The computational study of bridge effect in D-π-A photosensitive dyes, based on triphenylamine

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Abstract. For an efficient electron transfer from donor to acceptor unit, the heterocycles units play a crucial role as π-bridges in the Donor-π-Acceptor (D-π-A) organic sensitizers for dye-sensitized solar cells (DSSCs). A series of organic D-π-A dyes, based on triphenylamine donor (D), cyanoacrylic acid acceptor (A)and bridged by different π-conjugated spacer systems, are studied by density functional theory (DFT) and time-dependent DFT (TD-DFT) with the Becke 3-Parameter-Lee-Yang-Parr (B3LYP) functional and the 6-31G (d, p) basis set. Generally, the fundamental parameters, such as the HOMO and LUMO energies, of studying dyes have been discussed. The calculated results show that the narrow energy gaps (1.98 to 2.48 eV) and the large visible absorption bands (from 556.72 to 707.10 nm), suggest the studied compounds as promising light harvesters materials for organic solar cell applications. Furthermore, our theoretical results demonstrate that sensitizer D5 with the benzothiadiazole spacer has a broader absorption (707.10 nm) and the lower energy gap (1.98 eV) compare to other dyes; this opens a new way to design new efficient organic sensitizers for dye sensitized solar cells (DSSCs).

1. Introduction

The vast majority of global energy consumption is provided by the exploitation of non-renewable fossil resources. Although, the unavoidable depletion of this type of resources and the environmental impacts resulting from their consumption poses, due to the growing global energy demand, important questions concerning the guarantee of access to energy for future generations. In this context, renewable energies, such as wind, geothermal, biomass or solar energy, are today the subject of many important researches. Among these energies, solar energy is considered one of the promising alternatives as it is available aplenty from the sun. This energy could therefore represent a viable alternative to fossil fuels. Nevertheless, there is still a lot of progress to be made in this field, particularly in terms of the production cost of the modules.

Among the new concepts studied in the field of photovoltaics, dye-sensitized solar cells (DSSC) have been the subject of much research since the early work of O’Regan and Grätzel in 1991[1], involving less expensive production methods; they consist of semiconducting metal oxides photosensitized by a photosensitive dye. This type of photovoltaic cells has already shown high power
conversion efficiency (PCE), making it an excellent alternative to marketed silicon-based solar cells [2,3].

One of the major research challenges for the production of high performance photovoltaic cells is the development of new photosensitizers. The Ruthenium (Ru)-based sensitizers have been commonly used as efficient sensitizers, such as N3 and N719, and their PCEs (power conversion efficiencies) reach above 10% [4]. However, seeing that the Ru-based sensitizers have some limitations as the rareness and cost of Ru metal, many researchers are focusing on organic dyes as promising sensitizers, this is attributed to their low production cost, their flexibility manipulates and their environment friendly applications [5,6]. The organic dyes, almost all have an electron donor (D) and electron acceptor (A) connected with π-conjugated spacer, namely D-π-A dyes.

On the basis of studies carried out on certain D-π-A organic dyes, we have identified that triphenylamine (TPA) is among the best donors used in the construction of effective organic sensitizers due to its non-planar molecular configuration, resistant to aggregation [7,8]. Cyanoacrylic acid is chosen as the electron-accepting unit because of its high electron-withdrawing capacity and its high TiO₂ bonding capacity, which facilitates the injection of electrons [9]. In addition to the molecular engineering of donors and acceptors, the development of new types of π-spacers are one of the essential requirements to improve the optoelectronic parameters in D-π-A organic dyes, as it is crucial for the electron transfer from the donor to acceptor fragments and beneficial to the light harvesting ability.

In this study, we were systematically investigated theoretically five D-π-A sensitizers containing the TPA donor (D) unit and the cyanoacrylic acid acceptor (A) unit connected by different π-spacers such as phenyl, pyridine, thiophene, bithiophene and benzothiadiazole. The choice of these bridges units is justified by their performance in the same type of DSSCs. They are considered to be promising π-conjugated spacers in D-π-A organic dyes and have enhanced the efficiency of solar devices [10,11,12]. Therefore, we were interested in exploring the effect of this bridging on the geometries and optoelectronic properties. The presented study of these compounds depicted in Figure 1 could help to design more efficient photovoltaic organic materials, for aim to find the best material which is used as a π-spacer electron in dyes applied in dye-sensitized solar cells (DSSCs).

![Figure 1. Molecular structures of study dyes Di (i = 1 to 5).](image-url)
2. Computational Details
In this work, the geometrical and electronic properties are studied by the Density Functional Theory (DFT) using the B3LYP correlation exchange function (Becke's three-parameter hybrid functional, and Lee-Yang-Parr’s correlation functional), known to be the most hybrid functional used for a wide variety range of organic molecules, combined with 6-31G(d, p) basis set of neutral and doped forms [13-16].

The excitation energies, the wavelengths and oscillator strengths were simulated using Time Dependent Density Functional Theory method (TD-DFT). These calculations were carried out including solvent effects (tetrahydrofuran, THF) using the conductor-polarizable continuum model (CPCM). All calculations were performed with the Gaussian 09 packages [17].

3. Results and discussions
3.1 Geometrical properties
The geometrical configuration of all sensitizers Di (i=1-5) is optimized by DFT calculations at B3LYP/6-31G (d, p) level. The calculated dihedral angles θ between the donor group and π-spacer, the bond lengths (L1) between the donor group and π-spacer and those (L2) between the acceptor group and π-spacer for studying compounds are listed in Table 1.

Table 1. Geometrical parameters of the studied compounds calculated at the B3LYP/6-31G(d,p) level.

| Dyes | Forms | L1(Å) | L2(Å) | θ(°) |
|------|-------|-------|-------|------|
| D1   | Neutral | 1.47  | 1.45  | 30.51 |
|      | Cation   | 1.47  | 1.46  | 32.46 |
|      | Anion    | 1.46  | 1.42  | 23.75 |
| D2   | Neutral | 1.47  | 1.44  | 8.67  |
|      | Cation   | 1.48  | 1.46  | 10.66 |
|      | Anion    | 1.46  | 1.41  | 2.17  |
| D3   | Neutral | 1.45  | 1.42  | 18.19 |
|      | Cation   | 1.45  | 1.43  | 13.26 |
|      | Anion    | 1.44  | 1.39  | 1.72  |
| D4   | Neutral | 1.46  | 1.42  | 22.41 |
|      | Cation   | 1.45  | 1.43  | 9.63  |
|      | Anion    | 1.44  | 1.39  | 1.25  |
| D5   | Neutral | 1.47  | 1.42  | 30.78 |
|      | Cation   | 1.46  | 1.43  | 25.25 |
|      | Anion    | 1.47  | 1.40  | 22.69 |

For each dye, the calculated bond lengths L1 and L2 are in the range of 1.42-1.47 Å for the neutral forms. We can conclude that they don’t change significantly which implies that the change of spacer doesn’t have an effect on the bond lengths. However, during the doping process, the bond lengths of the negatively doped dyes become shorter, while the bond lengths for those positively doped become generally longer compared to the work done by our research group’ [18,19,20].

On the other hand, the dihedral angles for D1, D2, D3, D4 and D5 are 30.51°, 8.67°, 18.19°, 22.41° and 30.78° respectively, which indicates that the dihedral angle of the D2 is significantly smaller; this can be ascribed to the nitrogen atom (N) of pyridine ring which induces a coplanar structure by hydrogen bonding interaction between the nitrogen atom and phenyl hydrogen. In addition, the decrease of bond lengths, for the negatively doped dyes, is accompanied by a huge decrease of dihedral angles.
3.2. Electronic properties

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of study dyes are calculated by DFT method, the band gap is evaluated as the difference between the HOMO and LUMO energies. Table 2 summarizes the calculated electronic parameters obtained in the neutral and doped forms. The results were compared with available experimental data [7].

Table 2. Electronic properties of the studied compounds calculated at DFT/B3LYP/6-31G(d, p) level.

| Dyes | Forms | HOMO (eV) | LUMO (eV) | Egap (eV) | Egap$^{exp}$ (eV)$^a$ |
|------|-------|-----------|-----------|-----------|------------------|
| D1   | Neutral | -4.87    | -2.42    | 2.45      | 2.56             |
|      | Cation  | -8.18    | -4.61    | 3.57      |                  |
|      | Anion   | 0.15     | 1.41     | 1.56      |                  |
| D2   | Neutral | -4.91    | -2.54    | 2.37      |                  |
|      | Cation  | -8.20    | -4.82    | 3.38      | -                |
|      | Anion   | 0.32     | 1.46     | 1.78      |                  |
| D3   | Neutral | -4.94    | -2.46    | 2.48      |                  |
|      | Cation  | -8.07    | -4.96    | 3.11      | -                |
|      | Anion   | 0.33     | 1.47     | 1.8       |                  |
| D4   | Neutral | -4.9     | -2.49    | 2.41      |                  |
|      | Cation  | -7.84    | -4.89    | 2.95      | -                |
|      | Anion   | -0.46    | 1.32     | 1.78      |                  |
| D5   | Neutral | -4.82    | -2.84    | 1.98      |                  |
|      | Cation  | -7.65    | -5.11    | 2.54      | -                |
|      | Anion   | -0.90    | 0.76     | 1.66      |                  |

$^a$Experimental Gap Energies of the studied dyes (eV)[7].

The calculated Egap are in the range of 1.98-2.48 eV for neutral form, and increase in the following order: D5 < D2 < D4 < D1 < D3. We note that the energy gap decreases from the neutral to the negatively doped form, while increasing to the positively doped form. The weaker band gap of D5 indicates a significant effect of intramolecular charge transfer, which would cause an absorption spectrum shifted to red. This is attributed to thiadiazole compound inserted at the π-spacer.

On the other side, as shown in table 2, the obtained value at B3LYP/6-31G(d,p) level of energy gap for D1 is close to these obtained experimentally, this is attributed to the appropriate method used (DFT). In addition, this theoretical method will help us to identify the dyes with the most interesting optoelectronic properties for solar cell applications, and will guide us in the synthesis of these dyes and the experimental study of their optoelectronic properties.

As depicted in Figure 2, the HOMO orbital of D5 is delocalized over the donor (D), whereas the LUMO orbital shows distributions through the acceptor and π-spacer units, which indicates that there are good electron–separated states between HOMO and LUMO. These distributions enhance the Intra Charge Transfer (ICT) by facilitating the charge transfer from the electron donor to the acceptor.
Figure 2. Representation of HOMO and LUMO molecular orbitals of the D5 compound.

Figure 3. Sketch of the HOMO, LUMO and E_gap levels of the studied molecules.

For DSSC application the HOMO of the dye must be below the redox couple of I^-/I_3^- electrolyte and the LUMO of the dye must be situated above the TiO_2 conduction band (-4.0 eV) [21]. We note through the Figure 3 that all the five dyes are supposed to be injected very easily from the excited state S1 to the TiO_2 conduction band. On the other hand, these molecules that lose electrons could get electrons from the electrolyte.

3.3. Optical properties
The functional theory of time-dependent density (TD-DFT) has emerged as a powerful tool for theoretical processing of absorption spectra [22,23]. TD-DFT/B3LYP/6-31G (d, p) method was used to simulate the optical property of the studied dyes in the gas phase. Table 3 lists the maximum absorption wavelength (\(\lambda\)), oscillator strengths (f) and excitation energies (\(\Delta E\)) of each dye. The solvent effects were included in the calculation in order to predict the experimental spectra with a reasonable accuracy, seeing that most chemical processes occur in the solution phase [24]. Based on the previous experimental work, the tetrahydrofuran (THF) was used as solvent.
The analysis in Table 3 shows that the excitation energies are about 2eV for all the studied dyes. In addition, all compounds have an absorption maximum in the visible region of approximately 542 to 763 nm, which can be attributed to an Intramolecular Charge Transfer (ICT) between the different units [25].

The calculated wavelength $\lambda$ of study compounds decreases in the following order: D5 > D4 > D2 > D1 > D3, which is almost the same order of the band gaps. Furthermore, we remark that a near infra-red is realized (707 nm) of D5; its absorption spectrum covers the whole visible region then extends to the near infra-red (NIR) region, which indicates the strongest ICT interaction between units in D5. As a result, the calculated spectral data confirm that the introduction of benzothiadiazole as a $\pi$-spacer in D-$\pi$-A system could favorable the long wavelength light harvesting, beneficial for increasing the power conversion efficiency of the solar cells. The absorption maxima of all dyes are shifted by the solvent effect (THF): bathochromic displacement. The magnitudes of the spectral offset are about 50 nm for all dyes, this clearly indicated the significant influence of the solvent that lead to enhance the conjugation on the studied structures [26].

4. Conclusion
In summary, a series of D-$\pi$-A organic dyes were theoretically studied by introducing different $\pi$-conjugated spacers: phenyl, pyridine, thiophene, bithiophene and benzothiadiazole combined with triphenylamine and cyanoacrylic acid respectively as donor and acceptor, to understand the bridge impact on the optoelectronic properties of dyes. All geometric structures, electronic and optical properties were studied using DFT and TDDFT methods.

In view of the HOMOs, LUMOs, band gaps and wavelengths, we can conclude that the selected dyes can be used as units in dye sensitized solar cells. Overall, D5, with the benzothiadiazole $\pi$-spacer, should be the best photosensitizer for use in DSSC; this is due to his low band gap and his favorable absorption which allow a better light harvesting. Furthermore, the DFT study clearly reveals that the electron injection into the CB of TiO$_2$ and regeneration of dyes by $I_-/I_3^-$ where feasible.

This theoretical approach is a guiding tool to understand the structural relationships of these compounds and to design another new promising organic sensitizers for the future development of DSSCs.

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