ORIGINAL ARTICLE

Effect of Extended Conjugation on the Photosensitizers for DSSC: DFT and TD-DFT Study

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Abstract

Dye sensitized solar cells have achieved more than 12% efficiency[1][2] since 1991 when first metal organic photosensitizer was made by Gratzel based on ruthenium complex[3]. Here we have discussed the effect of extended conjugation on absorption spectra of the photosensitizers[4]. The designed dye molecules are based on donor- π -acceptor model. The designed dyes are named as S1 [**naphthalene-pyrrole-butanoic acid**] and S2 [**naphthalene-pyrrole-thiophene-butanoic acid**]. In both the systems naphthalene is the donor and butanoic acid is the acceptor moiety. The pyrrole is the bridging molecule in S1 and pyrrole along with thiophene are the bridging moiety in S2. Both the systems are optimized under the framework of density functional theory using B3LYP hybrid functional with 6-31+G(d,p) basis set and absorption spectra is calculated utilizing time dependent density functional theory at CAM-B3LYP functional on Gaussian *16W* software. The optimized geometries are also checked for their global minima on the potential energy surface through frequency calculation. The calculated absorption maxima of the S1 are at 286.66 nm and for S2 the absorption maxima are observed at 296.89 nm. The frontier molecular orbital energy gap HOMO-LUMO for S1 is found at 4.34 eV and for S2 it is 3.75 eV. This shows that the HLG energy reduces on increasing the π bridge molecule in the system which enhances the absorption maxima towards the red shift of the visible spectrum. The red shift of 10.23 nm in the absorption spectra is observed in the S2 system as compared to the S1. Thus, the effect of bridging on the absorption maxima shows that conjugation length plays a key role in enhancing the absorption spectra for the designed photosensitizer. Therefore, this study would help in designing the novel conjugated organic molecules as better photosensitizers for high-performance DSSCs.

Keywords: DSSC; DFT; TD DFT; CAM-B3LYP; D-π-A; D-π- π-A.

Introduction

Dye sensitized solar cells are semi-transparent, roll to roll printable and have low production cost which makes it environment friendly material than inorganic material based solar cells. Gratzel et.al. made the first DSSC based on ruthenium complex, which showed efficiency around 10% [1]. Since then metal free organic

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dyes are extensively explored in recent years [2,3]. The structure for designing the organic sensitizers for DSSC have donor, spacer and acceptor are connected all together to form a dye molecule [3,4]. While the other structures based on one donor and two acceptors or two donors and one acceptor are also utilized for making efficient sensitizers which has showed wide absorption region [4-6]. The tunability of the absorption region of the sensitizer is the key, which can be achieved either by increasing the electron donating strength or through the effecting bridging length or through the electron acceptor strength [7-10]. The widely utilized donor compounds are based on carbazole, phenothiazine, diphenylamine, coumarin etc. while the spacer or bridging compound is thiophene, thiazole, pyrrole etc. and the acceptor molecules are cyanoacetic acid, rhodamine acetic acid, napthalimide and benzolthiadiazole etc. Recent progress in the field of organic solar cells with new π-conjugated polymers, small molecules (SMs), fullerene-free acceptors (FFAs), all together with the better device configurations have shown significant improvement in power conversion efficiencies of single-junction Bulk Hetero Junction Solar Cells in the range of 10 to 16% [11-14]. In this paper, two novel dyes have been designed to look upon the effect of π bridging in the system. We have utilized one donor (naphthalene) and one acceptor (butanoic acid) approach along with one π bridge molecule and two π bridge molecules in the form of pyrrole and thiophene. Naphthalene is chosen as a donor

moiety expected to show good charge transport property in the designed system [15]. And butanoic acid is the strong electron acceptor which will act as an electron puller form the donor site of the dye molecule which is expected to reduce the recombination of the exciton pair. Therefore, butanoic acid is chosen as acceptor in this study [16-17]. The system first is based on (donor-π-acceptor) model S1 [naphthalene- pyrrole-butanoic acid] and system second is based on (donor-π- π-acceptor) model S2 [naphthalene-pyrrole-thiophene-butanoic acid]. Both the optimized dyes are shown in Figure 1. The designed molecules were targeted to show shift in the absorption region towards red side of the visible spectrum.

The charge transfer mechanism in the dye sensitized solar cells is typically takes place from the acceptor site of the dye which is also called the anchoring unit on the semiconducting material (e.g., TiO_2, SnO_2, ZnO, CuO etc.). As the dye molecule absorbs photon energy, it excites its electron to the excited state then this electron passes to the semiconducting material. And the oxidized dye gets regenerated through the electrolyte solution (e.g., iodide solution) which is used as filler in the dye based solar cells. For an efficient charge transfer from the sensitizer, the LUMO levels of the dye must be at higher position than the conduction band of the semiconducting material and HOMO levels of the dye must be at lower level of the electrolyte's redox potential [18-19].

(a)

(b)
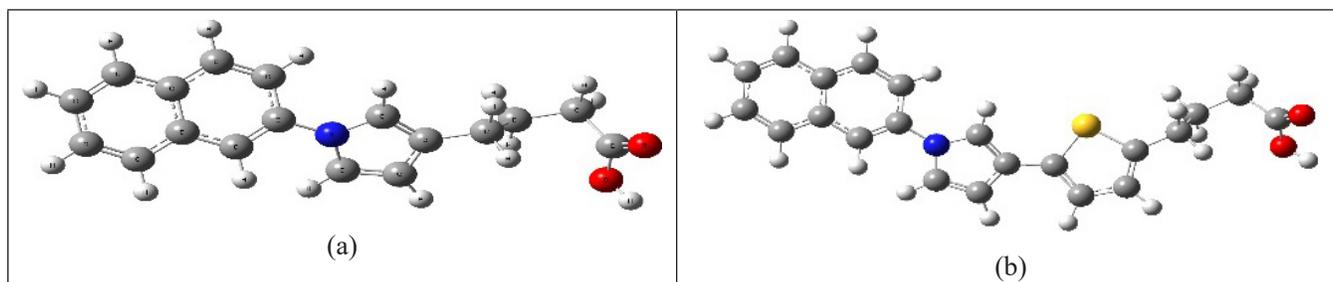
Fig. 1. (a) Optimized geometry of S1 (naphthalene-pyrrole-butanoic acid) at B3LYP/6-31+G(d,p) level; (b) Optimized geometry of S2 (naphthalene-pyrrole-thiophene-butanoic acid) at B3LYP/6-31+G(d,p) level.

Computational Details

Both the dye molecules were modelled on the Gauss View interface and then these are optimized using the density functional theory [20] at B3LYP and 6-31+G(d,p) level [21-22] on the Gaussian 16 package [23]. Density functional theory method has been extensively used in the theoretical

studies of organic molecules with B3LYP functional [24-27]. Frequency calculations were also performed to check the true global minima of the optimized systems. The vertical transition energy or absorption maxima is calculated using the TD DFT method with long-range corrected functional CAM-B3LYP/6-31+G(d,p) level.[28

Results and Analysis

To look for the effect of bridging in the molecule, careful spacer molecule is required to be chosen. Apart from simple D-π-A model the introduction of additional donors, acceptors, and extension of π conjugation reduces the HOMO-LUMO energy gap and redshifts the absorption maximum. In the D-π-A structure the HOMO level is mostly spread over the donor and π bridge molecule while the LUMO level spread over the bridging site majorly similarly for the D-π- π-A structure, which is shown in Figure 2. For efficient high absorption maxima, it is must that HOMO -LUMO Gap energy to be very low which could be achieved through the shifting of the LUMO levels of the dye molecule closer to the conduction band of the semiconducting material. Therefore, to lower

the LUMO levels of the dye molecule we need to engineer the bridging site in the dye molecule efficiently. Hence, in this paper we worked on the strategy of the double bridge model attached with donor and acceptor units. In the designed molecules, the chosen bridging unit is of pyrrole that lowers the LUMO level therefore it is suitable for designing efficient absorber dyes, while the second molecule which has two bridging molecules like pyrrole and thiophene also shows the lower LUMO level than the conduction band of the widely used titanium oxide. Here TiO_2 is taken as reference anode due to its better energy alignments with the dye molecule [29]. We have from literature the band gap of $TiO_2 \sim 3.2$ eV, [30-31]. Therefore, TiO_2 is taken as a photo anode here in the study of designed dye molecules.
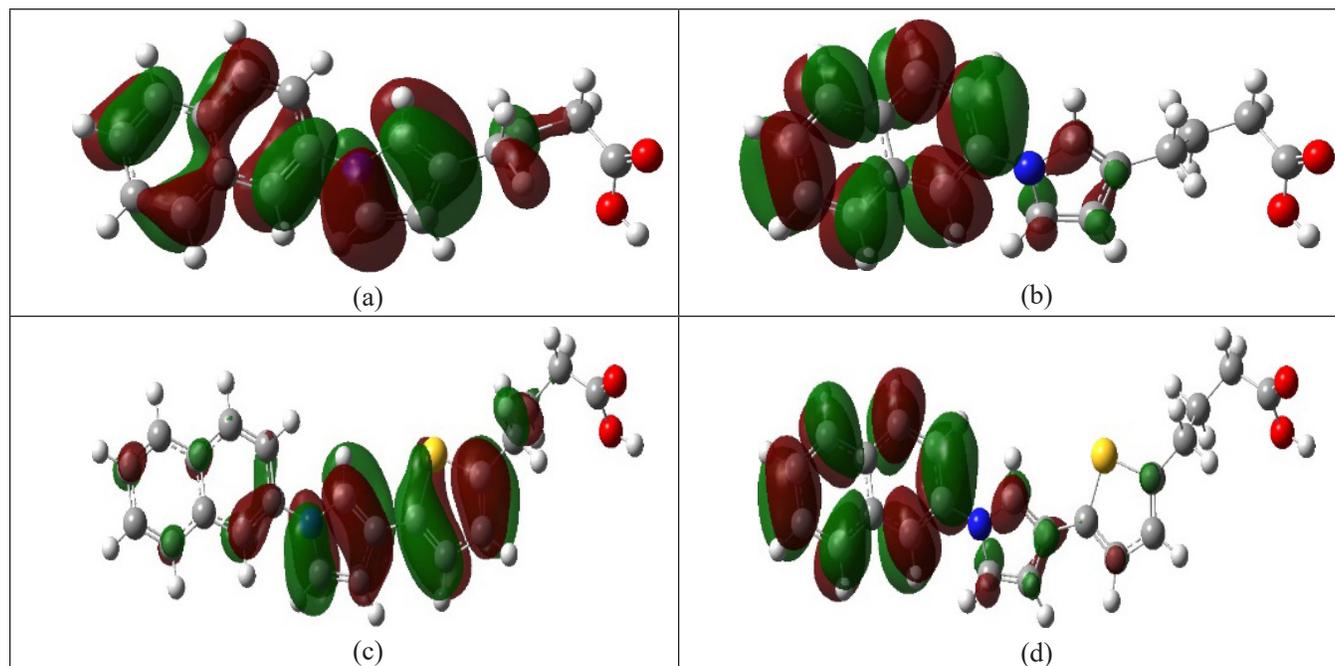
Fig. 2. (a) HOMO charge distribution of S1 (naphthalene-pyrrole-butanoic acid); (b) LUMO charge distribution of S1 (naphthalene-pyrrole-butanoic acid); (c) HOMO charge distribution of S2 (naphthalene-pyrrole-thiophene-butanoic acid); (d) LUMO charge distribution of Optimized geometry of S2 (naphthalene-pyrrole-thiophene-butanoic acid) designed dyes in the ground state.

Absorption spectra: In designing the dssc the role of absorption spectra is very critical. For efficient light harvesting the absorption maxima should be in the visible spectrum. In the designed dyes the system first S1 shows the absorption maxima at 286.66 nm and system second S2 shows the absorption maxima at 296.89 nm which is reported in Table 2. The probable reason of this high absorption wavelength in S2 as compared to the S1

system could be its strong extended conjugation length in the S2 system. In both the designed dyes the energy level of the LUMO lies very close to the conduction level of the semiconducting material, therefore the chosen model of D-π-A and D-π- π-A shows increased absorption wavelength in S2 system.

Photovoltaic properties: Photovoltaic parameters calculated for the designed dyes are Light Harvesting

Efficiency, Free energy of the charge injection, Open circuit voltage, Free energy of charge regeneration, Absorption maxima, Light harvesting efficiency.

The ground state oxidation potential (E) of a dye can be approximated as the negative of the dye's HOMO energy ($-E_H$). And the excited state dye regeneration driving force ($\Delta Greg$) [32] can be approximated as ($-(E_H) - 4.8$) eV, where -4.8 eV stands for the redox potential of $I^{-/}I^{3-}$ electrolyte couple. [33]

The free energy of electron injection ($\Delta Ginject$) [34] from the excited state of the dye to the semiconductor TiO_2 is defined as, $\Delta Ginject = (-E_H - 4.0 \text{ eV})$ where $E_{dye}^{*ox} = -E_H$ is the excited state oxidation potential and -4.0 eV stands for conduction band (CB) edge of the TiO_2 semiconductor. It is calculated as below:

$$\Delta G^{inject} = E_{ox}^{dye*} - E_{CB}^{TiO_2}$$

E_{dye}^{*ox} is approximated as the difference between the ground state oxidation potential of the dye and the absorption maxima energy, $E_{dye}^{*ox} = (-E_H) - \lambda max$.

And the difference between the energy of the LUMO (E_L) of the dye and the energy of the conduction band edge of SnO_2 is regarded as the open circuit voltage, $eV_{OC} = E_L - (-4.0)$. It is calculated as below:

$$Voc = E_{LUMO}^{dye} - C.B. (E_{TiO2})$$

From Table 1, it is clearly visible that both the designed dyes have lower HOMO energy levels i.e., for (system first it is at -5.91 eV and for system second it is -5.40 eV) than the Redox couple of the iodide solution (-4.8 eV) which confirms that designed dyes will have fast regeneration.

The HOMO LUMO gap of both the dyes are found to be 4.34 eV and 3.75 eV for system first S1 and system second S2 respectively.

Table 1. HOMO, LUMO, HOMO-LUMO Energy Gap Values in eV.

Dyes	HOMO Energy (eV)	LUMO Energy (eV)	HLG Energy (eV)
S1	-5.91	-1.57	4.34
S2	-5.40	-1.65	3.75

In Table 2, the LHE values for the designed dyes are reported as 0.127 eV and 0.728 eV for system first S1 and system second S2 respectively. This result concludes that S2 has higher LHE as compared to S1 which is expected from its extended conjugation length in the system.

Table 2. Computed maximum absorption wavelengths (λ_{max}), oscillator strengths (f), and light-harvesting efficiency (LHE), λ_{max}ICT of modeled dye sensitizers

Dyes	Absorption wavelengths (λ_{max}) (nm)	Oscillator strengths (f)	LHE (eV)	λ_{max}ICT in (eV)
S1	286.66	0.0594	0.127	4.325
S2	296.89	0.566	0.728	4.176

In Table 3, the $\Delta Ginject$ values for system first and second are -2.41 eV and -2.77 eV respectively, where the system second shows the most negative value which concludes that it has the high electron injection efficiency than system first which could be attributed to double bridging site is attached in the second system.

Table 3. Computed ΔGinject, E_{OX}dye*, E_{OX}dye, of all modeled dye sensitizers.

Dyes	ΔGinject Energy (eV)	E_{OX}dye* Energy (eV)	E_{OX}dye Energy (eV)
S1	-2.41	1.59	5.91
S2	-2.77	1.23	5.40

From Table 4, the dye regeneration energy is calculated, $\Delta Greg$ for system first is 1.11 eV and for system second is 0.60 eV. The system first shows the high value of the dye regeneration therefore it is concluded that dye first will be regenerated later as compared to the dye second. And the open circuit voltage for the system first is 2.43 eV and for system second it is 2.35 eV, which shows that both the systems have high open circuit voltage values. Therefore, in conclusion it can be inferred that designed dyes show similar photovoltaic properties and could be useful in designing the efficient photosensitizers.

Table 4. Computed dye regeneration energy ΔG (reg) and open circuit voltage Voc in (eV) for all dyes.

Dyes	Regeneration energy ΔG (reg) (eV)	open circuit voltage Voc in (eV)
S1	1.11	2.43
S2	0.60	2.35

Conclusion

In this study of effect of bridging on novel photosensitizers for DSSC which are based on D-π-A and D-π- π-A model. The system first is called S1 [naphthalene-pyrrole-butanoic acid] and system second is named as S2 [naphthalene-pyrrole-thiophene-butanoic acid]. From the results of HOMO and LUMO charge distribution, HOMO lies over the donor and π bridge in the ground state while LUMO was spread mostly over the acceptor moieties in both the dyes. From the HOMO and LUMO Plots, it was clearly noticed that the charge distribution is found over donor site mostly and some part of bridging molecule in both the dyes. The high absorption is found for system second as compared to the first that confirms that extended conjugation helps in shifting the maximum wavelength of absorption towards red site of the visible spectrum. We expect this study would be helpful in designing efficient photosensitizers for DSSC.

Conflicts of Interest: There are no conflicts to declare.

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