



Theoretical studies of squaraine and functionalized 2,1,3-benzothiadiazole molecules for solar cell applications

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ABSTRACT

Research on alternative renewable energy sources is of great interest because of increasing world energy demand and depleting non-renewable energy resources. Both organic and inorganic solar cells are an important category of alternative energy resources. Inorganic solar cells, being the most successful technology has demerits such as high cost, rigidity etc. Organic solar cell is a better alternative with power conversion efficiency more than 17%. Squaraine is an important class of electron donating compounds which has high absorption and emission in the visible to near IR region. Organic photovoltaic devices with squaraine-fullerene systems attained 8% power conversion efficiency, which denotes that squaraine compounds have the potential for future organic solar cells. Organic materials consisting of 2,1,3-benzothiadiazole as core functionalized with different chromophore and squaraine as arms and vice versa may be a potential molecule for the fabrication of various organic electronic devices. By understanding the band gap, excitation energies and light-harvesting capability the designed molecules can be effectively used in solar cell applications. Here we designed and studied different squaraine containing molecules whose geometry optimization and band gap calculations are done by time-dependent DFT method. © 2019 Elsevier Ltd. All rights reserved.

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1. Introduction

The interest in converting solar energy to electricity is swiftly growing owing to the very high demand for low cost renewable energy sources. The existing technology of solar cells employs inorganic materials and is generally referred as silicon solar cells. However another class of solar cells, based on organic molecules has inspired the scientific and industrial community. Organic solar cells will be the next generation photovoltaics because of their compatibility with flexible substrates, low manufacturing cost and wide range of applications [1–5]. Recently more than 17% power conversion efficiency (PCE) is reported for organic photovoltaic devices [6]. Squaraine (SQ) compounds are an important class of electron donating compounds for organic solar cells with high absorption and emission in visible to near IR region and high oscillator strength [7–9]. It was reported that squaraine molecules have a central four membered ring system with two electron-

donating groups [9] and usually these are derived from squaric acid [10]. In 1965 Triebs and Jacob reported about squaraine dye for the first time, when they treated pyrrole with squaric acid resulted in the formation of an insoluble product [11]. Squaraine was first used as photovoltaic layer for organic solar cells by Merritt and Hovel in 1976 [12]. Now there is a growing interest in SQ compounds to use in bulk-heterojunction solar cells [13]. Over these years PCE of SQ based organic solar cells has reached 8.3% [14].

Another promising molecule for the fabrication of organic photovoltaic devices is 2,1,3-Benzothiadiazole (BT) [15,16]. Its properties and chemical reactivity are ideal for the fabrication of organic electronic devices such as organic light-emitting diodes, organic solar cells etc and thus benzothiadiazole derivatives will be a potential molecule [17]. BT and its π -extended oligomers, polymers and copolymers are used as donor molecule in organic photovoltaics (OPVs) [18,19] and has achieved an efficiency of around 10% [20]. Therefore it is of great interest to explore the properties of combinations of BT and SQ molecules, two potential candidates for the fabrication of organic electronic devices.

Scientists are putting tremendous effort to push the efficiencies of organic solar cells to a value that is competent with their inor-

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ganic counter parts. Different approaches such as controlling the morphology of active layers, optimizing the band gap of the materials to enhance the short circuit current and increasing open circuit voltage and modelling new molecules to improve the light harvesting efficiency have been applied to enhance the efficiencies of OPVs. Oligomeric molecules with excellent photophysical and charge transport properties can be designed with the help of advanced software and computer facilities. Therefore, quantum chemical and density functional theory (DFT) methods can be used for designing and further studies of organic molecules for solar cell applications [21,22]. Thus, computational studies can be taken as a good guide for designing efficient organic molecules which may be an ideal candidate for the fabrication of organic photovoltaic devices.

In this paper we designed a series of oligomers with 2,1,3-benzothiadiazole as core and squaraine as arms and vice versa and studied the optimised geometry, optical properties, band gap, light harvesting efficiency and open circuit voltage by time-dependant DFT theoretical calculations.

2. Computational methodologies

All computational calculations were carried out with the Gaussian 09 package [23]. Geometry optimization of squaraine compounds are calculated using time dependant DFT method using B3LYP hybrid functional and 6-311G basic set.

The power conversion efficiency (η) can be calculated from the short-circuit current density (J_{SC}), the open-circuit photovoltage (V_{OC}) and fill factor (FF). It can be calculated by using Eq. (1).

$$\eta = \frac{FFV_{OC}J_{SC}}{P_{inc}} \quad (1)$$

where, P_{inc} is the incident solar power.

The V_{OC} is directly proportional to the difference between the HOMO energy (E_{HOMO}) of electron donor and the LUMO energy (E_{LUMO}) of electron acceptor [24,25]. In this case the squaraine molecules are electron donors and PC₆₀BM is the electron acceptor. V_{OC} can be calculated by using Eq. (2) [26–28].

$$V_{OC} = \frac{1}{e} (|E_{HOMO}(D)| - |E_{LUMO}(A)|) - 0.3 \text{ V} \quad (2)$$

where, e is the elementary charge and 0.3 V is an empirical value. Scharber and co-workers proposed the equation (2) using the E_{LUMO} value as -4.3 eV for PC₆₀BM [27,29].

The short-circuit current density (J_{SC}) can be determined by Eq. (3) [28].

$$J_{SC} = \int \lambda LHE(\lambda) \Phi_{inject} \eta_{collect} d\lambda \quad (3)$$

where, $LHE(\lambda)$ is the light-harvesting efficiency at a given wavelength, Φ_{inject} is the electron injection efficiency and $\eta_{collect}$ is the charge collection efficiency.

The light harvesting efficiency is estimated from oscillator strength (f) and can be determined by the Eq. (4) [30].

$$LHE = 1 - 10^{-f} \quad (4)$$

The oscillator strength is related to the λ_{max} , Φ_{inject} and associated with the driving force (ΔG_{inject}) of the electrons injected from the excited state of the molecule. Thus LHE as well as J_{SC} is influenced by ΔG_{inject} . It is calculated from the oxidation potential of the excited molecule ($E^{molecule*}$) and reduction potential of the conduction band (CB) of the semiconductor (E_{CB}). Here we use commonly accepted value, -4.00 eV [31]. ΔG_{inject} can be calculated using the Eq. (5) [31].

$$\Delta G_{inject} = E^{molecule*} - E_{CB} \quad (5)$$

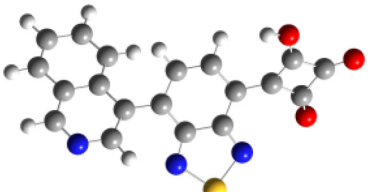
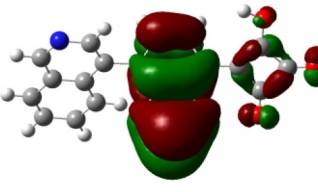
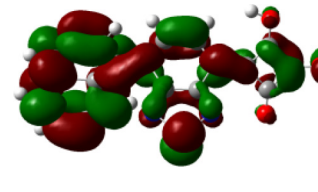
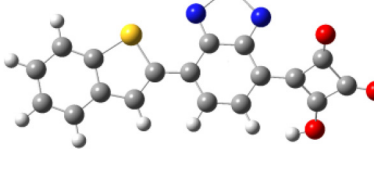
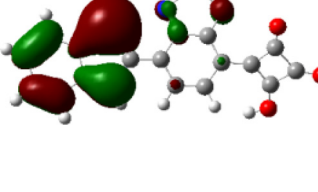
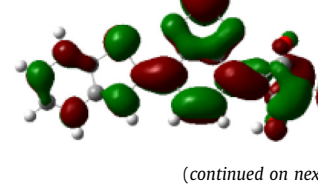
$E^{molecule*}$ can be calculated from the redox potential of the ground state of the molecule ($E^{molecule}$) and vertical transition energy by using the Eq. (6).

$$E^{molecule*} = E^{molecule} - \lambda_{max} \quad (6)$$

3. Results and discussion

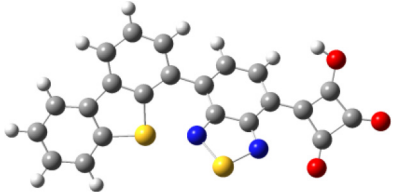
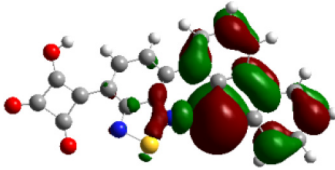
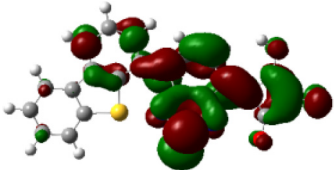
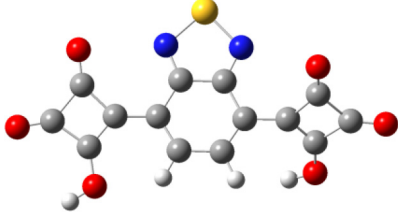
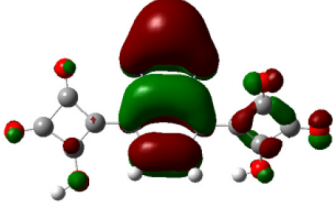
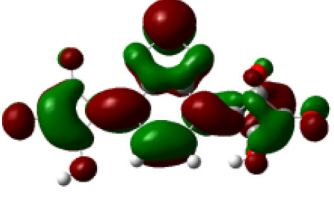
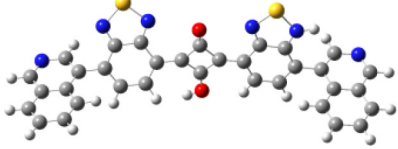
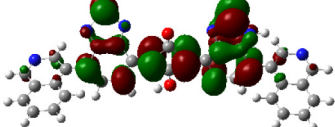
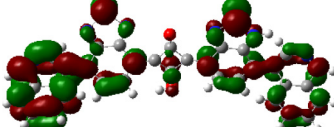
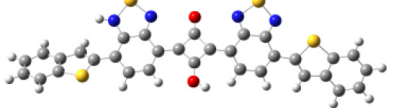
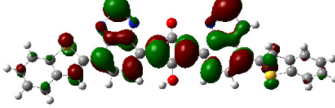
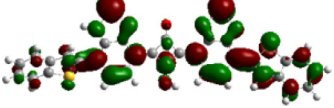

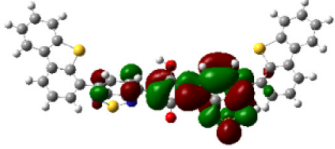
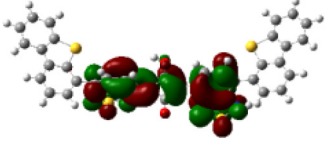
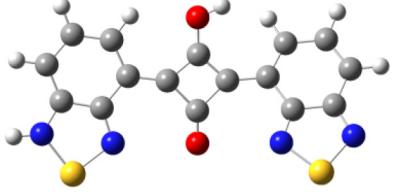
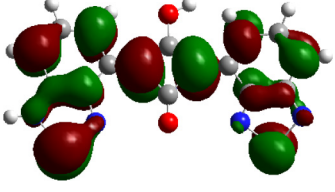
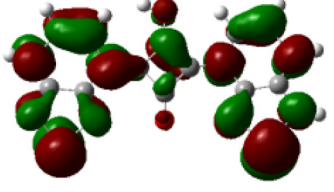
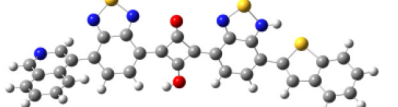
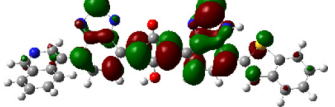
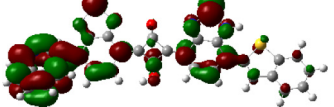
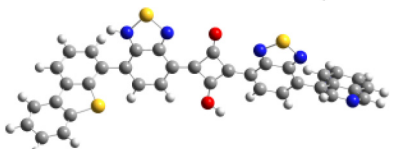
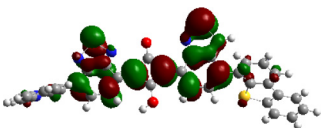
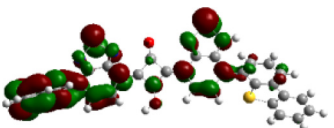
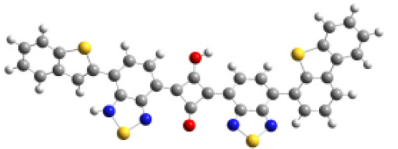
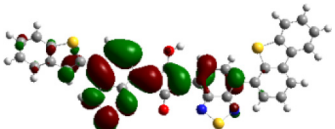
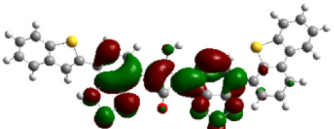
We have designed eleven different SQ and BT compounds. BT1-SQ (SQ₁), BT2-SQ (SQ₂), BT3-SQ (SQ₃) and SQ-BT-SQ (SQ₄) are compounds, in which BT is the central molecule, one arm of BT is substituted with SQ and other arm is substituted with different chromophoric groups such as isoquinoline, benzothiophene, dibenzothiophene and SQ respectively. BT1-SQ-BT1 (SQ₅), BT2-SQ-BT2 (SQ₆), BT3-SQ-BT3 (SQ₇) and BT-SQ-BT (SQ₈) are another set of compounds in which SQ is the central molecule and two sides of SQ are substituted with same substituent like isoquinoline derivative of BT (BT1), benzothiophene derivative of BT (BT2), dibenzothiophene derivative of BT (BT3) and 2,1,3-benzothiadiazole respectively. BT1-SQ-BT2 (SQ₉), BT1-SQ-BT3 (SQ₁₀) and BT2-SQ-BT3 (SQ₁₁) are another set with SQ as central molecule and both the arms of SQ are substituted with BT1 & BT2, BT1 & BT3, and BT2 & BT3 respectively. The optimized geometry, HOMO and LUMO of the designed molecules are summarized in Table 1.

Table 1
The optimized geometries of the designed molecules.

Compound	Optimized Geometry	HOMO	LUMO
BT1-SQ (SQ ₁)			
BT2-SQ (SQ ₂)			

(continued on next page)

Table 1 (continued)

Compound	Optimized Geometry	HOMO	LUMO
BT3-SQ (SQ ₃)			
SQ-BT-SQ (SQ ₄)			
BT1-SQ-BT1 (SQ ₅)			
BT2-SQ-BT2 (SQ ₆)			
BT3-SQ-BT3 (SQ ₇)			
BT-SQ-BT (SQ ₈)			
BT1-SQ-BT2 (SQ ₉)			
BT1-SQ-BT3 (SQ ₁₀)			
BT2-SQ-BT3 (SQ ₁₁)			

3.1. UV-visible data

Absorption values of the compounds are obtained from TD-DFT calculations. All absorption values are located in the visible region (400 nm to 700 nm) range except for SQ₄ (325.13 nm). The optical data of all the designed molecules are summarized in Table 2. The wavelength (λ_{\max}) are found to be in the increasing order

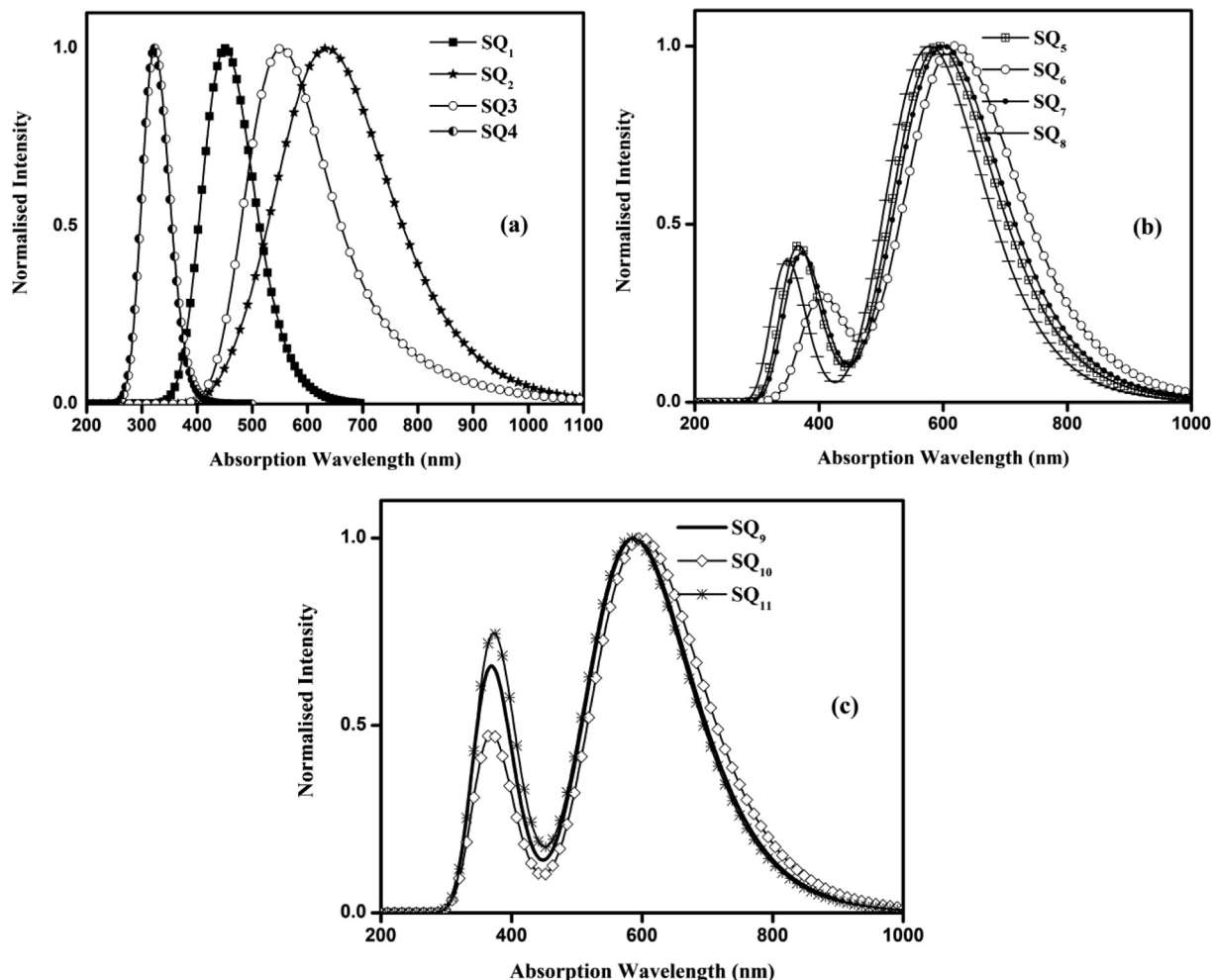
SQ₄ < SQ₁ < SQ₈ < SQ₁₁ < SQ₉ < SQ₅ < SQ₁₀ < SQ₇ < SQ₆ < SQ₃ < SQ₂. The absorption spectra of the oligomers are presented in Fig. 1.

3.2. HOMO-LUMO band gap

Band gap can be calculated from the difference between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molec-

Table 2Energy, λ_{\max} , HOMO, LUMO and Band gap of designed compounds calculated by TD-DFT B3LYP, 6–311 G.

Compound	Energy (au)	λ_{\max} (nm)	HOMO (eV)	LUMO (eV)	Band Gap (eV)
SQ ₁	-1509.43	451.14	-6.54	-3.82	2.72
SQ ₂	-1822.04	643.78	-6.15	-3.96	2.19
SQ ₃	-1975.69	626.38	-6.19	-3.90	2.29
SQ ₄	-1487.19	325.13	-7.78	-4.19	3.59
SQ ₅	-2568.36	592.31	-6.26	-3.99	2.27
SQ ₆	-3177.59	618.88	-6.18	-4.21	1.97
SQ ₇	-3482.81	600.58	-6.09	-3.99	2.10
SQ ₈	-1772.29	578.47	-4.79	-3.21	1.58
SQ ₉	-2872.98	588.04	-6.22	-3.37	2.85
SQ ₁₀	-3025.59	599.26	-6.16	-3.33	2.83
SQ ₁₁	-3330.21	585.14	-6.20	-3.35	2.85

**Fig 1.** UV-Vis spectrum of a) SQ₁-SQ₄ b) SQ₅-SQ₈ and c) SQ₉-SQ₁₁.

ular Orbital (LUMO). According to band theory HOMO and LUMO may be termed as the valence band and conduction band. The desirable band gap for an efficient photovoltaic system is in the range of 0.7–2.5 eV. From the calculation we found that the band gap of the designed oligomers varies in the range 1.58–3.58 eV. HOMO LUMO values and band gap of all the molecules are tabulated in Table 2. The compounds SQ₆, SQ₇ and SQ₈ have low band gap (1.97, 2.10 and 1.58) compared to other compounds and thus they can be used for the fabrication of organic photovoltaic devices.

3.3. Light harvesting energy (LHE) calculations

The LHE is calculated from the oscillator strength (f) of the molecule. From the values of λ_{\max} and f , we can see that there is

an optimum absorption (618.88 nm) for these molecules. Beyond and below this value f is decreasing and LHE is also decreasing. This can be explained by the dihedral angle, which is the angle between two intersecting planes. From this data we can also get the information about the planarity of molecule. In the first group (SQ₁–SQ₄), where BT is the central molecule, SQ₄ has the maximum LHE with 73.47% and has the lowest dihedral angle of 9.2°. The second group (SQ₅–SQ₁₁), where SQ is the central molecule, maximum LHE, 95.55% goes to SQ₆ with the lowest dihedral angle (25.02°) in the group. From this observation we can conclude that LHE is directly proportional to the oscillator strength and inversely proportional to the dihedral angle. The oscillator strength and LHE of these designed molecules are found to be in the order SQ₃ < SQ₂ < SQ₁ < SQ₄ < SQ₈ < SQ₁₁ < SQ₉ < SQ₁₀ < SQ₅ < SQ₇ < SQ₆.

Table 3
Calculated values of λ_{\max} , f , dihedral angle and LHE from TD-DFT calculations.

Compound	λ_{\max} (nm)	f	Dihedral Angle	LHE
SQ ₁	451.14	0.4977	34.87	0.6821
SQ ₂	643.78	0.3122	34.91	0.5127
SQ ₃	626.38	0.2454	37.67	0.4317
SQ ₄	325.13	0.5763	9.22	0.7347
SQ ₅	599.26	0.9777	29.39 (right)	0.8947
SQ ₆	618.88	1.3514	25.02 (right)	0.9555
SQ ₇	600.58	1.0316	28.79 (right)	0.9070
SQ ₈	578.47	0.7010	32.219 (right)	0.8009
SQ ₉	588.04	0.9148	30.11	0.8783
SQ ₁₀	599.26	0.9704	(angle of SQ- BT1) 29.46	0.8929
SQ ₁₁	585.14	0.9128	(angle of SQ-BT1) 30.20 (angle of SQ-BT3)	0.8778

Table 4
Calculated values of oscillator strength, LHE and V_{OC} of designed molecules from TD-DFT calculations.

Compound	f	LHE (eV)	V_{OC} (v)
SQ ₁	0.4977	0.6821	1.94
SQ ₂	0.3122	0.5127	1.55
SQ ₃	0.2454	0.4317	1.59
SQ ₄	0.5763	0.7347	3.18
SQ ₅	0.9777	0.8947	1.66
SQ ₆	1.3514	0.9555	1.58
SQ ₇	1.0316	0.90702	1.49
SQ ₈	0.7010	0.8009	0.19
SQ ₉	0.9148	0.8783	1.62
SQ ₁₀	0.9704	0.8929	1.56
SQ ₁₁	0.9128	0.8778	1.60

Calculated values of λ_{\max} , oscillator strength, dihedral angle and LHE are summarized in Table 3.

3.4. Open circuit voltage (V_{OC})

The V_{OC} is an important parameter used to predict the performance of a solar cell device. To evaluate this we need the E_{LUMO} of the acceptor and E_{HOMO} of the donor. Acceptor molecule is PC₆₀BM, one of the most widely used acceptor system [29]. The obtained V_{OC} values of designed oligomers are in the range of 0.19–3.18 eV. All the values are positive and this suggests that the electron transfer will be easy from the designed compounds to the PC₆₀BM; so we can use these compounds in OPV devices. The order of V_{OC} values of these compounds is as follows, SQ₈ < SQ₇ < SQ₂ < SQ₁₀ < SQ₆ < SQ₃ < SQ₁₁ < SQ₉ < SQ₅ < SQ₁ < SQ₄. The calculated values of oscillator strength, LHE and V_{OC} are shown in Table 4.

4. Conclusions

In this work TD-DFT calculations were performed for the studies of structural, electronic and absorption properties of symmetrical as well as unsymmetrical squaraine-2,1,3-benzothiadiazole based compounds (SQ₁ to SQ₁₁). The LHE values are related to the absorption maxima, oscillator strength and dihedral angle. The oligomers SQ₆ and SQ₇ have LHE above 90%, low band gap values and have V_{OC} values which are suitable for OPVs. Thus it can be concluded that SQ₆ and SQ₇ may be the potential molecules which can be used to fabricate OPV devices. Further studies of these oligomers are under progress in our laboratory.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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