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Research Article

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Posted Date: March 3rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-259041/v1>

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Quantum Chemical Investigation on D- π -A Based Phenothiazine Organic Chromophores with Spacer and Electron Acceptor Effect for DSSCs

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Abstract

In this work, the newly designed phenothiazine based organic dye (PT-BTBA, PT-EBTBA and PT-EBTEBA) derivatives were screened and investigated for dye-sensitized solar cells (DSSCs) application. The literature dye of SB covers the electron-donor (D) in phenothiazine and cyanoacrylic acid in electron-acceptor (A) based on D-A structure. In order to improving the π -conjugation and acceptor effects on the SB dye were investigated. The effect of D- π -A designed dyes on the optical absorption spectra and photovoltaic (PV) parameters were implemented by the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. Also, the hybrid functionals were initially evaluated to establish an accurate methodology for calculating the first-singlet absorption peak of SB dye. Consequently, TD-CAM-B3LYP functional and 6-311++G(d,p) theory were well match with the literature data. According to this result, phenothiazine-4-((7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)benzoic acid (PT-EBTEBA) dye has the strong group for more red-shifted and successfully electron inject into TiO₂ surface. It is expected to provide some theoretical guidance on designing photosensitive with new metal-free organic dyes for use in DSSCs yielding highly efficient performance.

Keywords: D- π -A Configuration; DFT and TD-DFT Calculations; CAM-B3LYP Functional; Electronic and Absorption Spectra; DSSCs.

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Introduction

Michael Gratzel and O'Regan groups were first developed by the dye-sensitized solar cells (DSSCs) in 1991, it was converted light energy into electricity [1]. In photovoltaic (PV) device, DSSCs components were contained the conduction band edge (CBE) of semiconductor titanium dioxide (TiO₂) surface, photoanode sensitized dyes, redox shuttle and counter electrode, respectively [2]. Furthermore, sensitizers can be divided into two categories: (i). Metal complex and (ii). Metal-free organic dye has one of the key components for high power conversion efficiency (PCE) in DSSCs. Recently, the scientific research report were conducted by PCE up to 24.2%, but the conventional electricity production process is still noncompetitive [3]. Metal-free organic sensitizers contain the donor (D), π -bridge (π) and acceptor (A) (D- π -A) have feasible flexibility for molecular proposal in DSSCs. Also, D- π -A pattern of the dyes were strongly desirable because of their several features, such as large absorption wavelength, high efficiency, tunable molecules with optoelectronic properties, lower cost large-scale production, easier preparation and purification, etc. [4-7]. Other major advantages of the organic sensitizers were cover the tunable absorption wavelength and PV properties over suitable molecular architecture [8, 9]. In literature, novel organic merocyanine [10], cyanine [11], hemicyanine [12], triphenylamine [13-16], dialkylaniline [17], phenothiazine [18], tetrahydroquinoline [19], coumarins [20-23], indoline [24-27] and carbazole [28] dyes were successfully investigated and proven for DSSCs application. For example, Kar groups reported on N, N'-dialkylaniline (NDI 6) based DSSCs were exhibits by PCE upto 19.24% [29].

Highly efficient organic photosensitizer for DSSCs must have the following properties [30]: First, dye absorbs most of the sunlight or light rays, a broad absorption range that covers together the Ultraviolet-Visible (UV-Vis) and near-infrared (N-IR) regions. Secondly, an intramolecular charge transfer (ICT) from electronic-D and A moieties is one of the main characteristics of organic DSSCs [31-35]. Third, the suitable energy level of the highest occupied molecular orbitals (HOMOs) must be below the redox potential I^- / I_3^- of the electrolyte. Consequently, the oxidized sensitizer that have lose electrons is then turned back to the ground state of a redox system. Also, lowest unoccupied MOs (LUMOs) of the dyes must be above the conduction band edge (CBE) of the TiO₂ semiconductor metal oxide. Thus, excited state molecules electrons can be efficiently injected into the TiO₂ surface. The D- π -A structure with

acceptor directly bonded to the semiconductor surface, which favor efficient charge transfer (CT) to the CBE of TiO₂ and regeneration to the ground state of dyes [36].

In 2011, Derong Cao synthesized a D-A based SB dye is a simple structure of the organic chromophore with a phenothiazine group as a donor and 2-cyanoacrylic acid as acceptor. The electron rich nature of a phenothiazine group were delivered a good spread for the electron movement from D to A. According to SB-based DSSCs were exhibits a power conversion efficiency (PCE) 2.91%, high photocurrent (6.13 mA cm⁻²) and photovoltage (709 mV) measured at under AM 1.5G irradiation [37]. The PCE of DSSCs was generally determined by the short-circuit current density (J_{sc}), open-circuit photovoltage (V_{oc}) and the fill factor (FF). Furthermore, the improvement of J_{sc} and V_{oc} would be significantly enhance the PCE.

Additionally, spacer and the acceptor group effects of dyes play a key role on TiO₂ surface. It has been improve efficiency of the organic solar cell. In this study, 4-(benzo[c]-[1,2,5]thiadiazol-7-yl)benzoic acid (BTBA), 4-(7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl)benzoic acid (EBTBA), 4-((7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)benzoic acid (EBTEBA) were used as the spacer and acceptor groups [38]. The designed dye names were denoted by PT-BTBA, PT-EBTBA and PT-EBTEBA. Scheme 1 display that the spacer and electron-A effect of the D- π -A sensitizers were under investigation. Furthermore, a detailed inspect on photosensitizing properties of PT-BTBA, PT-EBTBA and PT-EBTEBA derivatives were determined by density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. The calculated result PT-EBTEBA were represent that the smaller energy gap, vertical absorption coefficient obviously red-shift and development of organic DSSCs.

Computational Details

The quantum chemical investigation were recognized as a powerful instrument. It has been used to the electronic configuration and numerous belongings of dye sensitizers. The ground-state geometries of the designed dyes were fully optimized by DFT with the B3LYP [39] and 6-31G(d,p) theory. The optimized geometry results were executed by without any symmetry constraints, it has been broadly used for theoretical DSSCs research. The optimized dye structures were found at its local minima (no imaginary frequency modes) on the potential energy surfaces.

The previous TD-DFT valuation suggested that extremely efficient and reliable calculation of vertical excitation energies, photoabsorption spectra and PV properties [40, 41]. In reliability of DSSCs, the great effects of the exchange (XC) and long-range corrected (LC) functionals were used for absorption peak. In this work, XC & LC functionals such as B3LYP, CAM-B3LYP [42], P3PW91 [43] and ω B97XD [44] methods were analyzed for UV-Vis peak. From the functionals, SB dye absorption peak calculated values were listed in table 1. From the table, the absolute values were 507, 427, 508 and 398 nm, respectively. From the results, CAM-B3LYP functional was display nearly well matched to SB (439 nm) with errors of more or less 68, 12, 69 and 41 nm. Consequently, TD-CAM-B3LYP/6-311++G(d,p) theory has discovered to be the reliable functional for prediction of UV-Vis spectra. The solvent effects were included by the conductor-like polarizable continuum model (C-PCM) [45, 46]. During the research, as per literature tetrahydrofuran (THF) solvent were used in SB dye. Also, CAM-B3LYP was successfully employed for calculating the absorption spectra of the designed dyes. The absorption spectra were calculated by GaussSum 3.0 version [47]. The DFT and TD-DFT calculations of the dyes were accomplished by Gaussian 09w suite [48].

Results and Discussion

Screening of the Dyes and Optimized Structures

The spacer and electron acceptor groups are a key parameter with D- π -A structure for high-performance of organic DSSCs. We selected three functional types, which might be made for the addition of chemical modified in conjugation and acceptor. The substituent groups have been given as the collected from literature as discussed above. From the preceding study, those molecules are good performing for organic DSSCs application. In this manner, those dyes may be stimulated to the phenothiazine based dye derivatives. A newly designed dyes in PT-BTBA, PT-EBTBA and PT-EBTEBA were investigated by the DFT and TD-DFT systematically. The optimized geometric structures of the SB and designed dyes were performed by the B3LYP/6-31G(d,p) level of theory and shown in Fig. 1. As shown in figure, the geometry structures of the dyes were shown that the better coplanar configurations. Also, the coplanar structure designates that the photosensitizers were fully conjugated throughout the D- π -A pattern. It has been favorable for the photo-induced CT from the electron D-A and also accelerating electron

injection to the CBE of TiO₂ surface. Additionally, the introduced π -conjugation and acceptor part were favored to the broadening absorption wavelengths.

Electronic Structures and Frontier Molecular Orbitals (FMOs) of the Planned Dyes

Frontier molecular orbitals (FMOs) is a very crucial factor in defining the charge separated states of dye sensitizers [49]. The FMOs of PT-BTBA, PT-EBTBA and PT-EBTEBA were recognized with admire in electron CT states for all dyes. The influence of the spacer and acceptor in HOMOs and LUMOs were obtained at the optimized structures using B3LYP/6-31G(d,p) level and shown in Fig. 2. To make a capable charge-divided by photoabsorption, it is desirable that the HOMOs were predominantly contained in the donor fragment of phenothiazine and π -spacer, LUMOs were localized on the π -spacer and electron acceptor moiety of benzoic acid (generally on the anchoring area). The electron dispersal indicated that the best CT character among the HOMOs and LUMOs. As shown in Figure 2, isodensity contour plots of the all dyes were efficient for CT. The HOMOs and LOMOs energies shown that possible responsible for the development of PV properties in organic DSSCs. As displayed in table 2, HOMOs and LUMOs energy values were -5.30, -5.20, -5.12, -4.99 eV and -3.01, -2.95, -2.98, -2.92 eV, respectively. Moreover, the calculated energy gap (E_g) values of the studied compounds were 2.29, 2.25, 2.14, 2.07 eV, respectively.

The HOMOs energy level must have lower than the redox potential I^- / I_3^- of electrolyte (-4.80 eV) [50]. Similarly, all the LUMOs energies have to be capable of injecting electrons into the CBE of TiO₂ (-4.0 eV) surface [50]. According to fig. 3, all LUMOs energies dyes lie over the CBE of TiO₂ and the HOMOs were situated below the redox couple. As shown in figure 3 and table 2, energy levels of the all designed dye compounds has smaller E_g , compared to SB. In particular, PT-EBTEBA dye can be identified that the positive response to wider absorption region and regeneration with photo-oxidation manner.

Optical Absorption Properties

Firstly, the optical absorption peak of SB dye was used four different functionals (B3LYP, CAM-B3LYP, P3PW91 and ω B97XD) with THF solvent and TD-DFT calculation (Table 1 and Figure 1). According to the best of functional, designed dye derivatives have been calculated at TD-CAM-B3LYP/6-311++G(d,p) theory with THF medium. The simulated absorption spectra

and corresponding calculated vertical excitation energy (E), oscillator strengths (f), major and minor orbital contributions (%) of the dyes have been listed table 3 and shown in Fig. 4 and. From the figure, all the organic dyes have shown extensive visible around 600 nm, which is related to ICT character. Normally, the molecular dyes with broader wavelengths and enhanced molar extinction coefficients are predicted to have higher photo-to-current conversion efficiency of DSSCs performance [51].

As shown in table 3, the calculated maximum optical absorption wavelengths of the planned dyes were 388, 464 and 506 nm, respectively. In particular, PT-EBTEBA sensitizer has the longer absorption spectrum compared to other dyes and SB (427 nm). Also, the vertical excitation energies of the dyes were 2.68, 2.67 and 2.44 eV, respectively. All the derivative sensitizers have shown red-shifts, compared to SB dye. The longer wavelengths were assigned to the ICT among the D to electron-A, and the shorter peaks were assigned to the localized π - π^* transitions within organic dyes. Moreover, the strongest absorption spectra of dyes were arising from $n \rightarrow \pi^*$ transitions. From table 3, the E were decreased order: PT-EBTBA > PT-BTBA > PT-EBTEBA showing that there has a red-shifts when passing from PT-EBTBA. The calculated results indicated that a PT-EBTEBA sensitizer more redshift at the long-wavelength side, which was promoted to further increase of the corresponding DSSCs.

PV Properties

Power Conversion Efficiency

PCE of the DSSCs have been calculated by using Eq. (1) [52]:

$$\eta = \frac{J_{SC} V_{OC} FF}{P_{INC}} \quad (1)$$

Where P_{INC} designates incident power density. In DSSCs, V_{OC} is predominantly determined by the difference between redox electrolyte and CBE of TiO_2 . Commonly, the solution I^- / I_3^- is used as the redox shuttle, it is able to be taken as a constant. The shift of CBE can be determined by using the formulation to earlier studies [53]. The μ_{normal} is another crucial characteristic that delivers the vertical electronic charge dispersal in the dye molecules. As proven in figure S0 (supporting information), if μ_{normal} was excessive to a more extent shift of CBE the outcome has been large V_{OC} .

As shown in table 4, the dipole moment values of PT-BTBA, PT-EBTBA and PT-EBTEBA are 6.01, 7.80 and 8.31 Debye, respectively. Also, all the dyes may have possible response a larger V_{OC} . In particular, a higher values of PT-EBTEBA can be very good act for V_{OC} , compared to SB (4.55 Debye). Among three dyes, PT-EBTEBA may be the best performance for excessive conversion efficiency of DSSCs. As for J_{SC} , it is a crucial part for DSSCs calculated by the formulations previous study [54] and the corresponding factors are discussed below. In order to attain extreme J_{SC} , LHE of the dye molecules necessity to be as high as possible.

$LHE(\lambda)$ can be described by the following equation [55]:

$$LHE(\lambda) = 1 - 10^{-f} \quad (2)$$

Where f signifies oscillator strength of associated dye molecules related to the absorption peak. So as to provide a needful of the spacer and electron acceptor, we simulated to the absorption spectra of the dyes with affecting the LHE . The calculated LHE values of the PT-BTBA, PT-EBTBA and PT-EBTEBA dye molecules were given in the range from 0.76 to 0.92 a.u., respectively. Based on LHE of the sensitizers, the values have to be high as probable to maximize the photocurrent reply for DSSCs. As displayed in table 4 and figure 5a, PT-EBTEBA dye has the highest value of LHE . Hence, all the sensitizers provided more or less similar photocurrent. In specific, PT-EBTEBA dye is more than the SB and other dyes, it has beneficial for J_{SC} .

Electron Injection and Dye Regeneration

Another method of increasing J_{SC} influence factors of the dye regeneration (ΔG_{reg}) electron injection (ΔG_{inject}) and oxidation potential energy ($E_{OX}^{dye^*}$) was calculated by using principles as defined in a previous study [56] and the calculated values are listed in table 4. The electronic possessions of the dyes in the first-singlet excited state is a main feature to increase the organic DSSCs. Theoretically proposed that ΔG_{inject} from the dye sensitized in the first excited state to CBE of TiO_2 surface [57]. According to table 4, it is observable that the ΔG_{inject} calculated values are negative, which means that the excited state of the dye lies above the CBE of TiO_2 . As said

by Islam theory, $\Delta G_{inject} > 0.2$ eV [58]. Consequently, absolute calculated values of the all planned dyes are much than 0.2 eV. Also, ΔG_{inject} energy values are given in the range from -1.45 to -1.55 eV, respectively.

J_{sc} is also enhanced by regeneration efficiency (ΔG_{reg}) of the dyes. For a quicker CT, it is essential to lesser regeneration [59]. From Table 4, the absolute calculated values of the PT-BTBA, PT-EBTBA and PT-EBTEBA are 0.40, 0.32, and 0.19 eV, respectively. The ΔG_{reg} of the PT-EBTBA and PT-EBTEBA dyes can be fastest regenerated, which is increased for J_{sc} . Particularly, PT-EBTEBA dye is extreme PCE of the DSSCs.

Open-Circuit Photovoltage

Theoretical analysis of eV_{oc} was determined by using the formulations as defined in an earlier study [60]. The eV_{oc} calculated values are listed in Table 4 and presented in figure 5b. From the table, PT-BTBA, PT-EBTBA and PT-EBTEBA values are given in a range from 0.99 to 1.08 eV, in these values is a promising response to the efficient electron injection. Also, larger values of the LUMOs will produce the higher eV_{oc} , which is provided to PCE of the DSSCs.

According to figure 5b, it has shown that the PT-BTBA and PT-EBTEBA dyes larger eV_{oc} value, compared to SB dye. In specific, PT-EBTEBA dye has a higher eV_{oc} , which identify that the extraordinary performance of organic DSSCs. Therefore, PT-EBTEBA dye has used for the dye-sensitized, owing to their electron injection technique from the excited state sensitizers into the CBE of TiO₂ have been successful.

Exciton Binding Energy (E_b)

To get high PCE in DSSCs, the electron-hole pairs should be split into separate negative and positive charges to escape from recombination owing to coulombic forces. During this procedure, the binding energy need be overcome; that is, the dyes must take lower exciton binding energy to attain high PCE of DSSCs. The exciton binding energy was followed by using the formula in earlier studies [61, 62] and the values are listed in table 4. From the table, PT-BTBA, PT-EBTBA and PT-EBTEBA dyes absolute calculated values are 0.43, 0.53 and 0.37 eV, respectively. As shown in figure 5c and table 4, PT-EBTEBA dye is smaller value than the

other molecules and SB. It can be noted that PT-EBTEBA dye has lesser than the other sensitizers and SB (0.61 eV), which denotes that the excellent act for DSSCs.

Conclusion

A sequence of three isolated metal-free organic DSSCs totally on the PT-BTBA, PT-EBTBA and PT-EBTEBA became successful with spacer and electron acceptor. The molecular orbital electronic structures, absorption properties and PCE influence parameters of the dyes were investigated systematically. In this study, the DFT and TD-DFT methods were discussed in detail to planning dye products. The calculated outcomes suggest that the screened with a spacer and the electron acceptor in PT-EBTEBA has promising functional organization for D- π -A form. Furthermore, the calculated results imply that the PT-EBTEBA dye has strong light harvesting efficiency, electron injection, electron transition, dye regeneration, open-circuit photovoltage, exciton binding energy and increasing the dipole moment, which benefits to higher PCE of DSSCs. It has concludes that the choice of the appropriate screened with spacer and electron acceptor. Finally, these are very important for the molecular design of phenothiazine based highly efficient organic solar cells.

Acknowledgements

The authors extend their sincere appreciation to Researchers Supporting Project at King Saud University, Riyadh, Saudi Arabia for funding this research (2020/06).

Funding

King Saud University, Riyadh, Saudi Arabia (2020/06).

Conflict of interest

The authors declared that there is no conflict of interest.

Availability of data and material

All the data and electronic materials available for Gaussian program.

Code availability

Chemdraw, Gaussian 09w, Gaussview and Gausssum.

Authors' contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Figure Captions

- Scheme 1** Outlining of molecular structures for D- π -A System.
- Fig. 1** Optimized geometric structures of SB and designed dye molecules were calculated at B3LYP/6-31G(d,p) level of set.
- Fig. 2** The selected frontier molecular orbitals of the Planned dyes and SB were implemented on B3LYP/6-31G(d,p) level of theory.
- Fig. 3** The energy levels of the SB and PT-BTBA, PT-EBTBA, PT-EBTEBA dyes are calculated at B3LYP/6-31G(d,p) theory.
- Fig. 4** TD-DFT absorption spectra of designed sensitizers and SB are calculated at CAM-B3LYP/6-311++G(d,p) level of basis set in THF medium.
- Fig. 5a,5b,5c** Light harvesting efficiency, open-circuit photovoltage and exciton binding energy of the SB, planned dyes were performed by the CAM-B3LYP/6-311++G(d,p) level of theory.

Supporting Information

- Fig. S0** Dipole moment of the SB and designed molecules are calculated by B3LYP/6-31G(d,p) level of theory.

Highlights

- ❖ The phenothiazine-based organic dyes are designed and investigated.
- ❖ The absorption wavelength PT-EBTEBA was showed better than the SB and other molecules.

Figures

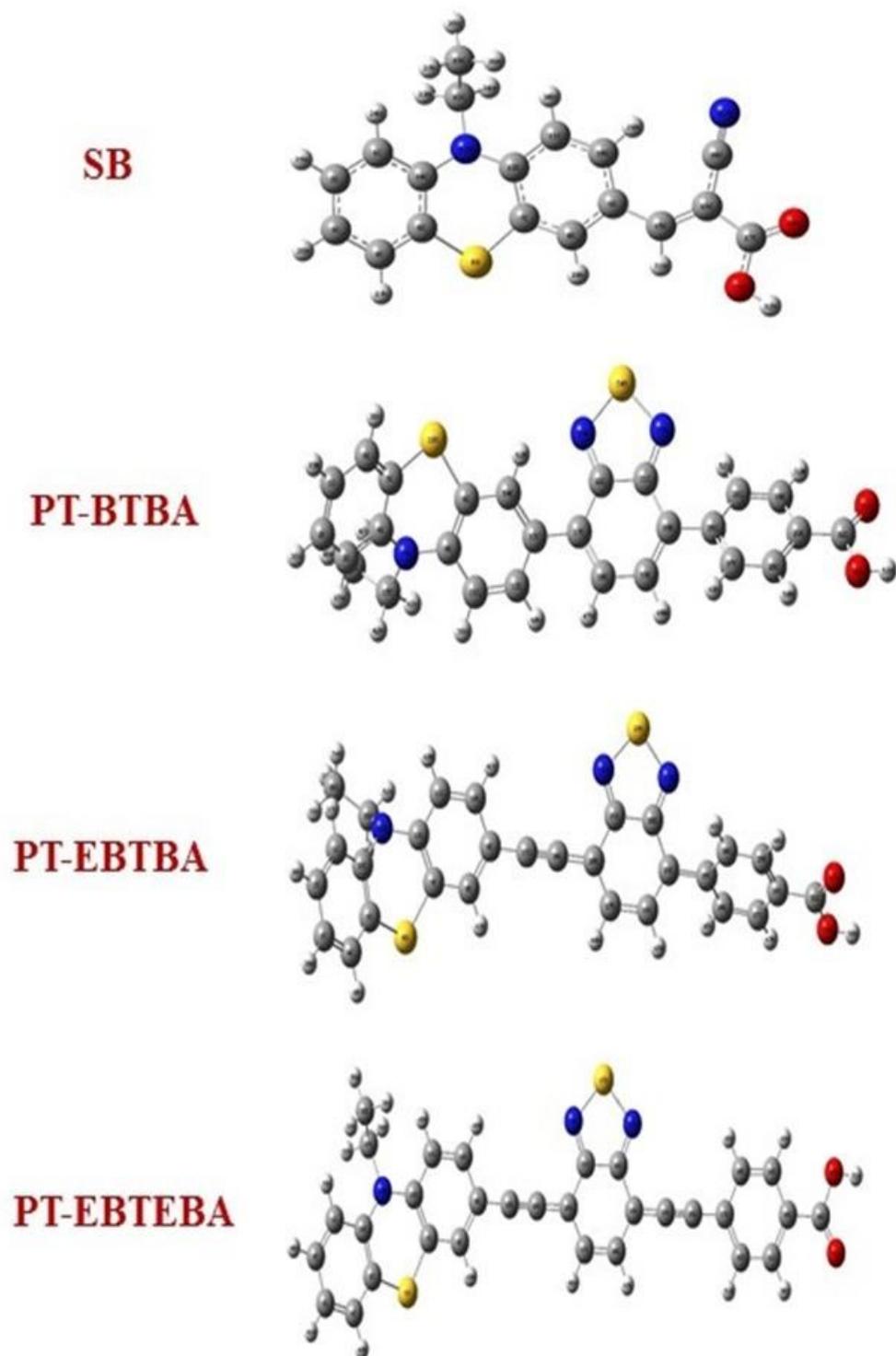


Figure 1

Optimized geometric structures of SB and designed dye molecules were calculated at B3LYP/6-31G(d,p) level of set.

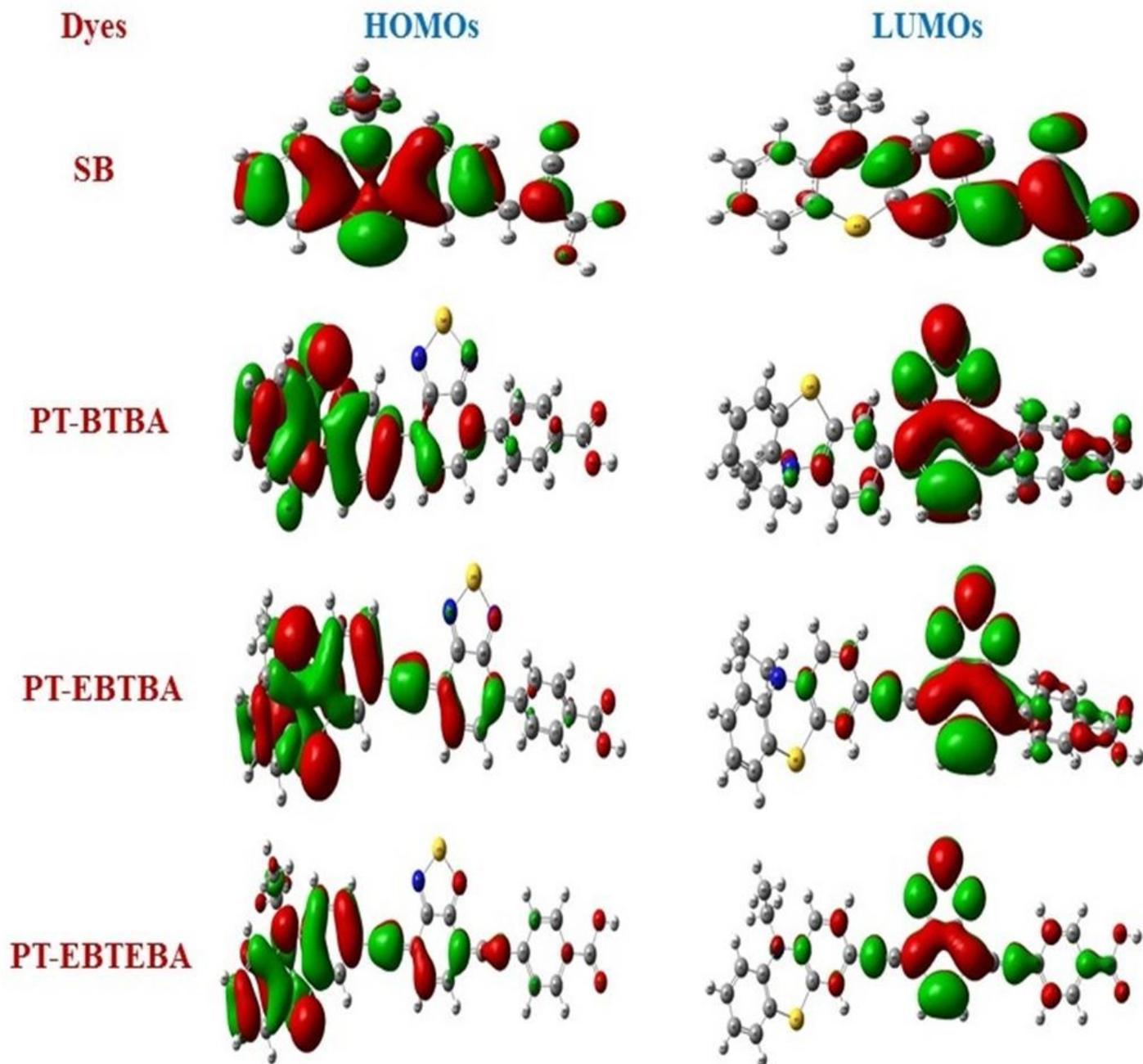


Figure 2

The selected frontier molecular orbitals of the Planned dyes and SB were implemented on B3LYP/6-31G(d,p) level of theory.

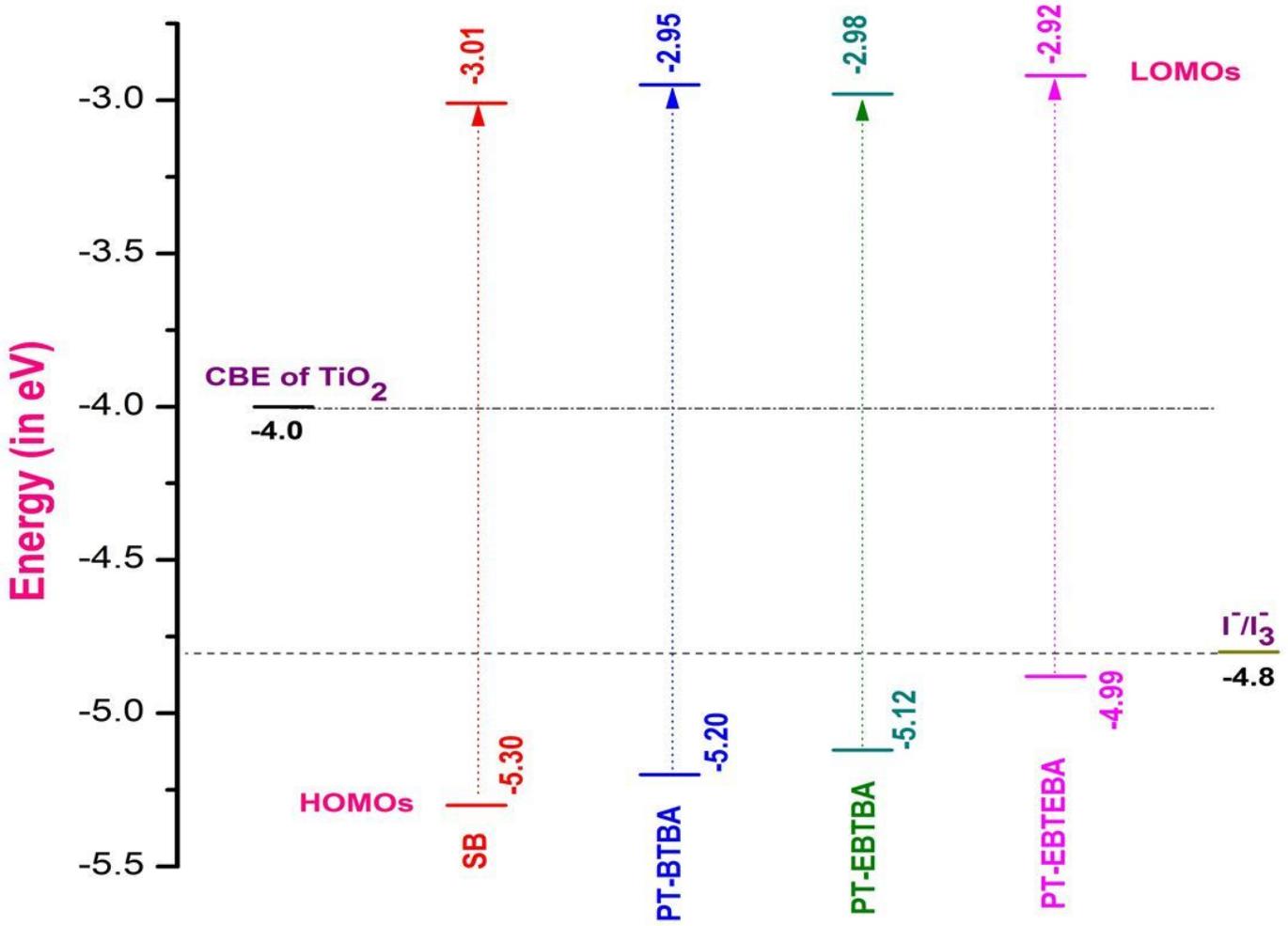


Figure 3

The energy levels of the SB and PT-BTBA, PT-EBTBA, PT-EBTEBA dyes are calculated at B3LYP/6-31G(d,p) theory.

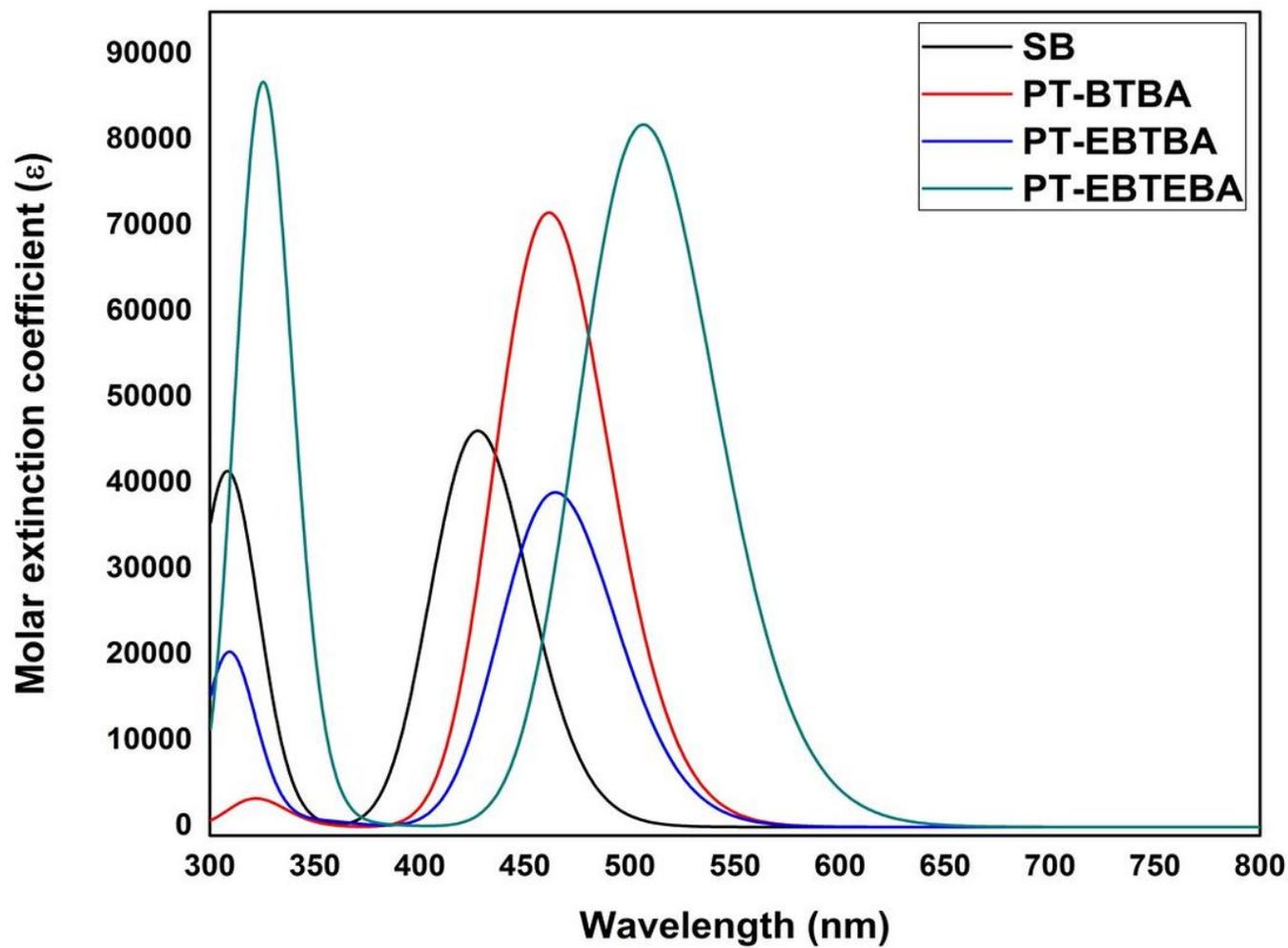
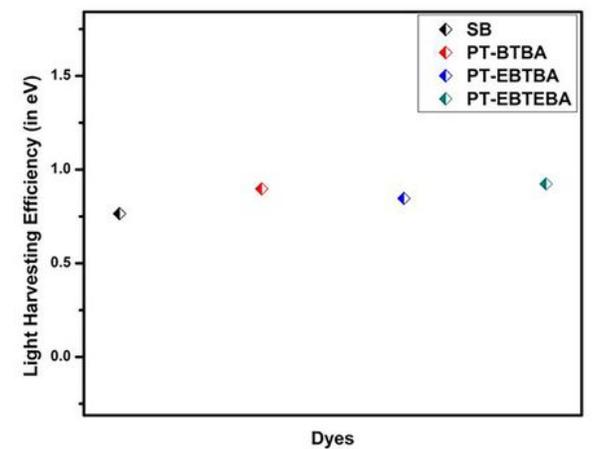


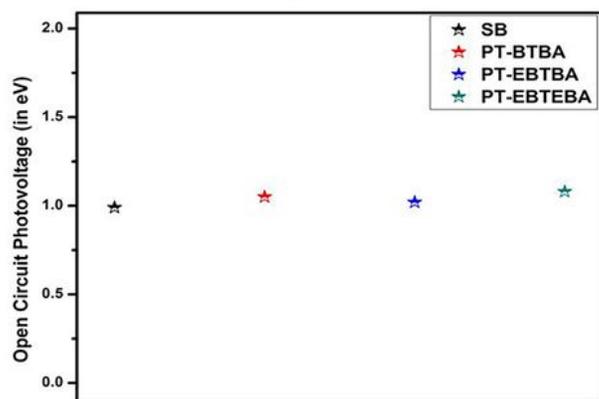
Figure 4

TD-DFT absorption spectra of designed sensitizers and SB are calculated at CAM-B3LYP/6-311++G(d,p) level of basis set in THF medium.



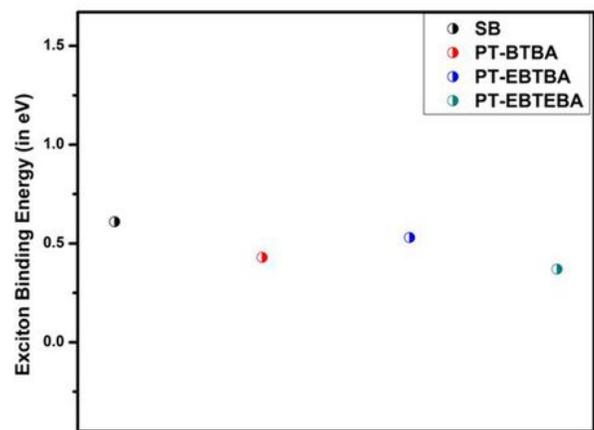
Dyes

a



Dyes

b



Dyes

c

Figure 5

Light harvesting efficiency, open-circuit photovoltage and exciton binding energy of the SB, planned dyes were performed by the CAM-B3LYP/6-311++G(d,p) level of theory.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

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