

Original Research

Designing and DFT Study of Thiophene-Based Hole Transport Materials for Applications in Organic and Efficient Perovskite Solar Cells

Shehla Gul¹, Javed Iqbal^{1,2,*}, Shaukat Ali¹, Yasir Jamil³

¹Department of Chemistry, University of Agriculture, 38000 Faisalabad, Pakistan

²Department of Chemistry, College of Science, University of Bahrain, 32028 Sakhir, Kingdom of Bahrain

³Department of Physics, University of Agriculture, 38000 Faisalabad, Pakistan

*Correspondence: Javed.Iqbal@uaf.edu.pk (Javed Iqbal)

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Abstract

A series of five thiophene bridged carbazole based molecules was designed by structural engineering of the reference molecule dibenzothiophene-dioxide (DBTO) using an acceptor alteration strategy. A density functional theory (DFT) investigation was conducted at the selected DFT functional B3LYP/6-31G (d, p) to evaluate optical and electronic properties of the reference (DBTO) and all designed molecules (DBTO-1 to DBTO-5). Several important characteristics, i.e., band gap (E_g), transition density matrix (TDM) analysis, dipole moment (μ), density of states (DOS) analysis, reorganization energies and open circuit voltage (V_{OC}) were investigated. All the newly drafted molecules show higher maximum absorption (λ_{max}) values in solvent (Dichloromethane) ranging from 386 nm to 457 nm when compared to the reference DBTO (276 nm). Notably, these molecules display increased V_{OC} values and better alignment of energy levels with perovskite materials. Lower reorganization energies for the electron (0.0227912–0.0250713 eV) as compared to DBTO (0.0404330 eV) reveal that the newly devised molecules display higher electron mobility rates, and hence, these small molecules can be used as proficient donor materials in high-performance organic solar cells (OSCs) and better hole transport materials (HTMs) for possible application in perovskite solar cells.

Keywords: hole-transport materials; thiophene derivatives; dibenzothiophene-dioxide; DFT/TD-DFT; reorganization energy; frontier orbital alignment; perovskite solar cells; organic solar cells; dopant-free HTM design

1. Introduction

The development of high-efficiency solar energy technologies has become an urgent global priority in response to escalating environmental concerns and the need for sustainable energy sources [1,2]. Among third-generation photovoltaic technologies, perovskite solar cells (PSCs) and organic solar cells (OSCs) have gathered significant attention due to their low fabrication costs, lightweight design, and tunable optoelectronic properties [3]. A critical component in the architecture of these devices is the hole transport material (HTM), which plays a pivotal role in charge extraction, transport, and interfacial stability. Conventional HTMs such as spiro-OMeTAD, while effective, suffer from drawbacks including complex synthesis and limited stability, prompting a vigorous search for alternative organic materials with tailored electronic characteristics [4,5,6,7].

In this context, thiophene-based π -conjugated systems have emerged as promising candidates due to their strong hole-transporting capabilities, excellent solubility, film-forming properties, and versatile synthetic tunability. Modifying the molecular structure of HTMs by engineering donor-acceptor (D-A) frameworks and end-capping moieties can significantly enhance their light-harvesting abil-

ity, energy level alignment, solubility, and charge mobility [8,9]. In particular, small-molecule HTMs incorporating electron-rich cores and electron-deficient substituents enable fine-tuning of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) levels, which is crucial for maximizing open circuit voltage (V_{OC}) and power conversion efficiency (PCE).

In this work, we report the rational design and density functional theory (DFT) investigation of a series of thiophene-based small molecules derived from a dibenzothiophene-dioxide (DBTO) core, functionalized with various electron-accepting moieties. The study aims to assess the electronic, optical, structural, and charge transport properties of these designed HTMs through a detailed computational approach. Parameters such as frontier molecular orbitals (FMOs), reorganization energies, dipole moments, light-harvesting efficiency (LHE), transition density matrix (TDM), and open circuit voltages were investigated. The results offer valuable insights into structure-property relationships and highlight the potential of these molecules as efficient HTMs for next-generation organic and perovskite solar cells.



2. Methods

DFT is used in this study to generate all computational simulations. All the geometries are optimized via Gaussian 09 software (Gaussian, Inc., Wallingford, CT, USA) [10] and the structures and results visualization were done using GaussView 6.0 program (Gaussian, Inc., Wallingford, CT, USA) [10]. Initially, four different DFT functionals have been used to optimize the reference molecule to obtain the most suitable method for the investigation of newly created molecules. To validate the chosen exchange–correlation functional, absorption maxima (λ_{max}) were compared using B3LYP, CAM-B3LYP, MPW1PW91, and ω B97XD (Supplementary Fig. 1, Supplementary Table 1) in solvent (CH_2Cl_2) using implicit solvent model IEF-PCM [11] and the gaseous phase. B3LYP and MPW1PW91 show moderate redshifts due to limited long-range charge-transfer treatment, whereas the range-separated functionals yield blue-shifted λ_{max} values, reflecting improved long-range electron–hole interactions. Overall, the selected function provides a reliable balance between accuracy and computational efficiency for predicting the optical properties of the studied systems. The optimized geometries for all designed molecules were obtained with the B3LYP functional along with 6-31G (d, p) basis sets due to its good accuracy of energy [12,13,14]. Frequency calculations were performed to confirm global minima for all molecules. Studying the distribution of charges in FMOs is essential to understanding and forecasting carrier injection and transport. Analysis including FMOs, TDM, density of states (DOS), electron affinity (EA) and ionization potential (IP), reorganization energy (RE) values, LHE, V_{OC} and PCE were calculated computationally. Additionally, binding energy (E_b), chemical hardness (η), electrophilicity (ω) and electronegativity (χ) index and, and dipole moment in gaseous (μ_g) and solvent CH_2Cl_2 phase (μ_s) were obtained using the same level of DFT. All the results have been demonstrated graphically utilizing Origin 6.0 software (OriginLab Corporation, Northampton, MA, USA), Multiwfn 3.8 (Beijing, China) and PyMolyze 1.1 (Stanford, CA, USA) [15,16].

3. Results and Discussions

3.1 Electronic Property

To improve the performance of photovoltaic (PV) cells, molecules must have the proper electronic structure which enhances their ability to extract and transfer electrons or holes [17,18,19]. In perovskite solar cells, the hole and electron transporting materials' HOMO levels (E_{HOMO}) and LUMO levels (E_{LUMO}) must be aligned with the perovskite material [20,21], while more negative E_{HOMO} and E_{LUMO} levels are essential for organic solar cells [22], which boosts charge transfer and open circuit photo-voltage of PVCs. Molecules such as DBTO-2 to DBTO-5, with HOMO values below -6.7 eV, may hinder hole extrac-

tion in PSCs and are therefore more suitable for OSC architectures. Therefore, the studies of E_{HOMO} and E_{LUMO} levels of investigated molecules are crucial. The investigated molecules (DBTO, DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5) are optimized at selected DFT levels. The optimized structures of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules are presented in Fig. 1. The E_{HOMO} and E_{LUMO} levels of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules are theoretically calculated from optimized geometries. As given in Table 1, the E_{HOMO} levels of the investigated molecules are -6.73 eV (DBTO), -6.01 eV (DBTO-1), -6.87 eV (DBTO-2), -5.85 eV (DBTO-3), -6.89 eV (DBTO-4), -7.05 eV (DBTO-5) and E_{LUMO} levels are -2.53 eV (DBTO), -2.14 eV (DBTO-1), -2.30 eV (DBTO-2), -2.81 eV (DBTO-3), -1.97 eV (DBTO-4), -1.52 eV (DBTO-5), respectively. The more negative E_{HOMO} increasing trend for the investigated molecules is $\text{DBTO-5} > \text{DBTO-4} > \text{DBTO-2} > \text{DBTO-3} > \text{DBTO} > \text{DBTO-1}$.

Table 1. Electronic properties of investigated molecules.

Molecules	HOMO (eV)	LUMO (eV)	E_g (eV)
DBTO	-6.73	-2.53	4.20
DBTO-1	-6.01	-2.14	3.87
DBTO-2	-6.87	-2.30	4.57
DBTO-3	-5.85	-2.81	3.04
DBTO-4	-6.89	-1.97	4.92
DBTO-5	-7.05	-1.52	5.53

HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; E_g , band gap.

The results showed that the addition of electron-withdrawing acceptors downshifts the HOMO levels of DBTO-2 to DBTO-5 molecules by 0.88 – 1.20 eV and stabilizes them to achieve the ideal molecules for photovoltaic cells which signifies better charge extraction and photovoltaic properties. Furthermore, uniform frontier molecular orbital (HOMO and LUMO) delocalization across the entire molecular backbone is an important factor for superior charge transport. In engineered molecules (DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5), the HOMO levels are smoothly concentrated over the donor portion and the LUMO levels on the acceptor portion as demonstrated in Fig. 2. In contrast, the HOMO level is completely focused on the whole molecule and the LUMO level is on the central portion of the reference DBTO molecule. In summary, the HOMO and LUMO distributions in engineered molecules are smoother and more uniform across the molecular skeleton than in the reference DBTO molecule. The valence band maximum (VBM) of typical lead-halide perovskites is assumed to lie in the range of -5.4 to -5.8 eV, which is consistent with widely reported experimental values.

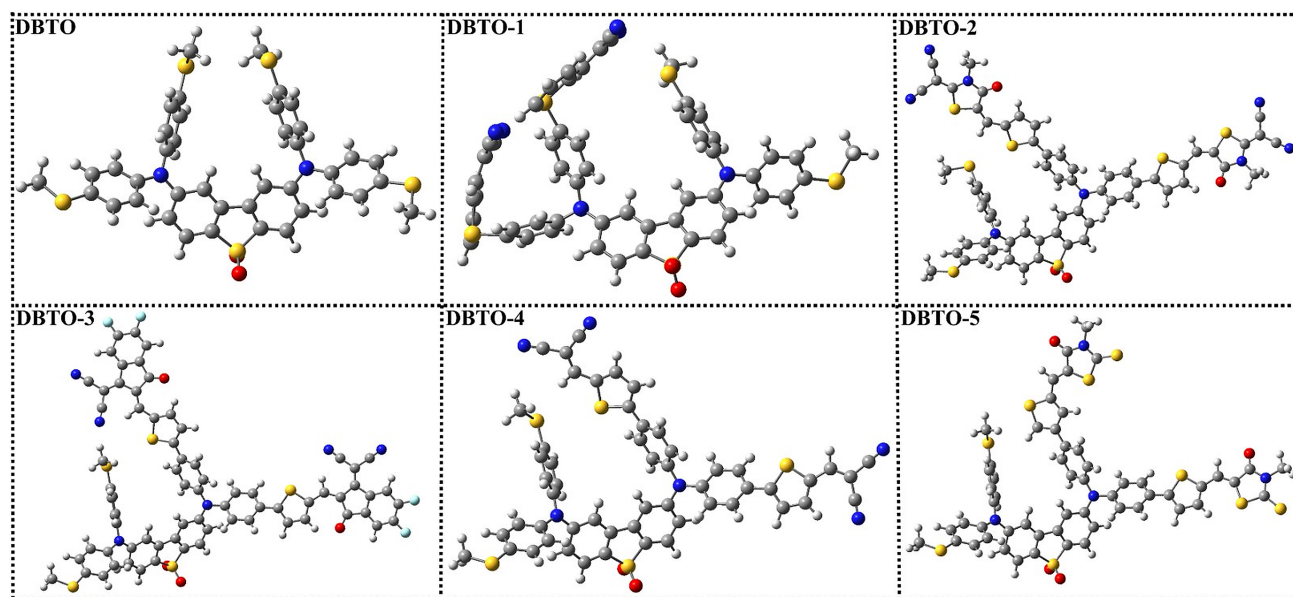


Fig. 1. Optimized structures of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules. DBTO, dibenzothiophene-dioxide.

3.2 Optical Property

The investigation of optical properties, i.e., LHE, maximum absorption ($\lambda_{\max}$), oscillator strength (f), and excitation energy (E_x) plays a vital role in modifying the ideal molecules based on absorption properties in the effective solar energy production [23,24,25,26]. These properties are studied by a selected time-dependent (TD)-DFT level in the gaseous and solvent (IEFPCM model is used in the solvent phase) phases. As presented in Tables 2,3, the $\lambda_{\max}$ of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules is located at 276 nm (DBTO), 464 nm (DBTO-1), 406 nm (DBTO-2), 436 nm (DBTO-3), 378 nm (DBTO-4), 368 nm (DBTO-5) in gaseous phase and 276 nm (DBTO), 435 nm (DBTO-1), 413 nm (DBTO-2), 457 nm (DBTO-3), 396 nm (DBTO-4), 384 nm (DBTO-5) in solvent (dichloromethane) phase as presented in Fig. 3. The increasing trend of $\lambda_{\max}$ is obtained as DBTO-1 > DBTO-3 > DBTO-2 > DBTO-4 > DBTO-5 > DBTO in the gaseous phase and DBTO-3 > DBTO-1 > DBTO-2 > DBTO-4 > DBTO-5 > DBTO in solvent (dichloromethane) phase with some bathochromic shift. The engineered DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5 molecules absorb in the 400 nm range which is non-competitive with perovskite absorption for perovskite solar cells, because this range prevents the molecules from competing with the perovskite layer, allowing the full consumption of light in the production of photocurrent generations. The finding indicated that engineered DBTO-1 to DBTO-5 molecules exhibited 92 nm to 188 nm more absorption than the DBTO reference owing to the incorporation of various acceptors, which increased the balanced conjugation, pushed the absorption to a maximum for photovoltaic cells, and decreased the excitation energies to the generation of excitons.

Table 2. Absorption parameters of all studied molecules (DBTO, DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5) in the solvent phase.

Molecules	$\lambda_{\max}$ (nm)	E_x (eV)	f	LHE
DBTO	276 nm	4.4837	0.6328	0.767
DBTO-1	435 nm	2.8881	0.1297	0.258
DBTO-2	413 nm	2.9381	2.6672	0.998
DBTO-3	457 nm	2.6737	2.0411	0.991
DBTO-4	396 nm	3.0760	1.9705	0.989
DBTO-5	386 nm	3.0759	1.7079	0.980

LHE, light-harvesting efficiency; $\lambda_{\max}$, maximum absorption; E_x , excitation energy; f , oscillator strength.

Table 3. Absorption parameters of all studied molecules (DBTO, DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5) in the gaseous phase.

Molecules	$\lambda_{\max}$ (nm)	E_x (eV)	f	LHE
DBTO	276	4.4835	0.5407	0.712
DBTO-1	464	2.3320	0.0113	0.025
DBTO-2	406	3.0290	2.5755	0.997
DBTO-3	436	2.7822	1.8891	0.987
DBTO-4	378	3.2219	1.8113	0.985
DBTO-5	368	3.2319	1.6144	0.976

As presented in Tables 2,3, the E_x of studied molecules is 4.4835 eV (DBTO), 2.3320 eV (DBTO-1), 3.0290 eV (DBTO-2), 2.7822 eV (DBTO-3), 3.2219 eV (DBTO-4), 3.2319 eV (DBTO-5) in gaseous phase and 4.4837 eV (DBTO), 2.8881 eV (DBTO-1), 2.9381 eV (DBTO-2), 2.6737 eV (DBTO-3), 3.0760 eV (DBTO-4), 3.0759 eV

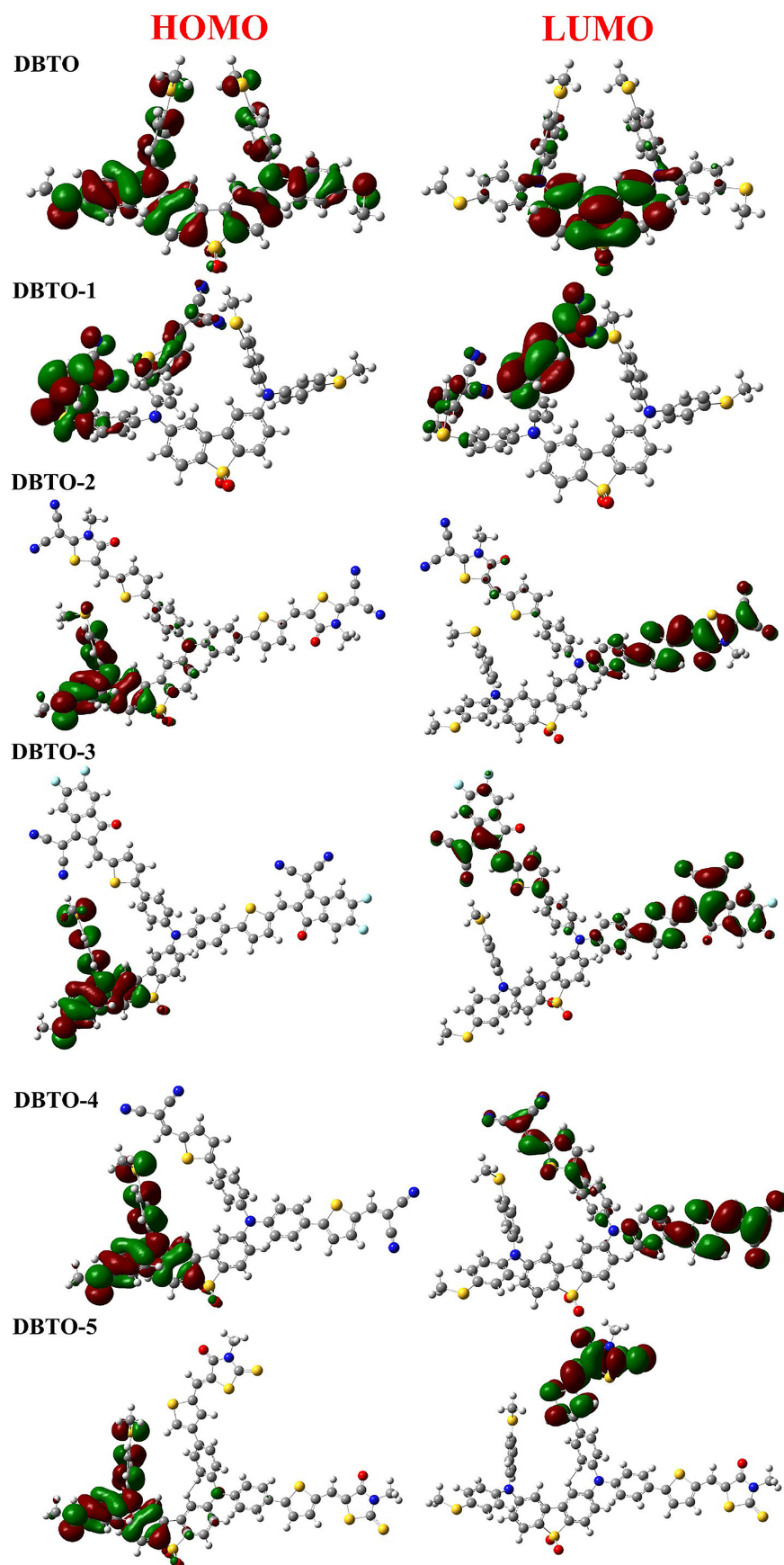


Fig. 2. HOMO and LUMO levels of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules.

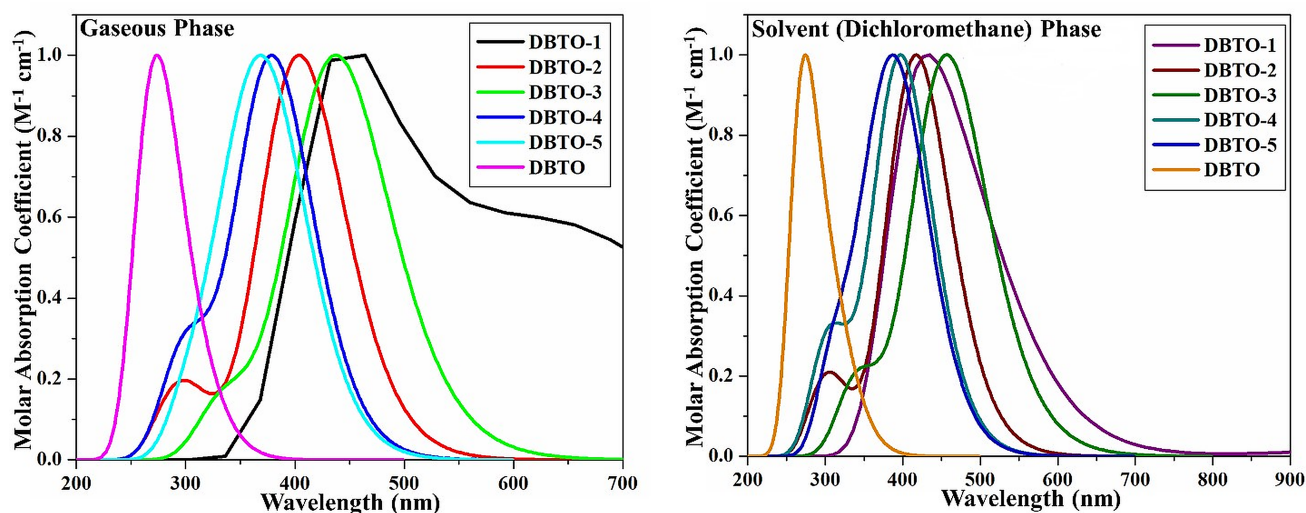


Fig. 3. UV-Vis spectra of DBTO, DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5 molecules. UV-Vis, ultra violet-visible.

(DBTO-5) in solvent (dichloromethane) phase. The increasing trend of E_x is obtained as DBTO > DBTO-5 > DBTO-4 > DBTO-2 > DBTO-3 > DBTO-1 in the gaseous phase and DBTO > DBTO-4 > DBTO-5 > DBTO-2 > DBTO-1 > DBTO-3 in the solvent phase, indicating that engineered DBTO-1 to DBTO-5 molecules required low energy to generate excitons compared to the DBTO reference. Furthermore, the possibility of molecules absorbing a photon is directly related to their f , which is an important parameter in understanding the absorption coefficient [27]. As presented in Tables 2,3, the f of studied molecules is 0.5407 (DBTO), 0.0113 (DBTO-1), 2.5755 eV (DBTO-2), 1.8891 (DBTO-3), 1.8113 (DBTO-4), 1.6144 (DBTO-5) in gaseous phase and 0.6328 (DBTO), 0.1297 (DBTO-1), 2.6672 (DBTO-2), 2.0411 (DBTO-3), 1.9705 (DBTO-4), 1.7079 (DBTO-5) in solvent (dichloromethane) phase. To evaluate the photocurrent flow of studied molecules, the LHE parameter is analyzed and calculated by $1-10^{-f}$ [28]. As presented in Tables 2,3, the LHE of studied molecules is 0.712 (DBTO), 0.025 (DBTO-1), 0.997 (DBTO-2), 0.987 (DBTO-3), 0.985 (DBTO-4), 0.976 (DBTO-5) in gaseous phase and 0.767 (DBTO), 0.258 (DBTO-1), 0.998 (DBTO-2), 0.991 (DBTO-3), 0.989 (DBTO-4), 0.980 (DBTO-5) in solvent (dichloromethane) phase. The f and LHE increasing trend of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules are obtained as DBTO-2 > DBTO-3 > DBTO-4 > DBTO-5 > DBTO > DBTO-1 in the gaseous and solvent phases. The results suggested that engineered materials (except DBTO-1) illustrated more f and LHE ability than the DBTO molecule, corresponding to a greater photocurrent flow and absorbing ability. The unusually low oscillator strength and LHE of DBTO-1 originate from its weaker intramolecular charge-transfer character and less effective conjugation, likely associated with molecular symmetry and reduced donor-acceptor electronic coupling compared to the other derivatives (Fig. 4).

3.3 Solubility and Stability

In photovoltaic cells, molecule solubility and stability via dipole moment and absolute hardness are strongly related to molecular morphology, film production, synthesis processing, charge transfer property, cost-effectiveness, and protection against external damage [29,30]. Superior solubility and stability of molecules improved the molecular morphology, film formation, processing, charge transfer ability, cost, and protection against external damage. Theoretically, the dipole moment of the engineered (DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5) and reference (DBTO) molecules is determined by the selected DFT level, while absolute hardness (η) is calculated using the formula [31]:

$$\eta = \frac{1}{2} (E_{LUMO} - E_{HOMO}) \quad (1)$$

As presented in Table 4, the dipole moment of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules is 7.7308 D (DBTO), 7.6349 D (DBTO-1), 6.5104 D (DBTO-2), 4.0488 D (DBTO-3), 6.4389 D (DBTO-4), 10.0699 D (DBTO-5) in the ground state and 9.5926 D (DBTO), 15.5470 D (DBTO-1), 6.9263 D (DBTO-2), 4.7290 D (DBTO-3), 7.1302 D (DBTO-4), 13.1041 D (DBTO-5) in the excited state as presented in Fig. 5. The results certify that engineered molecules (except DBTO-3) have comparable solubility compared to the reference DBTO molecule.

In studied molecules, the DBTO-5 molecule has better solubility which can improve the molecular morphology, film formation, processing, charge transfer ability, and enhance the efficiency of photovoltaic cells. Moreover, the η of the reference-DBTO and engineered DBTO-1 to DBTO-5 molecules is 1.52 eV (DBTO), 0.44 eV (DBTO-1), 2.29 eV (DBTO-2), 2.10 eV (DBTO-3), 2.46 eV (DBTO-

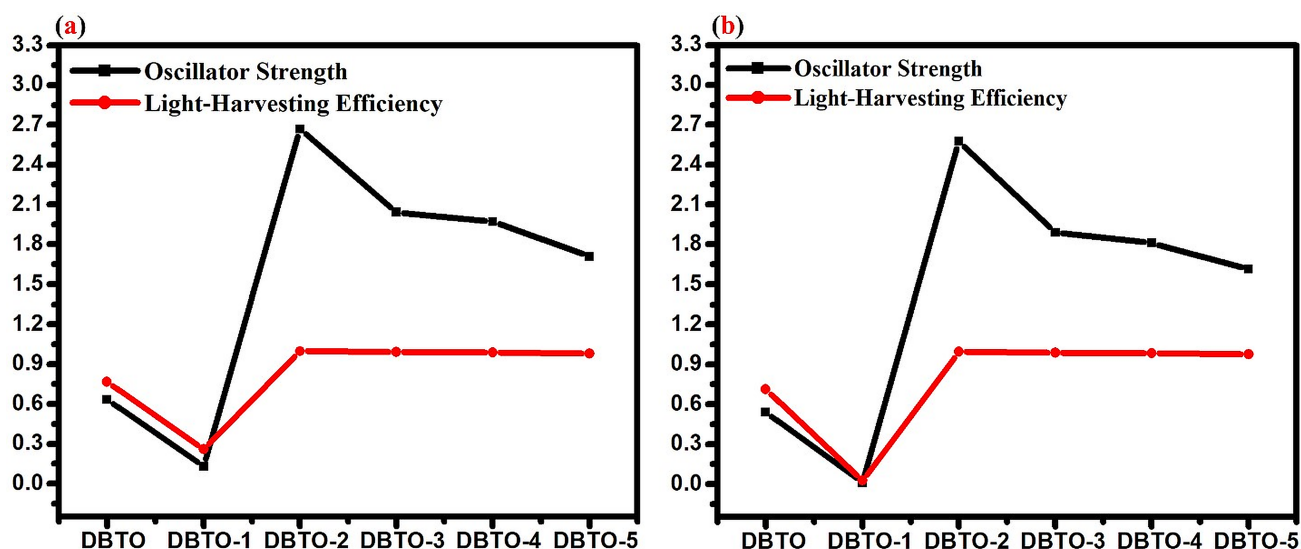


Fig. 4. Oscillator strength and light-harvesting efficiency in solvent (a) and gaseous (b) phases of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules.

Table 4. Dipole moment (in the ground and excited state) and absolute hardness (η) of studied molecules.

Molecules	$\mu_{\text{ground state (D)}}$	$\mu_{\text{excited state (D)}}$	η (eV)
DBTO	7.7308	9.5926	1.52
DBTO-1	7.6349	15.5470	0.44
DBTO-2	6.5104	6.9263	2.29
DBTO-3	4.0488	4.7290	2.10
DBTO-4	6.4389	7.1302	2.46
DBTO-5	10.0699	13.1041	2.77

4), 2.77 eV (DBTO-5). The increasing trend of η is obtained as DBTO-5 > DBTO-4 > DBTO-2 > DBTO-3 > DBTO > DBTO-1. The results demonstrated that engineered molecules (except DBTO-1) are more stable than the reference DBTO, enhancing the stability and providing more protection against external damage for photovoltaic cells.

3.4 Density of State Analysis

The DOS is an efficient method to analyze the electrical characteristics of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules [32,33,34]. By examining the contribution of sulfone-containing benzodithiophene-based core, diphenylamine, and acceptors (for engineered molecules) fragments to E_{HOMO} and E_{LUMO} of studied materials, the DOS gives information about their electronic structure and how it impacts their electrical and optical characteristics. The DOS analysis of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules was performed using selected DFT. To examine the population orbitals of studied materials, Milliken's charge evaluation was executed with PyMolyze 1.1 and colored line fragments (Fig. 6). The contributions of sulfone-containing benzodithiophene-based core, diphenylamine, and acceptors (for DBTO-1 to DBTO-5 molecules) frag-

ments to E_{HOMO} and E_{LUMO} formation of reference-DBTO and engineered DBTO-1 to DBTO-5 materials are shown in Table 5. The E_{HOMO} of engineered DBTO-1 to DBTO-5 molecules is formed from diphenylamine (81.1 to 93.7%) and sulfone-containing benzodithiophene-based core (0.0 to 18.6%) and E_{LUMO} is formed from diphenylamine (26.5 to 81.6%) and acceptor (28.0 to 73.5%), whereas E_{HOMO} and E_{LUMO} of reference-DBTO are formed from sulfone-containing benzodithiophene-based core and diphenylamine. The above findings demonstrated that charges are transferred from diphenylamine to the acceptor in engineered DBTO-1 to DBTO-5 molecules and from sulfone-containing benzodithiophene-based core to diphenylamine in the reference-DBTO molecule.

3.5 Transition Density Matrix

A TDM is an extensively utilized tool to describe the charge excitation phenomena such as separation processes, formation, overlapping, diffusion, recombination, and coherence in molecular fragments/atoms [35,36,37]. Moreover, the limited overlap among holes and electrons enables effective charge separation and enhances the efficiency of photovoltaic cells whereas more holes and electrons overlap, causing local excitations, charge recombination, and decreasing the efficiency and photocurrent den-

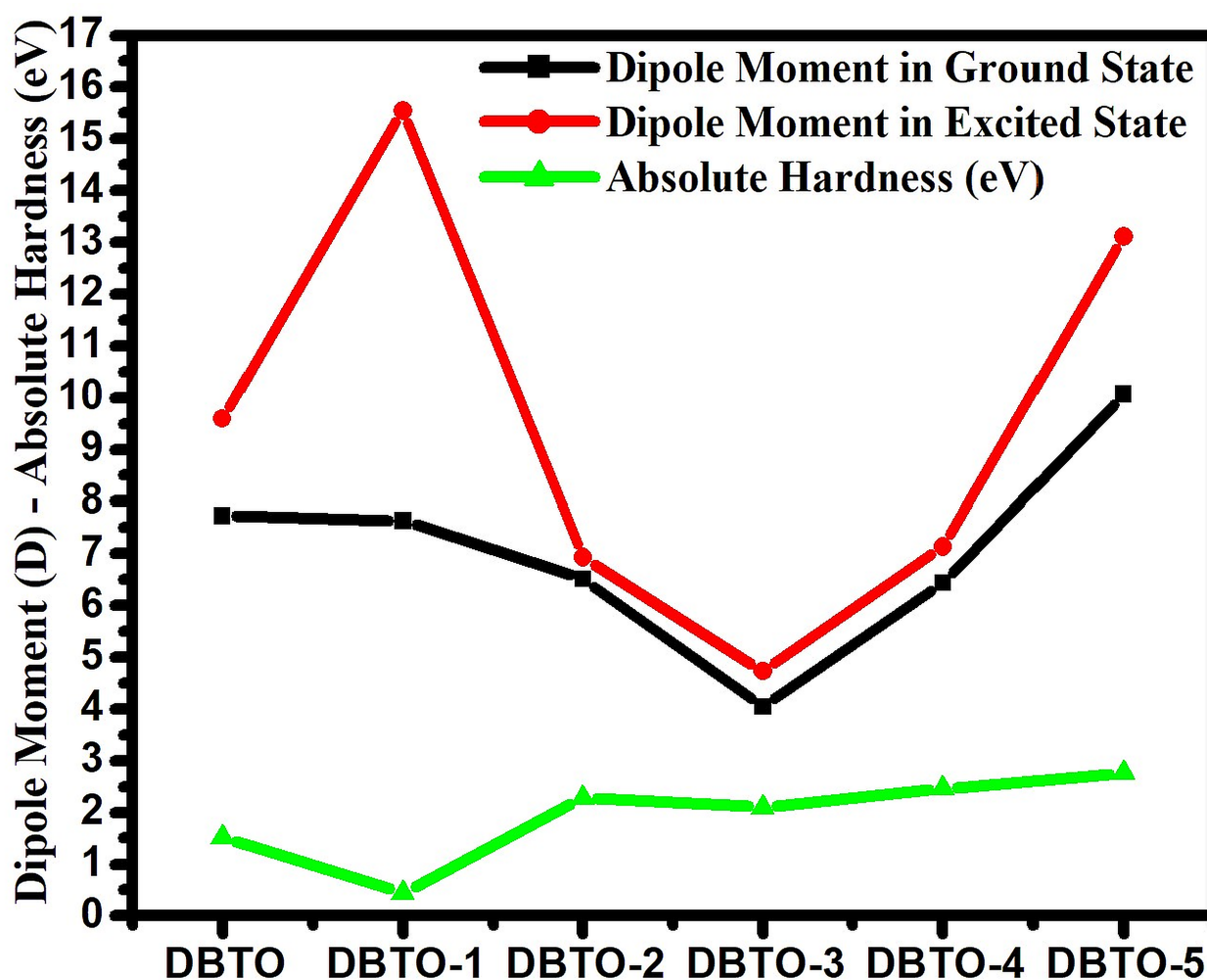


Fig. 5. Graphical representation of dipole moment and absolute hardness of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules.

sity of photovoltaic cells. Therefore, the TDM parameter is crucial which is employed through TD-DFT level and Multiwfn 3.8 software to investigate the reference-DBTO and engineered DBTO-1 to DBTO-5 molecules consisting of sulfone-containing benzodithiophene-based core, diphenylamine, and acceptors (for engineered molecules). As indicated in Fig. 7, engineered DBTO-1 to DBTO-5 molecules exhibit low consistency in distribution and excitation coherence across the molecular fragments due to stabilization of HOMO levels. The acceptor portion within the molecule is well-distributed and coherent, facilitating charge transfer from the acceptor to the benzodithiophene-based core. The TDM heat maps' off-diagonal x and y axes revealed a wide dispersion of holes-electrons on the benzodithiophene-based core, acceptors, diphenylamine, and bridges. The engineered DBTO-1 to DBTO-5 molecules show low overlap among holes and electrons, low exciton dissociation, low charge density, and charge transfer from benzodithiophene-based core to acceptor compared to the reference DBTO, enabling low

charge separation due to stabilization of HOMO levels. The TDM analysis is limited in predicting device-level performance. The TDM analysis correlates well with the frontier molecular orbital distributions and reorganization energies. In the engineered molecules, the donor-localized HOMO and acceptor-dominated LUMO lead to reduced hole-electron overlap, indicating enhanced intramolecular charge-transfer character. Notably, molecules exhibiting lower overlap in the TDM maps (e.g., DBTO-3 and DBTO-5) also show the lowest hole reorganization energies (λ_h), reflecting reduced structural relaxation upon oxidation. This consistency highlights that effective orbital delocalization and donor-acceptor separation contribute simultaneously to favorable excitation behavior and improved intrinsic hole-transport properties.

3.6 Reorganization Energy

Finding molecules with superior charge transport potential for efficient charge extraction is one of the key elements in enhancing photovoltaic cell efficiency [38,39].

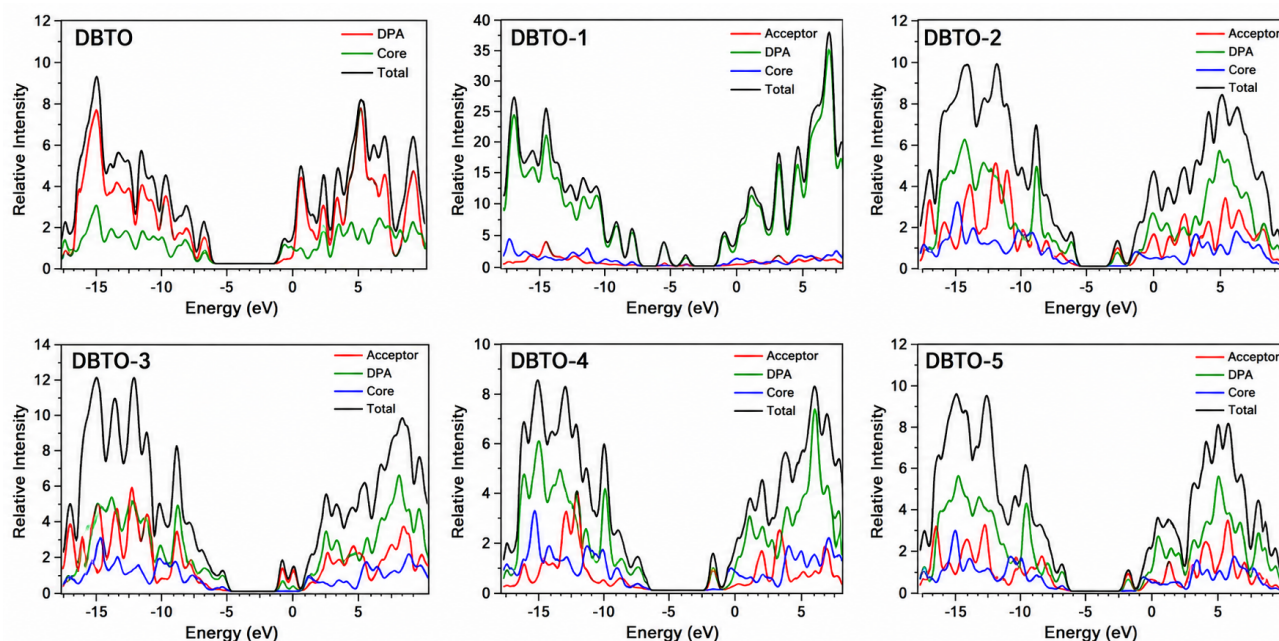


Fig. 6. DOS maps of the reference-DBTO and engineered DBTO-1 to DBTO-5 molecules. DOS, density of states.

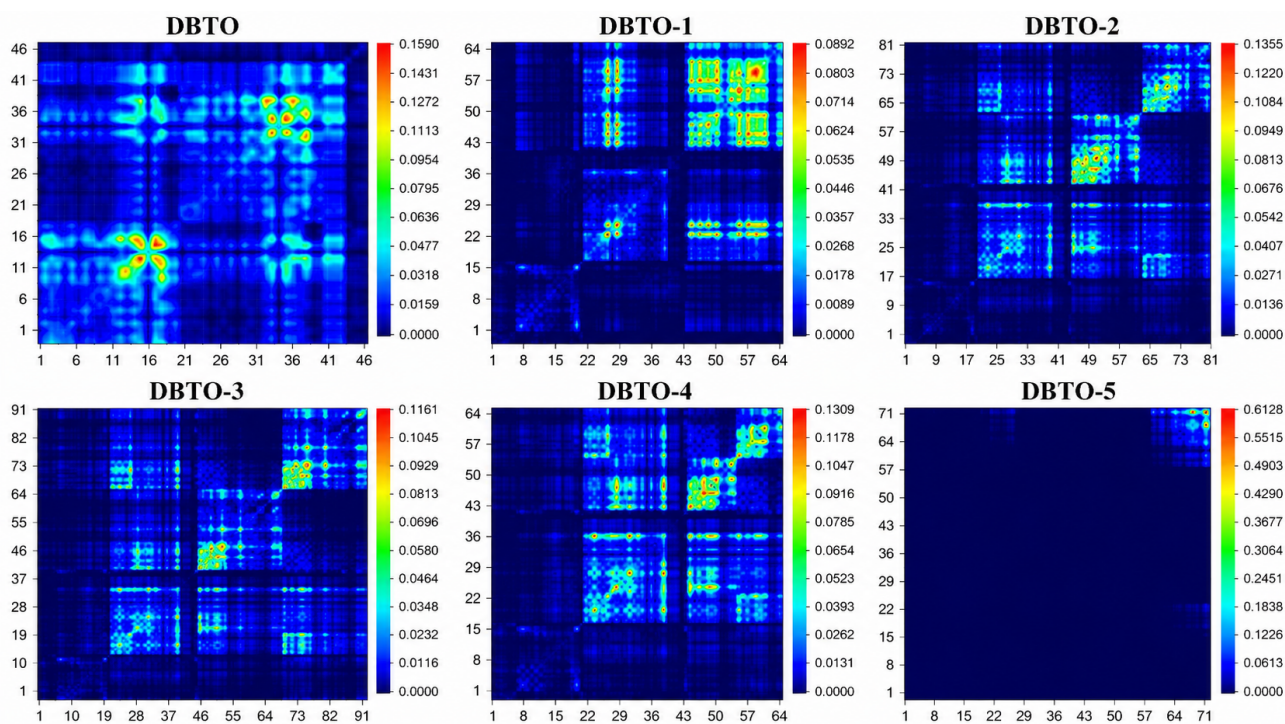


Fig. 7. TDM maps of studied materials. TDM, transition density matrix.

The Marcus theory indicates that the reorganization energy determines the charge transport potential [40,41]. The charge transport is based on a Marcus hopping regime, which is appropriate for molecular HTMs. Recent research indicates that substantial charge transport is more beneficial for molecules with smaller reorganization energies [31,42,43,44]. This is influenced favorably through coplanarity in the molecule core to promote charge delocal-

ization and fewer structural changes from the ground to oxidized configurations. Reorganization energies are organized into internal and external. In contrast to external reorganization energy, which is fairly insignificant as it does not affect charge transport potential, internal reorganization energy is associated with intermolecular modifications [45,46]. Internal reorganization energy of DBTO, DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5 molecules

Table 5. Contributions of sulfone-containing benzodithiophene-based core, diphenylamine, and acceptors (for DBTO-1 to DBTO-5 molecules) fragments to E_{HOMO} and E_{LUMO} formation of reference-DBTO and engineered DBTO-1 to DBTO-5 materials.

Molecules	Orbitals	DPA (%)	Core (%)	Acceptor (%)
DBTO	HOMO	73.5	26.5	-
	LUMO	13.1	86.9	-
DBTO-1	HOMO	93.7	0.0	6.3
	LUMO	81.6	0.4	18.0
DBTO-2	HOMO	81.4	17.5	1.1
	LUMO	54.4	0.4	45.3
DBTO-3	HOMO	83.3	16.6	0.0
	LUMO	26.5	0.1	73.5
DBTO-4	HOMO	84.3	15.4	0.3
	LUMO	64.8	0.3	34.9
DBTO-5	HOMO	81.1	18.6	0.3
	LUMO	45.2	0.0	54.8

for electron (λ_e) and hole (λ_h) are calculated through the following Eqns. 2,3.

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

$$\lambda_e = [E_0^- - E_-] + [E_-^0 - E_0] \quad (3)$$

The low reorganization energies arise from enhanced molecular planarity and structural rigidity, which reduce geometric relaxation between neutral and charged states and promote charge delocalization. As presented in Table 6, the λ_e of the reference-DBTO and engineered DBTO-1 to DBTO-5 molecules is 0.0404330 eV (DBTO), 0.0227912 eV (DBTO-1), 0.0886753 eV (DBTO-2), 0.0212969 eV (DBTO-3), 0.0250713 eV (DBTO-4), and 0.0208756 eV (DBTO-5) whereas the λ_h is 0.0145439 eV (DBTO), 0.0199852 eV (DBTO-1), 0.0199672 eV (DBTO-2), 0.0125379 eV (DBTO-3), 0.0143300 eV (DBTO-4), and 0.0129768 eV (DBTO-5). The decreasing trend of λ_e is DBTO-2 < DBTO < DBTO-4 < DBTO-1 < DBTO-3 < DBTO-5 while decreasing trend of λ_h is DBTO-1 < DBTO-2 < DBTO < DBTO-4 < DBTO-5 < DBTO-3. The DBTO-3, DBTO-4, and DBTO-5 molecules have lower hole reorganization energy than the DBTO reference while DBTO-1, DBTO-3, DBTO-4, and DBTO-5 molecules have lower electron reorganization energy compared to the DBTO reference, indicating their superior charge transport potential for efficient charge extraction in enhancing photovoltaic cell efficiency. The computed hole reorganization energies (λ_h) of DBTO-3 (0.0125 eV) and DBTO-5 (0.0130 eV) are significantly lower than those of benchmark HTMs such as

spiro-OMeTAD (~0.16–0.18 eV) and PTAA (~0.12–0.15 eV), and are comparable to or better than recently reported high-performance dopant-free small-molecule HTMs ($\lambda_h \approx 0.02$ –0.04 eV). These low λ_h values indicate reduced structural relaxation upon oxidation and suggest favorable intrinsic hole-transport characteristics.

Table 6. Reorganization Energies calculated for investigated molecules.

Molecule	λ_h (eV)	λ_e (eV)
DBTO	0.0145439	0.0404330
DBTO-1	0.0199852	0.0227912
DBTO-2	0.0199672	0.0886753
DBTO-3	0.0125379	0.0212969
DBTO-4	0.0143300	0.0250713
DBTO-5	0.0129768	0.0208756

λ_e , electron; λ_h , hole.

3.7 Open Circuit Voltage

V_{OC} is an essential metric for assessing the effectiveness of photovoltaic cells, which is generated by a photovoltaic cell when no current flows [47]. The calculated V_{OC} values represent theoretical upper limits derived from Scharber's model and do not account for interfacial recombination, energetic disorder, or morphological losses, which may reduce the experimentally achievable V_{OC} . In photovoltaic cells, the hole and electron transporting materials' HOMO and LUMO levels must be aligned with the perovskite material in perovskite solar cells and more negative HOMO and LUMO levels are essential for organic solar cells, which boosts charge transfer property and V_{OC} of PVCs [22,48]. Interface energetics, smooth morphology, superior charge transfer ability, easy film production, and synthesis processing also play crucial roles in enhancing the V_{OC} of photovoltaic cells [49,50]. Theoretically, the V_{OC} of DBTO, DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5 molecules are calculated for organic solar cells applications through the following Scharber's equation [51] where their HOMO levels are compared with the LUMO level (LUMO = -3.70 eV) of the acceptor phenyl-C61-butyric acid methyl ester (PC₆₁BM) [47].

$$V_{\text{OC}} = \frac{1}{e} (|E_{\text{HOMO}} \text{ of donor} - E_{\text{LUMO}} \text{ of acceptor}|) - 0.3 \quad (4)$$

As shown in Table 7 and Fig. 8, the V_{OC} of studied molecules is 1.85 V (DBTO), 0.01 V (DBTO-1), 2.87 V (DBTO-2), 2.73 V (DBTO-3), 2.89 V (DBTO-4), and 3.05 V (DBTO-5). The increasing order of V_{OC} is obtained as DBTO-5 > DBTO-4 > DBTO-2 > DBTO-3 > DBTO > DBTO-1. The findings demonstrated that the addition of various acceptors in engineered molecules (except DBTO-1) improved the morphology, charge transfer ability, film

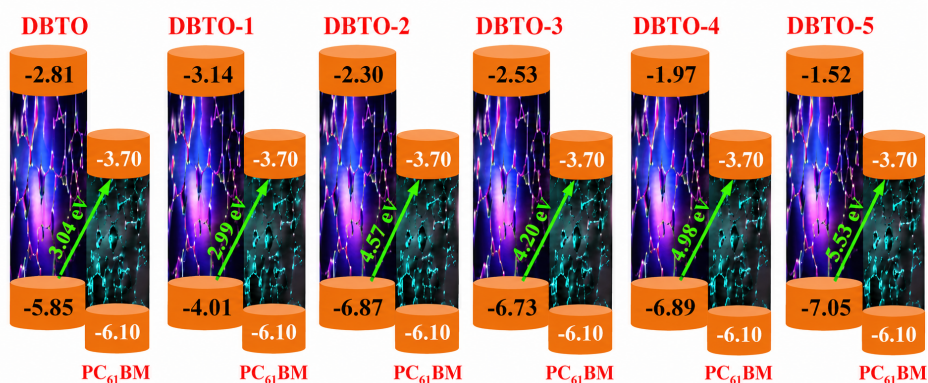


Fig. 8. Graphical representation of the open circuit voltage of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules.

production, and synthesis processing which explores the highest combination of DBTO-2, DBTO-3, DBTO-4, and DBTO-5: PC₆₁BM and boosts their V_{OC} and enhances the efficiency of photovoltaic cells. Thus, the engineered molecules (except DBTO-1) show promising potential for application as novel molecules in highly efficient solar systems.

Table 7. HOMO level, LUMO level, and V_{OC} of reference-DBTO and engineered DBTO-1 to DBTO-5 molecules.

Molecules	HOMO (eV)	LUMO (eV)	V _{OC} (V)
DBTO	-5.85	-2.81	1.85
DBTO-1	-4.01	-3.14	0.88
DBTO-2	-6.87	-2.30	2.87
DBTO-3	-6.73	-2.53	2.73
DBTO-4	-6.89	-1.97	2.89
DBTO-5	-7.05	-1.52	3.05
PC ₆₁ BM	-6.10	-3.70	-

V_{OC}, open circuit voltage; PC₆₁BM, phenyl-C61-butyric acid methyl este.

4. Limitations

This study is based solely on DFT and TD-DFT calculations and therefore reflects theoretical trends rather than exact experimental values. Device-level effects such as morphology, interfacial energetics, defect states, dopant influence, and charge recombination are not explicitly considered. The calculated open circuit voltages represent idealized upper limits derived from energy-level alignment models. Consequently, experimental synthesis and device fabrication are required to validate the predicted photovoltaic performance.

5. Conclusions

In summary, DBTO-1, DBTO-2, DBTO-3, DBTO-4, and DBTO-5 molecules are engineered which are based on

the benzodithiophene-based core, diphenylamine, and acceptors. The engineered DBTO-1 to DBTO-5 molecules exhibited 92 nm to 188 nm more absorption than the DBTO reference owing to the incorporation of various acceptors, which increased the balanced conjugation, pushed the absorption to a maximum for photovoltaic cells, and decreased the excitation energies to the generation of excitons. The results suggested that engineered materials (except DBTO-1) illustrated more *f* and LHE ability than the DBTO molecule, corresponding to a greater photocurrent flow and absorbing ability. The engineered molecules (except DBTO-3) have comparable solubility to the reference DBTO molecule. Furthermore, the engineered molecules (except DBTO-1) are more stable than the reference DBTO, enhancing the stability and providing more protection against external damage for photovoltaic cells. The DBTO-3, DBTO-4, and DBTO-5 molecules have lower hole reorganization energy than the DBTO reference while DBTO-1, DBTO-3, DBTO-4, and DBTO-5 molecules have lower electron reorganization energy compared to the DBTO reference, indicating their superior charge transport potential for efficient charge extraction in enhancing photovoltaic cell efficiency. The V_{OC} of engineered materials is 0.01 V (DBTO-1), 2.87 V (DBTO-2), 2.73 V (DBTO-3), 2.89 V (DBTO-4), and 3.05 V (DBTO-5) which is higher than the reference DBTO (1.85 V). The present results provide molecular-level screening and structure-property insights, and experimental validation and device-level studies are required to confirm actual photovoltaic performance.

Availability of Data and Materials

The datasets generated and analyzed during the current study are available from the corresponding author on reasonable request.

Author Contributions

SG: data curation, validation, visualization, writing—original draft; JI: conceptualization, methodology, investigation, formal analysis, writing—review, editing, supervi-

sion, project administration and funding acquisition; SA: supervision, data analysis, project administration and funding acquisition. YJ: supervision, data analysis, project administration. All authors contributed to the critical revision of the manuscript for important intellectual content. All authors read and approved the final manuscript. All authors have participated sufficiently in the work and agreed to be accountable for all aspects of the work.

Ethics Approval and Consent to Participate

Not applicable.

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Conflicts of Interest

The authors declare no conflicts of interest.

Supplementary Material

Supplementary material associated with this article can be found, in the online version, at <https://doi.org/10.31083/DJNB55195>.

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