

DFT Studies of Thiophene-based Sensitizers for Dye-Sensitized Solar Cells: Effects of Electron-Donating Heteroring Moieties on the Master Factors Enhancing the Photovoltaic Performance

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Abstract—This study focuses on the introduction of three conjugated compounds containing thiophene rings and the analysis of their applicability in dye-sensitized solar cells, to support the development of emerging materials for energy and sustainable technologies. The corresponding compounds were analysed theoretically using density functional theory (DFT) and time-dependent DFT (TD-DFT). These methods enable the determination of optoelectronic properties as well as the characterization of photogeneration and charge-transfer processes. The importance of theoretical calculations in materials science and engineering arises from their ability to address several experimental constraints and guide the design of efficient molecular compounds. The obtained results reveal relevant photovoltaic capabilities, and the studied photosensitizers exhibit desirable characteristics such as favorable absorption, good band gap, high light-harvesting efficiency (LHE), and practical open-circuit voltage (V_{oc}).

I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) represent a promising, cost-effective alternative to conventional photovoltaic technologies, characterized by their straightforward fabrication process and operational stability under diffuse light and elevated temperatures. Single-junction DSSCs have achieved certified power conversion efficiencies (PCEs) exceeding 13% [1]. However, commercial viability necessitates reaching efficiency levels of 15% or higher to compete effectively with established solar cell technologies [2,3]. Beyond efficiency, key challenges for DSSC commercialization include enhancing long-term device stability and reducing both material and manufacturing costs. The photoactive sensitizer dye is a critical component that dictates light absorption and subsequent light-to-electrical energy conversion within the DSSC architecture [4,5]. Despite two decades of intensive research dedicated to developing panchromatic dye sensitizers, particularly those based on synthetic ruthenium complexes, significant breakthroughs in cost-efficiency are becoming increasingly challenging.

The photoactive sensitizer is crucial for DSSC performance. Research into synthetic Ruthenium dyes is leading to important efficiencies, which exceed 11% under optimized

laboratory conditions and highlight the potential of this class of materials [6]. However, the high cost and toxicity of synthetic dyes necessitate the investigation of sustainable options. Sensitizers based on natural compounds offer a cost-effective, non-toxic, and biodegradable alternative. Efficiency can be optimized through careful selection and co-sensitization. This search for cost-effective and efficient chromophores has also intensified research into organic dyes, particularly those incorporating eco-friendly fragments. Thiophene-based D- π -A dyes are highly favored due to the ability of thiophene to enhance charge transfer and tune the electronic properties of the conjugated system, leading to optimized absorption spectra and energy levels for DSSC devices. The design of these synthetic dyes often draws parallels with naturally occurring compounds. For instance, thiophene and its derivatives are primarily recognized in nature as secondary metabolites produced by specific plant families, notably the Asteraceae. These natural thiophenes, often presented as oligomeric compounds, possess extended polyenic structures that enable strong light absorption in the visible spectrum, conferring yellow or orange pigmentation as described in Tagetes [7]. Thus, understanding the inherent chromophore properties of structures based on natural oligomers is essential for the rational design of eco-friendly next-generation sensitizers.

Herein, we developed a series of three sensitizers based on the D- π -A architecture with the aim of exploring and discussing the impact of varying donor units on photovoltaic performance for DSSCs. These compounds incorporate three substituent donor units: (1) ethyl-carbazole (Et-Cbz), (2) triphenylamine (TPA), and (3) bithiophene (2Th). In this study, we choose a typical structure where the 2Th is the common π -spacer and the acceptor is the most widely used cyanoacrylic group (Fig. 1). The dye-TiO₂ interaction plays an important role in the operation of DSSCs. Upon photoexcitation, the dye acts simultaneously as an electron-accepting and anchoring unit, promoting intramolecular charge transfer toward TiO₂, while ensuring efficient electron injection through its strong carboxylate-surface binding [8].

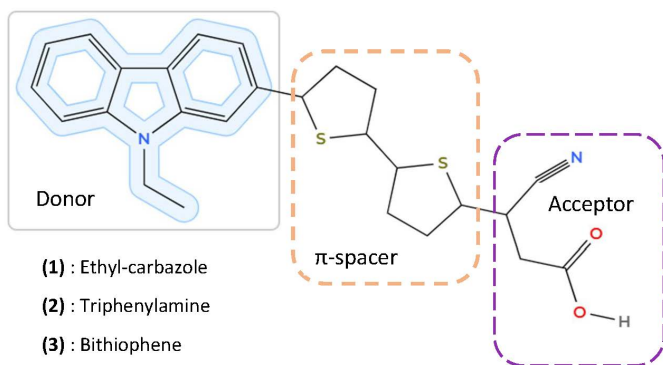


Fig. 1. Molecular structure of studied dyes.

TABLE I
THE HOMO, LUMO, ENERGY GAP, EA, AND IP ENERGY LEVELS (eV) FOR THE DYES CALCULATED BY DFT (B3LYP/ 6-31(G,D)).

Dye	HOMO(eV)	LUMO(eV)	E_g (eV)	EA	IP
1	-5.54323	-2.94672	2.596	1.80001	6.509
2	-5.34976	-2.98346	2.366	1.9174	6.307
3	-5.63004	-3.1138	2.516	2.06327	6.606

II. COMPUTATIONAL PROCEDURE

Density functional theory (DFT) method allows one to determine the optimized geometries, which is particularly useful for analyzing molecular structures and predicting quantum-chemical properties, providing essential information for the analysis of a material intended for a specific application [9,10]. The computational work was executed using the Gaussian09 software package [11]. All molecular structures were simulated using DFT in the gaseous phase. The optimized ground-state geometries were obtained using B3LYP hybrid functional with 6-31G(d,p). Vibrational calculations confirmed that these structures corresponded to true energy minima. Excited-state properties were investigated using time-dependent DFT (TD-DFT) with the CAM-B3LYP functional. Electronic transition energies and oscillator strengths were calculated from the TD-DFT results, utilizing the ground-state geometries previously obtained via DFT.

III. QUANTUM CHEMICAL PROPERTIES AND ELECTRONIC ENERGY LEVELS

The quantum chemical properties are reliably computed using the DFT (B3LYP/6-31G(d,p)) method. Table I lists the theoretical parameters of the studied molecular compounds. Generally, the ionization potential (IP) is evaluated as the difference between the ground state of the cation and the neutral molecule (S0). However, the electron affinity (EA) is given by the difference in energies: $EA = E_{\text{neutral}} - E_{\text{anion}}$, as shown in Fig. 2.

For efficient electron transfer from the redox electrolyte of iodide/triiodide, the HOMO level of all dyes show positive level relative to the redox couple potential ($E(I^-/I_3^-) = -4.8$ eV) [6,11,12], thereby enabling effective dye regeneration. Moreover, all calculated LUMO levels are positioned at a potential sufficiently higher than the conduction band edge

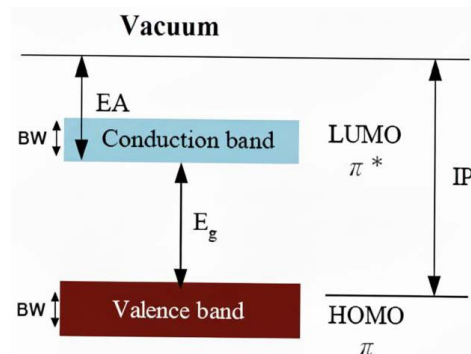


Fig. 2. Schematic representation of band structure for semiconductor materials.

of the TiO_2 photoanode to ensure favorable electron injection. Furthermore, the rapid kinetics of the dye regeneration, compared to the slower back-recombination of electrons from the semiconductor into the oxidized dye, is crucial for maintaining high device efficiency [13]. The compounds exhibit medium band gaps ranging from 2.3 to 2.6 eV. In fact, the insertion of 2Th in the oligomeric dye reduces the gap by about 0.08 eV compared with carbazole ring. However, TPA donor exhibits the smaller band gap energy compared to the other aromatic rings, which results in a significant reduction of 0.26 eV (Fig. 3).

As well, the examination of LUMO and HOMO energies is important because the relative ordering of occupied and virtual orbitals provides a reasonable qualitative indication of excitation properties and electronic density [14]. Figure 3 shows the HOMOs and LUMOs orbitals of the dye corresponding Et-Cbz substituent. The plot illustrates that the LUMO orbitals are mainly localized on the acceptor side of the cyanoacrylic region, whereas the HOMO orbitals are largely delocalized across the entire molecular framework.

IV. OPTICAL AND PHOTOVOLTAIC CHARACTERISTICS

The theoretical absorption spectrum was also obtained through the TD-DFT calculations. Figure 4 presents the UV-Vis absorption spectra of the three investigated chromophores (1–3). All molecules exhibit two distinct absorption domains. The high-energy band in the 300–350 nm region is attributed to localized $\pi-\pi^*$ transitions within the conjugated framework, whereas the lower-energy and more intense band between 380 and 500 nm arises from a characteristic intramolecular charge-transfer transition associated with the D- π -A architecture. Notably, compounds 2 and 3 display the strongest absorption intensities in the intramolecular charge-transfer region, reflecting enhanced electronic delocalization and more efficient donor-to-acceptor charge transfer. Moreover, we observe a very slight red shift from compound 1 to compound 3, which may indicate reduced electronic coupling between the donor and acceptor units for the Et-Cbz donor case. Overall, these spectral features underscore the sensitivity of the optical response to subtle structural modifications and provide insight into the optoelectronic behavior governing their potential applicability in the photogeneration mechanism.

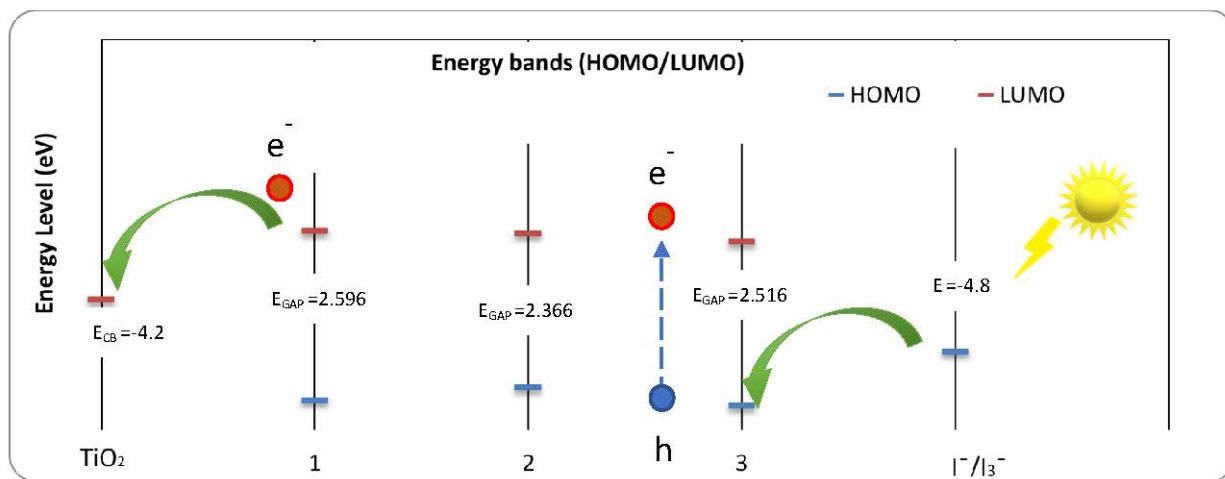


Fig. 3. Schematic energy level diagram of the studied dyes (1: Et-Cbz, 2: TPA, and 3: 2Th).

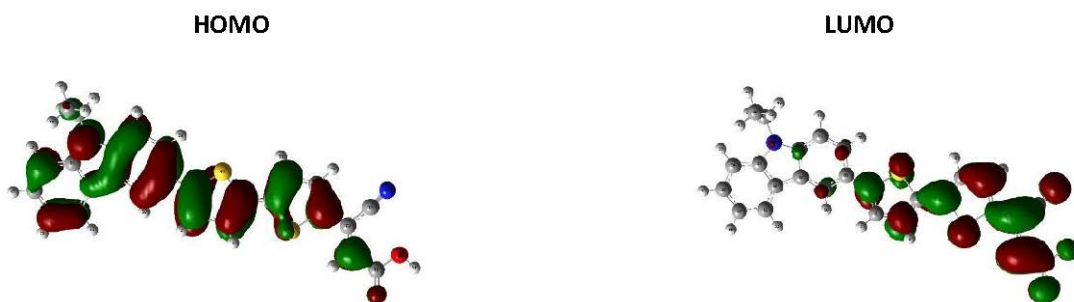


Fig. 4. DFT contour plots of FMO of the carbazole substituent dye (1) associated with the ground-state electronic structure.

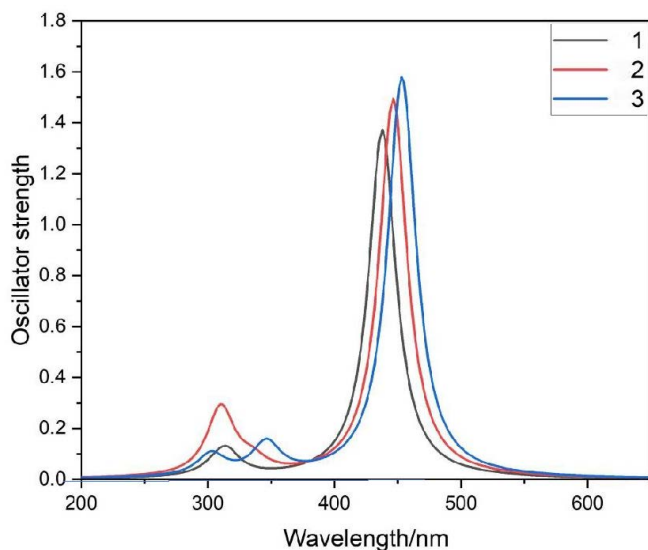


Fig. 5. TD-DFT computed absorption spectra of the three dyes (1: Et-Cbz, 2: TPA, and 3: 2Th).

To comprehensively assess the influence of various donor moieties on photogeneration, several key parameters were quantified by TD-DFT calculations, including the open circuit voltage (qV_{oc}), the force for electron injection (ΔG_{inj}), and the light harvesting efficiency (LHE), which describing

the percentage of incident light deduced from the calculated oscillator strength (OS) [15]: $LHE = 1 - 10^{-OS}$.

Basically, the power conversion efficiency (PCE) of the photovoltaic cell is proportional to the product of fill factor (FF) and the high short-circuit current density (J_{sc}). The V_{oc} and J_{sc} values present experimental values deduced from the J-V characteristics of the solar device under illumination intensity of 100 mW/cm^2 . The J_{sc} expression for DSSCs is defined as:

$$J_{sc} = \int LHE(\lambda) \Phi_{inj} \eta_{collect} d\lambda \quad (1)$$

where $\eta_{collect}$ is the charge collection efficiency and Φ_{inj} is the electron injection efficiency.

For the electron injection efficiency Φ_{inj} , it is directly linked to the driving force ΔG_{inj} of the electron obtained from the calculated oxidation potentials in the fundamental state (S0) and in the excited state (S*) denoted as E_{dye} and E_{dye}^* , respectively, [16,17]. Table II summarizes the photovoltaic parameters for all dyes.

Besides ΔG_{inj} , the total reorganization energy λ_{tot} also influences the kinetics of charge injection. Therefore, the λ_{tot} is crucial for assessing the relationship between the electronic structure and the resulting J_{sc} . Also, the corresponding dyes possess λ_{tot} energies inferior to 1 eV, the low λ_{tot} , which comprises both the hole and electron reorganization energies, can facilitate enhanced J_{sc} . In other words, these small λ_{tot}

TABLE II
TD-DFT/CAM-B3LYP/6-31 G(D,P) CALCULATED
PHOTOVOLTAIC PARAMETERS.

Dye	V _{oc} (V)	E _{dye} (eV)	E* _{dye} (eV)	ΔG _{inj} (eV)	LHE	λ _{tot} (eV)
1	1.053	5.543	2.71183	−1.288	0.9488	0.63945
2	1.016	5.350	2.57236	−1.428	0.9617	0.6602
3	0.886	5.630	2.89474	−1.105	0.9659	0.66503

values correspond to faster charge-carrier transport rates into the conduction band of TiO₂.

We find that for all dyes the LHE reaches 90%, and the corresponding efficiencies are: 0.9488, 0.9617, and 0.9659 for Et-Cbz, TPA, and 2Th, respectively. The compounds have negative values for ΔG_{inj}, which ensure spontaneous electron injection, essential for efficient dye regeneration. Moreover, ΔG_{inj} increases in the order: 2Th (1.10 eV)<Et-Cbz (1.29 eV)<TPA (1.43 eV). A larger ΔG_{inj} together with a high LHE, can also contribute to improving the photocurrent J_{sc} (Eq.*). As observed for Dye (2), the results indicate that the dye incorporating the TPA donor moiety is likely to deliver a higher J_{sc} than the other candidates listed in Table II. This observation is further supported by the smaller energy gap of the corresponding compound. In a recent study by Verma et al., a set of dyes incorporating thiophene as a π -spacer and thiadiazol-pyridine with benzotriazole as internal acceptor units was designed. The corresponding DFT results showed, in most cases, high photovoltaic descriptors with LHE = 0.97 and V_{OC} = 1.20 eV [18]. Compared to another previous experimental characterization of 2Th dyes employing bi-thienyl-benzonitrile derivatives as donors, a J_{SC} of 18.14 mA cm^{−2} and a V_{OC} of 0.676 V were reported [19]. In light of these studies, our results show a V_{OC} close to 1.0 eV and LHE of about 0.96, which fall within the same performance range as the best reported systems, indicating that the three dyes exhibit competitive optoelectronic properties.

V. CONCLUSION

We proposed three dyes by strategically modifying their molecular architecture D- π -A type, through variations in the donor moiety (1 = Et-Cbz, 2 = TPA, and 3 = 2Th). The primary goal was to investigate how varying the donor group influences energy levels, absorption spectra, and potential photovoltaic performance. Using calculations based on DFT and TD-DFT, we optimized the ground state of these molecules and characterized their essential optoelectronic properties. These calculations provided crucial insights into the HOMO–LUMO orbital configurations, band gap, absorption characteristics, and other key PV indicators. The quantum data and light absorption profiles confirm the potential of these sensitizers for applications in photonic systems. Furthermore, performance characteristics, such as LHE, V_{oc}, and ΔG_{inj}, suggest that these dyes are promising candidates for subsequent experimental testing.

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