



Untangling the effect of π -conjugation length on the opto-electronic properties of reactive dye-based sensitizer

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Abstract

Reactive dyes exhibit suitable opto-electronic properties, making them promising for dye-sensitized solar cell (DSSC) applications. The present study uses reactive orange 16 dye to design an efficient dye sensitizer for DSSC application using a donor– π –acceptor concept. The sensitizer structures and their electronic and optical properties were investigated using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. The molecular electrostatic potential maps, HOMO–LUMO distributions, and density of states plots were obtained for the optimized geometry. The analysis showed that the electronic properties of reactive orange 16 are enhanced due to the π -linkage, responsible for extending the conjugation length of the system. The TD-DFT calculations showed a bathochromic shift in the absorption spectra due to the introduction of the π -linker. The shift confirmed the conjugation's role in enhancing the sensitizers' electronic properties. The transitions were $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, and the transition with maximum oscillator strength was assigned to the H \rightarrow L excitation. The study showed that donor– π –acceptor concept-based sensitizers derived from reactive dyes favor DSSC applications. Hence, this study's findings could be used to design and develop more efficient dye sensitizers based on reactive dyes.

Keywords Reactive dye · Dye sensitizer · Π -linker · Solar cell · Conjugation · Bathochromic shift

1 Introduction

In the past few decades, constant efforts have been made to harness the energy derived from renewable sources to meet global energy demand. The magnitude of solar energy reaching the earth is four orders higher than the global energy consumption and thus has generated tremendous attention [1]. Solar photovoltaic cells convert light energy into electrical energy. However, photovoltaic cells' low energy conversion efficiency is the hurdle limiting their commercial application [2].

Presently, dye-sensitized solar cells (DSSC) (the third-generation solar cells) are of interest and are being explored to outweigh traditional solar cells in terms of efficiency,

simple manufacturing and economic viability [3]. In 1972, TiO₂ thin film-based DSSC was first proposed [4]. In 1991, a ground-breaking invention was made possible by Grätzel et al. [5] by introducing nanoporous TiO₂ electrodes with a rough surface and a solar-to-electricity conversion efficiency of 7%. In 2011, 12.3% solar-to-electricity conversion efficiency was reached for the DSSC made up of a Co(II/III) tris(bipyridyl)-based redox electrolyte, zinc porphyrin dye (YD2-o-C8) co-sensitized with another organic dye (Y123) [6]. Later, DSSC combined with a Co(II/III) tris(bipyridine)-based redox electrolyte and a zinc porphyrin dye was able to obtain a remarkable efficiency of 13.00% [7].

Generally, DSSC contains a sensitizer, photoanode, electrolyte, and counter electrode [8]. The dye sensitizer is essential to the DSSC as it collects light by energizing electrons and injecting them into the semiconductor's conduction band. Sunlight sensitizes the organic dye, which leads to electron injection. These energized electrons move into the conduction band of the semiconductor. The dyes used in DSSC must meet the following requirements: They should have a robust anchoring group, appropriate energy levels for efficient hole injection and dye regeneration, and the absorption range in the visible and near-IR regions [9]. Thus, the

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efficiency of the dye sensitizer can be greatly improved by suitable modification on the donor, π -spacer, and acceptor subunits. Compared to conventional metal-based dyes, metal-free organic offers several benefits such as high molar extinction coefficients, easy synthetic procedure, and cost-effective and flexible molecular design [10, 11]. Hence, metal-free dyes have attracted attention for applications in DSSCs. The choice of dyes also depends on their high light-absorbing capacity and high molar extinction coefficient [12].

Several organic dyes have been used as sensitizers for DSSCs [13–15]. Organic sensitizers are usually of a donor– π –acceptor (D– π –A) type, comprising of a donor unit (D), a π -linker (π), and an acceptor unit (A) [16]. The organic dye sensitizers based on D– π –A structures show photon–electron conversion through intramolecular charge transfer. However, for most pure organic dyes, the absorption maxima were found in a blue region, ultimately leading to a great loss in the utilization of sunlight [17]. Redshift in absorption maxima can be achieved by extending the π -conjugation of the metal-free organic dyes [18]. The aromatic heterocycles such as thiophene furan have been found to red shift the absorption wavelengths. Thus, they can be widely used as π -conjugated linkers [19, 20]. Because of its relatively lower resonance energy than thiophene, Furan has been found suitable to be used as a π -linker.

Numerous studies have investigated the role and effect of a π -linker in a dye sensitizer. Hua et al. [21] showed that the benzotriazole-based sensitizers with a furan moiety as spacers could improve the device efficiency and impart long-term stability. Tian et al. [22] have reported a series of donor–donor– π –acceptor structural organic dyes with different donor groups into the triphenylamine framework with starburst configuration for redshift absorption. Yin et al. [23] studied how the π -conjugation length affects the properties of the oligomers and their applicability in DSSCs. Zhang et al. [24] showed that the π -linker enhances the properties of dithiafulvenyl- π -phenothiazine dyes. Yen et al. [25] investigated the effect of π -linkers in the N-alkylphenoxazine-based sensitizer. Our previous study [26] showed that reactive dyes could be promising candidates for DSSC applications because of their optical and electrical properties. The findings revealed that reactive dyes exhibit many regions with electronegative potential. Moreover, they are structurally rich in functional moieties, allowing easy transformations to desired compounds.

The D– π –A strategy can significantly improve the electronic property of reactive dyes, and designs based on them can be explored for the DSSC applications. Despite the suitable properties, the literature shows little insight into exploring reactive dyes for DSSC applications. Further, the theoretical

discussions on the effect of different π -spacers having varying conjugation lengths on the electronic and photophysical properties of the dye sensitizer are limited. Theoretical discussion is necessary to understand the electronic properties of a dye sensitizer to save experimental time and achieve highly efficient designs in a shorter span. We chose reactive orange 16 (RO16) dye as a parent dye molecule to design the dye sensitizer in this study. Three different π -spacers containing heterocycles, namely 1,2-bis(2,5-dimethylthiophen-3-yl) cyclopent-1-ene (coded as BDT1), 4-hexyl-2,6-dimethyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (coded as BDT2), and 2,5,6,9-tetramethylnaphtho[2,1-b:3,4-b']dithiophene (coded as BDT3) were attached to it followed by an external acceptor unit ((E)-3-(7-cyano-2-methyl-2,3-dihydrobenzo[b]thiophen-6-yl)-2-methyl acrylic acid) (coded as BMA). The effect of varying conjugation length of the sensitizer system on its electronic properties is studied to establish the structures–properties relationship.

2 Computational details

This study investigated dye sensitizers based on RO16 using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations performed using Gaussian 09 software [27]. The ground-state geometries of the dye sensitizers were optimized using B3LYP functional and 6-311G basis set [28]. The geometry optimization converged after 27 cycles. To arrive at the most stable conformations, 67 (considering all the four reported molecules in this study) computations were examined for their structural aspects and energetics. Appropriate parameters such as the convergence criteria, the step size, and the trust radius for the optimization algorithm were chosen to balance the accuracy and efficiency of the optimization process. The rotation of the bonds was also considered to examine the 3D orientations of the molecules as the 3D arrangement of the system and its conjugation are strongly interrelated. The frontier molecular orbital analysis and HOMO–LUMO distribution were visualized using the Avogadro software [29]. GaussSum software was used to plot the DOS graphs [30]. The time-dependent DFT (TD-DFT) was employed for the excited-state computations. B3LYP/6-311++G(d,p) level of theory was used along with Coulomb attenuated method to obtain the absorption spectra and the oscillator frequencies [31]. The HOMO and LUMO energies and HLG value (difference between the energies of HOMO and LUMO energies) can be correlated with the electronic properties of the compounds. The HLG was calculated using the following equation:

$$\text{HLG} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$



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3 D- π -A design for RO16-based dye sensitizers

In this study, the structure modification of RO16 dye was based on the D- π -A concept. Three heterocyclic π -linkers, namely BDT1, BDT2, and BDT3, were attached to the RO16 at position X (Fig. 1) to enhance the electronic properties, optical absorption, and photovoltaic performances of RO16. These units were chosen because of their planar structure, extensible conjugation, and ability to form a D- π -A structure [32]. Here, the organic compounds derived from RO16 were used as donor fragments, BDT1, BDT2, and BDT3 as π -linkers and BMA as an acceptor group. In the D- π -A concept, a π -linker is attached to the dye molecule to increase the conjugation of the system. The conjugation length in a dye sensitizer is a key factor that dictates the electron flow within the sensitizer and directly affects the electronic properties of the sensitizer molecule [33]. However, conjugation is greatly affected by molecular geometry. In a planar molecule, the conjugation is maximum, and the deviation from the planar geometry reduces the π -conjugation due to the poor overlap between the orbitals involved in the π -bond formation. The effect of different BDT-based π -linkers and their conjugation length on the electronic properties of the sensitizer was studied.

4 Results and discussion

The DFT-optimized geometry of RO16 shown in Fig. 2a revealed that the three aromatic rings in the system were coplanar. The introduction of π -linkers results and an acceptor unit resulted in a non-planar geometry. The non-planar geometries of RO16-BDT1-BMA, RO16-BDT2-BMA, and RO16-BDT3-BMA is shown in Fig. 2. The non-planar geometry was mainly due to the bulky π -linkers and affected the extent of conjugation in the system.

The electrostatic potentials of RO16, RO16-BDT1-BMA, RO16-BDT2-BMA, and RO16-BDT3-BMA were visualized on their respective van der Waals surfaces and are shown in Fig. 3. The electrostatic surfaces are colored red (charge accretion regions) and blue (charge depletion regions). RO16 showed a charge accretion near the aromatic rings mainly due to the π -electron cloud of the aromatic benzene ring. The three sensitizer molecules exhibited more charge-accreted zones, with the aromatic hydrogens residing in charge-depleted zones. Among all the four molecules, RO16-BDT2-BMA showed maximum accretion of charges, indicating a suitable environment for the electron flow within the sensitizer.

Figure 4 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of RO16, RO16-BDT1-BMA, RO16-BDT2-BMA, and

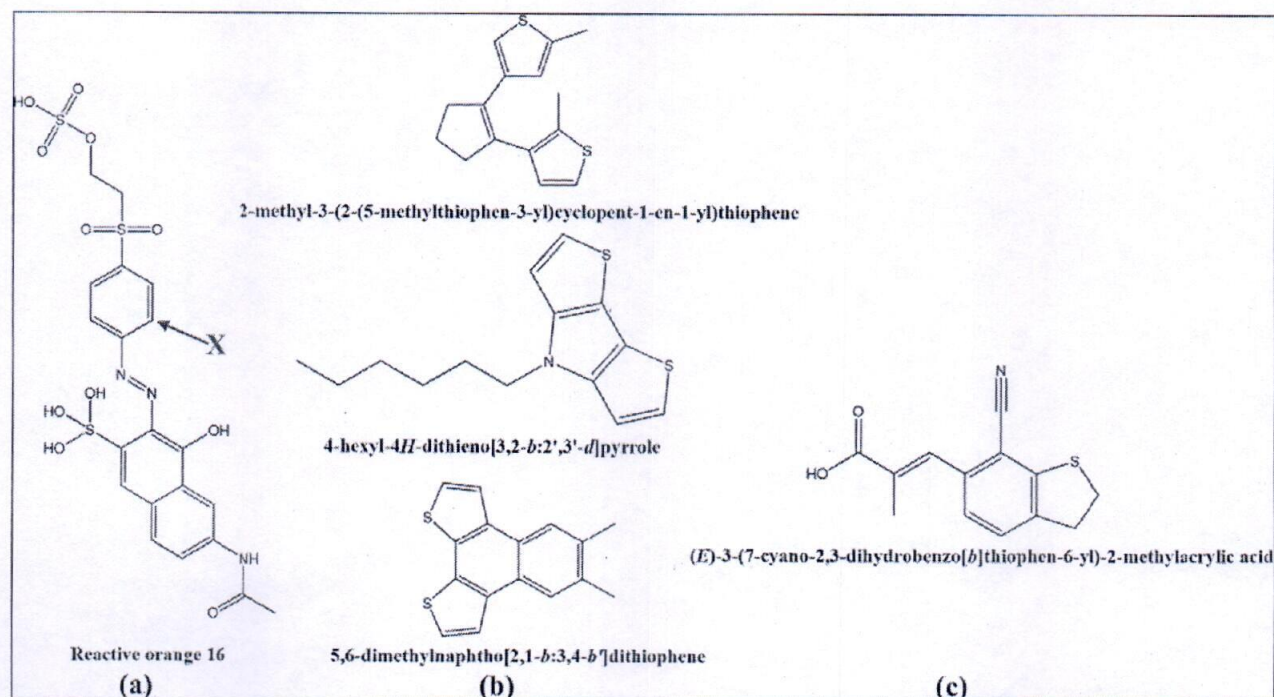


Fig. 1 D- π -A design for RO16 modified dye sensitizers. a RO 16 dye, b π -linkers, c acceptor

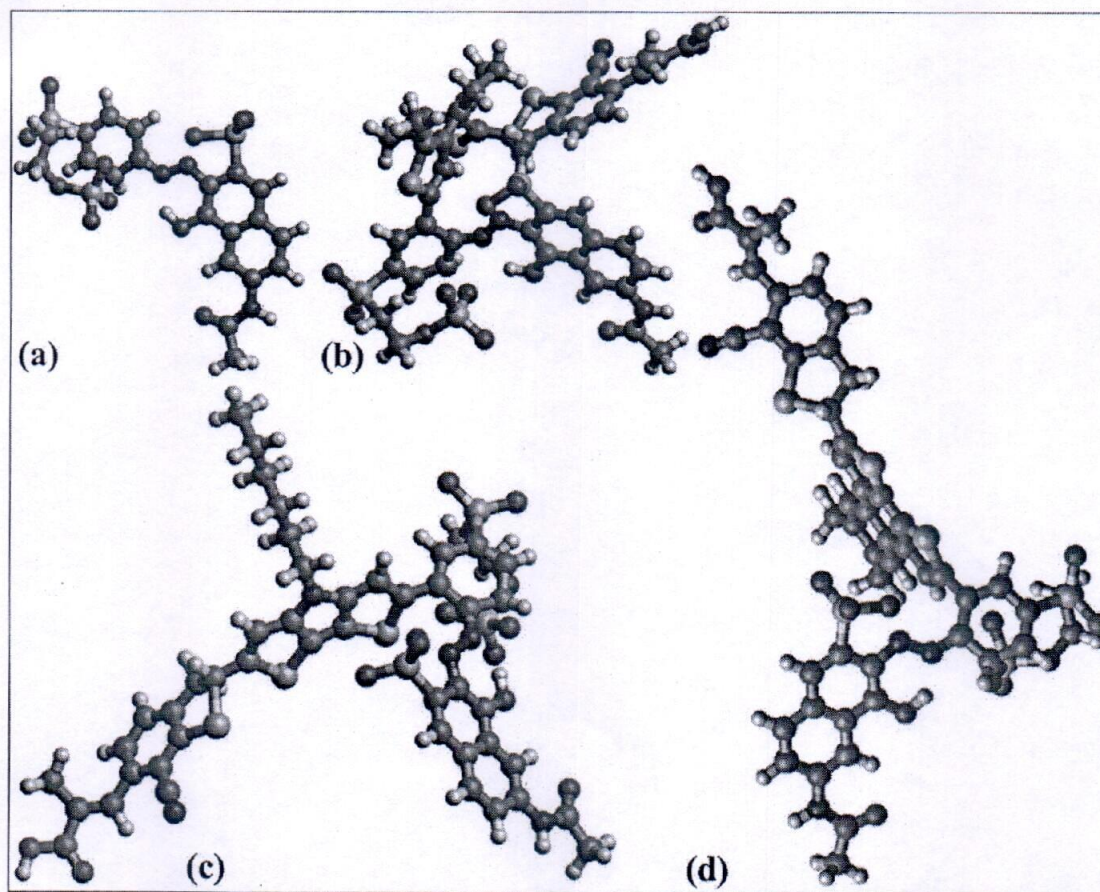


Fig. 2 DFT-optimized geometries of **a** RO 16, **b** RO 16-BDT1-BMA, **c** RO 16-BDT2-BMA, and **d** RO 16-BDT3-BMA dye sensitizers (red—O, yellow—S, green—Cl, blue—N, gray—C, white—H) (Color figure online)

RO16-BDT3-BMA. The HOMO of RO16 (Fig. 4a) was distributed throughout the molecule, with a large part on the aromatic rings. The LUMO resided on the S atoms of the $-\text{SO}_3\text{H}$ group with some contributions from the aromatic ring to which the $-\text{SO}_3\text{H}$ groups were attached. The HOMOs of RO16-BDT1-BMA, RO16-BDT2-BMA, and RO16-BDT3-BMA (Fig. 4b–d) showed a shift in the distribution toward π -linker. This indicated that although the non-planarity existed in RO16-BDT1-BMA, RO16-BDT2-BMA, and RO16-BDT3-BMA, the resonance effect remained active. The active resonance effect confirmed the possibility of electron displacement upon excitation within the molecules. The LUMO distributions of these three molecules were similar to RO16.

By comparing each system's HOMO and LUMO energies, the impact of conjugation was better understood (Table 1). A molecule with a lower HLG value requires less energy to excite an electron from the HOMO to the LUMO. The HOMOs of RO16-BDT1-BMA, RO16-BDT2-BMA, and RO16-BDT3-BMA had higher energies with the addition of a-linker, or when the molecule's conjugation was enhanced,

while the LUMOs remained stable. The destabilization of HOMO and stabilization of LUMO were well in accordance with the frontier molecular orbital theory, and the extent of orbital perturbations was proportional to the length of conjugation in the system [34]. The degree of conjugation was comparable in RO16-BDT1-BMA and RO16-BDT2-BMA, which similarly reduced the HLG value. The lowest HLG value for RO16-BDT2-BMA was 2.18 eV due to the highest energy perturbation of orbitals. The YD2-o-C8 and its variants were used to compare the probe molecule's HLG values [35]. As a result, the designed probe molecules might function as a sensitizer more effectively.

The DOS plots of the proposed sensitizer molecules are shown in Fig. 5. In RO16, the major contribution was due to the energy levels with energy ranging between -7.0 and -9.0 eV. After attaching the π -linkers to RO16, new energy levels appeared, which led to a decrease in the HLG of sensitizers. In all the D- π -A-type sensitizers, the density of electronic states varied appreciably, and an increased density was observed. New energy levels appeared mainly due to increased conjugation length through the π -linkers. The



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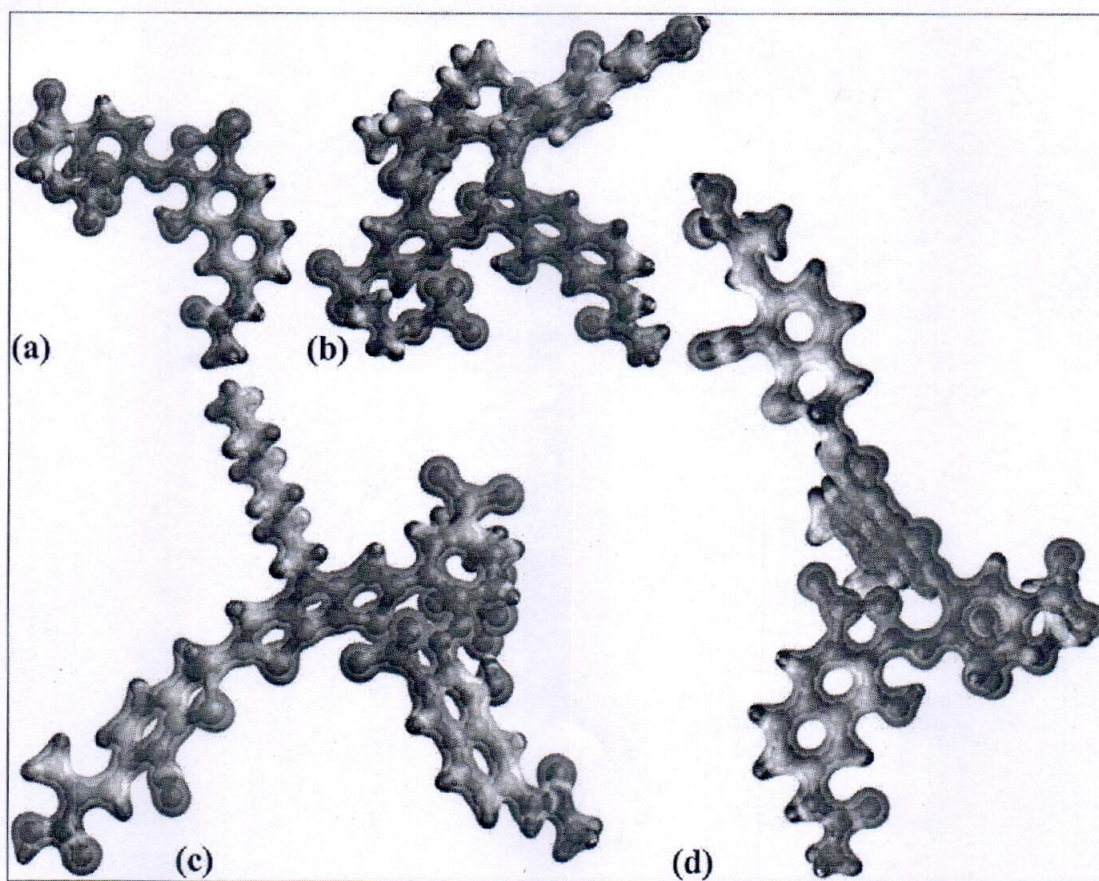


Fig. 3 Electrostatic potential maps for optimized geometries of **a** RO 16, **b** RO 16-BDT1-BMA, **c** RO 16-BDT2-BMA, and **d** RO 16-BDT3-BMA dye sensitizers (iso-value: 0.1)

DOS plots also confirmed the HLG values obtained from the HOMO–LUMO analysis.

TD-DFT studies were performed to gain insights into the optical properties of the dye sensitizers obtained from RO16 and to find their electronic transitions. Figure 6 shows the UV–visible absorption spectra of RO16 and the sensitizers derived from it (RO16-BDT1-BMA, RO16-BDT2-BMA, and RO16-BDT3-BMA). RO16 showed a very intense peak at 497.04 nm, while a bathochromic shift was observed in D– π –A-type sensitizers. The extended conjugation in the D– π –A system caused the shift in the maximum absorption. Effective photosensitizers typically have strong, broad absorption peaks in the visible region (400–750 nm). To photoexcite the dye, electrons must move from the HOMO to the LUMO, a process known as an intramolecular charge transfer transition. The HOMO and LUMO energy levels, particularly, are well separated in organic dye sensitizers. Electrons are injected into the oxide semiconductor's

conduction band because sunlight excites the dye. Small energy gap dyes are preferred since this transfer occurs from the dye sensitizer's excited states. They have maximum absorption red-shifted and exhibit relatively high light-harvesting efficiency. The transitions in all the sensitizers were mainly $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. These transitions arose due to the conjugated π bonds and the transitions between the non-bonded electron on the hetero atoms in the π -linkers and the adjacent π bonds. Table 2 summarizes the transitions taking place in the sensitizer molecules.

5 Conclusions

The structural, electronic, and optical properties of RO16 dye and the sensitizers based on donor– π –acceptor system derived from RO16, namely RO16-BDT1-BMA,

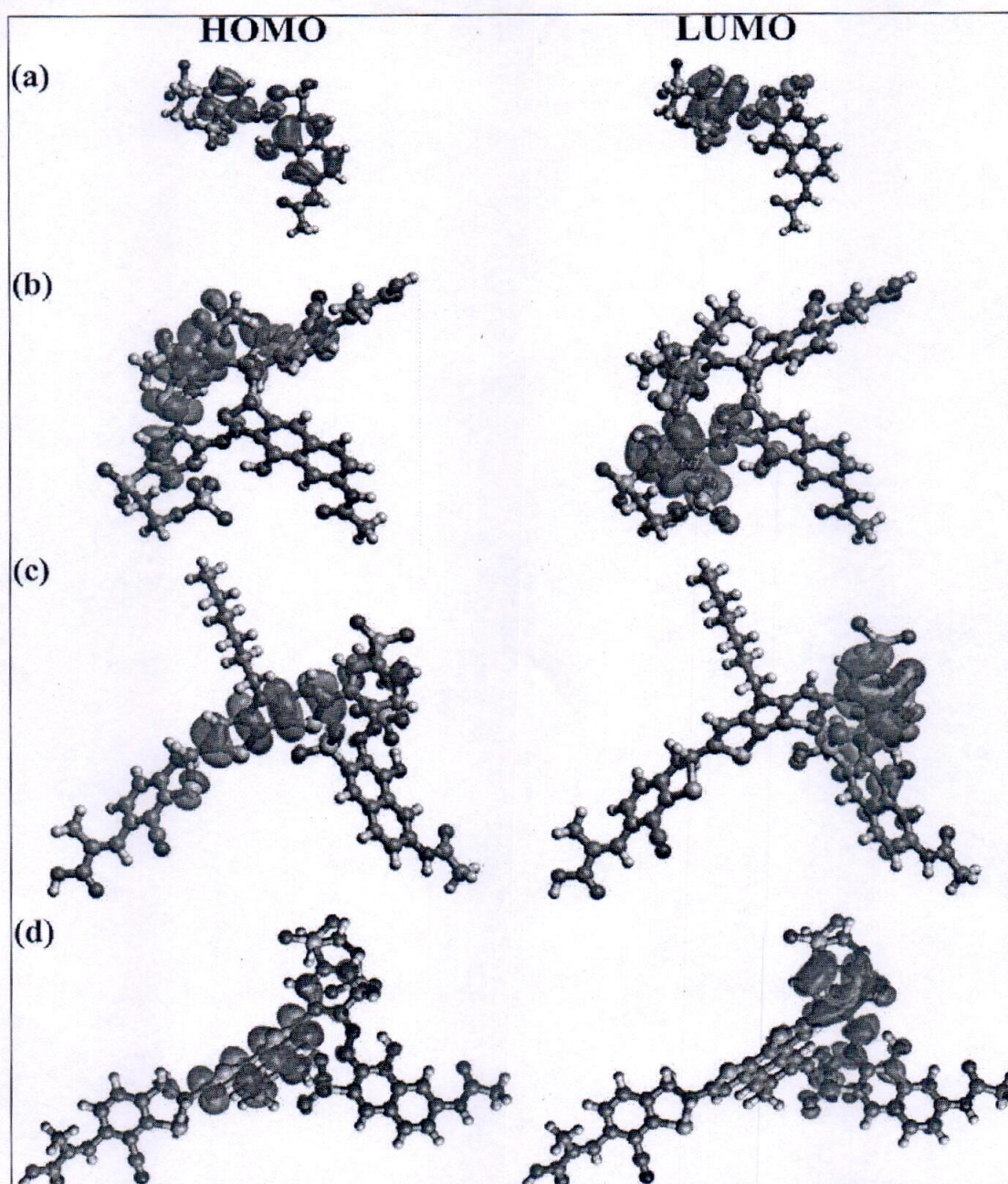


Fig. 4 HOMO–LUMO distributions for optimized geometries of a RO 16, b RO 16–BDT1–BMA, c RO 16–BDT2–BMA, and d RO 16–BDT3–BMA dye sensitizers

Table 1 HOMO–LUMO energy and HLG of sensitizers based on RO16 reactive dye

Properties	RO16	RO16–BDT1–BMA	RO16–BDT2–BMA	RO16–BDT3–BMA
HOMO	–5.77	–5.74	–5.34	–5.56
LUMO	–3.1	–3.28	–3.16	–3.29
HLG	2.67	2.46	2.18	2.27

RO16–BDT2–BMA, and RO16–BDT3–BMA, were examined using DFT and TD-DFT calculations. A non-planar geometry was observed for the D– π –A-type sensitizers that affected the extent of conjugation. The molecular electrostatic potentials revealed that all the sensitizers exhibited charge accretion regions, which increased slightly in the D– π –A-type sensitizers. HOMO–LUMO distributions showed a shift in the molecular orbital distribution



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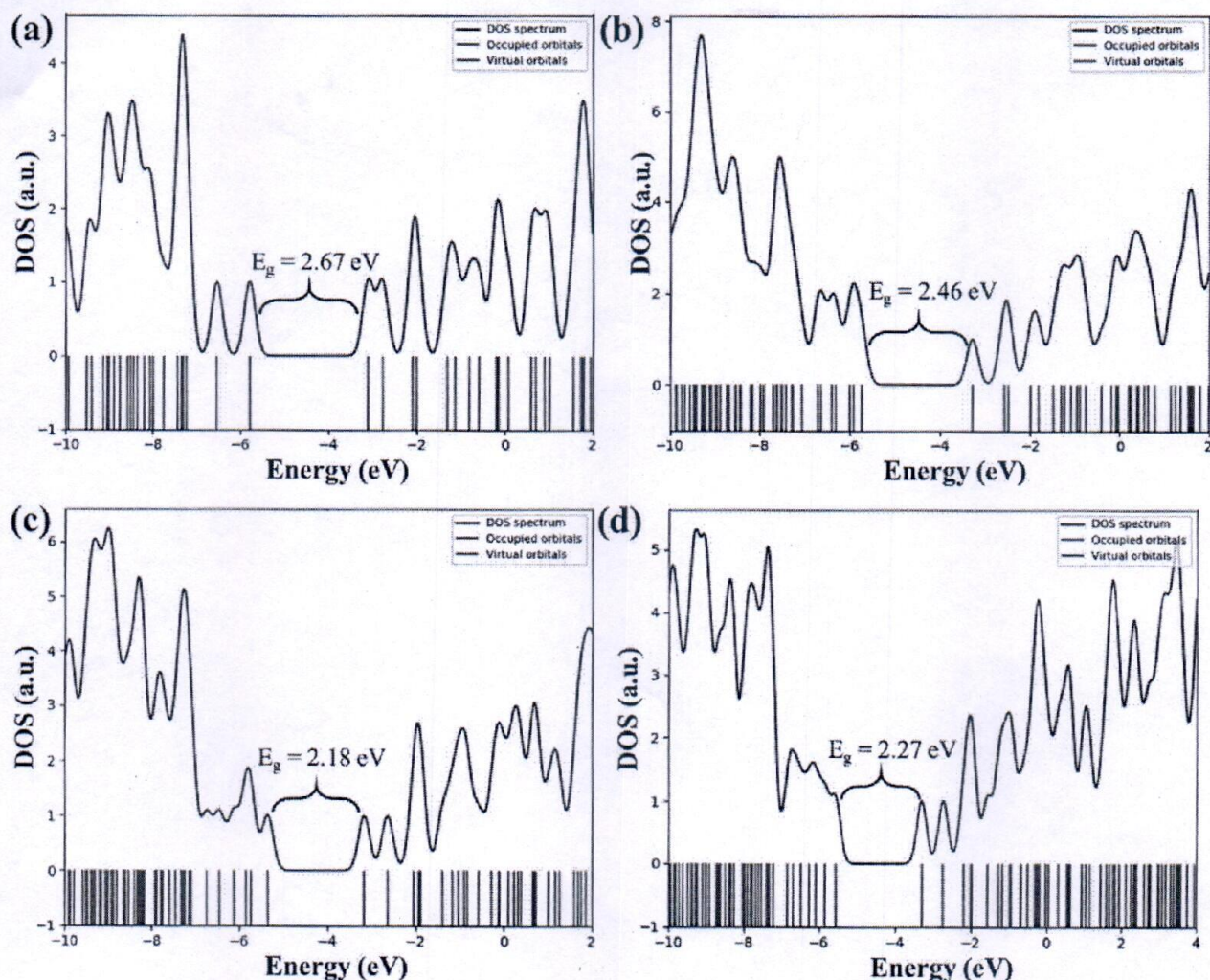


Fig. 5 DOS plots of a RO 16, b RO 16-BDT1-BMA, c RO 16-BDT2-BMA, and d RO 16-BDT3-BMA dye sensitizers

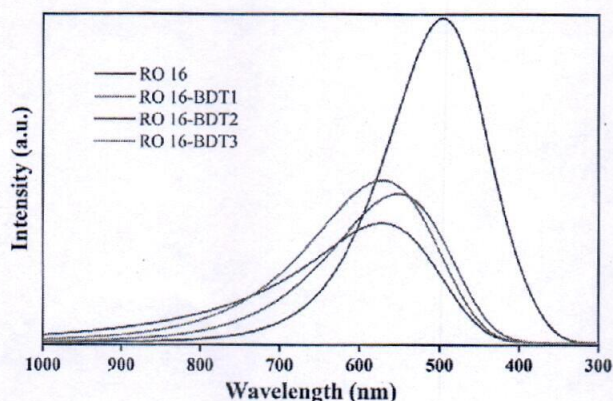


Fig. 6 The UV-visible spectra of dye sensitizers obtained from RO16

toward the π -linker than the RO16 dye molecule, where the molecular orbitals were spread over the molecule. The DOS plots confirmed new energy levels after the attachment of π -linkers, which arose due to the extended conjugation of the system. The results of TD-DFT calculations (transitions configurations) showed that for all dyes, HOMO \rightarrow LUMO transition is the main transition with large oscillator strength. In particular, RO16-BDT2-B was the most suitable sensitizer for the DSSC applications. The present study shows that reactive dyes are promising candidates for designing efficient sensitizers for DSSC applications. The present work could serve as a theoretical background in designing novel dyes and further improve the performance of DSSCs.

Table 2 TD-DFT parameters for dye sensitizers based on RO16

Adsorption							
Transition	λ (nm)	E (eV)	f	Transition	λ (nm)	E (eV)	f
RO16				RO16-BDT2-BMA			
H→L	497.04	2.49	0.4445	H→L	562.87	2.13	0.1158
H-1→L	415.53	2.98	0.0784	H-1→L	579.8	2.2	0.0305
H-2→L	564.22	2.19	0.0389	H-2→L	737.34	1.68	0.0279
RO16-BDT1-BMA				RO16-BDT3-BMA			
H→L	545.2	2.27	0.1417	H→L	569.45	2.17	0.1935
H-1→L	540.87	2.79	0.0262	H-1→L	536.06	2.31	0.0072
H-2→L	614.17	2.01	0.0307	H-2→L	691.36	1.79	0.0161

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Data availability The authors confirm that this article contains all the data supporting the findings of this study.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval Not applicable.

Consent for publication The authors gave their consent to publish the paper in this journal.

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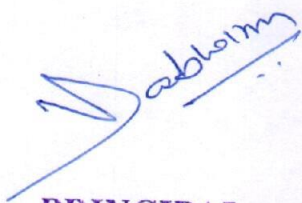


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