

Computational study of new pyranilidene-based D- π -A-A dyes: effect of the change of the auxiliary acceptor

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Abstract. In this study, four D- π -A-A molecules, based on pyranilidene as the donor, were developed by modification of the auxiliary acceptor. These molecules were theoretically studied using DFT and TD-DFT methods. The optoelectronic and photovoltaic properties were calculated as HOMO, LUMO, E_{gap} , V_{oc} (the open-circuit photovoltage), λ_{max} (the maximum absorption wavelength), E_{ex} (the vertical excitation energies), f (the oscillator strengths) in order to study the effect of auxiliary acceptor change on the enhancement of light absorption capabilities and increase of intramolecular charge transfer ICT. The findings indicate that the D4 dye performs better than the rest of the dyes as it is characterized by a low energy gap ($E_{\text{gap}}=1.549$ eV) and a maximum wavelength ($\lambda_{\text{max}}=758$ nm). Therefore, the D4 dye is a good candidate for use as a DSSC sensitizer.

Keywords: Pyranilidene, DSSC, TD-DFT, optoelectronic properties.

1 Introduction

Dye-sensitized solar cells (DSSCs) are among the most attractive alternatives to silicon-based solar cells because of their low cost, simple manufacturing procedure, and very acceptable power conversion efficiency (PCE) [1]. As a key component, sensitizers play a crucial role in increasing the PCE of DSSCs. Since 1991, when DSSC was first declared [1], ruthenium (Ru) has been used in sensitizers (N3, N719, and Z907), where a PCE greater than 10% has been obtained under simulated AM1.5 sunlight (100 mWcm⁻²) [2]. These ruthenium-based sensitizers have limited use due to the scarcity of Ru and its high price, prompting many researchers to focus their research on metal-free organic sensitizers, which have significant light-harvesting capacity due to high molar extinction coefficients, are environmentally friendly, and also feature low cost [3]. D- π -A structures are the most commonly used metal-free organic sensitizers. The pyranilidene moiety is considered one of the most efficient donors in photovoltaic devices [4]. Several units have also been explored as π -bridges to improve intramolecular charge transfer and increase light harvesting capabilities, such as thiazolothiazole [5]. Cyanoacrylic acid is frequently utilized as an electron-accepting moiety owing to its exceptional electron-withdrawal capacity and robust bonding ability to the TiO₂ semiconductor surface. These characteristics facilitate the injection of electrons [6]. In order to improve the photovoltaic performance of solar cells, several modifications have been made to D- π -A structures, such as the introduction of

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an auxiliary acceptor between the π -bridge and the A-acceptor to obtain the D- π -A-A structure [7]. The introduction of an auxiliary acceptor increases light-harvesting capacity by enhancing intramolecular charge transfer (ICT) and reducing the LUMO energy level of the dyes [8]. In the same context, keeping in mind previously reported studies [2], we designed four new dyes by changing the auxiliary acceptor, which is located between the π -bridge and the A-acceptor in the D- π -A-A structure, with auxiliary acceptors based on benzothiadiazole (D1), 2-methylbenzotriazole (D2), 2,3-dimethylquinoxaline (D3), and [1,2,5]thiadiazolo[3,4-g]quinoxaline (D4) (Fig. 1). In this theoretical study of these D- π -A-A dyes, a pyranilidene derivative was used as the D-electron donor, thiazolothiazole as the π -bridge and cyanoacrylic acid as the acceptor/anchor group. Using density functional theory (DFT) and time-dependent DFT (TD-DFT) the optoelectronic properties of all dyes were studied. In addition, the effect of various auxiliary acceptors on the geometries and electronic and optical properties was discussed for all dyes. Based on the results obtained, all the dyes studied can be used as sensitizers in DSSC.

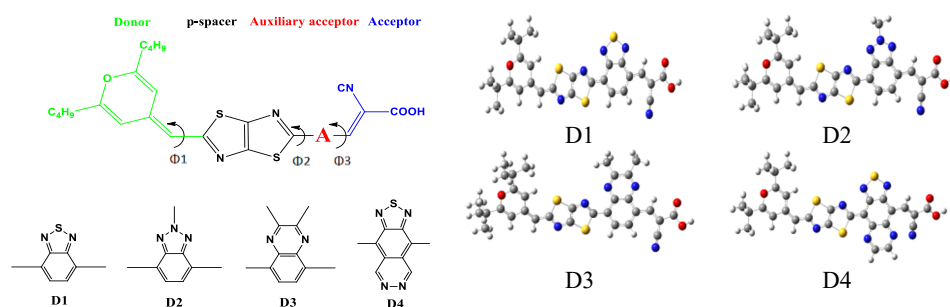


Fig. 1. The structure and optimized ground state structures of all dyes investigated.

2 Computational details

We performed all calculations using the Gaussian 09 program [9]. We optimized the neutral geometries of the designed dyes by the DFT approach using the hybrid functional B3LYP function [10] with the 6-31G (d,p) basis set [11]. We calculated the frequency of all structures to ensure that there was no imaginary frequency. To predict the optimized dye absorption spectra, the TD-DFT method was used with the CAM-B3LYP functional and the 6-31G (d,p) basis set. The Integrated Equation Form Polar Continuity Model (IEF-PCM) [12] was used to study the effect of the impact chloroform.

3 Results and discussion

3.1. Ground-state geometries

In Fig. 1, all optimized geometries of the D- π -A-A dyes are highlighted. Their specific geometric parameters are also shown in Table 1. For all dyes (D1-D4), the dihedral angle $\Phi1$ between the donor D and the π -bridge is between 178° and 180° , while $\Phi2$ the dihedral angle between the π -bridge and the auxiliary acceptor is between 146° and 179° and the dihedral angle $\Phi3$ between the auxiliary acceptor and the acceptor is between -150° and -180° , indicating that it is almost flat. Through these results, it appears to us that dyes D1 and D2 are characterized by a flat shape since all the dihedral angles are close to 180° , which leads to an improvement of the electron delocalization through these molecules [13].

Regarding the bond lengths, L1 (between the donor and the π -bridge), L2 (between the π -bridge and the auxiliary acceptor), and L3 (between the auxiliary acceptor and the acceptor), values between $1.422 \text{ \AA}$ and $1.459 \text{ \AA}$ were obtained for all dyes (D1-D4). This

indicates that the lengths of these bonds have a C=C character, which favors the intra-charge transfer (ICT) and means that there is an electron π delocalization between each group constituting the molecule.

Table 1. Φ_i (i=1,4) and Li (i=1,4) of studied dyes

Dyes	$\Phi 1$ (°)	$\Phi 2$ (°)	$\Phi 3$ (°)	$L1$ (Å)	$L2$ (Å)	$L3$ (Å)
D1	-179	179	-179	1.425	1.447	1.441
D2	180	179	-180	1.426	1.448	1.440
D3	178	146	-178	1.428	1.459	1.446
D4	179	-178	-150	1.422	1.440	1.442

3.2. Frontier molecular orbitals (FMOs)

The electronic distribution of frontier molecular orbitals (FMOs) is important when studying organic solar cells because it influences the effective charge transfer. In Table 2 and Fig. 2, the values of the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the energy difference ($E_{gap} = |E_{HOMO} - E_{LUMO}|$) for all dyes are reported using DFT/B3LYP/6-31(p, d). While the HOMO distributions were distributed to the donor and π -bridge for all molecules. On the other hand, the LUMO electron density is distributed to the auxiliary acceptor and the acceptor for all dyes. These molecules can therefore be considered donor dyes for TiO_2 .

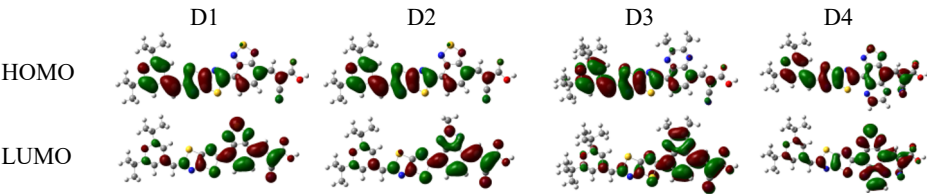


Fig. 2. The contour of HOMO and LUMO orbitals for the studied dyes D1-D4.

From the results obtained, it appears that the LUMO levels for all the dyes are higher than the conduction range of the TiO_2 semiconductor (-4.0 eV) [14], where their values are between -2.815 eV and -3.524 eV.

Table 2. Values of E_{HOMO} , E_{LUMO} , E_{gap} and V_{oc} for the studied dyes

Dyes	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	V_{oc} (eV)
D1	-5.147	-3.200	1.947	0.800
D2	-5.034	-2.880	2.154	1.120
D3	-5.014	-2.815	2.199	1.185
D4	-5.073	-3.524	1.549	0.476

This suggests that photo-excited electrons can be injected into the TiO_2 conduction band. For the HOMO levels of the dyes (D1-D4), they are confined between -5.014 eV and -5.147 eV, where they are lower than the redox potential of the I^-/I_3^- electrolyte (-4.6 eV) [15], which means the presence of a driving force for the regeneration of all dyes via the redox electrolyte. On the other hand, in DSSC it is possible to obtain a short-circuit current density J_{sc} with a high value, the smaller the energy gap, which also contributes to providing a wider wavelength region. The E_{gap} values for the dyes studied are between 1.549 eV and 2.199 eV.

3.3. Absorption Properties

The TD-DFT/CAM-B3LYP/6-31G(d, p)/IEF-PCM/chloroform level was chosen to study the spectral properties of the designed dyes. Table 3 shows the maximum absorption wavelength λ_{max} , the vertical excitation energies E_{ex} , and the oscillator strengths f for all the dyes studied. Fig. 3 shows the absorption spectra of these dyes. Looking at the spectra of all the dyes, they appear to have a similar profile, giving a main intense range of higher energies from 491 nm to 758 nm. It appears that the D4 molecule can harvest more light with a high λ_{max} , this study reports an increase in the efficiency of converting light-to-electricity in the solar cells examined. The absorption spectrum of these molecules shows a major absorption band attributed to the π - π^* transition.

Table 3. Absorption spectra data obtained at TD-DFT/ CAM-B3LYP/6-31G(d,p)

Dyes	$\lambda_{max}(nm)$	$E_{ex}(eV)$	f
D1	584	2.120	1.729
D2	535	2.315	1.987
D3	491	2.520	1.748
D4	758	1.635	1.421

Based on the results in Table 3, the excitation energy for dye D3 was 2.520 eV and decreases in the order: D3>D2(2.315 eV)>D1(2.120 eV)>D4(1.635 eV).

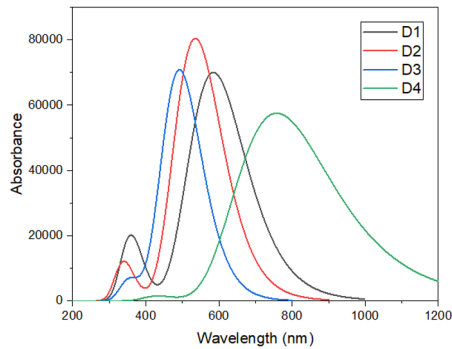


Fig. 3. Simulated UV–visible optical absorption spectra of all dyes.

3.4. Photovoltaic properties

In order to compare the performance of solar cells, we use the power conversion efficiency (PCE) which is proportional to the open-circuit voltage (V_{oc}), as shown in the following relationship (1) [16]:
$$PCE = \frac{J_{sc} V_{oc} FF}{P_{inc}} \tag{1}$$

Where J_{sc} is the short-circuit current density, V_{oc} is the maximum open-circuit voltage, FF is the fill factor, and P_{inc} is the incident solar power. The open-circuit voltage (V_{oc}) is one of the most important parameters used to evaluate the performance of a solar cell. It is acquired at zero level of current displaying showing highest voltage achieved from the solar cell devices. To achieve a high value for PCE, a high value for V_{oc} must be obtained. V_{oc} can be measured by calculating the energy difference between the LUMO of the acceptor and the HOMO of the donor in the solar cell. The theoretical value of V_{oc} can be calculated using equation (2) [17]:
$$V_{oc} = |E_{HOMO}^{Donor} - E_{LUMO}^{TiO2}| \tag{2}$$

Using the DFT/B3LYP/6-31G (d, p) method, E_{HOMO} , E_{LUMO} , and V_{OC} were determined for all the molecules studied as shown in Table 4. While the V_{OC} values obtained for all the dyes ranged from 0.476 eV to 1.185 eV, indicating the possibility of efficient electron transfer from the dye to the semiconductor TiO_2 .

4 Conclusions

In this paper, the electronic and optical properties of four dyes (D- π -A-A) were theoretically studied by changing the auxiliary acceptor, to be used as sensitizers in DSSC devices. The DFT/B3LYP/6-31G(d,p) method was used to perform the ground state geometries, while the excited state was calculated using the TD-DFT method to predict the absorption spectra of the studied dyes. Where the CAM-B3LYP functional provided an accurate maximum absorption wavelength λ_{max} compared to the experimental value. Moreover, the substitution of the auxiliary acceptor in the performed chemical structure improved the optoelectronic and photovoltaic properties of the designed molecules. Moreover, we found a significant decrease in the bandgap for the D4 molecule ($E_{\text{gap}}=1.549$ eV), and we also observed a significant bathochromic shift for the same D4 molecule, which is useful for increasing the efficiency of DSSCs. Finally, we found that lowering the bandgap of these molecules affects the absorption wavelength. Generally, all dyes can be considered promising candidates for good performance in DSSCs.

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