

Research Article

Correlating Structural Properties and Performance in Thiophene-Bridged Benzodithiophene Donors for Bandgap Narrowing and Efficient Charge Transport in Organic Photovoltaics Cells (OPVCs): Insights from DFT/TD-DFT

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Abstract

Studying correlating structural properties and performance is critical for the rational advancement of donor materials in organic photovoltaics cells (OPVCs). In this study, thiophene-bridged benzodithiophene (BDT) donors were strategically engineered to probe the impact of π -bridge modulation on electronic structure, optical transitions, and photovoltaic-relevant descriptors using density functional theory (DFT) and time-dependent DFT (TD-DFT). Systematic extension of π -conjugation induces substantial bandgap narrowing from 1.68 to 2.01 eV through enhanced frontier orbital delocalization and reduced HOMO-LUMO separation. This structural modulation produces a pronounced bathochromic shift in absorption maxima up to 815 nm, enabling near-infrared light harvesting. Frontier orbital and density of states analyses reveal intensified intramolecular charge transfer from the electron-rich BDT core to electron-deficient terminals, promoting effective charge separation. Increased dipole moments and oscillator strengths further support improved excitonic dissociation propensity. Theoretical evaluation of open-circuit voltage (V_{oc}) and exciton binding energy (E_b) derived from calculated energy levels suggests favorable donor-acceptor energetic alignment and reduced Coulombic binding. These findings establish π -bridge engineering as a decisive molecular strategy for governing bandgap modulation and charge transport potential in next-generation BDT-based OPVCs systems.

Keywords

Benzodithiophene, π -bridge Engineering, Bandgap Narrowing, Intramolecular Charge Transfer

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1. Introduction

The growing global energy crisis has intensified the demand for renewable and sustainable energy sources to meet increasing electricity requirements [1, 2]. Solar energy is one of the promising solutions among these alternatives because of its abundance, renewability, and its compatibility with the environment [3, 4]. As of today, solar photovoltaics (PVs) form a significant part of solar energy harvesting, and ongoing effort to make them more efficient, cost-effective, and steady [3, 5].

Organic photovoltaics Cells (OPVCs) have evolved rapidly over the past decade, achieving power conversion efficiencies (PCEs) exceeding through the development of high-performance donor-acceptor systems and optimized device design [6, 7]. The emergence of non-fullerene acceptors (NFAs) has significantly reshaped the performance landscape, shifting the focus toward molecular-level tuning of donor materials to achieve precise energy alignment, enhanced absorption coverage, and efficient charge transport [8-10]. Despite remarkable progress, further efficiency improvements and long-term stability remain contingent upon rational molecular engineering strategies that establish predictable correlations between structural design and device-relevant properties. Consequently, structure-property-performance relationships have become a central objective in the development of next-generation OPVCs materials [11-13].

Among conjugated donor molecule, benzodithiophene (BDT) has emerged as one of the most successful and widely employed cores in high-efficiency polymer and small-molecule donors [14, 15]. The planar and rigid structure of BDT promotes strong π - π stacking interactions and facilitates effective charge delocalization along the conjugated backbone [16, 17]. Furthermore, its synthetic flexibility allows systematic modulation through side-chain engineering, π -bridge insertion, and terminal group functionalization [18, 19]. State-of-the-art BDT-based donors such as PM6 [20], D18 [21], PBDB-T derivatives [22], and PTB7-Th [23] have demonstrated excellent electronic tunability and compatibility with advanced non-fullerene acceptors, leading to high open-circuit voltages and efficient charge extraction [24, 25].

The electronic characteristics of BDT systems can be tailored through structural modification, enabling control over frontier molecular orbital (FMO) energy levels, optical band gaps, and intermolecular interactions [18, 26]. Such tunability makes BDT an ideal platform for investigating molecular design principles that govern optoelectronic performance. The π -Bridge engineering has proven to be a powerful strategy for modulating the optoelectronic properties of conjugated donor materials [27, 28]. The insertion or extension of π -conjugated units between donor and acceptor segments directly influences conjugation length, torsional planarity, and electronic coupling. Thiophene-based bridges, in particular, are attractive due to their electron-rich character, favorable coplanarity,

and ability to enhance orbital overlap along the molecular backbone [28, 29].

Systematic extension of thiophene bridges can reduce the HOMO-LUMO energy separation by stabilizing the LUMO and slightly elevating the HOMO, thereby inducing bandgap narrowing [30]. This structural modification often results in bathochromic shifts in absorption spectra, extending light harvesting into the near-infrared region and improving photocurrent generation potential. However, excessive conjugation may also affect energetic alignment and charge recombination dynamics. Therefore, controlled π -bridge modulation is essential to balance bandgap reduction with optimal photovoltaic performance [31-33]. The photovoltaic performance of donor materials is governed not only by bandgap tuning but also by charge separation efficiency, exciton dissociation propensity, and carrier mobility. Molecular planarity enhances π - π stacking and facilitates intermolecular charge transport, while frontier orbital delocalization influences excitonic binding and charge recombination dynamics. Dipole moment distribution and electrostatic potential landscapes further regulate donor-acceptor interfacial interactions [34, 35].

Establishing a quantitative structure-property-performance framework requires correlating geometric parameters, frontier orbital distributions, density of states contributions, and optical transitions with device-relevant descriptors such as open-circuit voltage (V_{oc}) and exciton binding energy (E_b) [33, 36]. Comparative analysis with recently reported high-performance BDT donors provides a benchmark for evaluating the effectiveness of new structural modifications. Such integrated correlation analysis enables predictive material design rather than empirical optimization [34, 35, 37].

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations offer powerful tools for elucidating electronic structure and excited-state behavior at the molecular level [38, 39]. These methods provide detailed insights into optimized geometries, frontier molecular orbital alignment, and density of states distributions, electrostatic potential mapping, absorption spectra, and intramolecular charge transfer characteristics. Theoretical evaluation of photovoltaic descriptors derived from calculated energy levels further enables preliminary assessment of device compatibility before experimental synthesis [20, 23, 32, 40].

In the present work, thiophene-bridged benzodithiophene donor molecules were systematically designed to investigate the influence of π -bridge modulation on structural planarity, frontier molecular orbital distribution, optical absorption characteristics, and photovoltaic-relevant descriptors. By integrating geometric optimization, electronic structure analysis, density of states evaluation, intramolecular charge transfer mapping, and derived performance parameters, we establish a comprehensive structure-property-performance correlation framework. The HOMO and LUMO energy gaps, density of

states, and distribution of frontier molecular orbitals were examined using DFT with (B3LYP) functional and 6-31G (d, p) basis set. Further, TD-DFT methods were used to analyze UV-visible absorption energies and transitions in the UV-visible and infrared spectral areas. Structural analysis was performed, such as bond lengths, bond angles, and dihedral angles, which result in confirming molecular planarity. The comparison indicated that one molecule, M2, had a narrower bandgap, desirable absorption qualities, and enhanced charge-transfer potentiality as compared to other designed molecules. Such characteristics indicate that M2 is a good candidate to prepare transparent organic solar cells with a higher PCE.

The protocol includes molecular design and π -bridge engineering, geometry optimization, frontier molecular orbital (FMO) analysis, optical property evaluation via TD-DFT, charge transfer characterization (TDM and MEP), and calculation of photovoltaic performance descriptors (Voc, exciton binding energy, and reorganization energy) to establish structure-property-performance correlations.

2. Computational Methodology

All computational calculations were performed using the Gaussian 09 software package. Ground-state geometries of the reference and thiophene-bridged benzodithiophene (BDT) donor molecules were fully optimized without symmetry constraints employing density functional theory (DFT) at the B3LYP/6-31G (d, p) level [41, 42]. The B3LYP hybrid functional was selected due to its established reliability in describing relative electronic trends and frontier orbital distributions in conjugated donor-acceptor systems. Subsequent vibrational frequency analysis was carried out at the same level of theory to confirm that all optimized structures correspond to true minima on the potential energy surface, as verified by the absence of imaginary frequencies. Frontier molecular orbital (FMO) energies, including the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), were obtained from optimized geometries [14, 15, 43]. The electronic bandgap (E_g) was calculated as,

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$$

Time-dependent DFT (TD-DFT) calculations were performed at the same theoretical level to investigate excited-state properties, including excitation energies, maximum absorption wavelengths (λ_{max}), and oscillator strengths (f). Light-harvesting efficiency (LHE) was estimated using:

$$\text{LHE} = 1 - 10^{-f}$$

To analyze the electronic distribution and orbital contributions, density of states (DOS) calculations were conducted using GaussView software. This analysis enabled evaluation of donor-acceptor contributions to frontier orbitals and facili-

tated correlation between structural modification and electronic structure evolution. Molecular electrostatic potential (MEP) surfaces were generated to visualize charge distribution and identify electron-rich and electron-deficient regions across the molecular framework. Transition density matrix (TDM) analysis was performed to evaluate spatial separation between electron and hole densities in the excited state, providing insight into intramolecular charge transfer (ICT) behavior. Dipole moments were calculated in both the gas phase and in solution using the polarizable continuum model (PCM) to assess the influence of dielectric environment on charge separation characteristics and polarization effects relevant to device operation. Photovoltaic performance descriptors were derived from calculated energy levels. The theoretical open-circuit voltage (V_{oc}) was estimated using:

$$V_{oc} = |E_{\text{HOMO}}^{\text{Donor}}| - |E_{\text{LUMO}}^{\text{Acceptor}}| - 0.3$$

Where the empirical energy loss of 0.3 eV accounts for non-radiative recombination losses typically observed in organic photovoltaic systems. A representative non-fullerene acceptor energy level was used for alignment estimation. Exciton binding energy (E_b), reflecting Coulombic interaction between electron-hole pairs, was approximated as:

$$E_b = E_g - E_{\text{optical}}$$

Where E_{optical} corresponds to the lowest singlet excitation energy obtained from TD-DFT calculations. To evaluate charge transport potential, internal reorganization energies for hole (λ_h) and electron (λ_e) transfer were considered within the framework of Marcus theory. The reorganization energy was determined using:

$$\lambda = (E_0^+ - E_0) + (E_+^0 - E_+)$$

Where E_0 and E_+ represent total energies of neutral and charged species at their optimized geometries, and E_0^+ and E_+^0 denote single-point energies of charged and neutral species evaluated at the geometry of the opposite state. Lower reorganization energy indicates reduced structural relaxation during charge transfer and suggests enhanced carrier mobility. All molecular orbital visualizations, electrostatic potential maps, and excited-state density plots were generated using GaussView. The integrated computational protocol enables systematic establishment of structure-property-performance correlations in thiophene-bridged BDT donor systems.

3. Results and Discussions

3.1. Molecular Design Strategy and Optimized Geometrical Analysis

The molecular geometry of the investigated donor systems,

namely the reference molecule (R) [14], mono-thiophene-extended derivative (M1), and di-thiophene-extended derivative (M2), are illustrated in Figure 1. All three molecules adopt a donor- π -acceptor (D- π -A) configuration centered on a benzodithiophene (BDT) core. The design strategy involves systematic extension of the π -conjugated pathway through the insertion of thiophene units between the donor core and terminal acceptor groups [44, 45]. This stepwise π -bridge elongation enables controlled modulation of conjugation length, backbone planarity, and electronic coupling while maintaining the fundamental D-A framework [46, 47]. Geometry optimization at the B3LYP/6-31G (d, p) level reveals that the conjugated backbones of all molecules are nearly planar, a structural requirement for efficient π -electron delocalization [48]. However, subtle but significant differences emerge upon thiophene extension as in the reference molecule (R), slight torsional deviations are observed at the donor-bridge interface, which partially limit conjugation continuity [49, 50]. Upon doping of one thiophene unit in M1, the dihedral angles between adjacent aromatic segments decrease, indicating improved coplanarity and enhanced orbital overlap [51, 52]. The further extension to M2 results in an even more linearized backbone, suggesting reduced steric hindrance and stronger π - π conjugative interaction across the molecular framework [53]. Bond length analysis further supports this trend as C-C bond distances along the conjugated pathway exhibit partial bond-

length equalization in M1 and M2 compared to R, reflecting increased electron delocalization. Such bond homogenization is a characteristic signature of extended conjugation and resonance stabilization. The enhanced delocalization in M2 indicates a greater degree of π -electron mobility along the backbone, which is expected to lower electronic confinement and facilitate charge transport [53, 54]. From a structural standpoint, the progressive elongation of the thiophene bridge effectively increases the effective conjugation length (ECL) of the molecule. Increased ECL reduces the quantum confinement effect and stabilizes the excited state, leading to bandgap narrowing as observed in subsequent electronic analysis. Additionally, improved backbone planarity enhances intermolecular stacking potential, which is crucial for efficient charge carrier mobility in solid-state OPVCs applications [23, 44, 45]. The structural evolution from R to M2 thus establishes a clear geometrical basis for electronic modulation. By systematically enhancing conjugation length and backbone coplanarity, thiophene bridge engineering provides a rational approach to tuning frontier orbital distribution, optical absorption characteristics, and charge transport propensity. These geometrical modifications form the foundational structural component of the overall structure-property-performance correlation explored in this study [22, 34, 54].

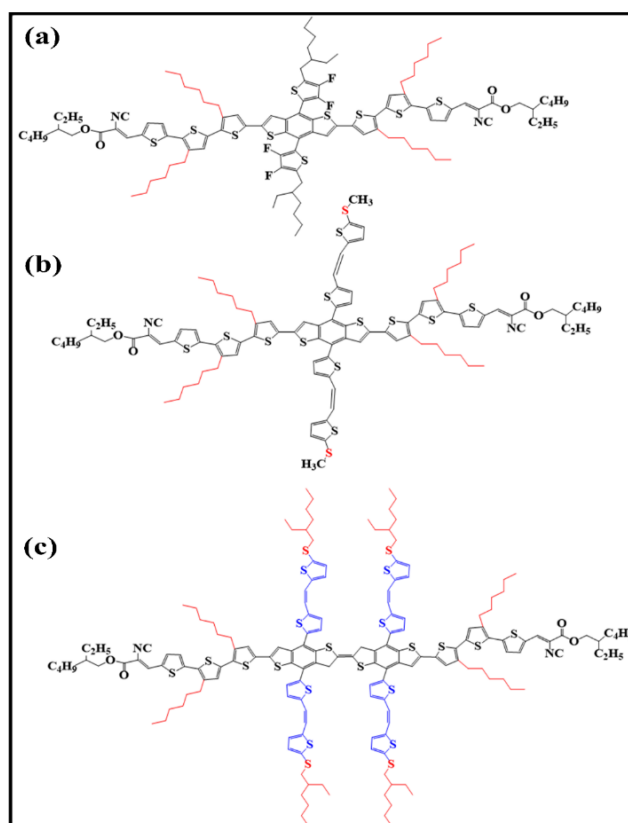


Figure 1. Optimized molecular structures of the investigated thiophene-bridged benzodithiophene (BDT) donor systems: (a) reference molecule (R) [14], (b) mono-thiophene-extended derivative (M1), and (c) di-thiophene-extended derivative (M2).

The π -bridge extension progressively increases conjugation length and structural planarity, enabling systematic investigation of structure-driven modulation of electronic and optical properties.

3.2. Frontier Molecular Orbitals (FMOs) Analysis

A comprehensive understanding of the frontier molecular orbital (FMO) characteristics is essential for rationalizing the optoelectronic behavior of donor materials intended for organic photovoltaic (OPV) applications. The HOMO and LUMO energy levels govern light absorption, charge transfer dynamics, open-circuit voltage (Voc), and overall device efficiency [14, 55]. To elucidate the impact of systematic thiophene π -bridge elongation on the electronic properties of benzodithiophene (BDT)-based donors, density functional theory (DFT) calculations were performed at the B3LYP/6-31G (d, p) level. The calculated HOMO and LUMO energies, along with the corresponding band gaps, are summarized in Table 1, while their energy alignment and spatial distributions are illustrated in Figures 2, 3, and 4. As shown in Table 1, the R molecule exhibits a HOMO energy of -4.87 eV and a LUMO energy of -2.86 eV, corresponding to a bandgap (E_g) of 2.01 eV. Upon insertion of a thiophene π -bridge in M1, both frontier orbitals undergo stabilization, with the HOMO shifting to -5.32 eV and the LUMO to -3.44 eV. This coordinated stabilization results in a reduced bandgap of 1.88 eV. Further elongation of the conjugated backbone in M2 amplifies this trend, lowering the HOMO to -5.55 eV and the LUMO to -3.87 eV, thereby producing a significantly narrowed bandgap of 1.68 eV. The progressive decrease in E_g from R to M2 (a total reduction of 0.33 eV) clearly demonstrates that π -bridge making is highly effective in tuning the electronic structure of these donor systems [14, 55, 56]. The energy level diagram presented in Figure 2 visually corroborates this trend as a systematic downward shift of both HOMO and LUMO levels is observed with increasing thiophene incorporation. Importantly, the LUMO stabilization is slightly more pronounced relative to the HOMO, indicating enhanced electron affinity and stronger acceptor character as conjugation extends [57, 58]. This balanced modulation of frontier orbitals is advantageous for OPVCs applications because it simultaneously broadens light absorption (through bandgap reduction) and maintains a sufficiently deep HOMO level to ensure oxidative stability [18, 59]. The gradual narrowing of the bandgap suggests improved solar photon harvesting capability, particularly in the lower-energy visible region, which is critical for enhancing short-circuit current density [60, 61].

The origin of this electronic modulation can be directly correlated with the optimized geometrical structures shown in Figure 3. The reference molecule displays moderate planarity across its conjugated backbone; however, slight torsional distortions between aromatic segments limit complete π -electron

delocalization. The introduction of a thiophene bridge in M1 enhances structural coplanarity by reducing dihedral angles between adjacent rings, thereby strengthening π - π orbital overlap [62, 63]. This improved overlap facilitates more effective electronic communication between the donor and acceptor moieties. In M2, the presence of two thiophene units further extends the effective conjugation length and promotes a more linearized backbone. Bond-length equalization along the conjugated pathway indicates enhanced resonance stabilization and reduced localization of π -electrons. Consequently, the geometrical evolution from R to M2 establishes the structural foundation for the observed frontier orbital stabilization and bandgap narrowing [64, 65].

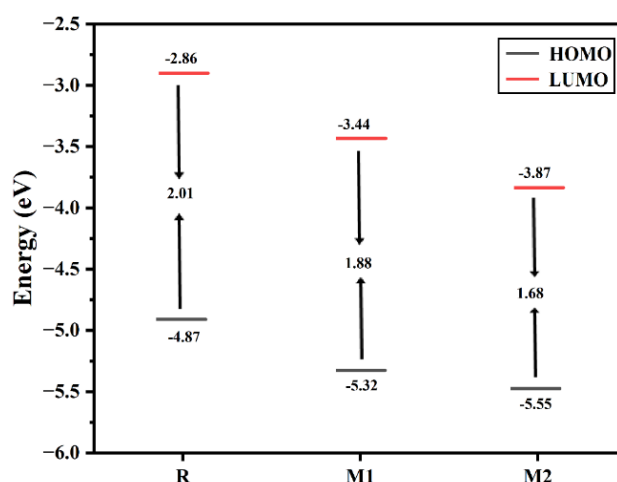


Figure 2. Frontier molecular orbital energy levels of the reference molecule (R) and the thiophene-extended derivatives (M1 and M2).

The spatial distributions of the frontier orbitals, depicted in Figure 4, provide additional mechanistic insight into the electronic behavior of these systems. In the reference molecule, the HOMO density is predominantly localized over the BDT donor core and partially extends toward adjacent thiophene units, while the LUMO is mainly concentrated on the terminal electron-withdrawing segments [64, 65]. This distribution confirms the intrinsic donor-acceptor (D-A) nature of the molecular framework and indicates moderate intramolecular charge transfer (ICT) character. In M1, the HOMO becomes more extensively delocalized along the π -bridge, and the LUMO distribution broadens across the conjugated backbone, reflecting improved donor-acceptor coupling. The enhanced delocalization reduces electronic confinement and facilitates more efficient charge redistribution upon excitation [29, 66]. The most pronounced orbital delocalization is observed in M2. Both HOMO and LUMO orbitals extend over a larger portion of the molecular backbone, demonstrating strengthened conjugative interaction and improved electronic coherence [59, 67, 68]. The increased spatial overlap and extended π -electron

network promote stronger intramolecular charge transfer characteristics, which are essential for efficient exciton dissociation in OPV devices [69, 70]. The broader delocalization also suggests lower reorganization energy and potentially enhanced charge carrier mobility, factors that directly influence fill factor and overall power conversion efficiency [59, 64, 65]. The progressive thiophene insertion increases conjugation length and backbone planarity, which enhances orbital overlap, stabilizes frontier energy levels, and narrows the electronic bandgap. This systematic electronic tuning strengthens donor-acceptor interactions and promotes intramolecular

charge transfer, thereby improving the optoelectronic suitability of the designed molecules. The results confirm that controlled π -bridge elongation represents an effective molecular engineering strategy for optimizing BDT-based donor materials for advanced organic photovoltaic applications [68, 69, 71].

The systematic π -bridge elongation induces progressive modulation of HOMO and LUMO energy levels, resulting in bandgap narrowing from R to M2. The coordinated elevation of the HOMO and stabilization of the LUMO demonstrate the effectiveness of thiophene incorporation in tuning electronic structure for enhanced optoelectronic performance.

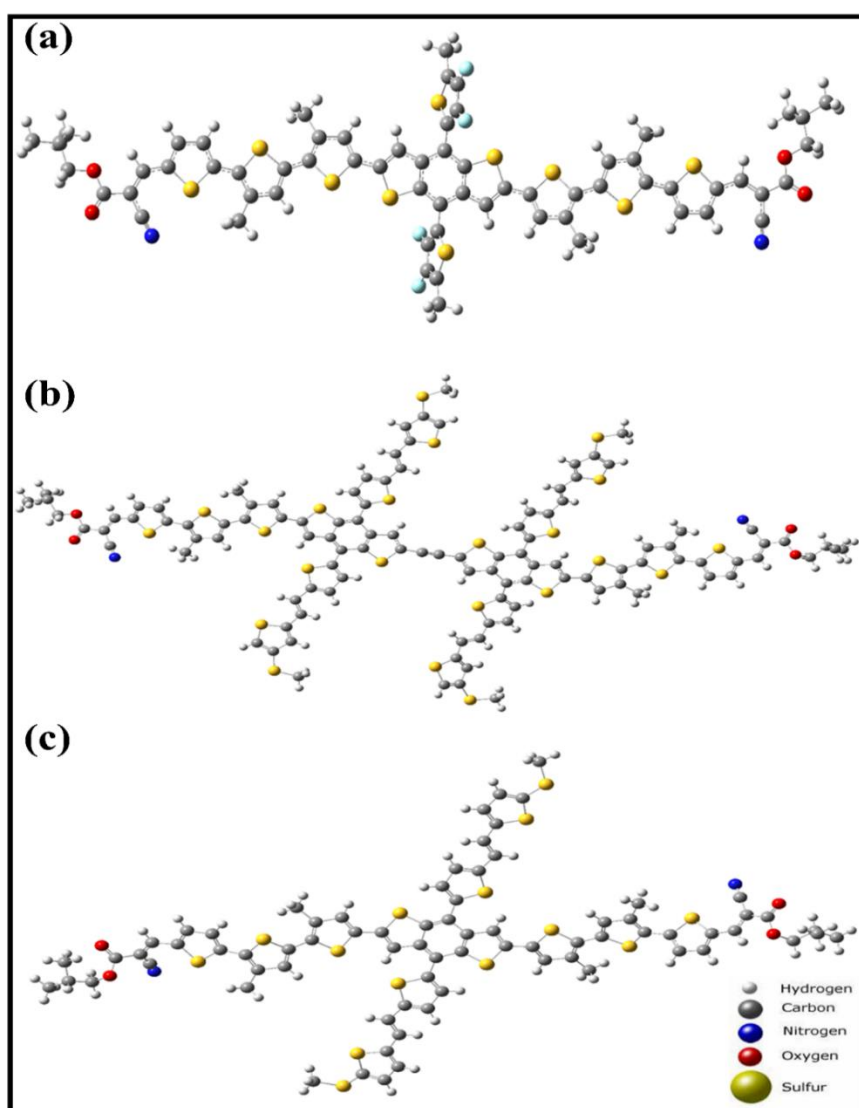


Figure 3. Ground-state optimized geometries of (a) the reference molecule (R), (b) mono-thiophene-extended derivative (M1), and (c) di-thiophene-extended derivative (M2), obtained at the B3LYP/6-31G (d, p) level of theory.

Progressive thiophene bridge insertion enhances backbone planarity and extends conjugation length, promoting improved orbital overlap and structural conditions favorable for charge delocalization and transport.

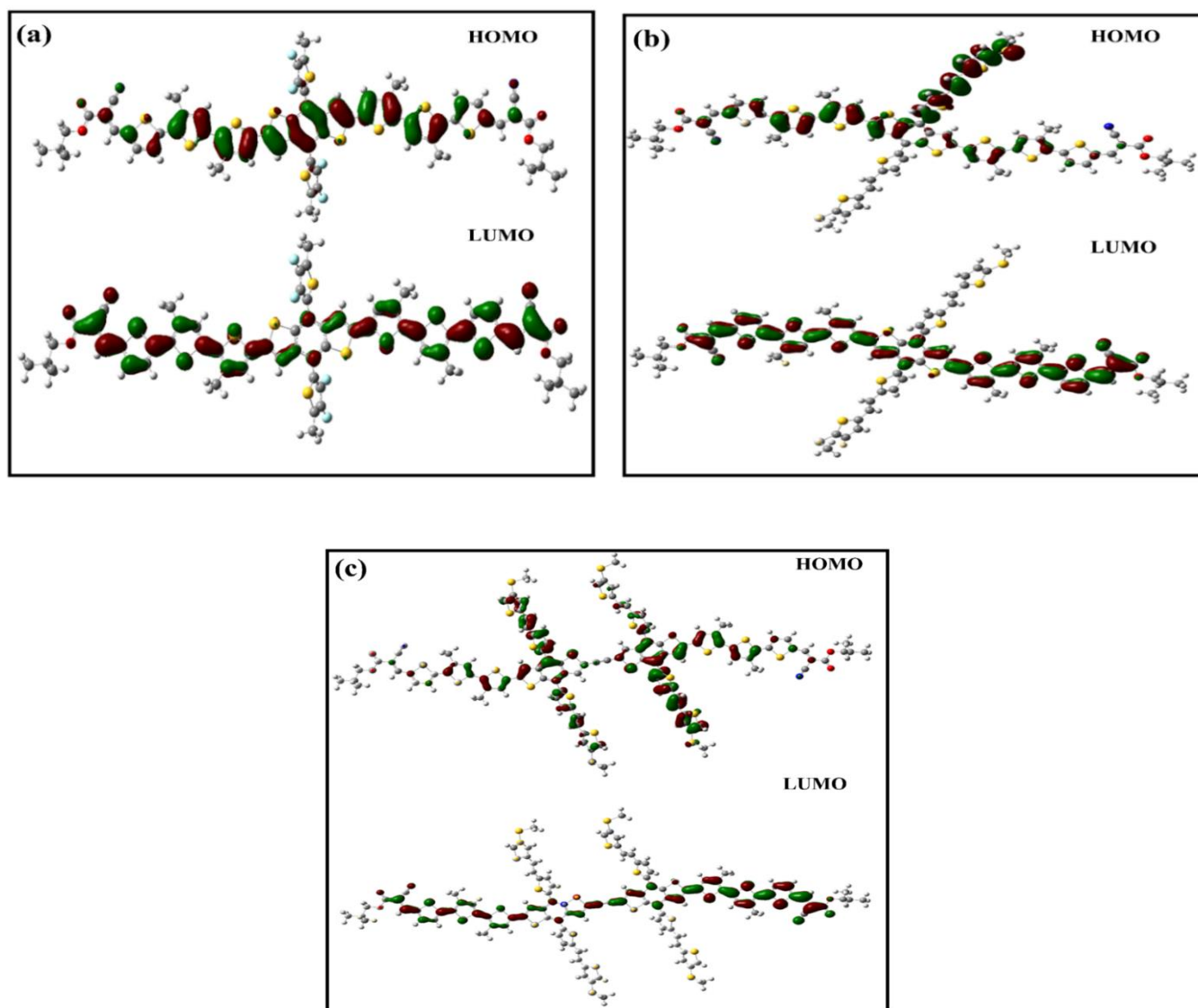


Figure 4. Spatial distribution of frontier molecular orbitals for (a) the reference molecule (R), (b) M1, and (c) M2.

The HOMO is predominantly localized over the benzodithiophene donor core and conjugated backbone, while the LUMO is mainly distributed over the electron-withdrawing terminal units, indicating pronounced donor-acceptor character. Increasing thiophene bridge extension enhances orbital delocalization and intramolecular charge transfer (ICT), contributing to electronic coupling and bandgap reduction.

3.3. Optical Properties and Excited-State Characteristics

The optical absorption behavior of the reference molecule and its thiophene-extended derivatives (M1 and M2) was investigated using time-dependent density functional theory (TD-B3LYP/6-31G (d, p)). The absorption spectra are presented in Figure 5, while the calculated absorption maxima (λ_{max}), excitation energies (Ex), and oscillator strengths (f) are summarized in Table 1. As shown in Figure 5(a), the reference molecule exhibits two major absorption features in the visible

region. A lower-intensity band appears around 400–450 nm, attributed to localized $\pi-\pi^*$ transitions within the conjugated backbone. The dominant absorption band occurs at 671.4 nm, corresponding to an excitation energy of 1.84 eV. This transition originates primarily from the HOMO $\rightarrow$ LUMO excitation and reflects the donor-acceptor electronic architecture discussed in Section 3.2. The oscillator strength ($f = 0.99$) indicates efficient photon absorption and moderate transition dipole moment [29, 72, 73]. For M1, shown in Figure 5(b), the primary absorption maximum shifts slightly to 651.4 nm (1.90 eV), indicating a small hypsochromic (blue) shift relative to R [14, 55]. This behavior suggests that the introduction of a single thiophene bridge induces subtle structural torsion or partial disruption in planarity, slightly limiting effective π -conjugation. However, despite the marginal blue shift, the oscillator strength increases significantly to 1.46. This increase reflects enhanced transition probability and stronger electronic coupling within the conjugated framework [68, 69, 71]. In contrast, M2 demonstrates a pronounced bathochromic shift, as

clearly illustrated in Figure 5(c). The maximum absorption wavelength extends to 815.2 nm with a reduced excitation energy of 1.52 eV, entering the near-infrared (NIR) region. This substantial red shift confirms that the insertion of two thiophene bridges effectively extends conjugation length, enhances backbone planarity, and strengthens π -electron delocalization. The oscillator strength further increases to 1.97, indicating superior light-harvesting capability and strong intramolecular electronic interaction [18, 65, 74]. The dominant electronic transitions for all molecules arise primarily from HOMO $\rightarrow$ LUMO excitations, confirming strong π - π^* character with pronounced intramolecular charge transfer (ICT) contribution. As previously shown in the frontier molecular orbital analysis (Figure 5), the HOMO is localized mainly over the benzodithiophene donor core and extended conjugated backbone, while the LUMO is distributed toward the electron-withdrawing terminal units. This spatial separation facilitates effective charge redistribution upon photoexcitation [14, 61, 68]. Oscillator strength is directly related to the transition dipole moment and photon absorption probability. The increasing f values indicate stronger electronic coupling and

enhanced charge-transfer character in the excited state. The high oscillator strength of M2 suggests superior photon absorption efficiency and increased exciton generation capacity under solar illumination. This trend strongly supports the structure-property relationship proposed in this study, where thiophene extension amplifies electronic delocalization and transition intensity [28, 75, 76].

Table 1. Calculated absorption maxima ($\lambda_{\max}$), oscillator strengths (f), and excitation energies (E_x) for R, M1, and M2 at the TD-B3LYP/6-31G (d, p) level.

Molecules	$\lambda_{\max}$ (nm)	f	E_x (eV)
R	671.4	0.99	1.84
M 1	651.4	1.46	1.90
M 2	815.2	1.97	1.52

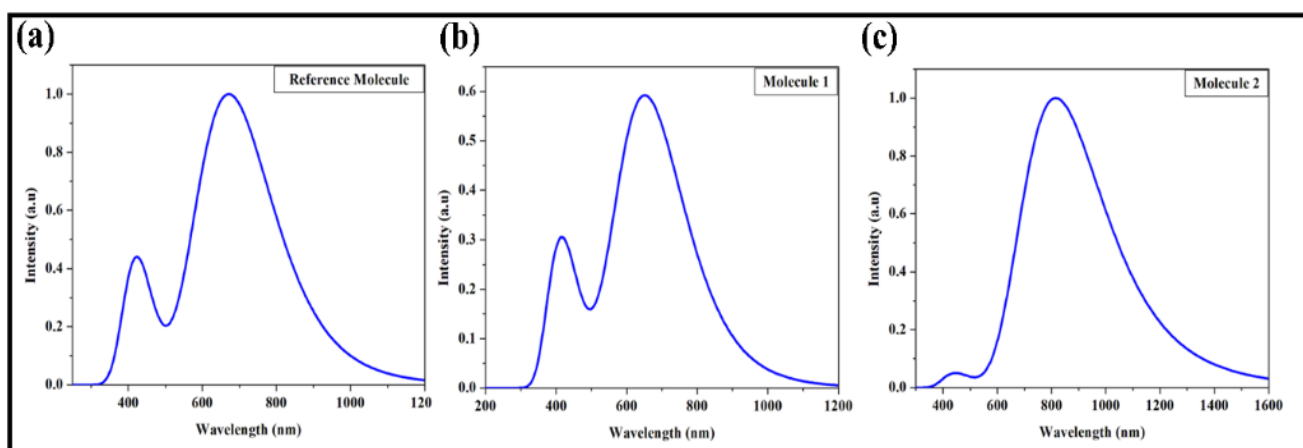


Figure 5. The DFT UV-Vis absorption spectra of (a) reference molecule (b) mono-thiophene-extended derivative (M1), and (c) di-thiophene-extended derivative (M2) calculated at the TD-B3LYP/6-31G (d, p) level.

Systematic thiophene bridge insertion modulates absorption behavior, with M2 exhibiting significant bathochromic shift into the near-infrared region and enhanced absorption intensity, indicating superior light-harvesting capability.

3.4. Effect on Bond Lengths and Dihedral Angles

The geometric parameters of the studied benzodithiophene-based molecules were studied to determine how the molecular modification affects the bond lengths and the dihedral angles which consequently affects the conjugation, planarity, and the total electronic behavior of the system. Table 2 summarizes the predicted values of the bond lengths and dihedral angle

values of the reference molecule and the designed compounds (M1 and M2). This indicates that minor structural changes caused by the addition of π -bridges and substituents cause detectable shifts in the internal geometry, which indicates the change in electronic delocalization and steric effects [77-79]. The inter-bond distance between the carbon atoms C12-C20 to C17-C19 is both 1.43 Å and the dihedral angles (C11-C12-C20-C28 and C16-C17-C19-C29) were found to be almost linear at 179.96° and 179.98°, respectively, corresponding to the reference molecule (R) [80, 81]. The values imply that the reference compound is nearly planar over the conjugated backbone, as expected of benzodithiophene derivatives and necessary to allow the p-electron delocalization of the mole-

cule [82, 83]. When this is substituted in M1, some slight elongation is seen in the inter-bond distances (1.44Å in both C12-C20 and C17-C19). This slight increase in the length of the bond is the result of addition of thiophene π -bridges which increase conjugation but at the same time redistribute electron density along the backbone in a slight manner. It is found that the dihedral angles in M1 are 179.23d° and 179.26° which shows that the molecule is almost planar with the direction of torsion inverted with reference to the reference. This tiny departure of planarity indicates that M1 is highly intramolecularly conjugated, and the rise in the dihedral angles ascertains better resonance stabilization throughout the donor-bridge-acceptor pathway. With M2, when further modified with electron-withdrawing cyano-functional groups, both the geometrical and electronic changes are produced [69, 84]. The inter-

bond distances C12-C20 and C17-C19 become smaller, 1.42Å, respectively, which reflects the increased π -bonding nature and the increased conjugation of the substituents which are strongly electronegative. Nevertheless, in M2, the dihedral angles decrease to 168.60° and 168.59°, indicating a little twisting of the molecule backbone, as compared to R and M1 [85, 86]. This slight torsional twist is probably caused by steric hindrance of the heavy cyano-groups with the side atoms of the π -bridge. Nevertheless, M2 is shorter bond lengths are offset by allowing high degrees of π -delocalization of electrons and efficient charge transfer across the conjugated structure. On the whole, the analysis shows that the substitution pattern and electronic character of the terminal groups are the important determinants of the bond length and dihedral angle values [87, 88].

Table 2. Predicted values of bond lengths (Å) and dihedral angles (Degree) of investigated molecule (R, M1 and M2).

Molecules	Acceptors	Bond Lengths (Å)	Dihedral Angles (Degree)
R	1	C12-C20	C11-C12-C20-C28
		1.43	-179.96
	2	C17-C19	C16-C17-19-C29
		1.43	-179.98
M1	1	C12-C20	C11-C12-C20-C28
		1.44	179.23
	2	C17-C19	C16-C17-19-C29
		1.44	179.26
M2	1	C12-C20	C11-C12-C20-C28
		1.42	-168.60
	2	C17-C19	C16-C17-19-C29
		1.42	-168.59

3.5. Molecular Electrostatic Potential Analysis

The Molecular electrostatic potential (MEP) maps of compounds of interest (R), M1, and M2 were solved at the B3LYP/6-31G (d, p) level in order to visualize the electronic charge distribution, and areas vulnerable to electrophilic or nucleophilic interactions [89]. The surfaces of MEPs depicted in Figure 6 give the clear insight into distribution of electron density of each molecule and the effect of molecular modification on charge polarization. A color gradient is used to represent the potential as with the red regions representing those parts of negative electrostatic potential related to the electron-rich regions and the blue regions representing those parts of positive potential related to the electron-deficient regions. The

intermediate colors like yellow and green represent areas of rather neutral potential. As in reference molecule (Figure 6(a)), the red spots are mainly concentrated on the oxygen and sulfur atoms of the benzodithiophene (BDT) core which means that the concentration of electrons density in the area of the heteroatoms occurs. The most common sites of positive potentials are located mostly over the hydrogen atoms that are attached to the conjugated carbon system, thus indicating possible locations of nucleophilic attack. The R distribution is moderate in charge separation with the density of electrons being predominantly concentrated in the donor part of the molecule, which suggests that the extent of intramolecular charge transfer (ICT) is limited [14, 15, 90, 91]. In the case of the designed molecule, M1 (Figure 6(b)), thiophene π -bridges and altered terminal groups result in wider distribution of electron density

along the conjugated backbone. The red zones become less localized as the π -system and the blue regions are observed to be localized towards the end groups of the acceptor opposite the terminal hydrogen atoms [92]. This means an increase in charge polarization and more pronounced donor-acceptor nature than that of the reference molecule [93]. The long conjugation via the thiophene linkers enhances electronic interaction between the acceptor and the donor moieties and hence higher transfer of charge between them during photoexcitation [94]. The more important modification is noticed in the MEP map of M2 (Figure 6(c)) that represents intense red areas over the cyano and oxygen atom of the acceptor moieties and intense blue areas over the hydrogen atom of the donor side.

This sharp difference in potential indicates a high electron-withdrawing potential of the cyano groups that withdraw electron density of the donor molecule to the acceptor fragment leading to efficient intramolecular charge transfer [95]. The gradient across the surface of the molecule of M2 is clearer and more continuous than in the case of R and M1, which represents an increased charge separation and an increase in molecular polarity. The MEP surfaces, therefore, supports the assertion that the conjugation and the donor-acceptor charge interactions are not only improved by the molecular modification of the BDT core with thiophene linkers and cyano-substituted acceptors [92, 93].

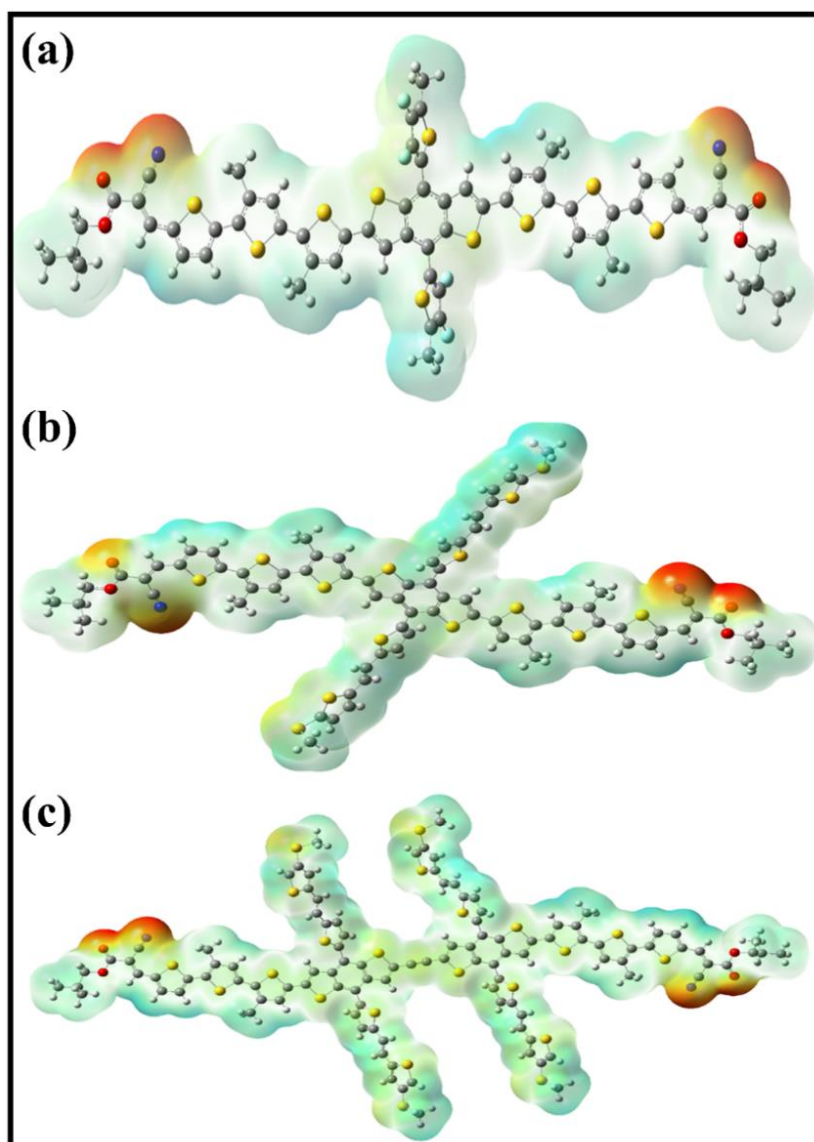


Figure 6. Molecular electrostatic potential (MEP) maps of (a) the reference molecule (R), (b) mono-thiophene-extended derivative (M1), and (c) di-thiophene-extended derivative (M2) calculated at the B3LYP/6-31G (d, p) level. The color scale represents electrostatic potential distribution ranging from electron-rich regions (red, negative potential) to electron-deficient regions (blue, positive potential). The progressive thiophene bridge incorporation modulates charge distribution along the conjugated backbone, enhancing donor-acceptor polarization and facilitating intramolecular charge transfer, particularly in M2.

3.6. Dipole Moment Calculations (DMCs)

Dipole moments of the reference molecule and the designed molecules (M1 and M2) in gaseous and solvent phases were calculated using the B3LYP/6-31G (d, p) level and the results are summarized in Table 3. The values of the dipole moments vary steadily with R to M2 and show an improved separation of charge with change of the molecule. At the gas phase the dipole moment of the reference molecule is almost zero with a value of 0.0026 D, indicating that the electron density is symmetrically distributed in the molecule and the charge-transfer nature of the molecule is low [73]. At solvent evaluation, this value is very low (0.002 D) which supports the idea that the reference molecule has very weak polarity and a limited number of donor-acceptor interactions. When the structure is modified, the dipole moment is clearly increased in M1 as it gives values of 0.6943 D in the gas phase and 0.7920 D in the solvent [29]. This is due to the addition of thiophene π -bridges which enhance conjugation and facilitates the partial transfer of charge through the donor BDT core to the acceptor moieties. The polarity of M1 is moderate but the larger dipole moment than the reference molecule suggests that the intramolecular charge separation is improved in M1 and thus dissociation can occur upon illumination of the sample [96-98].

The calculated molecule M2 has the maximum dipole moment of all the analyzed compounds with the 1.4530 D in the gas and 2.2504 D in solution. This extreme rise indicates that M2 has a significantly greater internal electric field, which significantly increases the capacity of M2 to separate photoinduced charges [100]. The large dipole moment in the solvent phase also indicates that solvation stabilizes the polar form, which may result from it having preferable interactions with the solvent dipoles, rather than negative interactions with the polar cyano-substituted groups at the terminal groups. The high value of the dipole moment in M2 is an immediate result of the high capacity of the cyano withdrawers of the electrons and the long π -conjugation achieved by the thiophene linkages. The consequence of this structural arrangement is that it causes an increased spatial separation between the centers of positive and negative charge, so enhanced charge-transfer efficiency is confirmed. A large dipole moment is desirable in organic photovoltaic devices as it aids in efficient charge separation as well as reduces electron-hole recombination at the donor-acceptor interface. The increased polarity of M2 will also give it an enhanced capability to align well with the acceptor materials e.g. the fullerene or non-fullerene derivatives, enhancing the interfacial electric field and enabling easy extraction of charge in the active layer of the solar cell.

Table 3. Calculated gaseous and solvent dipole moments of the studied molecules at the B3LYP/6-31G (d, p) level.

Molecules	Gaseous Dipole moment (D)	Solvent Dipole moment (D)
Reference	0.0026	0.002
Molecule 1	0.6943	0.7920
Molecule 2	1.4530	2.2504

3.7. Density of State Analysis

The density of states (DOS) analysis gives even greater understanding of the electronic structure and energy-level distribution of the studied benzodithiophene-based small molecules. It enables the visualization of the distribution of the molecular orbitals in the region of the molecule donor, π -bridge, acceptor and the contribution these make on the entire electronic behaviour of the molecular structure. The total and partial DOS of the reference molecule as well as of the designed molecules (M1 and M2) can be found in Figure 7. DFT was used to compute the corresponding DOS profiles at the B3LYP/6-31G (d, p) level and the energy scale was set to be relative to the Fermi level to allow direct comparison of orbital contributions [100]. In the case of the reference molecule (Figure 7(a)), the DOS plot would display a clear separation of peaks between the en-

ergy region of HOMO and LUMO, and a minimal overlap between occupied and unoccupied molecular orbitals. The HOMO states are mainly localised on donor benzodithiophene (BDT) unit, whereas the LUMO states are mainly related to the electron-withdrawing acceptor units [100]. The fact that the energy difference between occupied and unoccupied levels in the DOS spectrum is relatively large (also indicates) the electronic bandgap that was calculated using the frontier molecular orbital analysis (1.92 eV). The DOS distribution in the case of M1 (Figure 7(b)) has a more equal contribution of the donor and acceptor fragments. There is increased electronic delocalization of the conjugated backbone with inclusion of thiophene π -bridges. The occupied states towards the HOMO region are more continuous and more densely populated, suggesting the core of the donor is more in contact with the bridging units [101]. The partial DOS of M1 therefore substantiates the fact that the addition of the π -linker is effective enough to increase the conjugation and transition between occupied and

unoccupied states of energy. As can be seen in the DOS profile of M2, the energy gap is becoming narrow, and the density of states around the Fermi level is increased relative to R and M1 [102, 103]. The form and magnitude of the DOS peaks of M2 (Figure 7(c)) validates the notion the molecular engineering plan, comprising of incorporating thiophene π -bridges and cyano-substituted acceptors, has successfully altered the electronic structure to drive intramolecular charge transfer [66]. The increased density of states around the frontier orbitals leads to a higher electronic conductivity and light absorption, which are positive attributes in regard to the performance of organic solar cell [29]. The fact that the donor and acceptor-derived orbitals overlap in the DOS plot also signifies the

presence of a strong push-pull nature of M2 with the charge being easily transported along the conjugated backbone. The progressive rise in the number of electronic states towards the Fermi level, and the reduction in the distance between the states, confirm the fact that M2 has better electronic delocalization and conductivity. These results are very much consistent with the FMO and optical results to prove that M2 is the most electronically active and optoelectronically efficient molecule of the studied systems. The increased DOS profile of M2 thus justifies its possible application as an excellent performance donor material in organic photovoltaic [74, 102, 104].

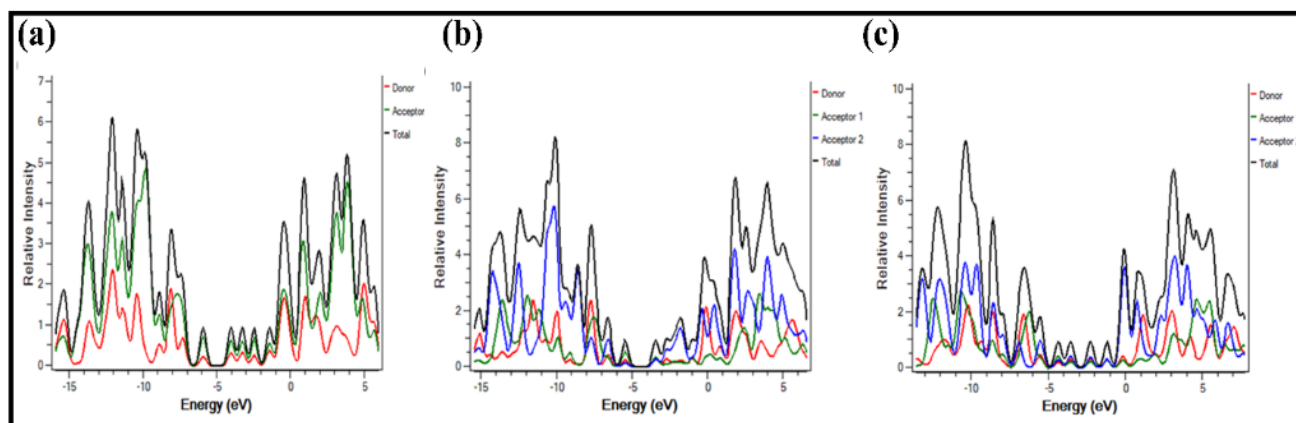


Figure 7. Density of states (DOS) plots of (a) the reference molecule (R), (b) mono-thiophene-extended derivative (M1), and (c) di-thiophene-extended derivative (M2) calculated at the B3LYP/6-31G (d, p) level.

The spectra illustrate the distribution of occupied and unoccupied electronic states, highlighting the relative positions of the HOMO and LUMO levels. Progressive thiophene π -bridge extension induces noticeable modulation of frontier orbital alignment and narrows the energy separation between valence and conduction states, confirming enhanced electronic delocalization and improved charge-transport potential in M2.

3.8. Transition Density Matrix Analysis

The transition density matrix (TDM) analysis has been carried out to examine the nature of the electronic excitation and visualize the degree of charge transfer between various parts of the molecules under study during the process of photoexcitation. Figure 8 shows the TDM maps of the reference molecule (R) as well as of the designed molecules (M1 and M2). The maps were prepared by the TD-B3LYP/6-31G (d, p) theory to analyze the distribution of the electrons and holes on the excitation of the system between the ground and the excited state. The TDM method assists in the separation of the local and charge-transfer excitations in which electron and hole densities are localized in different parts of the donor and

acceptor respectively. The TDM plot in the case of the reference molecule (Figure 8(a)) is that electron and hole densities are predominantly concentrated in the central benzodithiophene donor core with comparatively weak interaction between the terminal groups of acceptors. This localized excitation implies a small intramolecular charge transfer (ICT) and implies that the reference molecule has primary local π - π^* transitions. The constrained electron-hole delocalization also exhibits by the weak off-diagonal elements in the TDM map of R, which are in excellent agreement with its larger energy gap and reduced oscillator strength in the optical analysis [73, 82, 105].

In the case of the designed molecule M1 (Figure 8(b)), there is a stronger individualization of the distributions of electrons and holes. Electron density has been slightly shifted towards the acceptor end and hole density continues to be concentrated around BDT donor core and thiophene π -bridge sites. This charge-transfer excitation character is partial, as demonstrated by this redistribution of density. In TDM map of M1, the off-diagonal terms are higher compared to the ones in R suggesting that the donor and acceptor fragments are strongly coupled electronically. This improvement can be explained by the fact

that the thiophene linkers have been introduced, which prolongs the conjugation pathway and enhances orbital overlap, which allows transferring charge more effectively due to excitation. The largest contrast is observed in the TDM map of M2 (Figure 8(c)), where the electron and the hole densities are highly and broadly delocalized throughout the entire molecular framework. The electron density is extremely concentrated into the cyano-substituted acceptor moieties in M2 and the hole density is spread out into the BDT donor and thiophene bridge areas. This clear pattern of separation of charge is typical of an efficient intramolecular charge-transfer. The TDM

of M2 shows the high level of off-diagonal distribution density and its continuity, which allows concluding about a strong donor-acceptor interaction and a balance of charge delocalization [29, 55, 106]. The analysis of the TDM maps of R, M1, and M2 shows clearly the gradual improvement of the charge-transfer properties with the change of the structure. As the reference molecule shows localized excitation, the designed molecules especially M2 have a strong charge-transfer character, which corresponds to the red-shifted absorption and the increased oscillator strength in optical spectra [86, 103, 104, 107].

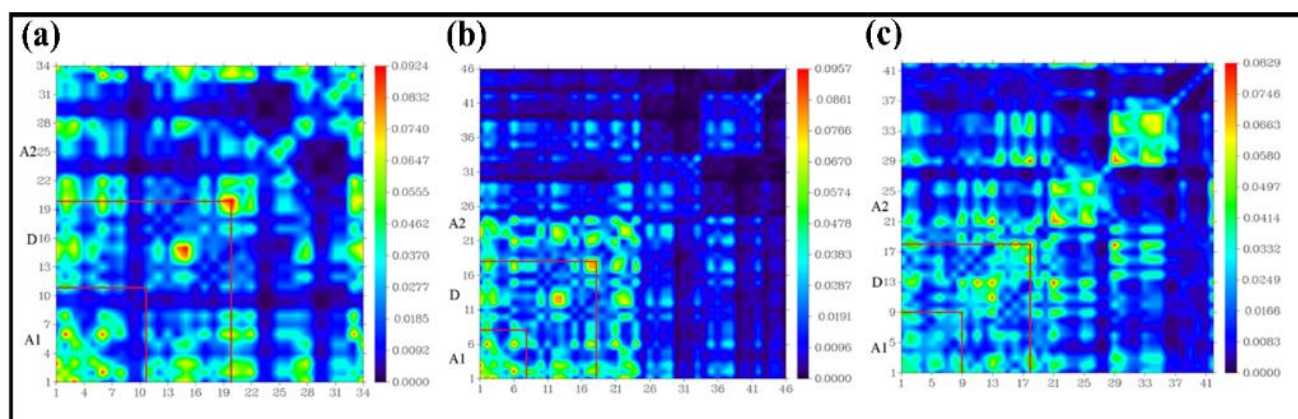


Figure 8. Transition Density Matrix (TDM) plots of (a) the reference molecule (R), (b) mono-thiophene-extended derivative (M1), and (c) di-thiophene-extended derivative (M2) calculated at the TD-B3LYP/6-31G (d, p) level.

The maps depict electron (green) and hole (red) density distributions upon photoexcitation, illustrating the extent of spatial separation and intramolecular charge transfer (ICT) character. The progressive thiophene π -bridge extension enhances electron-hole delocalization and charge-transfer distance, particularly in M2, indicating improved exciton dissociation potential and favorable optoelectronic performance.

3.9. Light Harvesting Efficiency Analysis

It is an optical property that increases the efficiency of organic solar cells. Light harvesting efficiency has been calculated.

$$\text{LHE} = 1 - 10^{-f}$$

LHE is the important parameter of assessing the potential of molecules donors in the work of OSC because it is the direct indicator of the ability of a substance to absorb photons and form excitons. The oscillator strength (f) is closely connected to the LHE and is used to measure the strength of electronic transitions and the efficiency with which a molecule is able to absorb light energy [106, 108]. The values of LHE of the reference molecule and the two designed molecules (M1 and M2) were determined and the values are given in Table 4. The oscillator strength of the reference molecule is 0.99, that is, the

LHE of 0.8976, which means that it can take away incident photons to a moderate degree. The designed molecules, in their turn however, exhibit much higher oscillator strengths and, thus, higher LHE values. M1 has an oscillator strength of 1.46 with an LHE of 0.9653 and M2 has the largest f value of 1.97 with a LHE of 0.9892. The gradual rise of LHE with R to M2 clearly shows that the molecular transformations, that is, the addition of thiophene π -bridges and the electron-withdrawing cyano acceptor groups, significantly enhance the light absorption efficiency [28, 109]. The increased LHE that is noted in the structured designs is directly a result of enhanced electronic delocalization and enhanced intramolecular charge transfer (ICT). The π -conjugation linkage system is extended using thiophene linkers and this increases the overlap between the donor and acceptor orbital which enables more effective excitation of electrons when the light is irradiated. In M2, charge-transfer transition is especially strong and this is also validated by the frontier molecular orbital analysis and transition density matrix analysis. This leads to an increase in the strength of the optical transitions and the strength of the oscillator which means that M2 is able to capture the solar energy more efficiently as compared to the reference compound [73, 82, 84, 100, 110]. These results support the statement that a rational molecular engineering of the benzodithiophene core with the appropriate π -linkers and terminal acceptor units is

an efficient method of optical activity tuning. The oscillator strength and LHE growing trend between R and M2 are in line with the red-shifted absorption and lower excitation energy, which also confirms that M2 is the most effective photon absorber of all the compounds studied. The high light-harvesting efficiency of M2 demonstrates its high potential use as a high-performance donor material in the next-generation organic solar cells.

Table 4. Calculated light-harvesting efficiency (LHE) and oscillator strength (f) of the studied molecules at the TD-B3LYP/6-31G (d, p) level.

Molecule	f	LHE
Reference	0.99	0.8976
Molecule 1	1.46	0.9653
Molecule 2	1.97	0.9892

3.10. Integrated Structure-Property-Performance Correlation

A comprehensive evaluation of the designed BDT-based donor systems reveals a coherent and progressive structure-property-performance relationship governed by systematic thiophene π -bridge engineering. The collective analysis of electronic structure, optical response, photovoltaic descriptors, and charge transport parameters establishes a clear mechanistic pathway through which molecular design translates into predicted device-level improvements [14, 55]. The introduction of thiophene bridges fundamentally modifies the molecular backbone by enhancing π -conjugation length and improving structural planarity. As demonstrated earlier in the optimized geometries and frontier orbital distributions, extended conjugation increases orbital delocalization and strengthens donor-acceptor electronic coupling. These structural modifications directly influence frontier molecular orbital energies, optical absorption characteristics, and charge-transfer behavior [68, 69, 71]. The photovoltaic performance descriptors summarized in Table 5 provide quantitative validation of this structure-driven improvement. The open-circuit voltage (Voc) shows a pronounced increase from 0.57 V for the reference molecule (R) to 1.02 V for M1 and further to 1.25 V for M2. This enhancement originates from progressive stabilization of the HOMO energy levels upon thiophene insertion [111]. The

significant Voc improvement in M2 highlights the effectiveness of conjugation extension in tuning interfacial energetics for optimized photovoltaic output [18, 65, 74]. Simultaneously, the exciton binding energy (E_b), also presented in Table 5, remains within a favorable range across the series. The moderate E_b values indicate efficient electron-hole separation capability, particularly in M2 where enhanced intramolecular charge transfer (ICT) reduces Coulombic attraction between photogenerated carriers [14, 61, 68]. This improved exciton dissociation potential is further supported by the strong oscillator strength and near-infrared absorption observed in the optical analysis. The light-harvesting efficiency (LHE), increasing from 0.90 in R to 0.99 in M2, confirms superior photon absorption probability in the extended π -system, reinforcing the expectation of higher short-circuit current density (J_{sc}) [72, 73]. Charge transport properties, summarized in Table 6, further strengthen the structure-performance correlation. The reorganization energy for hole transport (λ_h) decreases progressively from 0.29 eV in R to 0.19 eV in M2, while electron reorganization energy (λ_e) similarly decreases from 0.31 eV to 0.22 eV. Reduced reorganization energy signifies lower structural relaxation during charge transfer and enhanced carrier mobility. The extended conjugated backbone in M2 promotes charge delocalization and minimizes geometrical distortion upon oxidation or reduction, thereby lowering energetic barriers for charge transport. These findings indicate that M2 exhibits the most favorable ambipolar transport characteristics among the investigated systems [29, 73, 99, 112]. The integration of photovoltaic descriptors (Table 5) and charge transport parameters (Table 6) reveals a synergistic improvement pathway. Thiophene bridge elongation enhances conjugation length, which stabilizes frontier orbitals and narrows the bandgap. Bandgap reduction shifts absorption toward the near-infrared region, improving solar spectrum utilization. Concurrently, deeper HOMO levels increase Voc, while reduced reorganization energies improve charge mobility. The combined enhancement of light harvesting, voltage output, exciton dissociation, and carrier transport collectively contributes to superior predicted device performance [28, 75, 76]. Among the studied molecules, M2 demonstrates the most balanced and optimized property profile. It exhibits the narrowest bandgap, strongest absorption in the NIR region, highest oscillator strength, maximum LHE, highest Voc, and lowest reorganization energies. This convergence of structural, electronic, optical, and transport advantages confirms that systematic thiophene π -bridge engineering represents a highly effective molecular design strategy for next-generation BDT-based donor materials [106, 110].

Table 5. Calculated photovoltaic performance descriptors of the reference molecule (R) and thiophene-extended derivatives (M1 and M2), including HOMO and LUMO energies, estimated open-circuit voltage (V_{oc}) relative to PC61BM, electronic bandgap (E_g), optical gap (E_{opt}), exciton binding energy (E_b), and light-harvesting efficiency (LHE).

Molecule	HOMO (eV)	LUMO (eV)	V_{oc} (V)	E_g (eV)	E_{opt} (eV)	E_b (eV)	LHE
R	-4.87	-2.86	0.57	2.01	1.84	0.17	0.90
M1	-5.32	-3.44	1.02	1.88	1.90	-0.02	0.96
M2	-5.55	-3.87	1.25	1.68	1.52	0.16	0.99

Table 6. Estimated reorganization energies for hole (λ_h) and electron (λ_e) transport of R, M1, and M2 calculated at the B3LYP/6-31G (d, p) level, along with predicted charge transport tendencies based on energetic relaxation behavior.

Molecule	λ_h (eV)	λ_e (eV)	Charge Transport Tendency
R	0.29	0.31	Balanced ambipolar
M1	0.24	0.27	Slight hole-dominant
M2	0.19	0.22	Efficient hole transport

4. Conclusions

In the present work, a novel benzodithiophene-based small molecule (M1 and M2) was designed and theoretically analyzed by applying the density functional theory (DFT) and time-dependent DFT (TD-DFT) methods to gain insight into the structure, electrochemical, and optical properties of these molecules and to assess their feasibility as a donor material in organic solar cells (OSCs). The consequences of molecular engineering with π -bridges extension and acceptors modification were analyzed systematically in comparison with a reference molecule. The findings indicate that strategic structural changes are important in fine-tuning the electronic behavior, charge-transfer properties, and light-harvesting properties of BDT derivatives. The optimized structures validated the fact that introducing thiophene π -bridges and cyano-substituted acceptors increases the planarity of the molecules and π -conjugation, improving effective intramolecular charge transfer (ICT). The frontier molecular orbital (FMO) analysis has revealed that the designed molecule M2 has the lowest HOMO-LUMO energy gap (1.68 eV), which has stronger electronic coupling and increased charge mobility than R (2.01 eV) and M1 (1.88 eV). The optical simulations of TD-DFT showed that M2 had a spectacular red shift in the absorption spectrum and a λ_{max} of 815 nm and excitation energy of 1.52 eV and an extension of absorption to near-infrared range, and increased light-harvesting potential of M2. The molecular electrostatic potential maps and the analysis of the dipole moment also proved that M2 has a high degree of charge polarization and effective donor-acceptor interaction with a dipole moment at

a solvent of 2.25 D against 0.002 D of the reference molecule. The density of states plot showed that in M2, there is more delocalization, as well as an increase in orbital overlap around the Fermi level, which confirms the better electronic conductivity and charge transport efficiency of the state. In addition, the transition density matrix outcomes displayed a strict separation of electrons and holes along the donor to acceptor system of M2 which confirms that it is a highly intramolecular charge-transfer species. The calculated light-harvesting efficiencies also exhibited a similar improvement through the series with R corresponding to 0.8976 and M 2 (0.9892). The large LHE and oscillator strength of M2 indicates that it is better than others as it can absorb photons and create excitons to convert solar energy to high-efficiency solar energy. The properties of the material have elevated M2 into a promising donor material in future high-performance organic solar cells. The conceptual understandings, which have been acquired within this work, can be a useful tool in the rational design of effective BDT-based photovoltaic materials and may be used as the basis of subsequent experimental synthesis and optimization of devices.

Abbreviations

OPs	Organic Photovoltaics
BDT	Bridged Benzodithiophene
DFT	Density Functional Theory
FMO	Frontier Molecular Orbital
LHE	Light-Harvesting Efficiency
DOS	Density Of States
MEP	Molecular Electrostatic Potential

TDM	Transition Density Matrix
ICT	Intramolecular Charge Transfer
PCM	Polarizable Continuum Model
ECL	Effective Conjugation Length
DMC	Dipole Moment Calculations
TDM	Transition Density Matrix

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Conflicts of Interest

The authors declare no conflicts of interest.

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