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Design of new imidazole-derivative dye having donor-II-acceptor moieties for highly efficient organic-dye-sensitized solar cells

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ABSTRACT

In the present work, we have synthesised donors/acceptor substituted derivative of imidazole 4-(1-(3-chloro-4-nitrophenyl)-4,5-diphenyl-1H-imidazol-2-yl)benzoic acid (CNI) via one-pot synthetic method and has been characterized by spectroscopic methods such as ¹H-NMR, IR, SEM and EDX. The photophysical properties like, solvatochromic shift and quantum yield were estimated. Energy band gap of the CNI dye was calculated in various solvents using theoretical and experimental methods. Further, photosensitization of TiO₂ nanoparticles from CNI dye has been investigated using absorption, steady state and time resolved fluorescence methods. The increase in absorbance and decrease in fluorescence spectra with different concentrations of TiO₂ nanoparticles confirmed the possibility of interactions between dye and TiO₂ nanoparticles. Rehm-Weller relation suggests that, decrease in fluorescence of CNI dye was due to photo-induced electron transfer process and the Stern-Volmer studies suggest that, the fluorescence quenching mechanism was due to combined dynamic and static quenching process. The photo-induced electron transfer process has been used in solar energy harvesting applications by fabricating CNI dye sensitized solar cell. Photovoltaic energy conversion efficiency and fill factor of the CNI dye were found to be 1.85 % and 0.57 respectively.

1. Introduction

In the recent decade, percentage consumption of fossil fuel has increased with human population which is disastrous to the environment and because of which many researchers are worked on the renewable energy sources like solar energy, wind energy etc. Solar energy is one of the huge energy sources that can provide continuous energy for billion of year but conversion of solar energy in to solar power is a greater challenge. The solar cell is the device that can convert solar energy into solar electrical power and these cells are constructed using different material like, inorganic semiconductor and nanoparticles, organic dye, polymer etc. Amongst them Dye-sensitized solar cells (DSSCs) have proven to be attractive solar energy conversion tools because of their special characteristics features in terms they being environmental benign, relatively very easy fabrication, low-cost production, and more stable, which makes the way to high applications [1–10].

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Organic dye containing "Donor (D)-π conjugation bridge-acceptor (A)" groups having electron withdrawing and donating properties shows good absorption response in the visible light region, that improves the light harvesting and short circuit photocurrent properties of the solar cells [11]. Many investigators worked on DSSC till date and Huang *et al.* [12] developed hemicyanine derivatives based DSSC and got the efficiency in the range of 4.8%–5.1%. The thienothiophene substituted organic dye synthesized by Yang et al. [13] showed high solar energy-to electricity conversion efficiency of 6.23 %. Yanagida group [14] and Arakawa group [15] reported polyene dye or phenyl-conjugated oligoene dye which showed gain efficiency of 6.6 % and 6.8 %. A series of coumarin derivatives developed by Hara et al. [16–19] shown the efficiency of 7.7 %, which is comparable with that for N719 dye. Whereas, Uchida group [20] constructed DSSC without antireflection layer and reported 8.0 % of solar cells conversion efficiency. Recently, researchers developed mesoporous nano crystalline TiO₂ films based DSSCs with high photon-to-electricity conversion efficiency and method employed was economically benign. *Lohit et al.* [21] studied photosensitization of TiO₂ nanoparticles by 1,3,4-oxadiazoles derivatives in order to explore new dyes in the construction of solar cell. Gratzel group [22] reported the 9.03 % conversion efficiency for solar cells with D149 dye as sensitizer after optimizing nanocrystalline TiO₂ films. Ruthenium polypyridyl complexes were synthesized by Zhang et al. [2324] by using Squariane dye as co-sensitizer to improved its efficiency by 13 % than those sensitized with simple ruthenium polypyridyl complexes. The spectral response scope was widened the photovoltaic performance of solar cells was improved by co-sensitization of squaraine dye and polypyridyl ruthenium dye in a proper ratio.

Recently, organic molecules and polymers containing electron donor and acceptor group of imidazole have attracted considerable research interest due to their unique electro-optic properties. The conjugated chain is advantage in this polymers to the charge-transfer transition from the auxiliary electron donor to first an electron donor. After electron injection the charge recombination may be retarded because of decreasing positive charge density at the donor by electronic delocalization of the two substituents at positions 4 and 5 of the imidazolyl ring [25–31].

In view of this, we have synthesized donors/acceptor substituted derivative of imidazole 4-(1-(3-chloro-4-nitrophenyl)-4,5-diphenyl-1H-imidazol-2-yl)benzoic acid (CNI) and studied its photophysical and DSSC parameters using experimental and theoretical techniques in order construct new Dye-sensitized solar cells.

2. Experimental details

2.1. Materials and methods

Commercial Sigma Aldrich, India chemicals and reagents used for the synthesis of dyes. Analytical and HPLC grade solvents were purchased from Loba chemie. Pvt Ltd., India. Anatase Titanium dioxide nanoparticle (TiO_2 NPs) of average size of < 25 nm was purchased in powder form from Sigma Aldrich. The melting point was measured on a Boetius-Mikroheiztisch. TLC was performed by using from Merck KGaA silica gel 60 F254 (layer thickness 0.2 mm) TLC plates. ¹H-NMR spectrum were recorded using a Jeol with 400 MHz operating frequency in Dimethylsulfoxide (DMSO) solvent. IR spectra of the dyes were recorded using Nicolet 5700 FT-IR instrument. Scanning Electron Microscope (SEM) and Energy Dispersion X-ray Anlyser (EDAX) data were recorded by using Hitachi (Table top, Model TM 3000) instrument.

Carry-100 spectrophotometer, Hitachi F-7000 and ISS ChronoBH time correlated single photon counting spectrometer were used to study Absorption Fluorescence and Fluorescence lifetime measurements. Cyclic voltammetry (CV) studies were carried out using an electrochemical analyzer/ Work station (model: CHI1112C, USA) at 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte with a scan rate 1×10^{-3} Vs⁻¹.

Computational details: The optimized molecular geometry of the CNI dye was performed using the Gaussian09 software with the basis set B3LYP - 6-311 G (d,p). Optimized molecular geometry at the B3LYP level was verified with the vibrational frequency calculations at minimum potential energy surface (PES). Further, the electronic properties were computed for the molecule in the salvation state by applying IEFPCM model as implemented in Gaussian 09 software package. In order to estimate energy band gap and simulated UV–vis absorption spectra of the optimized molecule the basis set TD-DFT (B3LYP/6-311(d,p)) was used [32].

2.2. Procedure for 4-(1-(3-chloro-4-nitrophenyl)-4,5-diphenyl-1H-imidazol-2 yl)benzoic acid

In a 250 mL round-bottom flask, equimolar ratio of 3-chloro-4-nitroaniline (1 mmol, 0.172 g), benzil (1 mmol, 0.210 g), ammonium acetate (1 mmol, 0.75 g) and 4-formylbenzoic acid (1 mmol, 0.150 g) were take, to this 20 mL glacial acetic acid is added. The reaction mixture was then subjected to ultra sonication for 30 min and refluxed for 4-5 h on a heating mantle. The reaction was monitored by TLC (2:8, ethyl acetate:pet.ether mixture). After the completion of the reaction, the mixture was cooled to room temperature and poured into ice cold water. The reaction mixture was neutralized by aqueous sodium bicarbonate solution and the product was extracted with ethyl acetate. The crude product was then recrystallized by hot chloroform and ethyl acetate (2:6) to get analytically pure yield of 4-(1-(3-chloro-4-nitrophenyl)-4,5-diphenyl-1*H*-imidazol-2-yl)benzoicacid (**CNI**) with good yields (70–80 %). The chemical reaction was showed in Scheme 1.



Scheme 1. Synthetic route for construction of 4-(1-(3-chloro-4-nitrophenyl)-4,5-diphenyl-1H-imidazol-2 yl)benzoicacid (CNI).

2.3. Data characterization



Light yellow coloured solid, mp. 183–185 °C; IR (KBr cm⁻¹) v_{max} : 661 (C-Cl), 1250 (C-N), 1545 (N–O), 1600 (Ar, C = C), 1671 (C = N), 1736 (Carboxylic C = O), 2853 (Aliphatic C–H), 2924 (Ar-H), 3431 (Carboxylic O-H). ¹H-NMR (400 MHz, DMSO- d_{6} , δ ppm) 5.94–6.02 (m, 2H, ArH), 6.84–6.88 (t, 4H, J = 7.6 Hz, ArH), 6.99–7.03 (q, 3H, J = 1.2, 7.2 Hz, Ar-H), 7.24-7.31(m, 5H, Ar-H), 7.33–7.59 (m, 3H, Ar-H), 12.18 (s, 1H, Carboxylic O-H), Further, the formation of the compound CNI was confirmed by its Energy Dispersion X-ray Analyzer spectrum and all spectra are given in supplementary data (Scheme 1).

3. Result and discussion

3.1. Photophysical properties

The absorption band position of CNI molecule was investigated in different solvents and was shown in Fig. 1.

Fig. 1 shows the excitation maxima of the dye in a variety of solvents lies between 324 and 376 nm. On changing the media from non-polar to polar solvents CNI molecule showed tremendous redshift of 52 nm. The results revealed that, the solvents environment strongly enhances the intra molecular charge transfer and also there was possibility of $\pi \rightarrow \pi^*$ transition. On changing the polarity of the solvents the energy gap of the molecule varies these results in change of the position and shape of the absorption spectra. The values of the Stoke shift varies with respect to solvent environment giving an account of the specific interaction between the solute and solvent molecules.

The fluorescence band position of CNI molecule was investigated in different solvents depicted shown in Fig. 2. The fluorescence



Fig. 1. Normalised Absorption spectra of CNI in different solvents.



Fig. 2. Normalised fluorescence spectra of CNI in different solvents.

spectra of CNI was recorded using absorption maxima wavelength (λ_{max}^{abs}) in different solvents. From the Fig. 2, it was observed that fluorescence spectra of CNI shows most blue-shifted in benzene (λ_{max}^{emi} = 423 nm) and most red-shifted in dimethyl sulfoxide (λ_{max}^{emi} = 483 nm). The large solvatochromic shift between these two solvents was due to the dielectric constant. In summary, polarity, viscosity and proticity coupled with carboxylic group CNI molecules result in: (1) strong blue-shift and (2) temporal stability of obtained configuration between dye and solvent (solvation process).

A photo physical property of dyes such as, optical band gap is essential for designing of optoelectronic device like device dye sensitized solar cell (DSSC), Organic light emitting diodes (OLED's) etc., and it gives information about electronic excitation energy levels in organic material. In electronic transitions, the dyes absorbs photon in UV–vis spectral range and promote an electron from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) [33] and this can observed with the help of UV–vis spectrophotometer. The optical band (E_g) correlate with the energy of the long wavelength edge of the exciton absorption band. The optical band gap values (E_g) were determined from the onset of the low energy side of the absorption spectra (λ_{onset}) using Eq.1 and the values of optical band gap [33] in different solvent were summarized in Table 2.

$$E_{g} = \frac{1240}{\lambda_{onset}}$$
(1)

From Table 2 it was observed that, on changing solvent media from non polar to polar optical band decreased from 3.444 eV to 2.974 eV. This may be due to the formation of hydrogen bond between carboxylic functional group of the dye to the solvent environment and this effect increase with respect to increasing dielectric constant. From the literature, it was found that, low band gap molecules can be used with high efficiency in the area of light emitting materials, photovoltaic/optoelectronic applications and CNI molecule also show low optical band gap value as observed by others.

The fluorescence quantum yield (ϕ_s) [34] of the CNI dye was experimentally determined by comparing with standard fluorescent dye of known quantum yield [POPOP laser dye (ϕ_R = 0.97)] using Eq 2 in different solvents and the values are given in Table1.

$$\phi_s = \phi_R \frac{I_s OD_R n_s^2}{I_R OD_s n_R^2}$$
⁽²⁾

Where, ϕ , I, OD and n represent quantum yield, integrated fluorescence intensity, optical density and refractive index, S and R represent the sample and reference respectively. From the Table 1 it was observed that synthesised CNI dye was having good

Table 1	
Photophysical parameters of CNI dye.	

Solvent	λ_{max}^{abs} (nm)	λ ^{emi} max (nm)	Δλ. (nm)	Quantum yield	Fluorescence lifetime $< \tau >$ (ns)	χ^2
1,4-Dioxane	326	429	103	0.71	2.64	1.11
Benzene	330	445	115	0.66	2.62	1.14
Toulene	331	447	116	0.66	2.64	1.09
Tetrahydro furan	334	453	119	0.65	2.64	1.11
Ethyl acetate	345	459	114	0.65	2.69	1.14
Dichloromethane	349	461	112	0.65	2.72	1.09
Methanol	351	463	112	0.68	2.72	1.15
Ethanol	355	469	114	0.69	2.75	1.11
Acetonitrile	358	469	111	0.71	2.75	1.19
Dimethyl sulfoxide	371	471	110	0.71	2.79	1.11

Table 2

The values of HOMO-LUMO and chemical hardness.

	Experimental calculation	Theoretical calculation				
Solvent	Optical band gap E_g (eV)	HOMO (eV)	LUMO (eV)	Energy band gap E _g (eV)	η	
1,4-Dioxane	3.444	- 5.657	- 2.545	3.112	1.556	
Benzene	3.255	- 5.365	-2.229	3.136	1.568	
Toluene	3.229	-6.128	-2.984	3.144	1.572	
Tetrahydrofuran	3.147	-5.461	-2.312	3.149	1.575	
Ethyl acetate	3.123	-5.904	-2.751	3.153	1.577	
Dichloromethane	3.092	- 5.859	-2.667	3.192	1.596	
Methanol	3.047	-5.324	-2.115	3.209	1.605	
Ethanol	3.002	- 5.479	-2.224	3.255	1.628	
Acetonitrile	2.988	- 5.577	-2.316	3.261	1.631	
Dimethyl sulfoxide	2.974	-5.386	-2.114	3.272	1.636	

quantum yield and highly fluorescent. This is a necessary and most important property of a dye in order to explore in the field of optoelectronics.

Using pulsed excitation energy source, dye molecule can be excited to its excited state in solvent media. In the excited state dye molecule interacted with surrounding solvent molecule before returning to the ground state. These excited state solute-solvent interactions influence on the fluorescence life time of the excited molecule. Fluorescence lifetime measurements are the most sensitive measurement in order to understand the excited state behavior of the molecule. Therefore, the decay profile was fitted with biexponential function with χ^2 value close to unity [35]. The fluorescence lifetime of the dye was calculated in different solvent using Eq.3

 $I(t) = (A_1t_1 + A_2t_2)$ (3) Where t_1 and t_2 represented the short and longer lifetime components with their normalized amplitude



Fig. 3. Fluorescence decay profile of CNI dye (1 \times 10⁻⁵M) excited at 361 nm along with weighted residual plot in dimethylsulfoxide.



Fig. 4. Optimised molecular geometry of CNI molecule.

components A1 and A2 respectively and the average fluorescence lifetime of the CNI dye in different solvent were give in Table 1.

The fluorescence decay profile of the CNI dye is recorded in dimethylsulfoxide and is shown in Fig. 3 along with weighted residual plot. The fluorescence decay profile of the CNI dye in dimethylsulfoxide is best fitted with bi- exponential fitting model with χ^2 value is equal to 1.11 similarly fluorescence decay profile of CNI dye is recorded in different solvents and there fluorescence lifetime along with χ^2 values are given in Table 1. From the Table 1, it was observed that on changing media from nonpolar to polar, fluorescence lifetime increase from 2.64 ns to 2.79 ns. These results clear suggest that, the solvent polarity increase excited state lifetime of the electron.

The ground state optimized molecular structures of CNI dye is shown in Fig. 4. The Highest Occupied Molecular Orbit (HOMO) and Lowest Unoccupied Molecular Orbit (LUMO) of CNI dye in gaseous and dimethylsulfoxide are shown in Figs. 5–6. The luminescence property of organic molecule can be predicated on the basis of spatial distribution of molecular orbitals, mainly those of HOMO and LUMO. Generally, if the energy band gap between the HOMO and LUMO decreases, it is easier for the electrons of the HOMO to be excited. The synthesized molecule shows large HOMO value and small energy band gap which is essential properties for DSSC due to the strong electron-accepting ability of the electron-acceptor group is fundamentally a consequence of the large stabilization of the LUMO causes lowering of the HOMO-LUMO gap From the Fig. 5 it was observed that, CNI dye in gaseous phase the electron clouds of HOMO energy levels are all mainly located on the 1-chloro-2-nitrobenzene and this data strongly counts for good electron donating property of unit and LUMO energy levels are mainly concentrated on the 2,4,5-triphenyl-1H-imidazole unit, which is useful in the application of DSSC due to increase in the enhancement of electron transfer. HOMO-LUMO values are obtained by theoretical and experimentally (Cyclic Voltammeteric analysis) methods are in good agreement with each other.

Chemical hardness is a one of the important parameter in order to explore organic molecule in the field of optoelectronics. The chemical hardness (η) of the molecule can be calculated by using these HOMO–LUMO energy values. To denote resistance to deformation by mechanical force the hardness and softness were suggested [33]. Molecules with large HOMO–LUMO gap is hard which implies higher stability and opposing charge transfer since they oppose changes in their electron density and distribution. On



Fig. 5. Molecular orbital amplitude plots of HOMO and LUMO levels of CNI molecule in gaseous phase.



Fig. 6. Molecular orbital amplitude plots of HOMO and LUMO levels of CNI molecule Dimethyl sulfoxide.

contrary, molecules which require a small energy gap for its excitation are also termed as soft molecules. Hence, they are highly polarizable in nature [36].

The chemical hardness (η_{hard}) can be calculated using Eq. 4

$$\eta_{hard} = \frac{[E_{L} - E_{H}]}{2} \tag{4}$$

Where, E_H and E_L is the energy value of HOMO and LUMO respectively. The chemical hardness calculated from theoretical and experimental method is given in Table 2.

From Table 2 it was observed that, the small value of η and HOMO-LUMO energy gaps reflects that molecule are in soft in nature. The Molecular electrostatic potential map (MEPM) of the compound was used to Fig out the reactive sites for electrophilic and nucleophilic attacks and was also useful in biological detection and hydrogen bonding interactions studies [3738] and molecular electrostatic potential map is shown in Fig. 7. In addition, the MEPM is based on the molecular size, shape as well as positive, negative and neutral electrostatic potential region in terms of color grading. The different values of the electrostatic potential at the surface are represented by different colors; red represents regions of most negative electrostatic potential, blue represents regions of most positive electrostatic potential and [33]. It also provides an understanding of the relative polarity of the molecule. The molecular structure with its physicochemical property can be recognized.

In order to know the charge interrelated properties of the CNI, molecular electrostatic potential maps were plotted and are given in Fig. 8. From the Fig it was observed that, positive phases (blue colour) around the imidazole ring which consists of a nitrogen atom and all hydrogen atoms whereas, negative phases around the cyclohexanol ring consists of a oxygen atom.

Thermogravimetric analysis (TGA)

The ability of a material to form morphologically stable films is an important requirement for the successful operation of DSSC. The thermal stabilities of the CNI dye was studied by thermogravimetric analysis (TGA) under a nitrogen atmosphere and is shown in Fig. 8. The thermal and morphological stabilities of the CNI dye is summarized Table 3.

CNI was subjected to thermogravimetric analysis in the temperatures ranged from room temperature to 350 °C under nitrogen atmosphere. The TGA results revealed that first degradation was observed in the range of 35–70 °C with minor weight loss (1.27 %)



Fig. 7. Molecular electrostatic potential map of CNI.



Fig. 8. TGA/Derivative TGA thermograms of the CNI dye measured at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Table 3

Thermal and morphological stabilities of CNI dye.

dye	I-Degradation	II-Degradation	III-Degradation
	% wt loss	% wt loss	% wt loss
CNI	68.20–70.28°C	168.84–224.16°C	224.16–229.51°C0.604
	1.270 %	0.781 %	%

due to the evaporation of moisture content in the compounds. The major weight loss was observed in the range of 168–224 °C. These results revealed that, CNI dye have good thermal stability which can be used in the construction of the dye sensitized solar cells [39].

3.2. Spectroscopic studies

The absorption spectra of CNI dye of concentration 1×10^{-4} M in the absence and presence of TiO₂ NPs is recorded in dimethyl sulfoxide at room temperature and is shown in Fig. 9. From the Fig. 9, it was observed that, absorption spectra of CNI dye increase with increase in concentration of TiO₂ nanoparticle broadening of spectra without shifting the peak position and also there was no new absorption peak is found. This result revealed that, formation of ground-state complex between CNI dye TiO₂ nanoparticles was prohibited [21].

The steady state fluorescence and time resolved fluorescence spectra of CNI dye was recorded in the absence and presence of TiO_2 NPs in dimethylsulfoxide at room temperature NPs and are shown in Figs. 10–11. respectively. Table 4 represent the Fluorescence intensity and lifetime values of CNI dye in the absence and presence of TiO_2 NPs. From the Table 4, it was observed that fluorescence lifetime and intensity decrease with increasing concentration of the TiO_2 NPs. These spectral behaviors can be analysized using Stern-Volmer relation [35] and is given by (Eq 5 and 6)

$$\frac{I_o}{I} = 1 + k_{sv}[TiO_2] \tag{5}$$



Fig. 9. The absorption spectra of CNI dye in dimethylsulfoxide in the absence and presence of TiO_2 NPs.



Fig. 10. Steady state fluorescence spectra of CNI dye in the absence and presence of TiO2 NPs in dimethyl sulfoxide excited at 371 nm.



Fig. 11. Fluorescence decay curve of CNI dye in the absence and presence of TiO₂ NPs dimethyl sulfoxide.

Table 4 Values of TiO₂ concentrations, fluorescence intensity and fluorescence lifetime of CNI dye with corresponding χ^2 values.

TiO ₂ NPs Concentration x10 ⁻⁴ M	Fluorescence Intensity	Fluorescence Lifetime	χ^2
0	9704	2.79	1.11
1	8797	2.78	1.15
2	8021	2.77	1.11
3	7300	2.75	1.09
4	6655	2.73	1.12
5	6032	2.71	1.11
6	5256	2.70	1.15
7	4819	2.69	1.18
8	4431	2.68	1.13

$$\frac{\tau_o}{\tau} = 1 + k_{sv} [Tio_2]$$

Where,

 I_0 or τ_0 are fluorescence intensities or lifetime of CNI dye in the absence of TiO_2 NPs.

I or τ are the fluorescence intensities or lifetime of CNI dye in the presence of TiO_2 NPs.

Using steady state and time resolved fluorescence value of CNI dye Stern-Volmer (S–V) plot was drawn and is shown in Fig. 12. The values of S–V constant and bimolecular quenching are tabulated in Table 5. The S–V plot found to linear with intercept equal to unity and also variation in S–V constant obtained from both methods suggest that, fluorescence quenching was due to combined dynamic and static quenching process.

The magnitudes of bimolecular quenching constant obtained from both the methods suggest that short range interactions between

(6)



Fig. 12. Steady state and time resolved S-V Plot of CNI in dimethyl sulfoxide.

Table 5

Values of Stern-Volmer constant, bimolecular quenching constant and association constant of CNI dye.

Solvent	Steady state method		Time resolved metod		
	Stern-Volmer constant (k _{sv}) x10 ³ M ⁻¹	Bimolecular quenching Constant (k _q) x10 ¹¹ M ⁻¹ s ⁻¹	Association Constant (K_a) $x10^2M^{-1}$	Stern-Volmer constant $(k'_{s\nu})$ $x10^1 M^{-1}$	Bimolecular quenching Constant (k'_q) x10 ¹⁰ M ⁻¹ s ⁻¹
Dimethyl sulfoxide	1.057	3.789	5.768	8.829	3.164

CNI dye and TiO₂ NPs was occurred.

Further, stoichiometry and the association constant (K_a) of CNI dye with TiO₂ NPs are estimated from Benesi-Hilderbrand [40] equation (Eq 7),

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

Here all the terms in above equation have their usual meaning. 1/[Q] Vs $1/(I - I_0)$ plots for CNI dye-TiO₂ NPs system were drawn and are shown in Fig. 13. Benesi–Hilderbrand plot was perfectly linear and hence provide the evidence for the 1:1 stoichiometry between CNI dye and TiO₂ NPs. The association constant (K_a) was calculated by the ratio of intercept to slope and the values are given in Table 4. The 'K_a' values is almost in the same range (10²) of the previously reported values [21].

The absorption and emission spectra of CNI dye was observed from Fig. 16. suggest that non-overlap between absorption spectra of TiO_2 NPs and emission spectra of CNI dye. Which also suggests the possibility of resonance energy transfer between CNI dye and



Fig. 13. Benesi-Hildebrand linear analysis plot of all solute with varying concentration of TiO₂ NPs in dimethyl sulfoxide.



Fig. 14. CV curves of CNI were measured in dimethylsulfoxide in the presence of nBu₄NPF₆ at a scan rate of 100 mVs⁻¹.

 TiO_2 NPs is ruled out. Using Rehm-Weller relation the energy transfer from CNI dye to TiO_2 NPs can be estimated. The Rehm-Weller equation [41] as follows.

$$\Delta G_{et} = E_{1/2}^{ox} + E_{1/2}^{red} + E_s + C$$
(8)

Where,

 $E_{1/2}^{ox}$ is the oxidation potential of CNI dye,

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

 $E_{\rm s}$ is the excited singlet state energy of CNI dye and C is the coulombic term.

The cyclic voltammogram (CV) of CNI dye in dimethyl sulfoxide and acetonitrile has been displayed in Figs. 15 and Fig. 15. From the Fig, oxidation potentials of CNI dye were found to be 1.211 V and 1.012 V in dimethyl sulfoxide and acetonitrile respectively determined from cyclic voltammogram. E_s of CNI dye were 3.272 eV for dimethyl sulfoxide and 3.261 eV for acetonitrile respectively determined from absorption spectrum. Reduction potential of TiO₂ is -0.5 V. Substituting the values of E_s in Eq.8, ΔG_{et} values for dimethyl sulfoxide and acetonitrile were determined as -2.751 eV and -2.55 eV respectively and coulombic term was neglected since in polar solvents coulombic term was very small. From the magnitudes of ΔG_{et} it is observed that ΔG_{et} is greater in dimethyl sulfoxide than acetonitrile (less polar). These observations are the preliminary indications for the transfer of photo-generated electrons from CNI dye to TiO₂ NPs and allow us to fabricate DSSC

3.3. Fabrication of dye-sensitized solar cell

Commercial TiO₂ nanopowder (P25) was mixed in alpha-teripenol and ethyl cellulose to form TiO₂ paste. About 10 μ m thick TiO₂ layer was coated on FTO with an active area of 0.25 cm² by doctor-blade technique. TiO₂ photo-anode was annealed at 500 °C for 30 min and then soaked for sensitization at room temperature for 12 h in 10 mM of 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 μ m thick Surlyn film was used to fabricate cell. DSSC was completed upon the injection of the



Fig. 15. CV curves of CNI were measured in acetonitrile in the presence of nBu_4NPF_6 at a scan rate of 100 mVs⁻¹.



Fig. 16. Normalised absorption (D_A) and fluorescence (D_I) spectra of CNI in dimethyl sulfoxide.

electrolyte through the pre-drilled hole.

3.4. Photo-electrochemical measurement

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

HOMO = $-[E_{OX}^{ONSET} + 4.44]i$ (9)

The lowest unoccupied molecular orbital (LUMO) is equal to HOMO level minus Zero-zeroth energy (ΔE_{00}). Where, Zero-zeroth energy ($\Delta E_{00} = 1240/\lambda$) of the CNI dye alone is the intersection of the normalized absorption and fluorescence spectra (Fig. 16) and was found as 3.139 eV. Thus, LUMO level was found to be -2.312 V which lies well above the conduction band edge of TiO₂ (-0.5 V vs. NHE), ensuring the required driving force for electron injection from the dye into the TiO₂ semiconductor. Fig. 7 Fig. 17 shows the schematic theoretical energy level diagram of each component of dye sensitized TiO₂ electrode. Therefore solar cell sensitized by CNI dye was thus fabricated in order to investigate the solar to electricity conversion efficiency.

I–V characteristics of DSSCs were measured in the dark and under simulated solar light conditions. NREL certified silicon photodiode was used to calibrate output power to 1 sun. The conversion efficiency of DSSC based on photocurrent vs. voltage (I–V) curve was recorded with a Keithley source meter (Table 5).

The Efficiency (η) and fill factor (FF) [42] according to Eqs. (10) and (11) are

$$\eta = \frac{J_{sc} V_{oc} FF}{I_o} \times 100$$

$$FF = \frac{V_{max} \times i V_{max}}{J_{sc} \times i V_{oc}}$$
(10)
(11)

Where, V_{oc} , J_{sc} , 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 ($I_o = 1000 \text{ W/m}^2$). The plots of photo-current density (J) versus voltage (V) are shown in Fig. 18. and the values of V_{oc} , J_{sc} , η and FF are shown in Table 6. Photovoltaic conversion efficiency (η) of DSSCs



Fig. 17. The schematic energy level diagram of photo induced electron transfer from CNI to TiO_2 NPs.



Fig. 18. Photo-current density-voltage (J-V) characteristics of the best performed DSSCs both CNI dye.

Table 6 Optimized photovoltaic parameters values of CNI dye.

Dye	$V_{\rm oc}$ in mV	J _{sc} in mA cm ⁻²	FF	η
CNI	697.5	4.59	57.93	1.85

sensitized with CNI dyes is 1.85 % under AM 1.5 irradiation (1000 W/m^2). The photovoltaic conversion efficiency of CNI dye is lower than the standard dye may be due to lower value of molar extinction coefficient of CNI dye and may be due to some other regions which need further investigation

4. Conclusions

In the present work, photophysical and dye sensitized solar cell parameter of donor/acceptor substituted imidazole derivatives were carried out utilizing experimental and theoretical technique. Furthermore, to investigate the nature of interactions between TiO_2 nanoparticles and newly synthesized imidazole derivative-CNI dye, spectroscopic and electrochemical techniques were employed. For completeness, the association constant has been calculated from Benesi–Hildebrand relation and it suggests that there is a possibility of interaction between CNI dye and TiO_2 NPs. Fluorescence quenching of CNI dye in the presence TiO_2 NPs is due to combined static and dynamic quenching. The Rehm-Weller theory infers that, thermodynamically favorable electron transfer takes place between CNI dye to TiO_2 NPs. Thus, solar energy harvesting process has been investigated by using TiO2-CNI dye fabricated solar cell. Under optimized conditions, Photovoltaic conversion efficiency and fill factor of fabricated DSSC was found to be 1.87 % and 0.57 respectively. Further improvement of power conversion efficiency of DSSC may be achieved with further optimization of solar cell parameters.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ijleo.2019. 164074.

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