Computational investigations on acceptor substituent influence of metal-free efficient chromophores for optoelectronic properties

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Abstract
In this study, the computational studies of the PO₃H₂, CONHOH, and SO₂H (A1–A3) molecules were investigated for optoelectronic applications on the basis of tetrahydroquinoline (C1-1) dye. Besides, a detailed calculation of the molecular structures, energy levels, driving force of injection, regeneration, non-linear optical (NLO) property, chemical hardness, excitation binding energy, light-harvesting efficiency (LHE), absorption spectra, and photovoltaic (PV) parameters were all discussed in details using density functional theory (DFT) and time-dependent DFT (TD-DFT) methods. The optoelectronic properties of C1-1-based A1–A3 molecules are originated to be tuned by changing the position of the acceptor. To get a maximum absorption spectrum of C1-1, Becke’s three-parameter and Lee–Yang–Parr (B3LYP), Coulomb-attenuating method-B3LYP (CAM-B3LYP), and Head-Gordon model (ωB97XD) were used for the TD-DFT method. Results reveal that the TD-ωB97XD and 6-31G(d) combined functionals were provided reliable effects to the C1-1. Therefore, absorption spectra of the A1–A3 dyes were followed by the TD-ωB97XD/6-31G(d) techniques. The designed A1 dye displayed a smaller energy gap and red-shifted broadened spectra than the other dyes and C1-1 can be utilized to get a better PV properties. In addition, NLO properties of the A1–A3 chromophores were calculated by the polarizability and first-order hyperpolarizability. Consequently, A1 dye has a superior value of the NLO activity. This study will deliver a valuable reference to the upcoming molecular proposal of tetrahydroquinoline dyes for optoelectronic applications.

Keywords TD-ωB97XD Functional · D-π-A structure · DFT & TD-DFT calculations · NLO property

Introduction
Due to worldwide warming and faster exhaustion of fossil fuels, there is affordable attention to renewable strength in particular solar cells and solar energy. Particularly, dye-sensitized solar cells (DSSCs) have been concerned with the wonderful contract of scientific, methodological, and industrial interest due to low fabrication price and reasonably high solar energy conversion efficiency [1, 2]. Exquisite efforts in lots of aspects covering the semiconductor, counter electrode, electrolyte, and sensitizer were devoted for improving the electricity conversion efficiency. In DSSCs, dye is immersed by the light and anchored to the TiO₂ surface. Also, the ground state of the sensitizer has regenerated by the electrolyte, which included a redox mediator (I⁻/I³⁻) to give capable charge separation. To conclude, an electric power current can be produced. From these DSSCs, the dye molecules play an important part in their overall performance and are one of the most studied research [3]. The dye sensitizers had been fundamentally two classifications there are metal and metal-free dyes [4]. The metal-based complexes have mostly consisted of polypyridyl Ru(II) and porphyrins, which have proven to be capable of overall presentation [5]. However, these dyes were faced with the difficulties of limited resources, high price, and environmental issues, which limit importance by the uses in DSSCs.

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Alternatively, more researchers concentrated on metal-free dye sensitizers have involved a structural variety, ease of structural alteration, high molar extinction coefficient, and low price [6–9]. Up-to-date, many forms of organic dye molecules were made and verified for DSSCs [10]. Just an example, it has proven the efficiency around 20% and it has been reported by Kar groups [11]. Hence, chemical optimization of the organic dyes nevertheless requires in addition to the development of newly designed dyes.

Most of the above-stated highly capable metal-free organic dye molecules can be made of electron donor (D)-π-conjugated (π)-acceptor (A) (D-π-A) configuration. It can permit tuning of the optical and electronic belongings. From this point of view, the molecular constructions of the D-π-A organic dyes were modified with a change acceptor part. The D-π-A pattern resulted in the intramolecular charge transfer (ICT) from D-A via π-bridge, creating wide and extreme absorption spectra in the ultraviolet–visible (UV–Vis) region, despite the fact that the outstanding boost was made to use organic sensitizer for DSSCs. Therefore, the need of nevertheless widespread incentives inside the layout of more capable sensitizers can be designed.

In this regard, the theoretical study based on the density functional theory (DFT) and time-dependent DFT (TD-DFT) techniques may be excessive help within the layout of dyes. In these dyes with the advanced presentation, providing profound information on the excited states concerned within the absorption and electron injection procedures. Computational analysis has been beneficial kits to elude expenditure time and rate inside the photophysical belongings. In light of these, the sensible plans of organic dye organized with new state-of-art theoretical calculations were employed in some of the literature [12–16]. Computational analyses were broadly used for organic DSSCs [17]. A tetrahydroquinoline-based D-π-A dye was played a good representation in DSSCs application. In 2008, power conversion efficiency (PCE) of the C1-1-based DSSCs has provided by 4.4%, photovoltage (0.583 V) and photocurrent density (10.4 mA cm$^{-2}$) as stated by H. Tain et al. [18]. PCE of the photovoltaic (PV) device was especially determined through the short-circuit current density ($J_{SC}$), open-circuit photovoltage ($V_{OC}$), and fill factor (FF). In this manner, cyanoaacrylic acid was used as the acceptor group. The boost of $J_{SC}$ and $V_{OC}$ would be substantially growth in the PCE. Also, improvement of the electronic dipole moment ($\mu_{normal}$) would even be enhanced $V_{OC}$, which can be achieved higher efficiency. Additionally, the acceptor tuned influence of the dye performance played a major role inside the TiO$_2$ and improved the performance of DSSCs.

In the present study, a new type of organic dyes A1–A3 through the acceptor based on C1-1 was designed for NLO and DSSCs. Here, newly screened dye names along with PO$_3$H$_2$, CONHOH, and SO$_2$H (denoted as A1, A2, and A3) have been used for the electron-A groups. The C1-1-based A1–A3 molecular configuration of this study was illustrated in Scheme 1. Furthermore, these dyes were investigated by using DFT and TD-DFT methods with a view to design better dyes for DSSCs. The photophysical and absorption properties of the dyes were matched with the C1-1 sensitizer. Furthermore, A1–A3 dyes were explored to restrict the elements affecting the efficiency of DSSCs. As demonstrated, the creation of A1–A3 dyes would extensively develop the ability of D-π-A organic molecules. It has been evidencing that a small chemical alteration at the molecular schemes can essentially affect their PV performance. It is well identified that the tuning molecular modification system can prompt the absorption and physical belongings of the D-π-A structure. Later, NLO studies of the A1–A3 dyes were inspected into the polarizability and first-order hyperpolarizability. Accordingly, the acceptor tuning effect on A1 dye was the better NLO response. Finally, the theoretically studied results were shown that featured D-π-A organic dyes designed for optoelectronic as a promising candidature.

Scheme 1 Drawing of tuning molecular configuration for different anchor groups

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Computational details

Quantum chemical calculation has been a well-known device to study acceptor groups. It had been used to justify such compounds and provided for experimental work. The geometry of A1–A3 molecules in the gas phase was optimized via the DFT technique using Becke’s three-parameter functional and the Lee–Yang–Parr (B3LYP) \[19\] with 6-31G(d) levels of all dye atoms. The geometry calculations were found that there were no imaginary frequencies. Also, the geometry structures were exposed to local minima on the potential energy surfaces.

The different exchange–correlation (XC) and long-range corrected (LC) functionals were shown often regularly considerable effects using the TD-DFT to evaluate in UV–Vis spectrum. The TD-DFT technique has been currently raising widespread popularity in quantum chemical theory. The valuable device has been used for the excited state configuration. Furthermore, this method was worked well to the excited state geometry of the numerous dyes \[20\].

In literature, the computational concept was used to verify the solvent impact associated with the UV–Vis of the dyes \[22\]. The absorption spectra and molecular orbitals (MOs) energies in C1-1 dye were implemented on the different XC and LC functionals. The XC & LC involved in hybrid functionals such as B3LYP, CAM-B3LYP \[23\], and ωB97XD were reported \[24\]. The calculated absolute value of decided functionals were 579, 477, and 463 nm, respectively. All selected XC & LC calculated values were displayed in Fig. 1 and listed in Table 1. Moreover, compared with C1-1, B3LYP-, CAM-B3LYP-, and ωB97XD-calculated error values were 111, 09, and 05 nm, correspondingly. These effects show that the TD-ωB97XD has a desirable contract to C1-1. From the view of these factors, the TD-ωB97XD approach confirmed a minimal error value. Therefore, UV–Vis spectra of the A1–A3 molecules were calculated by the TD-ωB97XD/6-31G(d,p) technique. All calculations for the C1-1 and A1–A3 dyes were completed on DFT and TD-DFT with Gaussian 09w suite \[25\]. The absorption spectra were captured by the usage of GaussSum \[26\].

Results and discussion

Optimized structures of the A1–A3 dyes

As discussed in the previous section, the selected three main types of dyes were prepared from C1-1 based on the acceptor group. Acceptor alteration is an essential part of D-π-A building to achieve NLO and high PCE of a PV system. From the literature, the acceptor screening groups were extremely performed for the efficient DSSCs. In the present study, those components would be stimulated on the C1-1-based dyes for optoelectronic applications.

The optimized geometry structures of the A1–A3 molecules were calculated by using B3LYP hybrid functional and the 6-31G(d) basis set. The A1–A3 dyes in geometry structures were displayed in Fig. 2. To suggest dyes on the TiO2 anchoring group, viz., cyanoacetic acid, was changed to each of the molecules at the acceptor segment. It has been anticipated that the capability of dyes would keep the co-planarity amongst the anchoring group and the spacer part in order to facilitate that the CT process from D-A moieties to the semiconductor CBE of TiO2 effectively. As shown in the figure, all the dyes were revealed the co-planar structures. It has been indicated that the better electron delocalization and improved ICT properties.

Electronic transition of the A1–A3 dye structures

The molecular charge distribution of A1–A3 dyes was executed on the molecular orbitals (MOs) transition to explore the further vision. Based on the photoexcitation process, the electron spread of the highest occupied MOs (HOMOs) has shifted to the lowest unoccupied MOs (LUMOs). It has been contributed to the consequence of electron injection and dye regeneration processes. Commonly, D and A groups have accomplished the HOMO and LUMO energy levels of the D-π-A molecules. The HOMOs and LUMOs as well as their charge spreading were major aspects that describe the presentation of optoelectronic devices. Here, MOs of the A1–A3 dye derivatives in HOMOs and LUMOs were calculated by the B3LYP/6-31G(d) theory and distributions have shown in Fig. 3. The figure has exhibited the distribution of
The absolutely calculated HOMOs, LUMOs, and energy gap ($E_g$) values of the A1–A3 dyes were presented in Table 2. From the table, HOMOs energies values were given in the range from $-4.98$ to $-5.35$ eV and the LUMOs energies range from $-2.48$ to $-2.60$ eV. Furthermore, HOMOs energies were in the order of A1 < A2 < A3 and the LUMOs energies were in the following order: A1 < A2 < A3. From the above order, a higher LUMOs energies would enhance the open-circuit photo-voltage, important to obtain a higher efficiency in the DSSCs. The $E_g$ values of the dyes were increased order of: A1(−2.50) < A2(−2.62) < A3(−2.75). From the following order, A1 has the smallest $E_g$, compared to other molecules and C1-1 (−2.53 eV). Some reports demonstrated that the dyes with a smaller $E_g$ revealed better PV performance [27, 28]. It has been anticipated that the A1 dye with a lesser $E_g$, which has taken a maximum absorption wavelength for enhancing PV properties.

A1–A3 dye molecules in frontier molecular orbital analysis

Intramolecular charge transfer (ICT) plays a very significant role to determine the entire PV device. The ICT actions were justified from the FMOs contribution. The role of the dye strongly identified the ICT behavior by considering the FMOs system. The HOMO and LUMO plots were revealed the characteristics of π-type orbital features. Also, HOMOs have shown an antibonding character and the LUMOs a bonding characters about the two adjacent fragments. A strong electron-D group has a high HOMOs energy, while a strong electron-A group resulted in low LUMOs energies. FMOs of the A1–A3 compounds were computed by the B3LYP/6-31G(d) level and shown in Fig. 4. From the figure, CBE of TiO2, the redox potential of the electrolyte system was compared to the HOMOs and LUMOs. Furthermore, all LUMO levels of the A1–A3 dyes were lying above the CBE of TiO2 surface (−4.0 eV). It has been designated that the electron injection process could easily be injected from the excited state of dyes to the TiO2. The efficient and fastest electron injection technique was helpful to the enhancing performance of DSSCs. Meanwhile, all HOMOs levels of the A1–A3 molecules lie below the redox couple (−4.8 eV).
It has been confirmed that the charge regeneration of the dye sensitizer is important as per the literature [29].

Consequently, all the dyes were shown potential energies for specified large absorption UV–Vis spectra of the DSSCs. In particular, the A1 molecule has been identified as a positive applicant for the longer and wider wavelength absorption.

**Table 2** The HOMOs, LUMOs and energy gap ($E_g$) of the C1-1 and A1–A4 dyes were calculated by the B3LYP/6-31G(d) level of theory

| Dyes   | HOMOs (eV) | LUMOs (eV) | Energy gap ($E_g$) (eV) |
|--------|------------|------------|------------------------|
| C1-1   | −5.03      | −2.50      | 2.53                   |
| A1     | −4.98      | −2.48      | 2.50                   |
| A2     | −5.20      | −2.58      | 2.62                   |
| A3     | −5.35      | −2.60      | 2.75                   |

**Fig. 4** The FMOs energy levels of the C1-1 and A1–A3 dyes were calculated by using B3LYP/6-31G(d) method.
of the PV device. Furthermore, these dyes could be provided to the highest \( J_{SC} \) for enhancing the overall PCE of DSSCs.

### UV–vis absorption spectra analysis of the A1–A3 dyes

The optical absorption spectra were recorded for the C1-1 and planned dyes in ethanol solution by the CPCM-TD-\( \omega \)B97XD/6-31G(d) theory and presented in Fig. 5. The simulated results of the A1–A3 dyes were revealed the extreme peak in the 400–500-nm region. All dye molecules were shown that the strong wavelength in the absorption region, which have attributed to the \( S_0 \rightarrow S_1 \) states. Also, the absorption bands were contributed to the strong ICT between D-A groups. The calculated outcomes have shown that the maximum peaks of dyes were generally related to the smaller HOMOs-LUMOs gap. As seen in the figure, the lower absorption bands were calculated as 426 and 396 nm for A2 and A3, which was contributed to a \( \pi-\pi^* \) transition. The highest absorption peak has 489 nm for A1 dye that contributed to the ICT between HOMOs to LUMOs. It has been generated by an efficient charge-separated state. Also, A1 dye has the best tuned acceptor than the other dyes, due to their outspread absorption peak.

The computed vertical excitation energies (\( E \)) corresponding wavelengths (\( \lambda_{\text{max}} \)), oscillator strengths (\( f \)), LHE, and orbital contributions of the S1 state in A1–A3 dye values were listed in Table 3. As compared with dye C1-1, the initiations of A1 lead to 26-nm red-shift and A2 and A3 dyes were blue-shifted by 37 and 67 nm, respectively. The higher molar extinction coefficient is a very significant aspect of the light absorption ability of the dyes.

| Dyes | Wavelength Energy (eV) | Oscillator strength (f) | LHE | Major transitions |
|------|------------------------|------------------------|-----|-------------------|
| C1-1 | 2.67                   | 463                    | 1.843 | 0.985            |
| A1   | 2.53                   | 489                    | 1.918 | 0.987            |
| A2   | 2.90                   | 426                    | 1.767 | 0.982            |
| A3   | 3.13                   | 396                    | 1.907 | 0.987            |

Among all the dyes, A1 (13.89 \( \times \) 10^4 M⁻¹ cm⁻¹) and A3 (13.81 \( \times \) 10^4 M⁻¹ cm⁻¹) provide the highest molar extinction coefficient, compared to C1-1 (13.35 \( \times \) 10^4 M⁻¹ cm⁻¹). From these results, A1 has favored the highest light-harvesting capabilities and would improve photocurrent response in DSSCs.

### PV properties

#### Power conversion efficiency

Power conversion efficiency (PCE) of the DSSCs device were generally determined by the \( V_{OC} \), \( J_{SC} \), \( FF \), and intensity of the incident light (\( P_{INC} \)); it is expressed as follows Eq. (1) [30]:

\[
P_{CE} = \frac{V_{OC} J_{SC} FF}{P_{INC}}
\]

In DSSCs, \( V_{OC} \) is predominantly derived by the redox electrolyte and CBE of TiO\(_2\) surface. Commonly, \( I^-/I_3^- \) solution has been used as the redox couple, it has taken as a constant. So, the shift of CBE was calculated by using the formula as per the literature [31]. The dipole moment of the dye molecules has played some critical aspects in the electronic charge distribution. It has noticed that the highest dipole moment of the dyes leads to large a CBE shift of TiO\(_2\), which resulted in larger \( V_{OC} \). The A1–A3 dyes calculated from the vertical dipole moment values have presented in Table 4. From the above table, the absolute values were calculated as 16.58, 12.87, and 6.64 Debye, respectively. Here, A1 and A2 dyes have a larger dipole moments, compared to other molecules and C1-1 (10.94 Debye). Based on these results identified, the dyes leading to higher \( V_{OC} \) can be an excellent agreement with PCE.
The important factor of $J_{SC}$ was influenced by $\Delta G_{\text{reg}}$ of the A1–A3 dyes. From these influence factors, it has been performed with the dye and redox couple. From literature, to obtain faster CT needs of the low regeneration [37]. Accordingly, A1–A3 dyes were taken the lower dye regeneration efficiency of DSSCs. The absolute calculated $\Delta G_{\text{reg}}$ values of the C1-1 and A1–A3 dyes were displayed in Table 4. From the table, A1 dye has lower than the other dyes and C1-1 (0.23 eV); it has the fastest CT and extreme usage in PCE of the DSSCs.

### Theoretical open-circuit photovoltage

The maximum theoretical values of A1–A3 were calculated by the used formula as per the literature [38]. The $\epsilon V_{OC}$ absolute calculated values of the A1–A3 dyes were listed in Table 4. From the table, A1–A3 dyes have ranges from 1.40 to 1.52 eV, respectively. These values were abundant for a positive response to the electron injection process. Particularly, A1 dye has a larger $\epsilon V_{OC}$ compared to C1-1 (1.50 eV) and other dyes. It has been represented as the excellent overall performance of DSSCs. From these outcomes, the modified effect of A1–A3 molecules can be used as the dye-sensitized, because of the electron injection technique from the first singlet state dyes into CBE of TiO$_2$ and dye regeneration would be promising to the organic DSSCs.

### Exciton binding energies of the A1–A3 dyes

To get high PCE, the electron–hole pairs should be split into separate negative and positive charges to escape from recombination owing to Coulombic forces. During this procedure, the exciton binding energies ($E_b$) need be overcome; i.e., the dyes must take lower exciton binding energies to attain high PCE of DSSCs. The $E_b$ of A1–A3 dyes was evaluated by using the formula from the earlier study and the corresponding values were listed in the Table 4 [39, 40]. From the

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**Table 4** The calculated redox potential of the ground state ($E_{\text{OX}}^{\text{dye}}$), oxidation potential of the dye ($E_{\text{OX}}^{\text{dye}}$ in eV), absorption energy ($\lambda_{\text{max}}$ in eV), free energy change for electron injection ($\Delta G_{\text{inject}}$ in eV), dye regeneration ($\Delta G_{\text{reg}}$ in eV), open-circuit photovoltage ($\epsilon V_{OC}$ in eV), exciton binding energy ($E_b$), chemical hardness ($\eta$), and dipole moment ($m_{normal}$ in Debye) of the studied dye molecules at the TD-oB97XD/6-31G(d) level of theory in ethanol medium.

| Dyes   | $E_{\text{OX}}^{\text{dye}}$ (in eV) | $\lambda_{\text{max}}$ | $E_{\text{OX}}^{\text{dye}}$ | $\Delta G_{\text{inject}}$ | $\Delta G_{\text{reg}}$ | $\epsilon V_{OC}$ | $E_b$ | $\eta$ | $m_{normal}$ (Debye) |
|--------|---------------------------------|------------------------|----------------------------|---------------------------|------------------|------------------|------|------|-------------------|
| C1-1   | 5.03                            | 2.67                   | 2.36                       | -1.64                     | 0.23             | 1.50             | 0.14   | 1.03   | 10.94             |
| A1     | 4.98                            | 2.53                   | 2.45                       | -1.55                     | 0.18             | 1.52             | 0.13   | 0.98   | 16.58             |
| A2     | 5.20                            | 2.90                   | 2.30                       | -1.70                     | 0.40             | 1.42             | 0.28   | 1.20   | 12.87             |
| A3     | 5.35                            | 3.13                   | 2.23                       | -1.77                     | 0.55             | 1.40             | 0.38   | 1.10   | 6.64              |

The driving forces in electron injection and dye regeneration of the derivative dyes

The A1–A3 dye molecules of the electron injection ($\Delta G_{\text{inject}}$), oxidation potential energy ($E_{\text{OX}}^{\text{dye}}$), and dye regeneration ($\Delta G_{\text{reg}}$) were calculated by using the formulae in literature [34] and the corresponding values were listed in Table 4. The calculated results have shown that all these parameters were determined the $J_{SC}$ It has more probable to the theoretical calculations of the DSSCs. According to the earlier study, $\Delta G_{\text{inject}}$ as the unrelaxed excited state of sensitizers to the CBE of semiconductor substrate was anticipated successfully [35]. In view of Islam theory, it has $\Delta G_{\text{inject}} > 0.2$ eV [36]. Accordingly, A1–A3 dyes have greater than 0.2 eV. From the table, it has obvious that all $\Delta G_{\text{inject}}$ values of the A1–A3 dyes were negative. Therefore, a first singlet excited state of the dyes lies overhead the CBE of the TiO$_2$ surface successfully. From the table, A1–A3 dyes were given in the ranges from $-1.55$ to $-1.77$ eV among the first excited state dyes to CBE on TiO$_2$. Consequently, all the dye molecules have a probable D-π-A scheme and could be the best application in DSSCs.
table, A1–A3 dyes absolutely calculated values were 0.13, 0.28, and 0.38 eV, respectively. As shown in Table 4, A1 dye has smallest $E_b$ value than the other sensitizers and C1-1 (0.14 eV), which indicates an excellent act for DSSCs.

**Non-linear optical properties of the A1–A3 dyes**

In the past decade, numerous research groups studied non-linear optical properties (NLO) feedback to the usage of dye molecules [41–43]. A small $E_b$ results deliver the superior NLO belongings. The NLO performances were measured that the most sensitive systems to study the dye molecular patterns. As the probabilities of dye materials for NLO procedures were recognized, NLO belongings of such materials were examined by theoretical techniques. The NLO belongings indicate the response of a molecular system in an applied electric field. The polarizability ($\alpha$) describes the capability of an electric field to alter the electronic spreading of a dye molecule. The first higher order hyperpolarizability ($\beta$) designates the NLO response of molecular systems. Moreover, the NLO system has been convinced to the ICT in D-π-A organic dyes. Hence, NLO might be used as the chosen for PCE of CT dye molecules; it affects the $J_{SC}$ of DSSCs. In the D-π-A scheme, the NLO system alteration with the acceptor has linked to the PV demonstrations of the designed dyes.

In this work, NLO properties of the tensor components were calculated at used formulae in literature [28] and the corresponding values were listed in table S1. The $\alpha$ is directly correlated to the dipole moment and the $\beta$ is inversely proportional to the transition energies [44]. From table S1, the $\alpha$ absolutely calculated values were A1 (203 a.u.), A2 (199 a.u.), and A3 (196 a.u.), respectively. The greatest value of the A1 and A2 dyes was $(3.01 \times 10^{-23}$ e.s.u., and $2.95 \times 10^{-23}$ e.s.u.), compared to C1-1 $(2.55 \times 10^{-23}$ e.s.u.), except A3. The extreme value of $\beta$ is the best NLO activity of the dye and is closely connected with ICT. Accordingly, all the dyes are possible responses to the NLO system. As shown in table S1, the A1–A3 dyes the ranges from $4.44$ to $14.93 \times 10^{-30}$ e.s.u., respectively. In particular, A1 dye has minimum transition energy (2.53 eV got in TD-DFT technique) indicates the larger $\beta$ value of $14.93 \times 10^{-30}$ e.s.u. The quantum chemical studies were revealed that valuable in the details of the correlation among the electronic structure and its NLO response. The current outcomes demonstrate that the A1 is the most apt dye for usage in NLO properties.

**Chemical hardness**

Chemical hardness ($\eta$) is an appropriate parameter for studying the activity of chemical structures. It has defined as the second derivative energy with respect to the number of electrons [45, 46]. The $\eta$ may be a dependable measure to select the best sensitizer. The lower $\eta$ gets to higher conversion efficiencies. The earlier report on $\eta$ has signified the ICT transfer [47]. Therefore, lower $\eta$ denotes higher CT ability and thus could be a promising and more efficient. All the calculated $\eta$ values were listed in Table 4. From the table, it can be predicted that A1 (0.98 eV) has the best dye as compared to other sensitizers and C1-1 (1.03 eV). Also, these molecules have the greatest applicant for ICT. Overall, A1 dye have well suitable for together hole and electron carrying compared to C1-1.

**Conclusion**

In summary, a new D-π-A of the A1–A3 molecules was designed based on tetrahydroquinoline (C1-1) and made to use for optoelectronic applications. The ground-state and UV–Vis spectra of the A1–A3 dyes were executed by the DFT and TD-DFT methods. The substituted influence of the A1–A3 acceptor groups on the geometries and electronic structure, UV–Vis absorption, light-harvesting efficiencies, electron injection, dye regeneration, open-circuit photovoltage, exciton binding energies, chemical hardness, and PV properties were investigated successfully. The electron-separated state among the HOMOs and LUMOs has enhanced to the ICT. The A1–A3 dyes were revealed spatially overlapped HOMOs and LUMOs transitions. Moreover, it has shown that the acceptor parts have excessive effects on the optical belongings of A1–A3 dyes and the efficiency of the organic DSSCs. The NLO activity of the A1–A3 dyes was calculated by the polarizability and first-order hyperpolarizability, effectively. From the studied outcome, the A1 molecule has the best dye for NLO performance. Finally, a theoretical result has delivered that the elaborate research carried out for capable of organic dyes in D-π-A system to enhance the optoelectronic properties.

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**Data availability** All the data and electronic materials available for Gaussian program.

**Declarations**

**Competing interests** The authors declare no competing interests.
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