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Research Article

Cyanidin-Based Novel Organic Sensitizer for Efficient Dye-Sensitized Solar Cells: DFT/TDDFT Study

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Cyanidin is widely considered as a potential natural sensitizer in dye-sensitized solar cells due to its promising electron-donating and electron-accepting abilities and cheap availability. We consider modifications of cyanidin structure in order to obtain broader UV-Vis absorption and hence to achieve better performance in DSSC. The modified molecule consists of cyanidin and the benzothiadiazolylbenzoic acid group, where the benzothiadiazolylbenzoic acid group is attached to the cyanidin molecule by replacing one hydroxyl group. The resulting structure was then computationally simulated by using the Spartan'10 software package. The molecular geometries, electronic structures, absorption spectra, and electron injections of the newly designed organic sensitizer were investigated in this work through density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations using the Gaussian'09W software package. Furthermore, TDDFT computational calculations were performed on cyanadin and benzothiadiazolylbenzoic acid separately, as reference. The computational studies on the new sensitizer have shown a reduced HOMO-LUMO gap; bathochromic and hyperchromic shifts of absorption spectra range up to near-infrared region revealing its enhanced ability to sensitize DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSC), first introduced in 1991, are emerging as the most promising alternative to traditional silicon solar cells due to the low cost of fabrication and easy manufacturing process [1–4]. The sensitizer, which plays a major role in DSSC function, absorbs light and injects electrons to the conduction band of TiO_2 from its excited state. Sensitizers based on ruthenium [5, 6], zinc porphyrin [7, 8], and organic dyes [9] have been discovered and applied as efficient sensitizers for DSSC. Despite of the high efficiency of ruthenium and porphyrin sensitizers, environmental complication and sophisticated synthesizing procedures make it necessary to find for alternative efficient sensitizers.

Presently, many efforts are created to develop novel, reliable, efficient, and environmental-friendly sensitizers for real-world applications [5, 10, 11].

Natural dye molecules such as flavonoids, betalains, carotenoids, and chlorophylls are currently being tested as alternatives to the expensive sensitizers in the fabrication of DSSC, considering their electron-donating and electron-accepting abilities [12–16]. However, the efficiencies of DSSCs sensitized with natural dyes are still very poor, mainly due to the poor light-harvesting properties associated with them [17–20]. Therefore, the need to invent natural dye-based new dye with improved optical properties favorable to enhance efficiency of DSSC is a worthy solution.

In this study, a cyanidin, which belongs to flavonoids, based new organic dye is modeled and its suitability as a

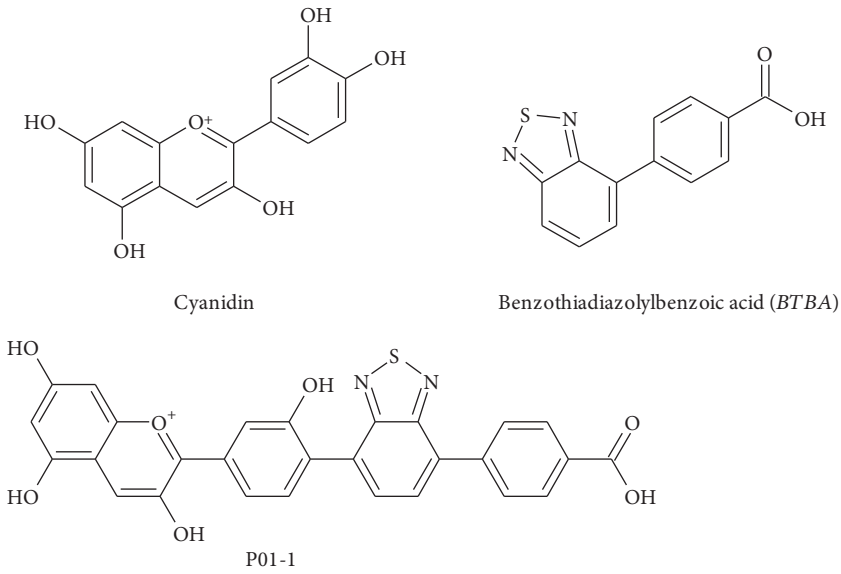

Figure 1: Fundamental molecular structure of cyanidin, *BTBA*, and *P01-1*.

novel sensitizer in DSSC is computationally tested using density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations. The new sensitizer, *P01-1*, is designed by attaching one of the hydroxyl groups on the benzene ring of cyanidin to the benzothiadiazolylbenzoic acid (*BTBA*) unit as shown in Figure 1. Following IUPAC rules, we have named the molecule (*P01-1*) as p-{5-[2-hydroxy-4-(3,5,7-trihydroxy-2-chromenyl)phenyl]-8-thia-7,9-diazabicyclo[4.3.0]nona-1(9),2,4,6-tetraen-2-yl}benzoic acid. In the design, we used benzothiadiazolylbenzoic acid as an electron acceptor by considering its strong electron withdrawing ability in some excellent dyes reported by Yao and coworkers [21]. The position of the *BTBA* substitution to cyanidin is based on our previous work [12]; TDDFT calculations of cyanidin revealed that the electron density cloud of the lowest unoccupied molecular orbital (LUMO) is highly localized and denser in the selected hydroxyl group.

2. Computational Details

The molecular structures of *P01-1*, cyanidin, and benzothiadiazolylbenzoic acid (*BTBA*) are computed using Spartan'10 software [22] to retrieve the molecular geometry coordinates. Both DFT and TDDFT calculations are performed using Gaussian'09W software [23]. The molecular structures of *P01-1*, cyanidin, and *BTBA* are fully optimized using Becke's three-parameter hybrid functional using Lee-Yang-Parr hybrid functional (B3LYP) [24] in ethanol. The electronic structures and total energies are calculated using 6-31g (d) basis set which adopted to describe metal-free atoms. All of the calculations include the solvation effect in ethanol using the polarizable continuum model (PCM) [25]. The lowest 5 singlet-singlet excitations are included in the TDDFT calculations. The models of electron density of various energy levels of the *P01-1* are visualized, and absorption spectra of *P01-1*, cyanidin, and *BTBA* are simulated using GaussView version 5.0 [26].

Table 1: Summary of DFT computational calculation of cyanidin, *BTBA*, and *P01-1* constituents in ethanol with geometry optimization.

Sensitizer	With geometry optimization		
	HOMO (eV)	LUMO (eV)	Energy gap (eV)
Cyanidin	−6.18	−3.39	2.79
BTBA	−6.33	−2.55	3.78
P01-1	−6.18	−3.66	2.52

The synthetic strategy to reach *P01-1* is by coupling cyanidin and bromo-benzothiadiazolylbenzoic acid together via Ullmann cross coupling reaction [27, 28]. Cyanidin can be extracted from natural flowers and fruits; benzothiadiazolylbenzoic acid (*BTBA*) can be synthesized by following a procedure reported by Yao and coworkers [21].

3. Results and Discussion

3.1. DFT Calculation. DFT calculations are performed on the *P01-1* molecule with a solvent effect on ethanol. For comparative purposes, we also performed calculations on cyanidin and *BTBA*. The results are summarized in Table 1. It is observed that the band gap value of *P01-1*, obtained after geometry optimization in ethanol, is smaller than HOMO-LUMO gap values of cyanidin and *BTBA* in ethanol.

3.2. HOMO-LUMO Energy Levels. Molecular orbitals and their properties such as corresponding energy are very useful to identify the best sensitizers for DSSCs. The highest occupied molecular orbital (HOMO) represents a donating ability of electrons; LUMO represents acceptability of electrons. For the efficient electron injection and regeneration

Table 2: Computed excitation energies in (eV), (nm), and the oscillator strength (f) of the cyanidin and *P01-1* obtained by TDDFT calculations at B3LYP/6-31g (d) level with the inclusion of geometry optimization under the solvation effect of ethanol.

Sensitizer	Optimized in ethanol			
	Calculated energy		Oscillator strength	MO configuration
	(eV)	(nm)	(f)	(coefficient)*
Cyanidin	2.52	492.16	0.583	H➔L = 0.695
	2.82	439.86	0.010	H-3➔L = 0.318
				H-2➔L = 0.467
				H➔L+1 = 0.211
	3.17	391.21	0.273	H-3➔L = 0.322
				H-2➔L = 0.192
				H-1➔L = 0.586
	3.88	319.36	0.025	H-4➔L = 0.687
	4.49	276	0.055	H-3➔L = 0.516
P01-1	2.18	567.75	0.795	H➔L = 0.703
	2.60	476.81	0.054	H-2➔L = 0.132
				H-1➔L = 0.665
	2.79	443.99	0.007	H-2➔L = 0.685
	3.00	413.81	0.312	H➔L+1 = 0.668
	3.22	385.11	0.148	H-4➔L = 0.613
				H-1➔L = 0.194
				H➔L+1 = 0.187

*Molecular orbitals with configuration coefficient < 0.1 are not shown.

processes, LUMO of sensitizer must be above the conduction band edge of TiO_2 (−4.0 eV) while HOMO of sensitizer must be below the energy level of the redox couple (−4.8 eV) [29–31]. The DFT calculations (see Table 1) show that the *P01-1* satisfies the conditions for efficient photo-energy conversion.

3.3. TDDFT Calculations and Absorption Spectra. TDDFT simulations are performed on the newly designed sensitizer *P01-1*, cyanidin, and *BTBA*, to gain perceptions on the excitation energy, electronic transition, optical properties, and UV-Vis absorption spectra for the singlet-singlet transition with hybrid functional B3LYP in ethanol solution. The lowest 5 singlet-singlet excitations are included in the TDDFT calculations.

The excitation energies, oscillator strengths, and molar extinction coefficient for the five states of *P01-1* and cyanidin calculated using B3LYP on 6-31g (d) basis set are shown in Table 2, and the computer simulated UV-Vis absorption spectra obtained for the *P01-1*, *BTBA*, and cyanidin via TDDFT calculations are depicted in Figure 2.

Oscillator strength expresses the strength of transitions to the excited states. The higher the oscillator strength, the higher the possibility for the molecule to be sensitized [32–36]. Except in the third excitation state, all other excitation states up to fifth excitation state have shown that oscillator strengths of *P01-1* are higher than those of cyanidin.

P01-1 has produced four significant oscillator strengths up to the fifth excitation states except third excitation state,

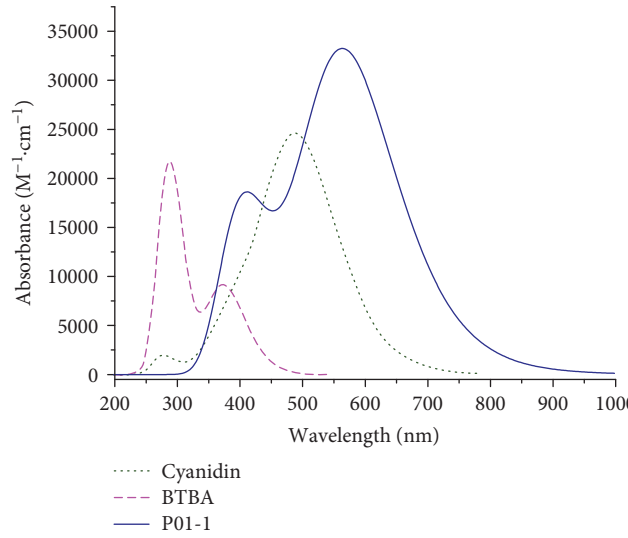

Figure 2: UV-Vis absorption spectra obtained for the *P01-1*, *BTBA*, and cyanidin via the output of TDDFT calculations with the solvation effect of ethanol solution.

while cyanidin only produced three significant oscillator strengths at the first, third, and fifth excitation states. This suggested that *P01-1* has more potential to be sensitized as compared to cyanidin. In addition, the λ_{max} values of the *P01-1* at each five excitation states shifted to longer wavelengths compared to λ_{max} of cyanidin by 75.59 nm, 36.95 nm, 52.78 nm, 94.45 nm, and 109.11 nm, respectively.

The absorption spectra of cyanidin and the *BTBA* extend only up to 800 nm and 550 nm. Interestingly, the absorption spectra of the *P01-1* have shown a redshift up to near IR of 1000 nm (Figure 2). The absorption bands of *P01-1* are more intense and broad in the visible region. The absorption maxima of *P01-1* has bathochromic shifts of 75.59 nm as compared to that of cyanidin. Furthermore, they have hyperchromic shifts of 8.577 ($10^3\,M^{-1}\cdot cm^{-1}$). These shifts in the modified dyes are favorable to effectively lead to an efficient sensitization.

3.4. Molecular Orbitals. The electron density clouds modelled at the transition of various energy levels that correspond to the first five excited states of *P01-1* are shown in Figure 3. At different energy levels, it could be observed that electron density clouds are localized in different regions of the *P01-1* molecule.

Almost all levels of the ground state energy such as HOMO-4, HOMO-2, HOMO-1, and HOMO levels of *P01-1* are π-type. At the HOMO, HOMO-1, and HOMO-3 levels, the electron density clouds are mostly delocalized over the entire molecule of *P01-1* but, at the HOMO-2 level, the electron density cloud is more localized in the benzene ring of the cyanidin unit of *P01-1*.

In the *P01-1* molecule, the electron cloud of LUMO is π^* type and the molecular orbital is localized at cyanidin unit. Here, the electron density cloud is observed to be denser in a chromenylium unit than the benzene dial on cyanidin unit of *P01-1*. The photogenerated electrons are excited to

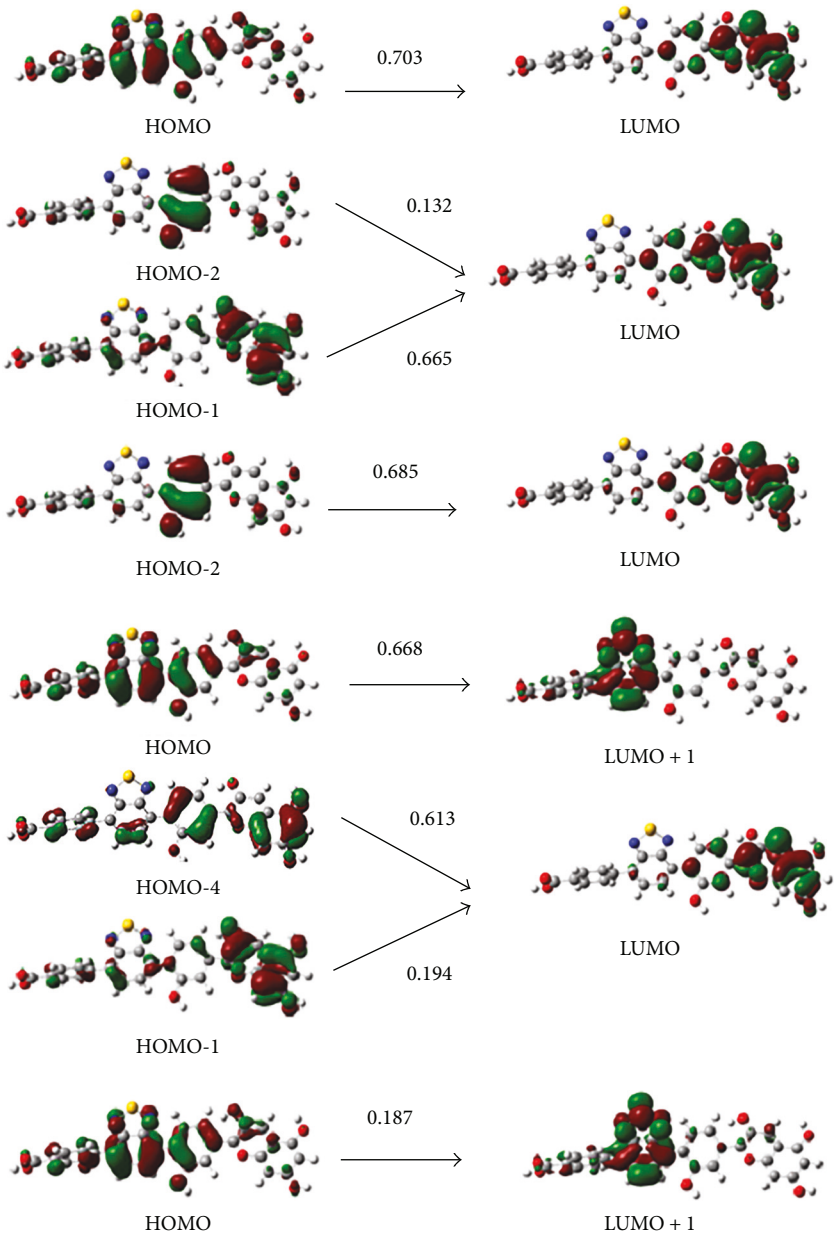

Figure 3: The behavior of electron density clouds at the various energy levels corresponding to the first five excited states of *P01-1* in ethanol using the TDDFT simulation with isovalue of contour = 0.03.

chromenylium unit on the electrode of TiO_2. Subsequently, electrons are easily injected into the conduction band of TiO_2 [32]. This electron injection is most possible from the chromenylium unit as it has denser electron density cloud in the LUMO π^* state. Therefore, the anchoring group of *P01-1* molecule that may efficiently inject electrons into the TiO_2 is deduced to be the hydroxyl group.

4. Conclusions

The molecular geometries, electronic structures, and absorption spectra of the newly designed molecules of the *P01-1* sensitizer are investigated by DFT and TDDFT computational analyses. By evaluating HOMO and LUMO energy levels obtained from DFT calculations of geometry-optimized structure of *P01-1* molecules with solvent effect in ethanol, *P01-1* satisfied the main requirement for efficient electron injection, where the LUMO level of *P01-1* is higher than the conduction band of the TiO_2 and the HOMO level of *P01-1* is sufficiently lower than the redox couple. Furthermore, the band gap of *P01-1* is smaller than that of cyanidin and *BTBA* in ethanol.

The UV-Vis absorption spectra reveal that the *P01-1* complex extends absorption spectra from 800 nm to 1000 nm range with bathochromic and hyperchromic shifts. All these results suggest a more promising sensitization ability of *P01-1* which is designed by modifying the sensitizer, cyanidin.

Disclosure

Kalpana Galappaththi permanent address is Institute of Technology University of Moratuwa, University of Moratuwa, Katubedda, Sri Lanka.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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