



Structurally modulated D- π -D-A_(Semiconductor) anchoring dyes to enhance the tunable NLO response: a DFT/TDDFT quest for new photovoltaic materials

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Abstract

In this paper, we designed new dyes (**D-1** to **D-5**) with anchoring groups to test their stability for semiconductor surfaces with silyl unit as dye-sensitized solar cells (DSSCs). To investigate their photovoltaic efficiency, density functional theory (DFT) calculations were conducted with these novel D- π -D-A_(Semiconductor) type structures using *N,N*-dimethylaniline and benzenesulfonate as electron donor (**D**) and a thiophene as π -conjugated spacers, with different semiconductor units as anchoring and electron acceptor units. A new dye structure as a reference (**Ref-D**) had been extended from methyl orange (**MO**) molecular structure with electron acceptor semiconducting units to improve the electronic transmission and increased maximum absorbance (λ_{max}) to derive these new dyes (**D-1** to **D-5**). The computed λ_{max} of **MO** was obtained by testing DFT functional to benchmark it with its experimental λ_{max} . Out of these functionals, the Coulomb-attenuating Becke, 3-parameter, Lee–Yang–Parr (CAM-B3LYP) functional having hybrid and long range correlation with 6-31G + (d,p) produced a nearly similar λ_{max} (459 nm) as of its experimental one (464 nm). Their ionization potentials (I₁) ranged between 2.65 and 5.31 eV which showed their good electron-donating nature. Their λ_{max} values ranged between 532 and 565 nm which had a considerable red shift from **Ref-D** (465 nm). The highest second-order nonlinear optical (NLO) response of 134,532 Debye-Angstrom⁻¹ was noted for dye **D-2** which had the shortest bandgap. The charge tripping analysis of all the dyes miscible with the **Ref-D** showed an exclusive shift from highest occupied molecular orbital (HOMO) of reference to lowest unoccupied molecular orbital (LUMO) of dye. The density of states (DOS) calculations were performed with the dye **D-5** to show that electronic transmission was from the dye towards the semiconductor in an efficient way. The inclusion of thiophene as π -conjugated spacer resulted in a significant increase in absorbance peak at around 80 nm. The DFT computed results offered an insight upon design of novel DSSCs with silyl anchoring groups for improved stability and efficiency. The present research is in a kind of prediction to develop new NLO materials with D- π -A design involving semiconductor as anchoring groups to attach with a DSSC surface.

Keywords Semiconductor anchoring · NLO · TD-DFT · NIR · UV–vis

Introduction

The scientific pursuit for nonlinear optical (NLO) materials which are essential in present photonics [1], optical communication system [2], and quantum chemical measurements [3] is a major topic in materials research. The fast advancement of optical science and technology has necessitated the establishment of innovative NLO materials [4] with broader application capabilities [5]. The use of environmental friendly renewable energy sources is of recent attention, and the issue is to improve the technology to satisfy the required demand [6]. Photovoltaic sensitive chemical dyes are one of

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the most promising potential renewable sources for harvesting solar energies to meet our requirements [7]. Gratzel et al. were the first to develop photosensitizer solar cells (DSSCs) as an innovative source of energy to traditional inorganic silicon-based photovoltaic modules [8]. However, the manufactured materials with NLO applications in the ultraviolet visible (UV–vis) and near infrared regions (NIR) are a very few [9]. The difficulty stems from the specific wavelength requirements and expensive exploration techniques. Metal-containing dyes have greater potential due to very broad absorbance range from UV–vis to NIR [10]. According to a recent study, using a co-adsorbent, ruthenium (Ru) containing dye may be increased [11]. The increased power conversion efficiency (PCE) created by metal-based dyes is difficult to synthesize, and the supply of Ru is restricted [12]. Such dyes also get leached from the semiconductor surface to make them environmental unfriendly [13]. As a result, solar cell dyes without any metal are a basic requirement for the viable green photovoltaic devices [14]. A great number of metal free dyes for solar cells application are designed by fabricating various electron poor and electron rich systems with a basic design of D- π -A type dye to attach with an electrode surface [15].

A dye chromophore, which is anchored upon any electrode surface, absorbs the light energy as the initial step inside the DSSC [16]. The charge separation is achieved next [17], followed by photoinduced electron injection (EIE) and electron hole (HIE) analysis at the interface of the dye and semiconductors interface [18], and the content related electron is inserted into the conduction band [19]. The D- π -A framework offers fair opportunities for modulating and optimizing improved efficiency in the DSSC system [20]. Specific units on a dye can be tuned to influence the electromechanical and optoelectronic characteristics of dye molecules [21]. The D, π -spacer, and anchorage components have been modified to produce more efficient photovoltaic solar modulation [22]. A reduced HOMO–LUMO energy bandgap has been considered to enhance NLO performance by enhancing electronic transition efficiency and decreasing the dye workflow [23]. The anchoring groups with their ability to bond with the electrode surface is also critical for all real-world applications [24]. Increased binding in involving anchor with the titanium (Ti) contained on the layer of the semiconductor ensures pertinent stability of the DSSCs and improves the rate of electron flow from dye to a semiconductor wafer or anchoring unit [25]. Various anchoring groups have recently been investigated which have been attributed to the prevalence of the robust electron-withdrawing units to act as electron carrier for establishing a relation to semiconductor surfaces [26].

In order to adhere to metal oxide substrates, dyes in dye-sensitized solar cells (DSSCs) need one or more molecular substituents to serve as an attachment point. The mechanism

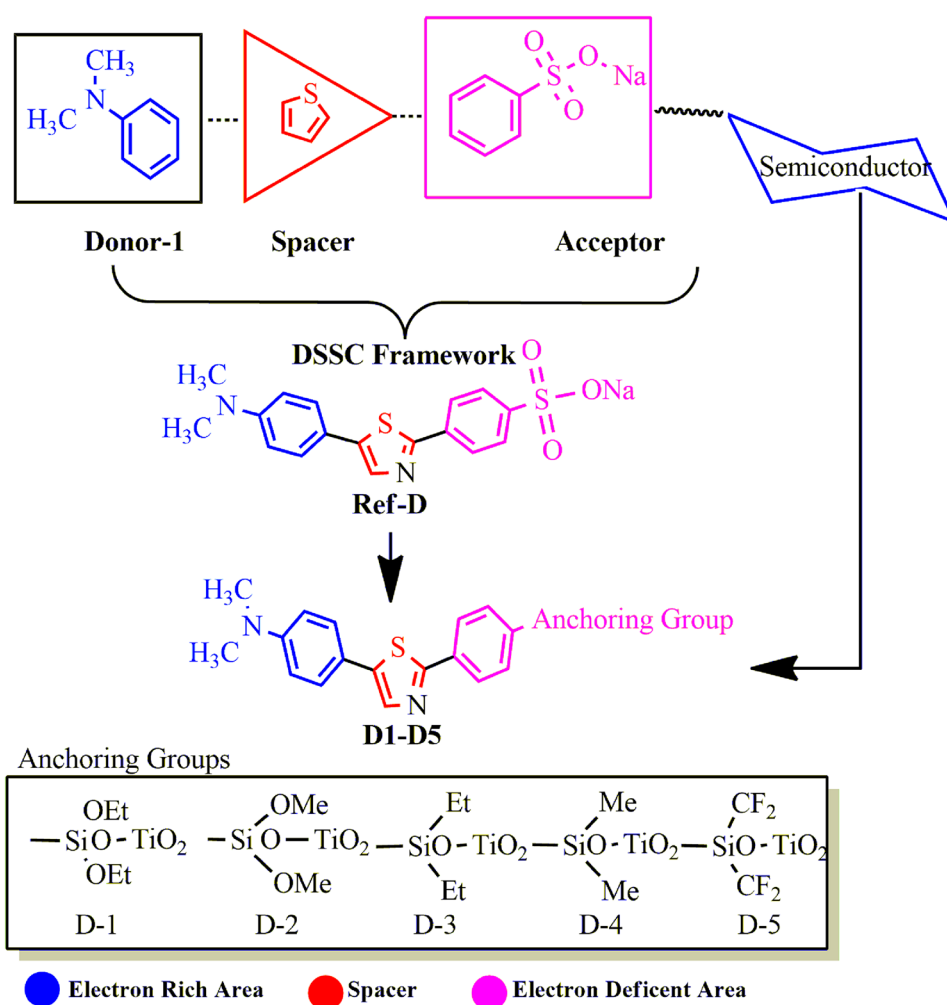
that starts the electrical device in a DSSC for electron injection is made possible by this adsorption. The exploration of new anchoring groups and an appreciation of the design of different DSSC anchors are essential steps in the creation of better DSSCs. Historically, dye anchoring groups in DSSCs have been carboxylic acid and/or cyanoacrylic acid moieties. A greater selection of materials is now accessible for DSSC dyes by the emergence of novel anchors recently. Additionally, the structural and chemical properties of these groups have fascinating implications at the interface of dyes and metal oxide surfaces. One of several key issues with DSSCs has been the destabilization of the cyanoacrylic acid component in moisture [27]. It has been observed that in the case of moisture in an electrolytic solution, a dye containing an anchoring may easily be released from its site [28]. The organosilicon-based compounds are reported to have a high binding affinity to anchoring surfaces by forming of Si–O–M type linkages [29]. There are various comparison investigations that employ ethoxysilyl groups as anchors, such as 4-(triethoxysilyl)azobenzene [30], (diethoxyphenylsilyl)azobenzene [31], and triethoxysilane [32]. This study focuses in particular on the structural features of such new dye anchoring units for silyl substituted DSSC surfaces. We have proved that the use of different anchoring groups as semiconductor material surfaced units in DSSCs to stabilize for semiconductor surfaces than dyes with some newly presented anchoring groups (Fig. 1).

Density functional theory (DFT)-based designs were adopted using straightforward electron donor (**D**) as *N,N*-diphenylamine and π -conjugated spacers with anchoring units to examine the effectiveness of DSSCs with anchoring units. We believe that additional research and comprehension of these novel forms of anchoring molecules for TiO₂ substrates can help us to create enhanced DSSCs as well as self-assembled monolayer-based innovations such as quantum dot-sensitized solar cells and water splitting devices.

Computational methodology

The present analysis was conducted using multiple long-range and range separated DFT driven functional with Gaussian 09 application [33]. To enhance the electronic conduction with improved maximum absorbance (max), a novel dye structure (**Ref-D**) was extended from molecular structure of methyl orange (**MO**) with electron acceptor semiconductor material units (**D-1 to D-5**). In order to select an appropriate basis set for DFT calculations, the experimental UV–vis spectra of **MO**, the starting material, was compared with several basis sets (B3LYP, CAM-B3LYP, B97-XD, and APFD) to get a benchmark result. Out of several range separated and long range basis sets, the Coulomb-attenuating Becke, 3-parameter, Lee–Yang–Parr (CAM-B3LYP) produced the

Fig. 1 Design of new D- π -D- $A_{(\text{Semiconductor})}$ type dyes (**D-1** to **D-5**) with new silyl anchoring groups



best closest value with the experimental values. The functional, which had long-range and hybrid correlation with 6-31G + (d,p), generated a λ_{max} (459 nm) that was very comparable to its experimental value (464 nm) (Fig. 2). The metrics for the dyes with a very D- π -D- $A_{(\text{Semiconductor})}$ designs

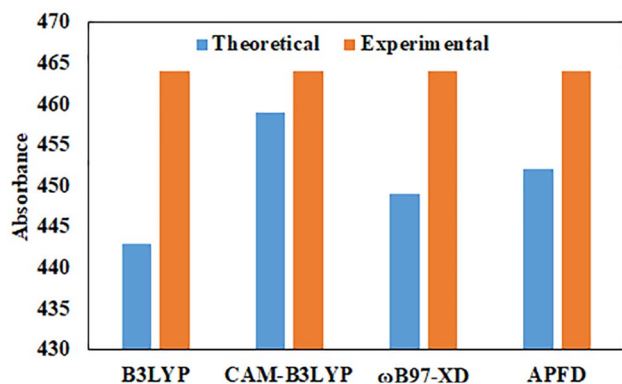


Fig. 2 Benchmarking of λ_{max} values of MO dye to select the most appropriate DFT functional

were studied with their frontier molecular orbitals (FMOs), natural bond orbital (NBO), density of state (DOS) studies, simulated UV–vis spectral analysis, and NLO properties in a gas and a solvent (chloroform).

An FMO investigation was used to figure out the energy bandgap, allowing the minimal energy required for the switch from HOMO to LUMO to be decided [34]. The hyperconjugative linkages and intramolecular charge carriers were found using NBO method [35]. The distribution of energy states was computed using the DOS computations. To study charge transfer, the UV–visible absorption spectra were obtained. The NLO and dipole moments of the dyes were calculated from the results of the dyes in solvent [36]. Results from extracted data using the Gaussview, Avogadro, and Chemcraft programs were used to derive the conclusions.

While researching the global reactivity parameters (GRPs), such as electron affinity (E_a), global electrophilicity index (ω), ionization potential (I1), global chemical potential (μ), electronegativity (χ), global hardness (η), and global softness (σ), the E_{LUMO} and E_{HOMO} have been used to depict reactivity

and stability [37]. The following formulas are used to decide various parameters utilizing Koopman's theory [38].

$$I1 = -E_{\text{HOMO}} \quad (1)$$

$$Ea = -E_{\text{LUMO}} \quad (2)$$

$$\chi = \left(\frac{IE + EA}{2} \right) \quad (3)$$

$$\eta = \frac{1}{2} E_{\text{LUMO}} - E_{\text{HOMO}} \quad (4)$$

$$\mu = -\left(\frac{IE + EA}{2} \right) \quad (5)$$

$$\sigma = \frac{1}{2\eta} \quad (6)$$

A single molecular system keeps track of energy constancy according to Parr's definition when it picks up extra charge on the surface out of its environment. It keeps an eye on energy consistency, according to Parr. Reactivity has a quality that makes it possible to classify things quantitatively.

$$\omega = \left(\frac{\mu^2}{2\eta} \right) \quad (7)$$

Another essential part that affects optical performance is the effectiveness of light harvesting. The highest charge-transfer sensitivity is seen in dyes with a high light-harvesting efficiency (LHE). The following formula (Eq. 8) may be used to calculate the LHE of dyes.

$$LHE = 1 - 10^{-f} \quad (8)$$

Open-circuit voltage (V_{oc}), a crucial measure for assessing the cost effectiveness of semiconductor technologies, is often calculated using the formula below.

$$V_{\text{OC}} = \frac{1}{e} ([E_{\text{HOMO}}(D) - E_{\text{LUMO}}(A)]) - 0.03 \quad (9)$$

The sum of the dyes was calculated using Eqs. (10) and (11) by employing their tensors, polarizability/hyperpolarizability.

$$\langle \alpha \rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (10)$$

$$\beta_{\text{tot}} = \left[(\beta_{\text{cxc}} + \beta_{\text{xyy}} + \beta_{\text{xzz}})^2 + (\beta_{\text{yyx}} + \beta_{\text{cxy}} + \beta_{\text{yzz}})^2 + (\beta_{\text{zxx}} + \beta_{\text{czz}} + \beta_{\text{yyz}})^2 \right]^{1/2} \quad (11)$$

Finding chemical bonds in designed dye materials that come from hyperconjugated interactions is made easier by NBO studies. As the transition from **D** components of the dyes to becoming electron acceptors, it offers a realistic view for analyzing intramolecular delocalization and electron density. The interaction between the **D** functions is increasingly important as stabilization energy increases. The stabilizing energy equation using a 2nd perturbation technique is Eq. (12).

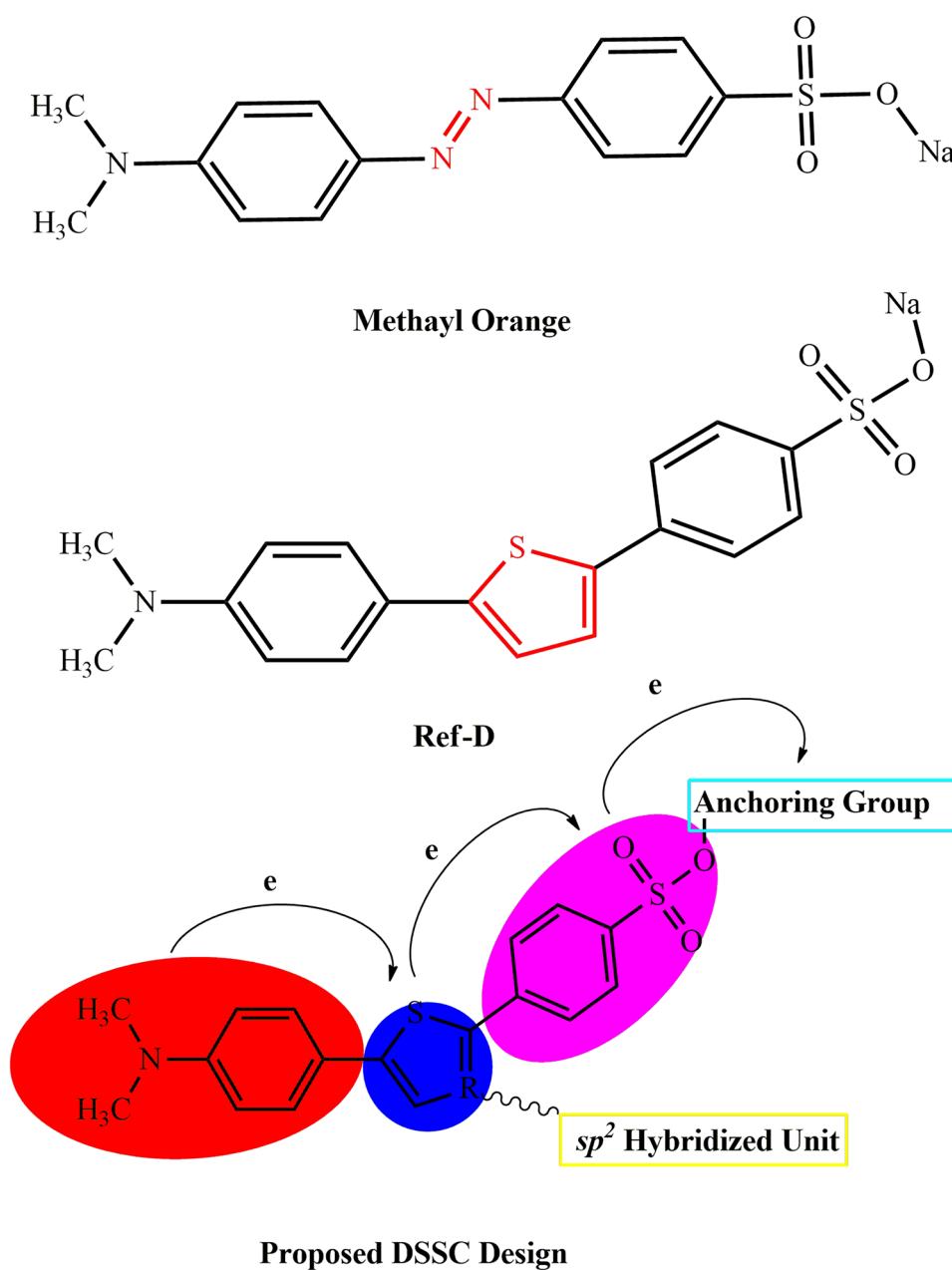
$$E^{(2)} = q_i \frac{(F_{ij})^2}{\epsilon_j - \epsilon_i} \quad (12)$$

Results and discussions

The developed DSSCs with anchoring units were studied in their D_1 - π - D_2 - $A_{(\text{Semiconductor})}$ designs. For theoretical ease, simple *N,N*-dimethylaniline was used as the electron D group in the dyes examined. First, a MO inspired reference dye (Ref-D) was designed in which the azo unit was converted into a spacer because azo units are often linked with their unstable nature. Then the dye Ref-D was further structurally modulated to create five new dyes (D-1 to D-5) which had a first electron donor (D_1), a π -spacer, a second donor (D_2), and linked anchoring units with electron-accepting ability with anchoring capability with a surface. We proposed silicone (Si)-based anchoring acceptors (A1–A5) including diethoxy(oxido(oxo)titanio)silane (A1), dimethoxy(oxido(oxo)titanio)silane (A2), dimethyl(oxido(oxo)titanio)silane (A3), diethyl(oxido(oxo)titanio)silane (A4), and (oxido(oxo)titanio)bis(trifluoromethyl)silane (A5) as previously they are proved with good actions. Similarly, efforts were made to investigate the significance of the anchoring groups in the DSSC efficiencies. We choose dye Ref-D as a reference system to investigate the parameters given and to carry out the proposed DSSCs for further investigation (Fig. 3). Because the azo unit in the reference system is recognized to be reactive across a wide range of experimental circumstances, so dye Ref-D was created with thiophene π -spacer to evaluate the efficacy of such DSSCs to the earlier dye system. The thiophene π -spacer was further accompanied by the doping of some sp^2 hybridized small units to further tune the photovoltaic performances. The introduction of a thiophene unit as a π -spacer group increases electron–hole, open-circuit voltage, and electron injection/hole characteristics for dyes. Thiophene has already been stated in the literature to be a superior spacer character over benzene.

We used thiophene as a spacer to investigate the factors influenced by such a group. In dye D-1, the maximum value (λ_{max}) shifts to a longer wavelength, while the other

Fig. 3 Proposed designs of the reference dye (**Ref-D**) and its derived dyes (**D-1** to **D-5**)



characteristics are still the same as in other dyes. *N,N*-dimethylaniline serves as a donor group in all of the newly developed dyes, while thiophene is connected to thiophene as a spacer unit.

To investigate the difference in the electronic dispersion of the proposed dye systems, the silyl anchoring groups as acceptors were used with electron-donating ($-OEt$, $-Me$, and $-Et$ groups) or electron-withdrawing ($-CF_3$ groups). In the instance of dye D-1, electron-donating ($-OEt$) groups are connected to the anchoring unit of Si atom. We modeled the Si anchoring group using the electron-donating methyl ($-Me$), ethyl ($-Et$), and electron-withdrawing ($-CF_3$) groups, which correspond to dyes 2, 3, and 4, respectively.

Orientation of dyes

To get a decent NLO efficiency from donor- π -linker-acceptor type dyes, the π -spacers must be evaluated. The purpose of this research is to design new possible NLO materials with various π -bridges and predict their photo activity, electronic, plus NLO properties for contemporary optical devices. These dyes were composed of three main parts that worked as a π bridge when combined. The C–C and C–H bonds are predicted to have lengths of 1.42–1.52 and 1.09–1.11 Å, respectively. The bond around the thiophene units like C(5)–N(13) and C(6)–N(37) had bonds that were 1.46–1.59 Å in their length. When considering the various angles, the calculated angles

were remarkably like one another, except for around the CF_3 group substitutions. The ring symmetry may be affected by the charged particle moieties on the aromatic rings, resulting in in-ring angles that are slightly more than 120° at the *meta* and *ortho* sites and slightly less than 120° at the modification point (Fig. 4). Similar results were seen for the bond angles of C(1)-C(6)-C(5) in dye Ref-D, which were 118.89° , C(5)-C(13)-N(17), and C(3)-C(9)-N(4), which were 143.1° and 120.0° . The imidazole ring and pyrimidine atoms C(7)-C(8)-N(33), C(1)-C(6)-N(6), and C(11)-C(12)-N(26) have corresponding bond angles of 120.7° and 121.3° . The structural composition

of the azole moiety was significantly altered by the inclusion of large donor atomic units, but the geometric conformation of the aromatic rings was left unaltered. The development of dyes with varying acceptor atoms involved the use of two phenyl-conjugates. The benzene ring of dye Ref-D with its dihedral angle was found to be between 117.65° and 118.09° .

It was found that the linked bond angles for C-C-N were 106° and 110° , respectively. The longitudinal benzene rings were found to be equivalent between 112.43° and 113.03° . The thiazole-facing benzyl circle C-C-C had a dihedral angle with 120° , so while the anchoring side by

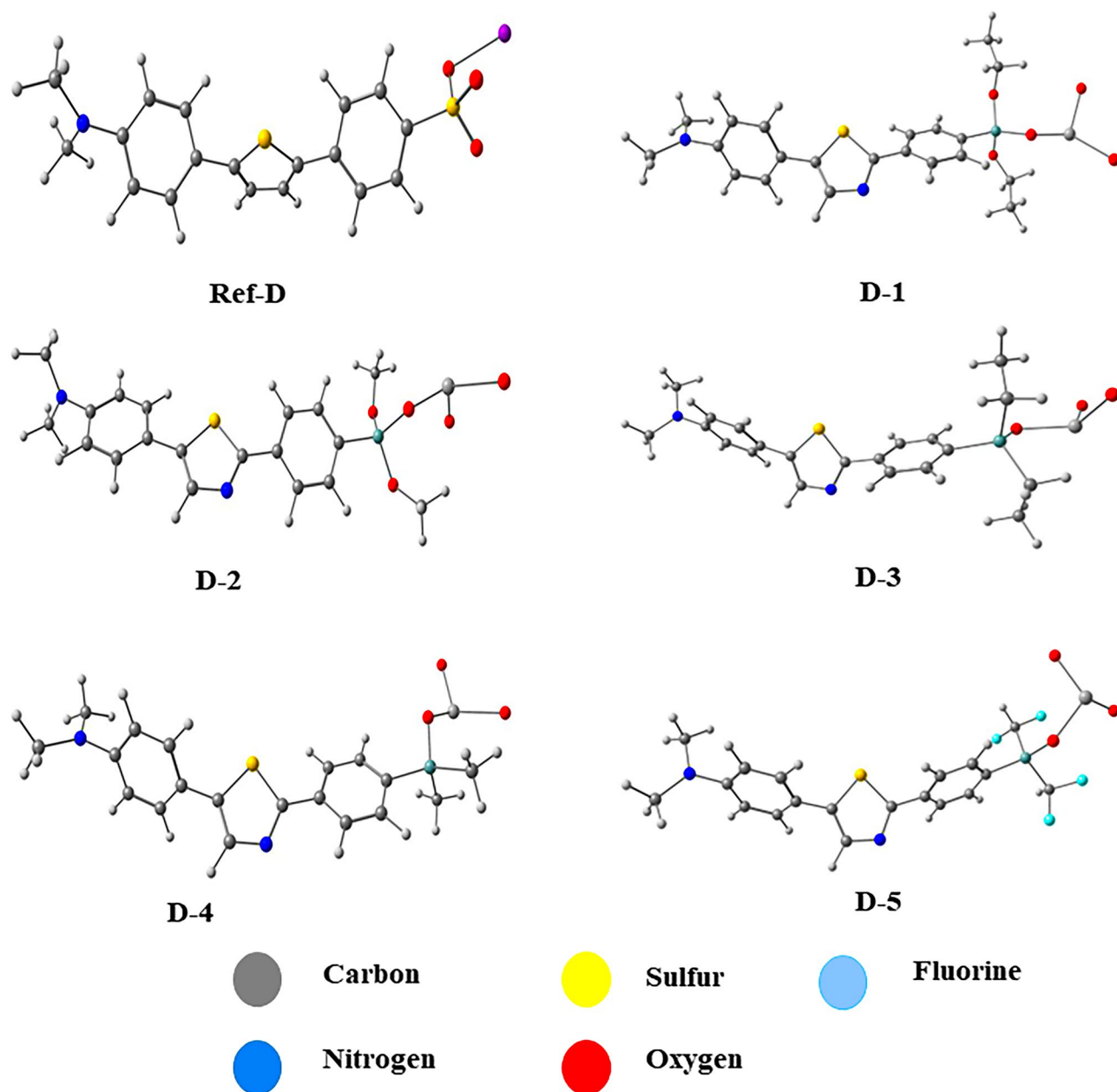


Fig. 4 DFT optimized geometries of reference dye (**Ref-D**) and newly designed dyes (**D-1** to **D-5**)

Table 1 Structural parameters like bond lengths (Å) and bond angles (°) of optimized structures of reference dye (Ref-D) and new dyes (D-1 to D-5)

Dyes	Bond lengths (Å)		Bond angles (°)	
Ref-D	R(1–2)	1.52	A(2–1–3)	117.3
	R(6–8)	1.41	A(27–2–28)	108.2
	R(6–33)	1.13	A(29–3–30)	108.2
D-1	R(1–2)	2.07	A(2–1–3)	109.8
	R(1–3)	2.07	A(2–1–22)	108.9
	R(12–23)	1.51	A(7–8–10)	119.9
D2	R(4–7)	1.49	A(5–4–7)	119.7
	R(5–30)	1.11	A(4–5–30)	111.3
	R(5–31)	1.11	A(4–5–31)	110.2
D3	R(2–32)	1.12	A(1–2–33)	112.9
	R(2–33)	1.12	A(1–2–34)	112.0
	R(2–34)	1.12	A(23–1–30)	106.7
D4	R(1–30)	1.11	A(1–21–2)	110.8
	R(2–21)	1.88	A(1–21–20)	108.6
	R(2–31)	1.11	A(1–21–22)	110.3
D5	R(3–4)	2.07	A(29–1–32)	110.2
	R(3–5)	2.07	A(21–2–30)	111.4
	R(3–22)	2.07	A(21–2–31)	110.0

side had such a geometrically exact displacement of 108°. The dihedral angles of C–C–N in the pyrrole part and C–N–N in the thiophene unit were, respectively, 106.43°–106.65° and 110.34°–110.39° (Table 1).

FMO analysis

A charge analysis of FMOs is crucial for predicting the chemical properties, physical permanence, electro-optic properties, and electronic wavelength of materials [39]. The acronyms for HOMO and LUMO stand for the propensity to take and distribute electrons, respectively. The dyes with their electron-poor part are represented by the LUMO, while its electron-rich part is represented by the HOMO (Fig. 5).

The proposed CT interaction of the dyes can be explained by a lower energy gap (E_g). There were 215 MOs in the dye Ref-D structure, 151 of which were occupied, and 64 of which were unoccupied. It is possible to see where the HOMO and LUMO are found across the dye materials. This suggested that HOMO and LUMO had a substantial orbital overlap, allowing the transition from ground state to excited state.

When calculating the GRP values using Koopmans' theorem, the HOMO/LUMO interactions were taken into consideration. To investigate the kinetics of compounds in diverse zones and be able to understand some factors associated with the respondents, it is significant to use DFT-based GRPs, such as I_1 , μ , E_a , χ , ω , electron-donating and electron-accepting (+) power, and η . The LUMO and

HOMO values control the E_a and I_1 , which are like dye materials due to their electron-accepting and -donating characteristics. The I_1 value decides the ability to donate electrons, and $I_1 = 5.68$ eV shows that dye D-4 has a very good donating capability. The dye D-2 may be employed in CT-related applications as per its higher positive (E_a) score. The HOMO orbitals were scattered around the system in dyes, although it was focused on the donor part and π -bridge in dye Ref-D from dyes D-1 to D-5. On the other side, the LUMO was discovered on the -bridge together with all the colors. The investigation showed a significant value since it affects how quickly a photosensitive dye may be duplicated throughout its electron transfer process. An electron-donating strategy that increases the HOMO energy level while also increasing the LUMO energy output can change the donor moiety (Table 2).

The electronic charge density diminishes because of the increasing photogenerated electron pushing power (energy differential between the LUMO and HOMO conduction and valence bands). In this investigation, the driving force of charge transfer increases as electronic charge density diminishes. As the electron density distribution over the HOMO and LUMO energy orbitals is essential for deciding the electrical behavior of the intended and reference compound Ref-D, the HOMO and LUMO of dyes were also referred as the valence and conductivity bands. While LUMOs are linked to anti-bonding tendencies, HOMOs have a bonding disposition. We show how the GRP values and the electron density transfer functions affect the distribution of FMOs. Between 54 and 99% of electrons were transferred in exciting states with B3LYP functioning. For the dyes D-1 to D-5, the E_g between E_{HOMO} and E_{LUMO} were found to be 2.28–3.33 eV. All the dyes showed lower E_g values than Ref-D (3.43 eV) to show their superior electronic conduction capabilities. The difference between Ref-D indicated that there was considerable intramolecular charge transfer (ICT), which caused the absorbance values to move towards to redshift. The dye Ref-D with end-capped silyl unit had a clearly strong electron-accepting action, which caused dye D-2 and D-5 to have lesser electron-accepting actions. The dye D-3 even from the reference dye Ref-D was a clue that the location and number of semiconductors are very important factors to consider when building unique OSCs like patterns.

Global chemical reactivity analysis

Analyzing FMOs is a useful method for knowing out how stable and photovoltaic a chemical is. An essential issue in absorption spectra for the physical modelling of material is the charge distribution studies over the FMOs, from HOMO to LUMO. The most crucial factor in figuring out the stability and chemical reactivity of new compounds is

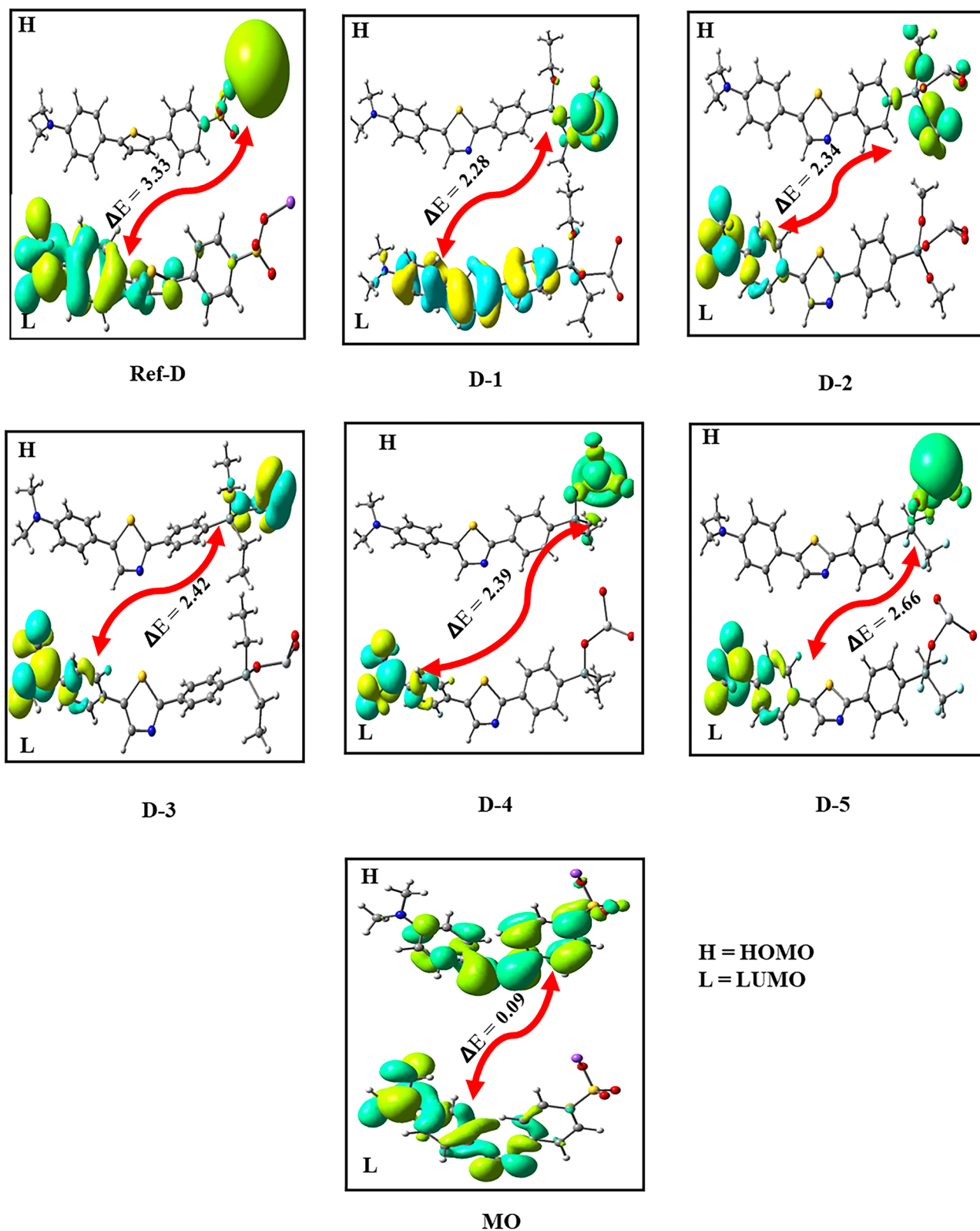


Fig. 5 An analysis of FMOs of reference dye (Ref-D) and new dyes (D-1 to D-5)

Table 2 Energies of HOMOs (E_{HOMO}), LUMOs (E_{LUMO}), with their energy gaps (E_g) in eV

Comp.	E_{H}	E_{L}	$E_g (\Delta E_{\text{H-L}})$
Ref-D	−5.31	−1.98	3.33
D-1	−2.66	−0.38	2.28
D-2	−2.75	−0.42	2.34
D-3	−2.67	−0.25	2.42
D-4	−2.65	−0.25	2.39
D-5	−2.70	−0.04	2.66

the bandgap ($E_{\text{LUMO}}-E_{\text{HOMO}}$). Smaller $E_{\text{LUMO}}-E_{\text{HOMO}}$ gaps are related to more reactive, less stable, and softer dye materials that are more polarized and start acting as a finer new competitor in supplying the best NLO response. In contrast, improved HOMO–LUMO prototype for a dye is related with its inertness, more consistency, and hard dyes. To take advantage of its relevance for their promising photoluminescence, the E_g across atomic orbitals was computed. The dye **D-4** had the lowest bandgap due to having the π -conjugated link and anchoring groups. Furthermore, after dyes **D-4** and **D-5**, which had two π -spacers and two and three acceptors, respectively, were more reactive. With phenyl π -spacers to close the E_g , silyl anchoring groups as electron acceptors had the greatest outcomes, according to the growing bandgap ordering of such dyes. Additionally, it was found that dyes with more π -spacers had E_g that were smaller, which stabilized a dye material more. Overall, the highest E_g value was discovered in dye **D-3**, while the lowest one was discovered in dye **D-4**. Figure 2 shows the results of a study on the charge distributions on the surfaces of orbitals. In HOMOs, the charge concentrations were uniform across the dye structure; in LUMOs, however, the charge densities are at the acceptor moiety and across π -spacers (Table 3).

The $E_{\text{LUMO}}-E_{\text{HOMO}}$ was used to stand for reactivity and stability by examining the GRP values, which includes such parameters as I , E_a , χ , η , μ , ω , and σ . The outcomes for the dyes under investigation were calculated from their molecular orbital analysis using the proper quantum chemistry implications. The ability of a substance to donate and

take electrons was figured out by its I as well as by measuring the amplitudes of its E_a values. The energy needed to remove one electron out of a dye is represented by the I . Increased I values imply stronger chemical stability and barrier properties. The I value for **Ref-D** was 5.31 eV, while the value for dye **D-4** was 2.65 eV. Their overall ranking was determined to be as follows: **Ref-D** (5.31) > **D-2** (2.75) > **D-5** (2.7) > **D-3** (2.67) > **D-1** (2.66) > **D-4** (2.65). Additionally, dye **Ref-D** had an E_a value of 1.98 eV, the highest value, while **D-5** value was just 0.04 eV. Overall, it was noticed that their order in descending order was as follows: **Ref-D** (1.98) > **MO** (0.77) > **D-2** (0.42) > **D-1** (0.38) > **D-3** (0.25) > **D-4** (0.25) > **D-5** (0.04). The results have suggested that the dye **Ref-D** and all of its derived dyes (**D-1** to **D-5**) had exceptional electron-accepting ability since the I values were discovered to be much greater than the E_a values. When evaluating μ , dyes with their chemical stability is considered. The overall descending order for all the dyes was compiled as follows: **MO** (−0.82) > **D-5** (−1.37) > **D-4** (−1.45) > **D-3** (−1.46) > **D-1** (−1.52) > **D-2** (−1.59) > **Ref-D** (−3.64). This has also to do with the χ of dyes, whereby low values show an easy uptake of electrons and describe electron attractions. The order of the dyes overall was determined to be **Ref-D** (3.64) > **D-2** (1.59) > **D-1** (1.52) > **D-3** (1.46) > **D-4** (1.45) > **D-5** (1.37) > **MO** (0.82). The examined dyes' higher η values suggest that they are stable, as shown by the dyes with negative μ values. Their overall order was noted as follows: **Ref-D** (1.66) > **D-5** (1.33) > **D-3** (1.21) > **D-4** (1.2) > **D-2** (1.17) > **D-1** (1.14) > **MO** (0.05). As softness is related inversely with the hardness, its order was reversal of the hardness values order. The overall descending order was noted as follows: **MO** (11.06) > **D-1** (0.44) > **D-2** (0.43) > **D-4** (0.42) > **D-3** (0.41) > **D-5** (0.38) > **Ref-D** (0.3). The order of the dyes with increasing E_g values matched the progression of their relative η . The electrophilicity was found in its decreasing order as follows: **MO** (7.42) > **Ref-D** (3.98) > **D-2** (1.08) > **D-1** (1.01) > **D-3** (0.89) > **D-4** (0.88) > **D-5** (0.7). This design was perfectly following the HOMO–LUMO bridging, proving that compounds with a substantial E_g value are regarded hard dye materials, having stronger stability, reduced reactivity, and resistant to electronic conformational change. The general ranking was as

Table 3 Global reactivity parameters (GRPs) of dye **Ref-D** and its new dyes (**D-1** to **D-5**)

Comp.	I	E_a	χ	μ	η	σ	ω
MO	0.86	0.77	0.82	−0.82	0.05	11.06	7.42
Ref-D	5.31	1.98	3.64	−3.64	1.66	0.30	3.98
D-1	2.66	0.38	1.52	−1.52	1.14	0.44	1.01
D-2	2.75	0.42	1.59	−1.59	1.17	0.43	1.08
D-3	2.67	0.25	1.46	−1.46	1.21	0.41	0.89
D-4	2.65	0.25	1.45	−1.45	1.20	0.42	0.88
D-5	2.70	0.04	1.37	−1.37	1.33	0.38	0.70

follows: the σ , which is related to its μ , is an added consideration. **D-2** (0.27) is the least reactive part and has the lowest σ value, while dye **D-4** (1.19) was found to be most reactive dye materials and has the highest σ value, according to the rising ordering of σ values, which is in direct contrast to the expanding E_g order. Characteristics of GRP showed a strong correlation with the HOMO–LUMO E_g order.

UV–visible analysis

Any photovoltaic system is a semiconductor that converts light energy into electrical energy [14]. This causes electrons from the valence band moving to the conduction band [40]. The optical characteristics of photovoltaic panels are widely studied using UV/vis/NIR spectroscopic techniques. The results showed that **Ref-D** had a red shift for the $\lambda_{\max}$ in comparison to **MO** (Fig. 6). However, the inclusion of sp^2 hybridized atom in the π -spacer part reduces the HOMO–LUMO E_g , causing the $\lambda_{\max}$ to shift to a higher wavelength (red shift).

Furthermore, the efficiency of these Si-containing anchoring dyes was compared using **MO** which is an experimentally documented dye with *N,N*-dimethylaniline as the donor, azo unit as a π -spacer, and cyanoacrylic acid as an anchor unit. The **Ref-D** had also been estimated at the same level. In gaseous, the largest **MO** value is 398 nm (Fig. 7).

This experimental measurement agreed well with the computationally estimated $\lambda_{\max}$ (401.63 nm) at the CAM-B3LYP/6-31G(d,p) level of theory using the CPCM model and chloroform as the solvent (Fig. 8).

Because chloroform is commonly employed as a solvent in DSSCs, it has been used in next computations. The overall order of the $\lambda_{\max}$ values in chloroform was noted as follows: **D-3** (576) > **D-4** (545) > **D-2** (542) > **D-5** (532) > **D-1** (511) > **Ref-D** (465). The major electronic transitions that were noted for these $\lambda_{\max}$ values were HOMO-1 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO,

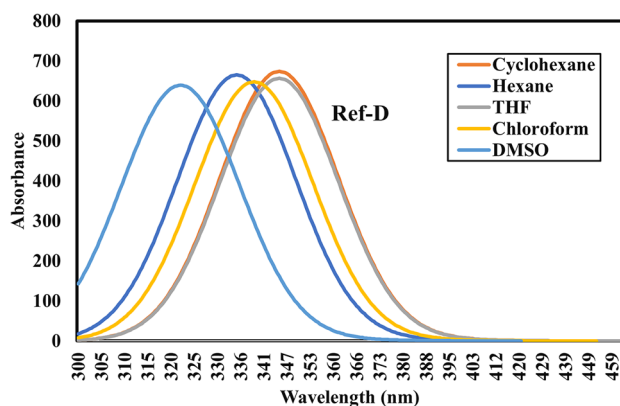


Fig. 6 Computed UV–vis analysis of reference dye (**Ref-D**) under different solvents

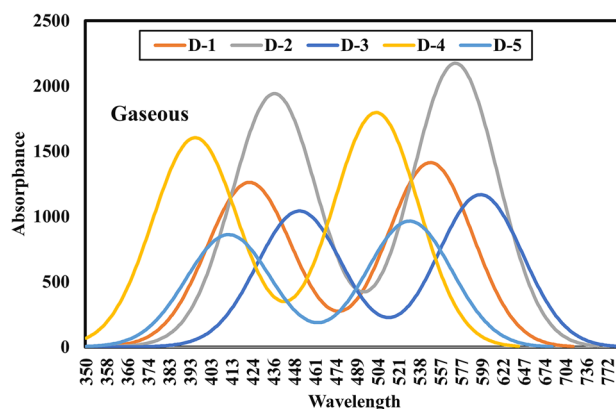


Fig. 7 Computed UV–vis analysis of reference new dyes (**D-1** to **D-5**) in gas

HOMO $\rightarrow$ LUMO + 1, and HOMO $\rightarrow$ LUMO + 2. The computed $\lambda_{\max}$ in ethanol solvent is 405.1 nm, which is quite like the experimental data. The efficiency of cyanoacrylic acid and Si-containing anchoring groups has been compared using **MO**. At the same level of theory, the **Ref-D** was computed. The $\lambda_{\max}$ obtained experimentally is 398 nm in ethanol. The research of materials that collect photons of natural sunlight is known as light harvesting [41]. This encompasses research into the light-harvesting characteristics of photosynthetic systems developed and constructed to stimulate photochemical processes or create solar fuels. The collection of sunlight photons is a critical stage in the photosynthetic activity. The pigment-binding proteins operate as absorbed energies to promote photochemistry. The LHE of newly designed materials can be calculated by the oscillator strength (f) of the $\lambda_{\max}$ values. In the present study, the **Ref-D** and all the new dyes had the LHEs in descending order as follows: **D-2** (0.6154) > **D-3** (0.1169) > **D-4** (0.0984) > **Ref-D** (0.0922) > **D-1** (0.0518) > **D-5** (0.0078) (Table 4).

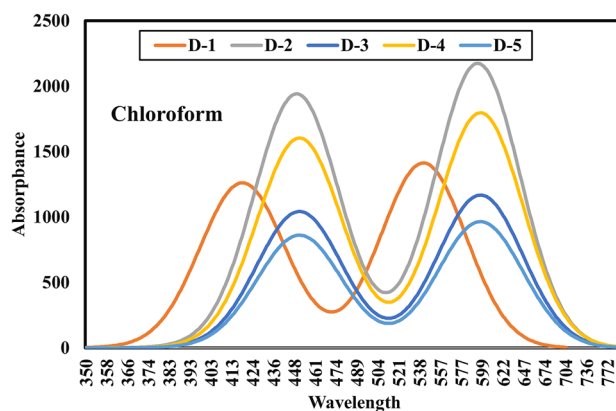


Fig. 8 Computed UV–vis analysis of reference new dyes (**D-1** to **D-5**) in chloroform

Table 4 Computed excited state parameters of dye **Ref-D** and its new dyes (**D-1** to **D-5**)

Dyes	State	E (eV)	$\lambda_{\max}$	f	Major transitions
Ref-D	1st	2.12	456	0.0512	HOMO-1 $\rightarrow$ LUMO
	2nd	1.39	465	0.0420	HOMO $\rightarrow$ LUMO
	3rd	2.34	398	0.0230	HOMO $\rightarrow$ LUMO + 1
D-1	1st	3.21	487	0.0123	HOMO $\rightarrow$ LUMO
	2nd	2.54	511	0.0231	HOMO $\rightarrow$ LUMO
	3rd	3.34	498	0.0032	HOMO-1 $\rightarrow$ LUMO
D-2	1st	2.45	502	0.0034	HOMO $\rightarrow$ LUMO
	2nd	1.56	542	0.415	HOMO $\rightarrow$ LUMO + 1
	3rd	2.32	454	0.0303	HOMO $\rightarrow$ LUMO
D-3	1st	2.12	497	0.0510	HOMO-1 $\rightarrow$ LUMO
	2nd	2.32	576	0.0540	HOMO $\rightarrow$ LUMO + 2
	3rd	2.21	456	0.0320	HOMO $\rightarrow$ LUMO + 1
D-4	1st	1.32	521	0.0430	HOMO $\rightarrow$ LUMO
	2nd	1.98	545	0.045	HOMO $\rightarrow$ LUMO
	3rd	2.87	432	0.009	HOMO-1 $\rightarrow$ LUMO
D-5	1st	3.421	458	0.005	HOMO $\rightarrow$ LUMO
	2nd	2.76	532	0.0034	HOMO $\rightarrow$ LUMO + 1
	3rd	2.21	467	0.0043	HOMO-1 $\rightarrow$ LUMO

The computed $\lambda_{\max}$ in gaseous state was 405.1 nm, which is quite like the experimental data. Furthermore, the efficiency of cyanoacrylic acid for anchoring groups was compared using an experimentally confirmed dye with *N,N*-dimethylaniline as the donor, thiophene as the π -spacer, and cyanoacrylic as the anchoring part. The dye **Ref-D** was computed at the same level. The $\lambda_{\max}$ found experimentally is 398 nm in ethanol solvent. This test result corresponds to the computed $\lambda_{\max}$ (401.63 nm) for the CAM-B3LYP/6-31G(d,p) level using CPCM and chloroform as solvent.

Nonlinear optical response

For these types of title dyes to be used in the field of nonlinear optoelectronic investigations, with structural insights [42], the bridging features leading in hyperpolarizability rise require FT-IR and FT-Raman spectrometric study [43]. When studying hyperpolarizability, the investigated material structural makeup is treated as distinct dye material structures. Most of the new dyes with their polarizability and hyperpolarizability tensors (a.u.) (Tables S12–S15) could well be computed using the preceding equation [44]. To carry out the desired results, an unconstrained open-shell CAM-B3LYP/6-31G + (d,p) was employed. More polarity was expected to result in smaller E_g values, which were inversely linked to their dipole moment. A significant NLO reaction was implied by a reduced E_g value, improved linear polarizability, and higher hyperpolarizability [45]. Employing chloroform as an organic solvent as well as the

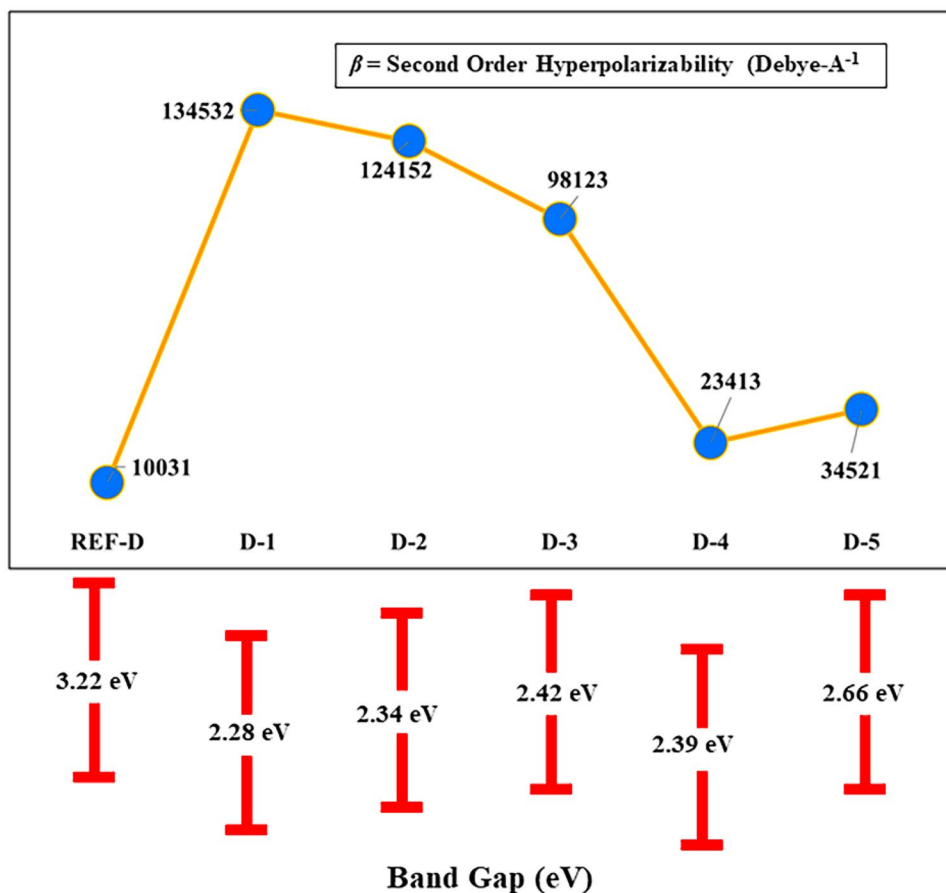
IEF-PCM modelling in computational analysis employing the TD-DFT approaches. The newly designed dyes with semiconductor anchoring groups as electron acceptors were simulated for their UV/visible spectra. Polarizability is negatively correlated with the HOMO–LUMO related E_g values. A small E_g is generally related with higher polarizability values. Smaller E_g values, larger linear polarizability (Fig. 9), and a substantial NLO responses are all predicted by optical metrics including dipole moment, HOMO–LUMO electron transfer allocations, oscillation strength, and related quantum chemical properties [46]. The relationship between $\lambda_{\max}$ and energy E_g was inverted. As the strength of the electron-drawing acceptor moieties linked to the donor rises, the E_g value gets smaller. Due to the impact of charge carrier dye materials at the terminals of dyes framework, absorbance intensity shifts to the top side. The early excited states of freshly formed small-donor dye material dye materials had average polarizability values in the descending order as follows: **Ref-D** (543) > **D-1** (1092) > **D-2** (987) > **D-3** (1321) > **D-4** (1231) > **D-5** (997). The hyperpolarizability values were noted as in their descending order: **D-1** (134,532) > **D-2** (124,152) > **D-3** (98,123) > **D-5** (34,521) > **D-4** (23,413) > **Ref-D** (10,031).

The highest wavelength of the **MO** (reference) was 528 nm. To further understand the excited state charge transfer process, the wavelength maxima ($\lambda_{\max}$) and energy transition characteristics from the most occupied to the least occupied d-orbitals were measured for the six singlet excitons. There is a reciprocal link including $\lambda_{\max}$ and so excitation energy as the $\lambda_{\max}$ lowers and the excited states grow as we move from $S_1 \rightarrow S_n$ vibrational modes to $S_0 \rightarrow S_n$ excited singlet state. Regarding the excited states of $S_1 \rightarrow S_n$ ($n=6$), the **Ref-D** absorbance intensity was 519, 518, and 481 nm correspondingly. The bathochromic shift of the **MO** molecules is 488 nm, while the E_g between the first and sixth singlet excited states is 0.869 eV. Due to its significant bandgap energy (E_g) and weak acceptor moiety, the dye **Ref-D** also displayed a small bathochromic shift in optical absorption [47]. Low energy CT has showed significant CT values in NLO compounds with substantial transition moments and oscillator strengths.

$$\beta_{CT} = \frac{\Delta\mu_{gm} + f_{gm}}{E_{gm}^3} \quad (13)$$

The **Ref-D** reflectance peak was separated by 12.12 nm with $\lambda_{\max}$ at 669 nm due to 2.63 eV exciting energy fluctuations from $S_1 \rightarrow S_6$. The dyes **D-3** and **D-4** have absorption wavelengths by 217 nm and 191.03 nm, respectively, and have different excitation energies by 1.082 eV and 1.612 eV. The excitation energy from the excited state of $S_0 \rightarrow S_n$ ($n=6$). The dye **D-4** had the easiest charge transfer since it has a greater excitation energy (1.32 eV) than the intended dyes that have the following descending order values: **D-5** (3.421) > **D-1**

Fig. 9 NLO analysis as a function of bandgap (E_g) changes of reference new dyes (**D-1** to **D-5**)



(3.21) > **D-2** (2.45) > **Ref-D** (2.12) > **D-3** (2.12) > **D-4** (1.32). The E is typically related to the energy needed for the first excitation. Because of the research, excitation energy is significantly lower than the E_g energy of suggested dyes. A linear link exists between the energy bandgap and the excitation strengths. Widening the E_g across HOMO and LUMO has several effects. The dipole moment is often associated with the stability of tiny organic solar cells in polar organic solvents. A higher dipole moment value improves the ability of OSC to process solutions. As a result, the solubility of a given dye material dye materials increases with increasing dipole moment, increasing material efficacy. The speedy and straightforward charge transfer is made easier by the highest maximum bending value, which also eases -conjugation. The dipole moment development of newly created dyes in their descending order was noted as follows: **Ref-D** (6.2036) > **D-2** (5.9726) > **D-1** (4.012) > **D-5** (3.7903) > **D-4** (3.4925) > **D-3** (2.6981). The production of donor components in identity thin film bulk heterostructure organic solar cell systems is significantly influenced by the dipole moment. While f_m^g stands in for the excited state dipole moment, f_m^s stands for the ground state dipole moment. Second-order polarizability is intrinsically linked towards the polarizability. Oscillator strength

in the ground state as well as absorption across n th wavelength range (nm). Relationship between total (blue line) and matching CT (red line) values for D-5. The process that may occur in the cube, E_m^{3g} , is inversely proportional to β while the excited state, f_m^g , is proportional to β . Large oscillator intensity and transitional moments have been seen in NLO compounds with low energy CT.

Molecular packing and charge tripping analysis

The phase dispersion is controlled by the donor–acceptor miscibility, which affects the NLO and other photovoltaic properties in lieu of their ability to trip the charges [48]. To get information about amorphous miscibility, the extent of molecular interaction of charge transport materials must be quantified. Miscibility assessment is quite useful in achieving the film shape (Fig. 10).

It has been stated that the best device photovoltaic properties may be achieved with the best miscibility and hence the best. All the newly developed dyes have been simulated for their miscibility and molecular studies by optimizing them at APFD level of DFT. The miscibility related quantum chemical parameter tends difficult to decide experimentally

as there are several approaches and a broad range of values for OSC devices are documented. Computational approaches are alternative ways for calculating the compressibility of a selected set of dye materials. The Blend module supplies many pair combinations for blending dye s. From their simulation boxes, the tripping of charges from the HOMO of **Ref-D** to the LUMOs of the respective dyes can be seen.

Density of states

The number of distinct stages that electrons have been permitted to hold at a certain energy level is known as the density of states (DOS) [49]. The evidence bought by FMOs from these dyes was supported at their DOS studies. The DOS profiles of

the compounds under investigation (Fig. 11) make it obvious that a significant acceptor character can alter the pattern of dispersion around the HOMO and LUMO. To illustrate the DOS study, we divided our dyes into two parts: the donor (the core unit) and acceptor (the end-capped group), which have been depicted by red and green lines, respectively. On the x -axis, the electronic framework at LUMOs was represented by positive numbers, while the dielectric loss at HOMO was depicted by negative values. The distance here between two was used to depict the E_g . It is helpful to look at the density of states of newly created dye before implementing the FMO ideas for their effects. Positive quantities on the x -axis denoted the electrical structure at LUMOs, while negative numbers showed the dielectric loss at HOMO.

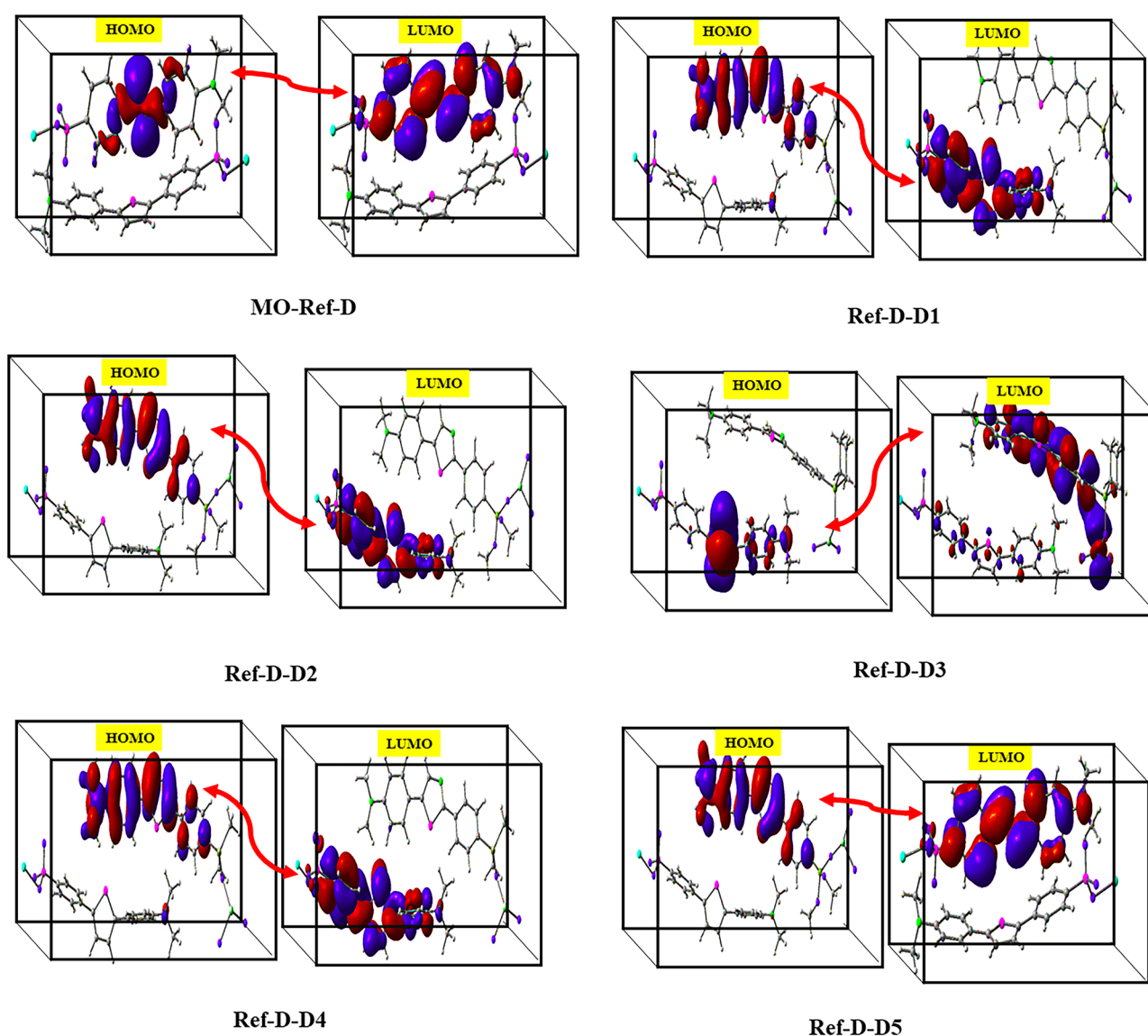


Fig. 10 Charge tripping analysis of new dyes (**D-1** to **D-5**) by optimizing their complexes at DFT level

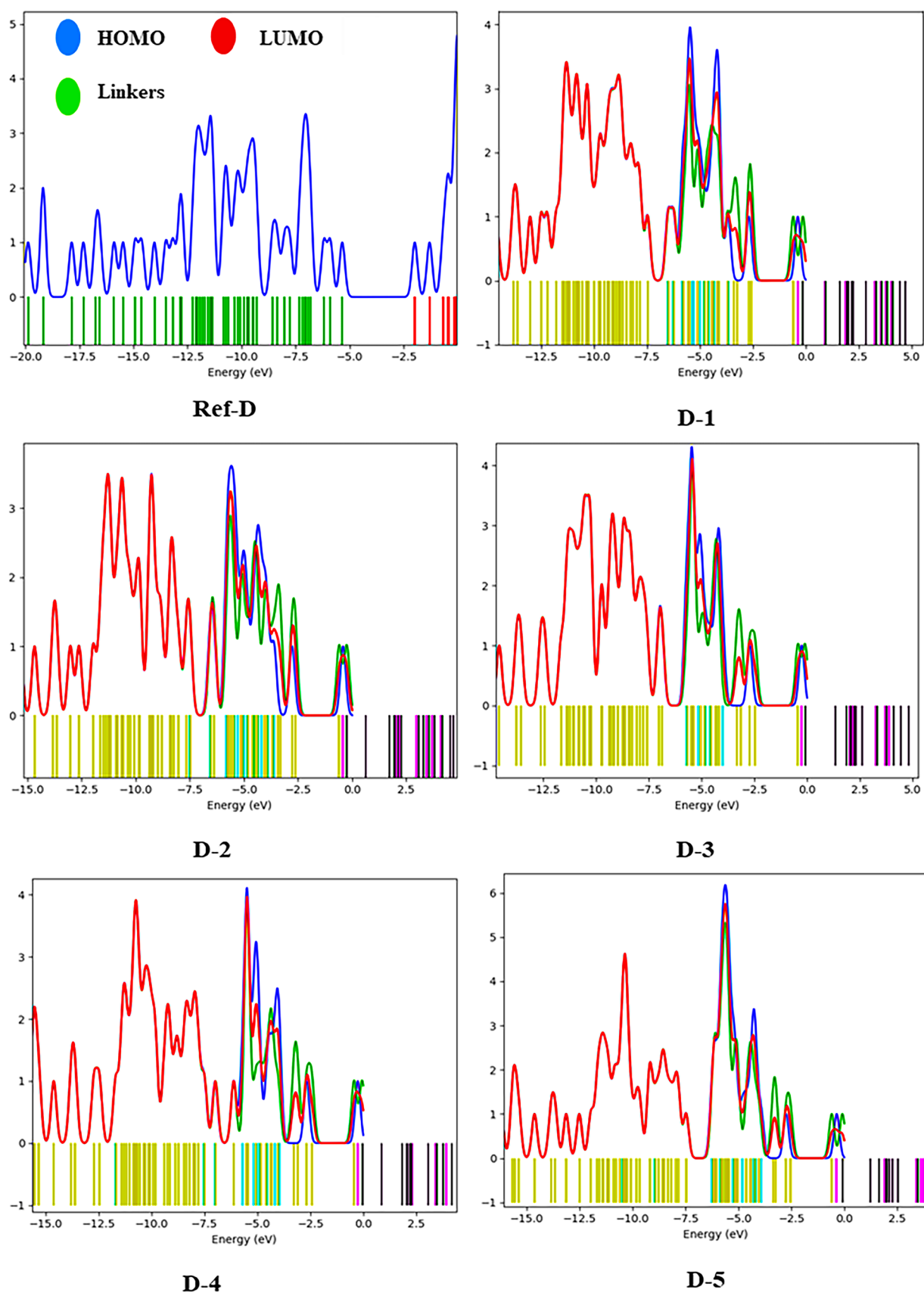


Fig. 11 Density of states analysis of dye **Ref-D** and its new dyes (**D-1** to **D-5**)

Table 5 Electron injection and hole analysis dye **Ref-D** and its new dyes (**D-1** to **D-5**)

Dyes	HIE (Au)	EIE (Au)	HIE (Al)	EIE (Al)
Ref-D	0.89	2.50	9.51	2.22
D-1	− 1.76	4.10	6.86	3.82
D-2	− 1.67	4.06	6.95	3.78
D-3	− 1.75	4.23	6.87	3.95
D-4	− 1.77	4.23	6.85	3.95
D-5	− 1.72	4.44	6.90	4.16

Electron hole injection

We are investigating a hole/electron injection barrier (HIE/EIE) from dyes towards the Al electrode as ($HIE = W$ of metal (E_{HOMO}) and $EIE = E_{\text{LUMO}}$ (W of metal)).

The declining order shown by the HIE of **Ref-D** and its new dyes for Au metal, the potential in descending order was seen as follows: **Ref-D** (0.89) > **D-2** (− 1.67) > **D-5** (− 1.72) > **D-3** (− 1.75) > **D-1** (− 1.76) > **D-4** (− 1.77). The same trend noted for Al electrode was seen as follows: **D-5** (4.44) > **D-3** (4.23) = **D-4** (4.23) > **D-1** (4.1) > **D-2** (4.06) > **Ref-D** (2.5). The trend for (Au) and (Al) for EIE of **MO** and its newly developed dyes also offered some intriguing results, with (Au) reported with the same pattern as follows: **Ref-D** (9.51) > **D-2**

(6.95) > **D-5** (6.9) > **D-3** (6.87) > **D-1** (6.86) > **D-4** (6.85). The Al electrode contrasted the subsequent tendency with one that was completely different, presenting it as follows: **D-5** (4.16) > **D-3** (3.95) > **D-4** (3.95) > **D-1** (3.82) > **D-2** (3.78) > **Ref-D** (2.22). The majority of dyes may function as excellent electrode materials, and the influence of the electrode is essentially nonexistent, according to the HIE and EIE analyses. They likewise reflect a metal tendency that is identical. Therefore, it may be inferred that while Al would be an excellent electrode material for investigations involving electron injection, Au can become a good possibility for electron holes (Table 5).

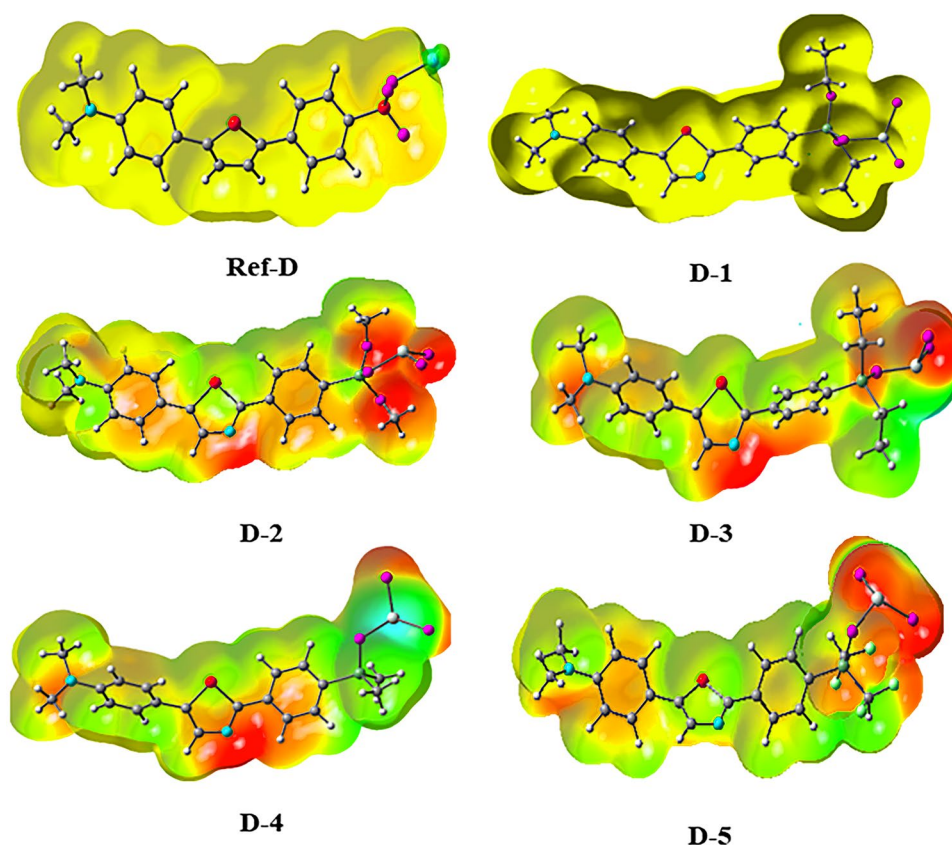
NBO analysis

Calculations of the distribution of electron densities across elements as well as the bonds that connect them are done using naturally localized orbitals. A method for finding acceptors and donors in various regions of the material is called NBO monitoring. This strategy can only be used to bring dye electrons through into semiconductor E_g when the C group acts as an anchoring factor. The dyes **D-1** and **D-2** in the dyes, as well as the **MO** itself, had negative NBO driven energies. The dyes **D-1** and **D-2** had fewer negative values than the **MO**, which suggested that a negative charge is transferred from **MO** to the newly established dyes **D-1**

Table 6 NBO analysis of dye **Ref-D** and its new dyes (**D-1** to **D-5**)

Dye	Donor (<i>i</i>)	Type	Acceptor (<i>j</i>)	Type	$E^{(2)}$	$E(j)E(i)$ (au)	F_{ij} (au)
D-1	Ti1-O2	π	Ti1-S12	π^*	0.28	0.38	0.013
	Ti1-O2	π	Ti1-O3	π^*	1.35	0.60	0.036
	Ti1-O2	π	Ti1-O22	π^*	1.21	0.59	0.034
	Ti1-O3	π	Ti1-O2	π^*	1.31	0.60	0.035
	S24	LP	C23-C25	π^*	8.78	0.26	0.060
D-2	Ti1-O3	π	Ti1-O22	π^*	1.17	0.59	0.033
	Ti1-O22	π	Ti1-S11	π^*	0.56	0.40	0.019
	Ti1-O22	π	Ti1-O2	π^*	1.36	0.62	0.037
	N4-C5	π	N4-C6	π^*	1.91	0.93	0.053
	N4-C5	π	N4-C7	π^*	1.56	0.95	0.049
D-3	N4-C5	π	C6-N36	π^*	0.64	0.99	0.032
	S24	LP	C26-N27	π^*	10.63	0.23	0.063
	N4-C5	π	C7-C8	π^*	1.14	0.65	0.037
	N4-C6	π	N4-C5	π^*	1.90	0.93	0.053
D-4	N4-C6	π	N4-C7	π^*	1.64	0.95	0.050
	N27	LP	C23-C25	π^*	1.52	0.91	0.034
	Ti1	π	Ti-O3	π^*	0.47	1.97	0.038
	Ti1	π	Ti-O2	π^*	0.25	1.99	0.028
	O22	π	Si19-O20	π^*	6.51	0.38	0.064
D-5	O22	π	Si19-O21	π^*	3.71	0.37	0.048
	N4-C6	π	C5-H32	π^*	0.64	0.99	0.032
	N27	LP	C13-C26	π^*	1.10	0.76	0.037
	N27	LP	C23-C25	π^*	1.52	0.91	0.048

Fig. 12 Electrostatically mapped surfaces of **Ref-D** and its new dyes (**D-1** to **D-5**)



to **D-5** during loading (Table 5). The study revealed that electronic densities were efficiently conveyed between donor through acceptor, resulting in an efficient charge condition where the most of donor and π -conjugated intermediate products had positive properties while all acceptors showed negative values. The enhanced charge transfer capabilities are found in the dyes with the greatest NBO values of energetic for the π -conjugated bond length, while variants with the lowest value have been researched and each dye was appeared to work well with others (Table 6).

Electrostatic potentials

The locations of proposed combination' electron-donating substitutions are revealed by molecular electrostatic potential (MEP) analyses, which enable the prediction of reactive species [50]. The colors red, blue, and green, respectively, reflect the negative, positive, and neutral sections of the MEP regions (Fig. 12).

Nitrogen atoms are the focus of the negative region (red), which suggests that such regions are vulnerable to electrophilic assaults [51]. The carbon and hydrogen atoms of CP/CP*, as well as those of dyes, are all covered by the positive (blue) zone, showing that nucleophilic interactions are possible at these sites. The parts of the dye material with no electrostatic charge are said to be neutral.

Conclusions

While in optoelectronic industry, organic materials with notable NLO characteristics are often used. By adjusting the various electronic group replaced chances to regulate their bandgap structure and their NLO sensitivities, nine newly created pull–push dyes with a D- π -D-A_(Semiconductor) framework were theoretically constructed from acceptor and donor components with π -spacers. Investigated is how different acceptors affect nonlinear kinetic energy modes. According to FMO testing, all the developed dyes showed extremely narrow E_g values, which had an impact on their other photovoltaic characteristics. The GRP values were shown to be related to lower values, higher ratings, and a narrower bandgap. The dyes displayed higher peak value and lower energy electronic interactions in the UV–vis band when comparing to the benchmark dye material. The production of electrostatic interaction in dyes in between donor (D) and acceptor (A) species was shown by an NBO research. Charge transport from D to A may have caused a large NLO reaction that led to this charge separation. The dyes had initial hyperpolarizability indices that were eight times greater than the standard. Our research should contribute to the creation of organic dyes with favorable properties for enhancing optical device performance. Additionally, by

applying π -poor vs π -rich semiconductor dyes to the dye-sensitive solar panels, a pull–push effect may be created to improve the NLO response.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11224-022-02070-3>.

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Author contribution Conceptualization: [SHS]; methodology: [AUH]; formal analysis and investigation: [MZ, MNZ]; writing—original draft preparation: [AUH]; writing—review and editing: [GM]; resources: [SHS]; supervision: [SHS].

Data availability All data generated or analyzed during this study are included in this published article and its supplementary information file.

Code availability Gaussian 09 W and Gauss view 5.1 are used for simulation and origin software is used to draw the plots.

Declarations

Ethics approval Not applicable.

Ethics declarations This work did not involve any human subjects.

Consent to participate This article does not have any studies with human participants or animals, clinical trial registration, or plant reproducibility performed by any author.

Consent for publication All authors have approved the paper and agree with its publication.

Competing interests The authors declare no competing interests.

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