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ORIGINAL RESEARCH

Highly efficient organic indolocarbazole dye in different acceptor units for optoelectronic applications—a first principle study

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Abstract

A series of novel organic dyes (ICZA1, ICZA2, ICZA3, ICZA4) with D-π-A structural configuration incorporating indolo[3,2,1-jk]carbazole moiety as donor (D) unit, thiophene as π-linker and 2-cyanoacrylic acid as acceptor unit were investigated using density functional theory (DFT) and time-dependent DFT (TD-DFT) methods. Indolo[3,2,1-jk]carbazole-based D-π-A dyes composed of different acceptor groups were designed. By modulating acceptor unit, the efficiency of D-π-A dye-based dye-sensitized solar cells (DSSCs) can be further improved. In the present work, four novel push-pull organic dyes only differing in electron acceptor, have been designed based on the experimental literature value of IC-2. In order to further improve the light harvesting capability of indolo[3,2,1-jk]carbazole dyes, the acceptor influence on the dye performance were examined. The NLO property of the designed dye molecules can be derived as polarizability and hyperpolarizability. The calculated value of ICZA2 dye is the best candidate for NLO properties. Furthermore, the designed organic dyes exhibit good photovoltaic performance of charge transfer characteristics, driving force of electron injection, dye regeneration, global reactivity, and light harvesting efficiency (LHE). From the calculated value of ICZA4 dye, it has been identified as a good candidate for DSSCs applications. Finally, it is concluded that the both ICZA2 and ICZA4 dyes theoretically agrees well with the experimental value of IC-2 dye. Hence, the dyes ICZA2 and ICZA4 can serve as an excellent electron withdrawing groups for NLO and DSSCs applications.

Keywords D-π-A · Metal-free sensitizers · DFT · NLO · LHE

Introduction

In 1991, Gratzel and coworkers have reported that dye-sensitized solar cells (DSSCs) are promising candidate for photovoltaic performance [1]. The working process of DSSCs requires that these dyes upon light absorption, photo-induced excited electron is then injected into the conduction band of semiconductor TiO_2 anode in a femtosecond lifetime by the anchoring group. Further, the presence of redox electrolyte regenerates the oxidized sensitizer. The oxidized dye is then neutralized to ground state by the I^-/I_3^- redox system [2]. There are two major categories sensitizers commonly used as (1) metal complexes and (2) metal-free organic dyes. Although N719 Ru(II)-polypyridyl photosensitizers have shown the highest performance of DSSCs exceeding 11.8% [3], in 2011, zinc porphyrin-based dye has the best power conversion efficiency (PCE) of DSSCs up to 12.3% [4]. Recently, Gratzel and Oxford University research teams independently developed a solid-state DSSCs PCE exceeding 15%, further creating a new record [5, 6].

Due to this, metal-free organic dyes and natural dyes have attracted considerable attention for their tunable electronic structure, absorption spectra and electrochemical properties, ease of molecular tailoring, and low cost processes [7]. Recent literature reports indicate achievement of PCE 13.1% using pure organic sensitizer C281, such as high PCE has been reached with a metal-free organic dye in DSSCs [8]. In 2017, Kar et al. using *N,N′*-dialkylaniline based (NDI 6) dye has

Highlights
- Four novel indolo[3,2,1-jk]carbazole-based dyes are designed by modifying electron acceptor.
- The lower E_g and larger absorption spectra will favors to light harvesting process.
- The better ICZA2-ICZA4 electron acceptor can be ascribed to enhanced LHE compare to IC-2.

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reached the best PCE of DSSCs in 19.24%. [9]. Several organic dyes such as coumarin [10, 11], polyene [12], indoline [13, 14], triphenylamine (TPA) [15], carbazole [16], tetrahydroquinoline [17], and phenothiazine [18] have been investigated for DSSCs and showed good photovoltaic performance. For example, a typical TPA-based dye (TPC1) reported by H. Tian and coworkers used in DSSCs as the sensitizer exhibits an impressive PCE of 5.3% [19]. Other major advantages of metal-free organic dyes are their tunable absorption and photochemical properties through suitable molecular design [20]. The most traditional organic efficient sensitizers are generally configuration made of electron donor (D), π-spacer, and electron acceptor (A) [21–23]. This D-π-A architecture produces an effective intramolecular charge transfer (ICT) from D to A during photoexcitation process [24].

In the study of Chunhua Luo in 2014, [25] indolo[3,2,1-jk]carbazole sensitized photovoltaic device exhibited a high PCE of 3.68%, photocurrent (9.78 mA cm^{-2}), and photovoltage (0.66 V) measured under illumination of AM1.5G simulated solar light (100 mW cm^{-2}) at room temperature. Additionally, the acceptor groups of organic dyes play an important role onto the semiconductor surface and enhance efficiency photovoltaic cell performance, namely PC, PN, PMN, and PR [26]. Different acceptor groups were employed in order to further increase the absorption spectra of the organic sensitizer. In the current study, the optoelectronic properties of D-π-A organic dyes with different electron acceptor groups have been studied using density functional theory (DFT) and time-dependent DFT (TD-DFT) approach in order to good sensitizing properties for DSSCs. Hence, in the present work, the NLO property of the designed dye molecules was analyzed through the static polarizability and first hyperpolarizability. The influence of photovoltaic properties of the DSSCs based on electron acceptor was under investigation.

Theoretical setup

The ground state geometries of these molecules were fully optimized without any symmetry constrains. Full geometry optimized structure were confirmed to be at its local minimum (no imaginary frequency modes) energy surface was found. The optimization of ground state structure are performed in DFT [27, 28] method with Becke's three-parameter and Lee-Yang-Parr (B3LYP) [29] hybrid functional using 6-31G(d, p) basis set on all atoms.

The TD-DFT calculations were performed to calculate the UV-Vis optical absorption spectra. In general, different exchange-correlation (XC) functionals for charge transfer (CT) excitations often show significant effects. To select suitable functional, the optical absorption spectra of IC-2 by different XC functionals, including B3LYP, CAM-B3LYP [30], and WB97XD, were calculated using [31] TD-DFT method. From three functionals, the absolute values of 468, 393, and 385 nm were compared to experimental absorption spectra 382 nm. It gives errors of 86, 11, and 03 nm, as shown in Table 1. From Fig. 1, TD-DFT optical absorption spectra of IC-2 was calculated at three hybrid functionals using in CH_2Cl_2 solution. While taking as reference value for further newly designed dye molecules, the three optical absorption wavelengths, with the help of TD-WB97XD functional with 6-31G(d,p) basis sets, were performed.

Therefore, TD-WB97XD functional with 6-31G (d,p) basis set were chosen for combining the conductor-like polarizable continuum model (CPCM) [32] in dichloromethane (CH_2Cl_2) solution to predict the optical absorption properties of designed dye molecules. All the calculations were performed with Gaussian 09 package [33]. The optical absorption wavelengths are obtained by using Gausssum [34].

Results and discussion

Screening of the electron withdrawing groups

The electron withdrawing groups play an important role in D-π-A organic structure and further influence the PCE of DSSCs performance. The acceptor molecules were collected from literature survey. In the previous study, the acceptor molecules are used in highly efficient organic DSSCs application. In this way, these molecules will be effected by the indolo[3,2,1-jk]carbazole-based dye derivatives. A series of metal-free organic dyes ICZA1-ICZA4 with D-π-A structure were designed in order to screen excellent electron withdrawing groups compared to IC-2. Structure of indolo[3,2,1-

Table 1 Experimental absorption spectra and computed absorption wavelength of the lowest excited state λ_{max} (nm) for the dye in CH_2Cl_2 solution, together with the calculated oscillator strength (f) and excitation configuration

Methods	λ_{max} (nm)	Oscillator strength (f)	LHE	Main configuration
B3LYP	468	0.80	0.841	HOMO→LUMO (99%)
CAM-B3LYP	393	1.36	0.956	HOMO→LUMO (77%)
WB97XD	385	1.40	0.960	HOMO→LUMO (71%)
Experiment	382	Taken from reference [24]		

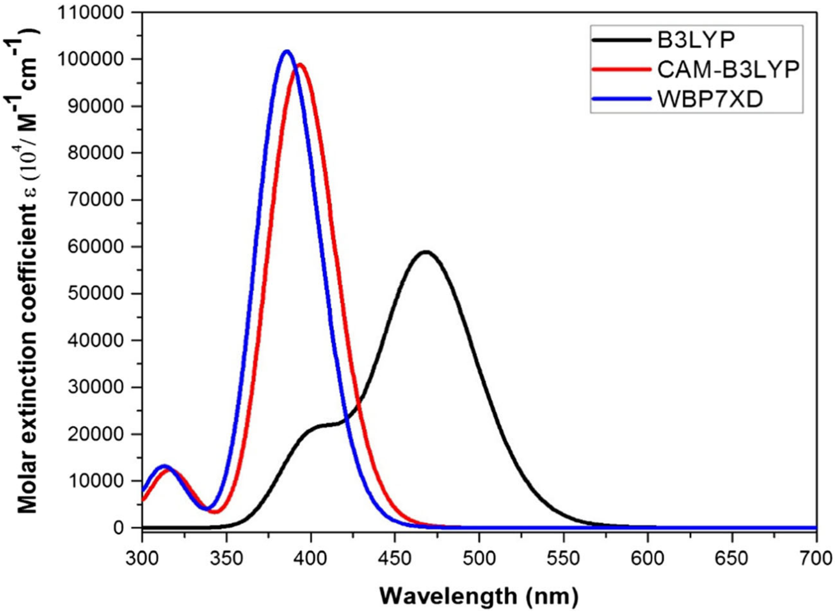


Fig. 1 TD-DFT optical absorption spectra of IC-2 calculated at hybrid functionals using CH_2Cl_2 solution

jk]carbazole was shown in Fig. 2. In order to explore considerably highly efficient indolocarbazole derivative dyes, tailoring of molecular design for D-π-A using different electron withdrawing groups were designed (ICZA1-ICZA4) as shown in Fig. 3. B3LYP/6-31G(d,p) were used for the optimization of indolo[3,2,1-jk]carbazole and four newly designed efficient sensitizers. Optimized geometric structures were shown in Fig. S0 (Supporting information). From the geometric structures explore that the electron acceptor effect of ICZA1-ICZA4 have shown coplanar structures, which might be favorable for the photo-induced electron CT and to broaden the optical absorption wavelength.

Intramolecular charge transfer effects

In DSSCs, the energy levels and corresponding orbitals distribution of frontier molecular orbitals (FMOs) are closely related to the intramolecular charge transfer (ICT) from electron donor to acceptor group of metal-free organic sensitizers [35]. It has a great effect on the optical absorption wavelength. Figure 4 shows the orbital spatial distribution of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the studied dye molecules. The HOMOs and LUMOs energy levels are very important aspects to explain efficient charge separation between donor and acceptor groups.

A strong D-π-A molecular structure has the character of the HOMOs are mainly contained on the donor parts to the π-conjugated spacer and LUMOs are mainly distributed on the electron acceptor moieties (anchoring group) when absorbed the photon in all dye sensitizers. The electron acceptor effect on the electronic properties by using various acceptor segments was investigated. The molecular orbitals (MO) contributions of HOMOs, LUMOs, and energy gap (E_g) are listed in Table 2.

Frontier molecular orbitals

The FMOs contribution is a very significant factor in determining the charge separated states of dye sensitizers [36]. In newly designed dye molecules, the HOMOs, LUMOs energy levels and their E_g values are among the most significant properties dominating the dye performance in photovoltaic devices. The smaller E_g values play an important role in broadening the visible absorption region, which improves the photoelectric properties of the dyes [37, 38]. The LUMOs are π*-orbitals of all the dye sensitizers are above the semiconductor conduction band edge (CBE) of TiO_2 (−4.0 eV) surface, and the HOMOs energy levels of π-orbitals are sufficiently below the redox potential of the I^-/I_3^- liquid electrolyte (−4.8 eV) system

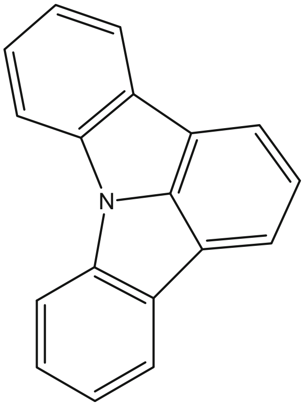


Fig. 2 Structure of indolo[3,2,1-jk]carbazole

Fig. 3 Tailoring of molecular design for D-π-A

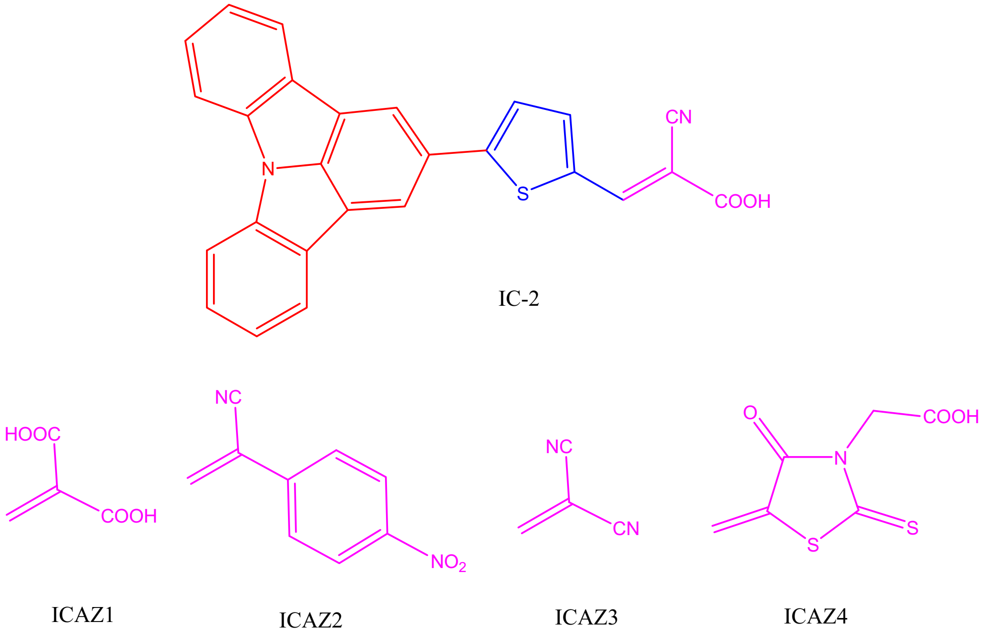


Fig. 4 The electronic structures of the IC-2 and ICZA1-ICZA4 calculated at B3LYP/6-31G(d,p) level of theory

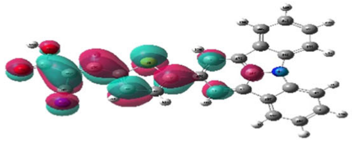
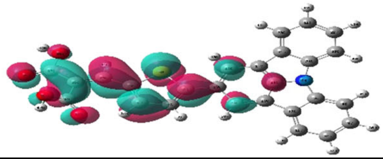
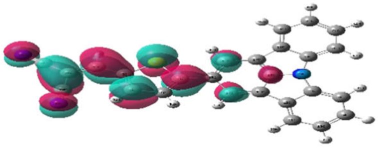
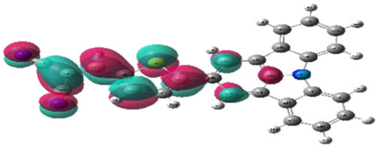
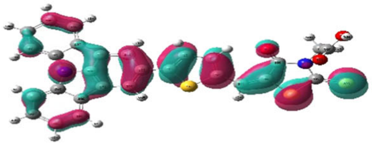
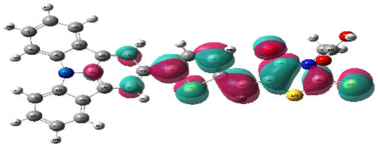
IC-2 HOMO	IC-2 LUMO
	
ICZA1 HOMO	ICZA1 LUMO
	
ICZA2 HOMO	ICZA2 LUMO
	
ICZA3 HOMO	ICZA3 LUMO
	
ICZA4 HOMO	ICZA4 LUMO
	

Table 2 The HOMOs energy (in eV), LUMOs energy (in eV), and energy gap (in eV) of IC-2, ICZA1-A4 dyes at B3LYP with standard basis set 6-31G(d,p) level of theory

Dyes	E_{HOMO} (in eV)	E_{LUMO}	Energy gap
IC-2	−5.73	−2.61	3.12
ICZA1	−5.57	−2.26	3.31
ICZA2	−5.66	−2.84	2.82
ICZA3	−5.84	−2.48	3.00
ICZA4	−5.48	−2.63	2.63

[39]. It is recommended that all the dye sensitizer should be capable of electron injection into the CBE of semiconductor and could be recombination process of electrons from the redox electrolyte. The HOMOs and LUMOs energies were calculated using B3LYP/6-31G(d,p) level of theory. The FMOs isodensity contour plots of IC-2, ICZA1-A4 were shown in Fig. 5. Four different structures of electron acceptor dyes were investigated. The HOMOs and LUMOs of the energy levels, with the increasing order of ICZA3 < ICZA2 < ICZA1 < ICZA4 and ICZA2 < ICZA4 < ICZA3 < ICZA1, respectively. The E_g values are between 2.63 and 3.31 eV. These results reveal that the sensitizers that have smaller E_g values show several characteristics beneficial to higher light harvesting efficiency (LHE) in the performance of DSSCs.

Global reactivity descriptors

The ionization potential (IP) and electron affinity (EA) of organic dyes give information about the charge-injection and charge transport character of the designed dye molecules [40]. The E_g between HOMOs and LUMOs for a molecule is an important parameter to determine electronic transport properties of DSSCs. The global chemical reactivity descriptors of molecules, chemical hardness (η), and softness (S) have been defined on the basis of E_{HOMO} and E_{LUMO} [41, 42].

By using Koopman's theorem [43] for closed-shell compounds of η and S can be defined as follows:

$$\eta\frac{(\mathrm{IP{-}EA})}{2} \tag{1}$$

Softness is a property of designed dye molecules that measures the extent of chemical reactivity.

$$S\frac{1}{2\eta} \tag{2}$$

where IP and EA can be obtained as IP = $-E_{\mathrm{HOMO}}$ and EA = $-E_{\mathrm{LUMO}}$.

All the calculated values of η and S of the designed dye molecules were listed in Table 3. From the table identified that the large HOMOs-LUMOs gap as a hard molecule and small HOMOs-LUMOs gap as a soft molecule while considering η. The stability of a molecule and its reactivity can be related to chemical η, which means that the dye molecules with least HOMOs LUMOs gaps have more reactive.

It is well identified that the higher the value of EA, the higher can be the electron transport ability. It is interesting to note that lower HOMOs-LUMOs gap of ICZA2 and ICZA4 shows lower IP values of 5.66 and 5.48 eV and higher EA values of 2.84 and 2.63 eV, respectively. This indicates that both the ICZA2 and ICZA4 dyes can be the best candidates for both hole and electron transport material compared with IC-2.

Non-linear optical study

The non-linear optical study (NLO) response of an isolated molecule in an electric field (E) can be represented as static polarizability (α), anisotropic polarizability ($\Delta\alpha$), and first hyperpolarizability (β) of the designed dye molecules were calculated using the following equation [44]:

$$\alpha_{tot} = \frac{1}{3}\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right] \tag{3}$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[\left(\alpha_{xx} + \alpha_{yy}\right)^2 + \left(\alpha_{zz} + \alpha_{xx}\right)^2 + 6\alpha_{xx}^2\right] \tag{4}$$

The third rank tensor of β can be described by 3 × 3 × 3 matrix.

$$\beta_0 = \left({\beta_x}^2 + {\beta_y}^2 + {\beta_z}^2\right)^{\frac{1}{2}} \tag{5}$$

$$\beta_0 = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{xxy} + \beta_{yyy} + \beta_{yzz}\right)^2 + \left(\beta_{xxz} + \beta_{zyy} + \beta_{zzz}\right)^2\right]^{\frac{1}{2}} \tag{6}$$

where α_{xx}, α_{yy} & α_{zz} polarizability tensor components, β_{zyy}, β_{zzz}, β_{xxx}, β_{xyy}, β_{xzz}, β_{xxy}, $\beta_{yyy} and \beta_{yzz}$ magnitude of the first hyperpolarizability tensor components. These constraints contribute in the non-linearity of the designed dye molecules.

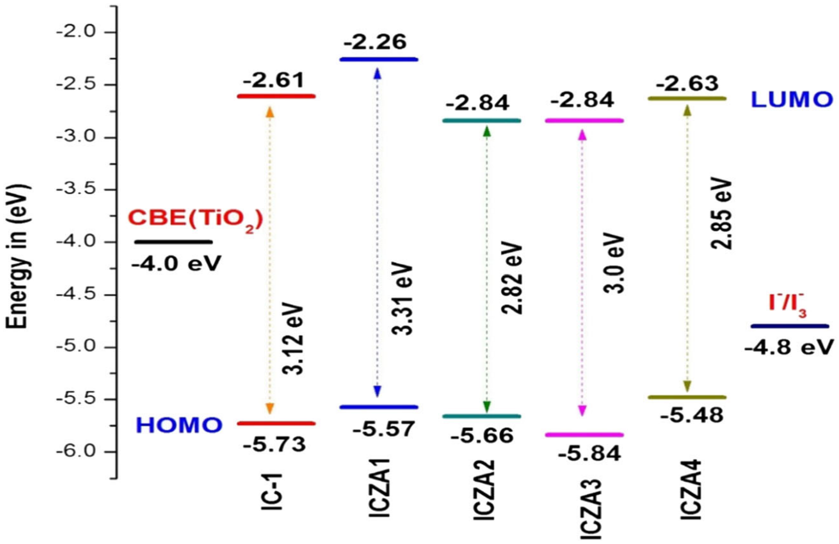


Fig. 5 FMOs of IC-2 and ICZA1-ICZA4 calculated at B3LYP/6-31G (d,p) level of theory

The highest molecular α and β exhibit good sensitizing property upon photoexcitation because it tends to decrease the aggregates formation on the surface of TiO_2 leads to better conversion efficiency. The calculated values were summarized in Table S1 and S2 (Supporting information). The α is directly proportional to the dipole moment and the β is inversely proportional to the vertical transition energy [45]. It has been observed that the α values of ICZA2 (231 a.u.), ICZA3 (193 a.u.), and ICZA4 (218 a.u.) are higher than that of the other molecules when compared to IC-2 (186 a.u.), except the value of ICZA1 (181 a.u.). The substitution effect of strong electron withdrawing groups of ICZA2 and ICZA4 dyes enhanced the α. The ICZA2 dye has the maximum value of α as 3.424×10^{-23} e.s.u. when compared with IC-2 as 2.764×10^{-23} e.s.u. The highest value of β, which is a measure of NLO activity of the molecular system, is related with the ICT, resulting from the electron cloud movement, through the acceptor framework of electron [46]. Accordingly, ICZA2 dye with minimum transition energy (2.92 eV obtained from TD-DFT calculation) exhibits the maximum β value of 11.424×10^{-30} e.s.u. A higher value of the β is important for active NLO performance and the present results indicate that the ICZA2 possess larger β value particularly which can be used for NLO applications.

Table 3 Global reactivity descriptors energy values of ICZA1-ICZA4 dyes at B3LYP/6-31G(d,p) level of theory

Dyes	IP in (eV)	EA	η	S
IC-2	5.73	2.61	1.56	0.32
ICZA1	5.57	2.26	1.65	0.30
ICZA2	5.66	2.84	1.41	0.35
ICZA3	5.84	2.48	1.68	0.29
ICZA4	5.48	2.63	1.42	0.35

Spectral analysis

The simulated optical absorption spectra of IC-2 and ICZA1-ICZA4 in dichloromethane solution were displayed in Fig. 6. It is obvious that all the dye sensitizers lie in the entire visible region of 410 nm. The calculated excitation wavelength, oscillator strength, LHE, and major orbitals transitions of IC-2, ICZA1-ICZA4 were shown in Table 4. The maximum absorption peak of ICZA4 is 423 nm and exhibits a large redshift of 38 nm compared to IC-2 (385 nm), which is consistent with the smaller E_g, while the presence of ICZA1 (366 nm) was blue-shifted 19 nm compared to IC-2. The longer absorption wavelength was assigned to ICT between the donor and electron acceptor moieties. All the absorption spectra also belonged to n-π* transitions. In Table 4, vertical excitation energies (E) were changed in decreasing order, ICZA4 > ICZA2 > ICZA3 > ICZA1, showing that there is a redshift when passing from ICZA4-ICZA1. We have also calculated the LHE is one of the important parameter which determines the efficiency of DSSCs.

LHE (λ) can be calculated according to the following [47]:

$$\mathrm{LHE} = 1 - 10^{-f} \quad (7)$$

where f represents oscillator strength of the dye sensitizer related to the $\lambda_{\max}$.

In Eq. 7, highest f and hence higher LHE were found for ICZA2. $\lambda_{\max}$ has the highest value for ICZA4 dye sensitizer for which LHE (1.65 a.u.). Therefore, according to LHE, ICZA4 dye should be the best sensitizer compared to IC-2 (1.40 a.u.), which has beneficial for larger short-circuit current density (J_{SC}). In all the studied dye molecules, the dominant absorption band has associated with HOMO-LUMO transition.

These results show that all dye sensitizers have only one band in the visible region ($\lambda_{\max} > 350$ nm). This also indicates

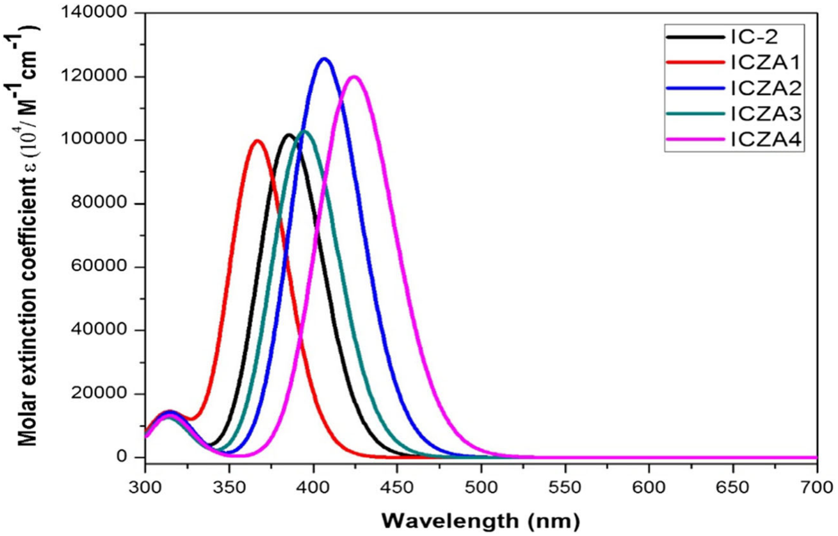


Fig. 6 TD-DFT absorption spectra of designed dyes and TC104 calculated at WB97XD/6-31G (d,p) level of theory in CH_2Cl_2 medium

that the ICZA4 could harvest more light at the longer-wavelength region, which can be helpful to further increase in the PCE of corresponding DSSCs.

Overall efficiency of DSSCs

As we know, the overall efficiency of DSSCs device is mainly determined byJ_{SC}, open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{IN}), it can be expressed as the following Eq. 8 [48]:

$$\eta = \frac{J_{SC}V_{OC}FF}{P_{IN}} \tag{8}$$

In DSSCs, V_{oc} can be described by the following [49]:

$$V_{OC} = \frac{E_{CB}}{q} + \frac{KT}{q} In\left[\frac{n_C}{N_{CB}}\right] - \frac{E_{redox}}{q} \tag{9}$$

where unit charge is q, thermal energy is KT, n_C is the conduction band (CB) of the electron number, N_{CB} is the accessible density of CB states, and E_{redox} is the oxidation potential of the liquid electrolyte.

TheV_{OC} is determined by energy difference between the CBE and redox electrolyte. Usually, the solution I^-/I_3^- is used as the redox potential, so we take it as a constant. ΔCBE is an important factor of V_{oc} and can be followed by [50]:

$$\Delta CBE = -\frac{q\mu_{normal}\gamma}{\varepsilon_0\varepsilon} \tag{10}$$

The outermost level concentration of dye sensitizer isγ, μ_{normal} is the dipole moment of individual molecular perpendicular to the boundary condition of the semiconductor and ε_0, ε it will be constants.

It is apparent that a large μ_{normal} will lead to greater extent shift of CBE which will result in largerV_{oc}. As shown in Table 4, ICZA1-ICZA4 values identified that the dipole moments are 6.52, 10.83, 8.98, and 12.06 Debye. The dyes ICZA2 and ICZA4 have the largest dipole moment, leading to largerV_{OC}. All four dyes were highly compared to IC-2 (10.35 Debye), except the values of ICZA1 and ICZA3. Among these dyes, ICZA4 can be the outstanding performance for improved efficiency of DSSCs.

TheJ_{SC} in DSSCs can be determined by the following [51]:

$$J_{SC} = \int LHE(\lambda)\Phi_{INJ}\eta_{coll}d\lambda \tag{11}$$

Table 4 Calculated at excitation wavelength in (nm and eV), oscillator strength (f), light harvesting efficiency (LHE), and major orbitals transition assignment of IC-2 and ICZA1-ICZA4 at TD-WB97XD/6-31G(d,p) level of theory in CH_2Cl_2 medium

Dyes	Excitation wavelength		Oscillator strength (f)	LHE	Major transitions (%)
	Energy (eV)	λ_{max} (nm)			
IC-2	3.21	385	1.40	0.960	HOMO→LUMO (71%)
ICZA1	3.38	366	1.37	0.957	HOMO→LUMO (72%)
ICZA2	3.08	406	1.73	0.981	HOMO→LUMO (65%)
ICZA3	3.14	394	1.41	0.961	HOMO→LUMO (71%)
ICZA4	2.92	423	1.65	0.977	HOMO→LUMO (77%)

Table 5 The calculated ground and excited-state oxidation potentials (in eV), vertical transition energies (in eV), dye regeneration (in eV), electron injection (in eV), and dipole moment (in Debye) of the dyes at TD-WB97XD/6-31G(d,p) level of theory in CH_2Cl_2 medium

Dyes	E_{OX}^{dye} (in eV)	λ_{max}^{ICT}	$E_{OX}^{dye^*}$	ΔG_{reg}	ΔG_{inject}	μ_{normal} (Debye)
IC-2 [25]	−5.73	3.21	2.52	0.93	−1.48	10.35
ICZA1	−5.57	3.38	2.19	0.77	−1.81	6.52
ICZA2	−5.66	3.08	2.58	0.86	−1.42	10.83
ICZA3	−5.84	3.14	2.70	1.04	−1.30	8.98
ICZA4	−5.48	2.92	2.56	0.68	−1.44	12.06

where *LHE* at a given wavelength of $\lambda_{max.}$ Φ_{INJ} is the electron injection efficiency and charge collection efficiency isη_{coll}. Hence, it is reasonable to assume that η_{coll} is a constant. Another way of growing $J_{SC}$is to improve the electron injection rate of free energyΔG_{inject}. $\Phi_{INJ}$is related to the driving force $\Delta G_{inject}$of electrons injecting from excited state of molecule to the semiconductor CBE of TiO_2.

ΔG_{inject} can be described by the following [52]:

$$\Delta G_{inject} = E_{OX}^{dye^*} - E_{CB}^{TiO_2} \tag{12}$$

where $E_{OX}^{dye^*}$ oxidation potential of the excited state of dye sensitizer and $E_{CB}^{TiO_2}$ CBE of TiO_2 in the reduction potential energy surface.

$E_{OX}^{dye^*}$ can be calculated by Eq. 13 [53–55]:

$$E_{OX}^{dye^*} = E_{OX}^{dye} - E \tag{13}$$

where E_{OX}^{dye} reduction potential of the ground state of dye, while *E* is a vertical excitation energy corresponding toλ_{max}. According to Islam investigation, when $\Delta G_{inject} > 0.2$ eV, the electron injection efficiency (Φ_{INJ}) is almost equal to one [56]. As shown in Tables 4 and 5, the absolute values of ΔG_{inject} for ICZA1-ICZA4 are much greater than 0.2 eV. So, it can be predicted that these sensitizers have driving force for the fast $\Delta G_{inject}$of excited state electrons into CBE of TiO_2.

J_{SC} is also influenced by the regeneration efficiency of sensitizer (η_{reg}), which can be determined by the driving force of regeneration ΔG_{reg}. It can be calculated by Eq. 14 [57]:

$$\Delta G_{reg} = E_{redox} - E_{dye} \tag{14}$$

According to the survey of Robson, the regeneration process of the dye can significantly influence the efficiency of DSSCs [58]. The ICZA3 dye having larger driving forces of regeneration can cause the improvement of η_{reg}. Finally, ICZA2 and ICZA4 will be the promising sensitizers due to their good PCE in DSSCs.

Conclusion

In summary, we have demonstrated that the dyes ICZA1-A4 can be transformed into suitable sensitizers especially in the higher molar extinction coefficient and longer-wavelength visible region of the solar spectrum. Photovoltaic properties of these D-π-A systems with different acceptor groups have been investigated by DFT and TD-DFT method. These dyes exhibit higher molar extinction coefficient and broad electronic absorption properties of DSSCs. Overall, a new type of ICZA1-A4 acceptor moieties were changed to different anchoring modes which can be successfully employed for DSSCs. In comparison with IC-2, the different acceptor segment of dyes ICZA2-ICZA4 have exhibited a higher absorption, LHE, smaller E_g, and obvious redshifts, for obtaining the improved PCE. The NLO property of the designed dye molecules were calculated at static polarizability and first hyperpolarizability values. It shows that the ICZA2 molecule possess better NLO performance. In particular, these results demonstrated that ICZA2 and ICZA4 acceptor moieties are promising electron withdrawing groups for high performance of DSSCs. Finally, to conclude, the promising D-π-A method has provided evidences with the electron withdrawing groups of ICZA2 and ICZA4 dyes for the further development of highly efficient metal-free organic dye sensitizer in practical application of DSSCs.

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Compliance with ethical standards

Conflict of interest The authors declared that they have no conflict of interest.

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