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Investigating the Use of Diketopyrrolopyrrole (DPP) Based Highly Conjugated Small Molecules in Organic Solar Cells

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Abstract

In this study, a series of three donor molecules (DPP-B, DPP-N and DPP-P) based on diketopyrrolopyrrole (DPP), sharing a similar backbone of D-π-A-π-D, were investigated. In these molecules, substituents such as pyrene, naphthalene and benzene act as electron donating end groups, and DPP acts as the central core unit. Additionally, thiophene was used as a bridge between donor and acceptor fragments. Theoretical calculations were carried out with the help of density functional theory (DFT) and time-dependent functional theory (TD-DFT). To optimize the geometry of the investigated molecules, DFT functional B3LYP/6-31g(d) was used, while TD-B3LYP/6-31g(d) was used to obtain optimal results from the calculations conducted during the molecules' excited state. After examining the results, DPP-P was determined to be the most suitable donor molecule among all the investigated molecules. This is due to the fact that it manifested a suitable e_g *value of 2.24 eV and showed a stronger absorption* λmax *at 611 nm. Hence, this study revealed that the investigated donor molecules are suitable for high performance organic solar cell devices.*

Keywords: conjugated polymers, density functional theory (DFT), organic solar cells, renewable clean energy, time-dependent functional theory (TD-DFT)

Introduction

The need for energy is increasing worldwide due to population and industrial growth. In the 21st century, prevention of energy crises is one of the most crucial problems that needs to be tackled. Available resources on the planet are getting exhausted due to the rapid growth of population and developmental activities [1]. Therefore, renewable energy sources must be investigated since they play an important role in nourishing the requirements of the people. Additionally, a sharp increase in the use of naturally existing solar energy has been observed because of the gradual increase in the interest of renewable clean energy [2].

Solar cells work on the principal of photovoltaic effect where extra energy is provided to electrons when they are activated in the presence of sunlight. In this phenomenon, the electrons get excited and transform from a lower energy state into a higher energy state when exposed to sunlight. As a result of this activation, the number of free electrons and holes will produce electricity [3].

The technology is silicon based (an inorganic material), it was initially used for the fabrication of solar cells. Research demonstrated that the efficiency rate of the solar cell is positively affected by the addition of organic semiconducting polymers. For this reason, both industry and the scholarly community focused on accelerating the improvements that could be made in these novel solar cells. Organic solar cells are the best alternative to inorganic photovoltaic technologies because of their light weight, sensitivity to low light levels, flexibility of the PV units, and eco-friendly fabrication and operation. These factors are also considered the main advantages of organic solar devices [4]

Organic photovoltaic consist of electron donating material and electron accepting materials. Small molecules and polymers are used as electron donating material in organic solar cells. Photovoltaic materials and devices based on polymers are attracting remarkable interest because of their advantages such as feasibility for large size and low weight [5]. Conversely, they also pose some problems when used. For example, polymers suffer from short exciton diffusion lengths and low charge mobility [6].

Small molecular donors are the best alternative of conjugated polymers. Small molecule based donors do not encounter the problems faced by polymers. In contrast, they have well-defined molecular structures, high purity, good charge transfer mobility, as well as definite molecular weights [7]. For this reason, recently for photovoltaic applications, donors based on small molecules have garnered the attention of the masses. The maximum power conversion efficiency of bulk heterojunction devices depending on small molecular donor materials has attained a power conversion efficiency of 7.38% [8]. Small molecular donors include oligothiophenes, oligoacenes, squaraines, and merocyanines dyes as well as diketopyrrolopyrrole-based small donors [9]. A study investigated how annealing enhances carrier transport in solar cells made up of small molecules. It analysed and made the capacitance–voltage measurements on CuPc/C60based solar cells. In these cells copper-phthalocyanine (CuPc)/C60 interface was incorporated into sodium to increase their power conversion efficiency. Another study designed twelve anisotropic molecules based on D-π-D and D-π-A-π-D topologies. It theoretically investigated efficiency by applying a double overlapping wave band strategy for organic photovoltaic applications [10].

Non-fullerene electron acceptor material use in organic solar cells has increased as compared to the fullerene acceptors since they have many intrinsic issues. Typically, there are four types of non-fullerene organic solar cells: small molecule donor-small molecule acceptor (M-M) [11], polymer donor-polymer acceptor (P-P) [12], polymer donor-small molecule acceptor (P-M) [13], and small molecule donor-polymer acceptor (M-P) [14]. Among these non-fullerene organic solar cells, a system consisting of small molecule based and donor-polymer based acceptors face many difficulties in device performance. They also have low PCE values due to having comparatively low electron movability of polymer acceptors and large polymer phase separation. Conversely, it should be noted that the change in the molecular structure of the donor molecule leaves a great impact on the optoelectronic properties of the material, especially on PCE and performance of devices. A study investigated four distinctive small molecules based on diketopyrrolopyrrole (DPP) having A–D–A type structure. In this study, units having different powers of electron-donation (thienothiophene vs. Naphthalene and thiophene vs. phenylene) and different molecular planarity (biphenylene vs. Naphthalene and bithiophene vs. thienothiophene) were systematically changed and used as electron-donating unit (D) [15]. The small molecules with strong donating units (thienothiophene or thiophene) have higher HOMO energy states as compared to those with weak donating units. A study designed three small molecules named BDFDPP, TBFDPP and BDTDPP as electron donating units in which the electron acceptor was the diketopyrrolopyrrole unit. They concluded that all three small molecular materials have excellent thermal stability, favorable solubility, absorption spectra in broad range, appropriate electrochemical energy level, and show power conversion efficiencies of 2.81%, 2.82%, and 3.19% respectively in bulk-heterojunction devices [16]. Another study demonstrated the potential of constructing high-performance organic solar cells (OSCs) by employing narrow band gap diketopyrrolopyrrole polymers and non-fullerene acceptors [17].

In this study, diketopyrrolopyrrole (DPP) is used as the electron donating unit to build conjugated molecules as a small molecule because it has a high charge transferring mobility, strong fluorescent performance, and exceptional stability. DPP also allows chemical structure modifications for more direct and reliable study of structure-properties relationship. Our work has been done on a series of electron donor molecules having D-π-A-π-D backbone structure, where thiophene is used as a bridge. In this work, various end groups (pyrene, naphthalene and benzene) are integrated within the backbone of the molecule. This is done to examine how fine transformations in the structure of the molecule influence the related optoelectronic properties.

2. Materials and Methods

In this study, the density functional theory calculations with different functional molecules using Gaussian 09 package [18] at the level of B3LYP/6-31g(d) were performed. It aimed to gain insight into the possible electronic properties and molecular geometries arising from the exisitng chemical structures of the molecules [19]. For the confirmation of regularity in the calculations and to match the results with experimental data, density functional theory (DFT) and time-dependent-DFT (TD-DFT) calculations hybrid functional and long range functional were used. Frequency calculations of each of the attained structures were achieved by using the same method which was used for geometry optimizations. Dihedral angles of DPP with different end groups, such as DPP-P than DPP-N and DPP-B, were found out to check their planarity and to get information about their intermolecular packing and optical bandgap. Additionally, material’s energy levels were calculated to investigate how the subtle changes in molecular structure affect relevant electronic properties. The HOMO, LUMO and gap (HOMO-LUMO) energies were analysed to find out their stable structures.The UV-Vis spectra of all the compounds at the TD-DFT level of theory were generated via simulation [20].

3. Results and Discussion

OSCs have molecules with conjugated backbone and contain the π-spacer that is centred between the donor and acceptor units of the molecule. They are claimed to be one of the most promising photovoltaic materials [21, 22]. This type of molecular structure lowers the value of E_g and assists in broadening the absorption spectrum so it has a longer wavelength. Furthermore, electronic energy levels in OSCs can be adjusted proficiently via changing the π-spacers, donor, and acceptor groups [23, 24].

In this study, a variety of organic small molecules were investigated. According to previous studies, diketopyrrolopyrrole (DPP) is believed to be a promising building block for small molecules because it has good charge carrier ability, exceptional stability, easy fabrication, and strong light absorption ability [25, 26]. Recently, a number of small molecules based on the diketopyrrolopyrrole have been reported to show better charge carrier ability, optical properties, and film morphology [27].

We have studied a series of small molecules (SMs) based on DPP having the backbone of D-π-A-π-D. In these SMs, DPP acts as an acceptor unit and the thiophene is used as the π-spacer between the donor and the acceptor units. Benzene, naphthalene, and pyrene were used as the end groups and play the task of donor units having the same backbone (Figure 1(a) and (b)).

3.1. Molecular Structures of DPP Based Highly Conjugated Designed Small Molecules

DPP-B

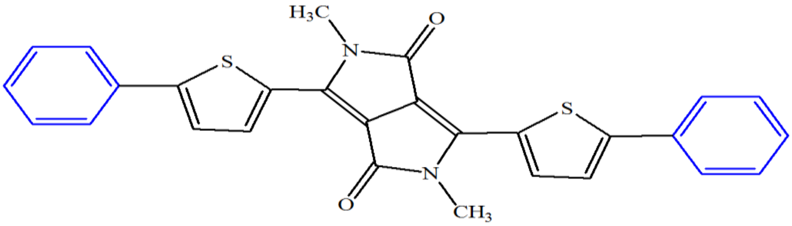
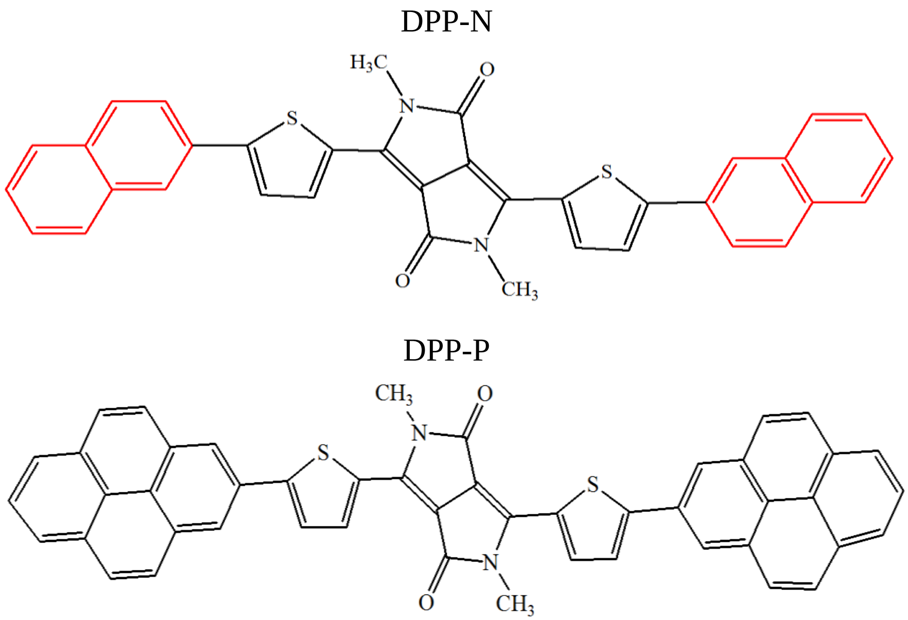


Figure 1. (a) Chemical structure of DPP-based analogues with different terminal groups DPP-B (benzene)



DPP-N

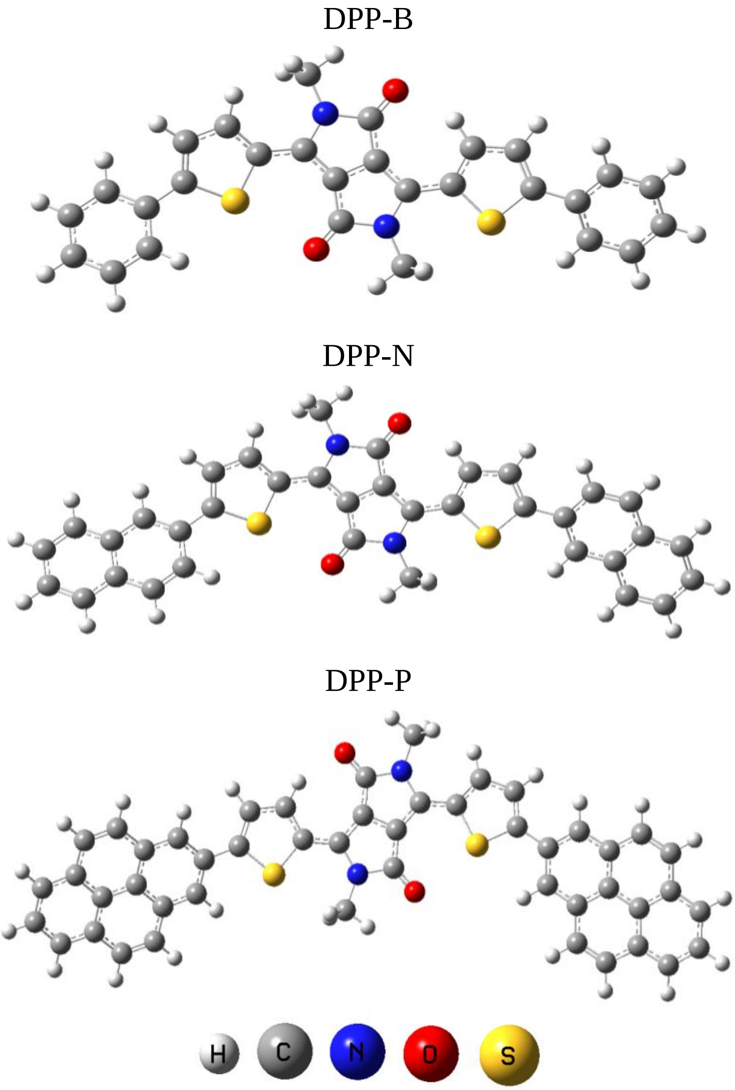
DPP-P

Figure 1. (b) Chemical structure of DPP-based analogues with the different terminal groups DPP-N (naphthalene) and DPP-P (pyrene)

Electronic and optical properties of the investigated molecules were computed by computational approach. The purpose of this study of molecular architecture is to investigate the effect of the subtle changes in the structure of molecules on the correlated optoelectronic properties [20]. Energies and the distribution patterns for the frontier molecular orbitals are plotted in Figure3 (a) and 3(b).

3.2. Optimization of Molecular Geometries

Optimization of investigated molecules was done in their ground states. The planar conformation of their optimized structures is illustrated in Figure 2 by using the DFT method. This method uses Becke's three parameter gradient-corrected exchange potential (B3LYP) level of the theory at basis set of 6-31G (d). This calculation was done at the neutral state with the singlet spin multiplicity. To optimize the ground state geometries, DFT was used to obtain a system that would be stable. For this reason, DFT is considered an important method in the field of computational chemistry.


DPP-B

DPP-N

DPP-P

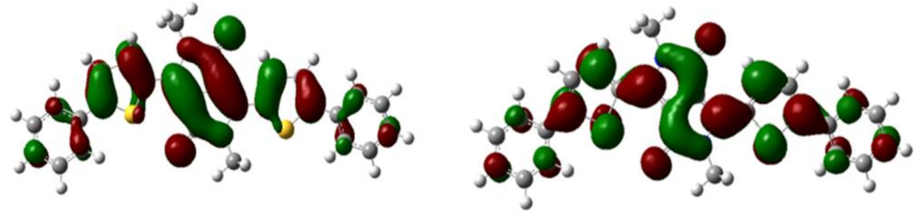
Figure 2. The schematic diagram of the investigated molecules and the optimized structures of DPP-P at B3LYP/6-31g(d) level of theory

3.3. Frontier Molecular Orbitals

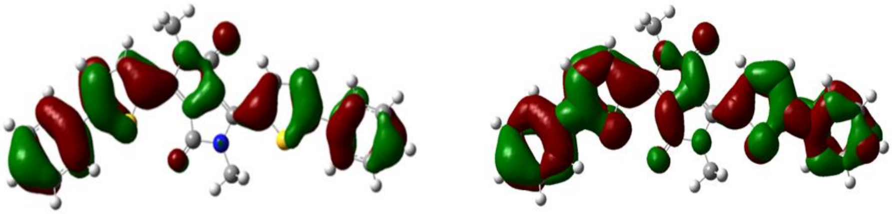
To analyse electronic and optical properties of molecules, the distribution patterns of the frontier molecular orbitals were examined. The distribution patterns of the FMOs, which include LUMO and HOMO of the investigated donor molecules at their ground state (S0), are shown in the figures which are given below. On the whole, structures of the investigated molecules and distribution patterns of FMOs were found to be extended. This means that a strong spatial overlap exists between the HOMOs and LUMOs of investigated molecules. As a result, greater optical absorption occurs during transition from HOMOs toward the LUMOs [27].

DPP-B

HOMO LUMO



HOMO-1 LUMO+1



HOMO-2 LUMO+2

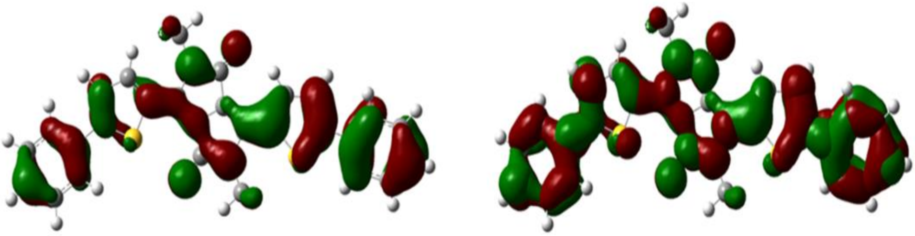


Figure 3. (a) Energy level diagrams of FMOs of DPP-B donor molecule

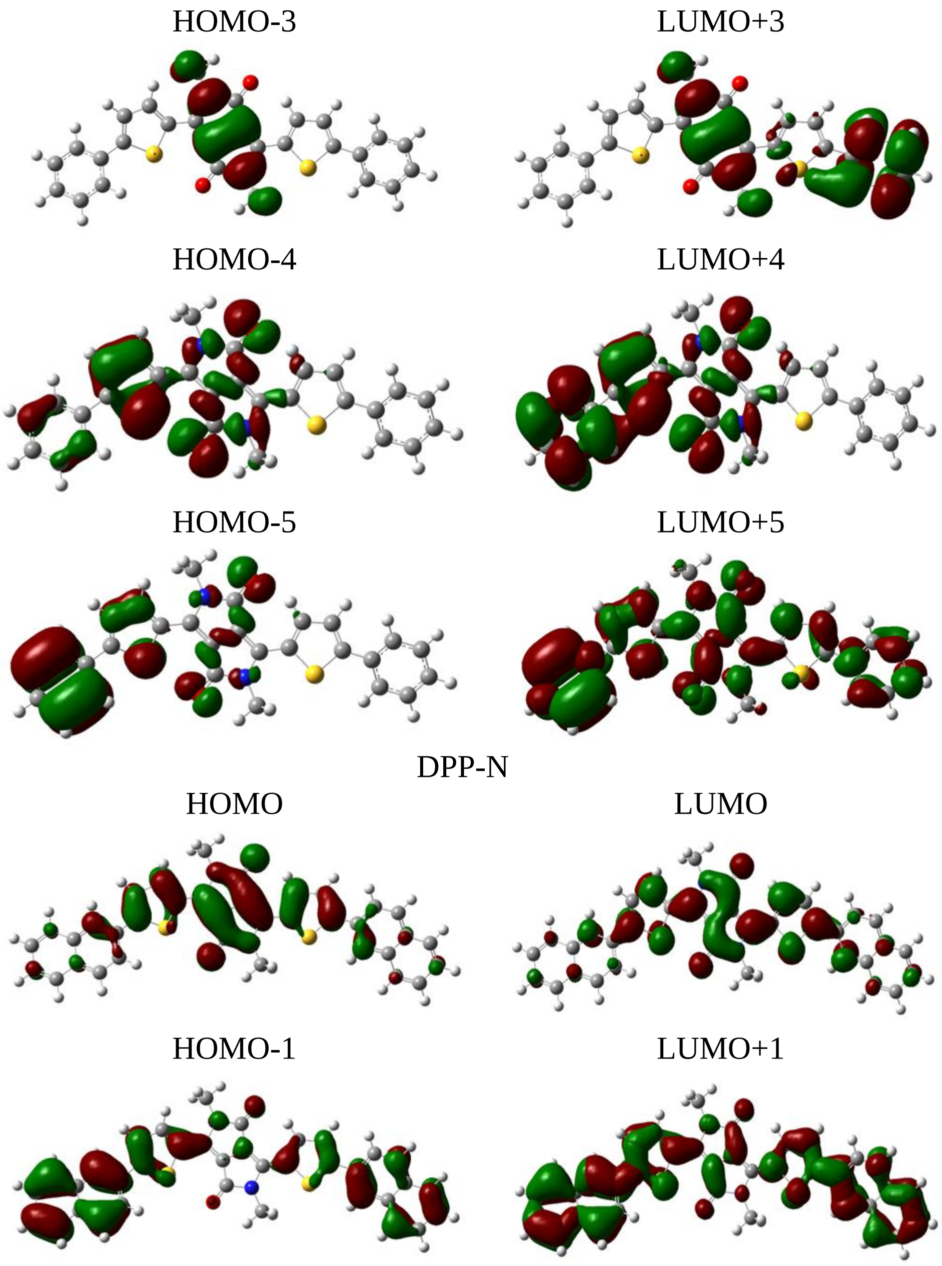


Figure 3. (b) Energy level diagrams of FMOs of DPP-B and DPP-N donor molecule

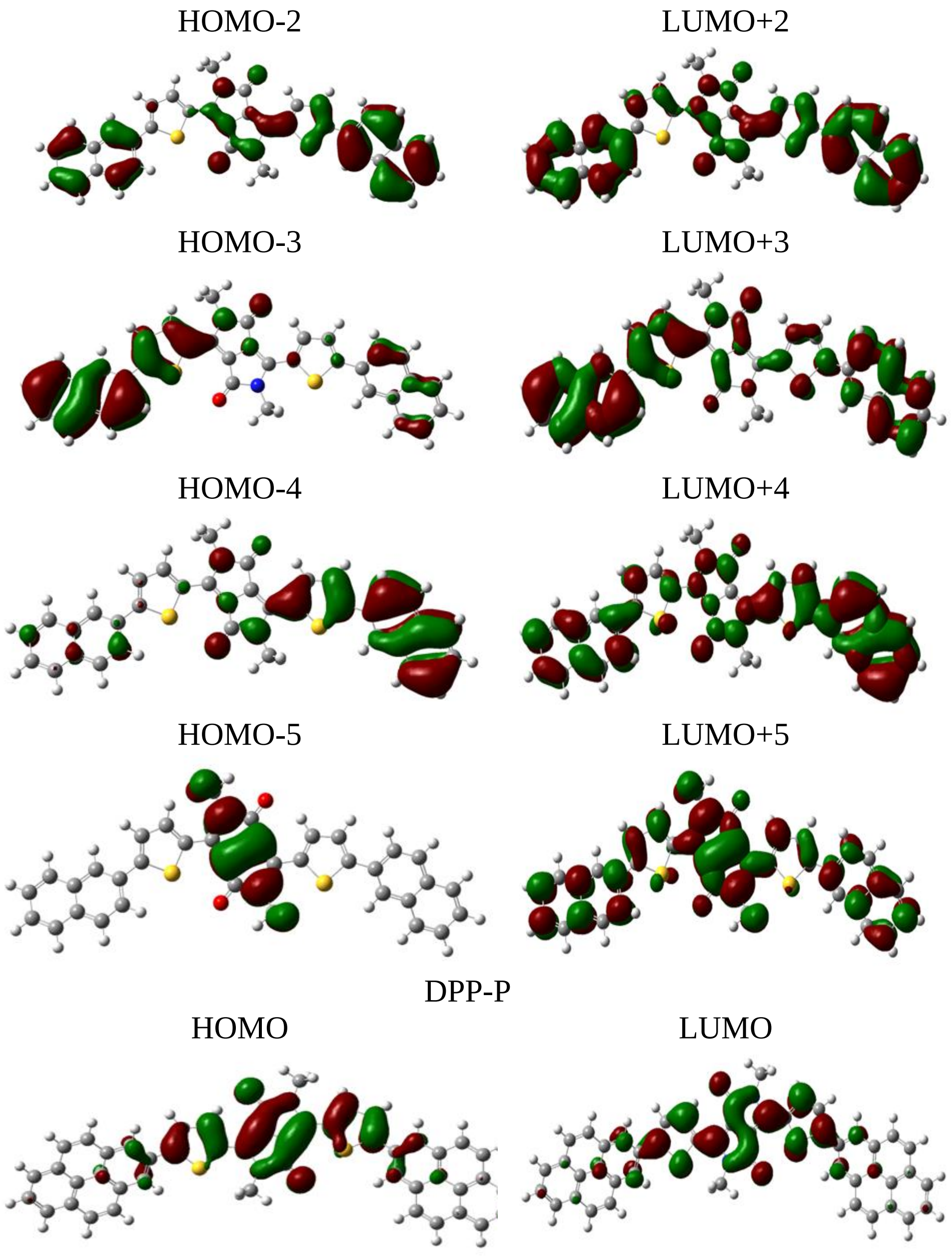


Figure 3. (c) Energy level diagrams of FMOs of DPP-N and DPP-P donor molecule

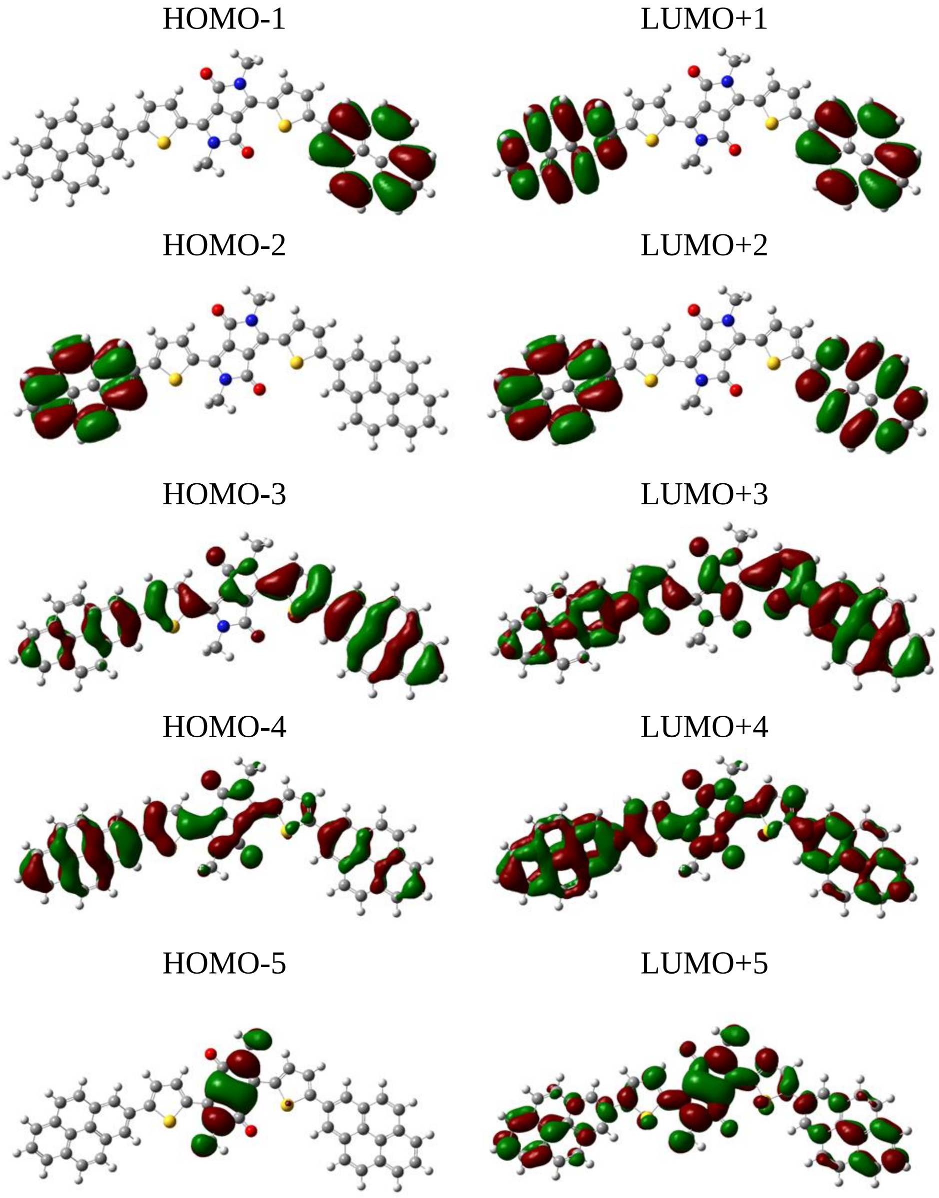


Figure 3. (d) Energy level diagrams of FMOs of DPP-P donor molecule

The molecules that were under observation were completely optimized at their ground state. Their qualitative molecular orbital representation of their HOMOs and LUMOs are shown in Figure 3(a) and 3(b). The structure and the reactivity of the molecules is explained with the help of their FMOs. Highest occupied molecular orbitals (HOMOs) are the bonding molecular orbitals which act as the electron donor or as the nucleophile, and lowest unoccupied molecular orbitals (LUMOs) are the anti-bonding molecular orbitals which act as the electrophile or as the electron acceptor. Localization and the delocalization of the electron density of the molecular orbitals is demonstrated in the Figure 3(a) and 3(b).

Electron densities of the molecular orbitals, which include the HOMOs and LUMOs, is shown in the green and red colours in the figures. To have a good charge transferring ability in a molecule, there should be a small energy gap in the HOMOs and LUMOs of the molecules. Through calculations, an analysis of E_{HOMO}, E_{LUMO} and E_g was accomplished to check the kinetic stability of the investigated molecules. E_g is basically the amount of energy which is necessary for the removal of one electron from ground state to a state of excitation.

Table 1. Optimized Values of Energies of HOMO, LUMO and Energy Gap (Eg) of HOMO-LUMO in eV at B3LYP/6-31g(d) Level of Theory

Molecules	HOMO (eV)	LUMO (eV)	E_g (eV)
DPP-B	-4.82	-2.55	2.27
DPP-N	-4.81	-2.55	2.26
DPP-P	-4.80	-2.56	2.24

Energies of HOMO, LUMO and the energy gap (E_g) between HOMO and LUMO was computed at the B3LYP function with 6-31g(d) basis set. Though the B3LYP method, it was found that the range of HOMO and LUMO energy levels was -4.82 eV to -2.55 eV. The calculated energy gap (E_g) of the optimized DPP-based small molecules with different donor groups by using B3LYP was between 2.24 eV to 2.27 eV (Table 1). The results of DPP based designed molecules were very close to the reference values.

The energy levels of the HOMO and LUMO of the investigated molecules, including DPP-B, DPP-N and DPP-P, was -4.82, -4.81, -4.80 and -2.55, -2.55, -2.56, respectively. The levels were close to the reference molecules; namely, DPP based C2-pyrene moieties [28] and DPP-OT-3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione(DPP(TBFu)$_2$) [29], where the OT refers to the unit of oligothiophene. It was found that the increasing order of energy level of HOMO is DPP-B < DPP-N < DPP-P, while DPP-P < DPP-N = DPP-B and the increasing order of energy gap is DPP-P < DPP-N < DPP-B. Thus, DPP based derivative is that DPP-P which has shown the smallest energy gap of HOMO and LUMO and has good absorption property as compared to others. The energy gap of the DPP-B and DPP-N are greater than that of DPP-P. Thus, the small value of the energy gap in DPP-P demonstrates a good charge transferring ability of this system from donor to the acceptor.

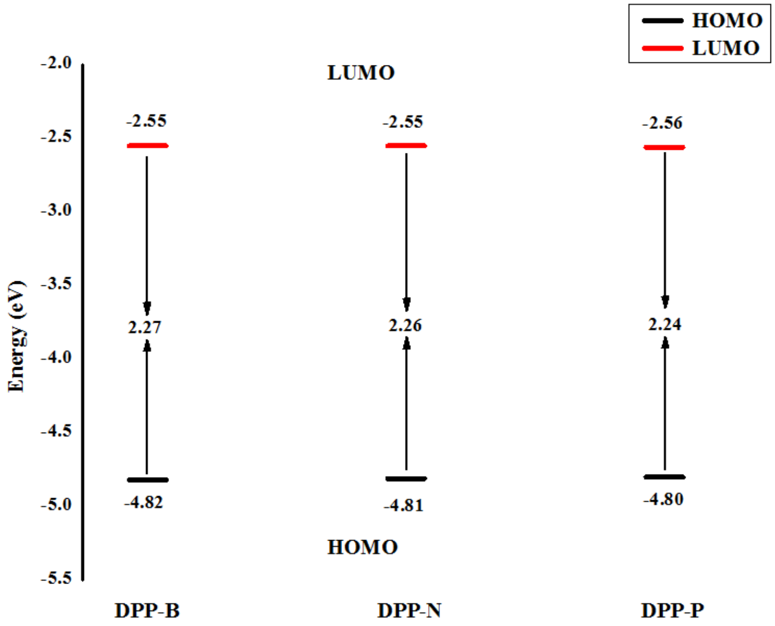


Figure 4. Evaluation of energies of HOMO and LUMO of the investigated molecules of DPP-B, DPP-N and DPP-P at B3LYP/6-31g(d) level of theory

Energy gaps have a strong link with the optical and electrical properties. The DPP-P molecule showed a small value in energy gap as compared to DPP-B and DPP-N because the value of the energy gap decreases as a result of an increase in the π electron delocalization in whole system. Small value of energy gap in the investigated molecules indicates the use of small amount of energy that is necessary for the excitation of electrons from one molecule to another. Molecules with a large energy gap absorb very small amounts of light of sun and thus demonstrate a narrow range of absorption. So, molecules with a small energy gap are preferred in such cases due to their optimal absorption spectra [30]. Thus, in this study, it is revealed that the DPP-P showed better results as compared to other molecules having narrow band gap value of 2.24 eV. The investigated molecules were completely optimized at their ground state. The energies of their HOMOs and LUMOs at the level of B3LYP/6-31g(d) are demonstrated in Figure 4.

3.4. Bond Lengths and Dihedral Angles of Investigated Molecules

In this study, we have calculated the bond lengths and dihedral angles of our investigated molecules, namely DPP-B, DPP-N, and DPP-P. The calculations are given in Table 4.2. We have also discussed the effect of donor groups as substituents on the inter bond length and dihedral angles. The inter bond length of benzene attached on the sides of the basic molecular structure of DPP-B as substituent was recorded as 1.46 A0 of C44-C14 and C36-C18. This means that the distance of these bonds is the same as in the DPP-B molecules, showing that there is no effect of the change in the position of the same substituent on the same molecule. Inter bond length for the attached substituents was also found to be 1.46 A0 for the DPP-B, DPP-N and DPP-P molecules, revealing that there is almost no effect of different substituents on the bond length of investigated donor molecules. In like manner, the inter bond length between the π-spacer (thiophene) and the basic structure of DPP was found to be 1.43 A0, revealing that there is almost no effect of the change in position of the same fragment.

Dihedral angles for the investigated molecules were found to be -1.59, -11.17, 25.23 and 24.65 for DPP-B; -1.77, -10.54, 23.04, and 23.61 for DPP-N; and -1.02, -10.73, -26.01, and 25.08 for DPP-P. DPP-P with smaller dihedral angles in comparison with DPP-B and DPP-N showed better planarity in its structure. It facilitates a better intermolecular packing, which results in the reduction in the optical band gap and an improvement in the charge transport.

Table 2. Calculated Values of Bond Lengths (A^0) and Bond Angles (Degree) of DPP-B, DPP-N and DPP-P Investigated Molecules

Molecules		**Bond Lengths (A^0)**	**Bond Angles ^{h}(Degree)**
DPP-B	1	C1-C11 1.43708	C3-C1-C11-C12 -1.59975
	2	C5-C21 1.43895	C4-C5-C21-S22 -11.17558
	3	C44-C14 1.46551	C49-C44-C14-S15 25.23081
	4	C36-C18 1.46641	C37-C36-C18-S22 24.65779
DPP-N	1	C1-C11 1.43671	C3-C1-C11-C12 -1.77699
	2	C5-C21 1.43855	C4-C5-C21-S22 -10.54772
	3	C42-C14 1.46356	C47-C42-C14-S15 23.04951
	4	C36-C18 1.46500	C37-C36-C18-C22 23.61512
DPP-P	1	C1-C11 1.43695	C3-C1-C11-C12 -1.02179
	2	C5-C21 1.43889	C4-C5-C21-S22 -10.73832
	3	C41-C14 1.46566	C46-C41-C14-S15 -26.01032
	4	C36-C18 1.46651	C37-C36-C18-S22 25.08953

The obtained results showed that the molecular structures of a linear molecule, based on the DPP, can be modified efficiently by selecting end groups properly. According to a previous report DPP-P showed closely packed crystal structure, having the greater overlap of the C2-pyrene unit. It was revealed that the end group of pyrene with extensive π-conjugation can express configuration with constructive packing for charge transfer[31]Thus, DPP-P showed better results in comparison with DPP-N and DPP-B due to its improved intermolecular packing with smaller dihedral angles.

3.5. Absorption Spectra

For the fabrication of a better photovoltaic material, the material should have an intense and broad absorption spectra [32]. DFT computations for the molecules utilizing the Gaussian 09 at B3LYP/6-31g (d) level were executed to find out the possible electronic properties and geometries of the molecules arising from chemical structures. With the increase in the amount of the delocalization in the structure of the molecule, greater amount of absorption occurs at the region of the spectrum with the longer wavelength. Thus, less energy is required for absorption and less energy gap is required between the energy levels of HOMOs and LUMOs. It is concluded that greater amount of delocalization of π-electrons reduces the energy gap, which in turn leads to stronger absorption at the maximum wavelength.

DFT and TD-DFT were used to compute and determine the electronic absorption spectra of optimized DPP-based designed molecules. Level of TD-B3LYP/6-31g(d) with chloroform as the solvent was used to calculate the absorption wavelength (λmax), excitation energy (Ex), and oscillator strength (*f*). Generally, greater oscillator strength demonstrates greater experimental absorption coefficients. The absorption spectrum computed at the TD-B3LYP/6-31g(d) showed very close resemblance with the experimental UV-Visible spectrum of reference molecules (DPP based C2-pyrene moieties (Lee et al., 2011) and the DPP-OT-3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP(TBFu)2) (Walker et al., 2009)). Figure 5 shows absorption spectra of the three investigated donor molecules. Table 3 represents the maximum wavelength (λmax) of represented absorption spectrum, excitation energy (Ex), main configurations (assignments), and oscillator strength (*f*) of designed donor molecules. For each molecule, 30 electronic transition states were calculated and only those transition states were selected which show the value of oscillator strength (*f*) equal or greater than the 0.1 ($f \geq 0.1$).

Table 3. The Values of Maximum Wavelength (λmax), Excitation Energy (Ex), Main Configurations (assignments) and Ooscillator Strength (*f*) of Investigated Donor Molecules at TD-B3LYP/6-31g(d) Level

Molecules	**Max. Wavelength λmax (nm)**	**Oscillation strength *f***	**Excitation Energy (eV)**
DPP-B	595	1.13	2.08
DPP-N	608	1.19	2.03
DPP-P	611	1.56	2.02

The analysis of the donor molecule's absorption spectra revealed that the DPP-P has the maximum value of absorption. Generally, solvent is introduced to adjust the energy values in the transition states so that very minimum amount of change takes place in the geometry of transition structure [2]. Thiophene π-spacer is used to improve the charge transferring ability. It causes intermolecular interactions, especiallyπ-π stacking, which results in the broadening of the UV-Visible absorption spectrum. It also causes longer effective conjugation length and an increase in ionization potential [33, 34].

To know the nature of electronic transitions in various regions, we investigated the absorption spectra of investigated donor molecules, namely DPP-B, DPP-N and DPP-P. Wavelength (λmax), excitation energy (Ex), oscillator strength (*f*), and main configurations (assignments) having relation with electronic configurations are calculated in Table 3. Simulated absorption spectra of the investigated donor molecules at TD-B3LYP/6-31g(d) level of theory are displayed in Figure 5.

All the investigated molecules showed a spectrum with wide absorption range of about 200-850nm. The value of λmax for the DPP-B molecule was found to be 595.62 and the value of oscillation strength (*f*) was found to be 1.1329. For the DPP-N molecule, the value of absorption wavelength was found to be 608.87 nm, which is higher than the DPP-B molecule.

Furthermore, the value of oscillation strength (*f*) for DPP-N was found to be 1.1933. For the DPP-P molecule, the value of absorption wavelength was found to be 611.32 nm, which is higher than the DPP-B and DPP-N molecule. The value of oscillation strength (*f*) for DPP-P was found to be 1.5664. Additionally, the values of excitation energy for DPP-P, DPP-N and DPP-B were found to be 2.0281, 2.0363, and 2.0816, respectively. Thus, it is concluded that DPP-B has higher value of excitation energy (2.0816) as compared to the other molecules. This molecule also demonstrates a blue shift with a decrease in λmax value and a greater oscillation strength.

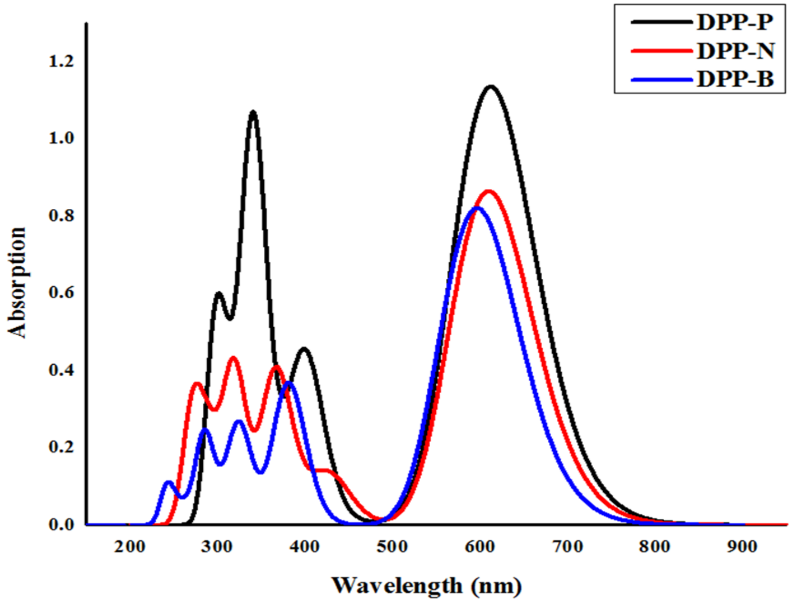


Figure 5. Simulated absorption spectra of the DPP-based analogues (DPP-B, DPP-N and DPP-P) in the chloroform solvent at TD-B3LYP/6-31g(d) level

HOMO and LUMO of all molecules showed that electron density is distributed over the whole structure of the molecule, especially on the acceptor region of the molecule. Our studies also revealed that the density of the charge in the HOMO-1 and LUMO+1 is equally dispersed over the molecule in the case of DPP-B and DPP-N. However, in the case of DPP-P, electron density resides towards the donor unit, especially in LUMO+1 of DPP-P. In HOMO-2 of DPP-B, electron density is distributed on the whole molecule, although in the case of DPP-N and DPP-P, electron density mostly resides over the donor units of the molecule due to an increase in conjugation and delocalization in the donor units. In LUMO+3 and LUMO+4, electron density is distributed on the whole structure of all molecules, showing that the electrons are completely delocalized. In HOMO+5, electron density resides on acceptor part, and in LUMO+5, electron density resides on the whole structure of the molecule.

The results of the Table 4 showed that the absorption spectrum of DPP-B reveals five absorptions in the spectrum's short wavelength region at 285, 321, 326 and 381 nm. They have the transitions of H – 1 → L+1, H – 4 → L, H → L + 2 and H - 2 → L, respectively. A strong absorption occurred at the 595 nm which showing a strong connection with main H → L electronic transitions. These electronic transitions can be recognized as π-π* transitions.

The absorption spectrum of DPP-N exhibits ten absorptions in the spectrum's short wavelength region at 270, 271, 281, 291, 296, 319, 362, 372, and 426 nm. They have the transitions of H – 1 → L + 3, H – 5 → L + 1, H – 2 → L + 2, H – 3 → L + 1, H – 9 → L, H – 1 → L + 1, H → L + 2, H – 4 → L, and H – 2 → L, respectively. A strong absorption occurred at 608 nm showing a strong connection with the main H → L electronic transitions. These electronic transitions can be documented as π-π* transitions.

The study of Table 4 revealed that absorption spectrum of DPP-P demonstrates seven absorptions in the spectrum's shortest wavelength region at 296, 304, 339, 342, 395, and 399 nm. They are connected with the transitions of H – 3 → L + 3, H – 9 → L, H → L + 4, H – 1 → L + 2, H – 3 → L and H – 4 → L, respectively. A strong absorption occurred at 611 nm showing a strong connection with the main H → L electronic transitions. These electronic transitions can be accepted as π-π* transitions.

Thus, DPP-P showed strong absorption at the broad range of spectrum at 611 nm as compared to the other molecules, namely the DPP-B and DPP-N. It is concluded that DPP-P demonstrates best results of absorption as compared to the others. These results showed that the absorption at the UV and visible region are due to the contribution of the π-conjugated electron donating groups which are sharing the same basic chain of DPP. It was noted that π-π* transitions occurred in the whole structure of the molecule.

Table 4. Calculated Values of Oscillator Strength (*f*), Maximum Wavelength (λmax), Excitation Energy (Ex) and Composition in Terms of the FMOs with the Related Character of the Investigated Molecules of DPP-B, DPP-N and DPP-P

	Transition states	**Maximum Wavelength (nm)**	**Oscillation strength (*f*)**	**Excitation energy (eV)**	**Assignments**
DPP-B	S0 → S1	595	1.1329	2.08	H → L (0.70) (π-π*)
	S0 → S4	381	0.4151	3.25	H - 2 → L (0.63) (π-π*)
	S0 → S7	326	0.2249	3.79	H → L + 2 (0.56) (π-π*)
	S0 → S8	321	0.1082	3.86	H – 4 → L (0.36) (π-π*)
	S0 → S16	285	0.2902	4.34	H – 1 → L+1 (0.66) (π-π*)
DPP-N	S0 → S1	608	1.1933	2.03	H → L (0.70) (π-π*)
	S0 → S3	426	0.1829	2.90	H – 2 → L (0.68) (π-π*)
	S0 → S6	372	0.2451	3.32	H – 4 → L (0.64) (π-π*)
	S0 → S8	362	0.3382	3.42	H → L + 2 (0.64) (π-π*)
	S0 → S12	319	0.4695	3.87	H – 1 → L + 1 (0.56) (π-π*)
	S0 → S18	296	0.1063	4.18	H – 9 → L (0.65) (π-π*)
	S0 → S19	291	0.1147	4.25	H – 3 → L + 1 (0.53) (π-π*)

	S0 → S23	281	0.1848	4.40	H – 2 → L + 2 (0.63) (π-π*)
	S0 → S24	271	0.1922	4.57	H – 5 → L + 1 (0.58) (π-π*)
	S0 → S25	270	0.1121	4.58	H – 1 → L + 3 (0.41) (π-π*)
DPP-P	S0 → S1	611	1.5664	2.02	H → L (0.70) (π-π*)
	S0 → S7	399	0.4530	3.10	H – 4 → L (0.62) (π-π*)
	S0 → S8	395	0.1534	3.13	H – 3 → L (0.46) (π-π*)
	S0 → S14	342	0.1831	3.61	H – 1 → L + 2 (0.51) (π-π*)
	S0 → S15	339	1.1922	3.64	H → L + 4 (0.44) (π-π*)
	S0 → S26	304	0.1785	4.07	H – 9 → L (0.45) (π-π*)
	S0 → S28	296	0.4195	4.17	H – 3 → L + 3 (0.53) (π-π*)

4. Conclusion

In this work, DPP based derivatives sharing a similar backbone of D-π-A-π-D were investigated. In these derivatives, pyrene, naphthalene and benzene act as electron donating end groups (in DPP-P, DPP-N, and DPP-B respectively), and DPP acts as the central core unit. Additionally, thiophene was used as a bridge between donor and acceptor fragments. It was also used for the computation of electronic, optical and photophysical properties. Their molecular structure was computed via Gaussian 09 to optimize their geometries and also to investigate their optoelectronic properties through DFT and TD-DFT. Excited states and electronic properties of investigated donor molecules were also calculated. The results revealed that all investigated molecules, namely DPP-P, DPP-N, and DPP-B, showed the appropriate E_g values of 2.24, 2.26, and 2.27 eV, respectively. At the level of TD-B3LYP/6-31g(d) and with chloroform as a medium, DPP-P showed strong absorption with an intense peak at 611 nm. The trend of absorption wavelength in nm for DPP-P, DPP-N and DPP-B was found to be: DPP-B < DPP-N < DPP-P. It was also noted that the absorption spectrum of DPP-P molecule was red shifted in comparison with other molecules. Hence, this study revealed that the investigated donor molecules can be used as photovoltaic material having a wide range of spectrum and they are extremely suitable for the high performance organic solar cells.

Conflict of Interest

The authors declare no conflict of interest.

References

[1] Shafiee S, Topal E. When will fossil fuel reserves be diminished?. *Energy policy*. 2009;37(1):181-9. https://doi.org/10.1016/j.enpol.2008.08.016

[2] Khan J, Arsalan MH. Solar power technologies for sustainable electricity generation–A review. *Renew Sustain Energy Rev*. 2016;55:414-25. https://doi.org/10.1016/j.rser.2015.10.135

[3] Green MA. Photovoltaic principles. *Physica E Low Dimens Syst Nanostruct.* 2002;14(1-2):11-7. https://doi.org/10.1016/S1386-9477(02)00354-5

[4] Scharber MC, Sariciftci NS. Efficiency of bulk-heterojunction organic solar cells. *Prog Polym Sci*. 2013;38(12):1929-40. https://doi.org/10.1016/j.progpolymsci.2013.05.001

[5] Shin WS, Jeong HH, Kim MK, et al. Effects of functional groups at perylene diimide derivatives on organic photovoltaic device application. *J Material Chem.* 2006;16(4):384-90. https://doi.org/10.1039/B512983D

[6] Nelson J. Organic photovoltaic films. *Curr Opin Solid State Mater Sci*. 2002;6(1):87-95. https://doi.org/10.1016/S1359-0286(02)00006-2

[7] Fitzner R, Elschner C, Weil M, et al. Interrelation between crystal packing and small-molecule organic solar cell performance. *Adv Mater*. 2012;24(5):675-680. doi:10.1002/adma.201104439 https://doi.org/10.1002/adma.201103177

[8] Zhou J, Wan X, Liu Y, et al. Small molecules based on benzo [1, 2-b: 4, 5-b′] dithiophene unit for high-performance solution-processed organic solar cells. *J Am Chem Soc*. 2012;134(39):16345-51. https://doi.org/10.1021/ja306865z

[9] Chen HJ, Wu HT, Hung KT, Fu SW, Shih CF. Sodium doping in copper-phthalocyanine/C60 heterojunction for organic photovoltaic applications. *Thin solid films*. 2013;544:249-53. https://doi.org/10.1016/j.tsf.2013.03.110

[10] Bibi S, Jia R, Zhang HX, Bai FQ. Effect of different topological structures (D-π-D and D-π-A-π-D) on the optoelectronic properties of benzo [2, 1-B: 3, 4-B́] dithiophene based donor molecules toward organic solar cells. *Solar Energy*. 2019;186:311-22. https://doi.org/10.1016/j.solener.2019.04.043

[11] Kwon OK, Park JH, Kim DW, Park SK, Park SY. An All-Small-Molecule Organic Solar Cell with High Efficiency Nonfullerene Acceptor. *Adv Material*. 2015;27(11):1951-6. https://doi.org/10.1002/adma.201405429

[12] Kim T, Kim JH, Kang TE, et al. Flexible, highly efficient all-polymer solar cells. *Nature Commun*. 2015;6(1):1-7. https://doi.org/10.1038/ncomms9547

[13] Lin Y, He Q, Zhao F, et al. A facile planar fused-ring electron acceptor for as-cast polymer solar cells with 8.71% efficiency. *J Am Chem Soc*. 2016;138(9):2973-6. https://doi.org/10.1021/jacs.6b00853

[14] Li Z, Lin JD, Phan H, et al. Competitive absorption and inefficient exciton harvesting: lessons learned from bulk heterojunction organic photovoltaics utilizing the polymer acceptor P (NDI2OD-T2). *Adv*

Funct Material. 2014;24(44):6989-98. https://doi.org/10.1002/adfm.201401367

[15] Choi YS, Jo WH. A strategy to enhance both VOC and JSC of A–D–A type small molecules based on diketopyrrolopyrrole for high efficient organic solar cells. *Org Electron*. 2013;14(6):1621-8. https://doi.org/10.1016/j.orgel.2013.03.031

[16] Fan L, Chen G, Jiang L, Yuan J, Zou Y. Benzodichalcogenophene-diketopyrrolopyrrole small molecules as donors for efficient solution processable solar cells. *Chem Phy*. 2017;493:77-84. https://doi.org/10.1016/j.chemphys.2017.06.007

[17] Pan L, Liu T, Wang J, et al. Efficient organic ternary solar cells employing narrow band gap diketopyrrolopyrrole polymers and nonfullerene acceptors. *Chem Material*. 2020;32(17):7309-17.

[18] Gaussian RA, Frisch MJ, Trucks GW, et al. Gaussian, Inc., Wallingford CT. 2009.

[19] Yuan J, Zhai Z, Li J, et al. Correlation between structure and photovoltaic performance of a series of furan bridged donor–acceptor conjugated polymers. *J Material Chem A*. 2013;1(39):12128-36. https://doi.org/10.1039/C3TA12210G

[20] Yuan J, Ma W. Diketopyrrolopyrrole based highly crystalline conjugated molecules for application in small molecule donor-polymer acceptor nonfullerene organic solar cells. *Org Electron*. 2016;39:279-87. https://doi.org/10.1016/j.orgel.2016.10.021

[21] Demeter D, Rousseau T, Leriche P, Cauchy T, Po R, Roncali J. Manipulation of the Open-Circuit Voltage of Organic Solar Cells by Desymmetrization of the Structure of Acceptor–Donor–Acceptor Molecules. *Adv Functional Material*. 2011;21(22):4379-87. https://doi.org/10.1002/adfm.201101508

[22] Sun Y, Welch GC, Leong WL, Takacs CJ, Bazan GC, Heeger AJ. Solution-processed small-molecule solar cells with 6.7% efficiency. *Nature Material*. 2012;11(1):44-8. https://doi.org/10.1038/nmat3160

[23] Yin B, Yang L, Liu Y, et al. Solution-processed bulk heterojunction organic solar cells based on an oligothiophene derivative. *Appl Phy Lett*. 2010;97(2):139. https://doi.org/10.1063/1.3460911

[24] Zhang J, Yang Y, He C, Li Y. Red-emission organic light-emitting diodes based on solution-processable molecules with triphenylamine core and benzothiadiazole-thiophene arms. *Sci China Chem*. 2011;54(4):695-8.

[25] Qiao Y, Guo Y, Yu C, et al. Diketopyrrolopyrrole-containing quinoidal small molecules for high-performance, air-stable, and solution-processable n-channel organic field-effect transistors. *J Am Chem Soc*. 2012;134(9):4084-7. https://doi.org/10.1021/ja3003183

[26] Murphy L, Hong W, Aziz H, Li Y. Influences of using a high mobility donor polymer on solar cell performance. *Org Electron*. 2013;14(12):3484-92. https://doi.org/10.1016/j.orgel.2013.09.024

[27] Jin R, Wang K. Rational Design of Diketopyrrolopyrrole-Based Small Moleculesas Donating Materials for Organic Solar Cells. *Int J Mol Sci*. 2015;16(9):20326-43. https://doi.org/10.3390/ijms160920326

[28] Lee OP, Yiu AT, Beaujuge PM, et al. Efficient Small Molecule Bulk Heterojunction Solar Cells with High Fill Factors via Pyrene-Directed Molecular Self-Assembly. *Adv Material*. 2011;23(45):5359-63. https://doi.org/10.1002/adma.201103177

[29] Walker B, Tamayo AB, Dang XD, et al. Nanoscale phase separation and high photovoltaic efficiency in solution-processed, small-molecule bulk heterojunction solar cells. *Adv Function Material*. 2009;19(19):3063-9. https://doi.org/10.1002/adfm.200900832

[30] Günes S, Neugebauer H, Sariciftci NS. Conjugated polymer-based organic solar cells. *Chem Rev*. 2007;107(4):1324-38. https://doi.org/10.1021/cr050149z

[31] Lee OP, Yiu AT, Beaujuge PM, et al. Efficient Small Molecule Bulk Heterojunction Solar Cells with High Fill Factors via Pyrene-Directed Molecular Self-Assembly. *Adv Material*. 2011;23(45):5359-63. https://doi.org/10.1002/adma.201103177

[32] Stübinger T, Brütting W. Exciton diffusion and optical interference in organic donor–acceptor photovoltaic cells. *J. Appl. Phys*.. 2001;90(7):3632-41.

[33] Young DC. A practical guide for applying techniques to real-world problems. *Comput Chem*. 2001;9:390.

[34] Kong H, Cho S, Lee DH, et al. The influence of electron deficient unit and interdigitated packing shape of new polythiophene derivatives on organic thin-film transistors and photovoltaic cells. *J Polym Sci A Polym Chem*. 2011;49(13):2886-98. https://doi.org/10.1002/pola.24724