ORIGINAL RESEARCH

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Theoretical Design of New Healthy Organic Dyes for Solar Cell Applications with Favorite Medicinal Effect

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Abstract

In this work, a computational investigation was used to design and study new materials based on carminic acid isomers as organic dyes for DSSCs. Density functional theory (DFT) was applied to report the ground state and the excited state characteristic was reported by utilizing time-dependent DFT (TD-DFT) methods. Some electronic, optical, photolytic and electron transfer properties are evaluated to achieve our study. The results indicate that modifying the chemical structure of a dye by doping improves light harvesting efficiency while reducing the driving force for electron injection and the potential of dye renewal while boosting dye aggregation on the electrode surface. The new structures dyes displays strong charge transfer absorption bands in the visible, excellent electronic, sufficient driving force and photoelectric conversion efficiency in comparison with carminic acid. Also, All suggested dyes have sufficient properties to achieve high PCE of the DSSCs. These results are adequate for a potential effective electron injection process. Accordingly, the theoretical methods are significant to provide experimental methods for designing new, highly efficient materials for optoelectronic applications. It was found that these dyes do not have any medical effect on human health.

Keywords

DFT, carminic acid, dye-sensitized, electronic structure, optical.

Imprint

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Introduction

The dye sensitized solar Cells (DSSCs) have stimulated the interest of industry and academic circles due to their high efficiency and inexpensive cost. Improvements in renewable power energy conversion have been a major object of research [1,2]. During 1991, Grätzel et al. were the first to use an organic electrolyte with a nanocrystalline electrode material with a larger specific surface area ratio in a DSSC [1,3]. The photochemical characteristics of various organic sanitizers have been widely studied in order to develop dyes with highest visible light absorption related to long-lived excited states [2,3]. However, significant work needs to be done in terms of designing novel sensitizers and determining the best employment conditions in enhancing photon-to-current conversion efficiency [1-4]. One of the most essential elements that influences the effectiveness of DSSCs is the dye's molecular structure. Dyes, which absorb solar radiation, mediate charge transfer between the semiconductor and the electrolyte [3-6]. The excited electron is injected into the semiconductor electrode while the oxidized dye is retrieved by the electrolyte, which then catches electrons from the reference electrode to continue the circuit [4,7]. The DSSC is based on four parts: a nanocrystalline photoanode, a counter electrode, a redox electrolyte and dye, the dyes of which is vital in estimating the PCE of DSSC's. The dyes can be separated into metal-free, metal-bearing, and natural dyes [8,9]. Quantum chemical approaches have become an effective option of exposing the relation between dye molecules' structures and properties, providing a strong theoretical foundation for the sensitive detection of high efficiency dyes [9.10]. Carminic acid is a low-cost dye with a simple structure. Furthermore, carminic acid, which is commonly used as a food and cosmetics colorant or as a paint pigment, has a diverse range of raw material sources and is environmentally friendly [11]. In this study, we utilized carminic acid as a sensitizer to evaluate the photosensitizer and electrical properties of DSSCs in studies aimed at understanding the relationship between chemical structure of dye and photoelectric characteristics. In order to analyze the theoretical results in depth, the significant factors influencing the efficiency of the eight derivative dyes

based on carminic acid (**Fig.1**) were evaluated by using DFT and TD-DFT functions.

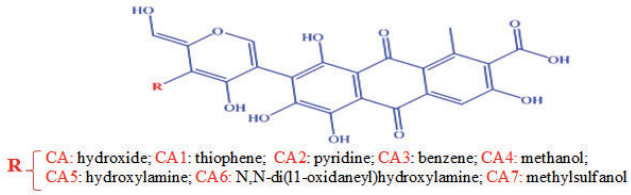

Fig. 1: Chemical structure drawings of the derivative dyes.

Method

Quantum chemical analysis has been used to understand the relationship between the physical, chemical properties and electronic structure of the designed dyes. The DFT/B3LYP method has been used to optimize the ground state structures of carminic acid and its derivative dyes, with a 6-311+G(d,p) basis set at the gas phase without any constraints [12]. Furthermore, the TD-DFT/B3LYP-6-311+G(d,p) level has been used to estimate the optical absorption, transition, electron excitations, and excitation energy of all dyes. Frequency investigation demonstrated that the optimized structures were true local minima on the potential energy surface without imaginary frequency [12,13]. All the calculations were simulated within the Gaussian 09 software with Gauss View 5.0.8 program to view the primary structure of the dyes and make available the database for it is input file [14,15]. The ultraviolet/visible spectra were simulated using the GaussSum program [16].

Results and Discussion

Geometrical Structure.

Fig. 2 represents the optimized structure of the reference (carminic acid) and the dyes modification by introducing subgroups. The carminic acid (CA) was first dye studded then; CA connected with an thiophene group (CA1), CA connected with pyridine (CA2), CA connected with benzenee (CA3), CA connected with methanol (CA4), CA connected with hydroxylamine (CA5), CA connected with N,N-di(l1-oxidaneyl)hydroxylamine (CA6), and CA connected with methylsulfanol (CA7) respectively. After optimization, the total energy () for CA, CA1, CA2, CA3, CA4, CA5, CA6, and CA7 was -0.288193, -0.1451779, -0.1585802, -0.3134708, -0.2396713, -0.214595, -0.233259, and -0.250869 a.u, respectively. The bond length values for the dyes investigated were found in are in line with data of experiment [17], as follows: C-C= 1.4245 to 1.4245, C-H=1.0768 to 1.0929, H-O=0.9717 to 0.9880, O-C=1.2625 to 1.3760, N-O=1.1969 to 1.3605, S-C=1.7234 to 1.7702. All of the dyes investigated exhibit similar coplanar configuration, according to their relaxed geometries as seen in Fig 2. This indicates that the coplanar molecule structure can enhance transfer of electrons from the donor to the acceptor.

Electronic Structures.

The distribution of sensitizer's frontier molecular orbitals (FMOs) is recognized to have a significant impact on charge transfer. The FMOs energy gap is a crucial characteristic of solar materials, where the PCE of solar cells is closely linked to FMOs energies and their energy band gaps. The open–circuit voltage and driving force for exciton dissociation are predicted by the energy gap. It also evaluates the chemical reactivity, dynamic stability, molecules' electron transport characteristics, chemical hardness, and softness [18]. To explore the impacts of functional groups on

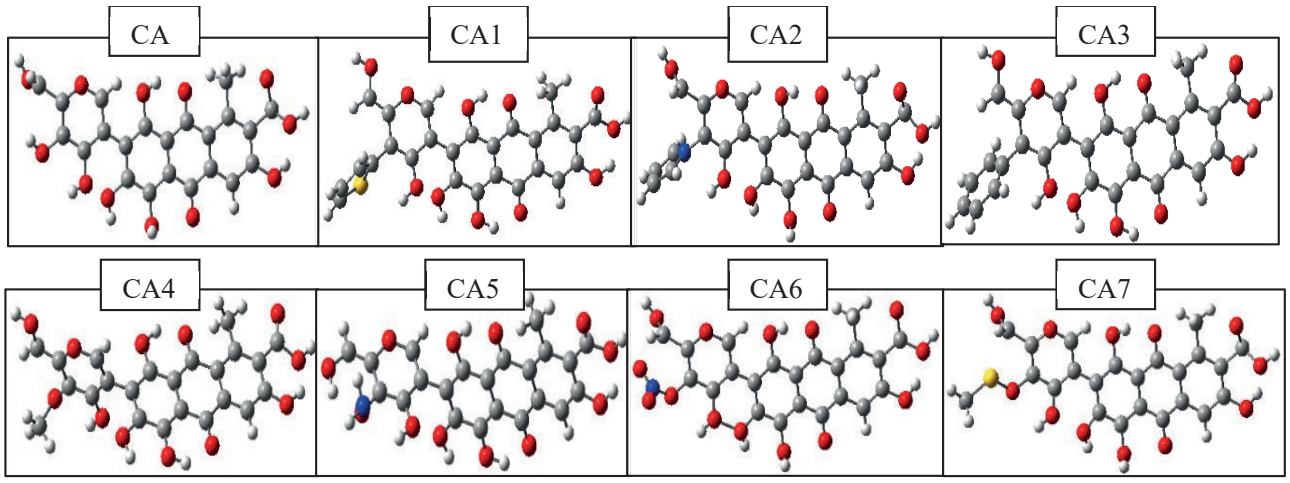

Fig 2. Optimized geometrical structures of carminic acid and CA1- CA7 dye.

the electronic and optical properties of the examined dyes, the energy levels graph of HOMOs, LUMOs and energy gap of CA and CA1–CA7, TiO_2 conduction band, and redox potential energy of the electrolyte are displayed in Fig. 3. The HOMO energy values are calculated to be; -5.9392, -5.0155, -5.0055, -5.0165, -5.0455, -5.0177, -5.0277 and -5.0577 eV for CA and CA1–CA7 respectively. Calculated HOMOs of CA and CA1-CA7 are found to be below the redox potential (-4.8 eV), resulting in quick dye regeneration and avoiding geminate recombination process between oxidized dye molecules and photo-injected electrons in the TiO_2 surface.

Also, the LUMO energy values for CA and CA1-CA7 are; -3.1170, -2.8898, -2.9954, -2.9975, -2.8754, -2.9628, -2.8823 and -2.9942 eV correspondingly. It appears from the results of LUMOs of CA and CA1-CA7 are found above the TiO2 CBE (- 4.0 eV) providing the thermodynamic driving force for favourable electron injection from the excited state dye to the CBE edge of TiO2. The energy gap value of reference CA is found to be 2.8222 eV which is noted as highest value of band gap among the designed molecules CA1-CA7), where differs from 2.0100- 2.1700 eV depending on the dye structures. The small energy gap in donor dyes aids in the generation of excitons and increases the efficiency of photo-excitation. Thus, all dyes have sufficient driving force for use as sensitizers in DSSCs and it is clear that the new dyes CA1-CA7 are better than the reference CA.

It is clear from Fig. 4 that the HOMO distribution is mainly on the left side of the dyes. The distribution of LUMOs, on the other hand, is primarily concentrated on the dyes' right side. the pattern of HOMOs and LUMOs shows that the HOMO-LUMO excitation has an intra-molecular charge transfer property and advantageous to an efficient solar cell. Because of this, there is a strong electronic connection between the dye's excited state and the semiconductor (TiO_2) conduction band, allowing for easy electron injection, and a high location of the HOMO on the donor end reduces the possibility of charge transfer between the injected electrons and the oxidized dye. This means that the electronic structures of these dyes are favourable to the solar cells' high overall efficiency.

Optical Characteristics

Novel sensitizers that can absorb in the visible area with significantly increased absorption coefficients are also required in the development of organic dyes for DSSCs. To understand the electronic transitions of the dyes investigated in this study, TD-DFT/ B3LY-

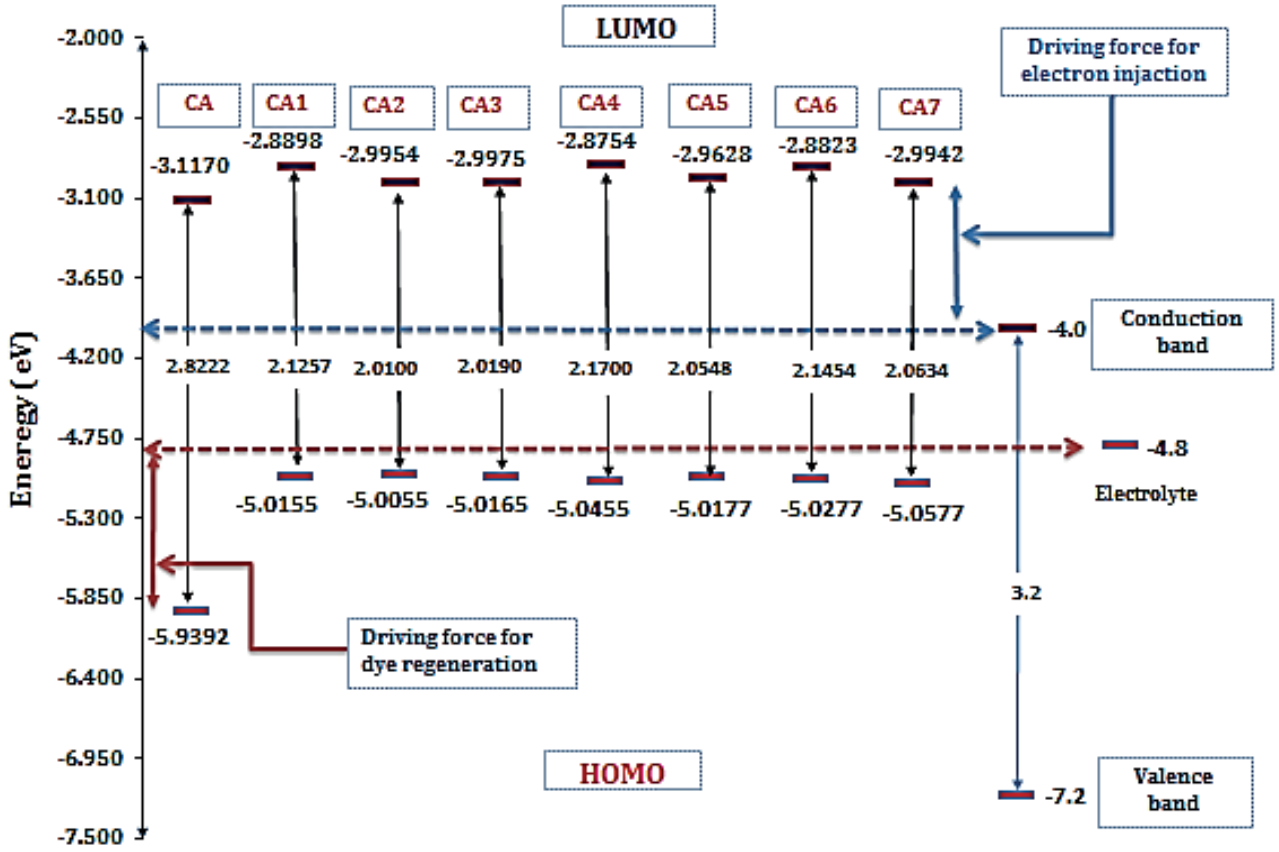

Fig. 3 Diagram E_{HOMO}, E_{LUMO} and E_g of all dyes, also TiO_2 and electrolyte.

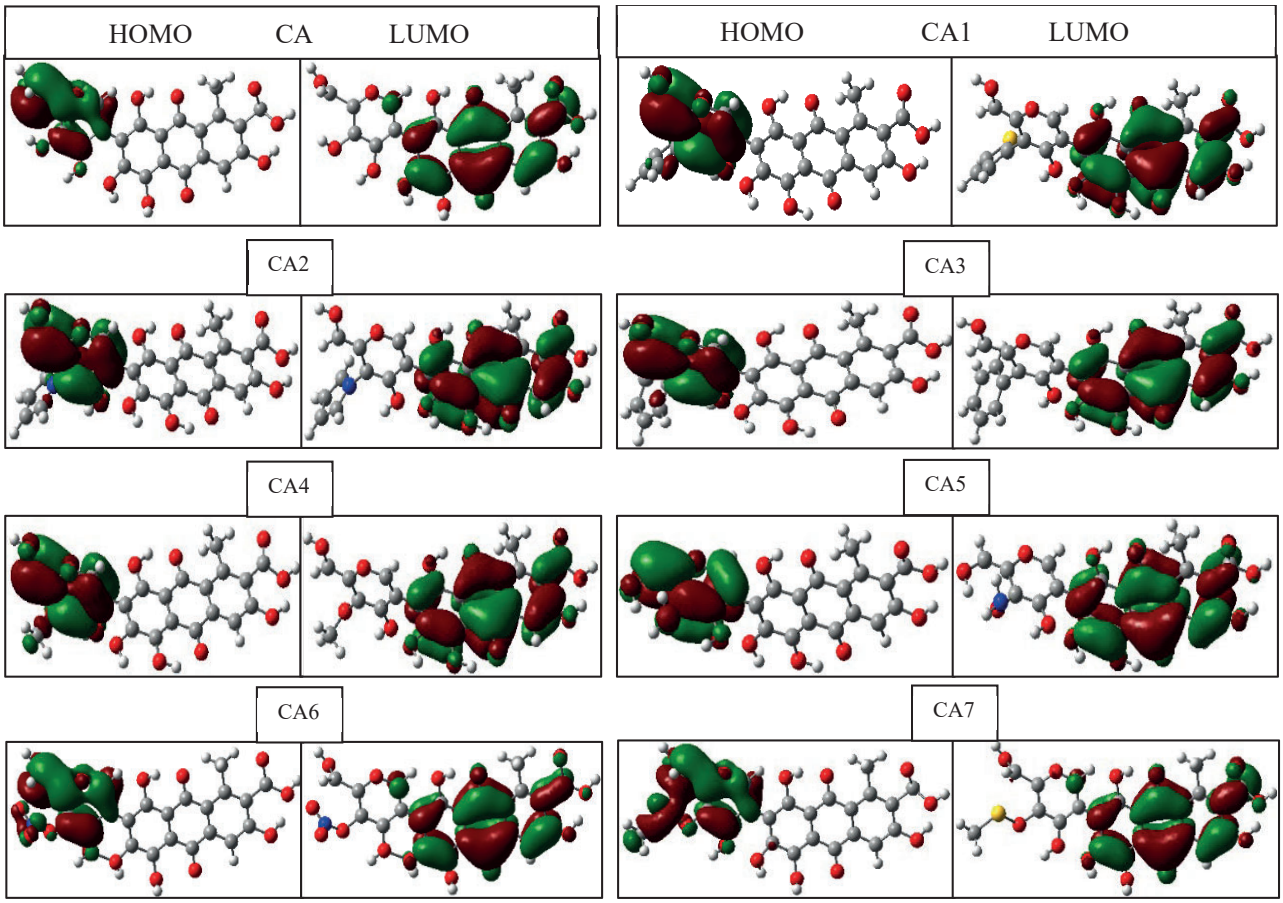

Fig. 4 the HOMOs and LUMOs distribution of the studied dyes.

P//6-311+G(d,p) simulations on electronic optical absorption were performed. **Fig. 5** illustrates the estimated absorption spectra for CA and CA1-CA7 dyes. The wavelength longer than 300 nm was listed in Table 1 because the absorption in visible and near-UV areas is the most significant region for photo-to-current conversion.

The major peaks in the carminic acid spectrum are at 2.053eV/415.502nm and 2.984eV/603.648nm 2.96 eV, which is very close to the experimental value [19]. The main peak spectrum of the CA1-CA7 dyes displays red-shifted in comparison to CA in the following order (Table 1): CA1 (2.776eV at 446.611nm and 1.994eV at 621.770nm, CA2 (2.911eV at 425.912nm and 2.030eV at 610.641nm), CA3(2.646eV at 468.541nm and 2.030eV at 610.643nm), CA4(2.782eV at 445.552nm and 1.867eV at 663.791nm), CA5(3.880eV at 319.502nm, 3.021eV at 410.393nm and 2.499eV at 495.951nm), CA6(2.905eV at 2.905nm and 2.302eV at 538.583nm) and CA7(2.699eV at 459.252nm and 1.738eV at 713.072nm), with the major transition from the HOMOs to the LUMOs orbital. Also, there is no type of wavelength affecting human health. All absorption bands in the visible region are typical or transitions. We note that the CA5 dye contains three main bundles, and this gives it the possibility of new transitions of importance. All dyes designed with high oscillator strength (*f*) compared to reference (CA), which means that they are more effective and efficient. The light harvesting efficiency (LHE) represents one of the important characteristics that determine the efficiency of dyes, that the higher its value, the more efficient and effective the dyes [6,8]. We note that all values of LHE for the designed dye are high compared to carminic acid, and this means that the new structures led to an improvement and increase in the efficiency of these dyes. These dyes display strong charge transfer absorption bands in the visible region.

Photovoltaic Properties

The photo-electronic properties of the excited-state of dyes are essential for improving the photoelectric performance of DSSCs. In this study, The significant parameters of JSC are: the open-circuit voltage, the lowest energy absorption, the oxidation potential energy, oxidation potential energy, free energy change, dye regeneration were calculated and listed in the **Table 2** using formulas from a previous study [6-19]. It was found that the value of for all the studied

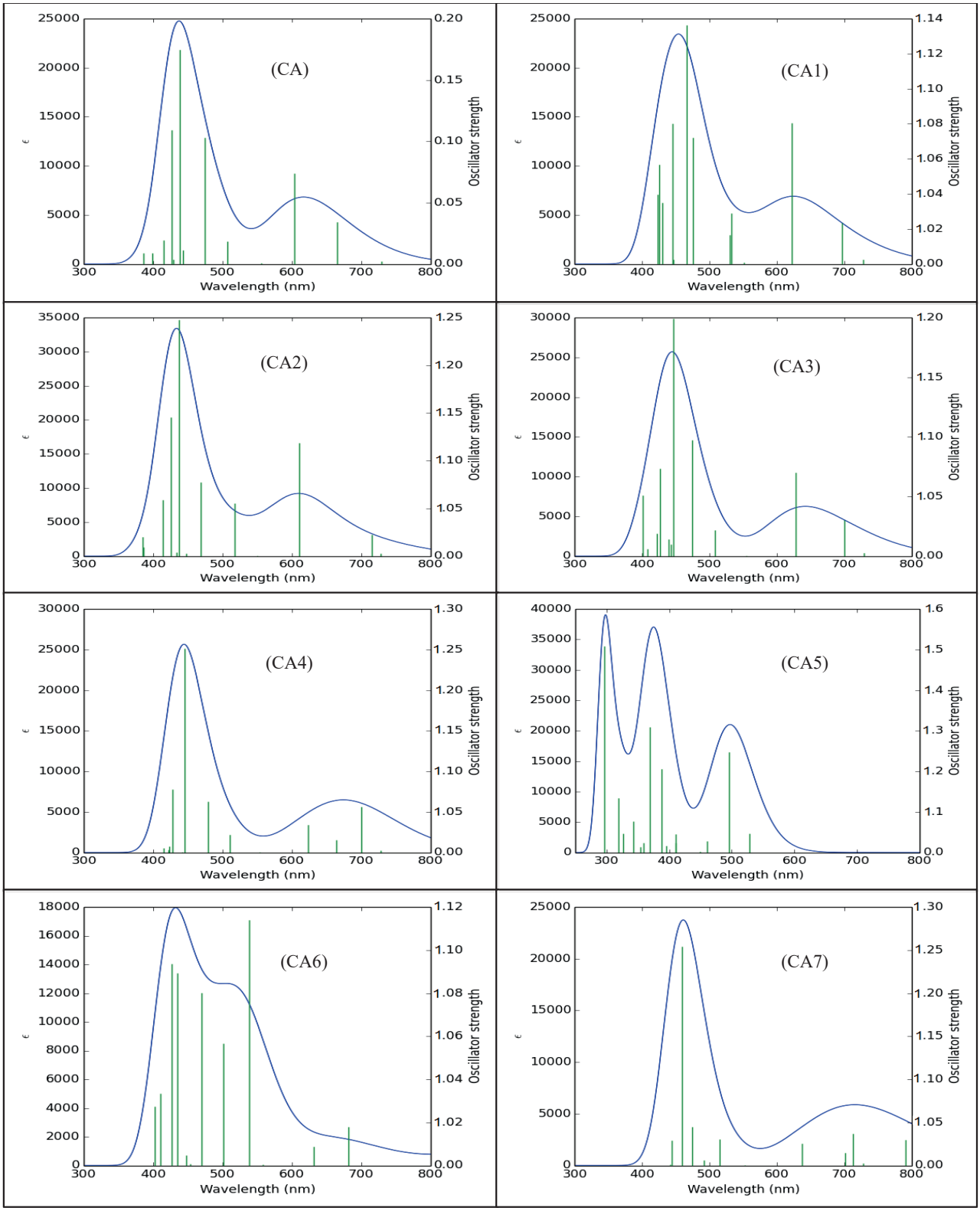

Fig. 5 Simulated absorption spectra for all dyes (CA-CA7).

dyes ranged between 0.805to 1.739eV, and it should be noted that these values are positive and good. This indicates the ease of transfer of electrons from dyes to the TiO2 conduction band. As it appears from the results that the values are negative for all studied dyes, and this indicates that the excited state of the designed dyes is above conduction band of TiO2. This means that the electron injection into the dyes will be spontaneous and preferring the electron injection from excited state of dye to the TiO2 conduction band. The is another characteristic that affects the efficiency of DSSCs. It is important to reduce the values of regeneration in order to achieve the electron transfer process quickly and this is noted in the value of in Table 1. This

Table 1

The characteristics of absorption spectra for all designed dyes.

Dyes	Excited state	(eV)	(nm)	f	LHE	Main Transition	%	Type transition
CA	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$	2.984 2.053	415.502 603.648	0.234 0.073	0.417 0.155	HOMO→LUMO+2 HOMO→LUMO	86% 76%	π → π* *n* → π*
CA1	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$	2.776 1.994	446.611 621.770	1.129 1.034	0.926 0.908	H-1→LUMO HOMO→LUMO+1	96% 90%	π → π* *n* → π*
CA2	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$	2.911 2.030	425.912 610.641	1.231 1.062	0.941 0.913	H-1→LUMO HOMO→LUMO	87% 90%	π → π* *n* → π*
CA3	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$	2.646 2.030	468.541 610.643	1.218 1.091	0.939 0.919	H-2→LUMO HOMO→LUMO	93% 86%	π → π* *n* → π*
CA4	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$	2.782 1.867	445.552 663.791	1.247 1.078	0.943 0.916	H-2→LUMO HOMO→L+2	91% 89%	π → π* *n* → π*
CA5	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$ $S_o \rightarrow S_3$	3.880 3.021 2.499	319.502 410.393 495.951	1.587 1.543 1.348	0.974 0.971 0.955	HOMO→LUMO H-1→LUMO HOMO→L+2	91% 86% 89%	π → π* π → π* *n* → π*
CA6	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$	2.905 2.302	426.745 538.583	1.128 1.091	0.926 0.919	H-1→LUMO HOMO→LUMO	93% 89%	π → π* *n* → π*
CA7	$S_o \rightarrow S_1$ $S_o \rightarrow S_2$	2.699 1.738	459.252 713.072	1.287 1.072	0.948 0.915	H-1→L+2 HOMO→LUMO	94% 90%	π → π* *n* → π*

Table 2

the photovoltaic properties of all dyes under study.

Dyes	$V_{OC}(TiO_2)$	E_{00}	E_{OX}^{dye}	E_{OX}^{dye*}	ΔG°_{inj}	ΔG^{regen}
CA	1.739	2.054	5.939	3.885	-0.115	1.139
CA1	0.815	1.994	5.015	3.021	-0.979	0.215
CA2	0.805	2.031	5.005	2.975	-1.025	0.205
CA3	0.817	2.031	5.017	2.986	-1.014	0.217
CA4	0.845	1.868	5.045	3.177	-0.823	0.245
CA5	0.818	2.500	5.018	2.517	-1.483	0.218
CA6	0.828	2.302	5.028	2.725	-1.275	0.228
CA7	0.858	1.739	5.058	3.319	-0.681	0.258

indicates that the studied dyes have sufficient properties to obtain high PCE of the DSSCs. These values are sufficient for a potential efficient electron injection process. Therefore, all the designed molecules can be suggested as the dye sensitized in DSSC.

Conclusions.

The chemical modifications were carried out for a well-performing organic dye sensitizer. Through rational chemical adaptations, the required qualities, such as electronic, optical, optical, redshift absorption spectrum, could be improved. Eight dye photosensitizers based on carminic acid isomers as organic dyes were simulated and reported using DFT//TD-DFT for develop new and more efficient organic dyes. The width and location of the first band in the UV-Vis spectra, the absorption threshold, and the LUMO energy with respect to the conduction band edge were chosen as appropriate parameters to evaluate the efficiency of these compounds as sensitizers in DSSCs. Also, the new designed dyes successfully lowered the energy gap depending on the dye structures. The LUMO levels of all designed dyes are much higher than the conduction band of TiO_2, suggesting that the photo-excited electron escapes easily from dye to TiO_2. The proposed new dyes showed significant improvement in the properties of dyes that will be used for organic solar cells such as charge distribution, spontaneous electron injection, open circuit voltage, driving force, redox, reasonable conversion, strong photosensitizing, harvesting properties during the photo-excitation process, and spectra absorption. Accordingly, all the

suggested dyes were seen to have good efficiency and therefore promising dye for organic solar cells and an important characteristic of these dyes is that they do not have any effect on human health.

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