Tuning the Optoelectronic Properties of Cross Conjugated Small Molecules Using Benzodithiophene As a Core Unit With Favorable Photovoltaic Parameters

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Abstract

In a recent study, cross conjugated molecules (**BDT-C1 to BDT-C6**) based on Benzo [1,2-b:4,5-b'] (BDT) as core units linked with different acceptor moieties are designed for encouraging photovoltaic applications. The optoelectronic study has been conducted by density functional theory (DFT) at B3LYP 6-31G (d, p) basis set combination by equating them with recently reported cross conjugated reference (**BDT-CR**) molecule and to study basic parameters such as frontier molecular orbital, density of states, reorganization energy, maximum absorption, dipole moment, transition density matrix (TDM) and open-circuit voltage (V_{OC}). Six new cross conjugated molecules (**BDT-C1 to BDT-C6**) with modified acceptor moieties are designed to evaluate their photophysical behavior in photovoltaic cells and the optoelectronic analysis of designed molecules indicates that among all cross conjugated molecules, **BDT-C3** molecule exhibited the lowest bandgap value (1.83 eV) and broad absorption (747 nm) spectrum in dichloromethane (DCM) due to extended conjugation in molecule than **BDT-CR**. TDM results reveal the easy dissociation of exciton due to the transfer of electron density in a diagonal direction from donor to acceptor moieties. The lowest value of electron mobility (0.0030 eV) and hole mobility (0.0027 eV) of **BDT-C4** indicates its excellent electron and hole transfer behavior. The newly architecture molecule **BDT-C5** displayed the highest V_{OC} value of 1.75 eV concerning **PC₆₁BM**. All above-mentioned outcomes reflects that our newly architecture cross conjugated molecules are suitable applicants for photovoltaic cells and can exhibit wonderful results in the quest of power conversion efficiency (PCE).

Highlights

- Benzodithiophene based cross conjugated molecules (**BDT-C1 to BDT-C6**) has been designed for photovoltaic applications.
- The recent investigated molecules exhibited good optoelectronic properties.
- The designed donor molecules showed significant charge transfer ability.

1. Introduction

Balance, accessible and consistent supply of energy is the basic, crucial and inevitable need for the development of modern societies. The global energy demand is increasing with time throughout history due to the rapid increase of human population, modernization and urbanization. In the coming years, the global energy demand will reach its maximum height to meet the energy requirements of human life [1, 2]. So, scientists and researchers are looking to explore alternative energy sources and renewable energy sources (tidal, wind power, biomass, solar energy) are considered to be environment friendly, abundant and inexhaustible to cope with the rapidly increasing current global energy demand without any environmental degradation. Among all of these potential alternatives, solar energy is propitious and of great interest with fascinating features to overcome the energy deficit. Solar energy is the cleanest, safe and appealing source of energy and photovoltaic cells are of various types such as gallium-selenide-based photovoltaic cells, monocrystalline silicon-based solar cell, dye-sensitized photovoltaic cell and

hybrid, solution-processed, perovskite and organic small molecules based solar cells. The silicon-based solar cell has remarkable efficiency but their use in energy conversion technology is limited due to many limitations such as high cost, rigid structure and complicated fabrication process which requires a high range of temperature and vacuum. While organic solar cells are the best alternative to silicon-based solar and their use in solar to energy conversion technologies is increasing day by day due to the use of small organic molecules. Organic solar cells gained more attention and have become to be an auspicious and potential technology because of their tremendous benefits including lightweight, environment friendly, low fabrication cost and mechanical stability [3]. PCE of 13% has been obtained for small molecule-based organic photovoltaic cells and many efforts have been exerted to attained further remarkable power conversion efficiency. Small molecule-based organic photovoltaic cells have many fascinating features in contrast to solution-processed polymer solar cells but still have some limitations like energy levels of donor molecules do not align with that of acceptor molecules, poor charge transport and film morphology which affect open-circuit voltage. To overcome the above-cited shortcomings, scientists and researchers have designed novel and efficient alternating small molecule donor materials [4-13]. Traditionally, fullerene-based acceptor molecules had been used to obtain the high PCE value. These frequent acceptor molecules allow efficient transport of charge and ultrafast charge separation but their optical absorption in the visible region is very poor and has highly complicated synthesis procedures as compared to small molecules and other polymers [14, 15]. Recently, highly efficient non-fullerene acceptor (NFAs) molecules are of great consideration and have to gain more attention because of the tenability of their optical properties and strong absorption of electromagnetic radiations in the visible region [16, 17].

Organic photovoltaic cells are evaluated by photovoltaic parameters, optoelectronic properties and opposite architecture. Concerning morphology, OPVs are contrived in viable methods. The first approach is to construct the OPVs as single layer OSCs comprise of only one active organic layer that is sandwich between two respective electrodes named anode and cathode. But this type of cell accounted for low conversion and quantum efficiency. The second strategy encompasses the electron donor (D) and acceptor (A) layer to enhance the operational performance of OPVs. The third and most important development approach to enhance the efficiency of OPVs is bulk heterojunction or dispersed OSCs comprised of a blend of donor and acceptor materials. This effective strategy can overcome the worldwide power outage by boost up the operational efficiency of OPVs.

Recently, benzo [1,2-b:4,5-*b'*]dithiophene (BDT) as a central fused core is of great interest due to its desirable quantum efficiency [18]. In photovoltaic cells, pi-conjugated organic semiconductors played a significant role in the ease of charge density transfer from D to A moiety resulted in high operational efficiency of the photovoltaic cell. BDT has been used as donor material and has exhibited efficient and excellent photovoltaic properties. The blend of small molecule-based donor and acceptor moieties enhances the optoelectronic properties of solar cells due to different substitutions on the BDT core unit [19-22]

Herein, we did a computational study on different cross conjugated molecules **BDT-C1 to BDT-C6** which possessed a fused core of BDT due to its peculiar behavior as it has symmetrical and planner structure,

excellent charge transport properties and structural modification versatility [23]. In the current initiative, the reference **BDT-CR** and new cross conjugated molecules **BDT-C1 to BDT-C6** consists of BDT as a donor (core unit) linked with different acceptors moieties via thiophene (see **Fig. 1**). The introduction of thiophene in all molecules can facilitate the charge shifting from the core to the end-capped acceptor groups at the terminal by alleviating conjugation and boost up the donating capability of BDT. The calculated optical and electronic features of cross conjugated novel molecules were equated with **BDT-CR** molecule [24] and the outcomes of all investigated optoelectronic properties suggest that these newly designed cross conjugated molecules could be used as a promising avenue to enhance the efficiency of the organic photovoltaic cell.

2. Computational Study

Gaussian 09 software [25] was used for all types of calculations of novel architecture molecules in the present chemical study. The Gaussview program was employed to construct the 3-D structures of the reference **BDT-CR** and designed molecules **BDT-C1 to BDT-C6** and also to visualize the output of these calculations. DFT which gives the most reliable results was implemented to evaluate the spectroscopic, electronic and electronic properties [26]. The geometry of cross conjugated **BDT-CR** molecule was optimized via four hybrid functionals named MPW1PW91[27], PBEPBE[28], B3LYP [29] and WB97XD using 6-31G (d, p) basis set method. The solvent effect was investigated using the integral equation formalism polarizable continuum model (IEPCM) (a solvation modal) by employing DCM as solvent [30]. An important approach known as Time-dependent density functional theory (TD-DFT) [31] with a functional method of B3LYP and basis set of 6-31G (d,p) was employed in both gaseous and solvent medium for modeling electronic and excited-state energy calculations. The absorption spectra of reference and all examined cross conjugated molecules were plotted using origin 6. 0 software [32]. The valid theoretical approach was selected by equating the calculated maximum absorption (λ_{max}) of the **BDT-CR** with that of experimental (λ_{max}) value. B3LYP was selected for geometry optimization and further calculations of all newly designed cross conjugated molecules due to the closest (λ_{max}) value of this method to experimental reported λ_{max} value as compared to other functional methods. Therefore selected functional B3LYP/6-31G (d,p) approach was employed for DOS calculation by using PyMolyze 1.1 software [33], TDM analysis by using Multiwfn 3.7 program [34], dipole moment and FMOs of reference **BDT-CR** and tailored molecules **BDT-C1 to BDT-C6**. Reorganization energy of **BDT-CR** and **BDT-C1 to BDT-C6** are divided into external and internal reorganization energy (λ_{ext} and λ_{int}). λ_{ext} concerns with the polarization effect in external environment while λ_{int} concerns with variation in internal structure. Herein, only the internal reorganization effect is of our interest and we discount the external effect in the current study due to our small donor molecules with a low dielectric constant value. Reorganization energy due to electron mobility (λ_e) can be determined from the below-mentioned equation (1)

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

E_0^- represents the neutral molecule energy of the optimized anion. E_0 represents the energy of a neutral optimized molecule E_0^- denotes the energy of anion of optimized neutral molecule and E_- denotes the energy of anion of optimized anion of neutral molecule. Likewise, reorganization energy due to hole mobility (λ_h) can be evaluated from the below-mentioned equation (2)

$$\lambda_h = [E_+^0 - E_0] + [E_0^+ - E_+] \quad (2)$$

E_+^0 represents the neutral molecule energy of optimized cation. While E_+^0 and E_+ signify cationic energy of the optimized neutral molecule and cationic energy of optimized cation of neutral molecule respectively.

3. Results And Discussion

3.1. Optimized geometry

The geometry of **BDT-CR** molecule was optimized via four distinct types of functionals such as B3LYP, PBEPBE, MPW1MP91 and WB97XD at 6-31G (d, p) level of theory to choose the best choice for novel architecture cross conjugated molecules. The **BDT-CR** cross conjugated molecule exhibited the λ_{max} values of 395, 554, 350 and 312 nm at B3LYP, PBEPBE, MPW1MP91 and WB97XD respectively. The above-mentioned values were sensibly equated with an experimentally reported λ_{max} value of 407 nm [35] and calculated λ_{max} of the **BDT-CR** molecule with B3LYP functional has close approximation with experimental value (see **Fig. 2**) so B3LYP was nominated as an appropriate method to intensify optoelectronic features and for further calculations of all investigated cross conjugated molecules. The optimized geometries of recently studied molecules **BDT-C1 to BDT-C6** which are the derivatives of cross conjugated **BDT-CR** and have donor-spacer-acceptor-arrangement has been portrayed in **Fig. 3**. Structure tailoring of cross conjugated **BDT-CR** molecule has been executed by keeping the donor fragment fixed and substituting the thiophene bridge with six different linkers name as 2-ethylidenemalononitrile (**BDT-C1**), (Z)-methyl 2-cyanobut-2-enoate (**BDT-C2**), (E)-2-(2-ethylidene-5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**BDT-C3**), benzo[c][1,2,5]thiadiazole (**BDT-C4**), 2-((E)-((E)-5-ethylidene-3-methyl-4-oxothiazolidin-2-ylidene)methyl)malononitrile (**BDT-C5**), (E)-5-ethylidene-3-methyl-2-thioxothiazolidin-4-one (**BDT-C6**). The ground state optimized configurations of **BDT-CR** and designed cross conjugated molecule (**BDT-C1 to BDT-C6**) with de-localization of pi-electrons can facilitate the charge mobility and can be recommended as good candidate for their applications in organic photovoltaic cells.

3.2. Frontier Molecular orbital (FMOs) and Density of state (DOS) analysis

The geometry of new architecture optimized molecules **BDT-C1 to BDT-C6** with B3LYP functional using 6-31G (d,p) basis set level has been exposed in **Fig. 3**. All optimized molecules have cross conjugated configuration exhibited donor-spacer-acceptor arrangement. Electronic distribution pattern of FMOs: highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) influences the photoelectronic properties of photovoltaic cells. FMOs are helpful to divulge the charge transition character of all investigated molecules.

The FMOs electronic distribution pattern of **BDT-CR** and designed cross conjugated designed molecules **BDT-C1 to BDT-C6** is presented in **Fig. 4**. The HOMO-LUMO bandgap ($E_{\text{HOMO}}-E_{\text{LUMO}}$) indicates the chemical reactivity of the substituted entities and molecules with small band gaps (E_g) are characterized as soft molecules because undoubtedly they have strong chemical reactivity and show low stability. **BDT-CR** molecule has an experimental HOMO energy value of -5.19eV and LUMO value of -2.38 eV with bandgap energy value of 2.81e V. In all devised cross conjugated designed molecule **BDT-C1 to BDT-C6**, charge carrier ability is enhanced via extended conjugation that is assisted by the electron delocalization within the molecular systems. Similarly, newly designed cross conjugated molecules **BDT-C1 to BDT-C6** exhibited the HOMO values of -5.51, -5.19, -5.41, -5.93, -5.50, -5.23 eV respectively and the trend of HOMO energy value is counted as **BDT-C4 > BDT-C2 > BDT-CR > BDT-C6 > BDT-C3 > BDT-C5 > BDT-C1**. The LUMO energy values for designed molecules BDT-C1 to BDT-C6 is counted as -3.39, -3.05, -3.57, -2.76, -3.34, -3.09 eV respectively and trend of LUMO energy value is found as **BDT-CR > BDT-C4 > BDT-C2 > BDT-C6 > BDT-C5 > BDT-C1 > BDT-C3**. The calculated energy gap value for **BDT-C1 to BDT-C6** molecules was noted as 2.12, 2.13, 1.83, 2.16, 2.16, 2.13 eV (**Table. 1**) with increasing trend of **BDT-CR > BDT-C4 = BDT-C5 > BDT-C1 > BDT-C2 = BDT-C6 > BDT-C3**.

Table 1. The HOMO-LUMO (eV) and band gap (eV) energy values for **BDT-CR** and **BDT-C1 to-BDT-C6** molecules

Molecule	HOMO (eV)	LUMO (eV)	Band Gap (eV)
BDT-CR	-5.22	-2.46	2.76
BDT-C1	-5.51	-3.39	2.12
BDT-C2	-5.19	-3.05	2.13
BDT-C3	-5.41	-3.57	1.83
BDT-C4	-4.93	-2.76	2.16
BDT-C5	-5.50	-3.34	2.16
BDT-C6	-5.23	-3.09	2.13

Among all these molecules **BDT-C3** cross conjugated molecule showed the lowest energy gap value because of electron-pulling nature of (E)-2-(2-ethylidene-5,6-diflouro-3-oxo-2,3-dihydro-1H-inden-1-

ylidene)malononitrile moiety at the peripheral position. FMOs representation depicts that HOMO electron density is restricted on the donor fragment while LUMO electron density is concentrated on the bridge and acceptor fragment of molecules. DOS analysis was performed for all these molecules and the outcomes from this analysis verify the pieces of evidence demonstrated by FMOs results. In the present investigation, the pictographic display of DOS analysis represented by blue, green and red color lines for donor, bridge and acceptor fragments of devised molecules showed that HOMO of all the designed molecules are identical, demonstrating that these occupied molecular orbitals are arising from a central core of the designed molecule resulting in the transfer of electrons within energy domain during excitation process (see **Fig. 5**). The LUMO of all molecules **BDT-C1 to BDT-C6** is almost the same with little variation indicating that lowest unoccupied orbital rising from acceptor unit of the molecules. Graphical representation of HOMO-LUMO and band gap values for **BDT-CR** and **BDT-C1 to BDT-C6** is exposed in **Fig. 6**.

3.3. Optical properties

Absorption properties are explored to envisage the working of photovoltaic cells. The spectra of **BDT-CR** were computed in the gaseous and solvent medium at four distinct DFT methods as shown in **Fig. 7**. For computing the electronic transition of **BDT-CR** and designed cross conjugated molecules (**BDT-C1 to BDT-C6**), absorption spectrum was recorded using B3LYP/6-31G (d, p) basis set combination in gas and DCM medium (**Fig. 8**). The experimental value of maximum absorption for reference **BDT-CR** molecule in both gas and DCM was found as 391 nm and 489 nm respectively. The recorded spectrum in the UV-visible region with an intense peak of design cross conjugated molecules seems to be a good approximation to show good photovoltaic properties in organic photovoltaic cells. The Calculated wavelength ($\lambda_{\max}$), oscillator strength (f_o), experimental wavelength ($\lambda_{\max}$) and excitation energy (ΔE) parameter for **BDT-CR** and all investigated molecules (**BDT-C1 to BDT-C6**) with B3LYP/6-31G (d,p) basis set combination are observed in both (gaseous and DCM) phases for photovoltaic performance (**Tables 2 and 3**). The **BDT-CR** and newly architecture cross conjugated molecules **BDT-C1 to BDT-C6** showed the $\lambda_{\max}$ at 391, 660, 659, 746, 614, 610 and 650 nm in a gaseous phase. The presence of DCM shifted the absorption towards red-shift with broader peaks as compared to the gas phase due to stabilized delocalized electrons.

The $\lambda_{\max}$ in the presence of a solvent for the reference **BDT-CR** and designed molecules **BDT-C1 to BDT-C6** was reported as 489, 665, 664, 748, 625, 633 and 649 nm respectively. So it was noted that solvent has a great effect to shift the absorption towards a longer wavelength. The order of $\lambda_{\max}$ in the presence of solvent among tailored molecules was noted as **BDT-C3 > BDT-C1 > BDT-C2 > BDT-C6 > BDT-C5 > BDT-C4 > BDT-CR**. Exceptionally, **BDT-C3** exhibited the highest red-shift value because of strong F atoms containing electron pulling acceptor moiety with extended conjugation. The aforementioned discussion predicts that **BDT-C3** highest absorption (in DCM and gaseous medium) and lowest bandgap value that profoundly makes it an effective candidate for solar cell applications.

Table 2. Estimation of Excitation energy (ΔE), oscillator frequency (f_o) and percent configuration interaction for **BDT-CR** and designed cross conjugated molecule **BDT-C1 to BDT-C6** in gaseous phase.

Molecule	$\lambda_{\text{max}}^{\text{cal}}$	$\lambda_{\text{max}}^{\text{exp}}$	Electronic Excitation	ΔE	f_o	Transition	% C.I.
BDTCR	391	470	$S_0 \rightarrow S_1$	3.16	0.34	H $\rightarrow$ L	69
BDT-C1	659	∞-∞-∞-∞-∞-∞-	-	1.95	0.45	-	65
BDT-C2	659	∞-	-	1.91	0.23	-	59
BDT-C3	746	∞-	-	1.74	0.26	-	59
BDT-C4	614	∞-	-	2.00	0.57	-	49
BDT-C5	610	∞-	-	1.96	0.59	-	65
BDT-C6	649	∞-	-	1.95	0.29	-	48

Table 3. Estimation of first excitation energy (ΔE), oscillator frequency (f_o) and percent configuration interaction (C.I) for **BDT-CR** and designed cross conjugated molecules **BDT-C1 to BDT-C6** in DCM solvent.

Molecule	$\lambda_{\text{max}}^{\text{cal}}$	$\lambda_{\text{max}}^{\text{exp}}$	Electronic Excitation	ΔE	f_o	Transition	% C.I.
BDT-CR	489	407	$S_0 \rightarrow S_1$	2.53	0.54	H $\rightarrow$ L	69
BDT-C1	665	-	-	1.86	0.67	-	66
BDT-C2	664	-	-	1.87	0.45	-	58
BDT-C3	748	-	-	1.65	0.27	-	62
BDT-C4	625	-	-	1.98	1.21	-	59
BDT-C5	633	-	-	1.95	0.88	-	66
BDT-C6	649	-	-	1.91	0.45	-	55

3.4 Transition Density Matrix

Transition density matrix (TDM) investigation of benzodithiophene-based cross conjugated small molecules was carried out for the estimation of transition nature and interaction of donor-acceptor groups during the excitation process. TDM describes the excitation process using a special map that displays electron-hole localization and transfer of charge density from donor to acceptor group [36, 37]. The selected B3LYP/ 6-31G (d, p) basis set combination was employed to evaluate the TDM analysis of **BDT-CR** and **BDT-C1 to BDT-C6** cross conjugated molecules

Hydrogen atoms do not play an important role in transition so we neglected them in our recent studied molecules. TDM outcomes were evaluated by dividing the newly architecture cross conjugated molecules into three basic fragments as donor (benzodithiophene core), Spacer (thiophene) and different acceptors groups. **Fig. 9** discloses the TDM display of **BDT-CR** and newly intended molecules (**BDT-C1 to BDT-C6**). The 2-D map indicates that in **BDT-CR** electron excitation is in the diagonal and off-diagonal character of donor and acceptor portion. The 2-D map of all tailored cross conjugated molecules presented outstanding diagonal charge transfer from BDT core to acceptor moiety via bridge representing smaller electron coupling in them and facilitates the easier exciton dissociation.

Another important parameter which helps to appraise the efficiency of organic photovoltaic cell is the binding energy and is a concrete tool helps to determine exciton dissociation potential and measures the Coulomb interaction of the hole and electron. The binding energy must be low for the dissociation of the exciton. Molecules with lower binding energy have a high potential of exciton dissociation during the transition to a higher energy state [37]. The binding energy of the **BDT-CR** and cross conjugated molecules **BDT-C1 to BDT-C6** was calculated from the following equation (3) to evaluate the efficiency of an organic photovoltaic cell.

$$E_b = E_g - E_x \quad (3)$$

Binding energy (E_b) can be determined from the energy difference of HOMO and LOMO (E_g) with first excitation energy (E_x) for **BDTR** and all designed cross conjugated molecules. The binding energy of **BDT-CR** and **BDT-C1 to BDT-C6** has been computed in **Table. 4**. The trend of exciton binding energy for cross conjugated novel molecules is found as **BDT-C6 > BDT-C1 = BDT-C2 > BDT-CR > BDT-C5 > BDT-C3 = BDT-C4**. A lower value of binding energy resulted in higher current charge density (J_{SC}) [38] and cross conjugated molecules **BDT-C3** and **BDT-C4** exhibited the lowest binding energy value than **BDT-CR** and other remaining molecules. So such molecules can be considered as well- suited for electronic excitation processes in photovoltaic cells.

Table 4. Excitation $E(s_1.s_0)$ (eV) and binding E_b (eV) energies for **BDT-CR** and **BDT-C1 to BDT-C6** in DCM.

Molecule	$E_{(s_1-s_0)}$ (eV)	E_b (eV)
	DCM	DCM
BDT-CR	2.76	0.23
BDT-C1	2.12	0.26
BDT-C2	2.13	0.26
BDT-C3	1.83	0.18
BDT-C4	2.16	0.18
BDT-C5	2.16	0.21
BDT-C6	2.13	0.94

3.5. Reorganization energy

Reorganization energy (RE) is an auspicious and significant parameter to evaluate the performance of photovoltaic cells by hole and electron mobility. It has an inverse relation with the transfer of charge in the photovoltaic cell. Reorganization energy of material must be low in order to obtain high charge mobility. It is used to find out the total transfer of charge between donor and acceptor moiety. Different factors affect the reorganization energy of cells but it is primarily affected by the geometry of anion and cation [39].

Consequently, for the evaluation of electron and hole charge transport features for current studied cross conjugated molecules (**BDT-C1 to BDT-C6**), we have calculated RE values that were linked with different cationic and anionic geometries determined by applying Equations (1) and 2). Electron and hole reorganization energy value (λ_e and λ_h) for **BDT-CR** and all designed cross conjugated molecules **BDT-C1 to BDT-C6** is tabulated in **Table 5**. Among all tailored molecules **BDT-C4** exhibited the lowermost λ_e (0.0030 eV) and λ_h (0.0027 eV) values. Charge transport is increased as the cation and anion movement rates are reduced. So, as the result of the existence of a strong electron pulling fragment, **BDT-C4** has the highest cationic and anionic charge movement rate as well as lowest binding energy among all recently developed chromophores. As a result, the customized molecule might be considered a promising choice for building OSCs with improved charge transfer capabilities.

Table 5. Reorganization energies with electron and hole mobilities (λ_e and λ_h) for reference **BDT-CR** and designed cross conjugated molecules **BDT-C1 to BDT-C6** at B3LYP method.

Molecule	λ_e	λ_h
BDT-CR	0.0147	0.0063
BDT-C1	0.0040	0.0068
BDT-C2	0.0181	0.0197
BDT-C3	0.0044	0.0147
BDT-C4	0.0030	0.0027
BDT-C5	0.0043	0.0031
BDT-C6	0.0043	0.0042

3.6 Dipole moment

Dipole moment is the fundamental attribute in the performance of proficient organic photovoltaic cells. Dipole moment has an effect on molecular solubility in organic solvents [40]. The dipole moment will be taken into account more when a molecule has more polar groups and high solubility in the solvent and also has a great influence on the charge mobility of the molecule with a high charge transfer rate during excitation [41]. The dipole moment of designed cross conjugated donor molecules also affect the self-assembly of molecules in the fabricating film which facilitates the fabrication process in solar cell device due to anti-parallel arrangement of adjacent molecules and can ultimately improve the crystallinity and order in bulk heterojunction organic solar cell device. The λ_h of molecules can be improved by increasing the strength of the dipole moment. When a molecule has a strong propensity to pack, boosting the dipole moment enhances its ability to self-assemble, resulting in a lengthy supramolecular chain that assists the mobility of charges by letting electrons and holes travel more easily [42].

The calculation of dipole moments for cross conjugated molecules **BDT-C1 to BDT-C6** was also carried out at the same functional and has a direct correlation with the molecular solubility. The calculated dipole moment of entitled molecules is shown in **Table 6**. The increased value of dipole moment resulted in smooth morphology. The calculated dipole moments for **BDT-CR** were found as 6.18 and 7.12 in lower and higher energy states respectively. The designed molecules **BDT-C1 to BDT-C6** have a ground state dipole moment value of 0.99, 5.42, 5.90, 4.58, 0.52, 5.51 Debye correspondingly. Similarly, all cross conjugated molecules have excited state dipole moments of 1.23, 7.23, 7.54, 5.61, 0.86, 6.86 Debye respectively. The values of dipole moment showed that all molecules have a greater value of dipole moment in a higher energy state (excited state) in contrast to the ground state. The order of calculated excited state dipole moment of **BDT-CR and BDT-C1 to BDT-C6** is found as **BDT-C3 > BDT-C2 > BDT-CR > BDT-C6 > BDT-C4 > BDT-C1 > BDT-C5**.

Table. 6 Calculated value of Dipole moments for BDT-CR and BDT-C1-BDT-C6 at B3LYP/6-31 G (d,p)

Molecule	μ_g (D)	μ_e (D)	$\mu_e - \mu_g$ (D)
BDT-CR	6.18	7.12	0.94
BDT-C1	0.99	1.23	0.24
BDT-C2	5.42	7.23	1.81
BDT-C3	5.90	7.54	1.64
BDT-C4	4.58	5.61	1.02
BDT-C5	0.52	0.86	0.33
BDT-C6	5.51	6.86	1.35

The results reveal that BDT-C3 has a higher dipole moment value than other proposed molecules because of its better solubility and photovoltaic stability in DCM. So, it can be recommended as a preferred candidate to be employed in the fabrication of thin film. The graphical representation of dipole moments for BDT-CR and newly architecture molecules (BDT-C1 to BDT-C6) is shown in Fig. 10

3.7. Open circuit Voltage (V_{OC})

V_{OC} is another crucial factor to estimate the organic photovoltaic device performance. It is the maximum voltage across the cell when no current flow and cell work at an open circuit [43]. Our designed donor molecules **BDT-C1 to BDT-C6** along with fullerene derivative PCBM as acceptor was used in ordered to evaluate the V_{OC} values. It is the energy difference between the HOMO energy level of the design donor cross conjugated molecule and the LUMO energy level of the **PC₆₁BM** polymer used as acceptor material. A high value of V_{OC} depends on the greater difference between the bandgap energy of HOMO and LUMO by keeping the HOMO at a low energy level and LOMO at a high energy level [44-47]. The energy gap was calculated between HOMO of newly architecture cross conjugated donor molecules and LUMO of illustrious **PC₆₁BM** acceptor material as shown in **Fig. 11**. **PC₆₁BM** was employed as acceptor material with HOMO and LUMO values of -6.1 and -3.7eV and optimized at selected B3LYP/6-31 G (d, p) basis set combination for quantum chemical exploration.

The following equation (4) can be used to calculate the V_{OC} of newly designed cross conjugated molecules.

$$V_{OC} = \frac{E_{LUMO \text{ of acceptor}} - E_{HOMO \text{ of donor}}}{e} - 0.3 \quad (4)$$

Herein, E is the energy gap of each investigated molecule and e is a charge on each molecule. The **BDT-CR** and designed donor molecules (**BDT-C1 to BDT-C6**) showed the expected V_{OC} value of 1.19, 1.69, 1.2, 1.55, 1.15, 1.75 and 1.26 eV respectively. All current studied designed cross conjugated molecules exhibited greater V_{OC} due to their low-lying HOMO levels. **BDT-C5** with heightened V_{OC} value indicates effective electron transport behavior from HOMO (donor) to LUMO (acceptor). So, we deduce that **BDT-C5: PC₆₁BM** composite could prove as an efficient active layer to boost up the working efficiency of organic photovoltaic cells.

Conclusion

In a recent quantum chemical investigation, cross conjugated molecules (**BDT-C1 to BDT-C6**) are designed to find their applications in an organic photovoltaic device. Different functionals (MPW1MP91, PBEPBE, WB97XD and B3LYP) are employed to optimize the geometries of customized cross conjugated molecules. All parameters (optical and electrochemical) were determined at selected B3LYP/6-31 G (d, p) basis set combination. All newly designed cross conjugated molecules consist of Benzo [1,2-b: 4,5-b'] core unit linked with distinct acceptor moieties through thiophene. The photovoltaic parameters of intended cross conjugated molecules are evaluated by equating them with **BDT-CR** molecule. The λ_{max} of **BDT-C1 to BDT-C6** in DCM solvent lies in the range of 489-748 nm exhibited red-shift behavior than **BDT-CR** (407 nm). The absorption values in presence of solvent (DCM) are found to be high than the gaseous phase, indicates that DCM played an important role to move the absorption band towards red-shift. The bandgap values for newly planned molecules (**BDT-C1 to BDT-C6**) fluctuate between 1.83 and 2.16 eV which are found to be less as compared to **BDT-CR** (2.76 eV) facilitated the electrons transfer from HOMO to LUMO energy level. The maximum value of dipole moment (7.54 Debye) of **BDT-C3** showed that the probability of recombination of charges is less in it as compared to other molecules. Among all tailored molecules **BDT-C4** has the highest electron and hole mobility value showed that this freshly designed molecule could have a plausibly greater chance of electron and hole transfer rate. 2-D map of TDM reveals that electron-density moves along diagonal direction allowing effective charge transfer from D to A. Moreover, calculated V_{OC} values of **BDT-C1-BDT-C6** concerning **PC₆₁BM** suggest that they could transfer the maximum amount of current and can prove as credible candidates for designing efficient photovoltaic cells. Hence, our newly designed cross conjugated molecules would exhibit profound consequences to enhance the optoelectronic features and PCE of the organic photovoltaic cells.

Declarations

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Authors' contributions:

1. Sana Majeed: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content.
2. Shafiq Ur Rehman: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content.
3. Anjum Zia: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically
4. Javed Iqbal: Made substantial contributions to the conception or design of the work; the acquisition, revised it critically for important intellectual content; approved the version to be published; and agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

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Figures

Figure 1

Sketch map of molecular structures of BDT-CR and designed cross conjugated BDT-C1-BDT-C6 molecules.

Figure 2

Column chart display demonstrating the calculated and experimental λ_{max} at four distinct DFT methods.

Figure 3

Optimized geometries of the BDT-CR and designed cross conjugated BDT-C1to BDT-C6 molecules

Figure 4

HOMO-LUMO distribution pattern of BDT-CR and cross conjugated BDT-C1 to BDT-C6 molecules.

Figure 5

Density of state (DOS) of BDT-CR and designed cross conjugated molecules BDT-C1-BDT-C6 around H=HOMO and L=LUMO

Figure 6

Graphical depiction of (a) HOMO and LUMO energy levels (b) band gap for BDT-CR and BDT-C1 to BDT-C6 molecules.

Figure 7

UV-visible absorption spectra for reference BDT-CR with four different functionals in both chloroform (right) and gaseous phases (left).

Figure 8

UV-Visible absorption spectra for cross conjugated designed molecules BDT-C1 to BDT-C6 in solvent (right) and gaseous phase (left)

Figure 9

Transition density matrix map for BDT-CR and designed BDT-C1 to BDT-C6 molecules where D = donor, B = bridge and A = acceptor.

Figure 10

Graphical display of dipole moments for BDT-CR and designed BDT-C1 to BDT-C6 molecules.

Figure 11

Estimated open circuit voltage of BDT-CR and BDT-C1 to BDT-C6 designed cross conjugated molecules with regard to PCBM polymer acceptor molecule.

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