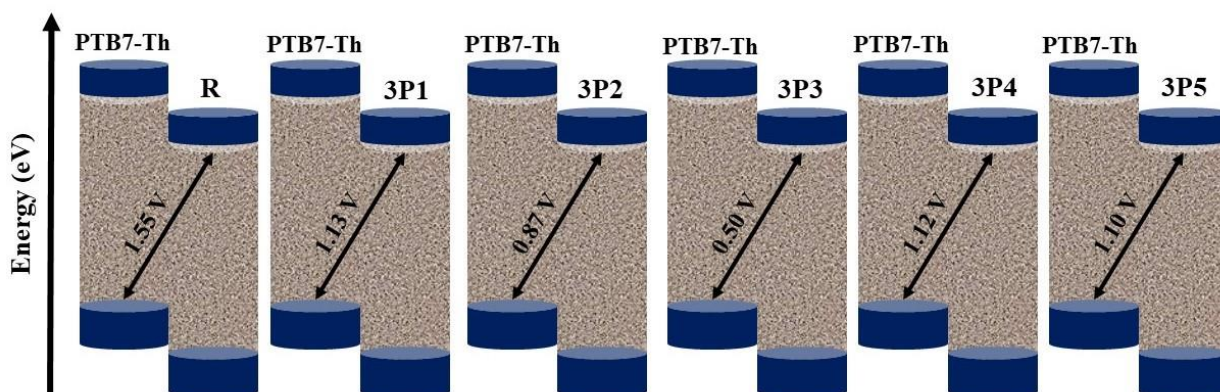


Figure 3. 6. Open circuit voltage of R and modelled molecules with donor polymer

3.4.3 Binding energy

Analysis of binding energy helps to see the binding of exciton in the active layer of solar cells. Low energy of binding allows easy dissociation of the exciton in the active layer. Easy dissociation of the exciton allows high excitation and easy transportation of charges from active layer towards the respective electrodes. For computations of binding energy, first principle excitation energy with band gap is used. Results of binding energy are expressed in Figure 3.7. The calculated value of E_b of reference is 0.567 eV and modelled

molecules have energy of binding as 0.451, 0.508, 0.417, 0.547, and 0.533 eV, for 3P1 to 3P5, accordingly.

Small values of binding energies are seen in all molecules. Modelled molecules have low values of exciton binding which suggest that the modelled molecules are more effective units for active layer of organic solar cells.

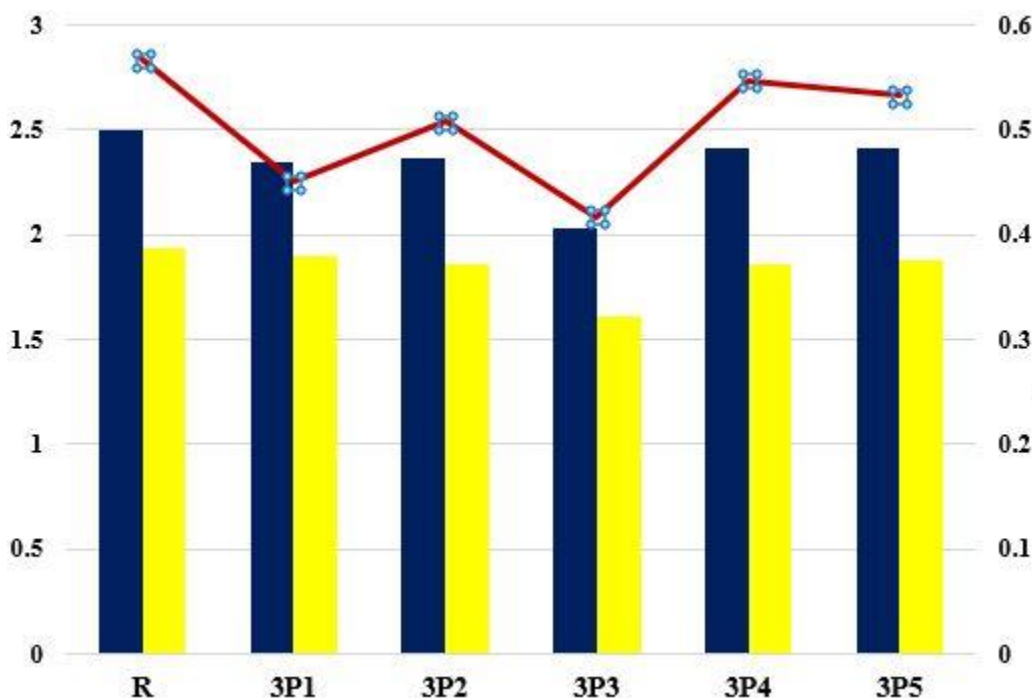


Figure 3. 7. Photophysical parameters and binding energies of R and modelled molecules

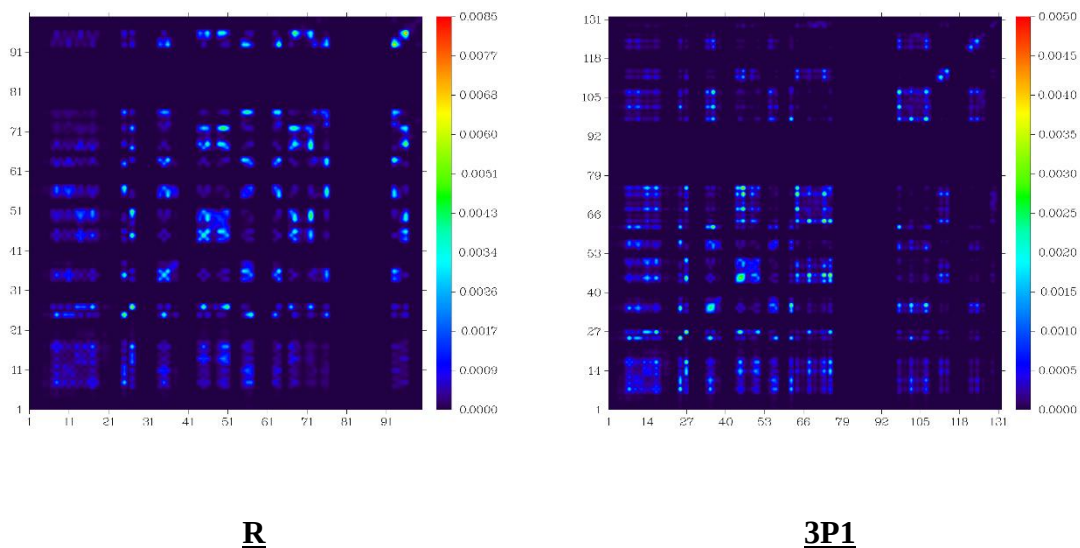
3.4.4 Transition density matrix

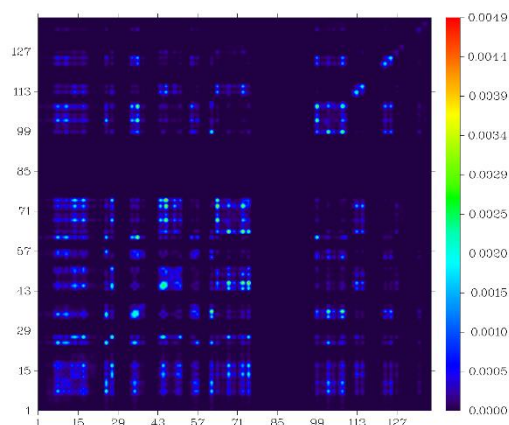
Location and amount of charge density on a certain place is a deciding factor for elucidating the presence of different components in a designed molecule. Moreover, location of charge density also confirms the series of transitions within a molecule. The presence of charge density in the form of heat map is an efficient way to explore the performance of different parts in the transportation of charges. In all transitions, different transitions participate

different role and the role of hydrogen in these transitions is very small therefore, it is being ignored.

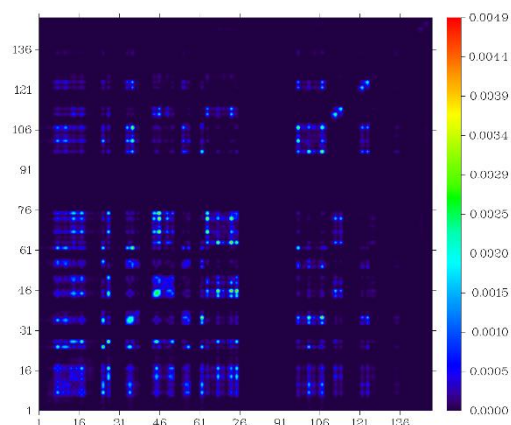
For simplification, the overall molecule is cut off into three section one consists of twisted backbone with out-of-plane rings that behaves as a donor part and two end-capped acceptors behave as acceptor units. The transitions are expressed in TDM map in Figure 3.8. In reference and modelled molecules, similar behavior of charge density is seen which confirms the effective alteration of end-capped units. The donor end helps to transport the charge density and acceptor ends effectively collect the charges. An electron coherence is seen in all the modelled molecules.

From transition density matrix maps, it is simply confirmed that the modelled molecules are effective contributors for high performance organic solar cell applications.

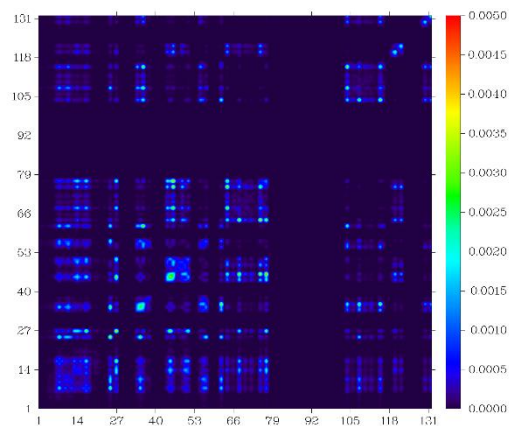




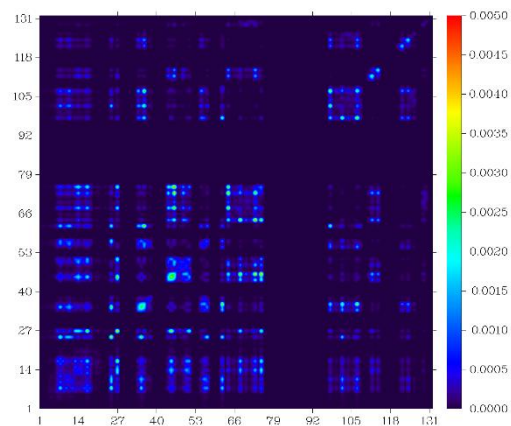
3P2



3P3



3P4



3P5

Figure 3. 8. TDMs of reference and modelled molecules

3.5 Outcomes

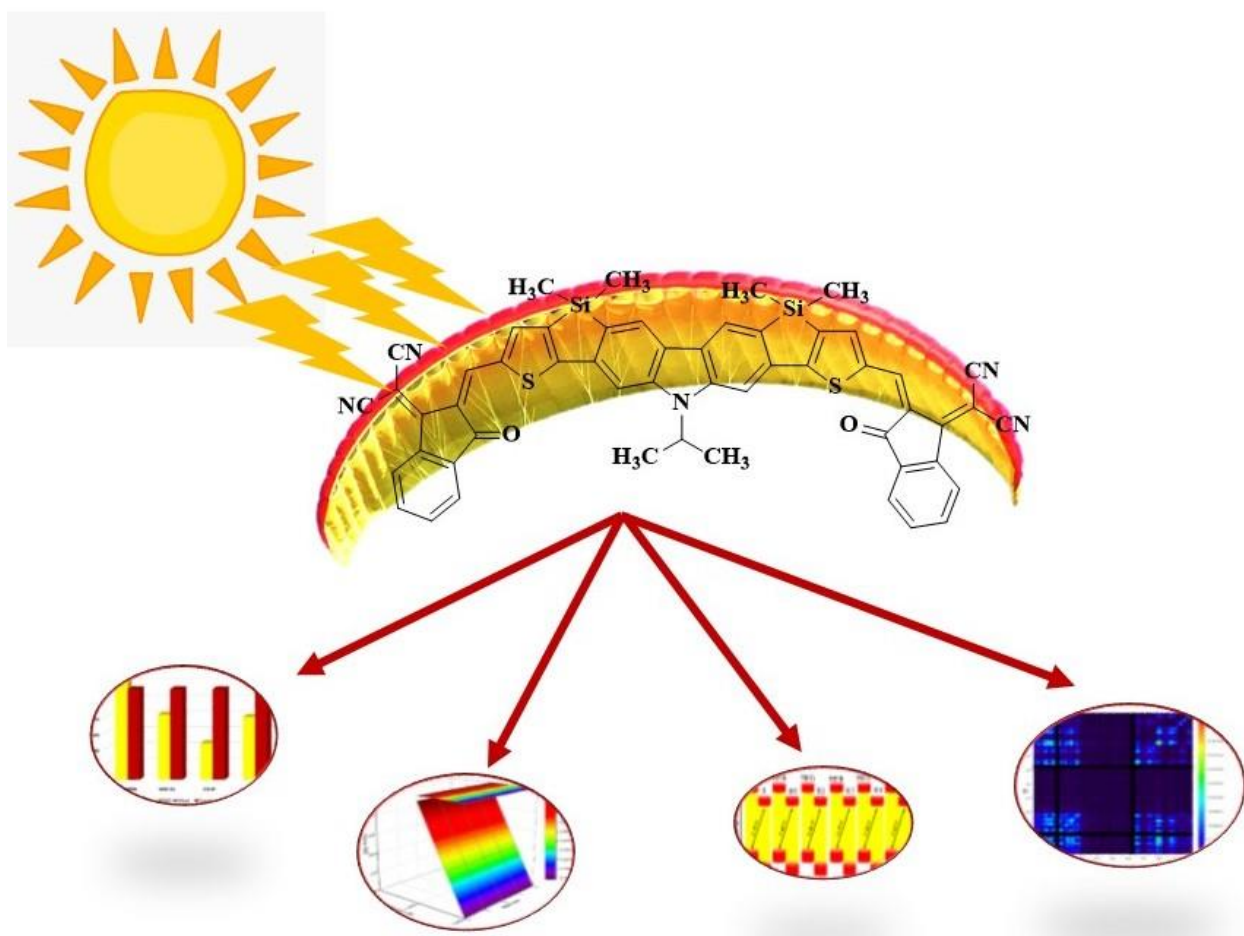
In conclusions, different quantum chemical techniques have been employed with the aid of DFT and TD-DT for exploring the photovoltaic characteristics of newly designed S-shaped acceptor molecules. In this study, end-capped modifications of acceptor molecules cause reduction in the value of electron reorganization energy (1.366 eV). Narrow energy

band gap (2.030 to 2.414 eV) with least values of excitation energy (1.745 to 1.891 eV) have been noted for 3P1 to 3P5. Small values of excitation energy cause easy excitation of charges in active layer with high charge mobility rate. Red-shift in the absorption spectrum of the 3P1 to 3P5 molecules (609 to 622 nm) in contrast to reference molecule (596 nm) is also noted. Further, small values of binding energy with good values of open circuit voltage are also noted for these S-shaped molecules. Transition density matrix analysis provides a detail of location and amount of charge density with all molecules that supports the presence of HOMO and LUMO distribution on all the designed systems. Results of different parameters have suggested that the designed S-shape molecules are efficient contributors for high performance organic solar cells.

CHAPTER 4

End-capped Modifications of Carbazole-based arc shaped

Fullerene Free Acceptor Molecules



4.1 Introduction

New photovoltaic technology is proved to be very beneficial for solving the environmental problems like environmental pollution [139]. In new photovoltaic technologies, the usage of bulk heterojunction solar cells gained huge attention of solar cell developers because of their light weight, very low toxic rate and high backup energies [106, 140].

In last few years, material scientists are busy in developing new materials based on high power conversion efficiencies [141]. Now these light conversion efficiencies are crossing the 18% limit due to development of new materials [142]. But certain limitations are associated with the use of these solar cells like their outdoor applications and large area for light harvesting [143].

Outdoor solar cells are important as they produced high PCE and better donor-acceptor combination [144, 145]. Now indoor solar cells are emerged as new high profile solar cells with high PCE and better donor/acceptor units. To enhance the working of new organic solar cells, new units are installed in indoor environment like light emitting diodes. So, for new indoor solar cells certain things are noted as it should cover the whole light absorption spectrum, i.e., 350 to 750 nm [146, 147].

Non-fullerene acceptor molecules are efficient materials for such light absorption capabilities [105, 148]. For designing the new acceptor materials some important fashion of designing is made like acceptor-donor-acceptor. Use of fused rings in the A-D-A fashion usually facilitates the transport of pi-electrons from one end to other end. The important way for high PCE is to enhance the open circuit voltage of the resultant molecules [149].

In previous years, different acceptor molecules were reported due to their high power conversion efficiencies like Y6, ITIC, ITCC, IO-4Cl and many more [150-153]. Among them, Y6 expressed high PCE due to efficient symmetry and configuration. Previously, Su and his co-workers efficiently synthesized new molecules named as DTSiC-IC and DTSiC-TC [154]. Among them, DTSiC-IC expressed high efficiency because of high light harvesting capability and fine levels of HOMO and LUMO.

Motivated from above synthesis, we decided to design new molecules based on DTSiC-IC (**R**) [154] by end-capped modification. In this way five new molecules are designed named as **EC1** to **EC5**.

4.2 Computational Methodology

In this comprehensive study, GaussView and Gaussian 6 was used for managing input and output files for different analysis. The absorption of reference molecule DTSiC-IC was tested on four methods like MPW1PW91 [155], M06-2X [156], B3LYP [157] and long range Cam-B3LYP [158] with 6-31G(d,p) [63,159-162,132] level of density functional and time-dependent density functional theory. After careful analysis of light absorption ranges, it is found that MPW1PW91 along with 6-31G(d,p) is the best option for further detail study.

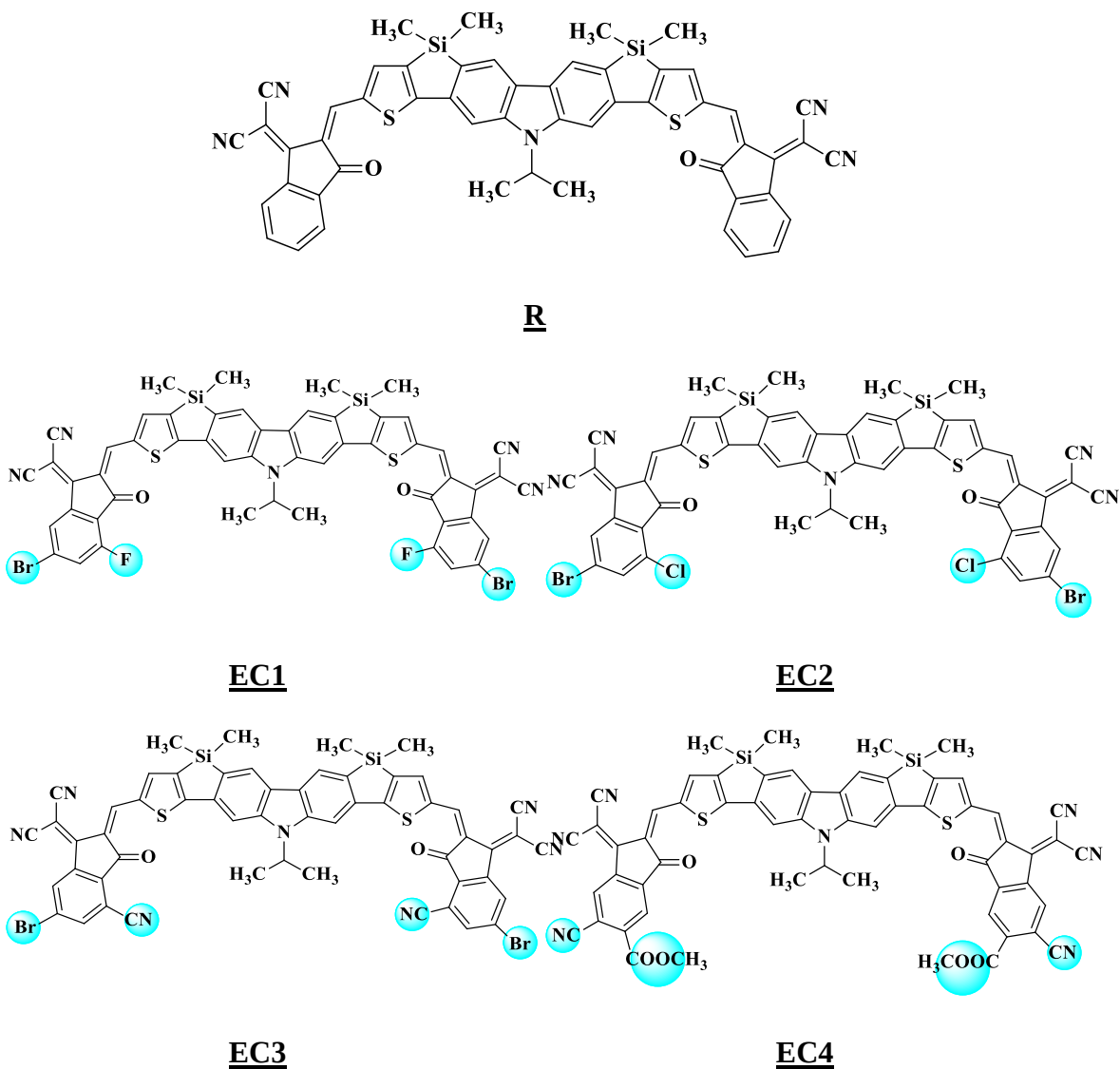
The internal reorganizational energy of the neutral, ionic and anionic species is considered through the following equations[129, 130, 134, 136, 163-165]:

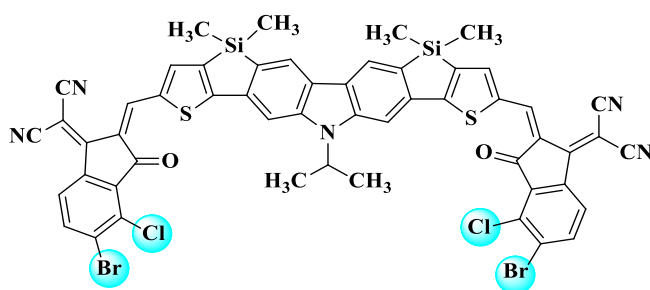
$$\lambda_{\text{electron}} = [E_0^- - E_-] + [E_-^0 - E_0] \quad (1)$$

$$\lambda_{\text{hole}} = [E_0^+ - E_+] + [E_+^0 - E_0] \quad (2)$$

4.3 Results and discussion

The end-capped alteration of the DTSiC-IC molecule [154] is made with bromine, fluorine, chlorine, and cyano groups. In this way five new molecules are made named as EC1 to EC5 as expressed in Figure 4.1. The use of bromine in the end-capped unit is highly beneficial as it elongates the absorption capacity with reduced band gap.





EC5

Figure 4. 1. Chemical structure of all molecules

Absorption of light was computed in dilute dichloromethane solvent and reference molecule showed an excellent absorption value of 651 nm at MPW1PW91, 602 nm at M06-2X, 566 nm at B3LYP and 599 at B3LYP. In all these computations, 6-31G(d,p) basis set was used. The experimental light absorption value was 634 nm for reference molecule. From Figure 4.2 and careful discussion, it is believed that MPW1PW91 with 6-31G(d,p) is the best option for further analysis.

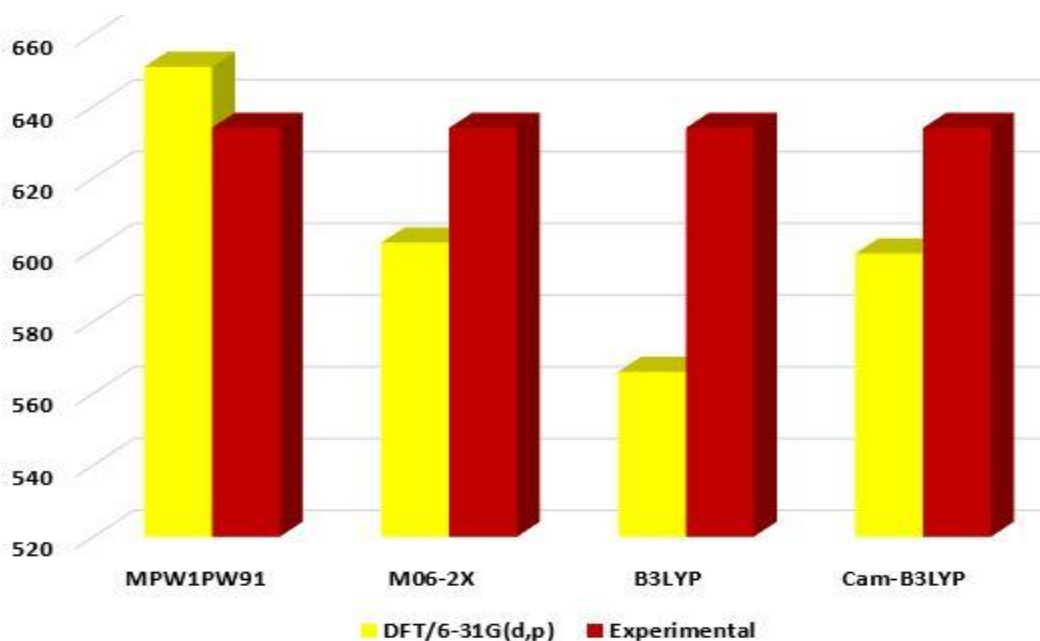


Figure 4. 2. Light absorption behavior of the reference molecule at different methods with 6-31G(d,p)

4.3.1 Position of frontier molecular orbitals

As mention above, MPW1PW91 with 6-31G(d,p) is used for further analysis, so initial optimization of the estimated molecules are done on same level of DFT. The fully stable geometries are expressed in Figure 4.3. The computed HOMO and LUMO distribution fashion is expressed in Figure 4.4.

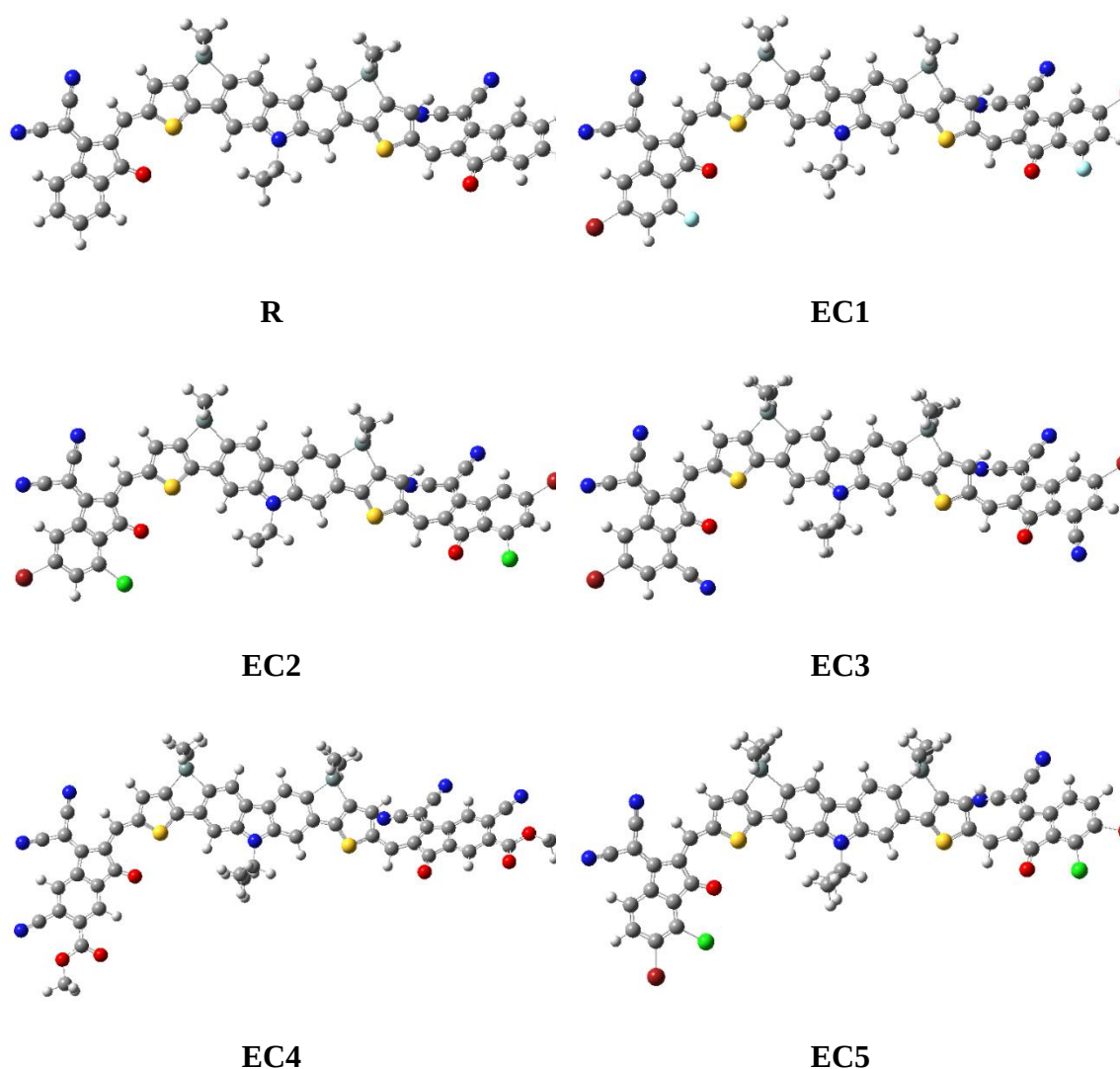


Figure 4. 3. Fully stable geometries of modelled molecules

The presence of HOMO and LUMO on the assigned parts is very helpful in deciding the performance of a molecule [124, 125, 127, 166]. The values of energy orbitals and band gap are expressed in Table 4.1. Reference shows HOMO and LUMO values as -5.643, and -3.166 with 2.477 band gap value. The HOMO of EC1 to EC5 is -5.795, -5.808, -5.943, -5.998, and -5.794 eV. And LUMO of EC1 to EC5 is -3.425, -3.445, -3.607, -3.747, and -3.414 eV, accordingly.

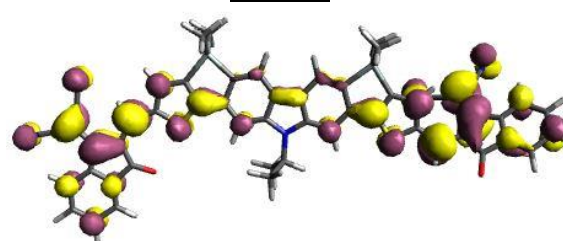
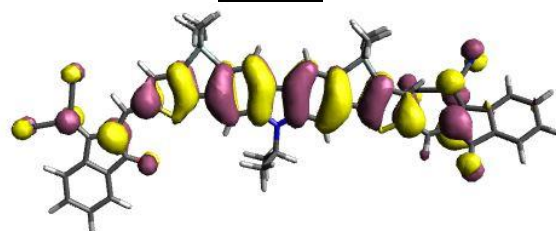
The computed band gap of EC1 to EC5 is 2.370, 2.363, 2.336, 2.251 and 2.380 eV, respectively. All the modelled molecules expressed least values of band gap which advocate that modelled molecules are efficient nominees for high performance with stable indoor organic solar cells. The least value was seen for EC4 modelled molecules which is because of efficient cyano group present in the end-capped of EC4. Overall, discussion communicates that modelled molecules enhance the shifting of charge density from lower to high level of orbitals

Table 4. 1: Orbitals energy with band gap for R, EC1 to EC5

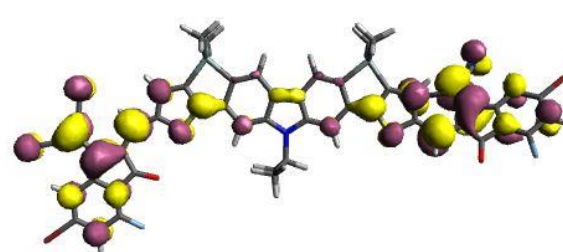
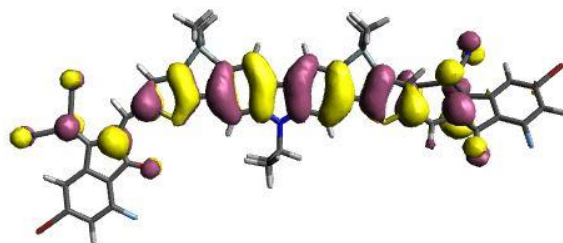
Molecules	HOMO energy	LUMO energy	Band gap
R	-5.643	-3.166	2.477
EC1	-5.795	-3.425	2.370
EC2	-5.808	-3.445	2.363
EC3	-5.943	-3.607	2.336
EC4	-5.998	-3.747	2.251
EC5	-5.794	-3.414	2.380

HOMO

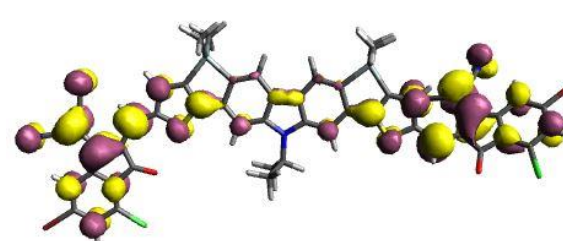
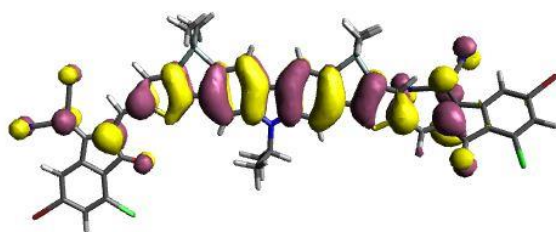
LUMO



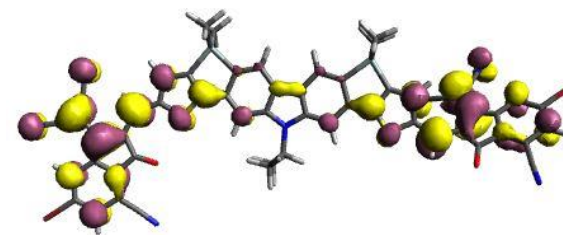
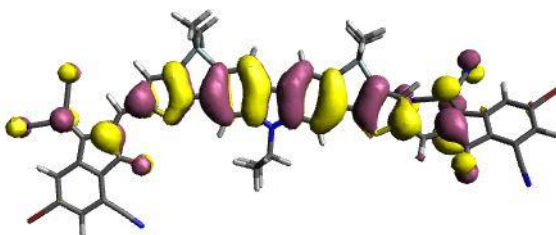
R



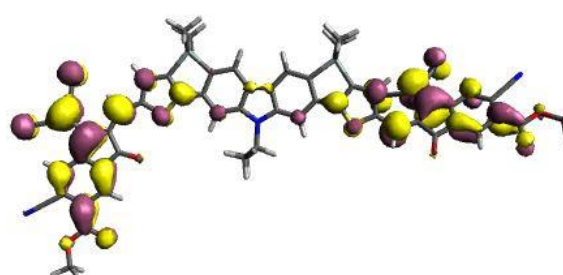
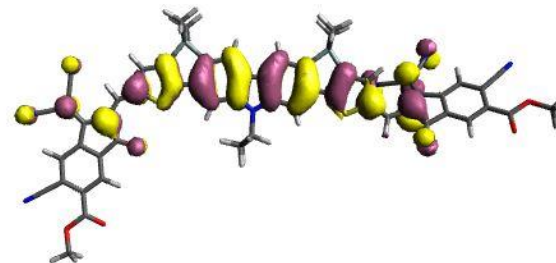
EC1



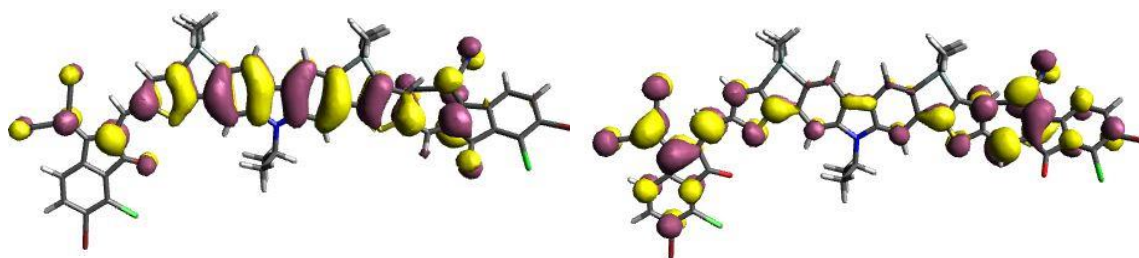
EC2



EC3



EC4



EC5

Figure 4. 4. HOMO and LUMO spreading pattern in modelled molecules

4.3.2 Light absorption properties

For the evaluation of the behavior and performance of a solar cell, the light absorption properties are computed with great concerns. In light absorption properties, some important factors are involved like oscillating strength, absorption maximum, major contribution of molecular orbitals, and excitation energy [117,126, 128, 167]. Results of these components are enclosed in Table 4.2.

The computed light absorption was 651 nm for reference which is close to experimental computed absorption value. EC1 to EC5, absorption values are computed as 677, 681, 680, 702 and 691 nm, accordingly. Modelled molecules disclosed red-shift in the absorption spectrum which is because of efficient end-capped units. Highest light absorption capability is again seen in EC4 molecule due to cyano and CH_3COO^- group.

Oscillating strength is also important as large values of f_{os} grantee the high light absorption and vice versa. From Table 4.2, it is evidently seen that modelled molecules expressed high values of oscillating strength that encourage the experimentalists for future synthesis of these molecules.

Table 4. 2: Absorption, oscillating strength, excitation energy with major contribution of EC1 to EC5

Molecules	Absorption maxima	Excitation (E _x) energy	Oscillating f _{os} strength	Major orbital contribution
R	651	2.16	2.78	HOMO→LUMO(98%)
EC1	677	2.02	2.98	HOMO→LUMO(99%)
EC2	681	2.06	2.98	HOMO→LUMO(99%)
EC3	680	2.03	2.91	HOMO→LUMO(99%)
EC4	702	1.99	3.11	HOMO→LUMO(99%)
EC5	691	2.05	2.83	HOMO→LUMO(99%)

4.3.3 Excitation energy

Low values of excitation energy also helpful in high light absorption [2, 118]. In reference the energy of excitation is noted as 2.16 eV, and for EC1 to EC5, it is 2.02, 2.06, 2.03, 1.99 and 2.05 eV, accordingly as shown in Figure 4.5.

All the modelled molecules show small values of excitation energy which communicated that modelled molecules are fine contributor for high performance organic solar cells. Again least value was noted for EC4 molecule, which is because of utilization of excellent cyano group that reduces the band gap and contributes more for high light absorption.

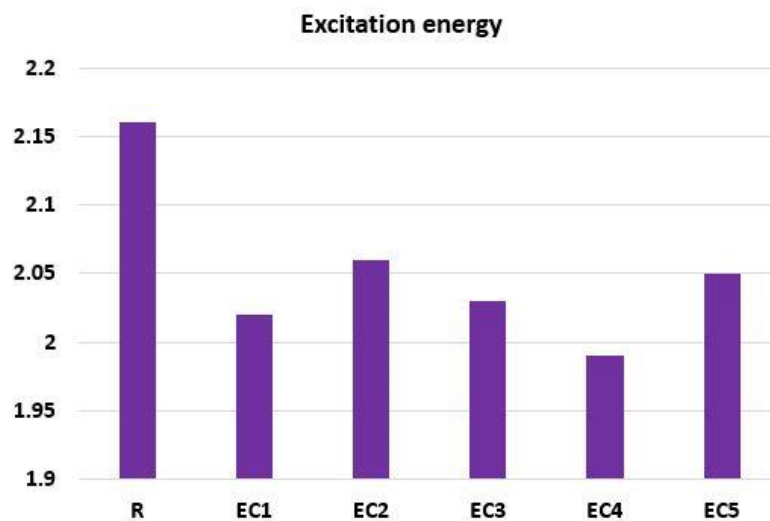


Figure 4. 5. Excitation energy of modelled molecules

4.3.4 Reorganizational energy

The presence of exciton in active layer of the solar cell determines the performance of the solar cell. The low values of reorganizational energy offer large light absorption with maximum PCE. The low values of reorganization proved to be beneficial for high movement of hole and electron in the active layer [133, 135, 168-174].

Table 4. 3: Electron, hole reorganization energy of EC1 to EC5 and R

Molecules	Electron reorganization energy	Hole reorganization energy
R	1.0045	0.0080
EC1	1.0022	0.0060
EC2	1.0021	0.0090
EC3	1.0043	0.0090
EC4	1.0020	0.0030
EC5	1.0031	0.0060

The computed results of reorganization energy of electron of reference is 1.0045 and for EC1 to EC5 is 1.0022, 1.0021, 1.0043, 1.0020, and 1.0031. Computed hole reorganization energy is 0.0800 for reference and 0.0060, 0.0090, 0.0090, 0.0030, and 0.0600 for EC1 to EC5, accordingly.

From above data and Figure 4.6, it is obvious that modelled molecules expressed small values of hole and electron reorganization energy which communicated that modelled molecules are effective molecules for high performance organic solar cell.

The presence of effective end-capped groups in the form of halogens and cyano in end-capped acceptor moiety encourages the experimentalists for future development of the stable organic solar cells.

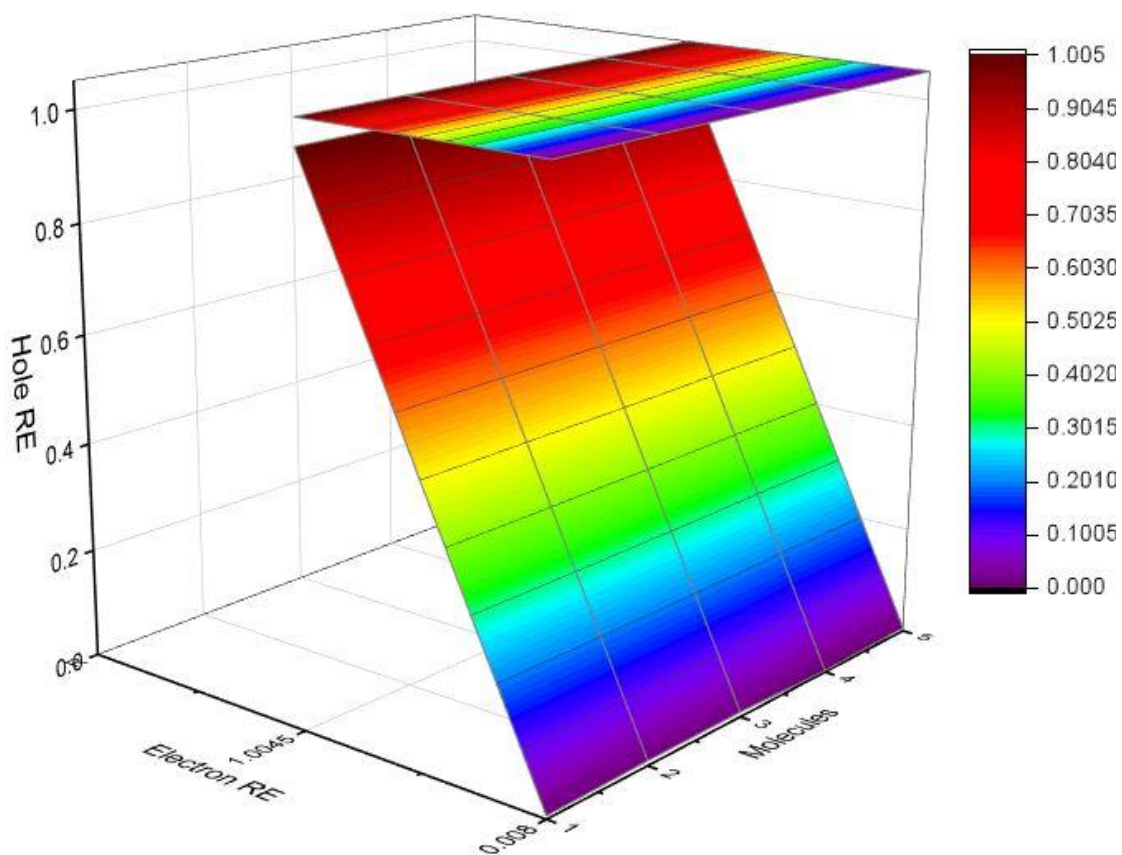


Figure 4. 6. Reorganization energy of hole and electron of modelled molecules

4.3.5 Open circuit voltage

For DFT based computation of open circuit voltage, certain factors are considered. The open circuit voltage is the total amount of current (whether it is photo-saturated or photo-generated) drawn from optical device [138, 175-179].

For theoretical estimation of the open circuit voltage, the orbital overlap is very important as the level of donor polymer and acceptor molecule could enhance the DFT based open circuit voltage values. For computation of open circuit voltage, PTB7-Th is considered as donor polymer with modelled acceptor molecules.

The computed results of open circuit voltage are 1.73 V for reference and 1.48, 1.46, 1.29, 1.15, 1.49 V for EC1 to EC5 (Figure 4.7). From results, it is estimated that EC5 molecule disclosed high value of open circuit voltage among modelled molecules which is due to efficient halogens in the end-capped unit of the modelled molecule. The sequence of high open circuit voltage is: **EC5> EC1> EC2> EC3> EC4**.

So, from above analysis it is advocated that modelled molecules are effective members for future organic solar cells.

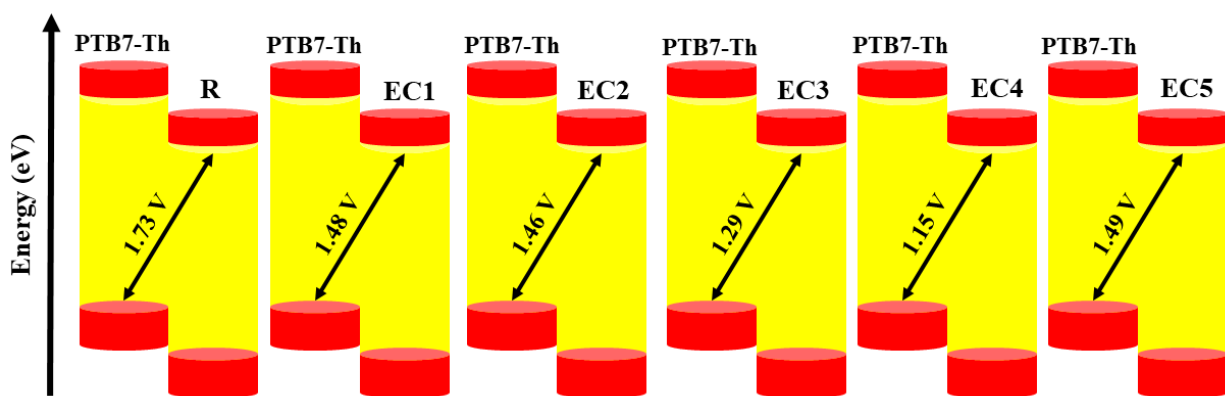


Figure 4. 7. Open circuit voltage of all modelled molecules with donor polymer

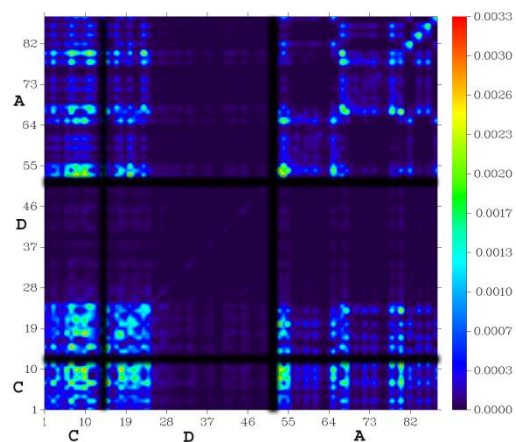
4.3.6 TDM estimation

Transition density matrix is used to locate the position of the charge within the molecule. The number and fashion of the transitions in the reported molecules is also estimated with the aid of the transition density matrix analysis.

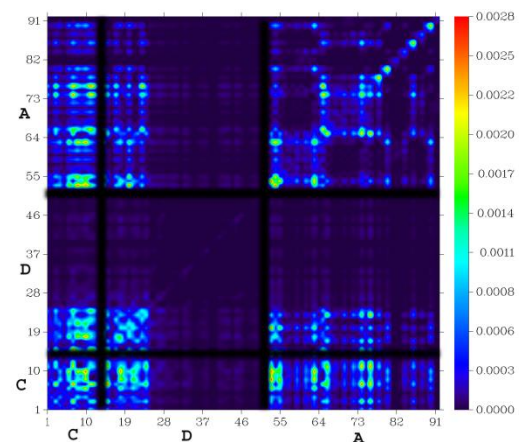
From one end to other end of the molecules, core plays important role as it provides path for the transport of the charge. Different atoms like sulfur, oxygen, nitrogen with carbon participated much in the transitions. But the role of hydrogen is very minor that is why its effect is being ignored during the computations.

MPW1PW91 with 6-31G(d,p) is used to simulate the transition density matrix plots of the reference and modelled molecules. Different parts like donor bridge donates the electron density and end-capped acceptor efficiently accepts electron density and core units facilitate them to do such activity as shown in Figure 4.8.

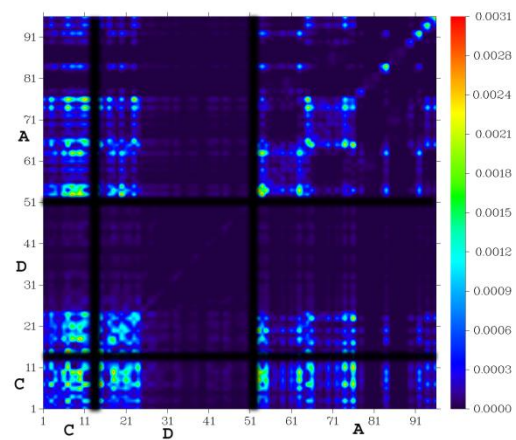
In all modelled molecules and reference same pattern of electron density transportation is seen which recommended that end-capped acceptor modifications with halogens and cyano group are efficient approaches for plotting new molecules for highly stable organic solar cells.



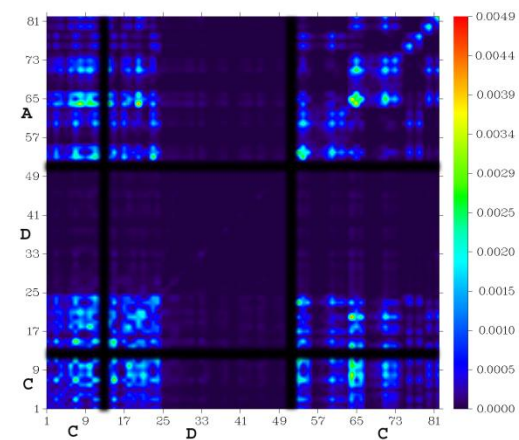
R



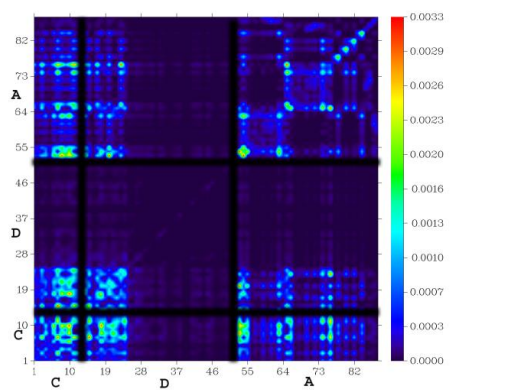
EC1



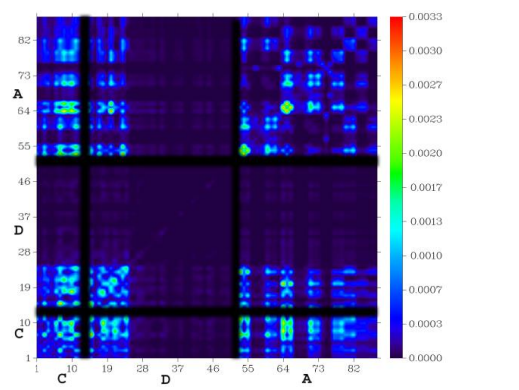
EC2



EC3



EC4



EC5

Figure 4. 8. Transition density matrix plots of the reference and modelled molecules.

Binding energy also measures the performance of the organic solar cells as it is related to the fill factor, Jsc and luminous flux. Binding energy is measured with the help of first principle excitation energy with energy band gap. The values of binding energy confirmed the exciton dissociation and related properties.

The computed data of binding energy is tabulated in Figure 4.9 which suggested that reference has binding energy value as 0.317 eV and EC1 to EC5 displayed binding energy value as 0.350, 0.303, 0.306, 0.261, and 0.330 eV, accordingly. Modelled molecules expressed least values of binding energy than reference molecule except EC1, and EC5. Molecule EC4 disclosed least value of E_b which communicated that EBC4 is the fine contributor for future development of the organic solar cells.

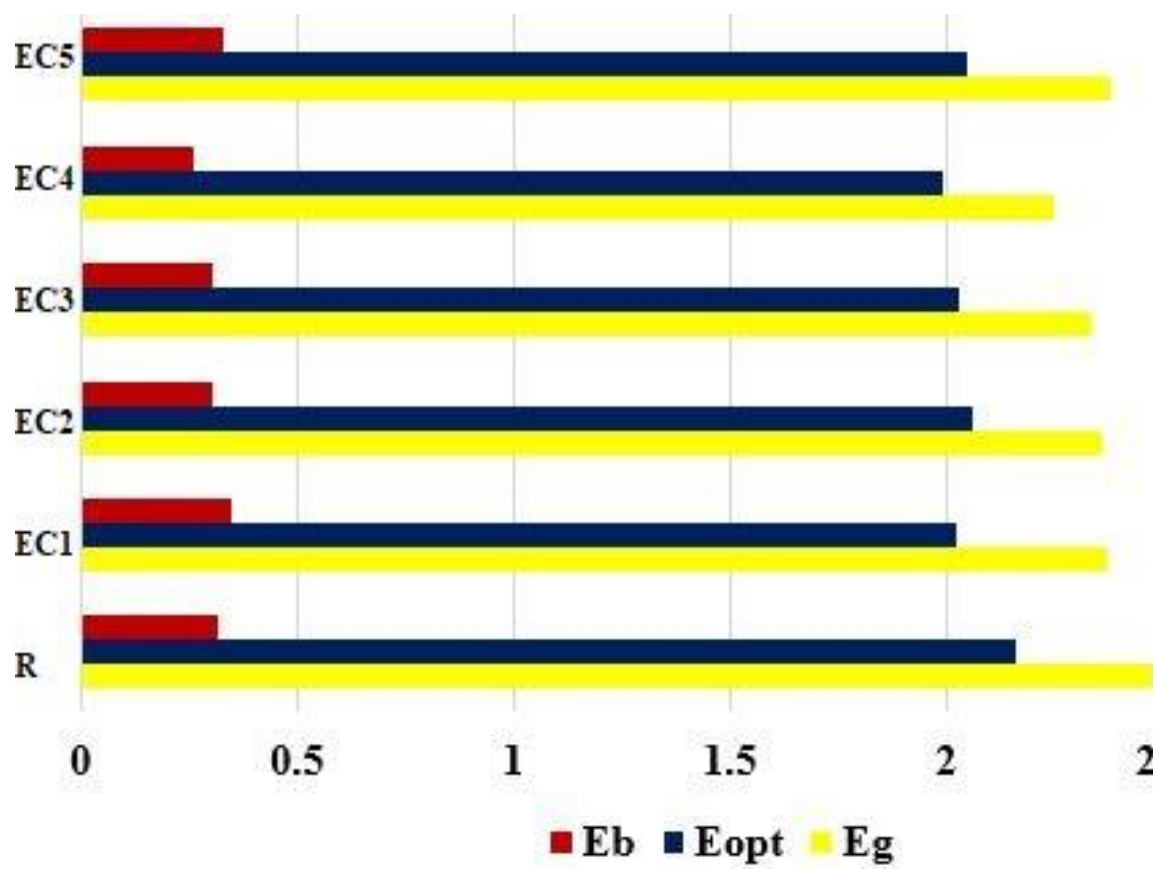


Figure 4. 9. Binding energy of reference and modelled molecules

4.4 Outcomes

Quantum chemical analysis of newly designed EC1 to EC5 molecules has been performed by using DFT and TD-DFT approach. Different halogens and cyano groups are used as end-capped units in newly designed molecules. Designed molecules (EC1 to EC5) expressed reduced or narrow energy band gap (2.251 to 2.380 eV) than reference molecule (2.477 eV). Good values of open circuit voltage ($V_{oc} = 1.29$ to 1.49 V) and small values of binding energies are noted for designed molecules. Further, least values of electron and hole reorganization energy allow high charge density mobility in EC1 to EC5 molecules. Red-shifting in the absorption spectrum of the EC1 to EC5 (677 to 702 nm) are noted in contrast to reference molecule (651 nm). Fine values of excitation energy with major contribution (99%) from lower orbitals to high orbitals are also noted in the designed molecules. Foregoing discussion and results of different analyses recommended that the designed molecules are efficient contributors for high performance indoor and outdoor organic solar cells.

CHAPTER 5

End-Capped and Bridging Core Alterations in π -conjugated

shaped A-D-A type small active layer molecules



5.1 Introduction

Since mid of 1990's, solution processed bulk heterojunction organic solar-cells (BHJ-OSCs) are proved to be very beneficial due to low cost, easy synthetic pathway and high energy conversion efficiencies. Additionally, bulk heterojunction OSCs also disclosed good efficiency along with various commercial applications [180-182]. And in last few years, there is enormous research on the development of non-fullerene acceptors (NFAs) and donor (D) molecular fabrication [1, 137, 138, 183, 184].

In these fullerene free acceptor molecules (AMs), some A-D-A type NFAMs are the most important and beneficial due to outstanding backbone and efficient absorption in near IR, visible and UV region [103, 104, 185]. In past, different acceptor molecules based on A-D-A were successfully synthesized and evaluated for their power conversion efficiencies [186, 187]. Further, these molecules also disclosed very high photovoltaic properties. Moreover, donor having fused rings when combined with efficient acceptor units, high photovoltaic properties were seen in few excellent solar cell materials [47, 109, 188].

In literature, Jen et al. designed and synthesized new molecules having long and fused rings that are attached with well efficient units [189]. These systems were unique and provided maximum yield in the form of power conversion efficiency [189]. In 2017, Chen et al. reported heptacyclic ring containing central core unit which expressed more than 10% power conversion efficiency when combined with a donor polymer [108].

BDF (benzodifuran) unit is very efficient due to furan rings which causes deeper highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital

(LUMO) level that directly affected the power conversion efficiency (PCE) of a solar cell. In addition, furan rings also facilitate the high charge mobility with high electronegativity caused by oxygen atom [190, 191]. Recently, Wang and his co-workers discovered and successfully synthesized small acceptor molecules having heptacyclic benzodi(thienocyclopentafuran) as a central unit [110]. These molecules unveiled high photovoltaic properties with an excellent charge mobility. Motivated from that report, we decided to design molecules having heptacyclic benzodi(thienocyclopentafuran) unit theoretically. Consequently, new five molecules are designed (after end-capped and bridging modification of **BFHIC-4F** [110]) and are theoretically characterized by using different analyses like alignment and level of FMOs, transition density matrix (TDM), reorganizational energy, optical properties, excitation energy, binding energy, and open circuit voltage. The results of all these analyses suggested that these theoretical designed molecules are efficient materials for solar cell applications.

5.2 Computational detail

The computations present in this paper are theoretically performed by employing GaussView and Gaussian 09 package of program. Reference molecule was studied by means of absorption maxima at four different methods (MPW1PW91 [155], B3LYP [157], CAM-B3LYP [192], and ω B97XD [158]) with 6-31G(d,p) [64, 169, 193] basis set. After careful analysis, B3LYP method with 6-31G(d,p) was selected for further analysis.

Reorganization energy (RE) is categorized into internal and external type of reorganizational energy. Internal RE belongs to internal changes like morphology and chemical structures and the other one, i.e. the external RE belongs to external environment

polarization which does not participate much and hence being ignored. Following equations are used to compute the RE for electron and hole, respectively [136, 162, 164, 172]:

$$\lambda_e = [E_0^- - E^-] + [E_-^0 - E_0] \quad (1)$$

$$\lambda_h = [E_0^+ - E_+] + [E_0^+ - E_0] \quad (2)$$

Additionally, different softwares are used like pyMolyze, Gauss sum, and Avogadro for drawing different graphs.

5.3 Results and their discussion

First, the reference molecule **R** [110] was optimized at MPW1PW91, B3LYP, CAM-B3LYP, and ω B97XD methods with 6-31G(d,p) basis set. Then absorption maxima values were also computed at same level. Theoretically computed absorption maxima values were 820, 758, 791, and 826 nm. While in experiment the measured absorption maxima value is 750 nm [110]. So, from above analysis it is crystal clear that B3LYP method with 6-31G(d,p) shows good coherence with experimental value as shown in Figure 5.1. And it allows us to proceed further by using B3LYP method.

End-capped modifications were made with different efficient units like chloro (**ZBCF1**), cyano (**ZBCF2**), cyano-fluoro (**ZBCF3**), and cyano-acetate (**ZBCF4**). And bridging core modifications were made with fused rings containing nitrogen combined with sulfur (**ZBCF5**) and sulfur atoms conjugate with oxygen atoms (**ZBCF6**) as shown in Figure 5.2 and 5.3.

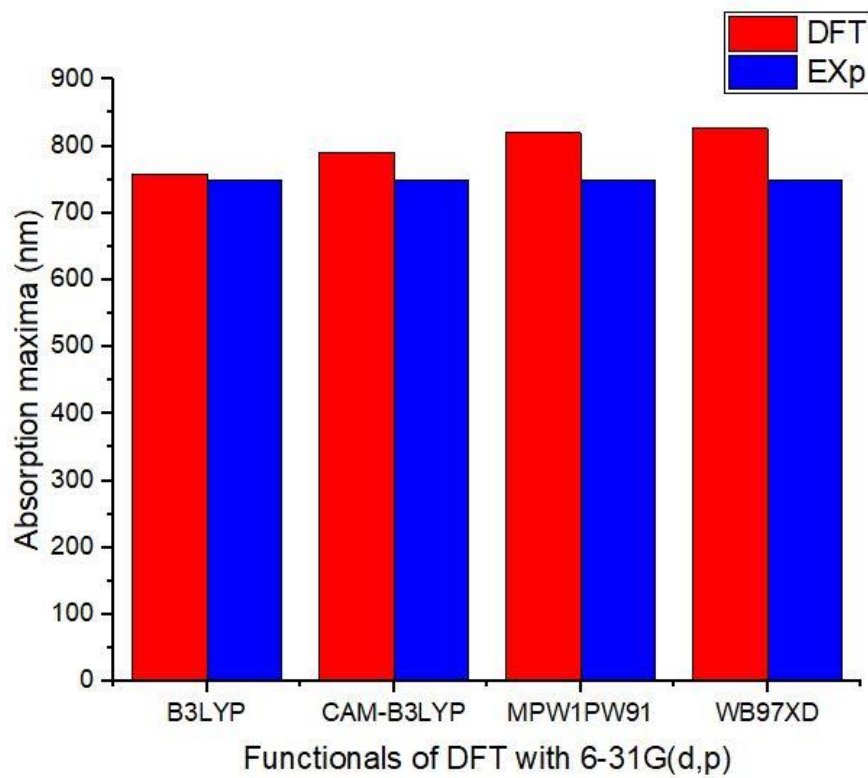
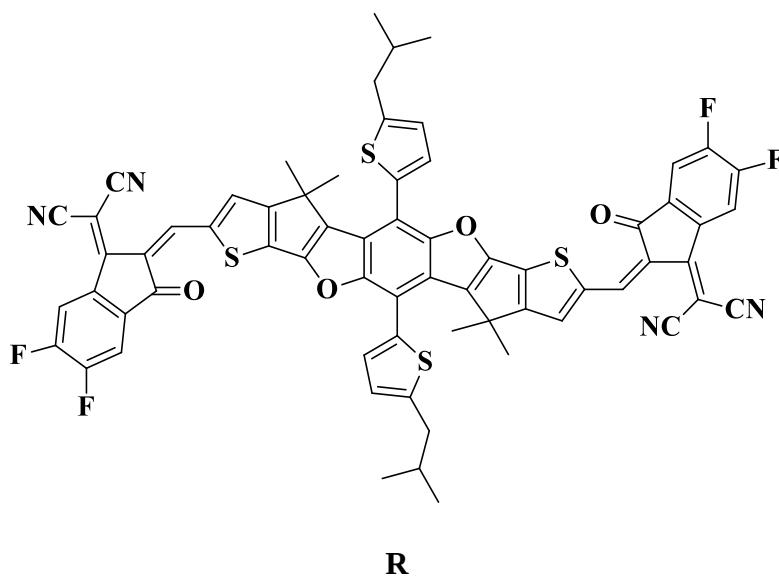


Figure 5. 1. Computed UV of R at different methods combined with 6-31G(d,p) level of DFT



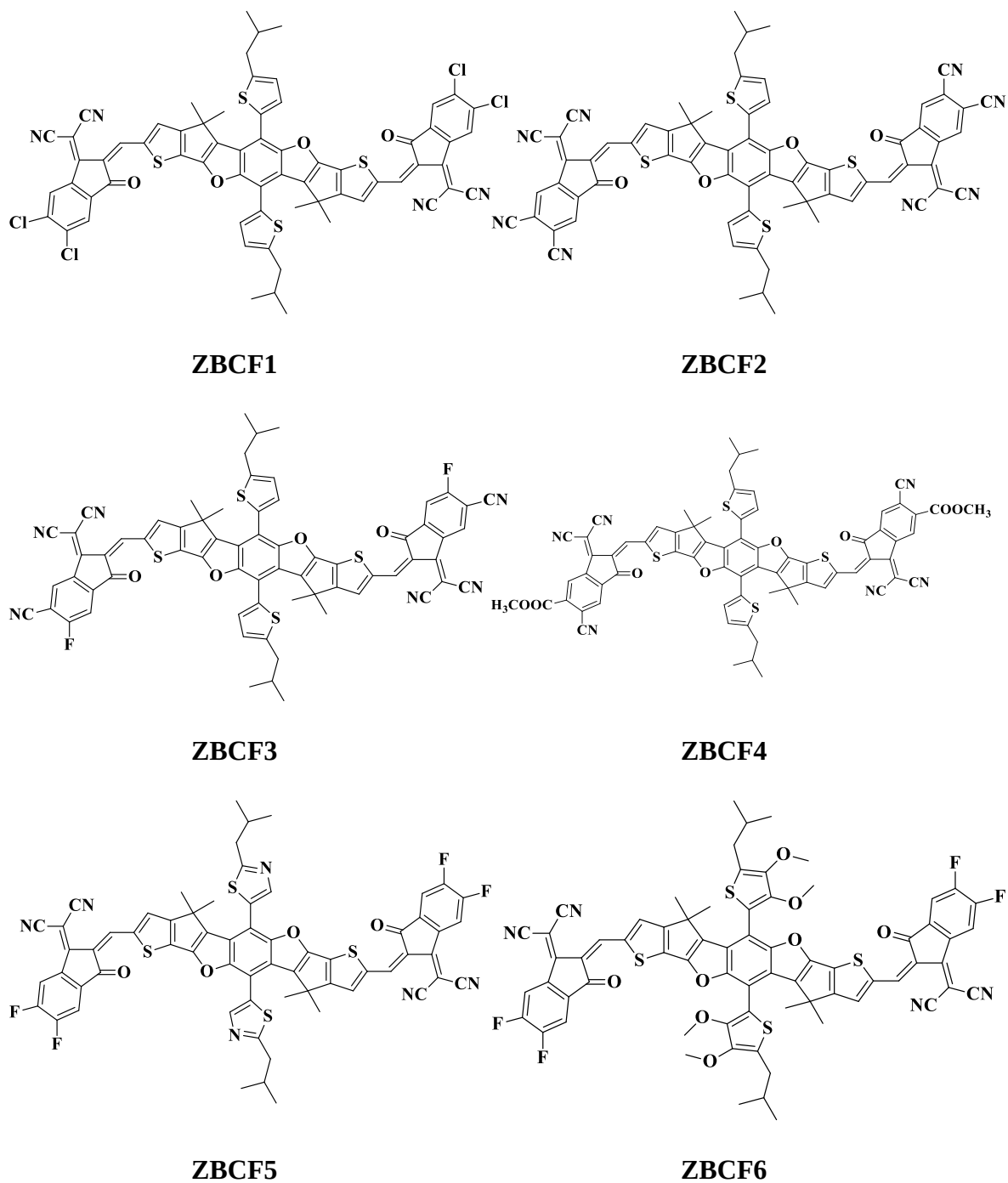
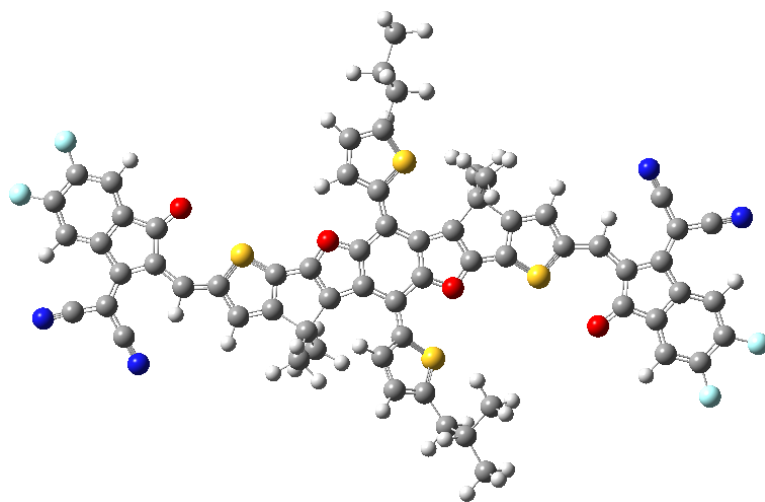


Figure 5. 2. Chemical structures of R and designed systems ZBCF1 to ZBCF6

5.3.1 Frontier molecular orbitals (FMOs)

The level of both theoretical orbitals, i.e. HOMO and LUMO matters a lot for defining the efficiency of a solar device. The gap between two molecular orbitals give us the band gap which directly related to shifting of charges between two orbitals [2, 118, 194, 195].

The narrow band gap allows high charge shifting and also allows high PCE. The optimized geometries of all systems are expressed in Figure 5.2. The computed results of molecular orbitals are listed in Table 5.1. The calculated HOMO and LUMO values of **R** are -5.175 and -3.349 eV, respectively at B3LYP/6-31G(d,p). The HOMO and LUMO values of **ZBCF1** to **ZBCF6** are -5.236, -5.508, -5.395, -5.421, -5.536, -5.144 and -3.454, -3.894, -3.612, -3.777, -3.543, -3.357 eV, sequentially.



R

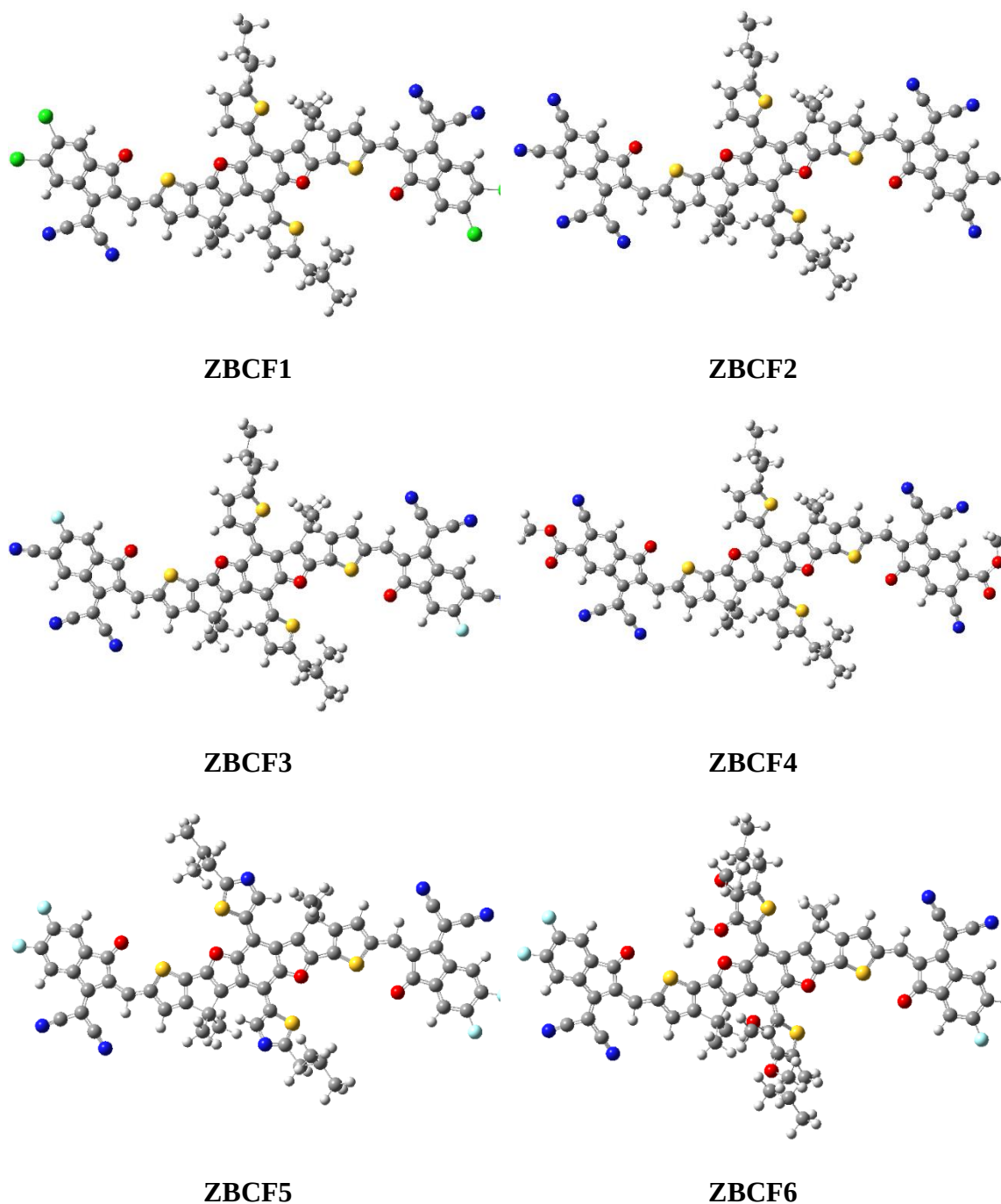


Figure 5. 3. Optimized structures of all studied molecules at B3LYP/6-31G(d,p).

The computed band gap results of **R** and **ZBCF1** to **ZBCF6** are 1.826, 1.782, 1.614, 1.783, 1.644, 1.693, and 1.787 eV, sequentially. All theoretically designed molecules expressed low band gap as compared to **R** that is because of efficient end-capped and bridge atoms modifications (Figure 5.3 and 5.4). Narrowest band gap is seen in **ZBCF2**

molecules ($E_g=1.614$ eV) and it is because of efficient cyano groups. Overall, theoretically planned molecules expressed better charge transfer between molecular orbitals, thus these molecules are good nominees for high performance solar cells.

Table 5. 1: The computed values of HOMO, LUMO and energy band gap

Systems	HOMO	LUMO	E_g
R	-5.175	-3.349	1.826
ZBCF1	-5.236	-3.454	1.782
ZBCF2	-5.508	-3.894	1.614
ZBCF3	-5.395	-3.612	1.783
ZBCF4	-5.421	-3.777	1.644
ZBCF5	-5.426	-3.733	1.693
ZBCF6	-5.144	-3.357	1.787

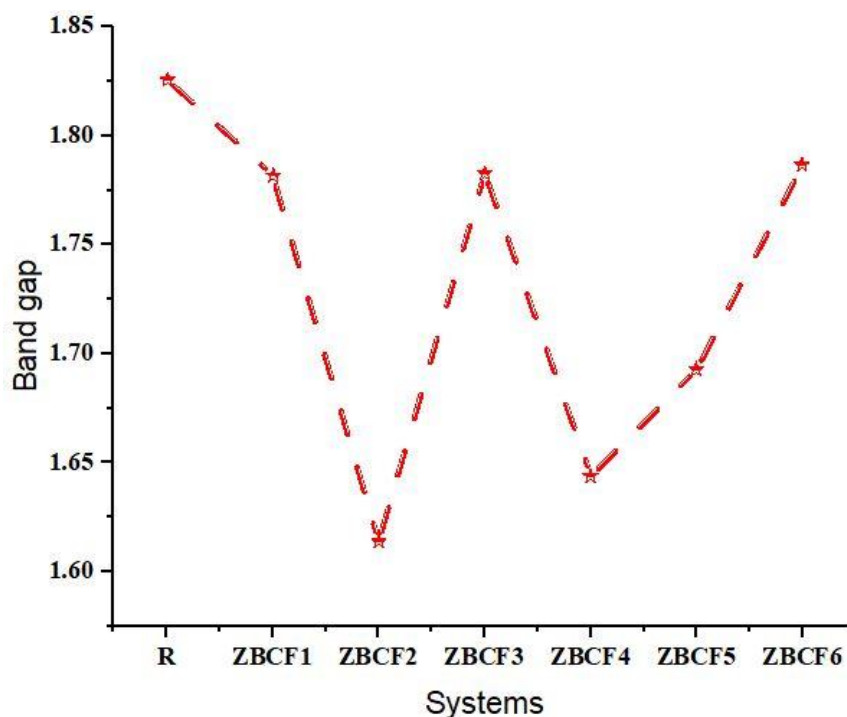


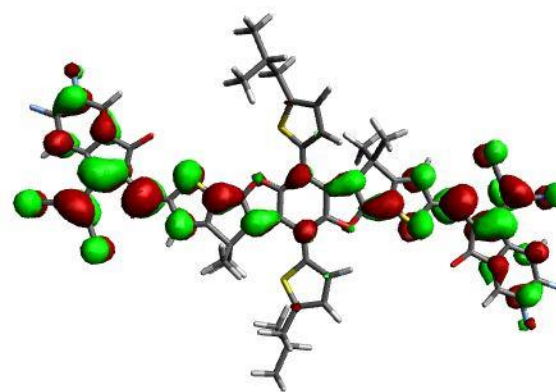
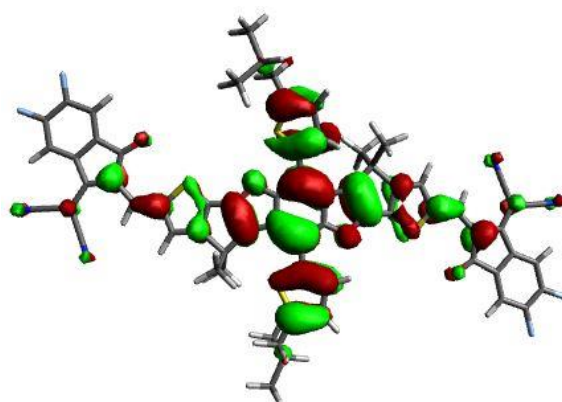
Figure 5. 4. Computed band gap of all theoretical proposed molecules at B3LYP/6-31G(d,p)

Distribution of frontier molecular orbitals also computed in order to unveil the position of both MOs on theoretically designed molecules as explained in literature as well [118, 195]. The distribution pattern of MOs of our studied molecules is shown in Figure 5.5.

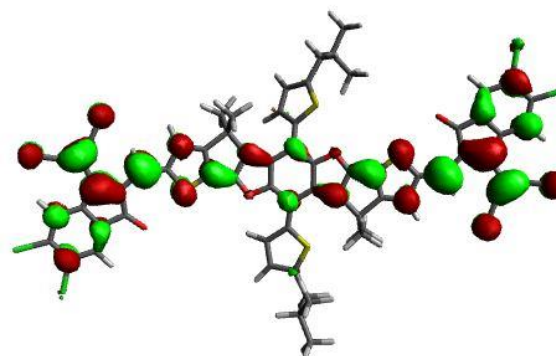
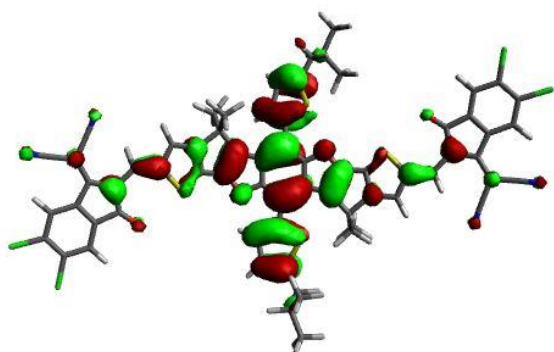
The HOMO of R is seen on central bridge atoms (donor) while LUMO is fully present on end-capped units. HOMO of **ZBCF1**, **ZBCF2**, **ZBCF3**, **ZBCF4**, **ZBCF5**, and **ZBCF6** is present on central donor units and LUMO is fully occupied by end-capped units. Presence of LUMO in **ZBCF1** to **ZBCF4** confirmed that these theoretical discussed molecules have better end-capped units and presence HOMO on central units in **ZBCF5** and **ZBCF6** confirms that bridge atoms modification is also a good technique to design and boost the charge transfer ability. Therefore, from foregoing analysis it is clear that these theoretical molecules are good nominees for highly stable solar cell applications.

HOMO

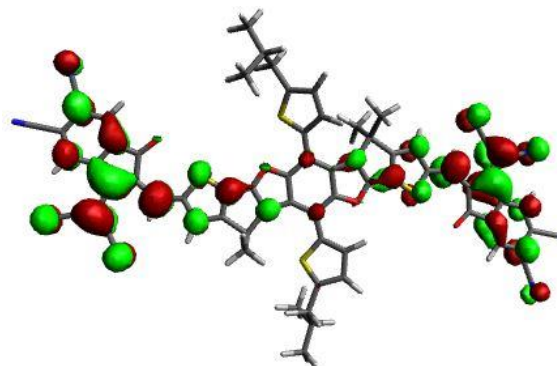
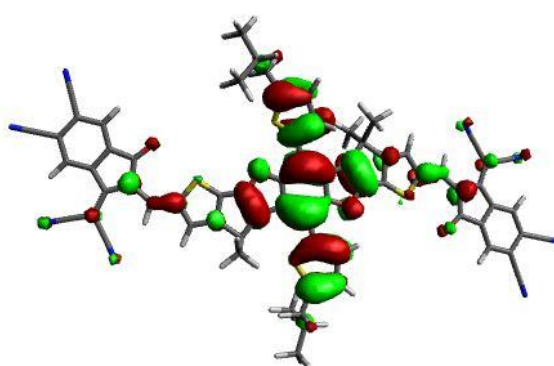
LUMO



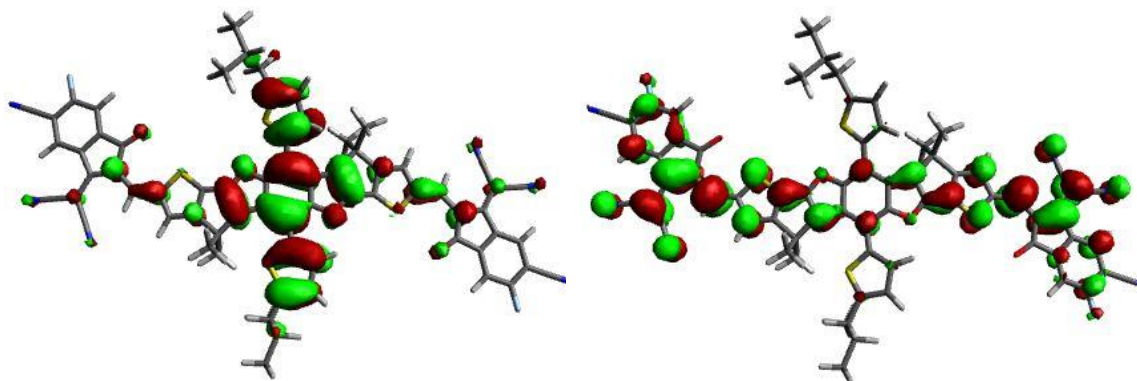
R



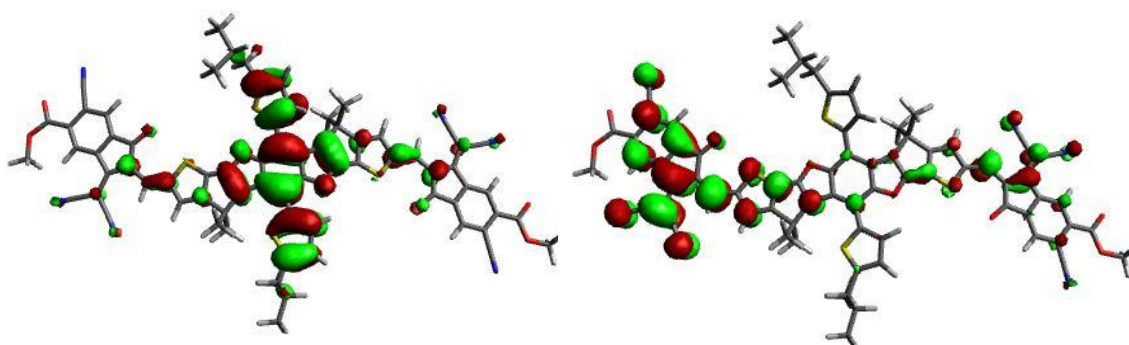
ZBCF1



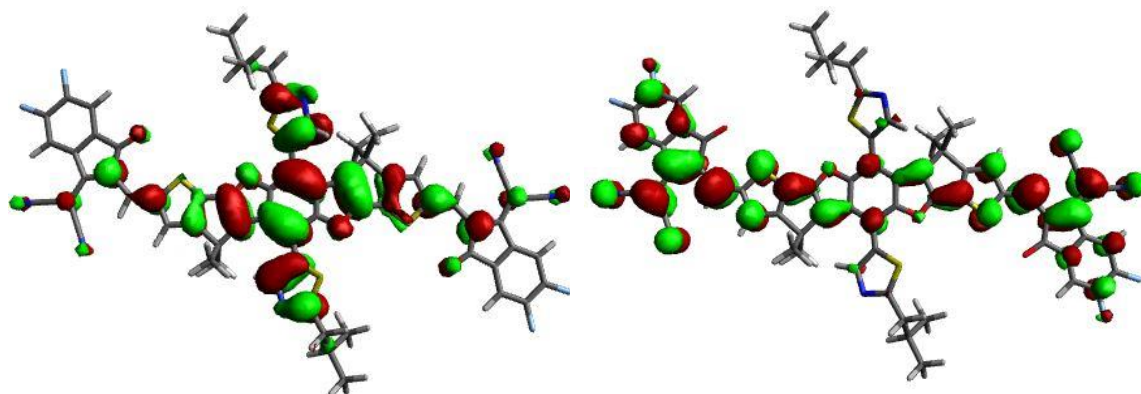
ZBCF2



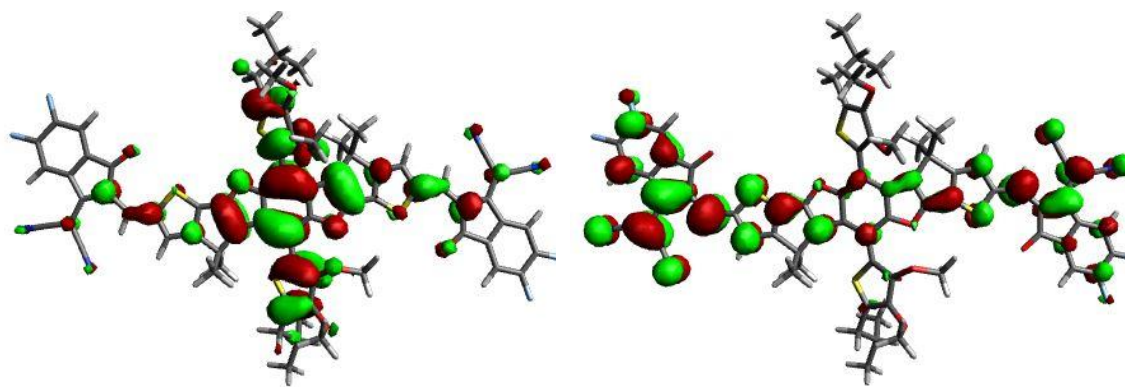
ZBCF3



ZBCF4



ZBCF5



ZBCF6

Figure 5. 5. HOMO and LUMO distribution on our studied systems.

5.3.2 Photovoltaic (PV) characteristics

The excitation energy with oscillating strength, absorption strength (wavelength) based on DFT and experiment and major contribution between molecular orbitals can be called as photovoltaic parameters of a solar cell [63, 124, 125, 127,159, 160].

The computed data of absorption parameters is given in Table 5.2. Reference molecule showed 758 nm absorption maximum in chloroform solvent (based on DFT computation) and 750 nm experimentally. The theoretically modelled molecules **ZBCF1** to **ZBCF6** expressed absorption maxima of 769, 802, 771, 792, 799, and 765 nm, sequentially. All theoretical planned molecules showed great bathochromic absorption in contrast to **R**. This shift is because of outstanding end-capped units and vital bridge atoms. Largest bathochromic shift was seen in **ZBCF2** molecule that is because of cyano units present in end-capped unit. The 2nd and 3rd largest bathochromic shift was observed in **ZBCF5** and **ZBCF4** molecules which is again because of efficient bridge atoms and end-capped units, respectively.

Table 5. 2: Wavelengths (nm), oscillating strength, excitation energy (eV) and contribution of all theoretical discussed molecules

Systems	Wavelength (DFT)	Experimental wavelength	Oscillating strength	Excitation energy (E _x)	Contributions HOMO→LUMO
R	758	750	1.192	3.301	(98%)
ZBCF1	769	---	1.998	3.288	(99%)
ZBCF2	802	---	2.012	3.269	(99%)
ZBCF3	771	---	2.019	3.299	(98%)
ZBCF4	792	---	2.012	3.291	(97%)
ZBCF5	799	---	2.011	3.283	(98%)
ZBCF6	765	---	1.997	3.301	(98%)

Excitation energy or energy of excitation participates well to demonstrate the performance of active layer molecules for solar cell applications. A least value of excitation energy offers high charge transfer along with better PCE.

The TD-DFT based computed excitation energy (E_x) values of **R** and **ZBCF1** to **ZBCF6** are 3.301, and 3.288, 3.269, 3.299, 3.291, 3.283, 3.301 eV, sequentially. From these values it is crystal clear that all theoretically planned molecules have least values of E_x which suggested that the designed molecules are efficient nominees for active layer that can boost the photovoltaic properties. The decreasing order of excitation energy is **R** = **ZBCF6** > **ZBCF3** > **ZBCF4** > **ZBCF1** > **ZBCF5** > **ZBCF2**. From foregoing discussion, it is clear that molecule having cyano units in end-capped has least value of E_x and highest charge transfer with better PCE.

The computed contribution between MOs is about or higher than 98% which confirmed that the planned molecules are best nominees for charge transfer reactions as shown in Table 5.2.

5.3.3 Reorganizational energy

The mobility of charges, i.e. electron and hole is inversely related to the reorganizational energy. Usually, the least amount of RE allows high mobility of charges. To detect the efficiency of a solar cell, RE plays a vital role. The active layer molecules with fine values of RE is efficient for high performance solar cells.

Reorganization energy (RE) in electron volt (eV) is categorized into internal and external type of reorganizational energy. Internal RE belongs to internal changes like morphology and chemical structures and the other one, i.e. the external RE belongs to external environment polarization which does not participate much and hence being ignored.

The computed values of RE are given in Table 5.3. B3LYP/6-31G(d,p) was used to compute RE of all modelled molecules (**R** and **ZBCF1** to **ZBCF6**). Reference molecule shows 2.101 as electron RE, while theoretically designed molecules like ZBCF1 to ZBCF6 show electron RE as 1.992, 1.723, 1.890, 1.771, 1.929, 2.094, accordingly. All theoretical planned molecules expressed least values of electron RE which confirmed that these designed molecules have surely large electron mobility in active layer.

Table 5. 3: Electron and hole reorganizational energy (eV)

Systems	Electron	Hole
R	2.101	1.229
ZBCF1	1.992	1.227
ZBCF2	1.723	1.311
ZBCF3	1.890	1.310
ZBCF4	1.771	1.302
ZBCF5	1.929	1.301
ZBCF6	2.094	1.301

Hole RE also computed in order to examine the hole mobility of discussed molecules in active layer. The computed hole RE is 1.229, 1.227, 1.311, 1.310, 1.302, 1.301, and 1.301 for **R** and **ZBCF1** to **ZBCF6** as shown in Figure 5.6. From foregoing discussion and analysis, it is crystal clear that theoretical proposed molecules are good nominees for active layer as electron and hole transport materials. The computed results also suggested that proposed molecules also good nominees for high performance organic solar cell applications.

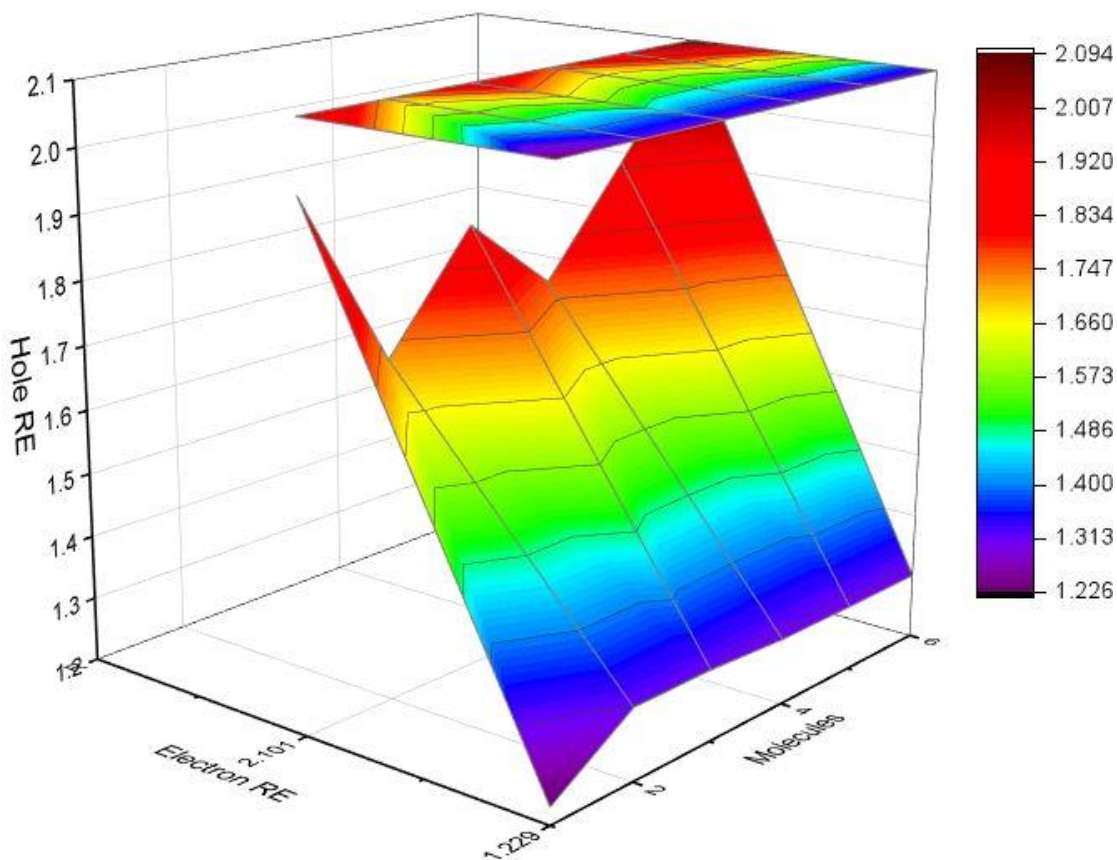


Figure 5. 6. Electron and hole RE of all the designed molecules at B3LYP/6-31G(d,p)

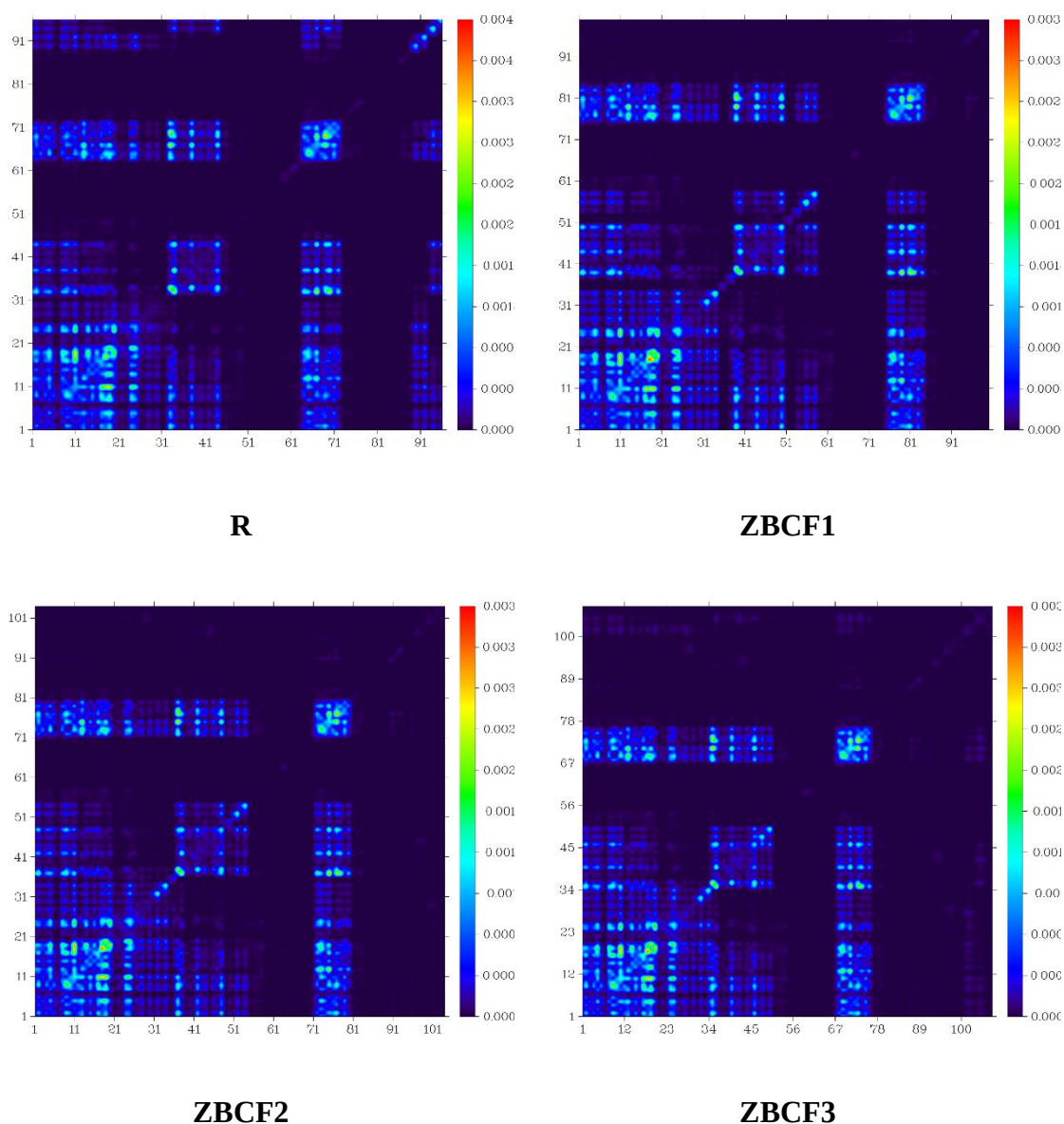
5.3.4 TDM Analysis

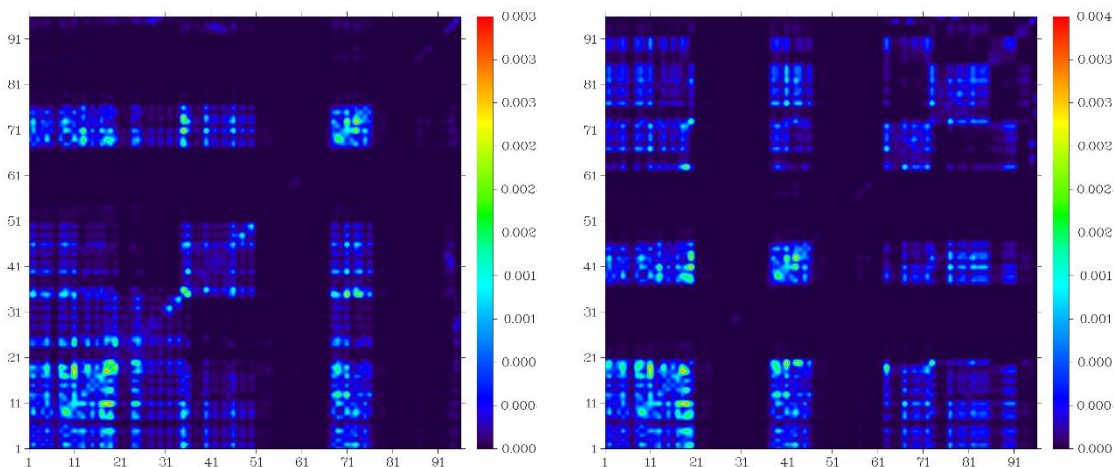
TDMs (transition density matrix) analysis highlights the transitions within a molecule from ground level to excited levels. The TDMs also unveil the targeted segmental transition within a molecule. Different transitions are studied and discussed within a molecule and shown by TDMs plot in Figure 5.7. Additionally, the location of donor and acceptor unit can also be unveiled through TDM plots.

All atoms present within a molecule participated in overall transitions but participation of hydrogen is small so its role is being ignored. B3LYP/6-31G(d,p) was employed to compute the overall TDMs and S_1 emission state is considered as shown in

Figure 5.7. In **R** molecule electron coherence is present on diagonal and similar pattern is present in all the proposed molecules.

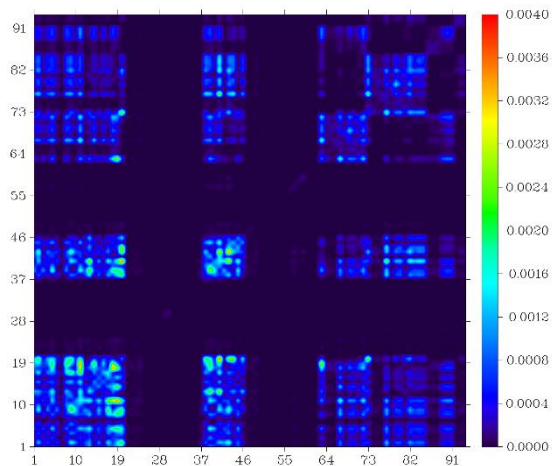
The presence of electron sector on donor unit and withdrawing of these electron density towards acceptor end suggested that end-capped efficient units withdraw electron density. The efficient bridge atoms mainly rich in electron density (oxygen and sulfur) facilitate electron density generation in **ZBCF5** and **ZBCF6** molecules.





ZBCF4

ZBCF5



ZBCF6

Figure 5. 7. TDMs of all theoretical discussed molecules in S_1 emission state

Binding energy is another important tool to unveil the performance of a solar cell. The first principle excitation energy along with energy band gap plays outstanding role for theoretical computation of binding energy. Generally, active layers with low value of binding energies offer high current charge density and high dissociation constant. Following equation is used to compute the binding energy of molecule:

$$E_b = E_{H-L} - E_{OPT} \quad (3)$$

Table 5. 4: Binding energy, excitation energy and band gap in electron volts (eV).

Systems	E_{H-L}	E_{OPT}	E_b
R			
	1.826	1.209	0.617
(BFHIC-4F)			
ZBCF1	1.782	1.203	0.579
ZBCF2	1.614	1.192	0.422
ZBCF3	1.783	1.189	0.594
ZBCF4	1.644	1.188	0.456
ZBCF5	1.693	1.199	0.494
ZBCF6	1.787	1.201	0.586

The computed values of binding energy of **R** and **ZBCF1** to **ZBCF6** are 0.617 and 0.579, 0.422, 0.594, 0.456, 0.494, and 0.586 eV respectively. All these molecules have least amount of binding energy, which indicates that the modelled molecules are good nominees for high performance solar cells. The order of binding energy is **R** > **ZBCF3** > **ZBCF6** > **ZBCF1** > **ZBCF5** > **ZBCF4** > **ZBCF2**. Molecule **ZBCF2** disclosed least amount of binding energy and probably will show high value of short-circuit current density (J_{sc}) as shown in Figure 5.8.

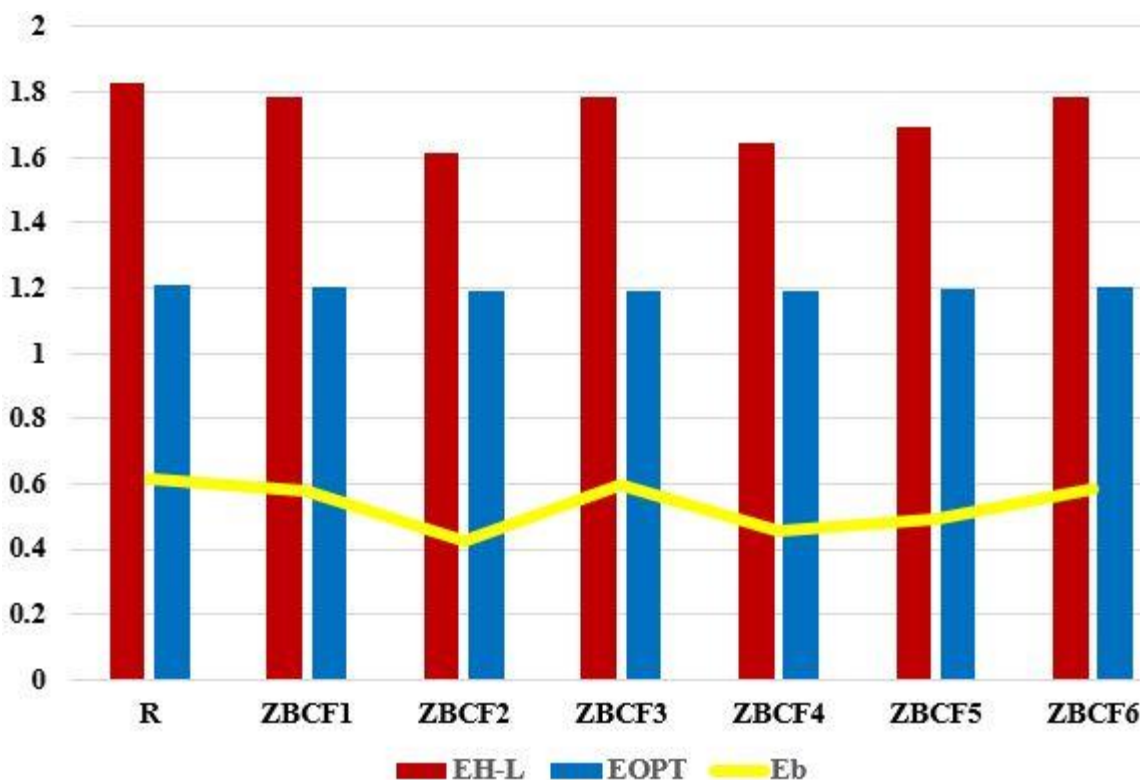


Figure 5. 8. The band gap, first principle excitation, and binding energy of all theoretically designed molecules at B3LYP/6-31G(d,p)

5.3.5 Open Circuit Voltage

The photovoltaic performance is also influenced due to results of V_{oc} (open circuit voltage). For computing V_{oc} , different parameters should be considered and measured like the level of both molecules (donor and acceptor). Additionally, the V_{oc} is computed from both type of current, i.e. photo-saturated and photo-concentrated. The V_{oc} is always measured at null voltage and at zero kelvin. At B3LYP/6-31G(d,p) level of DFT, the V_{oc} of all molecules is computed and results are expressed in Figure 5.9. Following equation is also proved helpful for computing total open circuit voltage values of all molecules in voltage (V):

$$V_{oc} = (|E_{HOMO}^D| - |E_{LUMO}^A|) - 0.3 \quad (4)$$

Here, E express elementary charge of donor and 0.3 is an empirical factor value.

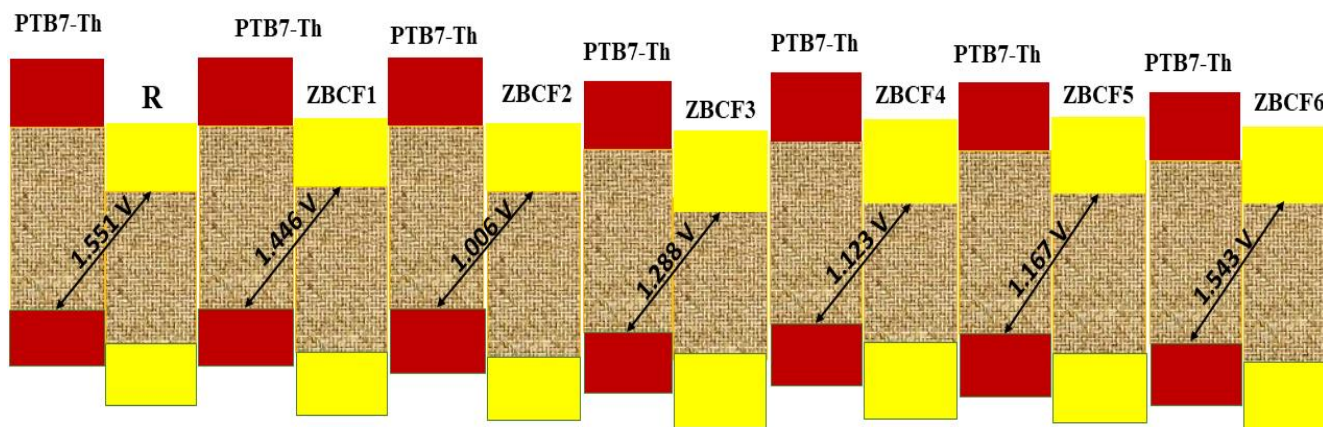


Figure 5. 9. V_{oc} of all the studied molecules with respect to PTB7-Th donor polymer

In this study, all NFAs are aligned with donor polymer (PTB7-Th) in order to compute the overall open circuit voltage. The theoretically computed V_{oc} values for **R** and **ZBCF1** to **ZBCF6** are 1.551, 1.446, 1.006, 1.288, 1.123, 1.167, and 1.543 V, respectively. All the theoretically designed molecules show good values of V_{oc} in contrast to reference molecule, that is because of efficient end-capped and bridge atoms. This arrangement not only boosted the open circuit voltage but also enhanced the absorption capabilities in NIR region. Overall, V_{oc} results suggested that the designed molecules are good nominees for high performance solar cell applications.

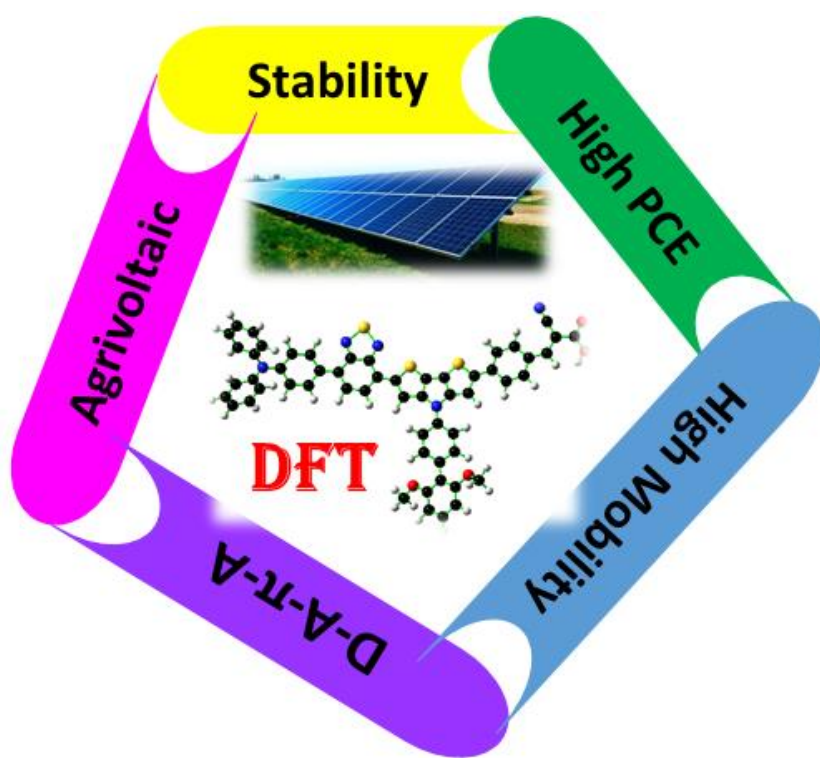
5.4 Outcomes

In conclusion, A-D-A type small organic molecules are theoretically designed and explored by employing DFT and TD-DFT calculations. Advanced quantum chemical techniques are used to express the photovoltaic response of newly planned molecules (**ZBCF1** to **ZBCF6**). Large bathochromic shift in NIR region (769 to 802 nm) was seen with narrow band gap values. Narrow band gap with large red-shifting allows maximum charge transfer which in return enhances the photovoltaic properties of designed molecules in contrast to **R** molecule. Low binding energy (0.422 to 0.586 eV) and excitation energy (3.269 to 3.301

eV) offer maximum J_{sc} values and easy transfer of charge density from ground to excited states. High open circuit voltage with least amount of reorganizational energy values allows high mobility of charges and large PCE. Transition density matrix analysis also confirmed the different type of transitions in designed molecules and also confirmed that electron coherence is present in all the studied molecules. To sum up, these newly designed molecules have expressed efficient photovoltaic properties. Thus, we recommend these novel type of systems to experimentalists for future development of high performance solar cells.

CHAPTER 6

Designing the D-A- π -A scheme of molecules as Donor systems for Applications in Solar Cells



6.1 Introduction

In order to enhance the energy production from solar devices, scientists of this field are busy to develop new photovoltaic (PV) devices [196, 197]. Researchers of this field are also involved in designing new PV technologies that not only improve the energy harvesting capability but also show integration in novel applications [113, 198, 199]. Following this line, photovoltaic devices are now used in agriculture sector and give an important application named as “agrivoltaics” (use of photovoltaic devices in agriculture field for production of energy that improved production rate of food) [200, 201]. In last few decades, silicon based photovoltaic were installed on greenhouses. But certain limitations are associated with silicon based photovoltaic like they are opaque and thus captured the transmitted light that ultimately reduce the plants productivity rate with bad plant growth [202, 203].

In modern era, use of organic solar cells or dye sensitizer cells as alternative of silicon based photovoltaic devices. Both devices, i.e. (organic solar cell [204, 205] or dye sensitizer cells [206]) are transparent with different colors, light and simple weight, and have low toxicity. Among them, dyes-based solar cells are commonly utilized in greenhouse-integrated solar cells because these solar cells absorb visible-region light, i.e. 400 to 800 nm. Plant’s chlorophyll *a* and *b* absorb red and blue light of visible spectrum for their regular activities [207, 208].

Designing of dyes sensitizer solar cells that absorb green region light while transmitting red and blue light is a hot topic for researchers [209]. In this field, many organic, tandem and dyes sensitizer solar cells are already reported in valuable literature.

N719 [210] and many diketopyrrolopyrrole-derivative based solar cells [211] (showed good efficiencies) were reported in past. More recently, many thiazolo[5,4-*d*] thiazole based dyes sensitizer were reported for solar cells that absorbed more light in green region of visible spectrum while transparent in red and blue region. D- π -A based dye TTZ8-12 reported in literature, in which donor end attached with acceptor end via efficient bridge atoms [114]. Therefore, in this way efficient dye sensitizer solar cell was prepared that showed good efficiency with excellent optoelectronic properties.

More recently, Dessi and his co-authors used addition acceptor group between donor and π -bridge atoms for improving the PV and optoelectronic aspects of green housed integrated solar cell [112]. They used 2,1,3-benzothiadiazole as internal acceptor unit that was attached with good donor unit giving **D-A- π -A** type backbone skeleton. They reported 3 new molecules named as BTD-DTP1, BTD-DTP2, and BTD-DTP3 by using D-A- π -A configuration. Among these molecules, **BTD-DTP3** [112] showed good efficiency with good optoelectronic properties. Due to unique backbone skeleton and application in green house, we theoretically proposed **GH1** to **GH5** molecules by modifying the acceptors units (end-capped) of **BTD-DTP3** molecule (consider as **R**) and examined the various parameters of theoretically designed molecules. Alignment of frontier molecular orbitals (FMOs), absorption maximum, and excitation energy along with oscillating strength, V_{oc} estimation, and transition density matrices (TDMs) of theoretical proposed molecules are observed by TD-DFT and DFT approaches. Finally, blend study of donor material with suitable acceptor polymer has also been performed for detecting charge shifting behavior of resultant molecules. Outcomes of our studied theoretical analyses advised that the

theoretical designed systems/molecules are very good nominees for highly stable green-house integrated solar cells.

6.2 Computational detail

In our research findings, Gaussian 09 W and GaussView 6.0 are used to perform various calculations and to manage output results (output results visualization). At first, **R** was fully optimized at five functionals (M06-2X [156], B3LYP [157], MPW1PW91 [155] , CAM-B3LYP [212], and ω B97XD [158]) along with 6-31G(d,p) level of basis set [63, 130, 138, 160, 179, 193] . Following it, the UV/Visible calculations of designed molecules were evaluated in organic solvent. By comparing the experimental and theoretical computed absorption maximum [112], functional MPW1PW91 with level 6-31G(d,p) of DFT was chosen for remaining computational analyses.

The reorganizational energy of electron and hole was theoretically computed by employing following equations [129-131, 133, 136, 164]:

$$\lambda_{\text{electron}} = [E_0^- - E_-] + [E_-^0 - E_0] \quad (1)$$

$$\lambda_{\text{hole}} = [E_0^+ - E_+] + [E_+^0 - E_0] \quad (2)$$

Where, E_0 , $E_{+/-}$, $E_0^{+/-}$ and $E_{+/-}^0$ define the energy at the neutral state, the energy at cation/anion state, the energy of excited state at the ground state geometry and the neutral energy at the excited state, respectively.

6.3 Results and discussion

6.3.1 Choice of appropriate method and level of DFT

At first, **BTB-DTP3** was fully optimized at five functionals with level 6-31G(d,p) of DFT. Then UV/Visible calculations of **R** were done at B3LYP, MPW1PW91, CAM-B3LYP, M06-2X and ω B97XD with level 6-31G(d,p) of TD-DFT in organic solvent (CHCl_3). The computed λ_{max} of **R** is 481 nm for B3LYP/6-31G(d,p), 534 nm for MPW1PW91/6-31G(d,p), 611 nm for M06-2X/6-31G(d,p), 546 nm for CAM-B3LYP/6-31G(d,p), and 577 nm for ω B97XD/6-31G(d,p). The experimental recorded absorption maximum is 518 nm in CHCl_3 solvent [112]. So, after careful analysis, method MPW1PW91 with level 6-31G(d,p) show best consistency with the experimental recorded absorption maxima as shown in Figure 6.1. Therefore, method MPW1PW91 with DFT level 6-31G(d,p) was used for further theoretical analysis and evaluations.

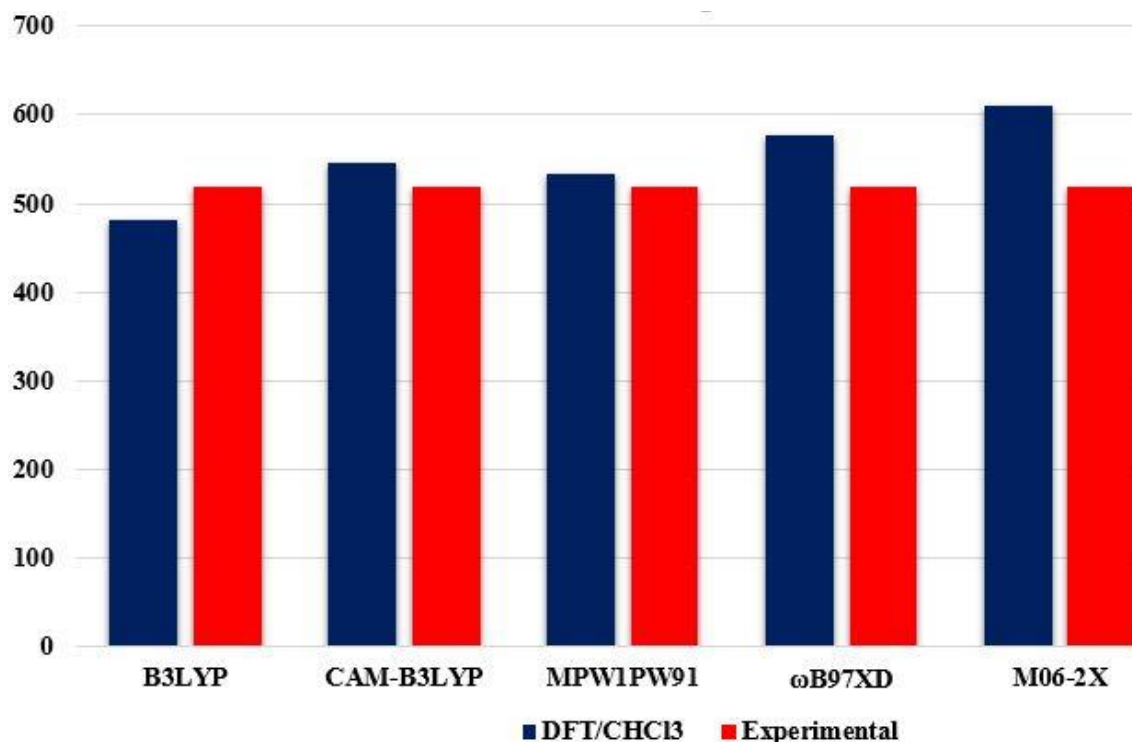


Figure 6. 1. UV-Visible recorded bar chart of reference molecule at different functionals

6.3.2 Chemistry of molecules

End-capped acceptor tailoring of reference molecule was made design five molecules (GH1), (GH2), (GH3), (GH4), (GH5) as illustrated from Figure 6.2. By using this approach, five new efficient molecules are designed for green house integrated solar cell applications. The relaxed geometries of theoretical proposed molecules are exhibited in Figure 6.3.

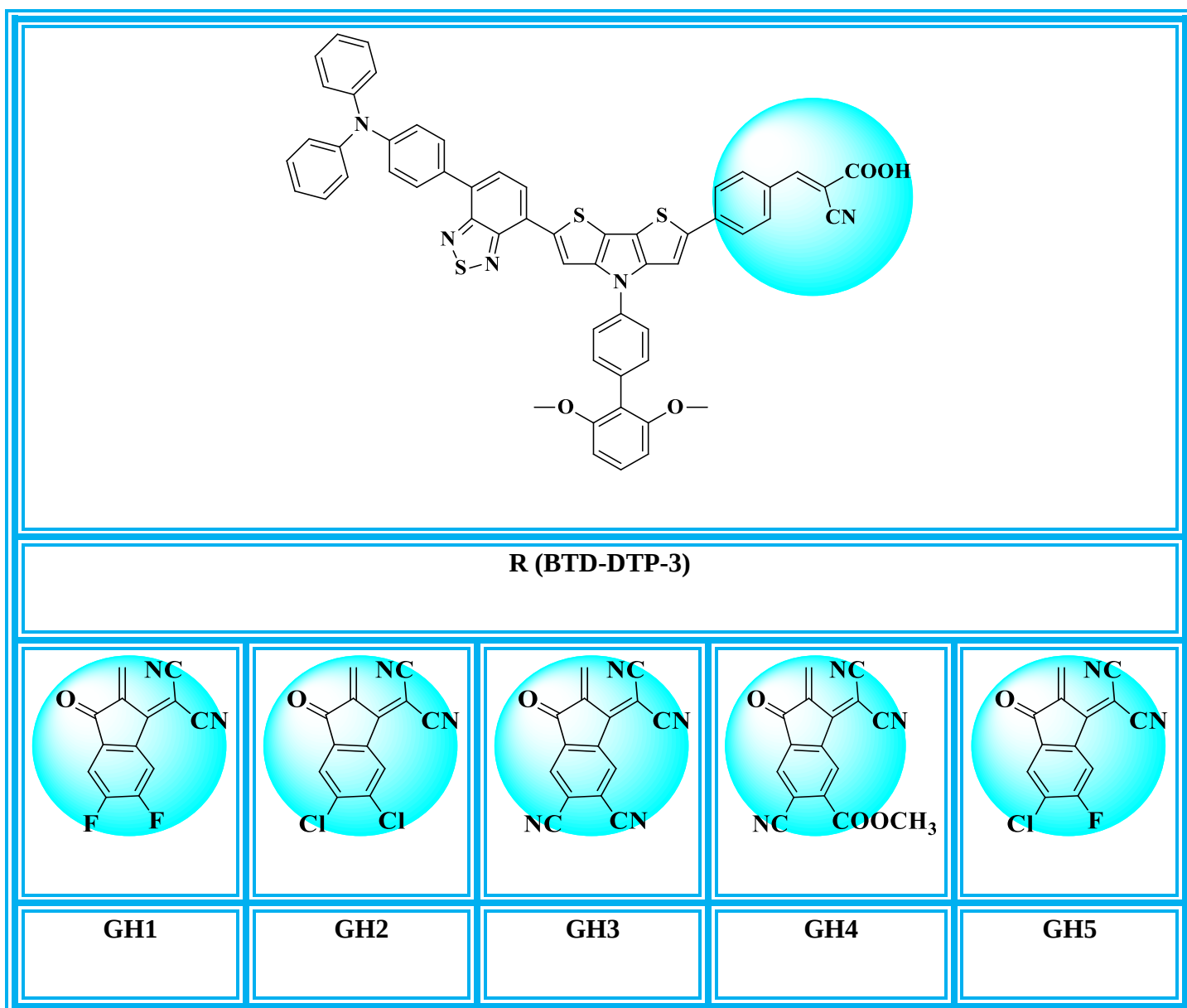


Figure 6. 2. Chemical structure of reference molecule and theoretically designed acceptor units

6.3.3 Frontier molecular orbital analysis

Frontier molecular orbitals (highest occupied and lowest unoccupied molecular orbitals) are involved in playing a tremendous role for measuring the performance of a solar cell [64, 168, 172, 178]. FMOs not only judge the photovoltaic properties but also charge transfer behavior of a molecule. The gap between HOMO and lowest unoccupied-MO is regarded as energy band gap. Energy band gap plays a crucial role to estimate the overall

charge transfer within a molecule [2, 117, 118]. Commonly narrow band gap provides more and quick charge transfer within a molecule and vice versa. Finally, a molecule with least band gap value is very important for designing well-ordered and well organized photovoltaic devices.

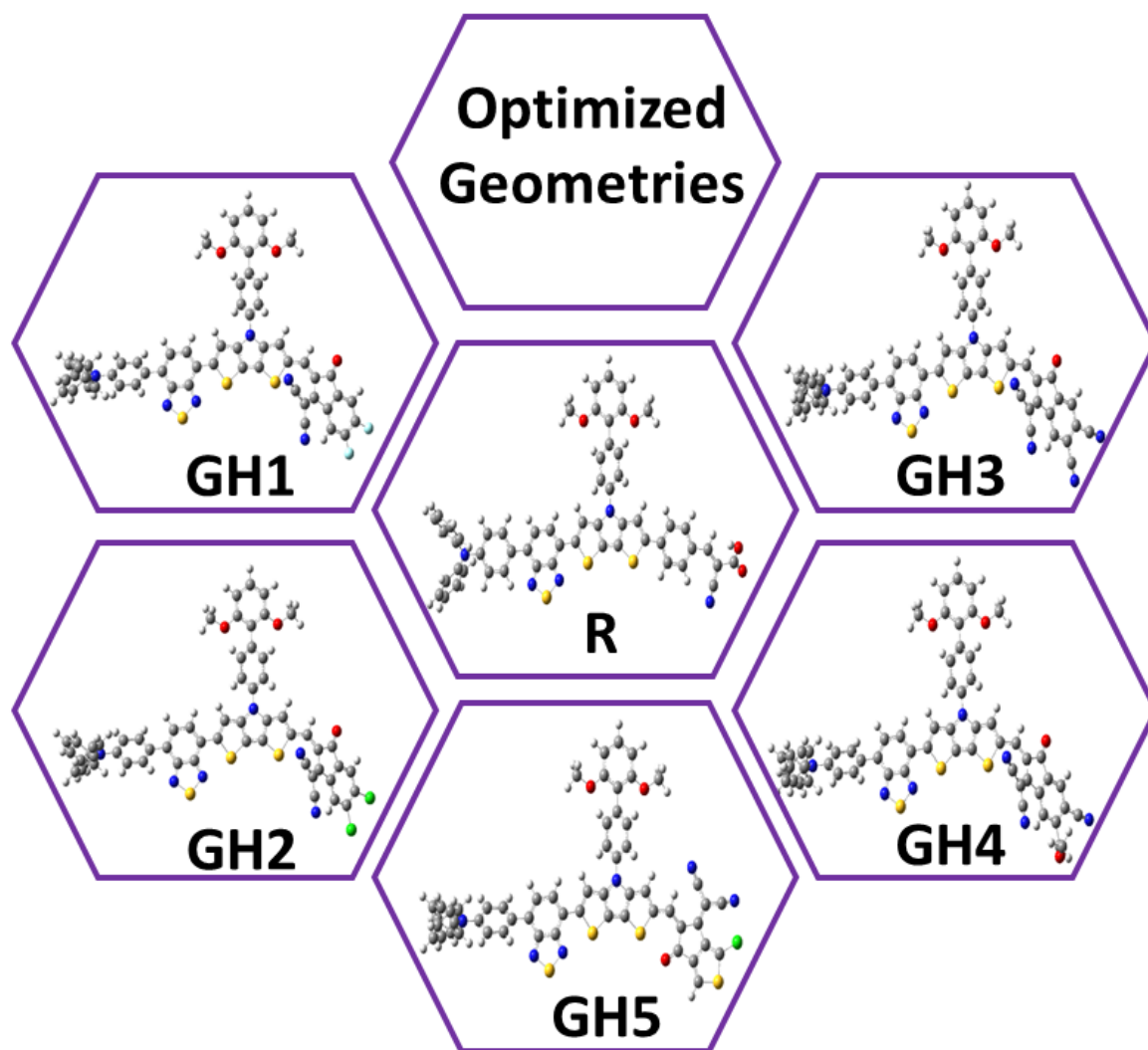


Figure 6. 3. Fully optimized structures of theoretically planned molecules

Orbitals energy and band gap of all theoretical proposed molecules are listed in Table 6.1. Method MPW1PW91 with level 6-31G(d,p) is applied to determine orbitals energy and band gap. Reference molecule and theoretically, designed molecules (**R**, **GH1** to **GH5**) intimate HOMO energy as -6.90, -6.20, -6.22, -6.32, -6.30, and -6.20 eV, accordingly. LUMO energy of **R**, **GH1** to **GH5** is -1.65, -2.08, -2.16, -2.50, -2.42, and -2.12 eV, sequentially. The computed band gap is 4.44 eV for **R**, 4.12 eV for **GH1**, 4.06 eV for **GH2**, 3.82 eV for **GH3**, 3.88 eV for **GH4**, and 4.08 eV for **GH5**. From data, it is crystal clear that the theoretical planned molecules displayed reduced band gap values in contrast to **R** which proposed that the theoretical planned molecules are well organized and efficient candidates for green house integrated solar cells. The HOMO and LUMO scattering on theoretical planned molecules are given in Figure 6.4. The descending order of band gap is: **R** > **GH1** > **GH5** > **GH2** > **GH4** > **GH3**.

Table 6. 1: HOMO and LUMO energies and band gap calculated at DFT level.

Molecules	E_{HOMO}	E_{LUMO}	$E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$
R	-6.09	-1.65	4.44
GH1	-6.20	-2.08	4.12
GH2	-6.22	-2.16	4.06
GH3	-6.32	-2.50	3.82
GH4	-6.30	-2.42	3.88
GH5	-6.20	-2.12	4.08

Among all theoretically studied molecules, least band gap value is computed for **GH3** molecule which is because of well-ordered cyano groups in end-capped acceptor moiety. Likewise, **GH4** and **GH2** indicated reduced band gap in contrast to reference

molecule which is because of cyanide (-CN) acceptor units. Overall, theoretical plotted molecules are cost-effective and efficient nominees for green house integrated solar cell applications.

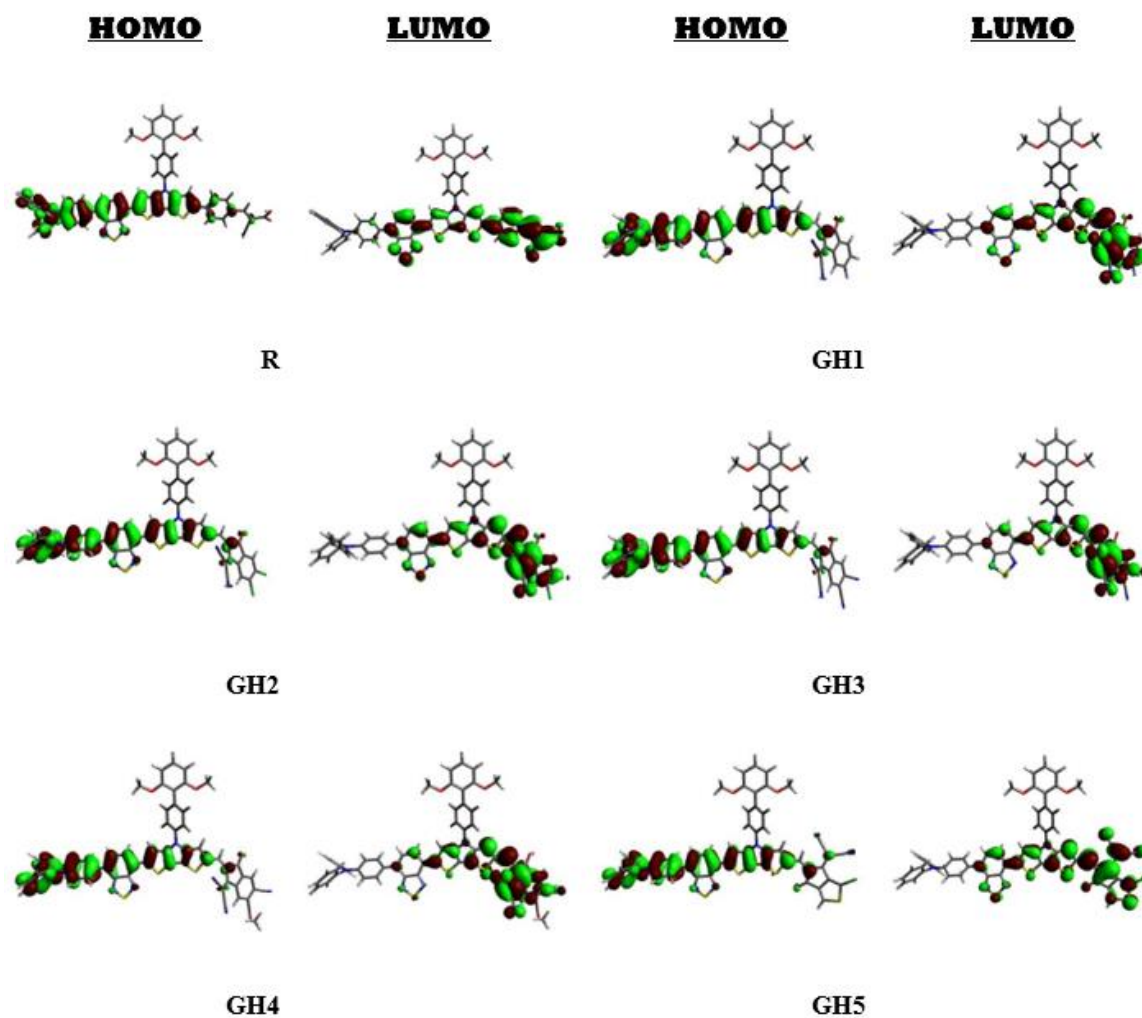


Figure 6. 4. HOMO and LUMO scattering on theoretical planned molecules

6.3.4 Density of states

Density of states (DOS) spectrum interpretation is a special criterion to guesstimate the working efficiency of a solar cell [137, 175]. DOS unveil the nature of all linking groups (that are present in a molecule) with charge transfer behavior. DOS is pure quantum mechanical technique which also estimate the presence of electron density per unit area in a molecule. Both properties boosted the performance of a solar cell. Method MPW1PW91 with DFT level 6-31G(d,p) was employed to take out DOS spectra (Figure 6.5). For a general acceptor or donor molecule, HOMO should cover donor parts and LUMO should be on acceptor unit. In present report, HOMO is majorly present on donor unit with small amount on bridge atoms whereas LUMO is majorly present on acceptor end with small amount on bridge atoms. The bridge atoms work as facilitators between donor and acceptor end. Same scattering pattern is observed in all theoretical planned molecules which advised that our end-capped acceptor tailoring with efficient chloro, cyano, fluoro functional groups is a key approach to design well-ordered and logical nominees for high performance greenhouse integrated solar cell applications.

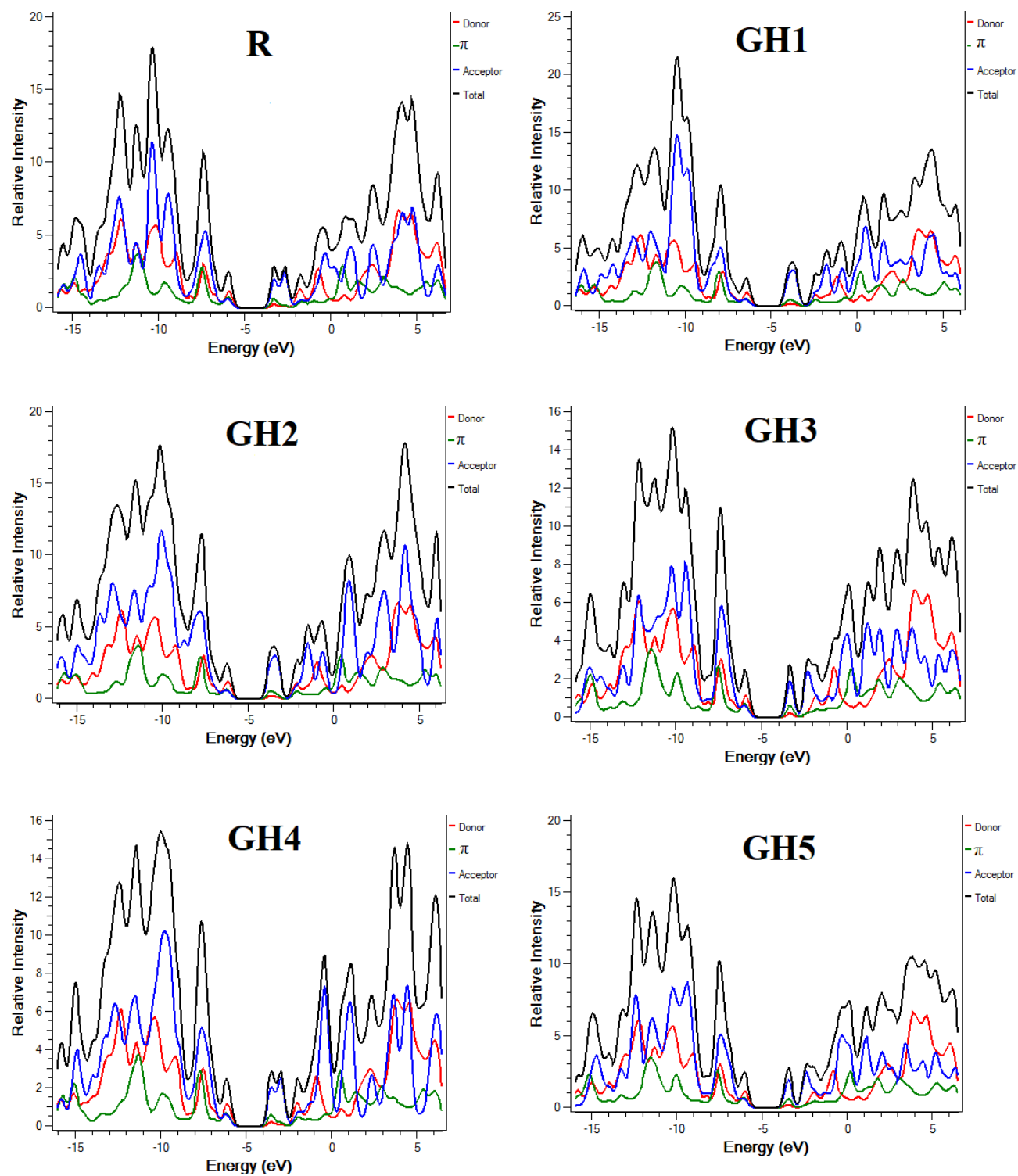


Figure 6. 5. DOS sketches of theoretical studied molecules at method MPW1PW91.

6.3.5 Photovoltaic properties

Absorption maximum, oscillating strength (f_o), excitation energy (E_x) and major assignment between molecular orbitals are key parameters that judge the photovoltaic aspects of a solar cell [134, 138, 169]. Certain factors are important to measure the photovoltaic efficiency of a solar cell like red-shifting with low value of E_x and high f_o with best charge shifting (HOMO→LUMO) always offer outstanding photovoltaic properties in a solar cell. As present report is on designing effective molecules for greenhouse integrated solar cell, therefore absorption in visible region is also an important factor for judging the photovoltaic properties of a molecule. Photovoltaic aspects of theoretically planned nominees are listed in Table 6.2.

The absorption maximum ($\lambda_{\max}$) value (experimental) of **R** in CHCl_3 solvent was 518 nm (visible region) [112]. The $\lambda_{\max}$ values of theoretical planned nominees are also measured in CHCl_3 solvent at MPW1PW91 along with level 6-31G(d,p) of TD-DFT. The $\lambda_{\max}$ values of **R**, and **GH1** to **GH5** are 534, 566, 572, 588, 582, and 583 nm, sequentially. All theoretically proposed molecules exhibited absorption maximum in visible region which advocated that these molecules are potential candidates for greenhouse integrated solar cell applications. Red-shifting in absorption spectrum is also noted for all designed molecules in contrast to reference molecule. Large bathochromic shift is observable in **GH3** molecule which is because of -CN acceptor unit. Likewise, molecules **GH4** and **GH5** intimate approximately similar values of absorption with bathochromic shift (by comparing with **R**) and this is perhaps due to additional functional groups in end-capped units of **GH4** and **GH5**. Interestingly, all molecules demonstrated good values of absorption maxima with most absorption in visible region. The descending schedule of $\lambda_{\max}$ values of all the

studied theoretical proposed molecules is: **GH3**> **GH5**> **GH4**> **GH2**> **GH1**> **R**. From foregoing analysis, it is crystal clear that these theoretically proposed molecules are nominees for highly stable greenhouse integrated solar cell applications.

Table 6. 2: TD-DFT calculations for the estimation of excited state properties

Molecules	λ_{max} (DFT)	λ_{max} (Exp)	E_x	f_o	MOs assignments HOMO→LUMO
R	534	518	2.61	1.94	98%
GH1	566	---	2.58	2.01	98%
GH2	572	---	2.50	2.04	99%
GH3	588	---	2.44	2.10	99%
GH4	582	---	2.35	2.06	99%
GH5	583	---	2.40	2.01	98%

Excitation energy (E_x) is basic criterion to decide the performance and working of a solar cell. Molecules in the active layer of a solar cell should have low values of E_x because low value of E_x causes high charge mobility and PCE of resultant molecule. **R** intimate E_x value of 2.61 eV in CHCl_3 solvent. The E_x value is 2.58 eV for **GH1**, 2.50 eV for **GH2**, 2.44 eV for **GH3**, 2.35 eV for **GH4**, and 2.40 eV for **GH5** molecule. Evidently all theoretical proposed molecules expressed least values of E_x in contrast to reference molecule. Lowest value of E_x is observed in **GH4** which is because of end-capped acceptor unit. **GH5** and **GH3** also displayed low values of E_x which is because of additional functional groups in the end-capped moiety of designed molecules. The descending order of E_x for all the modelled molecules including reference molecule is: **R**> **GH1**> **GH2**> **GH3**> **GH5**> **GH4**. From foregoing analysis, it is clear that the theoretically modelled

molecules are nominees for high performance greenhouse-integrated solar cell applications.

Simulated absorption spectrum of all the studied molecules in CHCl_3 solvent is displayed in Figure 6.6. All molecules show good excellent absorption peaks in visible region that recommended the proposed molecules are potential nominees for solar cell applications.

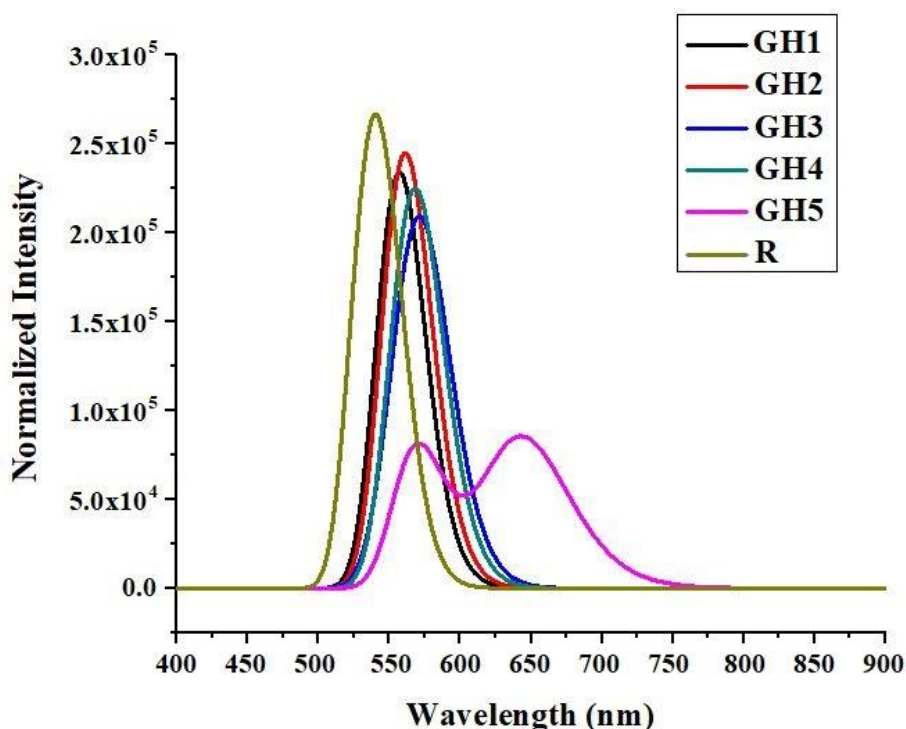


Figure 6. 6. Simulated absorption spectrum of all proposed molecules in CHCl_3 solvent

6.3.6 Reorganizational energy

Reorganizational energy (RE) of hole and electron is vital criterion to estimate the mobility of charges which in return examine the performance and working capability of a solar cell. From scientific point of view (solar cell basic criterion), there exist a mathematically

inverse relationship between mobility of charges and RE. Which means a molecule with less RE value should have high mobility of charges [195, 213].

From foregoing motivations, we also computed RE of theoretically proposed molecules at method MPW1PW91 with level 6-31G(d,p) of DFT and results are listed in Table 6.3.

The λ_h (hole-reorganizational energy) is 0.0165 eV for **R**, 0.0161 eV for **GH1**, 0.0159 eV for **GH2**, 0.0144 eV for **GH3**, 0.0147 eV for **GH4**, and 0.0154 eV for **GH5**. Interestingly, all quantum chemically proposed molecules displayed low λ_h values in contrast to **R**. And this perhaps due to introduction of efficient functional groups in end-capped acceptor moiety of **R**. Least value of λ_h is noted for **GH3** molecule which is surely due to narrow band gap and bathochromic shift in the absorption spectrum. Molecules **GH4** and **GH5** also expressed low values of λ_h which is because of extra functional groups in end-capped acceptor unit. Likewise, **GH2** and **GH1** proposed molecules show approximately close values of λ_h which is because of fluoro and chloro units in end-capped moiety of GH1 and GH2 molecules, sequentially. Overall, a decreasing trend of λ_h in all the proposed molecules is: **R** > **GH1** > **GH2** > **GH5** > **GH4** > **GH3**.

Table 6. 3: Reorganizational energies of electron and hole for all the molecules

Molecules	Reorganizational energy of electron (eV)	Reorganizational energy of hole (eV)
R	0.0306	0.0165
GH1	0.0303	0.0161
GH2	0.0309	0.0159
GH3	0.0301	0.0144
GH4	0.0303	0.0147
GH5	0.0305	0.0154

The λ_e (reorganizational energy of electron) is 0.0306 eV for **R** molecule. And λ_e is 0.0303, 0.0309, 0.0301, 0.0303, and 0.0305 eV for **GH1** to **GH5**, respectively. Macroscopically, all molecules disclosed comparable values of λ_e with **R**. Among all proposed molecules, **GH1**, **GH3**, **GH4**, and **GH5** expressed low values of λ_e in contrast of **R**, which is because of superb end-capped acceptor units as shown in Figure 6.7. Lowest λ_e is again observed for **GH3** molecule which is because of efficient end-capped cyano functional group. The decreasing trend of λ_e of all the studied molecules is: **GH2** > **R** > **GH5** > **GH1**=**GH4** > **GH3**.

From Figure 6.7 and foregoing discussion, it is evident and observable that all proposed frameworks are sensible nominees for greenhouse-integrated (GHI) solar cell

applications. Among all, **GH3** molecule displayed superb values of reorganizational energy of hole and electron. So, this molecule could be used as potentially approved efficient molecule for highly efficient GHI-solar cell applications.

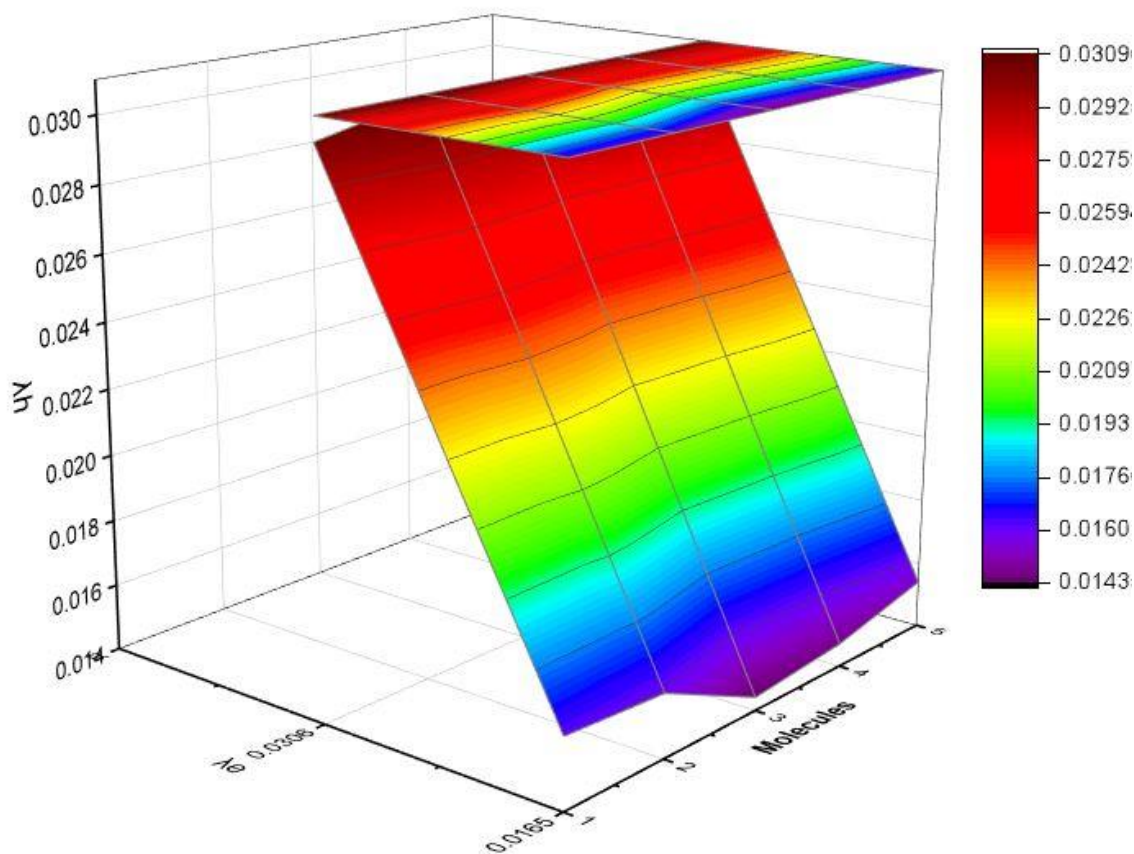


Figure 6. 7. The λ_e and λ_h values of all theoretical proposed models/molecules

6.3.7 Prediction of open circuit voltage

The V_{oc} , i.e. Open circuit voltage is demonstrated as the amount of current that is basically drawn from any PV (photovoltaic device) at null voltage. V_{oc} is important criterion to explain the working mechanism and performance of a solar cell. V_{oc} is highly depended on total photo-saturated and photo-generated current.

Scaling factors are important to measure the V_{oc} of a solar cell like the donor molecules in the active layer of a solar cell should be scaled with acceptor PC₆₁BM polymer. The HOMO level of donor and LUMO level of acceptor also play a crucial role to compute the overall V_{oc} . The open circuit voltage of proposed donor molecules with acceptor polymer is shown in Figure 6.8.

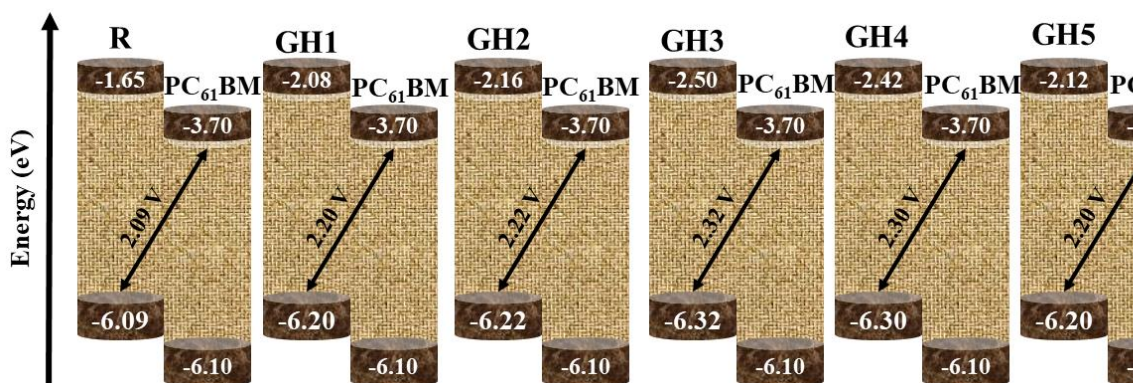


Figure 6. 8. V_{oc} of GH1 to GH5 with respect to PC₆₁BM polymer

The V_{oc} value is 2.09 V for **R**, 2.20 V for **GH1**, 2.22 V for **GH2**, 2.32 V for **GH3**, 2.30 V for **GH4**, and 2.20 V for **GH5**. Amazingly all theoretical planned molecule disclosed high value of V_{oc} in contrast to **R** molecule. High value of V_{oc} of a molecule recommended that molecule is potential nominee for high PCE. Generally, for computing PCE fill factor along with V_{oc} is used and in present report the computed values of V_{oc} of theoretical planned molecules are higher than **R**. Highest value of V_{oc} is noted for molecule **GH3** which is because of end-capped acceptor moiety of theoretically planned molecules boosted the V_{oc} values. The decreasing order of V_{oc} for all molecules is: **GH3** > **GH4** >

GH2> GH1=GH5> R. From foregoing discussion of Voc, it is crystal clear that the theoretical planned molecules are potential nominees for highly efficient GHI-solar cell applications.

6.3.8 Transition density matrix and binding energy

TDMs (analysis of transition density matrix) is an important criterion to evaluate the states of transition within a molecule which enhance PCE. TDMs estimation is also important in order to observe the total transition from lower level to higher level which is helpful to estimate the total charge density shifting behavior along with amount of total current charge density within a molecule. TDMs also unveil the nature and position of electron and hole density within a molecule.

For the sake of simplification, all theoretical proposed models are spliced into four components, i.e. **D** (donor), **A** (additional acceptor), π (bridge atoms), and **A** (end-capped acceptor). Hydrogen is a small electropositive atom and don't participate much in overall transitions, therefore, its role is being ignored throughout TDMs estimation.

Method MPW1PW91 with level 6-31G(d,p) of DFT was employed to simulate the TDMs plots of all model molecules and plots are shown in Figure 6.9. From plots, it is easily observable that donor atoms donate electron density, addition acceptor accept electron density. Next π -bridge atoms move this electron density from additional acceptor to end-capped acceptor because strength of accepting electron density of end-capped acceptor is more in contrast to additional acceptor. Same behavior of scattering of charge density is seen in all model molecules (**R** and **GH1** to **GH5**). The presence of well-ordered electron density in **GH1** to **GH5** molecules encouraged that end-capped acceptor

modification is an effective approach for designing highly efficient molecules for greenhouse integrated solar cell applications. Except **GH1** molecule, all other proposed molecules disclosed excellent charge distribution plots as shown in Figure 6.9, which recommended that these theoretical proposed model molecules are good nominee for charge transfer reactions.

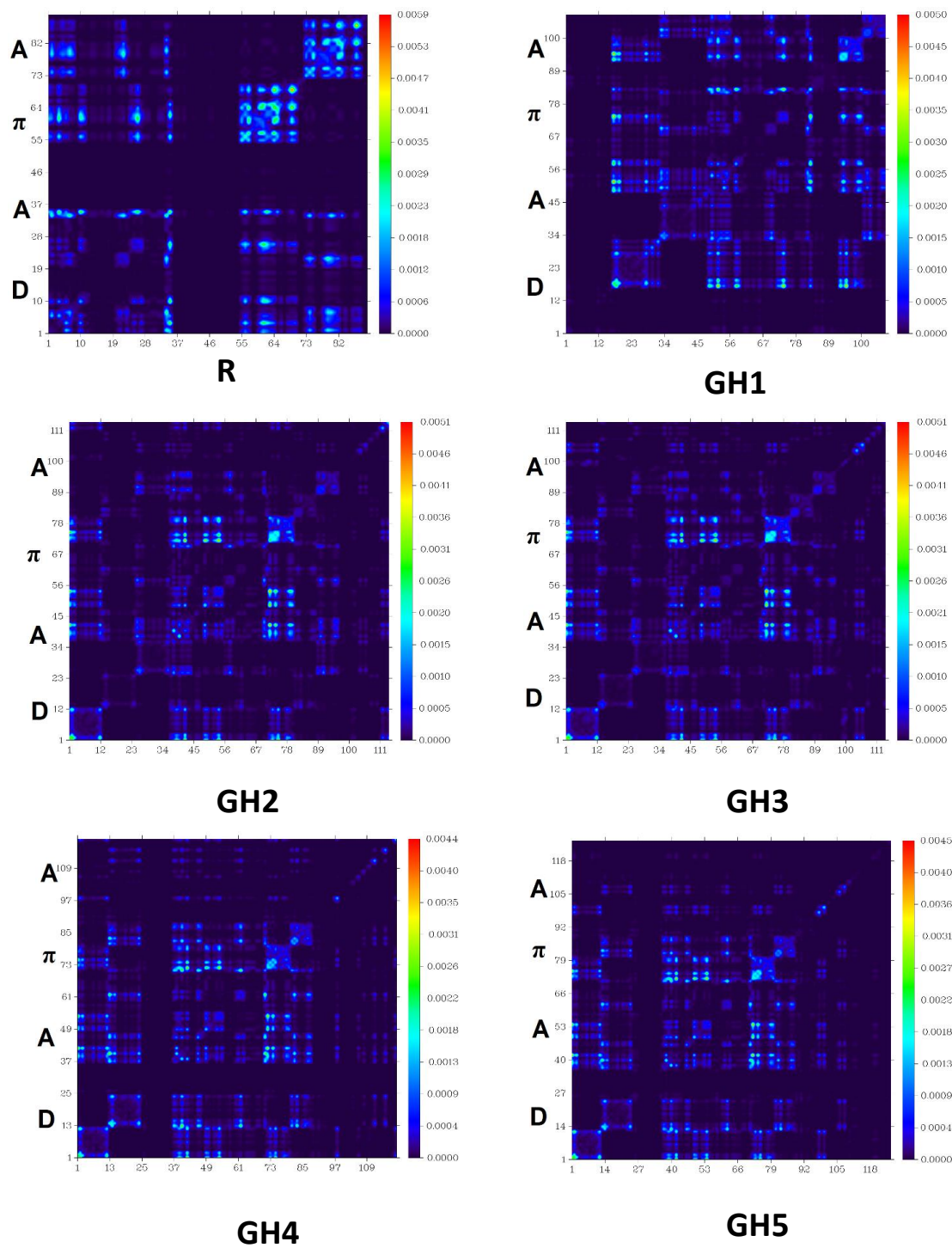


Figure 6. 9. TDMS plots of all theoretical studied molecules at method MPW1PW91

Binding energy (E_b) is still another criterion to unveil the performance of a solar cell with estimation of total current charge density. A general criterion is “low binding energy favors high power conversion efficiency with high charge transfer”. Low values of E_b is also offers high current charge density (J_{sc}). Motivated from these points, E_b of studied systems are also computed and results are expressed in **Figure 6.10**. There are some key factors which are evidently used to compute binding energy theoretically like E_{opt} (1st principle excitation energy), E_{H-L} (energy band gap). Below given equation is used to compute binding energy ^{29,30}:

$$E_b = E_{H-L} - E_{OPT} \quad (3)$$

E_b value is 1.83 eV for **R**, 1.54 eV for **GH1**, 1.56 eV for **GH2**, 1.38 eV for **GH3**, 1.53 eV for **GH4**, and 1.68 eV for **GH5**. Interesting, all theoretical proposed molecules framed low values of E_b which recommended that proposed model molecules are effective nominee of showing high current charge density with good exciton disassociation. High J_{sc} allows high PCE with high charge transfer. In all proposed model molecules, **GH3** exhibited least value of E_b which is because of end-capped acceptor unit. Macroscopically, all proposed model molecules disclosed low values of E_b which recommended that theoretical planned molecules are fine nominees for high PCE greenhouse integrated solar cell applications.

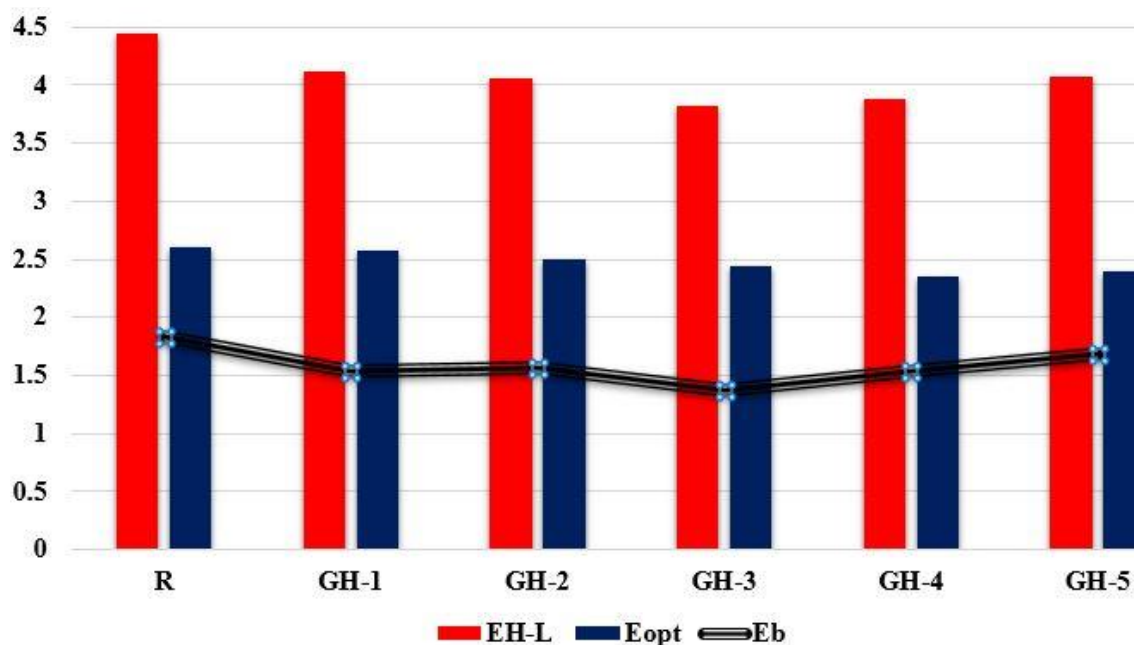


Figure 6. 10. Eb, E^{opt}, and EH-L values of all theoretical proposed model molecules

6.3.9 Study of Complex

Nature of theoretical planned molecules, charge transfer behavior and behavior of a molecule within a complex is important to study because these factors play a vital role for determining the PCE and maximum visible light harvesting capability. For blend study, donor and acceptor molecules are blended together. In studied report, proposed models/molecules are donor and should be blended with PC₆₁BM acceptor polymer. For blend formation only one efficient molecule is selected because of some exception properties. Among theoretically planned molecules, **GH3** disclosed outstanding values of **E_b**, **E_x**, **V_{oc}**, **E_g**, **λ_e**, **λ_h**, and **λ_{max}**. And **PC₆₁BM** is well recognized and well-known acceptor polymer for donor-acceptor type blend formation used for GHI-solar cells. The position of both components within blend is interesting with respect to charge transfer at interface. The optimized geometry of GH3/PC₆₁BM blend (at method MPW1PW91 along with level 6-31G(d,p)) is displayed in Figure 6.11. PC₆₁BM is present close to donor end of **GH3**

molecule which advised that maximum charge transfer occurs from donor to acceptor part which is evident from dipole vector position. The computed dipole vector is from donor end to acceptor polymer in optimized geometry.

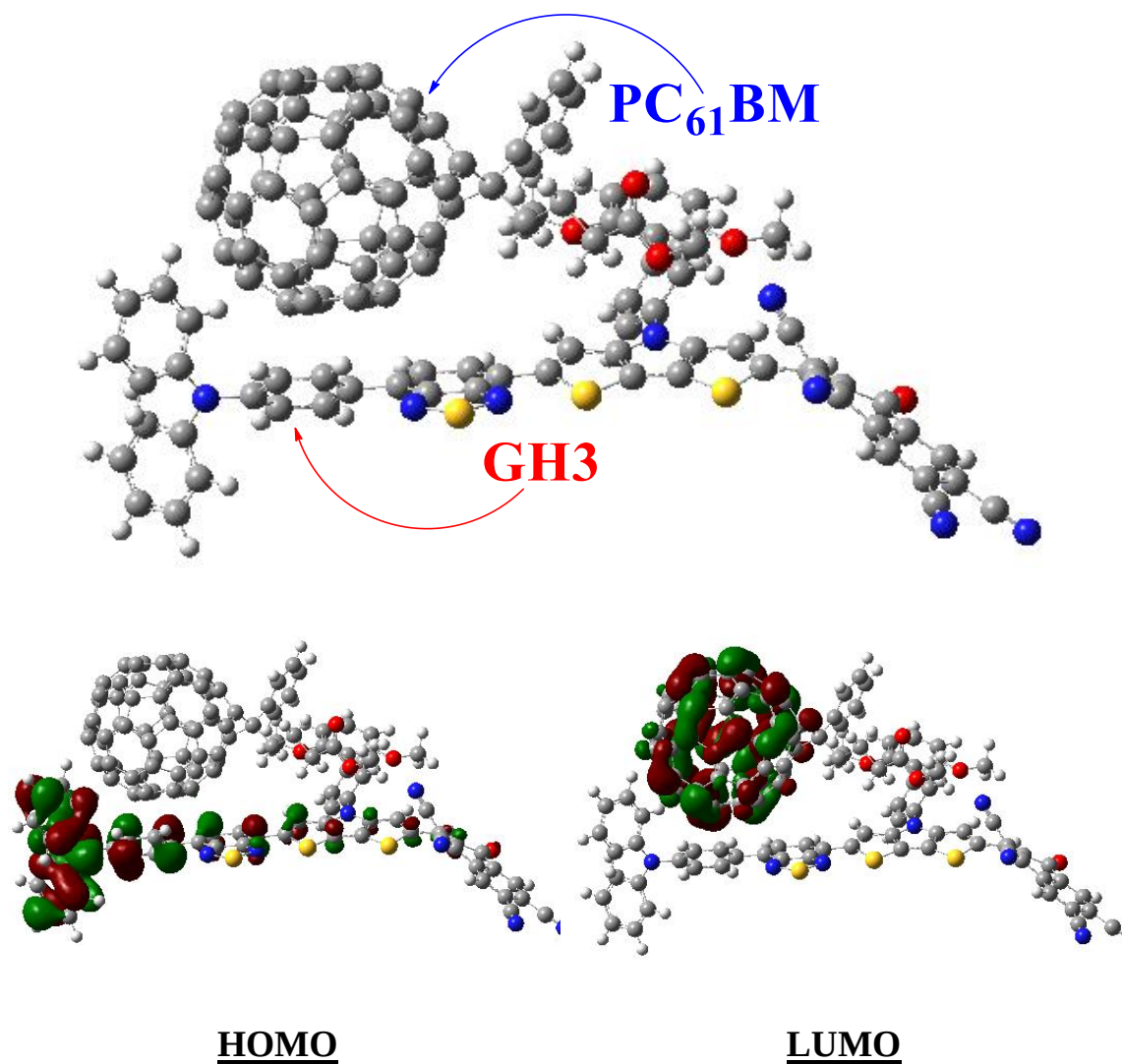


Figure 6. 11. GH3/PC₆₁BM blend: optimized geometry with HOMO and LUMO distribution in blend

In order to give theoretically solid evidence of charge transfer within blend, HOMO and LUMO density presence is being considered. Presence of HOMO on donor molecule and LUMO on acceptor polymer is an ideal condition for estimation of charge transfer within a blend. In current report, HOMO is present on **GH3** molecule and LUMO is present on PC₆₁BM polymer as evident from Figure 6.11. From foregoing discussion and presence of HOMO and LUMO, it is crystal clear that the designed molecule **GH3** is a potential nominee for development of highly stable GHI-solar cell applications.

6.4 Outcomes

Five donor compounds (GH1 to GH5) are theoretically designed. Theoretically proposed model molecules unveil narrow energy band gap ($E_g = 3.82$ to 4.12 eV) and red-shift in visible region ($\lambda_{\max} = 566$ to 588 nm) in contrast to reference molecule ($E_g = 4.44$ eV and $\lambda_{\max} = 534$ nm). Additionally, high open circuit voltage values ($V_{oc} = 2.20$ to 2.32 V) are gained by scaling designed donor molecules with PC₆₁BM polymer which advised that the theoretically planned molecules are excellent nominees for enhancing PCE of resultant solar cell. Low E_x and E_b values recommended that the proposed framework of these molecules are superb candidates for high J_{SC} . Low reorganizational energy of hole (0.0144 to 0.0161 eV) and electron (0.0301 to 0.0305 eV) also allows high charge mobility in proposed molecules. Finally, blend study of GH3/PC₆₁BM unveils the efficient charge transfer behavior of theoretically planned molecule. Results of all the foregoing observations suggested that the designed molecules are efficient candidates for highly stable greenhouse integrated solar cell applications.

CHAPTER 7

Concluding Remark

D- π -A based functional were analyzed for photovoltaic and nonlinear optical properties. Virtual high throughput screening method with the help of DFT was implemented on a library of molecules. Several functionals along with basis sets were applied. The functionals and basis sets which provided the reproducible results and near to the experimental findings were used for further analysis. All the selected compounds from the library of molecules are excellent NLO and solar cell materials. The studied compounds have large values of open circuit voltage, least binding and excitation energies. They also possess significant values of dipole moment, polarizability and second order polarizability to be considered as efficient nonlinear materials. Lower values of excitation energies and red shifting (increase in absorption maxima) were observed for the investigated compounds. The structural modification in most of the designed compounds was found plausible to improve the desired properties. They are also good nonlinear optical materials in comparison with urea.

Solar cells will be dominant in the field of new energy in the future and have great potential. We recommend the laboratory synthesis of our theoretically designed compounds for experimental scientists. In order to achieve high efficiency, effective light trapping, long exciton diffusion and new device schemes such as multi-junction structure have to be investigated. The efficiency of organic solar cells has improved steadily, and further research is needed to improve efficiency as well as reliability. Research progress and new development of new efficient solar cells still needed to be implemented for commercial and civil use. Several

compounds with different backbones were taken as reference from synthetic chemistry and studied for the organic electronics Computational design was carried out by end capped or bridging modification. Virtual high throughput screening was performed on a library of around a thousand molecules. The designed compounds with efficient results and most stable geometry were taken for further analysis. All the studied molecules expressed efficient photovoltaic and optoelectronic properties

7.1 Global Conclusion

D- π -A compounds are efficient materials for optoelectronic and light harvesting characteristics. Modifications in acceptor(A) and (bridge) π play important role to fine tune the electronic properties. Structure-property relationship has been studied to investigate the solar cell properties to attain high power conversion efficiencies. The electron-withdrawing property of the terminal acceptor units has a significant influence on the optical absorption properties, HOMO/LUMO energy levels, molecular ordering, charge carrier mobility and morphology of the resulting designed molecules.

7.2 Future Prospects

The designed compounds will be synthesized in the laboratory. All the designed compounds show excellent charge transfer properties so they will be considered for second and third order nonlinear optical properties. Further research will be done to improve efficiency as well as reliability of the solar cells.

CHAPTER 8

REFERENCES

- [1] L. Lu, T. Zheng, Q. Wu, A.M. Schneider, D. Zhao, L. Yu. *Chem. Rev.* **2015**, 115, 12666.
- [2] M.R.S.A. Janjua. *Inorg. Chem.* **2021**, 60, 2816.
- [3] M.U. Khan, M. Khalid, M. Ibrahim, A. A.C. Braga, M. Safdar, A . Al Saadi, M.R.S.A. Janjua, *J. Phys. Chem. C.* **2018**, 122, 4009.
- [4] M.R.S.A. Janjua, W. Guan, L.K. Yan, Z.M. Su, M. Ali, I.H. Bukhari. *J. Mol. Graph. Model.* **2010**, 28, 735.
- [5] M. Haroon, M.R.S.A. Janjua. *Mater. Today Commun.* **2021**, 26, 1018802
- [6] H.R. Allcock, E.C. Bissell, E.T. Shaw. *Inorg Chem.* **1973**, 12, 2963.
- [7] P. Gouzerh, Y. Jeannin, A. Proust, F. Robert. *Angew Chem Int Ed.* **1989**, 28, 1363.
- [8] S. Liu S, S.N. Shaikh. *Inorg Chem.* **1988**, 27, 3535.
- [9] Proust A, Thouvenot R, Herson P. *Dalton Trans.* **1999**, 1, 51.
- [10] H. Kwen, V.G. Young, E.A. Maatta. *Angew Chem Int Ed.* **1999**, 38, 1145.
- [11] Y. Du, A.L. Rheingold, E.A. Maatta. *J. Am. Chem. Soc.* **1992**, 114, 345.
- [12] A. Proust, R. Thouvenot, M. Chaussade, F. Robert, P. Gouzerh *Inorg Chim Acta.*, **1994**, 224, 81.
- [13] W. Clegg, R.J. Errington, K.A. Fraser. (Eds.: Pope M T): *Kluwer Academic Publishers, Dordrecht, The Netherlands.* **1994**, 113.

- [14] J. B. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh, E. A. Maatta. *J Am Chem Soc.* **2000**, 122, 639.
- [15] J.L. Stark, V.G. Young, E.A. Maatta. *Angew Chem Int Ed.* **1995**, 107, 2547.
- [16] J.L. Stark, A.L. Rheingold, E.A. Maatta. *J Chem Soc Chem Commun.* **1995**, 1165.
- [17] W. Clegg, R.J. Errington, K. Fraser. *Chem Commun.* **1995**, 4, 455.
- [18] Y. Wei, B. Xu, C.L. Barnes. *J Am Chem Soc.* **2001**, 123, 4083.
- [19] R.A. Roesner, S.C. McGrath, J.T. Brockman. *Inorg Chim Acta.* **2003**, 342, 37.
- [20] L. Xu, M. Lu, B. Xu, Y. Wei, Z. Peng. *Angew Chem Int Ed.* **2002**, 41, 4129.
- [21] M. Lu, Y. Wei, B. Xu, C.F. Cheung, Z. Peng, D.R. Powell. *Angew Chem Int Ed.* **2002**, 41, 1566.
- [22] C. Sanchez, F. Ribot, B. Lebeau. *J. Mater. Chem.* **1999**, 9, 35.
- [23] L. Benedicte, I. Plinio. *Chem. Soc. Rev.* **2011**, 40, 886.
- [24] M. Darder, M. Colilla, N. Larab, E. Ruiz-Hitzky. *J. Mater. Chem.* **2002**, 12, 3660.
- [25] Ritchie, J. E. In *Hybrid Materials: Synthesis, Characterization, and Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: **2007**, p 401.
- [26] F. De Souza, E. Leite. *ChemInform.* **2011**, 42.
- [27] E. Mathieu, G. Yann, G. David, W. Alain. *Anal. Bioanal. Chem.* **2013**, 405, 1497.
- [28] E. Karakhanov, A. Maximov, S. Kardashev, Y. Kardasheva, A. Zolotukhina, E. Rosenberg. Allen. *J. In Macromolecular Symposia*; Wiley Online Library. **2011**, 304, p 55.
- [29] L.A. Dias Carlos, R.A. Sá Ferreira, V. de Zea Bermudez. In *Hybrid Materials*; Wiley-VCH Verlag GmbH & Co. KGaA, **2007**, p 337.
- [30] D ARIVUOLI PRAMANA-J PHYS. **2001**, 57, 871

- [31] M. Nilsson, P. Lucas, T. Yoshida. *Sustainability*. **2013**, 5, 4124.
- [32] Y.W. Su, S.C. Lan, K.H. Wei. *Mater. Today*. **2012**, 15, 554.
- [33] B. Kippelen, J.L. Brédas. *Energy Environ. Sci.* **2009**, 2, 251.
- [34] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger. *Science*. **1995**, 270, 1789.
- [35] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia. *Science*. **2018**, 361, 1094.
- [36] Zhou H, Yang L, You W. *Macromolecules*, 2012, 45, 607–632
- [37] J.C. Hummelen, B.W. Knight, F. LePeq, F. Wudl, J. Yao, C.L. Wilkins. *J. Org. Chem.* **1995**, 60,532.
- [38] M.M. Wienk, J.M. Kroon, W.J. Verhees, J. Knol, J.C. Hummelen, P.A. Van Hal, R.A. Janssen, *Angew. Chem. Int.* **2003**, 115, 3493.
- [39] Y. He, H.-Y. Chen, J. Hou, and Y. Li. *J. Am. Chem. Soc.* **2010**, 132, 1377.
- [40] X. Guo, C. Cui, M. Zhang, L. Huo, Y. Huang, J. Hou, Y. Li. *Energy Environ. Sci.* **2012**, 5, 7943.
- [41] Z. Xiao, X. Geng, D. He, X. Jia, L. Ding. *Energy Environ. Sci.* **2016**, 9, 2114.
- [42] C. Yan, S. Barlow, Z. Wang, H. Yan, A.K.Y. Jen, S.R. Marder, X. Zhan. *Nat. Rev. Mater.* **2018**, 3, 18003.
- [43] Y. Geng, A. Tang, K. Tajima, Q. Zeng, E. Zhou. *J. Mater. Chem. A.* **2019**, 7, 64.
- [44] Y. Lin, J. Wang, Z.G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan. *Adv. Mater.* **2015**, 27, 1170.

- [45] Z. Xiao, S. Yang, Z. Yang, J. Yang, H.L. Yip, F. Zhang, F. He, T. Wang, J. Wang, Y. Yuan, *Adv. Mater.* **2019**, 31, 1804790.
- [46] Z. Xiao, X. Jia, D. Li, S. Wang, X. Geng, F. Liu, J. Chen, S. Yang, T.P. Russell, L. Ding. *Sci. Bull.* **2017** 62, 1494.
- [47] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P.A. Johnson. *Joule.* **2019**, 3, 1140.
- [48] H. Hu, K. Jiang, G. Yang, J. Liu, Z. Li, H. Lin, Y. Liu, J. Zhao, J. Zhang, F. Huang. *J. Am. Chem. Soc.* **2015**, 137, 14149.
- [49] S.H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee, A.J. Heeger. *Nat. Photon.* **2009**, 3, 297.
- [50] Roncali J, Leriche P, Blanchard P. *Adv Mater*, 2014, 26, 3821–3838
- [51] K. Li, Y. Wu, Y. Tang, M.A. Pan, W. Ma, H. Fu, C. Zhan, J. Yao. *Adv. Energy Mater.* **2019**, 9, 1901728.
- [52] T. Yan, W. Song, J. Huang, R. Peng, L. Huang, Z. Ge. *Adv. Mater.* **2019**, 31, 1902210.
- [53] J. Xiong, K. Jin, Y. Jiang, J. Qin, T. Wang, J. Liu, Q. Liu, H. Peng, X. Li, A. Sun. *Sci. Bull.* **2019**, 64, 1573.
- [54] Y. Lin, Z.-G. Zhang, H. Bai, J. Wang, Y. Yao, Y. Li, D. Zhu, X. Zhan. *Energy Environ. Sci.* **2015**, 8, 610.
- [55] Z. Xiao, X. Jia, L. Ding. *Sci. Bull.* **2017** 62, 1562.

- [56] X. Li, F. Pan, C. Sun, M. Zhang, Z. Wang, J. Du, J. Wang, M. Xiao, L. Xue, Z.G. Zhang, *Nat. Commun.* **2019** 10, 1.
- [57] Y. Yang, Z.-G. Zhang, H. Bin, S. Chen, L. Gao, L. Xue, C. Yang, Y. Li. *J. Am. Chem. Soc.* **2016**, 138, 15011.
- [58] Z. Zhou, W. Liu, G. Zhou, M. Zhang, D. Qian, J. Zhang, S. Chen, S. Xu, C. Yang, F. Gao. *Adv. Mater.* **2020** 32, 1906324.
- [59] Z.P. Yu, Z.X. Liu, F.X. Chen, R. Qin, T.K. Lau, J.L. Yin, X. Kong, X. Lu, M. Shi, C.Z. Li. *Nat. Commun.* **2019**, 10, 1.
- [60] H. Huang, Q. Guo, S. Feng, Z. Bi, W. Xue, J. Yang, J. Song, C. Li, X. Xu, Z. Tang. *Nat. Commun.* **2019**, 10, 1.
- [61] Y. Cui, H. Yao, L. Hong, T. Zhang, Y. Xu, K. Xian, B. Gao, J. Qin, J. Zhang, and Z. Wei. *Adv. Mater.* **2019**, 31, 1808356.
- [62] S. Pang, X. Zhou, S. Zhang, H. Tang, S. Dhakal, X. Gu, C. Duan, F. Huang, Y. Cao. *ACS Appl. Mater. Interfaces.* **2020**, 12, 16531.
- [63] M.U. Khan, R. Hussain, M.Y. Mehboob, M. Khalid, M.A. Ehsan, A. Rehman, M.R.S.A. Janjua. *Spectrochim. Acta A Mol. Biomol. Spectrosc. SPECTROCHIM ACTA A.* **2020** 118938.
- [64] M.U. Khan, R. Hussain, M. Yasir Mehboob, M. Khalid, Z. Shafiq, M. Aslam, A.A. Al-Saadi, S. Jamil, M.R.S.A. Janjua,. *ACS Omega.* **2020**, 37, 24125.

- [65] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.J. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, "D. 0109, Revision D. 01, Gaussian". *Inc., Wallingford, CT*. **2009**.
- [66] R.D. Dennington, T.A. Keith, J.M. Millam, "GaussView 5.0. 8". *Gaussian Inc*. **2008**.
- [67] V. Barone, M. Cossi. *J. Phys. Chem. A*. **1998**, 102, 1995.
- [68] M.E. Köse, W.J. Mitchell, N. Kopidakis, C.H. Chang, S.E. Shaheen, K. Kim, G. Rumbles. *J. Am. Chem. Soc.* **2007**, 129, 14257.
- [69] N.M. O'boyle, A.L. Tenderholt, K.M. Langner. *J. Comput. Chem.* **2008**, 5, 839.
- [70] Bhole, R. P.; Bhusari, K. P., *Med. Chem. Res.* **2011**, 20 (6), pp. 695-704.

- [71] El-Helw, E. A.; El-Badawy, A. A., *J. Heterocycl. Chem.* **2020**, 57 (6), pp. 2354-2364
- [72] Shehzad, M. T.; Khan, A.; Islam, M.; Halim, S. A.; Khiat, M.; Anwar, M. U.; Hussain, J.; Hameed, A.; Pasha, A. R.; Khan, F. A., *Bioorg. Chem.* **2020**, 94, pp. 103404.
- [73] Gerwick, W. H.; Proteau, P. J.; Nagle, D. G.; Hamel, E.; Blokhin, A.; Slate, D. L., *J. Org. Chem.* **1994**, 59 (6), pp. 1243-1245.
- [74] Suga, S.; Okajima, M.; Fujiwara, K.; Yoshida, J.-i., “Cation flow” method: a new approach to conventional and combinatorial organic syntheses using electrochemical microflow systems. *J. Am. Chem. Soc.* **2001**, 123 (32), pp. 7941-7942
- [75] Sengoden, M.; Vijay, M.; Balakumar, E.; Punniyamurthy, T., Efficient pyrrolidine catalyzed cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide “on water”. *RSC Adv.* 2014, 4 (97), 54149- 54157.
- [76] Bijev, A.; Prodanova, P., One-Step Synthesis of 2-Aminothiazoline Derivatives Free of Lachrymatory Intermediates. *Synth. Commun.* **2006**, 36 (21), pp. 3095-3101
- [77] Zhu, Y.-P.; Yuan, J.-J.; Zhao, Q.; Lian, M.; Gao, Q.-H.; Liu, M.-C.; Yang, Y.; Wu, A.-X., I₂/CuO-catalyzed tandem cyclization strategy for one-pot synthesis of substituted 2-aminothiozole from easily available aromatic ketones/ α , β -unsaturated ketones and thiourea. *Tetrahedron* **2012**, 68 (1), pp. 173-178.
- [78] Dalmal, T.; Appalanaidu, K.; Kosurkar, U. B.; Jagadeesh Babu, N.; Kumbhare, R. M., One-Pot Synthesis of 2-Imino-4-(trifluoromethyl) thiazolidin-4-ol Derivatives in a Three-Component Reaction: Application to Structurally Diverse Scaffolds of Biological Interest Through Subsequent Reactions. *Eur. J. Org. Chem.* **2014**, 2014 (12), pp. 2468-2479.

- [79] Sengoden, M.; Irie, R.; Punniyamurthy, T., Enantiospecific Aluminum-Catalyzed (3+ 2) Cycloaddition of Unactivated Aziridines with Isothiocyanates. *J. Org. Chem***2016**, *81* (22), pp. 11508-11513.
- [80] Ricci, P.; Khotavivattana, T.; Pfeifer, L.; Médebielle, M.; Morphy, J. R.; Gouverneur, V., The dual role of thiourea in the thiotrifluoromethylation of alkenes. *Chem. Sci.* **2017**, *8* (2), pp. 1195-1199.
- [81] Nigst, T. A.; Ammer, J.; Mayr, H., Ambident Reactivities of Methylhydrazines. *Angew. Chem. Int. Ed.* **2012**, *51* (6), pp.1353-1356.
- [82] Sun, J.; Ge, H.; Zhen, X.; An, X.; Zhang, G.; Zhang-Negrerie, D.; Du, Y.; Zhao, K., TBHP/AIBN-Mediated Synthesis of 2-Amino-thioazoles from Active Methylene Ketones and Thiourea under Metal-free Conditions. *Tetrahedron* **2018**, *74* (17), pp. 2107-2114.
- [83] Chupp, J. P., Reaction of electrophiles with enolizable N-hydrogen ketimines. *J. Org. Chem***1970**, *35* (7), pp. 2441-2443.
- [84] Akram, M.; Adeel, M.; Khalid, M.; Tahir, M. N.; Khan, M. U.; Asghar, M. A.; Ullah, M. A.; Iqbal, M., A combined experimental and computational study of 3-bromo-5-(2, 5-difluorophenyl) pyridine and 3, 5-bis (naphthalen-1-yl) pyridine: Insight into the synthesis, spectroscopic, single crystal XRD, electronic, nonlinear optical and biological properties. *J. Mol. Struct.* **2018**, *1160*, pp.129-141.
- [85] Shkir, M.; Muhammad, S.; AlFaify, S.; Irfan, A.; Patil, P. S.; Arora, M.; Algarni, H.; Jingping, Z., An investigation on the key features of a D- π -A type novel chalcone derivative for opto-electronic applications. *RSC Adv.* **2015**, *5* (106), pp. 87320-87332.
- [86] Khalid, M.; Ullah, M. A.; Adeel, M.; Khan, M. U.; Tahir, M. N.; Braga, A. A. C., Synthesis, crystal structure analysis, spectral IR, UV-Vis, NMR assessments, electronic

and nonlinear optical properties of potent quinoline based derivatives: interplay of experimental and DFT study. *J. Saudi Chem. Soc.* **2019**, 23 (5), pp. 546-560.

[87] García-Melchor, M.; Braga, A. A.; Lledós, A.; Ujaque, G.; Maseras, F., Computational perspective on Pd-catalyzed C–C cross-coupling reaction mechanisms. *Acc. Chem. Res.* **2013**, 46 (11), pp. 2626-2634.

[88] Dennington, R.; Keith, T.; Millam, J., GaussView, version 5. *Semichem Inc., Shawnee Mission, KS* **2009**.

[90] Andrienko, G. A., Chemcraft. Graphical Software for Visualization of Quantum Chemistry Computations. 2010.

[91] Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R., Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *J. Cheminform.* **2012**, 4 (1), pp. 17.

[92] Haroon, M.; Khalid, M.; Akhtar, T.; Tahir, M. N.; Khan, M. U.; Muhammad, S.; Al-Sehemi, A. G.; Hameed, S., Synthesis, crystal structure, spectroscopic, electronic and nonlinear optical properties of potent thiazole based derivatives: Joint experimental and computational insight. *J. Mol. Struct.* **2020**, 1202, pp. 127354.

[93] Socrates, G., Infrared and Raman characteristic group frequencies: table and charts. Ltd WJS 2001, 1-347.

[94] Perkampus, H. H., LJ Bellamy: The Infrared Spectra of Complex Molecules, Vol. 1, 3. Auflage, Chapman and Hall Ltd., London 1975, 433 Seiten, 32 Abb., 22 Tabellen, Preis:£ 8.—. *Ber. Bunsenges. Phys. Chem.* **1976**, 80 (1), pp. 99-100.

[95] Parr, R. G.; Szentpaly, L. v.; Liu, S., Electrophilicity index. *J. Am. Chem. Soc.* **1999**, 121 (9), pp. 1922-1924.

- [96] Khalid, M.; Hussain, R.; Hussain, A.; Ali, B.; Jaleel, F.; Imran, M.; Assiri, M. A.; Usman Khan, M.; Ahmed, S.; Abid, S., Electron donor and acceptor influence on the nonlinear optical response of diacetylene-functionalized organic materials (DFOMs): density functional theory calculations. *Molecules* **2019**, *24* (11), pp. 2096.
- [97] Prasad, P. N.; Williams, D. J., *Introduction to nonlinear optical effects in molecules and polymers*. Wiley New York: 1991; Vol. 1.
- [98] Khan, I.; Khalid, M.; Adeel, M.; Khan, M. U.; Khan, M. S.; Ahmad, N.; Ali, A.; Akram, M., Palladium-catalyzed synthesis of pyrimidine substituted diaryl ethers through Suzuki Miyaura coupling reactions: Experimental and DFT studies. *Optik* **2020**, *219*, pp. 165285.
- [99] Scrocco, E.; Tomasi, J., Electronic molecular structure, reactivity and intermolecular forces: an euristic interpretation by means of electrostatic molecular potentials. *Adv. Quantum Chem.* **1978**, *11*, pp. 115-193.
- [100] Mahalakshmi, G.; Balachandran, V., NBO, HOMO, LUMO analysis and vibrational spectra (FTIR and FT Raman) of 1-Amino 4-methylpiperazine using ab initio HF and DFT methods. *Spectrochim. Acta. A Mol. Biomol. Spectrosc.* **2015**, *135*, pp. 321-334.
- [101] Luo, Z.; Liu, T.; Ma, R.; Xiao, Y.; Zhan, L.; Zhang, G.; Sun, H.; Ni, F.; Chai, G.; Wang, J.; Zhong, C.; Zou, Y.; Guo, X.; Lu, X.; Chen, H.; Yan, H.; Yang, C. Precisely Controlling the Position of Bromine on the End Group Enables Well-Regular Polymer Acceptors for All-Polymer Solar Cells with Efficiencies over 15%. *Adv. Mater.* **2020**, *32* (48), pp. 2005942.

- [102] Sun, H.; Yu, H.; Shi, Y.; Yu, J.; Peng, Z.; Zhang, X.; Liu, B.; Wang, J.; Singh, R.; Lee, J.; Li, Y.; Wei, Z.; Liao, Q.; Kan, Z.; Ye, L.; Yan, H.; Gao, F.; Guo, X. A Narrow-Bandgap N-Type Polymer with an Acceptor–Acceptor Backbone Enabling Efficient All-Polymer Solar Cells. *Adv. Mater.* **2020**, *32* (43), pp. 2004183.
- [103] Yao, H.; Wang, J.; Xu, Y.; Zhang, S.; Hou, J. Recent Progress in Chlorinated Organic Photovoltaic Materials. *Acc. Chem. Res.* **2020**, *53* (4), pp. 822–832.
- [104] Jia, B.; Wang, J.; Wu, Y.; Zhang, M.; Jiang, Y.; Tang, Z.; Russell, T. P.; Zhan, X. Enhancing the Performance of a Fused-Ring Electron Acceptor by Unidirectional Extension. *J. Am. Chem. Soc.* **2019**, *141* (48), pp. 19023–19031.
- [105] Fukuda, K.; Yu, K.; Someya, T. The Future of Flexible Organic Solar Cells. *Adv. Energy Mater.* **2020**, *10* (25), pp. 2000765.
- [106] Zhan, L.; Li, S.; Xia, X.; Li, Y.; Lu, X.; Zuo, L.; Shi, M.; Chen, H. Layer-by-Layer Processed Ternary Organic Photovoltaics with Efficiency over 18%. *Adv. Mater.* **2021**, *33* (12), pp. 2007231.
- [107] Hu, Z.; Wang, J.; Ma, X.; Gao, J.; Xu, C.; Wang, X.; Zhang, X.; Wang, Z.; Zhang, F. Semitransparent Organic Solar Cells Exhibiting 13.02% Efficiency and 20.2% Average Visible Transmittance. *J. Mater. Chem. A* **2021**, *9* (11), pp. 6797–6804.
- [108] Kan, B.; Feng, H.; Wan, X.; Liu, F.; Ke, X.; Wang, Y.; Wang, Y.; Zhang, H.; Li, C.; Hou, J.; Chen, Y. Small-Molecule Acceptor Based on the Heptacyclic Benzodi(Cyclopentadithiophene) Unit for Highly Efficient Nonfullerene Organic Solar Cells. *J. Am. Chem. Soc.* **2017**, *139* (13), pp. 4929–4934.

- [109] Wang, R.; Zhang, C.; Li, Q.; Zhang, Z.; Wang, X.; Xiao, M. Charge Separation from an Intra-Moiety Intermediate State in the High-Performance PM6:Y6 Organic Photovoltaic Blend. *J. Am. Chem. Soc.* **2020**, *142* (29), pp. 12751–12759.
- [110] Wang, K.; Chen, J.; Hu, J.; Guo, X.; Zhang, M.; Li, Y. A Small Molecule Acceptor with a Heptacyclic Benzodi(Thienocyclopentafuran) Central Unit Achieving 13.4% Efficiency in Polymer Solar Cells with Low Energy Loss. *J. Mater. Chem. C* **2021**, *9* (8), pp. 2744–2751.
- [111] J. Li, W.D. Yao, X.H. Li. *Chem. Commun.* **2021**, *57*, 1109.
- [112] Dessì, A.; Chalkias, D. A.; Bilancia, S.; Sinicropi, A.; Calamante, M.; Mordini, A.; Karavioti, A.; Stathatos, E.; Zani, L.; Reginato, G. D–A– π –A Organic Dyes with Tailored Green Light Absorption for Potential Application in Greenhouse-Integrated Dye-Sensitized Solar Cells. *Sustain. Energy Fuels* **2021**, *5* (4), pp. 1171–1183.
- [113] Bernardo, G.; Lopes, T.; Lidzey, D. G.; Mendes, A. Progress in Upscaling Organic Photovoltaic Devices. *Adv. Energy Mater.* **2021**, pp. 2100342.
- [114] Dessì, A.; Calamante, M.; Sinicropi, A.; Parisi, M. L.; Vesce, L.; Mariani, P.; Taheri, B.; Ciocca, M.; Di Carlo, A.; Zani, L.; Mordini, A.; Reginato, G. Thiazolo[5,4- d]Thiazole-Based Organic Sensitizers with Improved Spectral Properties for Application in Greenhouse-Integrated Dye-Sensitized Solar Cells. *Sustain. Energy Fuels* **2020**, *4* (5), pp. 2309–2321.
- [115] Kim, J.-J.; Kang, M.; Kwak, O. K.; Yoon, Y.-J.; Min, K. S.; Chu, M.-J. Fabrication and Characterization of Dye-Sensitized Solar Cells for Greenhouse

Application. *Int. J. Photoenergy* **2014**, 2014, pp. 1–7.

[116] Mateen, F.; Ahsan Saeed, M.; Won Shim, J.; Hong, S.-K. Indoor/Outdoor Light-Harvesting by Coupling Low-Cost Organic Solar Cell with a Luminescent Solar Concentrator. *Sol. Energy* **2020**, 207, pp. 379–387.

[117] Janjua, M. R. S. A.; Khan, M. U.; Khalid, M.; Ullah, N.; Kalgaonkar, R.; Alnoaimi, K.; Baqader, N.; Jamil, S. Theoretical and Conceptual Framework to Design Efficient Dye-Sensitized Solar Cells (DSSCs): Molecular Engineering by DFT Method. *J. Clust. Sci.* **2021**, 32 (2), pp. 243–253.

[118] Janjua, M. R. S. A. How Does Bridging Core Modification Alter the Photovoltaic Characteristics of Triphenylamine-Based Hole Transport Materials? Theoretical Understanding and Prediction. *Chem. – A Eur. J.* **2021**, 27 (12), pp. 4197–4210.

[119] Hsu, C.-H.; Wu, J.-R.; Lu, Y.-T.; Flood, D. J.; Barron, A. R.; Chen, L.-C. Fabrication and Characteristics of Black Silicon for Solar Cell Applications: An Overview. *Mater. Sci. Semicond. Process.* **2014**, 25, pp. 2–17.

[120] Sun, R.; Wu, Y.; Guo, J.; Luo, Z.; Yang, C.; Min, J. High-Efficiency All-Small-Molecule Organic Solar Cells Based on an Organic Molecule Donor with an Asymmetric Thieno[2,3-f] Benzofuran Unit. *Sci. China Chem.* **2020**, 63 (9), pp. 1246–1255.

[121] Qin, J.; An, C.; Zhang, J.; Ma, K.; Yang, Y.; Zhang, T.; Li, S.; Xian, K.; Cui, Y.; Tang, Y.; Ma, W.; Yao, H.; Zhang, S.; Xu, B.; He, C.; Hou, J. 15.3% Efficiency All-

Small-Molecule Organic Solar Cells Enabled by Symmetric Phenyl Substitution. *Sci. China Mater.* **2020**, 63 (7), pp. 1142–1150.

[122] Brédas, J.-L.; Cornil, J.; Heeger, A. J. The Exciton Binding Energy in Luminescent Conjugated Polymers. *Adv. Mater.* **1996**, 8 (5), pp. 447–452.

[123] Wang, X.; Cui, X.; Lu, H.; Chen, Y.-N.; Liu, Y.; Zhou, Y.; Zhang, C.; Song, J.; Li, C.; Zhang, Z.; Bo, Z. Insights into Out-of-Plane Side Chains Effects on Optoelectronic and Photovoltaic Properties of Simple Non-Fused Electron Acceptors. *Org. Electron.* **2021**, 89, pp. 106029.

[124] Janjua, M. R. S. A. Deciphering the Role of Invited Guest Bridges in Non-Fullerene Acceptor Materials for High Performance Organic Solar Cells. *Synth. Met.* **2021**, 279, pp. 116865.

[125] Janjua, M. R. S. A. Theoretical Understanding and Role of Guest π -Bridges in Triphenylamine-Based Donor Materials for High-Performance Solar Cells. *Energy & Fuels* **2021**, 35 (15), pp. 12451–12460.

[126] Haroon, M.; Janjua, M. R. S. A. High-Throughput Designing and Investigation of D–A– π –A -Type Donor Materials for Potential Application in Greenhouse-Integrated Solar Cells. *Energy & Fuels* **2021**, 35 (15), pp. 12461–12472.

[127] Janjua, M. R. S. A. Quantum Chemical Design of D– π –A-Type Donor Materials for Highly Efficient, Photostable, and Vacuum-Processed Organic Solar Cells. *Energy Technol.* **2021**, 9 (10), pp. 2100489.

- [128] Janjua, M. R. S. A. Prediction and Understanding: Quantum Chemical Framework of Transition Metals Enclosed in a B₁₂N₁₂ Inorganic Nanocluster for Adsorption and Removal of DDT from the Environment. *Inorg. Chem.* **2021**, *60* (14), pp. 10837–10847.
- [129] Hussain, R.; Mehboob, M. Y.; Khan, M. U.; Khalid, M.; Irshad, Z.; Fatima, R.; Anwar, A.; Nawab, S.; Adnan, M. Efficient Designing of Triphenylamine-Based Hole Transport Materials with Outstanding Photovoltaic Characteristics for Organic Solar Cells. *J. Mater. Sci.* **2021**, *56* (8), pp. 5113–5131.
- [130] Mehboob, M. Y.; Hussain, R.; Adnan, M.; Irshad, Z. End-Capped Molecular Engineering of S-Shaped Hepta-Ring-Containing Fullerene-Free Acceptor Molecules with Remarkable Photovoltaic Characteristics for Highly Efficient Organic Solar Cells. *Energy Technol.* **2021**, *9* (5), pp. 2001090.
- [131] Afzal, Z.; Hussain, R.; Khan, M. U.; Khalid, M.; Iqbal, J.; Alvi, M. U.; Adnan, M.; Ahmed, M.; Mehboob, M. Y.; Hussain, M.; Tariq, C. J. Designing Indenothiophene-Based Acceptor Materials with Efficient Photovoltaic Parameters for Fullerene-Free Organic Solar Cells. *J. Mol. Model.* **2020**, *26* (6), pp. 137.
- [132] Khan, M. U.; Khalid, M.; Hussain, R.; Umar, A.; Mehboob, M. Y.; Shafiq, Z.; Imran, M.; Irfan, A. Novel W-Shaped Oxygen Heterocycle-Fused Fluorene-Based Non-Fullerene Acceptors: First Theoretical Framework for Designing Environment-Friendly Organic Solar Cells. *Energy & Fuels* **2021**, *35* (15), pp. 12436–12450.
- [133] Mehboob, M. Y.; Khan, M. U.; Hussain, R.; Fatima, R.; Irshad, Z.; Adnan, M.

Designing of Near-Infrared Sensitive Asymmetric Small Molecular Donors for High-Efficiency Organic Solar Cells. *J. Theor. Comput. Chem.* **2020**, *19* (08), pp. 2050034.

[134] Siddique, S. A.; Siddique, M. B. A.; Hussain, R.; Liu, X.; Mehboob, M. Y.; Irshad, Z.; Adnan, M. Efficient Tuning of Triphenylamine-Based Donor Materials for High-Efficiency Organic Solar Cells. *Comput. Theor. Chem.* **2020**, *1191*, pp. 113045.

[135] Mehboob, M. Y.; Hussain, R.; Irshad, Z.; Adnan, M. Role of Acceptor Guests in Tuning Optoelectronic Properties of Benzothiadiazole Core Based Non-Fullerene Acceptors for High-Performance Bulk-Heterojunction Organic Solar Cells. *J. Mol. Model.* **2021**, *27* (8), pp. 226.

[136] Khan, M. U.; Mehboob, M. Y.; Hussain, R.; Fatima, R.; Tahir, M. S.; Khalid, M.; Braga, A. A. C. Molecular Designing of High-performance 3D Star-shaped Electron Acceptors Containing a Truxene Core for Nonfullerene Organic Solar Cells. *J. Phys. Org. Chem.* **2021**, *34* (1) pp. 4119.

[137] Mehboob, M. Y.; Hussain, R.; Khan, M. U.; Adnan, M.; Ehsan, M. A.; Rehman, A.; Janjua, M. R. S. A. Quantum Chemical Design of Near-infrared Sensitive Fused Ring Electron Acceptors Containing Selenophene as Π -bridge for High-performance Organic Solar Cells. *J. Phys. Org. Chem.* **2021**, *34* (8) pp. 4204.

[138] Mehboob, M. Y.; Hussain, R.; Irshad, Z.; Adnan, M. Designing of U-shaped Acceptor Molecules for Indoor and Outdoor Organic Solar Cell Applications. *J. Phys. Org. Chem.* **2021**, *34* (8) pp. 4210.

- [139] Wu, J.-S.; Cheng, S.-W.; Cheng, Y.-J.; Hsu, C.-S. Donor–Acceptor Conjugated Polymers Based on Multifused Ladder-Type Arenes for Organic Solar Cells. *Chem. Soc. Rev.* **2015**, *44* (5), pp. 1113–1154.
- [140] Li, Y. Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption. *Acc. Chem. Res.* **2012**, *45* (5), pp. 723–733.
- [141] Steim, R.; Ameri, T.; Schilinsky, P.; Waldauf, C.; Dennler, G.; Scharber, M.; Brabec, C. J. Organic Photovoltaics for Low Light Applications. *Sol. Energy Mater. Sol. Cells* **2011**, *95* (12), pp. 3256–3261.
- [142] Lin, Y.; Firdaus, Y.; Isikgor, F. H.; Nugraha, M. I.; Yengel, E.; Harrison, G. T.; Hallani, R.; El-Labban, A.; Faber, H.; Ma, C.; Zheng, X.; Subbiah, A.; Howells, C. T.; Bakr, O. M.; McCulloch, I.; Wolf, S. De; Tsetseris, L.; Anthopoulos, T. D. Self-Assembled Monolayer Enables Hole Transport Layer-Free Organic Solar Cells with 18% Efficiency and Improved Operational Stability. *ACS Energy Lett.* **2020**, *5* (9), pp. 2935–2944.
- [143] Abdulrazzaq, O. A.; Saini, V.; Bourdo, S.; Dervishi, E.; Biris, A. S. Organic Solar Cells: A Review of Materials, Limitations, and Possibilities for Improvement. *Part. Sci. Technol.* **2013**, *31* (5), pp. 427–442.
- [144] Park, S.; Ahn, H.; Kim, J.; Park, J. B.; Kim, J.; Im, S. H.; Son, H. J. High-Performance and Stable Nonfullerene Acceptor-Based Organic Solar Cells for Indoor to Outdoor Light. *ACS Energy Lett.* **2020**, *5* (1), pp. 170–179.
- [145] Greenbank, W.; Djeddaoui, N.; Destouesse, E.; Lamminaho, J.; Prete, M.; Boukezzi, L.; Ebel, T.; Bessissa, L.; Rubahn, H.-G.; Turkovic, V.; Madsen, M. Degradation

Behavior of Scalable Nonfullerene Organic Solar Cells Assessed by Outdoor and Indoor ISOS Stability Protocols. *Energy Technol.* **2020**, 8 (12), pp. 2000295.

[146] Zhang, Y.; Yi, H.; Iraqi, A.; Kingsley, J.; Buckley, A.; Wang, T.; Lidzey, D. G. Comparative Indoor and Outdoor Stability Measurements of Polymer Based Solar Cells. *Sci. Rep.* **2017**, 7 (1), pp. 1305.

[147] Beuel, S.; Hartnagel, P.; Kirchartz, T. The Influence of Photo-Induced Space Charge and Energetic Disorder on the Indoor and Outdoor Performance of Organic Solar Cells. *Adv. Theory Simulations* **2021**, 4 (3), pp. 2000319.

[148] Duan, L.; Uddin, A. Progress in Stability of Organic Solar Cells. *Adv. Sci.* **2020**, 7 (11), pp. 1903259.

[149] Li, J.; Wu, Y.; Zhang, X.; Zeng, D.; Luo, Y.; Duan, X.; Gao, X.; Cai, P.; Zhang, Q.; Zhang, J.; Liu, Z. A New Fluorinated Pyran-Bridged A-D-A Type Small Molecular Acceptor for Organic Solar Cells. *Dye. Pigment.* **2020**, 175, pp. 108165.

[150] Tokmoldin, N.; Hosseini, S. M.; Raoufi, M.; Phuong, L. Q.; Sandberg, O. J.; Guan, H.; Zou, Y.; Neher, D.; Shoaee, S. Extraordinarily Long Diffusion Length in PM6:Y6 Organic Solar Cells. *J. Mater. Chem. A* **2020**, 8 (16), pp. 7854–7860.

[151] Khan, J. I.; Firdaus, Y.; Cruciani, F.; Liu, S.; Anthopoulos, T. D.; Beaujuge, P. M.; Laquai, F. Thienyl Sidechain Substitution and Backbone Fluorination of Benzodithiophene-Based Donor Polymers Concertedly Minimize Carrier Losses in ITIC-Based Organic Solar Cells. *J. Phys. Chem. C* **2020**, 124 (19), pp. 10420–10429.

[152] Cai, J.; Zhang, X.; Guo, C.; Zhuang, Y.; Wang, L.; Li, D.; Liu, D.; Wang, T.

Asymmetric and Halogenated Fused-Ring Electron Acceptor for Efficient Organic Solar Cells. *Adv. Funct. Mater.* **2021**, *31* (31), pp. 2102189.

[153] Yu, R.; Yao, H.; Xu, Y.; Li, J.; Hong, L.; Zhang, T.; Cui, Y.; Peng, Z.; Gao, M.; Ye, L.; Tan, Z.; Hou, J. Quadrupole Moment Induced Morphology Control Via a Highly Volatile Small Molecule in Efficient Organic Solar Cells. *Adv. Funct. Mater.* **2021**, *31* (18), pp. 2010535.

[154] Su, Y.-J.; Huang, S.-C.; Chen, T.-W.; Chueh, L.-C.; Cui, Y.; Hong, L.; Yao, H.; Hou, J.; Chen, J.-T.; Hsu, C.-S. Elucidating End-Group Modifications of Carbazole-Based Nonfullerene Acceptors in Indoor Applications for Achieving a PCE of over 20%. *ACS Appl. Mater. Interfaces* **2021**, *13* (22), pp. 26247–26255.

[155] Adamo, C.; Barone, V. Exchange Functionals with Improved Long-Range Behavior and Adiabatic Connection Methods without Adjustable Parameters: The MPW and MPW1PW Models. *J. Chem. Phys.* **1998**, *108* (2), pp. 664–675.

[156] Hussain, R.; Saeed, M.; Mehboob, M. Y.; Khan, S. U.; Usman Khan, M.; Adnan, M.; Ahmed, M.; Iqbal, J.; Ayub, K. Density Functional Theory Study of Palladium Cluster Adsorption on a Graphene Support. *RSC Adv.* **2020**, *10* (35), pp. 20595–20607.

[157] Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. B3LYP Augmented with an Empirical Dispersion Term (B3LYP-D*) as Applied to Molecular Crystals. *CrystEngComm* **2008**, *10* (4), pp. 405–410.

[158] Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10* (44), pp. 6615.

- [159] Mehboob, M. Y.; Hussain, R.; Asif Iqbal, M. M.; Irshad, Z.; Adnan, M. First Principle Theoretical Designing of W-Shaped Dithienosilole-Based Acceptor Materials Having Efficient Photovoltaic Properties for High-Performance Organic Solar Cells. *J. Phys. Chem. Solids* **2021**, *157*, pp. 110202.
- [160] Mehboob, M. Y.; Khan, M. U.; Hussain, R.; Hussain, R.; Ayub, K.; Sattar, A.; Ahmad, M. K.; Irshad, Z.; Saira; Adnan, M. Designing of Benzodithiophene Core-Based Small Molecular Acceptors for Efficient Non-Fullerene Organic Solar Cells. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2021**, *244*, pp. 118873.
- [161] Hussain, S.; Shahid Chatha, S. A.; Hussain, A. I.; Hussain, R.; Mehboob, M. Y.; Gulzar, T.; Mansha, A.; Shahzad, N.; Ayub, K. Designing Novel Zn-Decorated Inorganic B₁₂P₁₂ Nanoclusters with Promising Electronic Properties: A Step Forward toward Efficient CO₂ Sensing Materials. *ACS Omega* **2020**, *5* (25), pp. 15547–15556.
- [162] Mehboob, M. Y.; Hussain, R.; Khan, M. U.; Adnan, M.; Umar, A.; Alvi, M. U.; Ahmed, M.; Khalid, M.; Iqbal, J.; Akhtar, M. N.; Zafar, F.; Shahi, M. N. Designing N-Phenylaniline-Triazol Configured Donor Materials with Promising Optoelectronic Properties for High-Efficiency Solar Cells. *Comput. Theor. Chem.* **2020**, *1186*, pp. 112908.
- [163] Adnan, M.; Mehboob, M. Y.; Hussain, R.; Irshad, Z. Banana-Shaped Nonfullerene Acceptor Molecules for Highly Stable and Efficient Organic Solar Cells. *Energy & Fuels* **2021**, *35* (14), pp. 11496–11506.
- [164] Mehboob, M. Y.; Adnan, M.; Hussain, R.; Irshad, Z. Quantum Chemical Designing of Banana-Shaped Acceptor Materials with Outstanding Photovoltaic Properties for High-Performance Non-Fullerene Organic Solar Cells. *Synth. Met.* **2021**, *277*, pp.

116800.

[165] Akram, M.; Siddique, S. A.; Iqbal, J.; Hussain, R.; Mehboob, M. Y.; Siddique, M. B. A.; Naveed, S.; Ali, B.; Hanif, A.; Sajid, M.; Shoukat, S. End-Capped Engineering of Bipolar Diketopyrrolopyrrole Based Small Electron Acceptor Molecules for High Performance Organic Solar Cells. *Comput. Theor. Chem.* **2021**, *1201*, pp. 113242.

[166] Janjua, M. R. S. A. Hydrogen as an Energy Currency: Encapsulation of Inorganic Ga₁₂N₁₂ with Alkali Metals for Efficient H₂ Adsorption as Hydrogen Storage Materials. *J. Phys. Chem. Solids* **2022**, *160*, 110352.

[167] Ali, S.; Ul Hassan Shah, S. J.; Jamil, S.; Bibi, S.; Shah, M. U.; Islam Aqib, A.; Zaheer, T.; Rauf Khan, S.; Saeed Ashraf Janjua, M. R. Zirconium Nanoparticles-Poly (N-Isopropylacrylamide-Methacrylic Acid) Hybrid Microgels Decorated Graphene Sheets for Catalytic Reduction of Organic Pollutants. *Chem. Phys. Lett.* **2021**, *780*, pp. 138915.

[168] Zafar, F.; Mehboob, M. Y.; Hussain, R.; Khan, M. ammad U.; Hussain, A.; Hassan, T.; Rashid, M.; Shahi, M. N. End-Capped Engineering of Truxene Core Based Acceptor Materials for High Performance Organic Solar Cells: Theoretical Understanding and Prediction. *Opt. Quantum Electron.* **2021**, *53* (2), pp. 99.

[169] Adnan, M.; Mehboob, M. Y.; Hussain, R.; Irshad, Z. In Silico Designing of Efficient C-Shape Non-Fullerene Acceptor Molecules Having Quinoid Structure with Remarkable Photovoltaic Properties for High-Performance Organic Solar Cells. *Optik (Stuttg)*. **2021**, *241*, pp. 166839.

[170] Younas, F.; Mehboob, M. Y.; Ayub, K.; Hussain, R.; Umar, A.; Khan, M. U.; Irshad, Z.; Adnan, M. Efficient Cu Decorated Inorganic B₁₂P₁₂ Nanoclusters for Sensing

Toxic COCl₂ Gas: A Detailed DFT Study. *J. Comput. Biophys. Chem.* **2021**, 20 (01), pp. 85–97.

[171] Ahmed, M.; Imran, M.; Muddassar, M.; Hussain, R.; Khan, M. U.; Ahmad, S.; Mehboob, M. Y.; Ashfaq, S. Benzenesulfonohydrazides Inhibiting Urease: Design, Synthesis, Their in Vitro and in Silico Studies. *J. Mol. Struct.* **2020**, 1220, pp. 128740.

[172] Khan, M. U.; Mehboob, M. Y.; Hussain, R.; Afzal, Z.; Khalid, M.; Adnan, M. Designing Spirobifullerene Core Based Three-dimensional Cross Shape Acceptor Materials with Promising Photovoltaic Properties for <scp>high-efficiency</Scp> Organic Solar Cells. *Int. J. Quantum Chem.* **2020**, 120 (22) pp. 26377.

[173] Hussain, S.; Chatha, S. A. S.; Hussain, A. I.; Hussain, R.; Mehboob, M. Y.; Muhammad, S.; Ahmad, Z.; Ayub, K. Zinc-Doped Boron Phosphide Nanocluster as Efficient Sensor for SO₂. *J. Chem.* **2020**, 2020, pp. 1–12.

[174] Mehboob, M. Y.; Hussain, F.; Hussain, R.; Ali, S.; Irshad, Z.; Adnan, M.; Ayub, K. Designing of Inorganic Al₁₂N₁₂ Nanocluster with Fe, Co, Ni, Cu and Zn Metals for Efficient Hydrogen Storage Materials. *J. Comput. Biophys. Chem.* **2021**, 20 (04), pp. 359–375.

[175] Hussain, R.; Khan, M. U.; Mehboob, M. Y.; Khalid, M.; Iqbal, J.; Ayub, K.; Adnan, M.; Ahmed, M.; Atiq, K.; Mahmood, K. Enhancement in Photovoltaic Properties of N,N'-diethylaniline Based Donor Materials by Bridging Core Modifications for Efficient Solar Cells. *ChemistrySelect* **2020**, 5 (17), pp. 5022–5034.

[176] Mehboob, M. Y.; Adnan, M.; Hussain, R.; Farhad, A.; Irshad, Z. Butterfly-Shaped Hole Transport Materials with Outstanding Photovoltaic Properties for Organic

Solar Cells. *Opt. Quantum Electron.* **2021**, 53 (9), pp. 517.

[177] Bilal Ahmed Siddique, M.; Hussain, R.; Ali Siddique, S.; Yasir Mehboob, M.; Irshad, Z.; Iqbal, J.; Adnan, M. Designing Triphenylamine-Configured Donor Materials with Promising Photovoltaic Properties for Highly Efficient Organic Solar Cells. *ChemistrySelect* **2020**, 5 (25), pp. 7358–7369.

[178] Hussain, R.; Imran, M.; Mehboob, M. Y.; Ali, M.; Hussain, R.; Khan, M. U.; Ayub, K.; Yawer, M. A.; Saleem, M.; Irfan, A. Exploration of Adsorption Behavior, Electronic Nature and NLO Response of Hydrogen Adsorbed Alkali Metals (Li, Na and K) Encapsulated Al₁₂N₁₂ Nanocages. *J. Theor. Comput. Chem.* **2020**, 19 (08), pp. 2050031.

[179] Hussain, R.; Hassan, F.; Khan, M. U.; Mehboob, M. Y.; Fatima, R.; Khalid, M.; Mahmood, K.; Tariq, C. J.; Akhtar, M. N. Molecular Engineering of A–D–C–D–A Configured Small Molecular Acceptors (SMAs) with Promising Photovoltaic Properties for High-Efficiency Fullerene-Free Organic Solar Cells. *Opt. Quantum Electron.* **2020**, 52 (8), pp. 364.

[180] Espinosa, N.; Laurent, A.; Krebs, F. C. Ecodesign of Organic Photovoltaic Modules from Danish and Chinese Perspectives. *Energy Environ. Sci.* **2015**, 8 (9), pp. 2537–2550.

[181] Hou, J.; Inganäs, O.; Friend, R. H.; Gao, F. Organic Solar Cells Based on Non-Fullerene Acceptors. *Nat. Mater.* **2018**, 17 (2), pp. 119–128.

- [182] Xue, P.; Xiao, Y.; Li, T.; Dai, S.; Jia, B.; Liu, K.; Wang, J.; Lu, X.; Han, R. P. S.; Zhan, X. High-Performance Ternary Organic Solar Cells with Photoresponses beyond 1000 Nm. *J. Mater. Chem. A* **2018**, 6 (47), pp. 24210–24215.
- [183] Li, G.; Chang, W.-H.; Yang, Y. Low-Bandgap Conjugated Polymers Enabling Solution-Processable Tandem Solar Cells. *Nat. Rev. Mater.* **2017**, 2 (8), pp. 17043.
- [184] Gasparini, N.; Paleti, S. H. K.; Bertrandie, J.; Cai, G.; Zhang, G.; Wadsworth, A.; Lu, X.; Yip, H.-L.; McCulloch, I.; Baran, D. Exploiting Ternary Blends for Improved Photostability in High-Efficiency Organic Solar Cells. *ACS Energy Lett.* **2020**, 5 (5), pp. 1371–1379.
- [185] Cheng, P.; Li, G.; Zhan, X.; Yang, Y. Next-Generation Organic Photovoltaics Based on Non-Fullerene Acceptors. *Nat. Photonics* **2018**, 12 (3), 131–142.
- [186] Xu, Y.; Yao, H.; Ma, L.; Hong, L.; Li, J.; Liao, Q.; Zu, Y.; Wang, J.; Gao, M.; Ye, L.; Hou, J. Tuning the Hybridization of Local Exciton and Charge-Transfer States in Highly Efficient Organic Photovoltaic Cells. *Angew. Chemie* **2020**, 132 (23), pp. 9089–9095.
- [187] Kini, G. P.; Jeon, S. J.; Moon, D. K. Design Principles and Synergistic Effects of Chlorination on a Conjugated Backbone for Efficient Organic Photovoltaics: A Critical Review. *Adv. Mater.* **2020**, 32 (11), pp. 1906175.
- [188] Ge, J.; Xie, L.; Peng, R.; Fanady, B.; Huang, J.; Song, W.; Yan, T.; Zhang, W.; Ge, Z. 13.34 % Efficiency Non-Fullerene All-Small-Molecule Organic Solar Cells Enabled by Modulating the Crystallinity of Donors via a Fluorination Strategy. *Angew. Chemie Int. Ed.* **2020**, 59 (7), pp. 2808–2815.

- [189] Li, Y.; Gu, M.; Pan, Z.; Zhang, B.; Yang, X.; Gu, J.; Chen, Y. Indacenodithiophene: A Promising Building Block for High Performance Polymer Solar Cells. *J. Mater. Chem. A* **2017**, 5 (22), pp. 10798–10814.
- [190] Huo, L.; Huang, Y.; Fan, B.; Guo, X.; Jing, Y.; Zhang, M.; Li, Y.; Hou, J. Synthesis of a 4,8-Dialkoxy-Benzo[1,2-b:4,5-B']Difuran Unit and Its Application in Photovoltaic Polymer. *Chem. Commun.* **2012**, 48 (27), pp. 3318.
- [191] Warnan, J.; Cabanetos, C.; Labban, A. El; Hansen, M. R.; Tassone, C.; Toney, M. F.; Beaujuge, P. M. Ordering Effects in Benzo[1,2-B:4,5-b']Difuran-Thieno[3,4-c]Pyrrole-4,6-Dione Polymers with >7% Solar Cell Efficiency. *Adv. Mater.* **2014**, 26 (25), pp. 4357–4362.
- [192] Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, 393 (1–3), pp. 51–57.
- [193] Mehboob, M. Y.; Hussain, R.; Irshad, Z.; Adnan, M. Enhancement in the Photovoltaic Properties of Hole Transport Materials by End-Capped Donor Modifications for Solar Cell Applications. *Bull. Korean Chem. Soc.* **2021**, bkcs, pp. 12238.
- [194] Janjua, M. R. S. A. Quantum Chemical Designing Of Triphenylamine Dyes With D-A- π -A Configuration For Dye Sensitized Solar Cells: Molecular Engineering Through First-Principles Calculations. *J. Chil. Chem. Soc.* **2018**, 63 (1), pp. 3850–3854.
- [195] Janjua, M. R. S. A.; Liu, C.-G.; Guan, W.; Zhuang, J.; Muhammad, S.; Yan, L.-K.; Su, Z.-M. Prediction of Remarkably Large Second-Order Nonlinear Optical

Properties of Organoimido-Substituted Hexamolybdates. *J. Phys. Chem. A* **2009**, *113* (15), pp. 3576–3587.

[196] Zhang, D.; Fan, B.; Ying, L.; Li, N.; Brabec, C. J.; Huang, F.; Cao, Y. **2021**, Recent Progress in Thick-film Organic Photovoltaic Devices: Materials, Devices, and Processing. *SusMat* *1* (1), pp. 4–23.

[197] Faure, M. D. M.; Lessard, B. H. Layer-by-Layer Fabrication of Organic Photovoltaic Devices: Material Selection and Processing Conditions. *J. Mater. Chem. C* **2021**, *9* (1), pp. 14–40.

[198] Cao, Y.; Zhao, Z.; Bao, P.; Gan, Z.; Wang, H. Lateral Photovoltaic Effect in Silk-Protein-Based Nanocomposite Structure for Physically Transient Position-Sensitive Detectors. *Phys. Rev. Appl.* **2021**, *15* (5), pp. 054011.

[199] Rammal, M.; Lévêque, P.; Schlatter, G.; Leclerc, N.; Hébraud, A. Recent Advances in the Green Processing of Organic Photovoltaic Devices from Nanoparticle Dispersions. *Mater. Chem. Front.* **2020**, *4* (10), pp. 2904–2931.

[200] Ramin Shamshiri, R.; Kalantari, F.; C. Ting, K.; R. Thorp, K.; A. Hameed, I.; Weltzien, C.; Ahmad, D.; Mojgan Shad, Z. Advances in Greenhouse Automation and Controlled Environment Agriculture: A Transition to Plant Factories and Urban Agriculture. *Int. J. Agric. Biol. Eng.* **2018**, *11* (1), pp. 1–22.

[201] La Notte, L.; Giordano, L.; Calabrò, E.; Bedini, R.; Colla, G.; Puglisi, G.; Reale, A. Hybrid and Organic Photovoltaics for Greenhouse Applications. *Appl. Energy* **2020**, *278*, pp. 115582.

- [202] Kadowaki, M.; Yano, A.; Ishizu, F.; Tanaka, T.; Noda, S. Effects of Greenhouse Photovoltaic Array Shading on Welsh Onion Growth. *Biosyst. Eng.* **2012**, *111* (3), pp. 290–297.
- [203] Marrou, H.; Wery, J.; Dufour, L.; Dupraz, C. Productivity and Radiation Use Efficiency of Lettuces Grown in the Partial Shade of Photovoltaic Panels. *Eur. J. Agron.* **2013**, *44*, pp. 54–66.
- [204] Brus, V. V.; Lee, J.; Luginbuhl, B. R.; Ko, S.-J.; Bazan, G. C.; Nguyen, T.-Q. Hall of Fame Article: Solution-Processed Semitransparent Organic Photovoltaics: From Molecular Design to Device Performance (Adv. Mater. 30/2019). *Adv. Mater.* **2019**, *31* (30), pp. 1970219.
- [205] Lee, J.; Cha, H.; Yao, H.; Hou, J.; Suh, Y.-H.; Jeong, S.; Lee, K.; Durrant, J. R. Toward Visibly Transparent Organic Photovoltaic Cells Based on a Near-Infrared Harvesting Bulk Heterojunction Blend. *ACS Appl. Mater. Interfaces* **2020**, *12* (29), pp. 32764–32770.
- [206] Fakharuddin, A.; Jose, R.; Brown, T. M.; Fabregat-Santiago, F.; Bisquert, J. A Perspective on the Production of Dye-Sensitized Solar Modules. *Energy Environ. Sci.* **2014**, *7* (12), pp. 3952–3981.
- [207] McCree, K. J. The Action Spectrum, Absorptance and Quantum Yield of Photosynthesis in Crop Plants. *Agric. Meteorol.* **1971**, *9*, 191–216.
- [208] Brown, C. S.; Schuerger, A. C.; Sager, J. C. Growth and Photomorphogenesis of Pepper Plants under Red Light-Emitting Diodes with Supplemental Blue or Far-Red Lighting. *J. Am. Soc. Hortic. Sci.* **1995**, *120* (5), pp. 808–813.

- [209] Liu, Y.; Cheng, P.; Li, T.; Wang, R.; Li, Y.; Chang, S.-Y.; Zhu, Y.; Cheng, H.-W.; Wei, K.-H.; Zhan, X.; Sun, B.; Yang, Y. Unraveling Sunlight by Transparent Organic Semiconductors toward Photovoltaic and Photosynthesis. *ACS Nano* **2019**, *13* (2), pp. 1071–1077.
- [210] Kim, J.-J.; Kang, M.; Kwak, O. K.; Yoon, Y.-J.; Min, K. S.; Chu, M.-J. Fabrication and Characterization of Dye-Sensitized Solar Cells for Greenhouse Application. *Int. J. Photoenergy* **2014**, *2014*, pp. 1–7.
- [211] Duvva, N.; Raptis, D.; Kumar, C. V.; Koukaras, E. N.; Giribabu, L.; Lianos, P. Design of Diketopyrrolopyrrole Chromophores Applicable as Sensitizers in Dye-Sensitized Photovoltaic Windows for Green Houses. *Dye. Pigment.* **2016**, *134*, pp.472–479.
- [212] Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393* (1–3), pp. 51–57.
- [213] Janjua, M. R. S. A. Quantum Mechanical Design of Efficient Second-Order Nonlinear Optical Materials Based on Heteroaromatic Imido-Substituted Hexamolybdates: First Theoretical Framework of POM-Based Heterocyclic Aromatic Rings. *Inorg. Chem.* **2012**, *51* (21), pp. 11306–11314.

Vitae

Name :Muhammad Haroon
Nationality :Pakistani
Email :drharoon2020@gmail.com
Address :Syedan Colony Post office Dharema Tahsil and District
Sargodha 40100, Punjab Pakistan

Academic Background:

:PhD in Chemistry from King Fahd University of Petroleum and Minerals
Dhahran, 31261, Saudi Arabia CGPA 3.583/4.00
PhD in Chemistry from University of Sargodha Pakistan CGPA 3.21/4.00
Master's in chemistry From University of Sargodha Pakistan CGPA 3.20/4.00
Bachelor's in chemistry from university of Sargodha Pakistan CGPA 3.18/ 4.00
Bachelor of Education (B.Ed.) from Allama Iqbal Open University Islamabad,
Pakistan
Master of Education (M.Ed.) from Allama Iqbal Open University Islamabad,
Pakistan

Publications:

1. **M. Haroon**, A.A. Al-Saadi, M.R.S.A Janjua*, Insights into end-capped modifications effect on the photovoltaic and optoelectronic properties of S-shaped fullerene-free acceptor molecules: A density functional theory computational study for organic solar cells, *J. Phys. Org. Chem.***2022**. <https://doi.org/10.1002/poc.4314>
2. **M. Haroon**, M.R.S.A. Janjua*, Exploring the Effect of End-capped Modifications of Carbazole-based Fullerene Free Acceptor Molecules for High Performance Indoor Organic Solar Cell Applications, *J. Comput. Electron.* **2022**. <https://doi.org/10.1007/s10825-021-01838-w>
3. M.R.S.A. Janjua*, **M. Haroon**, R. Hussain, M. Usman, M.U. Khan, and W. A. Gill, Computational Engineering to Enhance the Photovoltaic (PV) by End-Capped and Bridging Core Alterations: Empowering the Future with Solar Energy through Synergistic Effect in D-A Materials, *Int. J. Quantum Chem.* (**2021**) e26821. <https://doi.org/10.1002/qua.26821>

4. **M Haroon**, M.R.S.A. Janjua*, High-Throughput Designing and Investigation of D–A– π –A-Type Donor Materials for Potential Application in Greenhouse-Integrated Solar Cells, *Energy Fuels* (2021) 35, 12461–12472 <https://doi.org/10.1021/acs.energyfuels.1c01726>
5. **M. Haroon**, M. Khalid, Z. Shafiq, M.U. Khan, M.R.S.A. Janjua*, High-throughput calculations and experimental insights towards the development of potent thiazoline based functional materials, *Mater. Today Commun.* (2021) 27, 102485 <https://doi.org/10.1016/j.mtcomm.2021.102485>