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Microwave assisted structural engineering on efficient eco-friendly natural dye alizarin for dye sensitized solar cells application

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ARTICLE INFO

Keywords: Dye sensitized solar cells Fluorescence quenching DFT HOMO-LUMO Photoinduced electron transfer

ABSTRACT

The novel eco-friendly natural dyes, (9E, 10E), -9, 10-bis(2-(4-nitrobenzylidene) hydrazono) -9,10 dihydroanthracene-1,2-diol (NHA) have been synthesised using the one-pot microwaveassisted solvent evaporation method, and physicochemical characterizations were carried out using ¹H NMR, ¹³C NMR, GC-MS, and FT-IR data. The photophysical properties of NHA dye were determined using experimental and theoretical techniques. The Stoke's shift shows a large bathochromic shift in polar solvents, which is due to the $\pi \rightarrow \pi^*$ transition. The ground-state optimization of NHA dye was carried out using density functional theory (DFT) with the B3LYP/6-31 G level basis set. The HOMO-LUMO and energy band gap values computed from density functional theory and absorption threshold wavelengths are good agreement with each other. Further, the effect of TiO₂ nanoparticles on NHA dye has been studied using spectroscopic and electrochemical techniques. It was observed that, NHA dye showed fluorescence quenching in the presence of TiO₂ NPs, which is due to the photo induced electron transfer process. The apparent association constant of the interaction between NHA dye and TiO2 nanoparticles is also calculated using the Benesi-Hildebrand model. The Rehm-Weller relation infers that thermodynamically favourable electron transfer takes place between dyes and TiO2 NPs. Further, the solar cell was constructed using NHA dye as a sensitizer, and the photovoltaic conversion efficiency was found to be 1.16%.

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https://doi.org/10.1016/j.ijleo.2023.171090

Received 29 September 2022; Received in revised form 29 May 2023; Accepted 18 June 2023 Available online 19 June 2023 0030-4026/ \odot 2023 Elsevier GmbH. All rights reserved.

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1. Introduction

Solar power is an attractive, clean, and renewable source. The sun emits enough solar power to fulfil the entire human energy demand. However, as of 2022, less than two percent of the world's energy came from solar. Historically, the conversion of solar energy into electrical energy has been expensive and relatively inefficient. Therefore, research focused on the development of high efficiency, low-cost, and environmentally benign solar cells is inevitable [1].

There has been a continuous effort in searching for affordable organic solar energies, among which, dye sensitized solar cells (DSSC) got maximum attention because of their ease of fabrication, low-cost, semi-flexibility, and semi-transparency. The conventional DSSC devices consist of a photoanode, dye sensitizer, redox electrolyte, and counter electrode. In the process of sunlight harvesting, organic dye plays an important role in most of the optoelectronic device. [2]. For example, electron injection into TiO_2 nanoparticle energy levels, and dye regeneration with the help of redox in the electrolyte. Subsequently, in recent studies on DSSC devices, the introduction of various organic dyes with fantastic and high-end optoelectronic properties has been highly sought. Among them, Donor- π -Acceptor (D- π -A) substituted organic dyes have fascinating advantages such as high abundance, a large molar extinction coefficient value, being less toxic, and a low cost of synthesis, which makes them superior over conventional metal dyes for DSSC [3–6].

The main characteristics of D- π -A substitute organic dyes include the pull-push tendency, which leads to an increase in the intramolecular charge transfer (ICT) from the donor to the acceptor through the π -bridge upon light absorption [7–9], which can red-shift the absorption spectrum compared to the typical $\pi \rightarrow \pi^*$ transitions in a conjugated organic molecule, which with the solar irradiation profile and beneficial to light harvesting. Moreover, the ICT process governs the inherent photovoltaic potential of a pure organic dye. Also, the D- π -A structure offers great potential for property tuning at electronic levels.

The HOMO and LUMO are feasible by changing D-, π -, and A-moieties and/ or bonding modes of dyes and assembling these to tune the dyes dynamically promising for electron injection into TiO₂ and dye regeneration. Furthermore, donor-localized HOMO-electrons and acceptor-localized LUMO-electrons are made feasible in the D- π – A structure, which renders the electron injection in TiO₂ [10, 11]. In quest of organic dyes containing the above properties for DSSC, a variety of molecules have been synthesized, viz, electron rich donors of carbazole [12], triarylamine [13], phenothiazine [14] and indoline [15]. Electron deficient anchoring acceptors of cyanoacrylic acid [16] and rhodanine-3-acetic acid [17], and conjugated bridges of oxadiazole [18] and imidizole [19]. Among them, Alizarin (1,2-dihydroxyanthraquinone) a heterocyclic aromatic compound that is widely present in the root of madder and has been used as a photosensitizer for TiO₂ nanoparticles in DSSC [20]. In addition to that, alizarin dyes based on thieno[3,2-b] thiophene conjugated bridges and cyanoacrylic acid acceptors have been applied to DSSC and exhibit excellent photoelectrical properties [21].

In light of the foregoing, we changed the natural alizarin dye in our study by inserting donor – π – acceptor substitution groups. Further, photosensitization of TiO₂ nanoparticles (~25 nm) by newly synthesised NHA dye has been studied using spectroscopic as well as electrochemical techniques.

2. Material and methods

The reagents employed in the synthesis of high purity commercial samples that were used as received (Fischer, Merck, and Sigma Aldrich). Reactions were carried out in an oven-dried RB flask. TLC was performed on alumina silica gel 60F254 (Fischer) detected by UV light (254 nm) and iodine vapors. The melting points were determined by open capillaries on a Buchi apparatus and are



Scheme 1. synthesis of bis-4-NBAlz (NHA).



Fig. 1. Normalised absorption (a) and fluorescence spectra (b) of NHA in different solvents.

uncorrected. The reaction sequence is applied for the synthesis of (9E, 10E)-9, 10-bis(2-(4-nitrobenzylidene) hydrazono)-9,10dihydroanthracen-1,2-diol(bis-4-NBAlz) using a stoichiometric mixture of alizarin and 4-nitro-phenyl-hydrazin in absolute ethanol, with a catalytic amount of acetic acid. The reaction mixture was placed in a conventional microwave oven and irradiated with microwave radiation to obtain a novel derivative of 1,2 dihydroxy – 9,10-anthraquinone. The structural identities and purities confirmed by 1 H NMR, IR, and MS (instrumentation details) were found to be in good agreement with the proposed structures. The absorption and fluorescence spectra were recorded using the Carry-100 and Hitachi F-7000 instruments, respectively. Cyclic voltammetry (CV) studies were carried out using an electrochemical analyzer/work station (model: CHI1112C, series, USA) at 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as a supporting electrolyte with a scan rate of 1 mVs⁻¹. The geometrical optimization of the synthesised dye was estimated by DFT calculations using the B3LYP/6–31 G and B3LYP/6–31 G (d,p) level basis set as implemented in the Gaussian 09 program package. The TiO₂ nanoparticles have been purchased from Sigma Aldrich Pvt. Ltd. India, and used without further purification.

2.1. Synthetic procedure

Stoichiometric mixture of alizarin (1) (1 equivance of 2 g, 0.0083 moles) and 4-nitro-phenyl-hydrazin (2) (2 equivance of 2.74 g, 0.0166 moles) is taken in 15 mL of absolute ethanol. A catalytic amount of acetic acid was added, and the reaction mixture was irradiated using microwave radiation for 2 min. A dark brown solution was obtained. The crude mixture was poured into ice cooled water with continuous stirring. The completion of the reaction was monitored by TLC, and then the brown coloured crude product was washed with water and dried. As obtained residue was further recrystallized from ethyl acetate to get analytically pure orange coloured NHA dye. The schematic synthesis of NHA is represented in Scheme 1, and spectral information is given in 2.2.

2.2. Spectral data characterization



(s, 2 H, Ar-H), 7.54 (d, 4 H, Ar-H), 7.5 (s, 3 H, Ar-H), 7.49 & 7.48 (s, 1 H, Ar-H), 4.7 (s, 2 H, Ar-OH). ¹³C NMR (100 MHz, DMSO, 6 ppm)

Table 1

Solvatochromic data of NHA.

Solvent	λ_a (nm)	$\lambda_{\rm f}$ (nm)	$\Delta\lambda$ (nm)	ϕ_s	Egopt	Fluorescence Lifetime (ns)
Benzene	423	468.0	45	0.44	2.931	2.51
Ethyl Acetate	426	473.0	47	0.49	2.911	2.52
Ethanol	428	479.0	51	0.49	2.897	2.51
Methanol	433	481.0	48	0.41	2.864	2.51
DMSO	434	484.0	50	0.41	2.857	2.54

164.2, 164.0, 152,3, 151.4, 150.1, 150.0, 148.2, 148.0, 143.4, 143.0, 129.9, 129. 1, 128.9, 128.3, 127.4, 127.2, 126.1, 125.7, 125.7, 125.2, 122.1, 123.6, 120.4, 119.3. IR (KBr) (v_{max} /cm⁻¹): 3400 (-OH stretching), 3020 (Ar-H), 1768–1628 (C=N-N = C), 1521–1329 (N-O), 711 (NO₂ deformation). Mass spectra of the compound showed molecular ion peak at *m/z*: 534 [M⁺] ion peak.

3. Results and discussion

3.1. Photo physical studies

The absorption and emission spectra of NHA dye with varying solvent polarity were shown in Fig. 1. The values of the absorption and emission maxima of the molecule are given in Table 1. The molecule shows a large bathochromic shift, which is due to the $\pi \rightarrow \pi^*$ transition from the alizarin to the nitrophenyl ring [22]. The quantum yields (Φ s) of the synthesised dye were experimentally determined by comparing them with the standard fluorescent dye of known quantum yield [POPOP laser dye ($\phi_R = 0.97$)] in different solvents using Eq. (1) and the values are given in Table 1. [23].

$$\phi = \phi_R \frac{I_s OD_R n_s^2}{I_R OD_s n_R^2} \tag{1}$$

Where, ϕ , I, OD and n represents quantum yield, integrated fluorescence intensity, optical density, and refractive index, and S and R represent the sample and reference, respectively. From Table 1, it was observed that synthesised dye has a good quantum yield and increases with an increase in solvent polarity. The change in quantum yield may be due to the formation of a hydrogen bond between the hydroxyl group of the NHA dye and the solvent environment. In addition, one possible mechanism for this effect is that a polar solvent can help stabilise the excited state of the molecule by forming a solvent shell around it. This can reduce the probability of non-radiative relaxation processes that would lead to heat dissipation rather than fluorescence emission. Polar solvents can also increase the rate of energy transfer from the excited molecule to the solvent, which can enhance the probability of fluorescence emission. This is because a polar solvent can have a higher refractive index and a higher dielectric constant, which can increase the local electric field and lead to more efficient energy transfer. However, it is important to note that the effect of solvent polarity on fluorescence quantum yield can depend on several factors, including the specific molecule, the electronic properties of its environment, and the type and concentration of the solvent [24].

In electronic transitions, the dye absorbs photons in the UV–visible spectral range and promotes an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [25] and difference between these two energy levels is called the energy band gap (E_g). The value of the energy band gap can also be determined from the onset low energy side of the experimentally recorded absorption spectra (λ_{onset}) using Eq.2 [25]. The values of the optical band gap in different solvents are given in Table 1.

$$E_{g} = \frac{1240}{\lambda_{onset}} (eV)$$
⁽²⁾

It was observed that, on changing solvent media from non-polar to polar, the optical band gap of NHA dye decreased from 2.931 eV to 2.857 eV. This may be due to the formation of a hydrogen bond between the hydroxyl functional group of the dye and the solvent environment. In addition, when an organic molecule is dissolved in a polar solvent, the polarity of the solvent can interact with the polar groups in the molecule, leading to a change in the distribution of electron density within the molecule. This interaction can result in a stabilization of the HOMO and LUMO energy levels, leading to a decrease in the energy band gap of the molecule. In addition, the solvent can also affect the overall geometry of the molecule, which can affect the overlap between the HOMO and LUMO orbitals and thereby influence the energy band gap. In a polar solvent, the molecular geometry may be altered due to changes in intermolecular interactions, leading to a decrease in the energy band gap [26].

The fluorescence lifetime of the molecule was calculated using pulsed excitation energy source and was calculated in a different solvent using Eq. (3).

$$I(t) = (A_1 \tau_1 + A_2 \tau_2)$$
(3)

Where τ_1 and τ_2 represent the short and longer lifetime components with their normalised amplitude components A_1 and A_2 respectively. The decay profile was fitted with a bi-exponential function with χ^2 value close to unity [26].

The fluorescence decay profiles of the NHA dye were recorded in dimethyl sulfoxide and are shown in Fig. 2. The fluorescence



Fig. 2. Fluorescence decay profile of NHA dye.

Table 2 The value of ΔE , E_{HOMO} and E_{LUMO} for NHA dye.

Theoretical model	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)
DFT-B3LYP-6–31 G	-5.758	-3.041	2.717
DFT-B3LYP-6–31 G (d,p)	-6.039	-2.897	3.141



Fig. 3. Optimised molecular geometry and molecular orbital amplitude plots of NHA in gaseous phase obtained using B3LYP/6-31 G level basis set.

decay profile of the NHA dye in dimethylsulfoxide is best fitted with a bi-exponential fitting model with χ^2 value equal to 1.01, similarly, the fluorescence decay profile of the NHA dye is recorded in different solvents, and their fluorescence lifetimes are mentioned in Table 2. The results revealed that, on changing media from nonpolar to polar, fluorescence lifetime increased from 2.51 ns to 2.54 ns. The interaction between the electronic excited state of the dye and the surrounding solvent media was observed, which was evident by the decrease in magnitude of the non-radiative rate constant upon an increase in solvent polarity [27].

The optimised ground state geometry of the NHA dye in the gas phase is determined theoretically by quantum chemical calculations. The computations were carried out using the Gaussian 09 W programme and analysed with the help of the Gauss View 5.0 visualisation program. The ground state geometry optimization is performed at the density functional theory (DFT) level of theory by employing the B3LYP (Becke, three-parameter, Lee-YangParr) functional with the 6–31 G and the polarization functions 6–31 G (d, p) level basis set. The optimized ground state molecular geometry, HOMO, and LUMO of the NHA dye were optimized using the DFT-B3LYP-6–31 G basis set and are shown in Fig. 3. The optimized ground state molecular geometry, HOMO, and LUMO of the NHA dye

(4)



Fig. 4. The absorption spectra of NHA dye in the absence and presence of TiO₂ NPs (1×10^{-4} M to 6×10^{-4} M) in acetonitrile.



Fig. 5. Steady state fluorescence spectra of NHA in the absence and presence of TiO₂ NPs in acetonitrile excited at 429 nm.

were also optimized using the DFT-B3LYP-6–31 G (d,p) levels basis set and are shown in Fig. S4. The energy band gap (ΔE) of NHA dye was calculated using energy level of HOMO (E_{HOMO}) and energy level of LUMO (E_{LUMO}) obtained from levels using Eq.4.

$\Delta E = E_{HOMO} - E_{LUMO}$

The value of ΔE , E_{HOMO} and E_{LUMO} were given in Table 2 and it was found that the energy value derived from various basis sets exhibits varying values. The variation in the energy value is due to the addition of diffuse functions in basis sets, such as the (d, p) functions in DFT-B3LYP-6–31 G (d, p), allows for better description of diffuse electron densities, which can be important for systems with extended or delocalized electronic states. These diffuse functions can have an impact on the energy levels, including the energy band gap.

luminescence property of organic molecules can be predicted based on the spatial distribution of molecular orbitals, mainly those of HOMO and LUMO. The synthesised molecule showed a large E_{HOMO} value and a small energy band gap, which are essential properties for DSSC applications. From Fig. 3, it was observed that, NHA dye in the gaseous phase; at HOMO level, electron clouds were concentrated all over the molecule, whereas at LUMO level, the electron clouds were mainly located at 9,10 dihydroanthracene-1,2-diol. These results strongly support the good electron donating property of synthesised dye, which is essential for the application of DSSC. HOMO-LUMO values were obtained by theoretical and experimental (Cyclic Voltammeteric analysis) methods that were in good agreement with each other.



Fig. 6. Fluorescence decay curve of NHA in the absence and presence of TiO₂ NPs acetonitrile.

Table 3		
Values of TiO ₂ concentrations, fluorescence intensit	ty and fluorescence lifetime NHA dye with corresponding χ^2	values.

TiO_2 NPs Concentration $\times \ 10^{-4} \ M$	Fluorescence Intensity	Fluorescence Lifetime (ns)	χ^2
0	7463	2.54	1.10
1	7023	2.52	1.11
2	6761	2.51	1.12
3	6483	2.49	1.09
4	6203	2.48	1.11
5	5953	2.47	1.14
6	5737	2.45	1.12



Fig. 7. Steady state and time resolved S-V Plot of NHA.

The absorption, fluorescence, and fluorescence life time spectra of NHA were measured in the presence of TiO₂ nanoparticles to understand photosensitization of TiO₂ nanoparticles (NPs) using NHA dye. The absorption spectra of 1×10^{-4} M NHA dye in the absence and presence of TiO₂ NPs (concentration of TiO₂ nanoparticle varied from 1×10^{-4} M to 6×10^{-4} M) were recorded in acetonitrile at room temperature, as shown in Fig. 4. It was observed that, absorption spectra of NHA dye increased with the increase in concentration of TiO₂ NPs without shifting the peak position, and no new absorption peak was found, which may be due to

Table 4

Values of Stern-Volmer constant, bimolecular qu	quenching constant ar	nd association constant	of NHA in acetonitrile.
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Steady state method			Time resolved method		
Stern-Volmer constant (k _{sv})	Bimolecular quenching Constant $(k_q) \times 10^{11} \ \text{M}^{-1} \ \text{s}^{-1}$	Association Constant (K_a) $\times ~10^2~M^{-1}$	Stern-Volmer constant ($\dot{k_{sv}}$) × 10 ² M ⁻¹	Bimolecular quenching Constant ($k_q^{'} angle imes 10^{10}~{ m M}^{-1}~{ m s}^{-1}$	
491	1.952	3.530	58	2.982	



Fig. 8. Benesi-Hilderbrand linear analysis plot NHA with varying concentration of TiO₂ NPs in acetonitrile for NHA.

nanoparticles ability to scatter the incident light more efficiently than bulk materials, leading to an increase in the overall amount of light that interacts with the organic molecule.

The result revealed that, the formation of a ground-state complex between dyes and TiO2 NPs was prohibited. The steady state fluorescence and time-resolved fluorescence spectra of NHA dye were recorded in the absence and presence of TiO₂ NPs in acetonitrile at room temperature and are shown in Figs. 5 & 6. Table 3 represent the fluorescence intensity and lifetime values of NHA dyes in the absence and presence of TiO₂ NPs. It was observed that fluorescence lifetime and intensity decrease with increasing concentration of the TiO₂ NPs (Table 3). These spectral behaviours can be analysed using the Stern-Volmer relation [27], which is given by

$$\frac{I_o}{I} = 1 + k_{sv}[TiO_2]$$

$$\frac{\tau_o}{I} = 1 + k_{sv}[TiO_2]$$
(5)

Where, I_0 or τ_0 are fluorescence intensities or lifetime of NHA dyes in the absence of TiO₂ NPs. *I* or τ is the fluorescence intensities or lifetime of NHA dyes in the presence of TiO₂ NPs.

Using steady state and time resolved fluorescence values of the NHA dye, a Stern-Volmer (S-V) plot was drawn (Fig. 7). The values of the S-V constant and bimolecular quenching were tabulated in Table 4. The S-V plot found to be linear with an intercept equal to unity and the variation in S-V constant obtained from both methods suggest that, fluorescence quenching was due to a combined dynamic and static quenching process. The magnitudes of bimolecular quenching constants obtained from both methods suggest that short range interactions occur between NHA dye and TiO₂ NPs.

Further, stoichiometry and the association constant (K_a) of NHA dye with TiO₂ NPs were estimated from the Benesi-Hilderbrand equation [28],

$$\frac{1}{(I-I_0)} = \frac{1}{K_a[C][Q]} + \frac{1}{[C]}$$
(7)

Here, all the terms in the above equation have their usual meaning. 1/[Q] Vs. $1/(I - I_0)$ plots for dye-TiO₂ NPs systems were drawn (Fig. 8).

The Benesi–Hilderbrand plot was perfectly linear, which provided evidence for 1:1 stoichiometry between dyes and TiO_2 NPs. The association constant (K_a) was calculated by the ratio of intercept to slope and the values (Table 3). The K_a value was almost in the same range (10²) as the previously reported values [28].

The cyclic voltammogram (CV) of NHA dye in acetonitrile and dimethyl sulfoxide has been displayed in Fig. 9. The E_s of NHA were



Fig. 9. CV curves of NHA were measured in dimethylsulfoxide (A) and acetonitrile (B) in the presence of nBu₄NPF₆ at a scan rate of 100 mVs⁻¹.



Fig. 10. Normalised absorption and fluorescence spectra of NHA in acetonitrile.

2.944 eV and 2.834 eV for dimethyl sulfoxide and acetonitrile respectively. The reduction potential of TiO_2 was obtained from the literature, which was -0.5 V [29,30]. The absorption and emission spectra of dyes observed in Fig. 10 suggested that there is a overlap between the absorption spectra of TiO_2 NPs and emission spectra of NHA. Furthermore, it was also suggested that there is a possibility of resonance energy transfer between dyes and TiO_2 NPs. Using the Rehm-Weller relation, the energy transfer from dye to TiO_2 NPs can be estimated. The Rehm-Weller equation [31] is as follows.

$$\Delta G_{et} = E_{1/2}^{ox} + E_{1/2}^{red} + E_s + C$$

Where,

 $E_{1/2}^{ox}$ is the NHA dye oxidation potential.

 $E_{1/2}^{red}$ is the TiO₂ reduction potential.

 E_s is the excited singlet state energy of NHA dye and C is the coulombic term. Substituting the values of E_s in Eq.8, the ΔG_{et} values for acetonitrile and dimethyl sulfoxide were determined as -3.593 eV and -3.342 eV respectively and the coulombic term was neglected since in polar solvents the columbic term was very small. The magnitude of ΔG_{et} is greater in acetonitrile than in dimethyl sulfoxide indicating a prominent thermodynamically favorable electron transfer process from NHA dye to TiO₂ NPs in acetonitrile than in dimethyl sulfoxide.

(8)



Fig. 11. The schematic energy level diagram of photo induced electron transfer from NHA to TiO₂ NPs.



Fig. 12. Photo-current density-voltage (J-V) characteristics of the best performed DSSC of NHA dye.

3.2. Fabrication of dye-sensitized solar cell

Commercial TiO₂ nano powder (\sim 25 nm) was mixed with alpha-teripenol and ethyl cellulose to form TiO₂ paste. A10 µm thick TiO₂ layer was coated on fluorine doped tin oxide (FTO) with an active area of 0.25 cm² by the doctor-blade technique. TiO₂ photoanode was annealed at 500 °C for 30 min and then soaked in 10 mM dye dissolved in tertbutyl alcohol and acetonitrile solution (1:1). A counter electrode was prepared by doctor-blade coating of the platinum paste on to the FTO surface, which was annealed at 400 °C for 10 min. A 25 µm thick Surlyn film was used to fabricate the cell. DSSC was completed upon the injection of the electrolyte through the pre-drilled hole.

3.2.1. Photo-electrochemical measurement

The electrochemical properties of dyes were explored by cyclic voltammetry (CV). The HOMO–LUMO band gap was derived from the difference between HOMO and LUMO energy levels. HOMO energy levels [32] were calculated using the following equation

$$HOMO = -\left[E_{OX}^{ONSET} + 4.44\right]eV$$
(9)

The lowest unoccupied molecular orbital (LUMO) is equal to the HOMO level minus zero-zeroth energy (ΔE_{00}). Where, zero-zeroth energy ($\Delta E_{00} = 1240/\lambda$) of the NHA dye alone is the intersection of the normalised absorption and fluorescence spectra (Fig. 10) and it was found to be 2.799 eV. Thus, the observed LUMO level was - 3.041 V which lies well above the conduction band edge of TiO₂ ensuring the required driving force for electron injection from the dye into the TiO₂ semiconductor. Fig. 11 shows the schematic

Table 5				
Optimized p	ohotovoltaic	parameters	values	of NHA.

V _{oc} (mV)	J_{sc} (mAcm ⁻²)	FF	η
613	4.31	46.29	1.16

theoretical energy level diagram of each component of the dye sensitized TiO_2 electrode.

The efficiency (
$$\eta$$
) and fill factor (FF) [33] according to Eqs. 10 and 11 are

$$\eta = \frac{J_{sc}V_{oc}FF}{I_o} \times 100$$
(10)
FF = $\frac{V_{max} \times qV_{max}}{J_{sc} \times qV_{oc}}$
(11)

Where, V_{oc} , J_{so} , V_{max} , J_{max} and I_0 are the open circuit voltage, short circuit current density, maximum power point voltage, maximum power point current density, and total incident irradiance ($I_0 = 1000 \text{ W/m}^2$). The plots of photo-current density (J) versus voltage (V) are shown in Fig. 12. The values of V_{oc} , J_{so} , η and FF are shown in Table 5. Photovoltaic conversion efficiency (η) of DSSC sensitized with NHA dyes was found to be 1.16% under AM 1.5 irradiation (1000 W/m²). The photovoltaic conversion efficiency of dyes is lower than that of standard dye, and this may be due to the lower value of the molar extinction coefficient of dyes or to some other regions that need further investigation.

4. Conclusion

In the present work, D- π -A substituted alizarin derivative (NHA) has been successfully synthesized and the photo physical properties of NHA dye were calculated using experimental and theoretical (density functional theory) techniques. The physicochemical characterizations confirmed the structure of the NHA dye. The Stoke's shift showed a large bathochromic shift in polar solvents which is due to the $\pi \rightarrow \pi^*$ transition. The HOMO-LUMO energy gap computed using density functional theory and absorption threshold wavelengths is found to be in good agreement. Further, the photosensitization of TiO₂ nanoparticles using NHA dyes has been studied using spectroscopic and electrochemical investigations. For completeness, the association constant has been calculated from the Benesi–Hilderbrand relation, which suggested that there was a possibility of interaction between dyes and TiO₂ NPs. Fluorescence quenching of NHA in the presence TiO₂ NPs is due to combined static and dynamic quenching. The Rehm-Weller theory infers that, thermodynamically favorable electron transfer takes place between dyes and TiO₂ NPs. Thus, the solar energy harvesting process has been investigated using TiO₂-dyes fabricated solar cells. The photovoltaic conversion efficiency of fabricated DSSC was found to be 1.16%. Further improvement of the power conversion efficiency of DSSC may be achieved with further optimization of solar cell parameters.

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.

Data Availability

Data will be made available on request.

Acknowledgments

One of the authors (Shashikant Walki) is thankful to the Principal and Staff, Hirasugar Institute of Technology, Nidasosi-Karnataka, India, for the continuous support and encouragement. Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2023R24), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ijleo.2023.171090.

References

^[1] T. Ozden, A countrywide analysis of 27 solar power plants installed at different climates, Sci. Rep. 12 (2022), https://doi.org/10.1038/s41598-021-04551-7.

- [2] R. Ameta, S. Benjamin, S. Sharma, M. Trivedi, Dye-sensitized solar cells, Sol. Energy Convers. Storage.: Photochem. Modes 4 (2015) 85–113, https://doi.org/ 10.1201/b19148.
- [3] Z.S. Huang, C. Cai, X.F. Zang, Z. Iqbal, H. Zeng, D. Bin Kuang, L. Wang, H. Meier, D. Cao, Effect of the linkage location in double branched organic dyes on the photovoltaic performance of DSSCs, J. Mater. Chem. A Mater. 3 (2015) 1333–1344, https://doi.org/10.1039/c4ta05652cS.
- [4] Liu, Y. Jiao, Y. Ding, X. Fan, J. Song, B. Mi, Z. Gao, Position engineering of cyanoacrylic-acid anchoring group in a dye for DSSC applications, Dyes Pigments 180 (2020) 108470–108480, https://doi.org/10.1016/j.dyepig.2020.108470.
- [5] Z. Yao, H. Wu, Y. Li, J. Wang, J. Zhang, M. Zhang, Y. Guo, P. Wang, Dithienopicenocarbazole as the kernel module of low-energy-gap organic dyes for efficient conversion of sunlight to electricity, Energy Environ. Sci. 8 (2015) 3192–3197, https://doi.org/10.1039/c5ee02822a.
- [6] Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li, P. Wang, Donor/acceptor indenoperylene dye for highly efficient organic dye-sensitized solar cells, J. Am. Chem. Soc. 137 (2015) 3799–3802, https://doi.org/10.1021/jacs.5b01537.
- [7] C.T. Li, F.L. Wu, C.J. Liang, K.C. Ho, J.T. Lin, Effective suppression of interfacial charge recombination by a 12-crown-4 substituent on a double-anchored organic sensitizer and rotating disk electrochemical evidence, J. Mater. Chem. A Mater. 5 (2017) 7586–7594, https://doi.org/10.1039/c6ta11091f.
- [8] E. Gabrielsson, H. Ellis, S. Feldt, H. Tian, G. Boschloo, A. Hagfeldt, L. Sun, Convergent/divergent synthesis of a linker-varied series of dyes for dye-sensitized solar cells based on the D35 donor, Adv. Energy Mater. 3 (2013) 1647-1656, https://doi.org/10.1002/aenm.201300367.
- [9] S. Haid, M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J.E. Moser, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, P. Bäuerle, Significant improvement of dye-sensitized solar cell performance by small structural modification in π-conjugated donor-acceptor dyes, Adv. Funct. Mater. 22 (2012) 1291–1302, https://doi.org/10.1002/adfm.201102519.
- [10] Y. Wu, W. Zhu, Organic sensitizers from D-π-A to D-A-π-A: Effect of the internal electron-withdrawing units on molecular absorption, energy levels and photovoltaic performances, Chem. Soc. Rev. 42 (2013) 2039–2058, https://doi.org/10.1039/c2cs35346f.
- [11] W. Zhang, Y. Wu, H. Zhu, Q. Chai, J. Liu, H. Li, X. Song, W.H. Zhu, Rational molecular engineering of indoline-based D-A-π-A organic sensitizers for longwavelength-responsive dye-sensitized solar cells, ACS Appl. Mater. Interfaces 7 (2015) 26802–26810, https://doi.org/10.1021/acsami.5b08888.
- [12] L.L. Tan, L.J. Xie, Y. Shen, J.M. Liu, L.M. Xiao, D. Bin Kuang, C.Y. Su, Novel organic dyes incorporating a carbazole or dendritic 3,6-diiodocarbazole unit for efficient dye-sensitized solar cells, Dyes Pigments 100 (2014) 269–277, https://doi.org/10.1016/j.dyepig.2013.09.025.
- [13] E. Gabrielsson, H. Ellis, S. Feldt, H. Tian, G. Boschloo, A. Hagfeldt, L. Sun, Convergent/divergent synthesis of a linker-varied series of dyes for dye-sensitized solar cells based on the D35 donor, Adv. Energy Mater. 3 (2013) 1647–1656, https://doi.org/10.1002/aenm.201300367.
- [14] X.X. Dai, H.L. Feng, Z.S. Huang, M.J. Wang, L. Wang, D. Bin Kuang, H. Meier, D. Cao, Synthesis of phenothiazine-based di-anchoring dyes containing fluorene linker and their photovoltaic performance, Dyes Pigments 114 (2015) 47–54, https://doi.org/10.1016/j.dyepig.2014.10.016.
- [15] X. Qian, R. Yan, C. Xu, L. Shao, H. Li, L. Hou, New efficient organic dyes employing indeno[1,2-b]indole as the donor moiety for dye-sensitized solar cells, J. Power Sources 332 (2016) 103–110, https://doi.org/10.1016/j.jpowsour.2016.09.138.
- [16] M. Saad Ebied, M. Dongol, M. Ibrahim, M. Nassary, S. Elnobi, A.A. Abuelwafa, Effect of carboxylic acid and cyanoacrylic acid as anchoring groups on Coumarin 6 dye for dye-sensitized solar cells: DFT and TD-DFT study, Struct. Chem. 33 (6) (2022) 1921–1933.
- [17] A.S. Steparuk, R.A. Irgashev, E.F. Zhilina, V.V. Emets, V.A. Grinberg, E.V. Tekshina, S.A. Kozyukhin, New thieno [3, 2-b] indole conjugates with 5-(methylene) rhodanine-3-acetic acid in dye-sensitized solar cells, Mendeleev Commun. 32 (4) (2022) 523–526.
- [18] L. Naik, I.A.M. Khazi, G.H. Malimath, Studies on photosensitization of TiO₂ nanoparticles by novel 1,3,4-oxadiazoles derivatives, Optik 183 (2019) 732–741, https://doi.org/10.1016/j.ijleo.2019.02.145.
- [19] S. Walki, L. Naik, H.M. Savanur, Y. K.C, S. Naik, R. M.K, G.H. Malimat, K.M. Mahadevan, Design of new imidazole-derivative dye having donor-Π-acceptor moieties for highly efficient organic-dye-sensitized solar cells, 164074-1640, Optik 208 (2020), https://doi.org/10.1016/j.ijleo.2019.164074.
- [20] I. Abubakari, N.S. Babu, S. Vuai, J. Makangara, Optical and photovoltaic properties of substituted alizarin dyes for dye-sensitized solar cells application, Energy Sources, Part A: Recovery, Util. Environ. Eff. 43 (2021) 2569–2582, https://doi.org/10.1080/15567036.2020.1836083.
- [21] C. Sun, Y. Li, J. Han, B. Cao, H. Yin, Y. Shi, Enhanced photoelectrical properties of alizarin-based natural dye via structure modulation, Sol. Energy 185 (2019) 315–323, https://doi.org/10.1016/j.solener.2019.04.078.
- [22] L. Naik, C.V. Maridevarmath, I.A.M. Khazi, G.H. Malimath, Photophysical and computational studies on optoelectronically active thiophene substituted 1,3,4oxadiazole derivatives, J. Photochem. Photobio. A Chem. 368 (2019) 200–209, https://doi.org/10.1016/j.jphotochem.2018.09.038.
- [23] S.M. Tsui, W. Chu, Quantum yield study of the photodegradation of hydrophobic dyes in the presence of acetone sensitizer, Chemosphere 44 (2001) 17–22, https://doi.org/10.1016/S0045-6535(00)00379-9.
- [24] J. Hoche, A. Schulz, L.M. Dietrich, A. Humeniuk, M. Stolte, D. Schmidt, T. Brixner, F. Würthner, R. Mitric, The origin of the solvent dependence of fluorescence quantum yields in dipolar merocyanine dyes, Chem. Sci. 10 (2019) 11013–11022, https://doi.org/10.1039/c9sc05012d.
- [25] P. Makula, M. Pacia, W. Macyk, How to correctly determine the band gap energy of modified semiconductor photocatalysts based on uv-vis spectra, J. Phys. Chem. Lett. 9 (2018) 6814-6817, https://doi.org/10.1021/acs.jpclett.8b02892.
- [26] K.K. Rohatagi-Mukherjee, Fundamentals of Photo-chemistry, Wiley Eastern, New Delhi, 1992.
- [27] J.R. Lackowicz. Principles of Fluorescence Spectroscopy, third ed., Springer, New York, 2006.
- [28] R. Wang, Z. Yu, Validity and reliability of benesi-hildebrand method, Acta Phys. Chim. Sin. 23 (2007) 1353–1359, https://doi.org/10.1016/S1872-1508(07) 60071-0.
- [29] Y. Liu, A. Hagfeldt, X.R. Xiao, S.E. Lindquist, Investigation of influence of redox species on the interfacial energetics of a dye-sensitized nanoporous TiO₂ solar cell, Sol. Energy Mater. Sol. Cells 55 (1998) 267–281, https://doi.org/10.1016/S0927-0248(98)00111-1.
- [30] Z.S. Wang, T. Yamaguchi, H. Sugihara, H. Arakawa, Significant efficiency improvement of the black dye-sensitized solar cell through protonation of TiO₂ films, Langmuir 21 (2005) 4272–4276, https://doi.org/10.1021/la050134w.
- [31] D. Rehm, A. Weller, Kinetics of fluorescence quenching by electron and H-atom transfer, Isr. J. Chem. 8 (1970) 259–271, https://doi.org/10.1002/ ijch.197000029.
- [32] S.H. Yoo, J.M. Kum, S.O. Cho, Tuning the electronic band structure of pcbm by electron irradiation, Nanoscale Res Lett. 6 (2011) 1–7, https://doi.org/10.1186/ 1556-276X-6-545.
- [33] Solar cells—Operating principles, technology and system applications, Solar Energy. 28 (1982). https://doi.org/10.1016/0038-092x(82)90265-1.