

DFT and TDDFT investigations of photovoltaic properties of triphenylamine based dyes: Impact of π -spacer tuning for DSSC with iodine and copper based redox shuttle

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ABSTRACT

A series of dyes with a donor- π -acceptor (D- π -A) framework based on triphenylamine (TPA) were theoretically designed to enhance the photovoltaic performance of dye-sensitized solar cells (DSSCs). Based on an experimentally reported TPA dye containing a benzo[c][1,2,5] thiadiazole(Dye1) π -spacer, five new dyes were modelled by including benzo[c]thiophene(Dye2), 4,4'-bibenzo[c]thiophene(Dye3), 2H-benzo[d][1,2,3]triazole (Dye4), 2H,2'-H-4,4'-bibenzo[d][1,2,3]triazole(Dye5), and 4-(benzo[c]thiophen-4-yl)-2H-benzo[d][1,2,3]triazole(Dye6) as π -spacers. Density Functional Theory and Time-Dependent Density Functional Theory were employed to study their electronic structures, charge transfer properties, and photovoltaic performance. All dyes showed negative Gibbs free energy for electron injection into TiO₂, signifying favourable charge transfer. The dye2 with benzo[c]thiophene spacer exhibited the highest open-circuit voltage, while those with dye5 and dye6 showed faster regeneration, particularly with copper-based redox shuttles. These candidates demonstrated high light-harvesting efficiency and ideal energy alignment, indicating their potential for high-efficiency DSSCs. These findings show that the π -spacer tuning is an effective strategy for optimizing dye performance in DSSCs.

1. Introduction

The growing concerns about global warming and the rising consumption of fossil fuels have sparked significant attention in developing energy conversion technologies and promoting zero-carbon emissions to achieve long-term sustainability [1]. The world energy landscape comprises both renewable and non-renewable sources, with solar fuel representing one of widely abundant sustainable energy resources [2,3]. Non-fossil fuel that is renewable resources currently contributes approximately 19 % of the world energy supply [3]. The share of electricity generation from renewable resources, like wind and solar energy, has been increasing exponentially on a global scale. Low-cost materials and cutting-edge solar technologies are encouraging solutions to the depletion of fossil fuels and control global warming [4]. Electrical energy represents an important component of the overall energy use and is implemented in different industrial facilities for electricity production, transportation, and heating [5]. Solar photovoltaics are an efficient process of converting solar energy to electrical energy. Nevertheless,

the expense of silicon-based solar cells and the reliance on less green chemistry have thwarted their ubiquity. As a result, research is being carried out on low-cost and sustainable alternative materials of the different solar technologies, third-generation solar cells have proven particularly interesting.

An alternative promising route to traditional Si-based solar cells is a DSSC [6] originally invented by O'Regan and Grätzel. This technology overcomes silicon-based photovoltaic systems limitations, such as energy-intensive manufacturing processes, limited effectiveness at dim lighting conditions, and substantial servicing requirements. These benefits have motivated research towards next-generation photovoltaic cells, and especially DSSCs [7,8]. DSSC device consists of the photo-electrode with the dye-adsorbed porous TiO₂, the counter electrode, and the electrolyte serving as the redox shuttle. Despite significant improvements, the efficiencies of these devices remain inferior to those of contending technologies. The sensitizer plays a pivotal role in DSSCs, making the modelling and synthesis of novel organic molecules with a focus of intensive research over past 15 years [9].

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Organic dyes have been extensively studied as alternatives to highly efficient transition-metal complex sensitizers due to their advantages, including high flexibility in molecular design, elevated molar extinction coefficients, cost-effective and straightforward synthetic methods, enhanced long-term chemical stability, and reduced ecological footprint [10,11]. The key factors to consider in modelling of dye include its effectiveness in light harvesting, electron injection, and dye regeneration, while preventing issues such as molecular stacking and charge recombination. Organic sensitizers with diverse dye architectures, such as donor-acceptor (D-A), D- π -A [12–14], D-A- π -A [15–17], D-D- π -A [18] and D- π - π -A [19], have been extensively explored for their ability to efficiently harvest solar light in DSSCs. These architectures play a key role in tuning light absorption properties and charge transfer dynamics of the dyes. Study focused on optimizing different key parameters, including light-harvesting efficiency, charge injection, and recombination rates, by systematically varying the positions and electronic properties of donor, acceptor and π -spacer moieties. The systematic studies on their positional and structural effects have guided to design of potential candidates for efficient DSSCs with much better absorption, making it an important practical direction for photovoltaic [20–22].

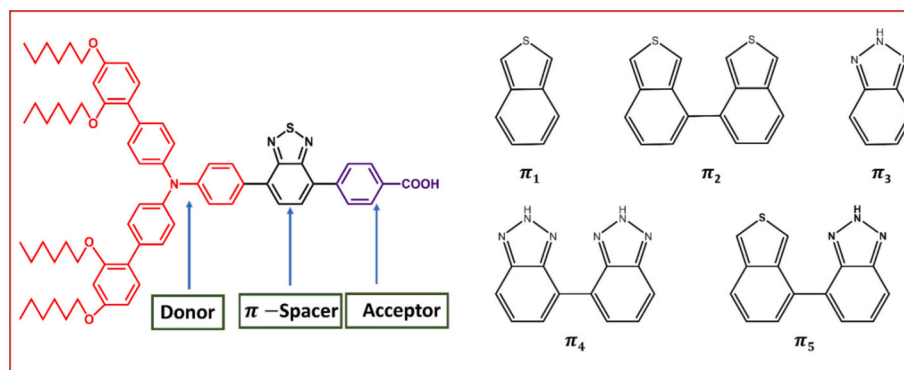
Based on previous studies on DSSCs, it is known that donor materials such as triphenylamine (TPA) significantly improve cell performance [23]. Also, triphenylamine, a well-studied organic unit with strong electron-donating character that enhances DSSCs light-harvesting ability and charge transport as well [24–33]. TPA plays a beneficial role in photovoltaic performance for D- π -A structures in which it is introduced as an electron donor as it promotes efficient electron injection into semiconductor and reduces recombination losses. TPA also contributes to long-term stability of dyes in DSSCs. The use of TPA-based dyes is being gradually explored since research shows that TPA-based dyes can provide favourable optical properties like broad absorption in the visible region, along with electronic properties suitable for energy conversion, making them a popular choice in efforts to enhance the DSSC efficiency.

This study aims to design and model new dyes to enhance the efficiency of DSSCs. Using the experimentally reported TPA-based donor dye (Dye1; (4-(7-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)benzoic acid)) [34], we modelled five Dyes with D- π -A architectures (Dye2, Dye3, Dye4, Dye5 and Dye6; see Scheme 1 and Scheme S1 of SI). The dyes were modelled by incorporating π -spacer groups into the parent dye (Dye1). Specifically, the π -spacer groups introduced to the reference dye (Dye1) for Dye2, Dye3, Dye4, Dye5, and Dye6 are benzo[c]thiophene, 4,4'-bibenzo[c]thiophene, 2H-benzo[d][1,2,3]triazole, 2H,2'H-4,4'-bibenzo[d][1,2,3]triazole and 4-(benzo[c]thiophen-4-yl)-2H-benzo[d][1,2,3]triazole, respectively. A comprehensive study was performed on the

electronic, chemical and optical properties of these π -spacers to appreciate their influence on the photovoltaic activity of the dyes. This study analyses the effect of the π -spacers modification on DSSC photovoltaic efficiency. These include a detailed study of electronic and chemical parameters such as energy gap, ionization potential and electron affinity. Then, optical and photovoltaic properties of the dyes, including excitation energy, absorption wavelength, dye regeneration, charge injection, oscillator strength, LHE, and V_{OC} were studied.

2. Computational detail

TPA donor-based dyes were modelled with GaussView 6.1 [35], and their geometries were optimized using Gaussian 16 software [36]. Calculations were performed using DFT and employing the hybrid B3LYP [37,38] functional with the 6-311G(d,p) [39] basis set. To ensure the reliability of our methodology, we benchmarked with different functionals (B3LYP, M06-2 $\times$ [40], wB97XD [41], and MPW1PW91 [42]) with the 6-311G(d,p) basis set (see Table S1). These were used to calculate the energy gap of the reference dye (dye1) and compared with its experimental value. Among the tested functionals, B3LYP predicted as the closest match to experiment, while the others showed larger deviations. Therefore, the B3LYP/6-311G(d,p) level of theory was chosen as the most suitable for describing both the ground-state geometries and the electronic properties of the modelled dyes. To study the donor-acceptor interactions in the molecular system, NBO analysis was performed. This method considers the interactions between the occupied orbitals (donor orbitals) of one subsystem and unoccupied orbitals (acceptor orbitals). These interactions are analysed in NBO to provide a good understanding of charge transfer, delocalization and orbital overlap stabilization [43]. Such analysis is important for understanding electronic structures and intramolecular interactions in the dyes, particularly in the cases of π - π^* conjugation and electron donor-acceptor dynamics in these systems. Using ORCA 4.2 [44] with the ZORA method to retain proper relativistic contribution to spectral properties, the electronic spectra were computed. This is particularly, the case in systems where relativistic corrections play an important role in the spectral behaviour, where this approach allows for accurate modelling of electronic transitions and energy levels. The excitation energies were calculated using TDDFT with B3LYP functional and the TZVP basis set [45,46]. The solvent environment was simulated with the polarizable continuum model [47], considering tetrahydrofuran (Dielectric constant (ϵ) = 7.25; refractive index = 1.407) as the solvent. Analysis of UV spectra and respective molecular orbitals was performed using the QMForge 3.2 software [48]. DOS was calculated using GaussSum [49] software. For enhanced clarity in the visual representation, hydrogen



Scheme 1. Chemdraw structure of TPA donor based **Dye 1** (4-(7-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)benzoic acid), and **Dye2** (4-(7-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)benzo[c]thiophen-4-yl)benzoic acid), **Dye3** (4-(7-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)-[4,4'-bibenzo[c]thiophen-7-yl)benzoic acid), **Dye4** (4-(7-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)-2H-benzo[d][1,2,3]triazol-4-yl)benzoic acid), **Dye5** (4-(7-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)-2H,2'H-[4,4'-bibenzo[d][1,2,3]triazol]-7-yl)benzoic acid) and **Dye6** (4-(7-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)benzo[c]thiophen-4-yl)-2H-benzo[d][1,2,3]triazol-4-yl)benzoic acid).

atoms were omitted from the structures. Details of theoretical calculation of photovoltaics parameters are in supporting information.

3. Results and discussion

3.1. Experimental section

The dye based on a triphenylamine donor (Dye1) was synthesized by

Dan Zhang et al. [34], integrating a bulky donor group, N-(2',4'-bis(dodecyloxy)-[1,1'-biphenyl]-4-yl)-2',4'-bis(dodecyloxy)-N-phenyl-[1,1'-biphenyl]-4-amine. This was characterized by electrochemical and UV-Vis absorption spectra, and the photovoltaic performance of DSSCs was evaluated using J-V and IPCE measurements under calibrated solar and indoor light sources [34]. The donor architecture, rich in long alkyl chains and extended aromatic systems, is designed to enhance solubility and reduce intermolecular aggregation. The resulting dye, Dye1 shows

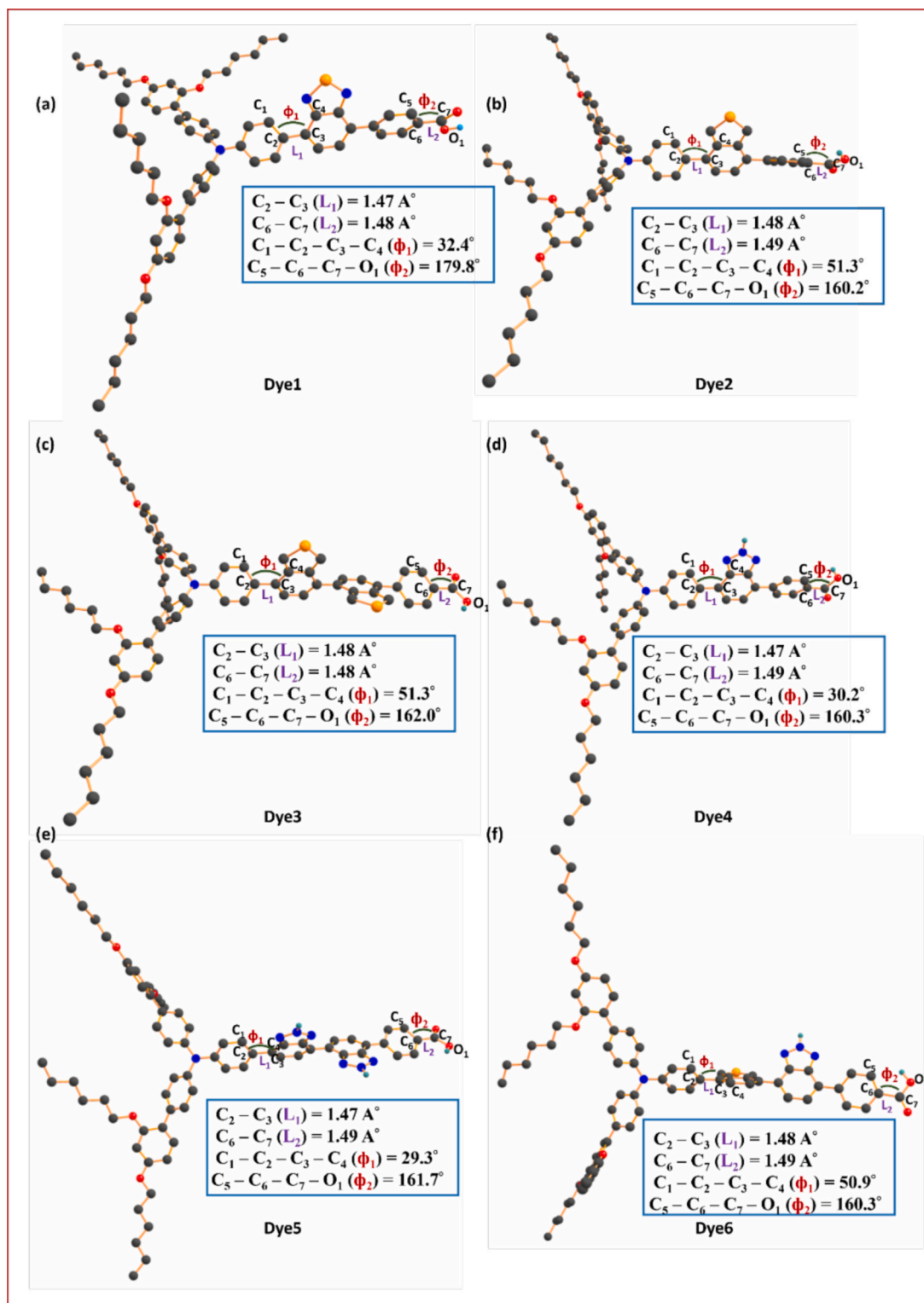


Fig. 1. Optimized structure of the dyes (a) Dye1, (b) Dye2, (c) Dye3, (d) Dye4, (e) Dye5 and (f) Dye6.

high open-circuit voltage (V_{OC}) in dye-sensitized solar cell applications. This alteration is attributed to the careful tailoring of the electron acceptor unit, which shows better intramolecular charge transfer and energy level alignment. Furthermore, Dye1 exhibits enhanced dye-loading capacity on TiO_2 photoanodes, which contributes to its higher light-harvesting efficiency and overall photovoltaic performance.

3.2. Structure of triphenylamine (TPA) based dyes

Optimized structure of the experimentally reported TPA dye (Dye1) (Fig. 1(a) and Table 1)) having D- π -A configuration. Triphenylamine serves as the donor unit, facilitating electron donation within dye molecule. This unit is strategically linked to a thiadiazol-4-yl group (C_2 - C_3) with a bond length of L1 (1.47 Å) and a dihedral angle Φ_1 (32.4°). The thiadiazol-4-yl group acts as a π -spacer, enhancing charge transport efficiency by expanding π -conjugation and reducing energy gap between these. Further, the π -spacer is linked to benzoic acid with L2 (1.48 Å) and Φ_2 (179.8°). Benzoic acid serves as the acceptor unit, playing a vital part in capturing electrons, thus finalising the electron transfer process started by donor and enabling effective dye participation in electron transfer reactions.

All the modelled dyes exhibit a D- π -A configuration. In Dye2 and Dye3, the donor is connected to benzo[c]thiophene and 4,4'-bibenzo[c]thiophene, respectively, both having L1 of 1.48 Å and Φ_1 of 51.3°. The π -spacer is linked to acceptor unit with L2 values of 1.49 Å and 1.48 Å, and dihedral angles Φ_2 of 160.2° and 162.0°, respectively (Fig. 1(b) and 1(c)). Dye4 and Dye5 feature 2H-benzo[d][1,2,3]triazole and 2H,2'H-4,4'-bibenzo[d][1,2,3]triazole as π -spacers units, with slightly varied L1 (1.47 Å) and Φ_1 values (30.2° and 29.3°, respectively) and are linked to acceptors with L2 of 1.49 Å and Φ_2 values of 160.3° and 161.7°, respectively (Fig. 1(d) and 1(e)). Dye6 incorporates a π -spacer, 4-(benzo[c]thiophen-4-yl)-2H-benzo[d][1,2,3]triazole, with L1 of 1.48 Å and Φ_1 of 50.9° and is connected to an acceptor unit with L2 of 1.49 Å and Φ_2 of 160.3° (Fig. 1(f) and Table 1)). Despite these alterations in π -spacers units, all dyes follow a similar structural trend with slight differences in dihedral angles and linker lengths.

3.3. Impact of dihedral angle on the performance of dye molecules in DSSCs

The performance of dye molecules in DSSCs is related to the dihedral angle of the dye molecule. It directly affects the extent of π -conjugation and the spatial arrangement of the molecular sections, such as donor, π -spacer, and acceptor units. A dihedral angle that closely follows the planarity of these units encourages faster electronic coupling and, consequently, greater charge transfer across the molecule. In contrast, high or twist dihedral angles may break π -conjugation that reduce the electron mobility and increase energy losses. Dihedral angle also influences orbital overlap, changing dye absorption properties and the dye's ability to harvest light [50,51]. The dihedral angle needs to be carefully screened to optimize the electronic characteristics as well as device performance on the whole for DSSCs, making it a significant factor in molecular design.

The computed results show that Dye1 is predicted as the highest dihedral angle (179.8°), signifying an almost planar structure (see

Table 1). This enhanced planarity leads to a better π -conjugation and improved charge delocalization, leading to more efficient electron injection into the semiconductor surface. In contrast, Dyes 2–6 display lower dihedral angles (160°–162°), suggesting small deviations from planarity. This non-planarity can introduce steric hindrance, reducing π -conjugation and potentially affecting light absorption and electron transfer efficiency. The reduced conjugation in these dyes may lead to lower electron injection rates and increased charge recombination, eventually impacting DSSC performance.

3.4. Frontier molecular orbital (FMO)

The distribution of FMOs within sensitizer plays an essential role in facilitating charge transfer. Here, the HOMO values are computed for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 (in eV) are −4.89, −4.89, −4.84, −4.88, −4.82 and −4.83, respectively (see Fig. S1 and S2). The LUMO values are computed for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 (in eV) are −2.60, −2.02, −2.10, −2.21, −2.29 and −2.29, respectively (See Fig. S1 and S2). The energy gaps for dyes Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 (in eV) are computed to be 2.29, 2.87, 2.74, 2.67, 2.53, and 2.54, respectively (see Fig. 2).

To enable effective charge migration from LUMO of dye to the CB of TiO_2 , energy levels of the oxidized species of the dye must match those of the reduced species of the TiO_2 . This arrangement allows electron transfer between the two components to percolate spontaneously. Moreover, the energy level LUMO of dye should be more than TiO_2 CB (−4.0 eV) [52] to initiate an efficient charge injection. To assure sufficient hole injection, HOMO level of dye must be lesser than the redox potential value of iodine-based redox shuttle (I^-/I_3^-) which is (−4.80 eV) [53].

The LUMO energies of all the modelled dyes are more than the CB of TiO_2 , and HOMO energies are lower than redox potential of redox mediator. These energy alignments show that all the dyes have enough driving force, which makes them ideal candidates to be used as dyes in DSSCs. In addition to the evidence for the effect of FMOs on the charge transfer mechanism, the DOS analysis is carried out to find out the role of the individual molecular segments of dye; donor, π -spacer and acceptor [23,41,54] (see Fig. 3). In the graph, the red regions correspond to the DOS, while green and black regions represent bonding and anti-bonding orbitals, respectively, with negative energy values. The charge dispersal within these orbitals, encompassing both donor and acceptor moieties, significantly influences the chemical properties of a molecule. A bonding orbital having a value of zero shows an absence of interaction with other bonding orbitals.

3.5. Global reactivity descriptors

FMOs are vital for understanding the dyes electronic properties and reactivity which includes; Ionization potential (IP), electron affinity (EA), electronegativity (χ), electrophilicity index (ω),

hardness (η), softness (s), and chemical potential (μ) [54,55] (See Table S2). The calculated values of η for the dyes; Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 (in eV) are 1.14, 1.43, 1.37, 1.33, 1.26, and 1.27, respectively, (see Table S2).

Among the studied dye, Dye 1 ($\eta = 1.145$) has the lowest η value, indicating it is the softest dye with potentially better electron injection ability, but may be less stable and more prone to charge recombination. Dye 2 ($\eta = 1.435$) shows the highest chemical hardness among the six dyes. This suggests that about the most electronically stable, but may also be slightly less efficient in terms of electron injection compared to softer dyes. Dyes 3 (1.37), 4 (1.335), 5 (1.265), and 6 (1.27) have intermediate values, indicating a favourable balance between electron injection efficiency and dye stability.

The ω measures the energy of stabilization of a system when it accepts electrons from an outside source. As by Domingo et al. [56],

Table 1
Computed bond length (L) and dihedral angle (Φ) for dyes.

Dyes	C_2 - C_3 (L_1)	C_1 - C_2 - C_3 - C_4 (Φ_1)	C_6 - C_7 (L_2)	C_5 - C_6 - C_7 - C_8 (Φ_2)
Dye1	1.47 Å	32.4°	1.48 Å	179.8°
Dye2	1.48 Å	51.3°	1.49 Å	160.2°
Dye3	1.48 Å	51.3°	1.48 Å	30.2°
Dye4	1.47 Å	30.2°	1.49 Å	160.3°
Dye5	1.47 Å	29.3°	1.49 Å	161.7°
Dye6	1.48 Å	50.9°	1.49 Å	160.3°

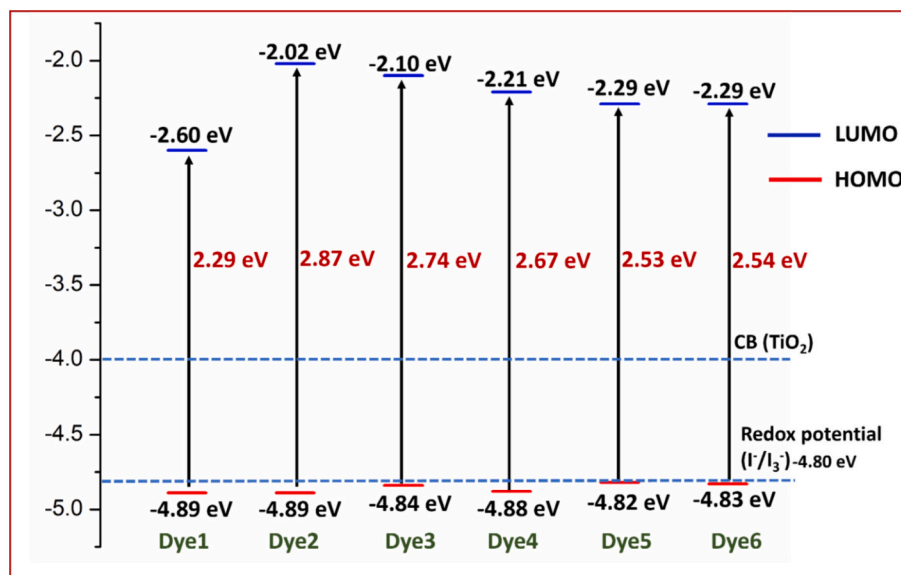


Fig. 2. Computed energy gaps of dyes (Dye1-Dye6) with comparison to the semiconductor conduction band and redox shuttle energy level.

organic systems can be divided into three classes according to their electrophilicity index (ω): strong electrophiles with $\omega > 1.5$ eV; moderate electrophiles with ω from 0.8 to 1.5 eV; and weak electrophiles with $\omega < 0.8$ eV. The value of electrophilicity index for the dyes follows the order of Dye1 (6.12 eV) > Dye4 (4.70 eV) > Dye5 (4.99 eV) > Dye6 (4.98 eV) > Dye3 (4.39 eV) > Dye2 (4.15 eV). These indicate the good electron-accepting ability of these dyes, making them highly active electrophiles. The electronegativity value of Dye1 is found to be the lowest value (-3.74 eV) suggests its higher stability (see Table S2) and the value increases from Dye1 to Dye6. Softness (S) value of Dye1 - computed as the highest (0.43 eV), reflecting its highest capacity to respond to variations in electron density (see Table S2). These softness variations highlight the dyes with different electronic characteristics with Dye1 potentially offering superior reactivity in applications due to its enhanced softness.

3.6. Molecular electrostatic potential (MEP) maps

The MEP maps provide a 3D visualization of electrostatic potential energy around a molecule in space [57–65]. Fig. S3 illustrates the MEP surfaces of the dyes. The electronegative potential.

values for the dyes are computed as (a) Dye1: -5.163×10^{-2} , (b) Dye2: -6.170×10^{-2} , (c) Dye3: -6.374×10^{-2} , (d) Dye4: -6.757×10^{-2} , (e) Dye5: -6.755×10^{-2} , and (f) Dye6: -6.959×10^{-2} (see Fig. 5). According to the MEP maps, Dye6 shows the highest electronegative potential among all dyes in the series. The red-coloured regions surrounding the oxygen atom in the benzoic acid units signify areas highly conducive to electrophilic attacks. This suggests that these regions exhibit a strong negative electrostatic potential, making them attractive to electrophiles. On the other hand, the green-coloured areas observed over donor and spacer segments of dye indicate neutral zones with relatively balanced electrostatic potential.

4. Natural bond orbital (NBO) analysis

NBO analysis is an important approach to study delocalization of electron density from donor to acceptor orbitals of the molecules [66–69]. This method provides valuable insights into characteristics of bonding and antibonding orbitals. Using second-order perturbation theory, it quantitatively evaluates interaction energy $E^{(2)}$, which represents an approximation of off-diagonal elements of the NBO Fock matrix. Eq. (1) demonstrates how this approach can be utilized to

calculate the stabilization energy $E^{(2)}$ corresponding to the delocalization from donor orbital (i) to acceptor orbital (j).

$$E^{(2a)} = \Delta E_{ij} = q_i \frac{F^2(i, j)}{\epsilon_j - \epsilon_i} \quad (1)$$

Table 2 summarises the intramolecular hyperconjugative interactions in the studied dyes, highlighting the weak, moderate, and strong $\pi \rightarrow \text{LP}^*$, $\sigma \rightarrow \sigma^*$, and $\pi \rightarrow \pi^*$ transitions. In Dye1, the $\pi(\text{C1-O8})$ to $\pi^*(\text{C2-C3})$ transition exhibits the highest $\pi \rightarrow \pi^*$ energy at 4.22 kcal/mol (see Fig. S4), while the $\sigma(\text{C59-O71})$ to $\sigma^*(\text{C58-C63})$ and $\sigma(\text{C33-O45})$ to $\sigma^*(\text{C32-C37})$ transitions show the lowest $\sigma \rightarrow \sigma^*$ energy at 1.60 kcal/mol. Table S3 shows the transition for Dye2. This transition from $\pi(\text{C75-O77})$ to $\pi^*(\text{C43-C44})$ (see Fig. S5) shows $\pi \rightarrow \pi^*$ transition computed at 1.31 kcal/mol. Conversely, transitions $\sigma(\text{C22-O33})$ to $\sigma^*(\text{C21-C26})$ shows the lowest $E^{(2)}$ value for $\sigma \rightarrow \sigma^*$ transitions, at 1.60 kcal/mol. Additionally, the $\sigma(\text{C75-O76})$ to $\sigma^*(\text{C42-C43})$ transition corresponds to the highest energy $\sigma \rightarrow \sigma^*$ interaction, with an $E^{(2a)}$ value of 4.18 kcal/mol. Table S4 shows the transition for Dye3 (see Fig. S6) where $\sigma(\text{C84-O86})$ to $\sigma^*(\text{C57-C84})$ shows the lowest $E^{(2)}$ value for $\sigma \rightarrow \sigma^*$ transitions, at 1.31 kcal/mol. Additionally, $\sigma(\text{C84-O85})$ to $\sigma^*(\text{C56-C57})$ transition corresponds to highest energy $\sigma \rightarrow \sigma^*$ interaction, with an $E^{(2a)}$ value of 4.18 kcal/mol. Table S5 presents the transition for Dye4 (see Fig. S7). This transition from $\pi(\text{C72-O73})$ to $\pi^*(\text{C42-C43})$ shows $\pi \rightarrow \pi^*$ transition energy, computed at 4.18 kcal/mol. Conversely, the transitions $\sigma(\text{C72-O74})$ to $\sigma^*(\text{C43-C44})$ shows the lowest $E^{(2)}$ value for $\sigma \rightarrow \sigma^*$ transitions, at 1.32 kcal/mol. Additionally, the $\sigma(\text{C37-C40})$ to $\sigma^*(\text{C36-C37})$ transition corresponds to the highest energy $\sigma \rightarrow \sigma^*$ interaction, with an $E^{(2a)}$ value of 3.95 kcal/mol. The transition for Dye5 is shown in Table S6. This transition from $\pi(\text{C78-O79})$ to $\pi^*(\text{C50-C51})$ (see Fig. S8) shows $\pi \rightarrow \pi^*$ transition computed at 4.19 kcal/mol. Conversely, the transitions $\sigma(\text{C78-O80})$ to $\sigma^*(\text{C51-C52})$ shows lowest $E^{(2)}$ value for $\sigma \rightarrow \sigma^*$ transitions, at 1.32 kcal/mol. Additionally, the $\sigma(\text{C6-C36})$ to $\sigma^*(\text{C36-C37})$ transition corresponds to the highest energy $\sigma \rightarrow \sigma^*$ interaction, with an $E^{(2a)}$ value of 3.89 kcal/mol. The transition for Dye6 is shown in Table S7. This transition from $\pi(\text{C78-O79})$ to $\pi^*(\text{C50-C51})$ (see Fig. S9) shows the $\pi \rightarrow \pi^*$ transition computed at 4.20 kcal/mol. Conversely, the transitions $\sigma(\text{C78-O80})$ to $\sigma^*(\text{C51-C52})$ show the lowest $E^{(2)}$ value for $\sigma \rightarrow \sigma^*$ transitions, at 1.31 kcal/mol. Additionally, the $\sigma(\text{C45-C48})$ to $\sigma^*(\text{C44-C45})$ transition corresponds to the highest energy $\sigma \rightarrow \sigma^*$ interaction, with an $E^{(2a)}$ value of 3.91 kcal/mol.

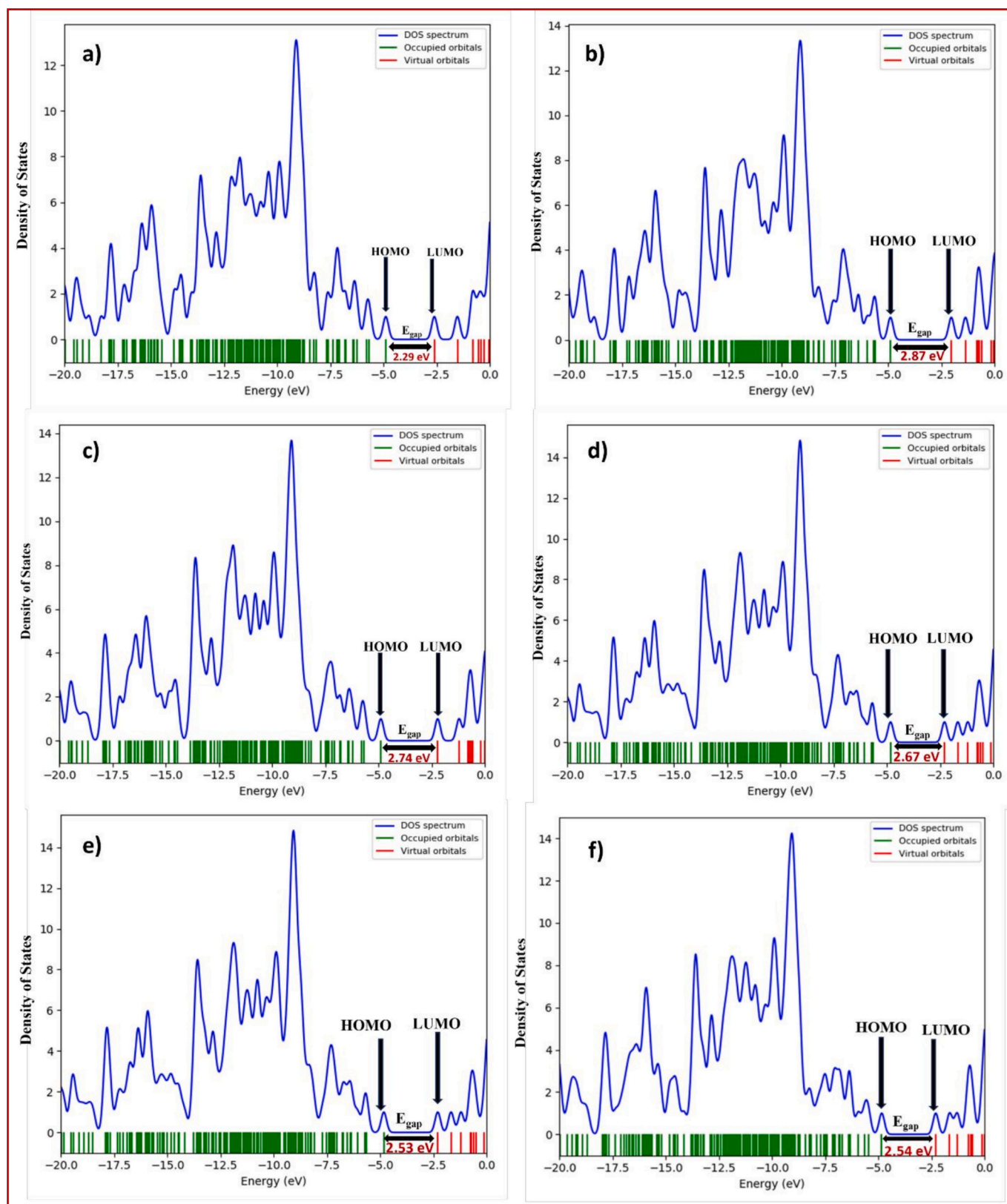


Fig. 3. DOS graph of dyes (a) Dye1, (b) Dye2, (c) Dye3, (d) Dye4, (e) Dye5 and (f) Dye6.

5. Non-linear optics (NLO)

NLO properties, including isotropic polarizability ($\langle\alpha\rangle$), anisotropy of polarizability ($\Delta\alpha$), and total hyperpolarizability (β_{tot}), play a vital role

in comprehending the electronic and optical behaviour of organic photovoltaic materials [70–73]. These properties offer valuable insights into how the materials interact with electric fields and contribute to their efficiency in photovoltaic applications.

Table 2

Significant donor-acceptor interactions and second order perturbation energies of TPA dye.

Donor NBO (i)	Acceptor NBO (j)	E ^(2a) kcal/ mol	E(j)-E(i) ^b (a. u.)	F (i,j) ^c (a. u.)
σ (C22-N25)	σ*(N25-C55)	2.35	1.19	0.047
π (N25-C29)	π*(C22-N25)	2.35	1.19	0.047
σ (C52-C55)	σ*(C22-C63)	3.66	1.21	0.060
σ (C18-C19)	σ*(C17-C18)	4.02	1.23	0.063
σ(C5-C15)	σ*(C15-C16)	4.03	1.24	0.063
π(C1-O8)	π*(C2-C3)	4.22	0.41	0.041
σ(O9-H82)	σ*(C1-C2)	3.90	1.17	0.061
σ(C1-O9)	σ*(C2-C7)	1.71	1.50	0.045
σ(C1-C2)	σ*(C6-C7)	2.60	1.26	0.061
σ (C59-O71)	σ*(C58-C63)	1.60	1.48	0.044
σ(C61-O64)	σ*(C59-C60)	1.61	1.47	0.044
σ(C26-C32)	σ*(C32-C37)	3.65	1.21	0.060
σ(C33-O45)	σ*(C32-C37)	1.60	1.48	0.044
σ(C35-O38)	σ*(C33-C34)	1.62	1.47	0.044

Dye molecules exhibit higher α , enhanced β , superior LHE, and a well aligned ground-state and excited-state oxidation potentials with redox potential and the CB of semiconductor hold substantial promise as candidates for DSSCs. The evaluation of the nonlinear optical properties of these dyes provides critical insights into their potential for improving energy conversion efficiency in photovoltaic applications (see Table 3).

The μ is a critical parameter that significantly influences the distribution of electronic charge within the framework of the modelled dye molecules. The computed dipole moment values for the dyes show that Dye5 exhibits the highest μ value (See Table 3), suggesting its enhanced charge separation capabilities and overall superior performance in comparison to the other dyes. This higher dipole moment shows that Dye5 has a higher charge transfer efficiency which is one of the key factors during the photoexcitation process [19].

Polarizability is naturally associated with a molecule's dipole moment showing how the electronic distribution within a system responds to an external electric field. The calculated polarizability (α) values for the dyes are as Dye1 (−460.64 a.u.), Dye2 (−478.56 a.u.), Dye3 (−555.63 a.u.), Dye4 (−471.79 a.u.), Dye5 (−540.59 a.u.), and Dye6 (−547.09 a.u.). Among these, Dye3 shows the highest polarizability (−555.63 a.u.), followed closely by Dye6 (−547.09 a.u.) and Dye5 (−540.59 a.u.), indicating that these dyes are more polarizable and could reveal superior optical properties. Dye1 shows the lowest polarizability (−460.64 a.u.) and, a comparatively lower ability to interact with the external fields. The higher polarizability of Dye3, Dye5, and Dye6 makes them promising candidates for DSSC because of improved NLO properties.

The computed β values for the dyes were found to be as Dye1 reveals

a β value of 1295.92 a.u., Dye2 shows an enhanced β value of 2995.44 a.u., Dye3 further increases to 4438.44 a.u., Dye4 achieves 3217.71 a.u., Dye5 slightly surpasses Dye3 with a β value of 4441.74 a.u., and Dye6 closely follows with 4357.08 a.u. Dye5 shows the highest hyperpolarizability, outdoing Dye3. This shows that Dye5 is possibly the most efficient candidate for NLO applications due to its higher β value. Dye5 performance suggests a more favourable D- π -A interaction or electronic configuration compared to the others. Consequently, Dye5 stands out as the best dye for applications requiring high NLO efficiency.

In NLO calculations, urea is frequently used as a benchmark due to its well-documented NLO properties [64–67]. All the compounds in our study showed responses that were substantially higher than those of urea. This notable enhancement underscores the superior NLO performance of modelled dyes, indicating their strong potential for application as efficient nonlinear optical materials in advanced photonic and optoelectronic technologies. This comparative analysis provides important insights into the promising attributes of modelled dyes, paving the way for their utilization in practical NLO devices.

6. Transition Density matrix (TDM)

Transition Density Matrix (TDM) analysis has been employed to gain an understanding of how the charge is distributed and how electronic coherence is maintained among the donor, π -bridge, and acceptor units in the excited state [74]. This approach allows for a detailed visualization of charge-transfer pathways and interaction strengths between molecular fragments. TDM analysis is conducted using the Multiwfn 3.8 software package [75]. TDM plots for Dye1 through Dye6 (see Fig. 4) visually represent the electron-hole coherence and charge reorganization behaviour in the excited states of the modelled dyes. In each plot, the x-axis resembles the positions of electron holes, while the y-axis shows the positions of excited electrons. The dye frameworks are segmented into distinct regions; donor, π -spacer, and acceptor labelled on axes. These partitions facilitate an understanding of charge transfer pathways between molecular fragments. Colour gradients ranging from blue to red signify the intensity of electron density transitions, with red signifying high transition probabilities. Prominent diagonal elements, particularly in all six dyes, show significant intra-fragment charge retention suggesting that electron-hole pairs are partially localized within the same moiety. However, the presence of off-diagonal features particularly in Dye2, Dye4, and Dye6 shows effective charge transfer between different regions, particularly from the donor to the acceptor through the π -spacer. The bright green and red areas adjacent to the diagonal in Dye1, Dye3, and Dye6, highlight extensive electron delocalization and a well-distributed transition density throughout the dye molecules. The TDM analysis confirms that the modelled dyes exhibit

Table 3

Computed total static dipole moment (μ), the mean polarizability (α), anisotropy of the polarizability ($\Delta\alpha$) and the first-order hyperpolarizability (β) for the studied ligands and their complexes. (μ in Debye; α , β and $\Delta\alpha$ are in atomic unit (a.u.)).

Property	Urea	Dye1	Dye2	Dye3	Dye4	Dye5	Dye6
μ	1.3197	9.5987	9.2420	12.8431	10.0226	14.0818	12.9585
α_{xx}	–	−477.611	−551.8787	−681.6146	−562.0748	−670.910	−672.9065
α_{yy}	–	−453.093	−433.5924	−478.8709	−419.7854	−453.317	−468.6408
α_{zz}	–	−451.219	−450.2127	−506.4226	−433.5375	−497.565	−499.7483
α	–	−460.641	−478.5612	−555.6360	−471.7992	−540.597	−547.0985
$\Delta\alpha$	–	25.50632	110.914062	190.468292	135.936072	199.189	190.625175
β_{xxx}	–	−750.131	−2242.1908	−4097.0444	−2710.4363	−4185.56	−4088.2912
β_{yyy}	–	344.5286	397.6130	105.4787	423.0254	71.0888	107.0068
β_{zzz}	–	10.6172	32.0785	31.9807	−31.1878	14.7146	6.8007
β_{xxy}	–	−311.823	−425.9525	−219.0110	−281.1508	−153.755	−186.7677
β_{xyx}	–	324.3338	739.4729	614.3235	709.0606	564.1494	522.1026
β_{xxz}	–	−211.070	−633.2394	−372.5191	−581.7931	−37.4189	−132.2527
β_{xzz}	–	−40.3378	−52.7573	−63.6522	30.4903	−68.3352	−46.8082
β_{yzz}	–	−60.4097	−67.6477	−63.7421	−147.2531	−85.9794	−83.2573
β_{yyz}	–	−106.397	−51.2859	44.5940	−171.6739	16.8414	37.8111
β	–	1295.924	2995.4403	4438.44979	3217.7124	4441.749	4357.0828

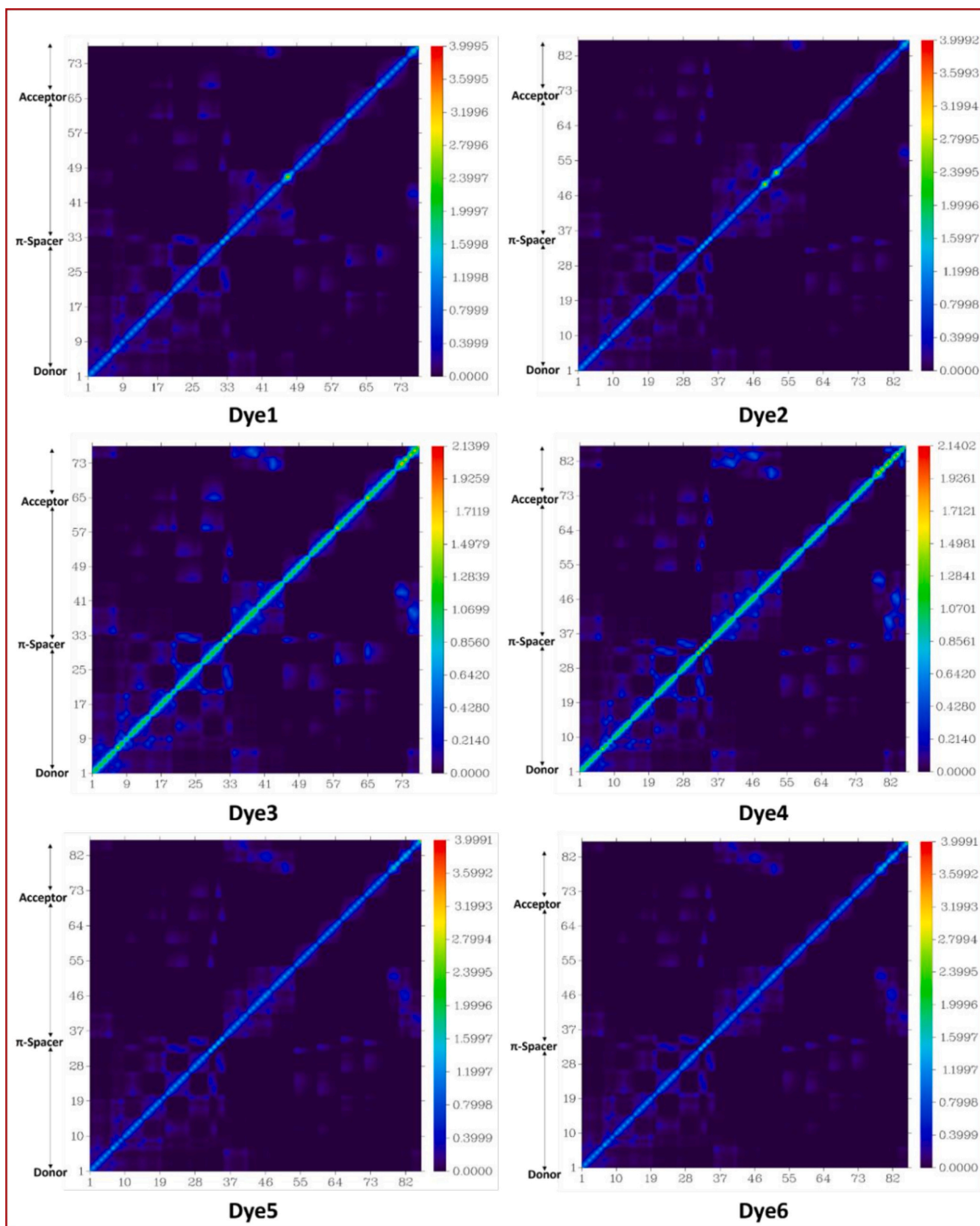


Fig. 4. TDM graphs for excited state of Dye1 to Dye6.

coherent and delocalized excited-state charge distributions. This behaviour is crucial for efficient light absorption and charge transport, making these dyes promising candidates for applications in DSSC.

7. Absorption spectra analysis for dyes

The absorption spectrum analysis of Dye1 (see Fig. 5 and Table S8) shows six prominent absorption peaks occurring at 287 nm, 353 nm, 405 nm, 471 nm, 549 nm, and 948 nm correspond very well with the experimental outcomes [34]. Each of these peaks corresponds to unique electronic transitions indicative of intramolecular charge transfer processes. At a peak of wavelength at 287 nm, a $\pi \rightarrow \pi^*$ electronic transition was observed, characterized by a 14.8 % contribution from HOMO(H)-1 (α) to LUMO(L) + 3(α) orbital excitation, with an oscillator strength (f) of 0.17 and a light-harvesting efficiency (LHE) of 33 %. At 353 nm, another $\pi \rightarrow \pi^*$ transition was detected, involving a 36.4 % contribution from H(α) to L + 2(α) orbitals. This transition exhibited f value of 0.48 and LHE of 67 %, indicating strong light absorption in this region. At a wavelength of 405 nm, the $\pi \rightarrow \pi^*$ transition was primarily attributed to a 45.1 % involvement from H-3(α) to L(α), with f value of 0.23 and LHE value of 42 %. For the transition at 471 nm, 41.5 % contribution from H-5(α) to L(α) was observed, showing f value of 0.06 and LHE of 13 %, indicative of relatively lower absorption efficiency. The peak at 549 nm corresponds to a $\pi \rightarrow \pi^*$ transition with 42.6 % involvement from H(α) to

L + 1(α). This transition has f value of 0.27 and LHE value of 47 %, highlighting significant light-harvesting potential. At 948 nm, the $\pi \rightarrow \pi^*$ transition involved a 49.3 % contribution from H(α) to L + 3(α), with f value of 0.21 and LHE value of 39 %, reflecting moderate absorption efficiency in the near-infrared region.

These observations suggest a strong correlation between higher oscillator strength and light-harvesting efficiency, emphasizing the role of enhanced π -conjugation in dye performance. Analysis of the HOMO-LUMO plots reveals that charge migration predominantly occurs from donor region of dye to acceptor region through the π -spacer. This effective charge transfer to the acceptor, which is connected to the semiconductor (TiO₂), ensures efficient charge injection into the semiconductor, a critical factor for dye-sensitized applications.

An absorption spectrum analysis of Dye2 (see Fig. S10 and Table S8) reveals five absorption peaks (in nm) at 283, 354, 427, 455, and 625, each corresponding to unique electronic transitions indicative of intramolecular charge transfer processes. At 283 nm, a $\pi \rightarrow \pi^*$ electronic transition was identified, characterized by a 40.4 % contribution from the H-2(α) to L + 2(α) excitation. This transition exhibited f value of 0.51 and LHE of 70 %. At 354 nm, another $\pi \rightarrow \pi^*$ transition was observed, involving a 40.4 % share from H(α) to L + 2(α) orbitals. This transition demonstrated f value of 0.54 and LHE of 72 %, indicating strong absorption in this region. The transition at 427 nm was attributed to a 29.6 % share from H-1(α) to L(α), with f value of 0.19 and LHE of 36 %.

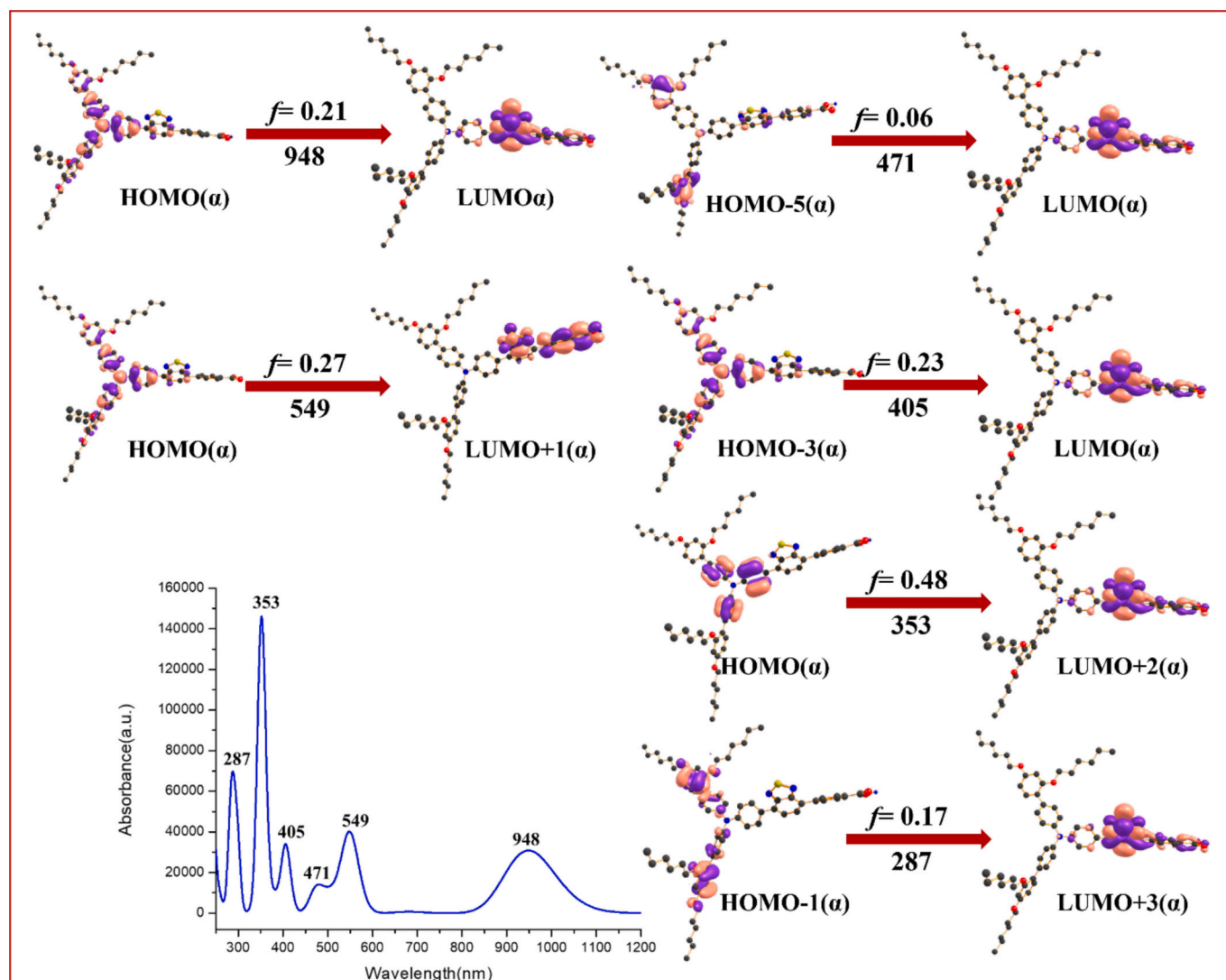


Fig. 5. TDDFT simulated electronic spectrum of Dye1.

Similarly, at 455 nm, a $\pi \rightarrow \pi^*$ transition involved a 32.8 % share from H(α) to L + 1(α), with f value of 0.17 and LHE of 33 %. Lastly, the peak at 625 nm corresponded to a $\pi \rightarrow \pi^*$ transition with a 48.9 % share from H(α) to L(α). This transition exhibited f value of 0.28 and LHE of 48 %, highlighting significant light-harvesting potential at longer wavelengths.

The absorption spectrum of Dye3 (see Fig. S11 and Table S8) reveals seven distinct absorption peaks at wavelengths of 271, 283, 356, 416, 482, 524, and 643 nm. Each peak corresponds to specific electronic transitions, highlighting intramolecular charge transfer processes. At 271 nm, a $\pi \rightarrow \pi^*$ electronic transition is observed with a 35.8 % share from the H-1(α) to L + 3(α) orbital excitation, f value of 0.005, and LHE of 2 %. The peak at 283 nm also involves a $\pi \rightarrow \pi^*$ transition, featuring a 30.6 % share from H-3(α) to L + 3(α), f value of 0.06, and LHE of 13 %, indicating efficient light absorption. At 356 nm, a prominent $\pi \rightarrow \pi^*$ transition is primarily attributed to a 42.6 % share from H(α) to L + 3(α), with f value of 0.61 and LHE of 76 %, demonstrating high light-harvesting capability. The transition at 416 nm involves a 32.1 % share from H-2(α) to L(α), f value of 0.19, and LHE of 36 %, reflecting moderate absorption efficiency. The peak at 482 nm corresponds to a $\pi \rightarrow \pi^*$ transition with a 40.3 % share from H-1(α) to L(α), f value of 0.14, and LHE of 28 %. At 524 nm, a $\pi \rightarrow \pi^*$ transition is characterized by a 46.8 % share from H(α) to L + 2(α), f value of 0.0001, and LHE of 1 %. Lastly, the transition at 643 nm involves a 47.0 % contribution from H(α) to L(α), with f value of 0.18 and LHE of 34 %. These findings show the diverse electronic transitions in Dye3, each contributing to its absorption spectrum and charge transfer dynamics.

The absorption spectrum analysis of Dye4 (see Fig. S12 and Table S8) reveals the four peaks at 281, 345, 430, and 668 nm the intramolecular charge transfer processes. At 281 nm, a $\pi \rightarrow \pi^*$ transition occurs, characterized by a 30.1 % contribution from H-2(α) to L + 2(α) orbital excitation, f value of 0.19, and a LHE of 35.5 %. The peak at 345 nm corresponds to another $\pi \rightarrow \pi^*$ transition with a 27.7 % share from H(α) to L + 3(α), f value of 0.57, and LHE of 73 %. At 430 nm, the $\pi \rightarrow \pi^*$ transition is primarily attributed to a 25.5 % share from H(α) to L + 1(α), with f value of 0.35 and LHE of 55.3 %. Lastly, the transition at 668 nm involves a significant 49.2 % share from H(α) to L(α), exhibiting f value of 0.49 and LHE of 67.6 %.

The absorption spectrum analysis of Dye5 (see Fig. S13 and Table S8) reveals five distinct absorption peaks at wavelengths of 287, 357, 429, 523, and 738 nm. At 287 nm, the spectrum exhibits a $\pi \rightarrow \pi^*$ electronic transition, primarily involving a 16.6 % contribution from the H-5(α) to L + 1(α) orbital excitation. This transition is characterized by f value of 0.10 and LHE of 11 %. The peak at 357 nm also corresponds to a $\pi \rightarrow \pi^*$ transition with a significant 44.1 % share from H(α) to L + 3(α) orbitals, displaying f value of 0.55 and a much higher LHE of 72 %. The peak at 429 nm, arises from a $\pi \rightarrow \pi^*$ transition, primarily attributed to a 46.6 % share from H-4(α) to L(α). This transition exhibits f value of 0.01 and a relatively low LHE of 1 %. At 523 nm, the transition involves a 48.0 % share from H(α) to L + 1(α), with f value of 0.27 and an LHE of 47 %. Finally, the peak at 738 nm corresponds to a $\pi \rightarrow \pi^*$ transition, predominantly involving a 49.0 % share from H(α) to L(α). This transition is characterized by f value of 0.36 and LHE value of 57 %. These findings underscore the electronic transitions and charge transfer processes intrinsic to Dye5, highlighting its potential for light-harvesting applications.

The absorption spectrum analysis of Dye6 (see Fig. S14 and Table S8) reveals six distinct peaks at wavelengths of 272, 299, 357, 423, 518, and 735 nm. At 272 nm, a $\pi \rightarrow \pi^*$ electronic transition was identified, predominantly resulting from a 34.6 % contribution of H-3(α) to L + 5(α) orbital excitation. This transition demonstrated f value of 0.004 and LHE of 1 %. The 299 nm peak corresponds to another $\pi \rightarrow \pi^*$ transition with a 19.7 % share from H-2(α) to L + 4(α), exhibiting f value of 0.11 and LHE of 23 %. A notable $\pi \rightarrow \pi^*$ transition was observed at 357 nm, primarily attributed to a 27.7 % share from H-1(α) to L + 1(α). This transition exhibited a significant f value of 0.75 and a high LHE of 83 %. At 423

nm, a $\pi \rightarrow \pi^*$ transition involving a 42.7 % share from H-3(α) to L(α) was detected, with f value of 0.05 and LHE of 11 %. The transition at 518 nm corresponds to a 41.0 % share from H(α) to L + 1(α), characterized by f value of 0.30 and LHE of 5 %. Lastly, the 735 nm peak is associated with a $\pi \rightarrow \pi^*$ transition resulting from a 48.2 % share from H(α) to L(α), with f value of 0.20 and LHE of 37 %. These transitions collectively highlight the intricate charge-transfer processes and the efficiency of Dye6 in light absorption across a wide spectral range, making it a promising candidate for optoelectronic and photovoltaic applications.

These findings highlight a significant relationship between the oscillator strength and more the LHE where higher the oscillator strength then the LHE will be also more. The examination of HOMO-LUMO plots provides insights into the charge migration mechanism, which predominantly occurs from donor region of dye to the acceptor region via the π -spacer. This efficient charge transfer pathway ensures that the acceptor, which is directly linked to TiO₂, facilitates robust charge injection into the semiconductor material. Such efficient charge injection is a pivotal factor in achieving high performance in dye-sensitized applications, contributing to improved energy conversion efficiencies.

8. Photovoltaic parameters

The photovoltaic parameters for the investigated dye-sensitized solar cells (DSSCs), including excited-state oxidation potentials $E_{ox}^{dye^*}$, free energy changes for electron injection ΔG_{inj} , regeneration energy levels ΔG_{reg} for both iodine and copper-based electrolytes, light-harvesting efficiencies (LHE), open-circuit voltage V_{oc} , and short-circuit current density J_{sc} are summarised and analysed below and details of theoretical calculation of photovoltaics parameters are in supporting information.

8.1. Photovoltaic parameters with traditional iodine redox shuttle

Several parameters are analysed to evaluate the performance of DSSCs and efficacy of dyes in conjunction with a redox shuttle. This includes Gibbs free energy change for regeneration (ΔG_{reg}), which shows the ease of regeneration of dye upon electron injection, and Gibbs free energy change for injection (ΔG_{inj}), which reveals efficiency of the transfer of electron from dye to the semiconductor CB. Another important parameter is LHE, which is a measure of the capability of the dye to absorb sunlight efficiently and convert it into energy. The open-circuit voltage (V_{oc}), the maximum potential difference under zero current flow, and the short-circuit current density (J_{sc}) serve to index current. The dyes show negative ΔG_{inj} values, confirming their high efficiency for electron injection to the CB of TiO₂. The negative Gibbs free energy of injection indicates that the injection is thermodynamically spontaneous and the process of the electron transfer is smooth, this is the key to improve the performance of DSSC [21,23]. Such favourable energy parameters ensure effective interaction between excited dye molecules and the TiO₂ surface, facilitating the transfer of electrons with minimal energy loss. Computed ΔG_{inj} values (in eV) for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 are found as -2.61, -2.61, -2.64, -2.71, -2.65, and -2.64, respectively. Dye4 shows the most negative value (-2.71 eV), indicating the highest thermodynamic driving force for electron injection, followed by Dye5 and Dye6. Dye1 and Dye2, although all the dyes still indicate favourable electron injection capabilities. Overall, the progressively more negative ΔG_{inj} values correlate with a higher potential for enhancing DSSC efficiency.

LHE measure the capability of dye to capture and utilize light energy effectively. It reflects the proportion of absorbed photons that are converted into usable energy. Maximum LHE (at wavelength/ oscillator strength) for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye 6 are found to be 67 % (354 nm/0.48), 72 % (354 nm/0.54), 76 % (356 nm/0.61), 73 % (345 nm/0.57), 72 % (357 nm/0.55) and 83 % (357 nm/0.75). This

observation underscores the significant role of extended π -conjugation systems for enhancing the oscillator strength and LHE. The increase in π -conjugation length contributes to greater delocalization of electrons, which in turn enhances the absorption of light and the overall electronic transition probability. As a result, molecules with larger π -conjugation systems exhibit improved stability and efficiency. Among these modelled dyes, Dye6 stands out due to its high LHE, favourable wavelength, and strong oscillator strength.

V_{OC} refers to the maximum voltage under open-circuit conditions, where no external load is connected to the device (DSSC), and the current flow is zero. It represents the potential difference between the positive and negative terminals of the DSSC. This voltage arises due to the separation of photogenerated charge carriers within the active layer of the DSSC. The computed V_{OC} values for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 are as 1.40, 1.98, 1.90, 1.79, 1.71, and 1.71 eV, respectively.

Among these, Dye2 exhibits the highest V_{OC} (1.98 eV), suggesting better charge separation and potential for efficient energy conversion. Dye3 (1.90 eV) and Dye4 (1.79 eV) indicating good performance, while Dye5 and Dye6 (both 1.71 eV) show comparable, slightly lower efficiencies. Dye1 has the lowest V_{OC} (1.40 eV, closer to the experimental reported value of 1.17 eV [34], reflecting relatively lower photovoltaic efficiency compared to the others (see Table 4). The regeneration of a dye (ΔG_{reg}) means the renewal of a dye in DSSCs. This plays a significant role in defining the efficiency of the dye regeneration process, which is important for the working operation of DSSCs. The oxidized dye molecule can transfer an electron into the CB of the TiO_2 , and then the dye can be restored to its ground state by gaining the electron from the RS within the electrolyte, and then this can regenerate the dye. ΔG_{reg} confirms that the regeneration process is energetically favourable and the process continues. The computed ΔG_{reg} values for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 are as 0.9, 0.9, 0.4, 0.8, 0.2, and 0.3 eV, respectively. Dye5, with the smallest ΔG_{reg} of 0.2 eV, displays the most favourable regeneration, followed by Dye6 (0.3 eV) and Dye3 (0.4 eV). Dye4 (0.8 eV), Dye1 (0.9 eV) and Dye2 (0.9 eV) need more energy for regeneration, making them less efficient. Therefore, Dye5 and Dye6 are the most promising dyes for efficient dye regeneration in DSSCs.

J_{SC} represents an important parameter that measures the photocurrent generated per unit area when the circuit is closed, allowing the maximum current flow under zero external resistance. The computed J_{SC} values for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 are as 1.74, 1.87, 2.00, 1.97, 1.90 and 2.19 mA/cm², respectively. The value of J_{SC} for Dye6 is the maximum among the three and therefore, it is the most efficient dye for photocurrent generation. Dye3, Dye4 and Dye5 are the next best dyes, and Dye3 has slightly better performance than the other two. Dye1 has the lowest J_{SC} , showing that it generates the minimum photocurrent under the same conditions. The graphical representation of the photovoltaic parameters for all the dyes are shown in Fig. 6 and S15 to S19.

8.2. Photovoltaic parameters with copper redox shuttle

The photovoltaic performance of the modelled dyes remains constant for both iodine-based and copper-based redox shuttles, with similar ΔG_{inj} , LHE, V_{OC} , and J_{SC} values. The redox potential value for the copper

redox shuttle is -4.67 eV as shown in Fig. S20 [23]. However, a prominent difference lies in the regeneration energy (ΔG_{reg}) influences the dye regeneration process and overall DSSC efficiency. In the iodine-based redox shuttle, the ΔG_{reg} values range from 0.2 eV to 0.9 eV. The computed ΔG_{reg} values for Dye1, Dye2, Dye3, Dye4, Dye5 and Dye6 are as 0.22, 0.22, 0.17, 0.21, 0.15, and 0.16 eV, respectively. Among these, Dye5 and Dye6 shows the lowest ΔG_{reg} values, signifying a more favourable regeneration process. The use of a copper-based redox shuttle further enhances dye regeneration, attributed to the redox potential of the Cu(I)/Cu(II) couple being well-aligned with the HOMO levels of the dyes. This facilitates rapid electron transfer, especially for Dye5 and Dye6 (See Table 4). This improvement suggests that copper-based redox shuttles facilitate faster electron transfer to the oxidized dye, helping faster dye regeneration and confirming sustained photocurrent generation. The lower regeneration energy in the copper system reduces energy losses, making it a promising alternative to traditional iodine-based electrolytes for improved DSSC performance. The graphical representation of the photovoltaic parameters for all the dyes are shown in fig. S21 to S26.

9. Comparative analysis of dye performance for DSSCs

Based on a thorough analysis of the photovoltaic parameters, Dye6 predicted as the best candidate for effective DSSCs among the studied dyes. It has the highest J_{SC} of 2.19 mA/cm², which indicates more generation of photocurrent. Moreover, the thermodynamic injection driving force ($\Delta G_{inj} = -2.64$ eV) for Dye6 ensures efficient electron injection. The light-harvesting ability of Dye6 is revealed by the high maximum ϵ value (83 % at $\lambda = 357$ nm) (high oscillator strength (0.75)), indicating the strong capacity of light capture. Dye2 yields the highest V_{OC} of 1.98 eV, indicating ideal charge separation and high energy conversion potential; however, the photocurrent generation and light absorption capacity of Dye6 is much higher in comparison to Dye2, hence making it the best overall performer. Dye3 follows Dye6 with a decent performance characterized by $J_{SC} = 2.00$ mA/cm², $\Delta G_{inj} = -2.64$ eV, and $V_{OC} = 1.90$ eV making it a good competitor as well. Similarly, Dye4 ($J_{SC} = 1.97$ mA/cm², $\Delta G_{inj} = -2.71$ eV) also shows highly favourable electron injection however its V_{OC} (1.79 eV) is found as the lower than that of Dye3, thus falling after Dye3. Dye5 leads to a J_{SC} value of 1.90 mA/cm² and a ΔG_{inj} of -2.65 eV; however, it also ranks slightly lower than Dye4 due to its lower J_{SC} as well as its V_{OC} (1.71 eV). With the lowest J_{SC} of 1.74 mA/cm², ΔG_{inj} of -2.61 eV, and a V_{OC} of 1.40 eV, Dye1 is the least efficient in photocurrent generation, charge separation, and regeneration energetics, and thus the most sub-optimal choice for DSSC. In the iodine-based redox shuttle, Dye5 (0.2 eV) and Dye6 (0.3 eV) show the most favourable regeneration. Conversely, the copper-based redox shuttle shows a significant enhancement in dye regeneration, with ΔG_{reg} value for Dye5 (0.15 eV) and Dye6 (0.16 eV) showing the most efficient regeneration. Here, Dye6 is found as the best-performing dye overall, excelling in photocurrent generation, electron injection, and light absorption, followed by Dye3, Dye4, and Dye5, with Dye1.

Table 4

Key photovoltaic parameters affecting DSSC performance with Iodine/Copper based redox shuttle.

Dyes	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{ox}^{dye+} (eV)	ΔG_{inj} (eV)	ΔG_{reg} (eV) Iodine	ΔG_{reg} (eV) Copper	LHE (%)	V_{OC} (eV)	J_{SC} (mA/cm ²)
Dye1	-4.89	-2.60	1.39	-2.61	0.9	0.22	67	1.40	1.74
Dye2	-4.89	-2.02	1.39	-2.61	0.9	0.22	72	1.98	1.87
Dye3	-4.84	-2.10	1.36	-2.64	0.4	0.17	76	1.90	2.00
Dye4	-4.88	-2.21	1.29	-2.71	0.8	0.21	73	1.79	1.97
Dye5	-4.82	-2.29	1.35	-2.65	0.2	0.15	72	1.71	1.90
Dye6	-4.83	-2.29	1.36	-2.64	0.3	0.16	83	1.71	2.19

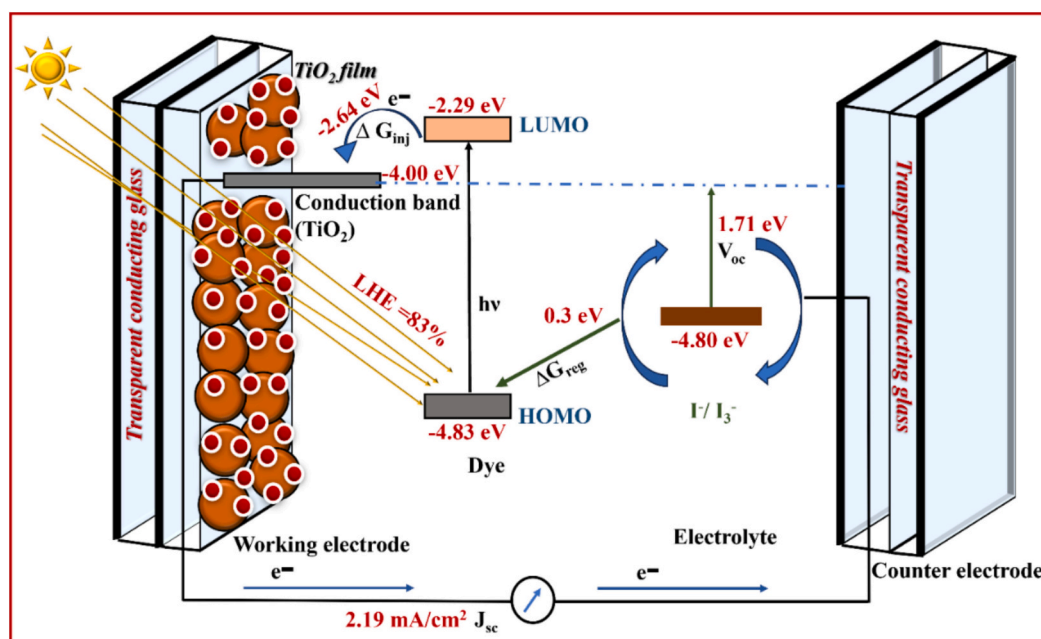


Fig. 6. Graphical illustration of the photovoltaic parameters of Dye 6, highlighting its superior performance among the studied dyes.

10. Effect of altering π -spacers on photovoltaic performance

The alteration of π -spacer groups in the parent dye significantly impacts their photovoltaic performance, as evidenced by the detailed analysis of their electronic and optical properties. The π -spacers introduced into the parent dye (Dye1) include benzo[c]thiophene for Dye2, 4,4'-bibenzo[c]thiophene for Dye3, 2H-benzo[d][1,2,3]triazole for Dye4, 2H,2'H-4,4'-bibenzo[d][1,2,3]triazole for Dye5, and 4-(benzo[c]thiophen-4-yl)-2H-benzo[d][1,2,3]triazole for Dye6.

These alterations affect the electronic energy levels, absorption characteristics, and overall photovoltaic parameters. Among the dyes, Dye6 stands out due to its superior photovoltaic performance, with the highest J_{sc} of 2.19 mA/cm² and maximum light-harvesting efficiency of 83 % at $\lambda = 357$ nm. Its relatively low thermodynamic injection $\Delta G_{inj} = -2.64$ eV ensures efficient electron injection into the semiconductor, while its high oscillator strength (0.75) shows its ability to effectively absorb light. In comparison, Dye2, while demonstrating the highest V_{oc} of 1.98 eV, has a lower J_{sc} and LHE, limiting its overall efficiency. The energy gap plays an important role in these, with Dye6 having the lowest energy gap of 2.11 eV, facilitating better light absorption and charge transfer. Conversely, Dye2 exhibits the highest energy gap of 2.87 eV, correlating with reduced LHE. Following Dye6, Dye3 and Dye4 exhibit promising photovoltaic characteristics, with Dye3 showing a J_{sc} of 2.00 mA/cm² and Dye4 achieving efficient electron injection ($\Delta G_{inj} = -2.71$ eV). Although Dye5 and Dye6 displays efficient regeneration with a ΔG_{reg} with both the iodine and copper redox shuttle. Altering the π -spacer groups significantly influences the dyes photovoltaic properties, with Dye6 (see Fig. 6) emerging as the most efficient candidate for DSSC applications. This study highlights the importance of π -spacer selection to optimize charge transfer, light absorption, and overall efficiency in DSSC. The graphical representation of the photovoltaic parameters for all the dyes with iodine and copper based redox shuttle are shown in fig. S15 to S25.

The relationship between the open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) for the series of dyes under investigation (Dye 1 to Dye 6). Dye 1 shows the lowest V_{oc} at 1.40 eV and the lowest J_{sc} of 1.74 mA/cm². Notably, a substantial increase in the open-circuit voltage from 1.40 eV (Dye 1) to 1.98 eV (Dye 2) correlated positively with an enhancement in J_{sc} from 1.74 mA/cm² to 1.87 mA/cm². However, beyond Dye 2, the relationship between V_{oc} and J_{sc} exhibited an

inverse trend. Specifically, despite a gradual decrease in V_{oc} from Dye 2 (1.98 eV) to Dye 6 (1.71 eV), J_{sc} values showed an overall upward trajectory, peaking at 2.19 mA/cm² for Dye 6. This inverse correlation suggests the addition of additional π -spacers extends conjugation length, improving electron delocalization and injection efficiency, thus enhancing current density despite a slight reduction in open-circuit voltage. Consequently, the data highlights (see Table 4) an optimal balance wherein moderate open-circuit voltage values favour higher current densities, potentially maximising the photovoltaic efficacy of these dyes.

11. Conclusion

This study focused on the modelling of dyes to enhance device efficiency, building on the experimentally reported TPA donor-based dye (Dye1) with a D- π -A arrangement. Five dyes (Dye2, Dye3, Dye4, Dye5, and Dye6) were modelled by incorporating diverse π -spacer groups into the parent dye structure (see Scheme 1). Using DFT and TDDFT methods, the study systematically evaluated how these π -spacers influence the electronic, optical, and photovoltaic properties of the dyes for their potential application in DSSCs. FMO analysis shows that all the dyes HOMO lies below the redox shuttle value (iodine) which is -4.8 eV and the LUMO value above the conduction band of the semiconductor (TiO₂) is -4.0 eV. This shows that all the modelled dyes are suitable for the DSSC application. The electronegative potential values for the dyes are computed as (a) Dye1: $-5.163e^{-2}$, (b) Dye2: $-6.170e^{-2}$, (c) Dye3: $-6.374e^{-2}$, (d) Dye4: $-6.757e^{-2}$, (e) Dye5: $-6.755e^{-2}$, and (f) Dye6: $-6.959e^{-2}$. According to the MEP maps, Dye6 shows the highest electronegative potential among all the dyes in the series. The NBO analysis reveals the variation in electronic behaviour across the dye molecules, with Dye1 exhibiting the most significant $\pi \rightarrow \pi^*$ interaction, while Dye2 displays weaker electronic coupling. Additionally, the higher-energy $\sigma \rightarrow \sigma^*$ transitions observed in all the dyes suggest their structural stability and potential for efficient electron transfer. NLO calculations reveal that all dyes in this study exhibit significantly higher responses compared to urea, underscoring the superior NLO performance of the modelled dyes.

This improvement shows their strong potential for application in DSSCs. TDDFT analysis shows that the FMO plots offer valuable insights into the charge migration that occurs from the donor region of the dye to the acceptor region through the π -spacer. This efficient charge transfer

pathway confirms that the acceptor, directly connected to the semiconductor (TiO_2), facilitates effective charge injection into the semiconductor (TiO_2). The photovoltaic parameters recognize Dye6 as the most promising candidate for DSSCs. Dye6 achieves the highest J_{SC} of 2.19 mA/cm^2 , indicating exceptional photocurrent generation. Its low thermodynamic injection driving force ($\Delta G_{\text{inj}} = -2.64 \text{ eV}$) further shows efficient electron injection. Additionally, Dye6 exhibits outstanding LHE with a maximum of 83 % at $\lambda = 357 \text{ nm}$, and a f value of 0.75, reflecting its ability to capture and utilize light. The higher photocurrent generation and light absorption capabilities found as the top-performing dye overall in Dye6 followed by Dye3, Dye4, Dye5, Dye2 and Dye1. Computed photovoltaics parameters show that Dye6, Dye3, and Dye4, as the best-performing among the modelled dyes, predict better photovoltaic and light-harvesting properties that make them highly suitable for DSSC. Their strong absorption capabilities, efficient charge transfer, and higher light-harvesting efficiencies enable them to function effectively under low-light conditions. This adaptability makes them ideal for situations where direct sunlight is not readily available, such as indoor, shaded outdoor areas, or urban environments, highlighting their potential for advanced PV systems and sustainable solar technologies.

CRedit authorship contribution statement

Sumit Sahil Malhotra: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Anitam Yadav:** Writing – original draft, Methodology, Data curation. **Mukhtar Ahmed:** Writing – original draft, Investigation, Data curation. **Abdullah Saad Alsubaie:** Writing – review & editing, Visualization, Conceptualization. **Manoj Kumar Gupta:** Writing – review & editing, Formal analysis, Conceptualization. **Azaj Ansari:** Writing – review & editing, Supervision, Software, Methodology, Conceptualization.

Declaration of competing 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemphys.2025.112913>.

Data availability

No data was used for the research described in the article.

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