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# Influence of donor substitution at D−π−A architecture in efficient sensitizers for dye-sensitized solar cells: first-principle study

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**Abstract.** Using density functional theory and time-dependent density functional theory, we theoretically studied a new series of five novel metal-free organic dyes, namely D1–D5, for application in dye-sensitized solar cells based on donor–π-spacer–acceptor (D−π−A) groups. In this present study, five different donor groups have been designed based on triphenylamine–stilbene–cyanoacrylic acid (TPA–St–CA). The electronic structures, UV–visible absorption spectra and photovoltaic properties of these dyes were investigated. Different exchange-correlation functionals were used to establish a proper methodology procedure for calculation and comparison to experimental results of dye TPA–St–CA. The TD-WB97XD method, which gives the best correspondence to experimental values, is discussed. The calculated results reveal that the donor groups in D2 and D3 are promising functional groups for D−π−A. In particular, the D2 dye showed small energy levels and red-shift, negative $\Delta G_{inject}$, fastest regeneration and largest dipole moment and exciton binding energy when compared with TPA–St–CA.

**Keywords.** Organic dye; density functional theory; long-range correlational functional; electronic and absorption spectra.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention in recent years as they offer the possibility of low-cost conversion from photon to electrical energy and thus they have been regarded as the next generation photovoltaic (PV) devices [1]. The widespread commercialization of the PV cells is still limited, mainly because of their high prices as compared with the amount of energy produced from them. According to the recent scientific research conducted, power-conversion efficiency reaches up to 24.2% [2]; however, photovoltaics is still non-competitive with the conventional electricity production process. In this regard, DSSCs have received extensive attention in recent years because of their easy processing and low cost [3–6].

The major components of the DSSCs are made up of three main parts: (i) a photosensitized dye coat of a semiconductor (usually $TiO_2$); (iii) a counter-electrode and (iii) an electrolyte solution, stable in its oxidized form, thus allowing its redox electrolyte (usually $I^-/I_3^-$). Therefore, photosensitizers have been investigated as they play an important role for efficient DSSCs. In this context, photosensitizers are divided into the metal (inorganic)-based and metal-free (organic) sensitizers.

To date, much attention has been paid to the development of novel metal complexes as sensitizers; however, this effort is not desirable for cost-effective environment-friendly PV systems because these metals are rare and expensive [7–9]. Organic dyes are widely available at low cost with various structures, and they also have been actively studied for their large absorption spectrum coefficients in the $\pi-\pi^*$ transitions. Metal-free organic dye sensitizers such as cyanines [10,11], hemicyanines [12,13], triphenylamine (TPA) [14–17], porylenes [18–20], coumarins [21–23], porphyrins [24,25] and indoline-based [26–28] dyes have been developed for DSSCs. Due to the advantage as a photosensitizer in DSSCs, the organic dyes with D−π−A structure have been intensively evolved [29–32].

In the past decade, some effective strategies for molecular design have been demonstrated. The basic structure of metal-free sensitizers are like the structure of D−π−A, in which the electron donor (D) and electron acceptor (A) must contain the anchoring group (π). The PV properties of such organic dyes can be used by selecting suitable groups within the D−π−A structure [33]. The electron-donating group (D) is designed to be an electron-rich moiety, linked through a π-conjugated spacer to the electron-acceptor group (A), an
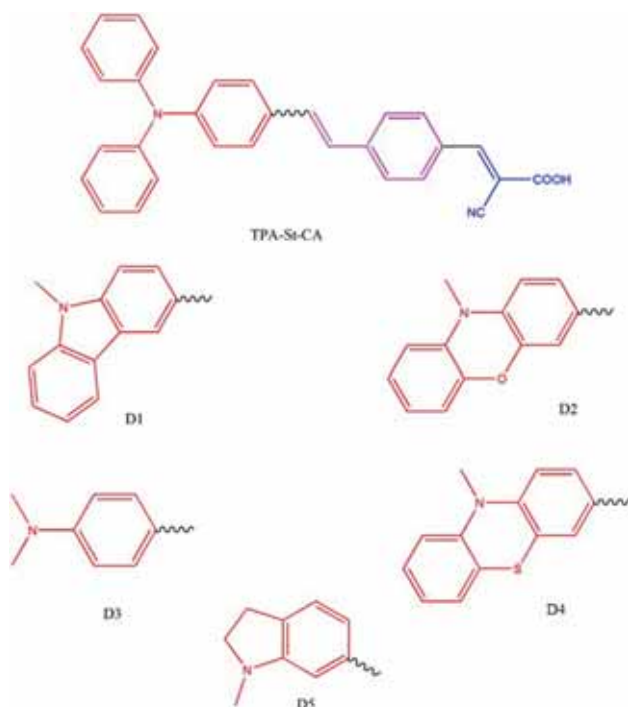
**Scheme 1.** Sketching of molecular structures for different donors, π-linker and acceptors.

electron-poor moiety directly anchoring to the semiconductor surface (TiO₂). Modification of optical and electrochemical properties of donors is expected and further influences their performance in DSSCs.

In the current study, we focus on implementing density functional theory (DFT) and time-dependent DFT (TD-DFT) methods for the organic dyes in DSSCs. In this context, we have employed different donor segments and investigated their significance in DSSCs. Computational studies have been widely used in the study of DSSCs [34,35]. They are motivated by the advantages, which include easy modification of anchoring groups, strong electron withdrawing strength and multiple anchoring sites. Scheme 1 displays the various types of donor-based D−π−A sensitizers under investigation. Using TPA–St–CA dye as a prototype, we further designed a series of new D−π−A structure dyes by adopting different donor groups and stilbene as the conjugator; cyanoacrylic acid is the most widely used electron acceptor. Thus, one aim of this work is to make models that can optimize the DSSC performances through a rational molecular design [36]. Finally, we recommend a type of novel donor derivatives, organic dyes with near-infrared light harvesting, for highly effective DSSCs.

## 2. Computational details

The geometrical structures of different donor derivatives of five systems were considered, and their structures are shown

in supplementary figure S0. The optimization of ground state structures is performed using DFT with B3LYP level and different basis sets. Through this work, we can see that there are no imaginary frequencies.

Previous investigations indicate that TD-DFT is highly efficient and accurate in the calculation of vertical excitation energy, electronic properties and optical absorption spectra [37,38]. Regarding reliability, use of different exchange-correlation (XC) functionals for charge-transfer excitations often shows significant effects. There are many suitable functionals; we adapt different XC functionals, which include B3LYP [39] and long range-correlational (LC) CAM-B3LYP [40] and WB97XD [41] in the TD-DFT calculations to evaluate the optical absorption wavelength of TPA–St–CA. From the three functionals, we get the values 589, 426 and 408 nm (table 1); when we compare with the experimental value of 386 nm, the errors are 203, 40 and 22 nm, respectively. We chose the best functional, which gave the best value for the optical absorption wavelength. We use the TD-WB97XD functional with 6-31G(d) [42] basis sets for further designing of new dye molecules. We select the conductor-like polarizable continuum model (CPCM), which is more useful to predict the optical properties in ethanol solution [43]. We used functionals and also basis sets from Gaussian 09 packages [44]. The absorption spectra are obtained using Gausssum [45].

## 3. Results and discussion

### 3.1 *Screening of the electron donor groups*

The electron donor group is a key factor in D−π−A structure for high-performance DSSCs device with organic dye. The experimentally synthesized organic dye TPA–St–CA is shown in supplementary figure S0. We have taken donor molecules from TPA–thiophene–cyanoacrylic acid [46]. But thiophene is varied from remaining donor and acceptor.

The selected dyes (D1–D5) are obtained using carbazole, phenoxazine, N,N-dimethylbenzenamine, phenothiazine and indoline, which replace TPA. The optimized geometric structures of the donor groups D1–D5 are nonplanar, which favour the electron donor to the electron acceptor.

### 3.2 *Frontier molecular orbitals of energy levels*

Figure 1 shows the frontier molecular orbitals (FMOs) of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels for the D1–D5 in ethanol solution. The FMOs contribution is very important in determining the charge-separated states of sensitizing dyes [47]. It is known that the distributed FMOs of the sensitizers have a significant influence on the electronic charge–transfer character of dyes. Significant charge transfer from the electron donor to electron acceptor moieties proved that these dyes would be good sensitizers.

**Table 1.** Experimental absorption maxima and computed excitation energies of the lowest excited state $\lambda_{max}$ (nm) for the dye in ethanol solution, together with the calculated oscillator strength ($f$) and excitation configuration.

| Methods | $\lambda_{max}$ (nm) | Oscillator strength ($f$) | Main configuration |
|---|---|---|---|
| B3LYP | 589 | 1.05 | HOMO → LUMO (100%) |
| CAM-B3LYP | 426 | 1.86 | HOMO → LUMO (75%) |
| WB97XD | 408 | 2.07 | HOMO → LUMO (64%) |
| Experiments | 386 | Taken from reference [59] | |

The HOMOs are π orbitals of dyes that are mainly localized over the donor group and the LUMOs are π* orbitals delocalized through the cyanoacrylic acid group; the photoinduced electron is transferred from the excited state of organic dye to the semiconductor surface. The π-characters of these orbitals contributed to high molar extinction coefficients of dyes. These results show that the LUMO energies of D1–D5 are higher than the conduction band edge (CBE) of the TiO$_2$ electrode (–4.0 eV) [48]. In addition, the HOMO energies of TPA–St–CA and D1–D5 are lower than the potential (−4.8 eV) of the $I^-/I_3^-$ redox electrolyte [49]. Therefore, these organic dye molecules could get electrons quickly from the redox couple. Figure 2 depicts the HOMO and LUMO energy levels of these organic dyes at B3LYP/6-31++G(d,p) level of theory. The energy gap values of TPA–St–CA and D1–D5 are listed in table 2.

On comparing D1–D5, the energy gap of D2 dye should be a suitable candidate for DSSCs. However, the HOMO energy level of D2 dye is so close to the redox potential of the electrocouple that it has only a low reduction driving force.

### 3.3 *Optical absorption properties*

The optical absorption spectra of D1–D5 dye molecules and TPA–St–CA in ethanol solution using the TD-WB97XD/6-31G(d) are shown in figure 3. All the dyes displayed a broad visible region around 500 nm, which was assigned to intramolecular charge transfer (ICT). From table 3, the maximum absorption peaks of D1, D2, D3, D4 and D5 are 397, 415, 416, 395 and 385 nm, respectively; D2, D3 exhibit red-shifts and D1, D4, D5 exhibit blue-shifts when compared with the reference dye TPA–St–CA (408 nm). The dominant absorption spectra of the D2, D3 dye molecules lie in the visible region, which are shown in figure 3. From table 3, vertical excitation energies ($E$) decrease in the order D5 > D4 > D1 > D2 > D3, showing that there are red-shifts for D1, D4, D5 when compared with reference dye TPA–St–CA. The absorption spectra also belonged to π − π* transitions. These results indicated that the D2, D3 dye molecules could show more absorption at longer wavelengths, which promotes further increase of the photon-to-current conversion efficiency of the corresponding DSSCs.

### 3.4 *PV properties*

The solar-to-electricity conversion efficiency of the DSSC devices is determined by the short-circuit current density ($J_{SC}$), the open-circuit photovoltage ($V_{OC}$), the fill factor (FF) and the intensity of the incident light $P_{IN}$; it is calculated from the following equation [50]:

$$\eta = \frac{J_{SC} V_{OC} FF}{P_{IN}}. \tag{1}$$

For DSSCs, $V_{OC}$ can be calculated as follows [51]:

$$V_{OC} = \frac{E_{CB}}{q} + \frac{KT}{q} \ln \left[ \frac{n_C}{N_{CB}} \right] - \frac{E_{redox}}{q}. \tag{2}$$

$V_{OC}$ is determined by the energy difference between the semiconductor CBE and the redox electrolyte potential. Usually, the solution $I^-/I_3^-$ is used as the electrolyte; hence, we consider it as a constant. $\Delta$CBE is the main factor that influences $V_{OC}$; it can be expressed as follows [52]:

$$\Delta CBE = -\frac{q \mu_{normal} \gamma}{\varepsilon_0 \varepsilon}, \tag{3}$$

where $q$ is the elementary charge, $\gamma$ is the outermost level molecular concentration, $\mu_{normal}$ is the dipole moment of molecules perpendicular to the boundary of the semiconductor and $\varepsilon_0$, $\varepsilon$ are constants. As shown in supplementary figure S1, if $\mu_{normal}$ is high it leads to a greater extent shift of CBE, which results in larger $V_{OC}$. From table 4, the dipole moments of D1, D2, D3 and D4 are 9.45, 10.46, 9.59 and 9.47 D, respectively. The moments of all four dyes (D1–D4) are high compared with that of TPA–St–CA, except for the value of D5 (7.20 D). Among the four dyes, D2 can be the best performer for high conversion efficiency.

The $J_{SC}$ is defined by the relation between TiO$_2$ and absorption coefficient of the sensitizer. $J_{SC}$ is determined by the following equation [53]:

$$J_{SC} = \int LHE(\lambda) \Phi_{INJ} \eta_{coll} d\lambda, \tag{4}$$
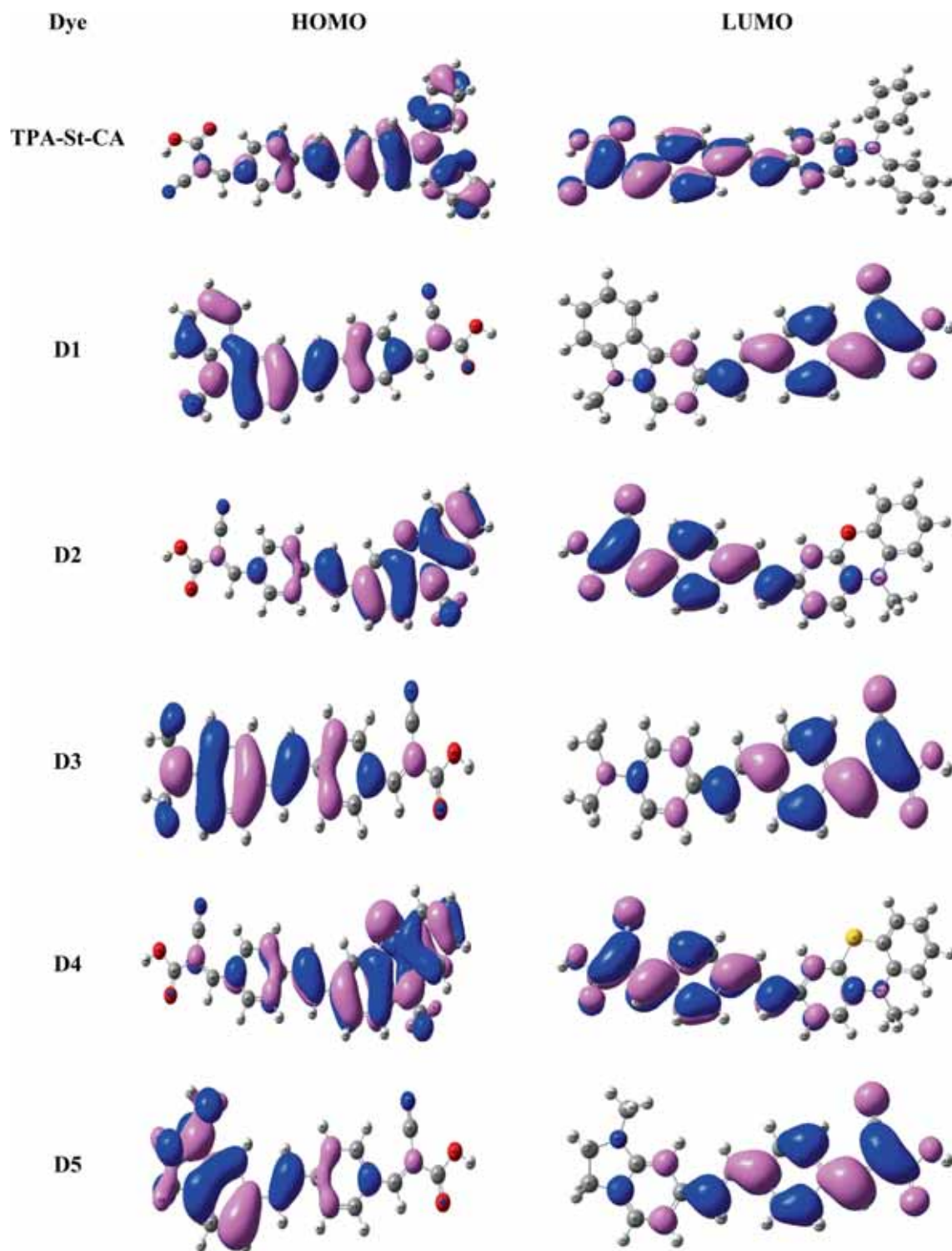
**Figure 1.** The selected frontier molecular orbitals of the designed dyes with different donor groups calculated using B3LYP/6-31++G(d,p) level of theory.

where LHE is the light harvesting efficiency at a given wavelength, $\Phi_{INJ}$ is the electron injection efficiency and $\eta_{coll}$ is the charge collection efficiency. For DSSCs the electrode is the same; the only difference is the various sensitizers; hence, $\eta_{coll}$ can be considered as a constant [53].
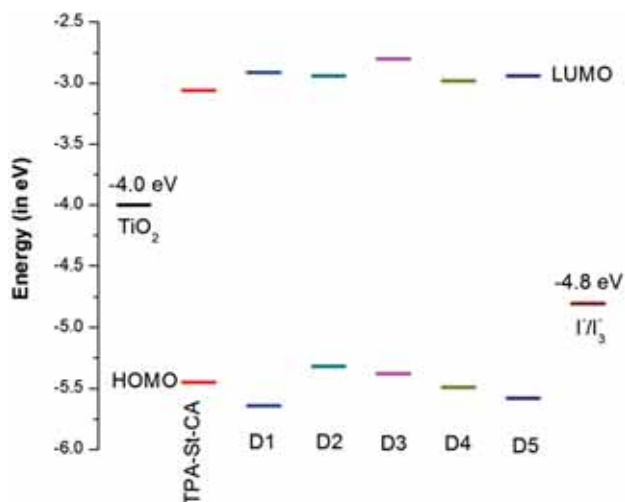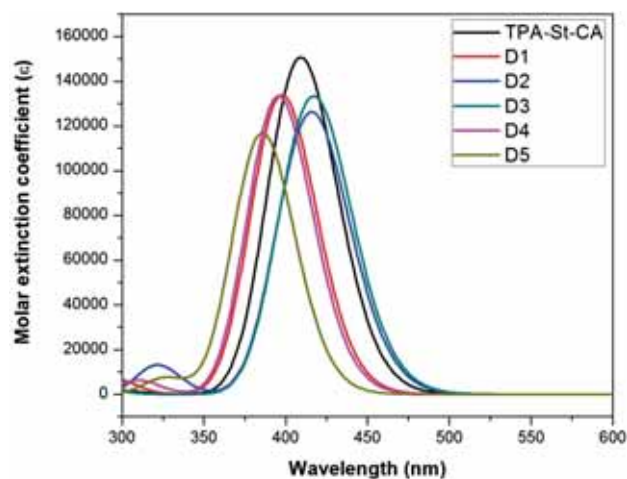
**Figure 2.** The energy levels of the TPA–St–CA and D1–D5 calculated using B3LYP/6-31++G(d,p) level of theory.



**Figure 3.** Calculated TD-DFT absorption spectra of designed dyes and TPA–St–CA in ethanol medium calculated using WB97XD/6-31G(d) level of theory.

LHE($\lambda$) is mainly determined by the oscillator strength ($f$) as follows [54]:

$$LHE = 1 - 10^{-f}, \quad (5)$$

where the oscillator strength of the dye is associated with the $\lambda_{max}$. As discussed earlier, the light harvesting efficiency (LHE) and the electronic injection free energy ($\Delta G_{inject}$) are the two main influencing factors of $J_{SC}$. In order to give an intentional impression about how the donor groups affect the LHE, we stimulated the UV–visible absorption spectra of the dyes. Increased oscillator strength might enhance the LHE value and would give rise to increasing overlap with the solar spectrum, especially in the entire visible range. As shown in table 3, the LHE values for these dye molecules are given in the range 0.985, 0.981, 0.985, 0.985 and 0.975. This means that all the sensitizers give more or less similar photocurrent. Another way of enhancing $J_{SC}$ is to improve the electronic injection rate of free energy $\Delta G_{inject}$.

$\Delta G_{inject}$ can be estimated as follows [55]:

$$\Delta G_{inject} = E_{OX}^{dye^*} - E_{CB}^{TiO_2}. \quad (6)$$

Here, $E_{OX}^{dye^*}$ is the oxidation potential of the dye in the excited state and $E_{CB}^{TiO_2}$ is the reduction potential energy of the TiO$_2$ conduction band. These results are displayed in table 4; we find that these sensitizers have negative values of $\Delta G_{inject}$. The values of D2–D5 are more negative than that of experimentally synthesized TPA–St–CA, except for D1. D2 dye has the largest $\Delta G_{inject}$; $J_{SC}$ is also influenced by the regeneration efficiency of dye ($\eta_{reg}$), which is determined by the driving force of regeneration $\Delta G_{reg}$. It can be expressed as follows [56]:

$$\Delta G_{reg} = E_{redox} - E_{dye}. \quad (7)$$

From table 4, we get the values of D1–D5 as 0.84, 0.52, 0.58, 0.69 and 0.78. Where D1, D4 and D5 have bigger driving force of regeneration; they have better $\eta_{reg}$, compared with

**Table 2.** Frontier molecular orbital energy levels and the corresponding energy gap of the different dye molecules in B3LYP using different basis sets.

| | 6-31G(d) | | | 6-31++G(d, p) | | | 6-311++G(d, p) | | |
|---|---|---|---|---|---|---|---|---|---|
| Dyes | HOMO (eV) | LUMO (eV) | Energy gap (eV) | HOMO (eV) | LUMO (eV) | Energy gap (eV) | HOMO (eV) | LUMO (eV) | Energy gap (eV) |
| TPA–St–CA | −5.20 | −2.71 | 2.49 | −5.45 | −3.06 | 2.39 | −5.51 | −3.11 | 2.40 |
| D1 | −5.34 | −2.54 | 2.80 | −5.64 | −2.91 | 2.73 | −5.69 | −2.94 | 2.75 |
| D2 | −4.99 | −2.58 | 2.41 | −5.32 | −2.94 | 2.38 | −5.38 | −2.97 | 2.41 |
| D3 | −5.09 | −2.44 | 2.65 | −5.38 | −2.80 | 2.58 | −5.42 | −2.83 | 2.59 |
| D4 | −5.21 | −2.63 | 2.58 | −5.49 | −2.98 | 2.51 | −5.54 | −3.01 | 2.53 |
| D5 | −5.30 | −2.59 | 2.71 | −5.58 | −2.94 | 2.64 | −5.64 | −3.00 | 2.64 |

**Table 3.** Calculated maximum absorption wavelength $\lambda_{max}$ (nm) and corresponding vertical excitation energies in eV, oscillator strength ($f$), orbital transitions and light harvesting efficiency (LHE) of the studied dyes in ethanol medium calculated using the TD-WB97XD/6-31G(d) level of theory.

| Dyes | Wavelength | | Oscillator strength ($f$) | LHE | Orbitals contribution | |
|---|---|---|---|---|---|---|
| | Energy (eV) | $\lambda_{max}$ (nm) | | | Major | Minor |
| TPA–St–CA | 3.03 | 408 | 2.071 | 0.991 | H-1 → L (21%), H → L (65%) | H → L+1 (9%) |
| | 4.05 | 306 | 0.015 | 0.033 | H-4 → L (11%), H-1 → L (43%), H → L+1 (31%) | H-2 → L (3%), H → L (3%), H → L+5 (3%) |
| | 4.33 | 286 | 0.028 | 0.062 | H-7 → L (87%) | H-1 → L+4 (5%), H → L+4 (3%) |
| D1 | 3.12 | 397 | 1.847 | 0.985 | H-2 → L (12%), H → L (73%) | H-1 → L (4%), H → L+1 (5%) |
| | 4.14 | 298 | 0.067 | 0.142 | H → L+1 (36%), H → L+2 (30%) | H-2 → L (8%), H-2 → L+1 (3%) H-1 → L (3%), H-1 → L+2 (8%) |
| | 4.31 | 287 | 0.040 | 0.087 | H-3 → L (14%), H-2 → L (16%), H-1 → L (26%), H → L+1 (11%), H → L+2 (12%) | H-1 → L+1 (9%), H → L (4%) |
| D2 | 2.98 | 415 | 1.742 | 0.981 | H-1 → L (18%), H → L (74%) | H → L+1 (12%) |
| | 3.85 | 321 | 0.181 | 0.340 | H-1 → L (47%), H → L+1 (28%) | H-3 → L (6%), H → L+3 (3%), H → L+5 (4%) |
| | 4.30 | 287 | 0.007 | 0.015 | H → L+3 (65%) | H-2 → L (2%), H-2 → L+1 (4%), H-1 → L (5%), H → L (3%), H → L+2 (8%) |
| D3 | 2.97 | 416 | 1.839 | 0.985 | H-1 → L (13%), H → L(77%) | H → L+1 (7%) |
| | 4.26 | 290 | 0.021 | 0.960 | H-4 → L (12%), H-1 → L (53%), H → L+1 (28%) | H → L (2%) |
| | 4.42 | 280 | 0.020 | 0.045 | H-3 → L (81%) | H-1 → L+2 (7%), H → L+2 (8%) |
| D4 | 3.13 | 395 | 1.840 | 0.985 | H-1 → L (22%), H → L (62%) | H-2 → L (3%), H → L+1 (9%) |
| | 3.99 | 310 | 0.084 | 0.175 | H-1 → L (35%), H → L+1 (29%) | H-3 → L (7%), H-2 → L (2%), H-1 → L+1 (2%), H-1 → L+2 (3%), H → L (4%), H → L+2 (6%), H → L+5 (3%) |
| | 4.30 | 288 | 0.009 | 0.020 | H → L+2 (69%) | H-4 → L+1 (2%), H-2 → L+1 (3%), H-1 → L (7%), H → L (3%) |

**Table 3.** (*continued*)

| Dyes | Wavelength | | Oscillator strength ($f$) | LHE | Orbitals contribution | |
|---|---|---|---|---|---|---|
| | Energy (eV) | $\lambda_{max}$ (nm) | | | Major | Minor |
| D5 | 3.21 | 385 | 1.613 | 0.975 | H-1 → L (30%), H → L (55%) | H-2 → L (4%), H → L+1 (7%) |
| | 3.79 | 326 | 0.103 | 0.211 | H-1 → L (49%), H → L (16%), H → L+1 (20%) | H-1 → L+1 (7%), H → L+3 (2%) |
| | 4.41 | 280 | 0.023 | 0.051 | H-3 → L (84%) | H-2 → L+2 (2%), H-1 → L+2 (7%), H → L+2 (3%) |

H—HOMO; L—LUMO.

**Table 4.** Calculated redox potential of the ground state ($E_{dye}$ in eV), oxidation potential of the dye ($E^*_{dye}$ in eV), absorption energy ($\lambda_{max}$ in eV), free energy change for electron injection ($\Delta G_{inject}$ in eV), driving force of regeneration ($\Delta G_{reg}$ in eV), exciton binding energy ($E_b$ in eV) and dipole moment (in Debye) of the studied dye molecules in ethanol medium using the TD-WB97XD/6-31G(d) level of theory.

| Dyes | $E_{dye}$ (eV) | $\lambda_{max}$ (eV) | $E^*_{dye}$ (eV) | $\Delta G_{inject}$ (eV) | $\Delta G_{reg}$ (eV) | $E_b$ (eV) | $\mu_{normal}$ (D) |
|---|---|---|---|---|---|---|---|
| TPA–St–CA | 5.45 | 3.03 | 2.42 | − 1.58 | 0.65 | 0.64 | 9.26 |
| D1 | 5.64 | 3.12 | 2.52 | − 1.48 | 0.84 | 0.39 | 9.45 |
| D2 | 5.32 | 2.98 | 2.34 | − 1.66 | 0.52 | 0.60 | 10.46 |
| D3 | 5.38 | 2.97 | 2.41 | − 1.59 | 0.58 | 0.39 | 9.59 |
| D4 | 5.49 | 3.13 | 2.36 | − 1.64 | 0.69 | 0.62 | 9.47 |
| D5 | 5.58 | 3.21 | 2.37 | − 1.63 | 0.78 | 0.57 | 7.20 |

reference dye TPA–St–CA (0.65). However, D2 dye molecule can provide the fastest regeneration for increasing $J_{SC}$.

To attain high energy-conversion efficiency, the electron and hole pairs should be dissociated into separate positive and negative charges and escape from the recombination due to Coulombic attraction. This process requires overcoming the binding energy; that is, the dye molecules should possess less exciton binding energy for high energy conversion. Here, the exciton binding energy is calculated using the formula [57,58]

$$E_b = E_g − E_x = E_{H–L} − \lambda_{max}, \tag{8}$$

where $E_g$ is the band gap and is approximated as the HOMO–LUMO energy difference and $E_x$ is the optical gap. From table 4, it can be observed that the exciton binding energy of D1 and D3 is the same and is equal to 0.39 eV, which is lesser than that of the other molecules.

## 4. Conclusion

A novel series of five D−π−A metal-free organic DSSCs dyes (D1–D5) were designed based on a highly effective electron donor modification. We have systematically investigated electronic structures, optical absorption and PV properties of these dyes. In this study, we used DFT and TD-DFT methods. The results indicate that the donor groups D2 and D3 are promising functional groups for D−π−A structure. In particular, the calculated results indicate that the D2 electron donor group permits strong electron transfer due to fast electron injection and dye regeneration, and large dipole moment, which results in a higher power conversion efficiency. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties of the other compounds and further to design novel materials for fabrication of efficient organic solar cells.

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