Influence of a Local Electric Field on the Light Harvesting Efficiency of a Cyclopentadithiophene-Bridged D-A- π -A Indoline Dye on Pure and N-doped TiO₂ Surfaces

Kadali Chaitanya^a, B Mark Heron^b, Xue Hai Ju^{a,1}

^aKey Laboratory of Soft Chemistry and Functional Materials of MOE, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

^bDepartment of Chemical Sciences, School of Applied Sciences, University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK

ABSTRACT

The primary objective of this paper is to study the influence of the local electric field at the dye/semiconductor (pure and nitrogen doped TiO₂) interface on the performance of dye sensitized solar cells (DSSCs). In this regard, as a first step, we explored the influence of electric field on the performance of the WS-51 dye by computing its properties in an electric field up to 15×10^{-4} a.u. The electronic and optical properties of an established, efficient, donor-acceptor- π -acceptor dye in different electric field strengths were probed with density functional theory (DFT) and time-dependent DFT. The calculated results indicate that, under an electric field, the dye shows significant changes in absorption spectrum due to considerable changes in molecular structure. The TD-DFT results indicate that the absorption spectrum of the dye in acetonitrile solution have shown a blue shift with decreasing molecular extinction coefficient by rising electric field strength. Secondly, we investigated the dye adsorbed on Ti₄₈O₉₆ and Ti₄₈O₉₅N clusters. In the applied field off state, the absorption spectrum of the dye/Ti₄₈O₉₅N system is red shifted with an improved molecular extinction coefficient as compared to the dye/Ti₄₈O₉₆ system, indicating that the nitrogen doped TiO₂ surface is more favourable for enhancing the efficiency of the DSSCs. Finally, the calculated results suggested that the light harvesting efficiency (LHE) of the dye/ Ti₄₈O₉₅N system is higher than that of the dye/ Ti₄₈O₉₆ system. But, under an electric field the LHE of the dye on Ti₄₈O₉₆ and Ti₄₈O₉₅N clusters is likely to decrease with increasing electric field strength. The photon to current response of the DSSCs is limited by the local electric field generated at the dye – semiconductor interface. Finally, results indicate that the doping of a nitrogen atom in TiO₂ moderates the electric field intensity at the dye – semiconductor interface. Therefore, the results obtained in this study will provide a valuable reference for understanding the role of local electric field for the further optimization of DSSCs.

¹ * Corresponding author. E-mail: xhju@njust.edu.cn; Tel: +86 25 84315947-801; fax: +86 25 84431622

1. INTRODUCTION

In the last few decades numerous researchers have been captivated by molecular engineering of sensitizers for dye sensitized solar cells (DSSCs) for the progression of next generation solar cells due to their economical production cost, easy scale-up, and flexible structural modification[1-3]. Among the different types of sensitizers, metallo-organic dye sensitizers (MODs), such as ruthenium [4] or zinc porphyrin [5,6] show photoconversion efficiency (PCE) between 11–13%. Instead, cheap metal free organic dye sensitizers (MFODs), such as triphenylamine derived dyes [7-9] and indoline derived dyes [10], appear to be the most promising candidates for DSSCs.

So far the donor – π -bridge – acceptor (D- π -A) design has been widely exploited for tailoring organic dyes due to their efficient intramolecular charge transfer (ICT) after photo-irradiation [10,11]. Recently, several researchers have suggested that the introduction of low bandgap electron-withdrawing units (such as benzothiadiazole, benzotriazole, quinoxaline, phthalimide and diketopyrrolopyrrole) [12] between the electron donor part and the π framework, thus constructing D-A- π -A featured sensitizers, can not only modulate the energy levels, absorption spectra, and photovoltaic performance, but also greatly improve the photostability of the organic dye sensitizers. For instance, WS-51 (see Fig. 1), one of the D-A- π -A dyes, employing an indoline derivative as the electron donor, cyanoacetic acid as the electron acceptor/anchor and a benzo[*c*][1,2,5]thiadiazole (BT) as the additional acceptor in the dioctyl-substituted 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) π -bridge, exhibited an excellent IPCE response with good interfacial interactions. It is also important to note that, in DSSCs the efficiency of very few indoline dye derivatives based on the standard iodine electrolyte are capable of achieving 9% efficiency. However, **Chai** et al. [13] were the first to surmount this barrier and reported an efficiency of 10.1% with iodine redox couples for WS-51.

In DSSCs, the photoabsorption is controlled by the dye sensitizer layered on the n-type semiconductor (mostly TiO₂) surface. Upon irradiation the excited electron in the dye molecule is injected into the semiconductor conduction band in an ultrafast femto- to pico-second time scale. Later, the oxidized dye molecules are regenerated in microseconds by an iodide/triiodide redox couple². The gap between the interfacial electron transfer rates is attributable to the inconsistency of molecular orbitals of the sensitizer and thermodynamic driving force between the two interfacial processes. Although some studies [2,8,12] open these fundamental operational principles of DSSCs, the exact working mechanism is still not fully understood due to a local electric field being established at the interface, inevitably created between the oxidized dye molecules and electrons in the TiO₂ causes a Stark effect on the nearby dye molecules, of DSSC device [14].

It has recently stated that local electric fields > 1 MV/cm, can show a significant unidirectional shift of the ground-state absorption spectrum [15]. Because, a single electron injected into semiconductor conduction band can affect the ground-state spectrum of many sensitizers, so the absorption change allied with the electric field will be rather enormous. For instance, in 2010, Cappel et al.,[16] and Ardo et al.,[17] independently using electrochromism / electroabsorption and photoinduced absorption (PIA) techniques observed a Stark effect in D149 and P1 based DSSCs. They suggest that electric field can induce changes in the absorption spectra of the dye molecule adsorbed on the semiconductor surface. Similarly, in 2013, using transient absorption spectroscopy Burdzinski et al.,[18] reported that the average rate for screening of electric fields for D149 adsorbed on TiO_2 in the presence of acetonitrile was $5 \times 10^3 \text{ s}^{-1}$. Also, using high level computational techniques De Angelis et al.,[19] observed the major spectral changes of a neutral dye molecule in the presence of local electric fields.

Recent investigations also exposed that N-doped TiO_2 as a promising photocatalytic material for a photovoltaic applications due to the beneficial effects of nitrogen on the electronic and optical properties of the TiO_2 [20,21,22]. Even though vast numbers of experimental results are published, appropriate information of the surface chemistry at the oxide interface and the role of the nitrogen atom in the physical features of the semiconductor are still inadequate. So, for a comprehensive understanding of the dye solar cell performance and the roles of the dye on an N-doped semiconducting surface, the structural and electronic properties of the dye under electric fields generated due to the Stark effect is of crucial importance. In this concern, we have selected the promising indoline based WS-51 dye and inspected its electronic absorption characteristics on a TiO_2 surface and an N-doped TiO_2 surface with and without electric field effect using quantum mechanical calculations centered on DFT and TDDFT which are believed to be most promising way ahead. Such state-of-the art theoretical calculations have been successfully employed to various sensitizers used in DSSCs [23,24]. The molecular structure of the dye WS-51 studied in this work is shown in Fig. 1. The results obtained in this study will certainly provide a useful reference to the future design and optimization of indoline derivatives for DSSC applications.

Figure 1

2. THEORY AND COMPUTATIONAL DETAILS

In DSSC, photo conversion efficiency (η) of solar cell device is determined by following equation [2,8]

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{inc}} \dots\dots\dots (1)$$

Where V_{OC} is open circuit photo voltage, J_{SC} is short circuit current density, FF is fill factor and P_{inc} is incident solar power. Here J_{SC} can be expressed as [2,8]

$$J_{SC} = q \int \eta_{IPCE} \phi_{Ph}^{source}(\lambda) d\lambda \quad \dots\dots\dots (2)$$

and η_{IPCE} also written as

$$\eta_{IPCE} = LHE \phi_{inject} \eta_{collect} \quad \dots\dots\dots (3)$$

where LHE is light harvesting efficiency, ϕ_{inject} is quantum yield of electron injection, $\eta_{collect}$ is efficiency of collecting the injected electrons at the back contact and q is charge of electron.

The LHE in above equation is expressed as

$$LHE = 1 - 10^{-A} = 1 - 10^{-f} \quad \dots\dots\dots (4)$$

where A and f are the absorbance and oscillator strength of the dye associated to the λ_{max}^{ICT} .

The V_{OC} in equation (1) is the difference between the electrolyte redox potential and the quasi-Fermi level of electrons in the semiconductor and can be expressed as [2,8]

$$V_{OC} = \frac{E_c + \Delta CB}{q} + \frac{k_b T}{q} \ln \left(\frac{n_c}{N_{CB}} \right) - \frac{E_{redox}}{q} \quad \dots\dots\dots (5)$$

In this expression q denotes the charge of electron, n_c is the number of electrons in conduction band, N_{CB} is the accessible density of states in conduction band, k_b is the Boltzmann constant, T is the temperature and ΔCB is the shift of conduction band energy of semiconductor when dye adsorbed on it and can be expressed as

$$\Delta CB = - \frac{q \mu_{normal} \gamma}{\epsilon \epsilon_0} \quad \dots\dots\dots (6)$$

where, μ_{normal} is the dipole moment of single dye molecules perpendicular to the surface of the semiconductor substrate and γ is the surface concentration of the dye. ϵ_0 and ϵ represent the vacuum permittivity and dielectric permittivity, respectively.

Initially, the equilibrium geometry of WS-51 dye in the ground state was obtained at different electric field strengths ($0 - 15 \times 10^{-4}$ a.u) at the B3LYP/6-31G** level using Gaussian 09 program²⁵. Later, we performed a single point calculation of optimized structures of WS-51 to obtain the ground and excited state dipole moment and polarizability at different electric field strengths. In order to reduce the computational time and complexity, the long alkyl chains in dye WS-51 have been replaced with methyl groups; analogous simplification has shown that it could capture the essential character of realistic organic dyes while not changing the relative trend of the obtained results. The excited state properties of molecules in acetonitrile solvent using conductor-

like polarizable continuum model (CPCM) in the self-consistent reaction field (SCRF) theory [26] were investigated with the CAM-B3LYP/DGDZVP method.

In the second step, we have optimized the dye on pure and nitrogen doped TiO_2 surfaces at the GGA/PBE/DNP level of theory using the Dmol³ program [27]. Where, the nitrogen doping model ($\text{Ti}_{48}\text{O}_{95}\text{N}$) was made by replacing one surface oxygen atom of $\text{Ti}_{48}\text{O}_{96}$ as suggested in the literature [28]. We used all electron option instead of pseudopotential for the basis sets. We used Grimme method for DFT-D correction. Lastly, making use of the optimized geometries from Dmol³, we have calculated the excited state properties of the dye on the pure and N-substituted TiO_2 complexes in acetonitrile solvent at the CAM-B3LYP/3-21G(d) level using the Gaussian 09 program. To understand the nature of electronic excitations, the excited states were analysed by constructing the frontier molecular orbitals (FMOs) within the Avogadro program [29].

3. RESULTS AND DISCUSSION

3.1. Molecular Structure of dyes.

Table 1

Generally, the performance of the DSSCs is critically dependent on the molecular geometry of the dye sensitizers. The literature indicates that, a non-planar configuration can reduce the charge recombination in the charge separated states; a planar geometry of the π -conjugated linker can broaden the absorption spectrum and increase the short circuit current density (J_{SC}) [9,13]. Therefore in order to know the performance of the WS-51 dye in an electric field, we have optimized the geometry of the investigated dye by applying an electric field along the x-direction at the B3LYP/6-31G(d,p) level of theory. The results show that the WS-51 dye, which has a non-planar structure, limits unfavourable intermolecular aggregation and molecular packing. However, in D-A- π -A sensitizers, the efficiency of the electron conduction is not only affected by the twist angle between the donor unit and auxiliary electron-withdrawing group (θ_1); but also affected by the auxiliary electron-withdrawing group and π -conjugated plane (θ_2) [9,13]. The calculated results indicate that the auxiliary acceptor and π -conjugated moieties have better planarity in WS-51 which assisted the efficient electronic communication between the donor and acceptor moiety. The variation of the structural parameters θ_1 and θ_2 of WS-51 in the external electric fields are presented in Table 1. From Table 1, one can notice that the twist angle θ_1 and θ_2 increases with increasing applied external electric field. This indicates that under an external electric field the molecular structure of WS-51 dye slightly increases the non-planarity as compared to their ground state structure. As a result, WS-51 dye shows significant changes in its electronic properties under different electric field strengths.

3.2. Electronic properties of dyes

Generally, the electronic excitations and transition characteristics of dye sensitizers depends on the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the dye sensitizer [9]. So the most accurate evaluation of the molecular orbitals is essential. Several studies reported that HOMO and LUMO energy levels can be obtained with reasonable accuracy using the B3LYP method [4]. For this reason, as a first step, we have computed the HOMO and LUMO values of WS-51 in acetonitrile with B3LYP functional using three different basis sets (6-31G(d,p), 6-311++G(d,p) and cc-PVDZ) and compared these results with the available experimental data. The calculated results indicate that the HOMO and LUMO energy levels obtained with 6-311++G(d,p) correlate better with the experimental data than the other two basis sets (6-31G(d,p) and cc-PVDZ). Secondly, in order to understand the influence of local electric field on the electronic properties of the dye sensitizer WS-51, we have calculated the potential levels of the sensitizer at different electric field strengths using the B3LYP/6-311++G(d,p) level. The calculated E_H , E_L , and E_g along with other parameters are presented in Table 2.

Table 2

A vast number of studies on DSSCs expound that the HOMO and LUMO energy levels of the dyes must be near to the conduction band energy level of the TiO_2 electrode and iodide/triiodide redox mediator [2,8,9,11]. Perhaps, for superior dye regeneration, the HOMO level must be lower than the iodide/triiodide redox couple with a sufficient driving force of 0.2 – 0.3 eV and at the same time the LUMO level must be higher than the TiO_2 conduction band to the extent the light absorption will be limited by the efficient electron injection [2,8,9]. From Table 2, we can observe that in the external field off condition, the HOMO and LUMO energy levels of the WS-51 dye are higher and lower than the TiO_2 conduction band and redox potential, respectively. It is interesting to observe that in an external electric field the HOMO and LUMO energy levels of the investigated dye were decreased and increased, respectively, with increasing field strength which suggests that the driving force required for excited-state electron injection and dye regeneration will increase. But, a sufficiently low driving force for excited-state electron injection and dye regeneration is a prerequisite for enhancing J_{SC} and V_{OC} . This indicates that the rise in driving force for excited-state electron injection and dye regeneration beyond the limiting value, due to setting up of local electric fields at the interface, decays the device performance.

3.3. Energy gap

In DSSCs, energy gap is an important parameter which is unswervingly associated with absorption characteristics and J_{SC} [9]. In order to enhance the J_{SC} , the energy gap of the sensitizer needs to be decreased by either lowering the LUMO energy level or raising the HOMO energy level. In order to better understand how the HOMOs and LUMOs of investigated dye were influenced by the local electric field, we have presented the frontier molecular energy levels of WS-51 dye under different electric field strengths in Fig. 2.

Figure 2

We observe that the calculated energy gap of the investigated dye without electric field matches well with the experimental values and thus validates the choice of computational model. In the off field state, the energy gap of WS-51 dye is 2.080 eV and is increasing steadily with increasing electric field strength. This indicates that the energy gap of dye with electric field is greater than that of the one without electric field. The energy gap of WS-51 dye decreases in the order of field = 15 (2.227 eV) > field = 10 (2.185 eV) > field = 5 (2.094) > field = 0 (2.080). From Fig. 2, we can perceive that in WS-51 the energy levels are well separated from the HOMO and LUMO, but HOMO - 4, HOMO - 5; LUMO + 3, LUMO + 4 are energetically very close. Mostly these orbitals (HOMO - 4, HOMO - 5 and LUMO + 3, LUMO + 4) have contributions from carbon atoms of the indoline group. From Fig. 2, it can also be seen that as the electric field strength increases, the energy difference between the HOMOs is decreases and LUMOs is increases. These results suggest that the investigated dye exhibits a blue-shifted electronic absorption spectra with increasing electric field strength due to the increase of the gap between HOMO and the LUMO energy levels.

3.4. Dipole moment and polarizability

As a general rule, a high molecular dipole moment [30] and polarizability [31, 32] are needed for a dye to be employed in efficient DSSCs. When there is no external field, our results indicate that the dipole moment of WS-51 in the gas phase (acetonitrile solvent) is 14.205 D (17.446 D) (see Table 1). When an electric field of strength 5×10^{-4} a.u was applied along the x-direction, the dipole moment of WS-51 dye is reduced by ~3%. Upon increasing the electric field strength, the dipole moment of this dye decreases gradually and creates a down shift in the conduction-band potential of the semiconductor electrode and thus, minimizes the V_{OC} . On the other hand, the calculated results indicate that the molecular polarizabilities of WS-51 dye decreases with increasing electric field strength. Due to this the local concentration of acceptor species at the semiconductor surface decreases and surges the time of electron recombination [31].

3.5. Optical properties

Generally, the absorption spectra of indoline based D-A- π -A derivatives exhibit three major electronic absorption bands: i) the band from the localized aromatic $\pi \rightarrow \pi^*$ transitions in the range 300–400 nm, ii) the ICT band in visible region (around 540 nm), and iii) the additional absorption band or shoulder from secondary orbital transition (near 450 nm). The absorption spectrum of WS-51 dye in mixed solvent solution ($\text{CHCl}_3:\text{CH}_3\text{OH}$, v/v = 4:1) exhibits an intense band at 551 nm [13]. This band is attributed to the $\pi \rightarrow \pi^*$ ICT originating from the indoline entity and part of BDT and CPDT to the electron accepting cyanoacrylic acid. The absorption spectra of WS-51 with and without an electric field was investigated at the CAM-B3LYP/DGDZVP level in acetonitrile solution is presented in Fig. 3.

Figure 3

Table 3

In the field off condition, the simulated absorption spectrum of WS-51 presented in Fig. 3 contains the peaks at 551, 435 and 306 nm, which are analogous to the experimental values 551, 460 and 314 nm, respectively. Thus, the absorption spectrum simulated at different electric field strengths with the current computational method is valid. The calculated vertical excited singlet states, oscillator strengths of WS-51 dye in acetonitrile solvent along with available experimental data are presented in Table 3. The calculated results show that the intense band at 551 nm predominantly undergoes HOMO- $\rightarrow$ LUMO (66%). The other strong absorption at 306 nm is mainly originated from two transitions HOMO- $\rightarrow$ L+2 (37%) and HOMO- $\rightarrow$ L+3 (27%). The additional band at 435 nm contributed by the excitation of H-1- $\rightarrow$ LUMO (34%) and HOMO- $\rightarrow$ L+1 (46%). On the other hand the simulated absorption spectra of WS-51 dye under different electric field strengths revealed that the maximum absorption band (λ_{max}) was blue shifted by ~20 nm with increasing electric field from 0 to 15×10^{-4} a.u. (see Fig. 3). The blue shift of λ_{max} is due to an increase in the band gap of the WS-51 dye under external electric field. Normally, the probability of absorption by a molecule depends on the molecular extinction coefficient (ϵ). Large values of ϵ indicate a high probability of absorption at a given wavelength leading to better conversion efficiencies. But our results show that the molecular extinction coefficient of λ_{max} decreases with increasing electric field strength. As a result, the conversion efficiency of WS-51 dye will decay with increasing electric field strength as a consequence of a decrease in ϵ .

In order to comprehensively understand the influence of the local electric field on the intramolecular charge transfer with in the dye, in Fig. 4 the charge density difference between the excited and ground states of WS-51 dye under different electric field strengths have been presented. From Fig. 4 we can observe that in field off condition, the density depletion zones (blue) are mostly

located on the donor unit and small percentage on conjugated spacer segments, while the regions of density enhancement (red) are localized on the conjugated spacer groups and the acceptor moiety, indicating adequate intramolecular charge transfer taking place when the transition occurs. On the other hand, in the field on condition (see Fig. 4), we notice that the density depletion zones and density enhancement regions on the donor and acceptor units are reducing and shrinking gradually with increasing electric field strength. This indicates that during the electronic transition the intramolecular charge transfer within the dye is decreasing with increasing electric field strength.

To assist the above discussion we have computed the molecular orbital composition of HOMO and LUMO energy levels of the WS-51 dye at different electric field strengths and these compositions are presented in Table 4. The results show that donor contribution to HOMO energy level and acceptor contribution to the LUMO energy level is decreasing with increasing electric field strength. These results indicate that the electron injection into TiO₂ surface decreases under electric field due to weakening of electron coupling between dye-TiO₂ surfaces.

Figure 4
Table 4

3.6. Stark effect on the absorption spectrum

Recent studies [16,17] report that the local electric fields acting on the ground state dye molecules could lead to a change in the absorption spectrum due to the Stark effect. The deviation in transition frequency ($\Delta\nu$) due to a peripheral electric field (E) is given by

$$\Delta\nu = -\Delta\vec{\mu} \cdot \vec{E} - \frac{1}{2} \vec{E} \cdot \Delta\alpha \cdot \vec{E} \quad \dots\dots\dots (7)$$

The change in the absorption spectrum as a function of local electric field can be obtained from a Taylor expansion of A around transition frequency at $E = 0$ as given below

$$\Delta A = -\frac{dA}{d\nu} \Delta\mu \vec{E} + \frac{1}{2} \left(\frac{d^2 A}{d\nu^2} \Delta\mu^2 - \frac{dA}{d\nu} \cdot \Delta\alpha \right) \vec{E}^2 \quad \dots\dots\dots (8)$$

where $\Delta\vec{\mu}$ is the change in dipole moment and $\Delta\alpha$ is the change in polarizability between the ground and excited state of the molecule. Therefore we have calculated the ground and excited state dipole moment and polarizability of WS-51 dye at different electric field strengths using B3LYP/6-31G(d,p) level of theory (Table 5). The calculated results show that the transition frequency and amplitude of the absorption change are increased with increasing electric field strength. Because, the applied electric field points in an opposite direction to $\Delta\mu$, the ground and excited states of the dye are destabilized. Due to this the gap between ground and excited state being increased by $\Delta\nu$, a resulting blue shift of the absorption spectrum is observed.

Table 5

3.7. Charge injection (ΔG_{inj}^0) and dye regeneration (ΔG_{reg}^0)

In order to know how the charge injection and dye regeneration parameters are affected under local electric field, we have calculated ΔG_{inj}^0 and ΔG_{reg}^0 using following equations³³

$$\Delta G_{inj}^o = E_{OX}^{Dye*} - E_{CB}^{TiO_2} \dots\dots\dots (9)$$

$$\Delta G_{reg}^o = E(I_3^- / I^-) - E_{OX}^{Dye} \dots\dots\dots (10)$$

where $E_{OX}^{Dye*} = E_{OX}^{Dye} - \lambda_{max}^{ICT}$ is the oxidation potential of the dye in the excited state, λ_{max}^{ICT} is the energy of the ICT and $E(I_3^- / I^-)$ is the redox potential energy level of the iodide/triiodide (-4.8 eV).

The calculated results are presented in Table 6. From Table 6 one can notice that in the field off condition the calculated values compare well with the experimental results. The calculated results indicate that the decrease in charge injection of WS-51 dye under electric field as compared to field off condition. Conversely, the dye regeneration of WS-51 dye also gradually increases with increasing electric field strength. This causes the major loss in PCE of DSSCs due to the energy dissipation as heat in the regeneration reaction.

Table 5
Figure 5

3.8. Dye adsorption on pure and nitrogen substituted titanium dioxide substrates

Generally, in DSSCs, the rate of charge transfer depends on the strength of interaction between dye and semiconductor, whereas, the coupling strength depends on the adsorption energy of the dye-TiO₂ system i.e., larger the adsorption energy stronger the electron coupling between the dye anchoring group and semiconductor substrate and thus, the more the rate of charge transfer is³⁴. Recent studies suggest that dyes linked to the TiO₂ substrate through a bidentate bridging mode are more constructive and stable for efficient charge injection due to shorter bidentate binding as compared to other bridging modes [34]. Therefore, to know the charge transfer kinetics between the dye sensitizer and the semiconductor surface the adsorption energy of WS-51 on Ti₄₈O₉₆ and Ti₄₈O₉₅N substrates *via* bidentate bridging with the two interface O-Ti bonds using DFT method has been studied. The optimized lowest energy structures of two systems (WS-51/Ti₄₈O₉₆ and WS-51/Ti₄₈O₉₅N) are presented in Fig. 5. The computed results show that the adsorption energy of WS-51/Ti₄₈O₉₅N system is similar to that of the WS-51/Ti₄₈O₉₆ system, whereas, the bond distances between the Ti atom and the O atom of dye are in the 2.034 – 2.101 Å range for both the systems. These effects suggest that the binding strength between the dye and semiconductor substrate can be

improved by substituting the nitrogen atom into TiO_2 substrate [28]. Therefore, the charge transfer rate will increase greatly and boosts the performance of the DSSCs device.

Figure 6

Figure 7

3.9. Optical properties of WS-51 dye adsorbed on $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ substrates

In order to understand the variation of optical properties of the dye adsorbed on pure and nitrogen doped TiO_2 substrates the electronic absorption spectrum of dye on $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ substrates using the CAM-B3LYP method with 3-21G* basis set have been investigated. The simulated absorption spectra of the investigated systems in the field off and the field on conditions are presented in Fig. 6. The calculated energy gap of $\text{Ti}_{48}\text{O}_{96}$ ($\text{Ti}_{48}\text{O}_{95}\text{N}$) cluster from molecular orbital energy levels in acetonitrile solution (see Fig 7) overestimate 5.005 eV (4.653 eV) the experimental value 3.20 eV (3.02 eV). However, the optical gap obtained from the $S_0 \rightarrow S_1$ transition for $\text{Ti}_{48}\text{O}_{96}$ (3.73 eV) and $\text{Ti}_{48}\text{O}_{95}\text{N}$ (3.20 eV) clusters (see Fig. 6 (a)) are rather comparable with the experimental data [35] and support the validity of the current computational method for analysis of optical properties of this dye on $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ clusters. From Fig. 7 one can also notice that the energy gap of $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ clusters decreases upon dye adsorption. This is generally due to the insertion of occupied energy levels of dye between HOMO and LUMO gap of the substrates. The energy level alignment of the WS-51 dye on the $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ clusters were shown in Fig. 7a. The energy gap of the WS-51/ $\text{Ti}_{48}\text{O}_{96}$ is decreased by $\sim 25\%$ upon doping the semiconductor substrate with a nitrogen atom and suggests that the possibility of red shift absorption spectra of WS-51/ $\text{Ti}_{48}\text{O}_{95}\text{N}$ systems as compared to that of WS-51/ $\text{Ti}_{48}\text{O}_{96}$ system. However, when WS-51/ $\text{Ti}_{48}\text{O}_{96}$ and WS-51/ $\text{Ti}_{48}\text{O}_{95}\text{N}$ systems are placed in an external electric field, the energy gap of the systems increase with increasing electric field strength. From Fig. 7 we can observe that the HOMO and LUMO energy levels of the WS-51/ $\text{Ti}_{48}\text{O}_{96}$ and WS-51/ $\text{Ti}_{48}\text{O}_{95}\text{N}$ systems are free from mixing of other molecular orbitals in field off and field on conditions. The HOMO of the systems having dye character, whereas, the LUMO of the systems having same character as the substrate.

The absorption spectrum of WS-51 dye on a $3\ \mu\text{m}$ TiO_2 film has two peaks at 533 nm and 450 nm [13]. The broad and intense peak at 533 nm exhibited a ~ 20 nm blue shift as compared to the isolated dye. In the field off condition, our calculated results (see Fig. 6) overestimated the experimental results and predicted the absorption peaks extending from 350 – 750 nm with a weak peak at 468 nm and a strong peak at 630 nm. Alternatively, when the WS-51 dye was placed on a $\text{Ti}_{48}\text{O}_{95}\text{N}$ substrate, the absorption spectra exhibited an 8 nm red shift with a better extinction

coefficient as compared to the WS-51/Ti₄₈O₉₆ system (see Fig. 6). On the other hand, when the dye was linked to the Ti₄₈O₉₆ or Ti₄₈O₉₅N system and placed in electric field a blue shift of absorption spectra was exhibited relative to that of the field off condition. From Fig 6 we can also observe that the molecular extinction coefficient of the charge transfer peak at higher wavelength is decreasing with increasing electric field strength ($0 - 15 \times 10^{-4}$ a.u.) for both WS-51/Ti₄₈O₉₆ and WS-51/Ti₄₈O₉₅N systems (see Fig 6b & 6c). The reason for reducing molecular extinction coefficient under electric field is due to peculiarities in alignment and symmetry of the unoccupied orbitals, which led to unfavourable orbital coupling between the dye and semiconductor substrate. The molecular extinction coefficient of a different peak observed at lower wavelength increases under an electric field but it is not conducive to charge transfer. The assignments of the observed peaks with the most significant transitions along with oscillator strength are presented in Table 7. From Table 7, it is evident that all the transitions take place from HOMO or HOMO-1 of the system and keeps the dye character. Where, the unoccupied states involved the transition from LUMO to LUMO + 18. For example, in field off condition, the main excitation $S_0 \rightarrow S_1$ at 630 nm in WS-51/Ti₄₈O₉₆ system having contribution from H-1->L+2 (32%), HOMO->L+17 (32%), HOMO->L+18 (11%) and in the case of WS-51/Ti₄₈O₉₅N system, the excitation observed at 653 nm having contribution from HOMO->L+15 (34%) and HOMO->L+16 (32%). The HOMO in each of the systems has localized only on the dye. This is confirmed by the visualization of the MOs with the Avogadro software. Fig. 8 is an isosurface plot of the LUMOs pertaining to WS-51/ Ti₄₈O₉₆ (WS-51/Ti₄₈O₉₅N) system with and without electric field, showing the contribution from both the dye and semiconductor substrate.

Figure 8

In order to better understand the electron injection from dye to semiconductor substrate, the electron density difference maps (EDDM) pertaining to the charge transfer peak in the absorption spectra of WS-51/Ti₄₈O₉₆ and WS-51/Ti₄₈O₉₅N systems under different electric field strengths are presented in Fig 8. From Fig. 8 we can observe that in the field off condition, the positive regions (blue) are mostly located on the donor unit, slightly on π -conjugated unit of dye and semiconductor substrate, however, the negative region (red) is confined to the π -conjugated unit and the acceptor moiety, which is indicative of passable electron injection from the dye to the semiconductor surface in an electronic transition. Conversely, we observe that the positive regions on the donor unit of dye are reducing gradually with increasing electric field strength. This reveals that during the electronic transition the degree of electron injection from the dye to semiconductor substrate is decreasing with increasing electric field strength due to weakening of the electron donating ability of the indoline unit.

Table 7

3.10. Influence of local electric field on J_{SC} and V_{OC}

In equation 3, if ϕ_{inject} and $\eta_{collect}$ are almost equal to unity, then J_{SC} is determined by the LHE of the dye adsorbed on the film. So in order to enhance the J_{SC} , the LHE must be as large as possible. Thus, we calculated the LHE of WS-51 dye on $Ti_{48}O_{96}$ and $Ti_{48}O_{95}N$ clusters with and without an electric field at the CAM-B3LYP/3-21G(d) level and the results are presented in **Table 7**. The absorption Stark spectrum (ΔA) as the change in absorption spectrum peak area in an external electric field is obtained as $\Delta A = A(E \neq 0) - A(E = 0)$. Recently, Cappel et al [16], reported that the Peak Area calculation method is more precise and accurate than the conventional maximum absorption method to quantify the photon to current response. Therefore, we have adopted the Peak Area calculation method to compare with the LHE, because the Peak Area calculation method covers all the electronic transitions in the complete area of the absorption spectra. If peak area is larger, the photocurrent response is greater i.e., the higher the LHE. The Peak Area for the dye on $Ti_{48}O_{96}$ and $Ti_{48}O_{95}N$ clusters has been obtained using following equation

$$A\% = \frac{A - A_{Ref}}{A_{Ref}} \dots\dots\dots (11)$$

where A and A_{Ref} are the peak area of the WS-51 dye on the semiconductor substrate with and without the local electric field in the acetonitrile solution. In the field off condition, the results indicate that the Peak Area of WS-51/ $Ti_{48}O_{95}N$ system is larger than that of the WS-51/ $Ti_{48}O_{96}$ system (see **Table 7**). This suggests that the LHE of the WS-51 dye improves by substituting the nitrogen atom in the TiO_2 semiconductor. However, in the field on condition the situation is different in both the systems; the peak area tends to decrease with increasing electric field strength. This indicates that the electric field leads to minimize the LHE of the systems than that of the field off condition.

Another significant factor that effects the performance of the DSSCs is V_{OC} . Numerous studies revealed that V_{OC} is unswervingly associated with the shift of the conduction band edge (ΔCB) of the semiconductor [12]. Where, ΔCB is influenced by the dipole moment of single dye molecules vertical to the surface of the semiconductor. Because, the dye adsorbed on the semiconductor substrate induces changes in structural parameters, dipole moment and charge density, consequently the conduction band edge of the semiconductor substrate adjusts. So as to improve the V_{OC} , the dipole moment of the dye – semiconductor system must be as large as possible. The calculated results show that WS-51 dye adsorbs on the $Ti_{48}O_{96}$ or $Ti_{48}O_{95}N$ substrate almost upright with their total dipole moment making an angle of 45° with the substrate. From

Table 6 we can also observe that the total dipole moment of the WS-51 dye on $\text{Ti}_{48}\text{O}_{96}$ substrate is slightly lower than that of the $\text{Ti}_{48}\text{O}_{95}\text{N}$ substrate. However, in the field on condition, the dipole moment of the WS-51 dye linked to the $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ substrates decreases with increasing electric field strength. This suggests that under an electric field the CB edge of the semiconductor shifts downward, thus the gap between the electrolyte redox potential and the quasi-Fermi level of the semiconductor moderates i.e., V_{OC} decreases. Finally, this study specifies that the doping of a nitrogen atom in TiO_2 controls the electric field intensity to some extent at the dye – semiconductor interface.

4. CONCLUSIONS

A ‘first principles’ study has been carried out to gain insight into the effect of a local electric field on the performance of the indoline based WS-51 dye on pure and nitrogen doped TiO_2 surfaces. In the field off condition, the ground and excited state properties of the isolated dye calculated with the B3LYP and CAM-B3LYP functionals compare well with the experimental data and suggest that DFT and TD-DFT methods are reliable and suitable for predicting electronic and optical properties of the sensitizer. The TD-DFT results show that, due to the Stark effect, the WS-51 dye exhibited a blue shifted absorption spectrum with rising electric field strength. This is due to the changes in molecular structure of WS-51 dye under an electric field. The calculated results indicate that the adsorption energy of the WS-51/ $\text{Ti}_{48}\text{O}_{95}\text{N}$ system is somewhat larger than that of the WS-51/ $\text{Ti}_{48}\text{O}_{96}$ system. In the field off condition, the absorption spectrum of WS-51/ $\text{Ti}_{48}\text{O}_{95}\text{N}$ system is red shifted with improved molecular extinction coefficient as a result of the lowering of its energy gap as compared to WS-51/ $\text{Ti}_{48}\text{O}_{96}$ system. However, under an electric field, the absorption peak diminishes and blue shifts with increasing electric field strength and eventually decreases the LHE of the WS-51/ $\text{Ti}_{48}\text{O}_{95}\text{N}$ and WS-51/ $\text{Ti}_{48}\text{O}_{95}\text{N}$ systems. The EDDM indicate that the charge transport between WS-51 molecule and $\text{Ti}_{48}\text{O}_{95}\text{N}$ substrate is improved due to their better binding strength as compared to the dye on the $\text{Ti}_{48}\text{O}_{96}$ substrate. It is also shown that the electron injection from the dye to semiconductor substrate decreases with increasing electric field strength due to weakening of electron donating ability of indoline unit. On the other hand, the decrease in dipole moment of the WS-51 dye linked to the $\text{Ti}_{48}\text{O}_{96}$ substrate and $\text{Ti}_{48}\text{O}_{95}\text{N}$ substrate with increasing electric field strength signifies that under an electric field the gap between the electrolyte redox potential and the quasi-Fermi level of the semiconductor moderates due to a down shift of the semiconductor conduction band edge. In summary, all the above results suggest that the setting up of a local electric field at the dye – TiO_2 interface opposite to the direction of dipole moment decreases the LHE, J_{SC} and V_{OC} of the dye sensitizer. But, doping of a nitrogen atom in TiO_2

moderates the electric field intensity at the dye – semiconductor interface and consequently improves the performance of the DSSCs.

ACKNOWLEDGEMENTS

We are grateful for the financial support from the National Science Foundation of China (No. 21372116) and the Project Funded by China Postdoctoral Science Foundation (No.2015M581802) for supporting this work.

REFERENCES

1. O'Regan B, Gratzel M, A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal Tio₂ Films. *Nature* 1991; 353, 737-740.
2. Hagfeldt A, Boschloo G, Sun, L Kloo, L Pettersson H, Dye-Sensitized Solar Cells. *Chemical Reviews* 2010; 110, 6595-6663.
3. Bach U, Lupo D, Comte P, Moser J. E, Weissortel F, Salbeck J, Spreitzer H, Gratzel M, Solid-State Dye-Sensitized Mesoporous Tio₂ Solar Cells with High Photon-to-Electron Conversion Efficiencies. *Nature* 1998; 395, 583-585.
4. Nazeeruddin M. K, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B, Grätzel M, Combined Experimental and Dft-Tddft Computational Study of Photoelectrochemical Cell Ruthenium Sensitizers. *Journal of the American Chemical Society* 2005; 127, 16835-16847.
5. Yella A, Lee H. W, Tsao H. N, Yi C, Chandiran A. K, Nazeeruddin M. K, Diau E. W, Yeh C. Y, Zakeeruddin S. M, Gratzel M, Porphyrin-Sensitized Solar Cells with Cobalt (Ii/Iii)-Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science* 2011; 334, 629-34.
6. Mathew S, Yella A, Gao P, Humphry-Baker R, CurchodBasile F. E, Ashari-Astani N, Tavernelli I, Rothlisberger U, Nazeeruddin Md, K, Grätzel M, Dye-Sensitized Solar Cells with 13% Efficiency Achieved through the Molecular Engineering of Porphyrin Sensitizers. *Nat Chem* 2014; 6, 242-247.
7. Zhang G, Bala H, Cheng Y, Shi D, Lv X, Yu Q, Wang, P, High Efficiency and Stable Dye-Sensitized Solar Cells with an Organic Chromophore Featuring a Binary [Small π]-Conjugated Spacer. *Chemical Communications* 2009; 2198-2200.
8. Clifford J. N, Martinez-Ferrero E, Viterisi A, Palomares E, Sensitizer Molecular Structure-Device Efficiency Relationship in Dye Sensitized Solar Cells. *Chemical Society Reviews* 2011; 40, 1635-1646.

9. Zhang X, Xu Y, Giordano F, Schreier M, Pellet N, Hu Y, Yi C, Robertson N, Hua J, Zakeeruddin S. M, Tian H, Grätzel M, Molecular Engineering of Potent Sensitizers for Very Efficient Light Harvesting in Thin-Film Solid-State Dye-Sensitized Solar Cells. *Journal of the American Chemical Society* 2016; 138 (34), 10742-10745.
10. Yang J, Ganesan P, Teuscher J, Moehl T, Kim Y. J, Yi C, Comte P, Pei K, Holcombe T. W, Nazeeruddin M. K, Hua J, Zakeeruddin S. M, Tian H, Grätzel M, Influence of the Donor Size in D- π -A Organic Dyes for Dye-Sensitized Solar Cells. *Journal of the American Chemical Society* 2014, 136 (15), 5722-5730.
11. Horiuchi T, Miura H, Sumioka K, Uchida S, High Efficiency of Dye-Sensitized Solar Cells Based on Metal-Free Indoline Dyes. *Journal of the American Chemical Society* 2004; 126, 12218-12219.
12. Wu Y, Zhu W, 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* 2013; 42, 2039-58.
13. Chai Q, Li W, Liu J, Geng Z, Tian H, Zhu W.-h, Rational Molecular Engineering of Cyclopentadithiophene-Bridged D-a-II-a Sensitizers Combining High Photovoltaic Efficiency with Rapid Dye Adsorption. *Scientific Reports* 2015; 5, 11330.
14. Kanemoto K, Domoto S, Hashimoto H, Origin of Stark Signals Induced by Continuous Photoirradiation for Working Dye-Sensitized Solar Cells Revealed by Photoinduced Absorption Measurements. *The Journal of Physical Chemistry C* 2014; 118, 17260-17265.
15. Sampaio R. N, O'Donnell R. M, Barr T. J, Meyer G. J, Electric Fields Control $\text{TiO}_2(\text{E}^-) + \text{I}_3^- \rightarrow$ Charge Recombination in Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry Letters* 2014; 5, 3265-3268.
16. Cappel U. B, Feldt S. M, Schöneboom J, Hagfeldt A, Boschloo G, The Influence of Local Electric Fields on Photoinduced Absorption in Dye-Sensitized Solar Cells. *Journal of the American Chemical Society* 2010; 132, 9096-9101.
17. Ardo S, Sun Y, Staniszewski A, Castellano F. N, Meyer G. J. Stark Effects after Excited-State Interfacial Electron Transfer at Sensitized TiO_2 Nanocrystallites. *J. Am. Chem. Soc.* 2010; 132, 6696-6709.
18. Burdzinski G, Karolczak J, Ziolek M, Dynamics of Local Stark Effect Observed for a Complete D149 Dye-Sensitized Solar Cell. *Physical Chemistry Chemical Physics* 2013; 15, 3889-3896.
19. Pastore M, De Angelis F. Computational Modelling of Stark Effects in Organic Dye-Sensitized TiO_2 Heterointerfaces. *J. Phys. Chem. Lett.* 2011; 2, 1261-1267.

20. Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y, Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science* 2001; 293, 269-271.
21. Ma T, Akiyama M, Abe E, Imai I, High-Efficiency Dye-Sensitized Solar Cell Based on a Nitrogen-Doped Nanostructured Titania Electrode. *Nano Letters* 2005; 5, 2543-2547.
22. Roose B, Pathak S, Steiner U, Doping of Tio₂ for Sensitized Solar Cells. *Chemical Society Reviews* 2015; 44, 8326-8349.
23. Le Bahers T, Pauporte T, Scalmani G, Adamo C, Ciofini I, A Td-Dft Investigation of Ground and Excited State Properties in Indoline Dyes Used for Dye-Sensitized Solar Cells. *Physical Chemistry Chemical Physics* 2009; 11, 11276-11284.
24. Preat J, Michaux, C Jacquemin, D Perpète, E. A, Enhanced Efficiency of Organic Dye-Sensitized Solar Cells: Triphenylamine Derivatives. *The Journal of Physical Chemistry C* 2009; 113, 16821-16833.
25. Frisch M. J, Trucks G. W, Schlegel H. B, Scuseria, G. E Robb, M. A, Cheeseman J. R, Scalmani G, Barone V, Mennucci B, Petersson G. A, et al. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.
26. Wang Y, Li H, Excited State Geometry of Photoactive Yellow Protein Chromophore: A Combined Conductorlike Polarizable Continuum Model and Time-Dependent Density Functional Study. *The Journal of Chemical Physics* 2010; 133, 034108.
27. Delley B, From Molecules to Solids with the Dmol3 Approach. *The Journal of Chemical Physics* 2000; 113, 7756-7764.
28. Chen Q, Tang C, Zheng G. First-principles study of anatase (1 0 1) surfaces doped with N. *Physica B: Condensed Matter* 2009; 404 (8–11), 1074-1078.
29. Hanwell M. D, Curtis D. E, Lonie D. C, Vandermeersch, T, Zurek E, Hutchison G. R, Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. *Journal of Cheminformatics* 2012; 4, 1-17.
30. Liu B, Wang B, Wang R, Gao L, Huo S, Liu Q, Li X, Zhu W, Influence of Conjugated [Small Pi]-Linker in D-D-[Small Pi]-a Indoline Dyes: Towards Long-Term Stable and Efficient Dye-Sensitized Solar Cells with High Photovoltage. *Journal of Materials Chemistry A* 2014; 2, 804-812.
31. Bruder I, Ojala A, Lennartz C, Sundarraj S, Schöneboom J, Sens R, Hwang J, Erk P, Weis J, Theoretical and Experimental Investigation on the Influence of the Molecular Polarizability of Novel Zinc Phthalocyanine Derivatives on the Open Circuit Voltage of Organic Hetero-Junction Solar Cells. *Solar Energy Materials and Solar Cells* 2010; 94, 310-316.

32. Nishida J.-i, Masuko T, Cui Y, Hara K, Shibuya H, Ihara M, Hosoyama T, Goto R, Mori S, Yamashita, Y, Molecular Design of Organic Dye toward Retardation of Charge Recombination at Semiconductor/Dye/Electrolyte Interface: Introduction of Twisted Π -Linker. *The Journal of Physical Chemistry C* 2010; 114, 17920-17925.
33. Pastore M, Mosconi E, De Angelis F, Grätzel M, A Computational Investigation of Organic Dyes for Dye-Sensitized Solar Cells: Benchmark, Strategies, and Open Issues. *The Journal of Physical Chemistry C* 2010; 114, 7205-7212.
34. Nazeeruddin M. K, Humphry-Baker R, Liska P, Grätzel M. Investigation of Sensitizer Adsorption and the Influence of Protons on Current and Voltage of a Dye-Sensitized Nanocrystalline TiO₂ Solar Cell. *The Journal of Physical Chemistry B* 2003; 107 (34), 8981-8987.
35. Ansari S. A, Khan M. M, Ansari M. O, Cho M. H. Nitrogen-doped titanium dioxide (N-doped TiO₂) for visible light photocatalysis. *New Journal of Chemistry* 2016; 40 (4), 3000-3009.

Figures

WS-51
($\lambda = 551 \text{ nm}$, $\eta = 10.1\%$)

Figure 1. Chemical structure of WS-51.

Figure 2 Energetic levels of frontier molecular orbital of WS-51 dye in acetonitrile solvent under different electric field strength calculated at the B3LYP/6-311++G(d,P) level. Experimental energy gap of the WS-51 dye is given in parenthesis for reference.

Figure 3 Calculated absorption spectra of WS-51 dye in acetonitrile solution at different electric field strengths using CAM-B3LYP/DGDZPV level of theory. The figure in the inset shows the comparison between calculated and experimental spectrum of WS-51 in field off condition.

Figure 4. HOMO, LUMO, and electron density difference maps (EDDM) between the excited and ground states of WS-51 dye with and without electric field. The contour thresholds for molecular orbitals and density differences are 0.02 and 0.0002 a.u., respectively. The blue and red colors indicate a decrease and increase of charge densities, respectively.

Figure 5 Optimized bidentate bridging mode and adsorption energy of the WS-51 dye on the $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ clusters calculated by PBE/DNP on DMol³ program.

Figure 6 CAM-B3LYP/3-21G(d,p) calculated absorption spectra of (a) $\text{Ti}_{48}\text{O}_{96}$ and $\text{Ti}_{48}\text{O}_{95}\text{N}$ clusters in field of condition (b) WS-51 dye on $\text{Ti}_{48}\text{O}_{96}$ and (c) WS-51 dye on $\text{Ti}_{48}\text{O}_{95}\text{N}$ surfaces with and without applied electric field.

Figure 7 Energy level alignment of (a) Ti₄₈O₉₆, WS-51-Ti₄₈O₉₆, Ti₄₈O₉₅N and WS-51- Ti₄₈O₉₅N systems in field off condition (b) WS-51-Ti₄₈O₉₆ and (c) WS-51- Ti₄₈O₉₅N in field-on condition calculated at the CAM-B3LYP/3-21G(d) level.

Figure 8 Isosurface plots of HOMO, LUMO, interacting orbital and electron density difference maps of WS-51 dye on Ti₄₈O₉₆ and Ti₄₈O₉₅N surfaces. The contour threshold for isosurfaces is 0.0002 a.u. The blue and red colors specify a decrease and increase of charge density, respectively.

Tables

Table 1 Important structural parameters θ_1 and θ_2 ($^\circ$), dipole moment in Debye (ρ), polarizability in a.u (α) of WS-51 dye in gas and solvent phase calculated at the B3LYP/6-31G** level.

Properties	<u>Field ($\times 10^{-4}$ a.u)</u>			
	<u>Gas Phase</u>			
	0	5	10	15
θ_1	30.454	31.041	31.496	31.789
θ_2	0.227	0.202	0.319	0.379
ρ	14.205	13.833	13.484	13.149
α^*	825.637	819.413	814.574	811.030
<u>Solvent Phase</u>				
	0	5	10	15
θ_1	33.406	33.981	34.406	34.669
θ_2	0.032	0.024	0.078	0.056
ρ	17.446	16.937	16.467	16.021
α^*	1175.094	1159.970	1148.082	1139.093

* Polarizability: 1 au= 1.648777×10^{-41} C²-m²-J⁻¹

Table 2 HOMO and LUMO energy in eV (E_H and E_L), Energy gap in eV (E_g) of WS-51 dye in acetonitrile solvent calculated with the B3LYP method. Experimental values are given in parenthesis¹³.

Electric Field Strength (x 10 ⁻⁴ a.u)	Basis set	E_H	E_L	E_g
0		(5.320)	(3.490)	(1.830)
	6-31G(d,p)	-4.879	-2.938	1.941
	cc-PVDZ	-5.081	-3.054	2.026
	6-311++G(d,p)	-5.238	-3.157	2.080
5	6-311++G(d,p)	-5.244	-3.150	2.094
10	6-311++G(d,p)	-5.274	-3.088	2.185
15	6-311++G(d,p)	-5.282	-3.055	2.227

Table 3 Absorption properties of the WS-51 dye in acetonitrile solution at different electric field strengths calculated at the CAM-B3LYP/DGDZVP level. Experimental data given in parenthesis.¹³

Electric Field Strength (x 10 ⁻⁴ a.u)	λ (nm)	ϵ (M ⁻¹ cm ⁻¹)	f	Major contributions
0	550 (551)	143905 (43000)	1.984	H-1->LUMO (21%), HOMO->LUMO (66%)
	435 (460)	11576 (27800)	0.158	H-1->LUMO (34%), HOMO->L+1 (46%)
	306 (314)	28752 (22700)	0.387	HOMO->L+2 (37%), HOMO->L+3 (27%)
5	533	137694	1.903	H-1->LUMO (11%), HOMO->LUMO (79%)
	421	12752	0.164	H-1->LUMO (27%), HOMO->L+1 (55%)
	303	25647	0.343	H-2->LUMO (21%), HOMO->L+2 (30%)
10	529	130635	1.801	HOMO->LUMO (89%)
	412	15482	0.206	H-1->LUMO (21%), HOMO->L+1 (65%)
	301	24847	0.1934	H-2->LUMO (48%)
15	531	122023	1.679	HOMO->LUMO (91%)
	405	20988	0.279	H-1->LUMO (15%), HOMO->L+1 (73%)
	307	22870	0.2565	H-1->L+2 (10%), HOMO->L+2 (49%)

Table 4 Percentage of donor, acceptor and spacer units contribution to HOMO and LUMO energy levels

Electric Field (x 10 ⁻⁴ a.u)	Molecular orbital contribution (%)							
	HOMO				LUMO			
	Donor	Acceptor	CPDT	BTB	Donor	Acceptor	CPDT	BTB
0	67	2	15	15	3	27	40	30
5	49	5	28	19	4	19	34	43
10	28	8	45	20	5	13	27	55
15	14	11	56	19	5	8	22	65

Table 5 The ground and excited state dipole moment in a.u, polarizability in a.u, change in transition frequency ($\Delta\nu$) in eV and change in absorption spectrum (ΔA) in eV calculated at the B3LYP/6-31G(d,p) level of theory.

Properties	Electric field strength ($\times 10^{-4}$ a.u)			
	0	5	10	15
ρ_{gs}	5.589	5.442	5.305	5.173
α_{gs}	825.637	819.413	814.574	811.030
ρ_{es}	13.169	13.248	13.763	13.740
α_{es}	2173.244	2196.169	2262.646	2275.083
$\Delta\mu$	7.580	7.806	8.458	8.566
$\Delta\alpha$	1347.607	1376.756	1448.072	1464.053
$\Delta\nu$	0.000	0.110	0.248	0.391
ΔA	0.000	0.069	0.082	0.071

Table 6 Ground and excited state redox potentials (E_{ox}^{dye*} and E_{ox}^{dye*}); charge injection and dye regeneration driving forces (ΔG_{inj}^0 in and ΔG_{reg}^0) of WS-51 calculated at B3LYP/6-311++G(d,p) level

Electric field (x 10⁻⁴ a.u)	E_{ox}^{dye} (eV)	λ_{max}^{ICT} (nm)	E_{ox}^{dye*} (eV)	ΔG_{inj}^0 (eV)	ΔG_{reg}^0 (eV)
0	-5.238	2.254	-3.157	-1.816	0.438
5	-5.244	2.326	-3.150	-1.882	0.444
10	-5.274	2.343	-3.088	-1.869	0.474
15	-5.282	2.334	-3.055	-1.852	0.482

Table 7 Calculated electronic properties of WS-51 dye on Ti₄₈O₉₆ and Ti₄₈O₉₅N substrates at CAM-B3LYP/3-21G(d,p) level

Electric field (x 10 ⁻⁴ a.u)	E _H (eV)	E _L (eV)	E _g (eV)	ρ (D)	$\lambda_{\max}$ (nm)	E ₀ (eV)	ϵ (M ⁻¹ cm ⁻¹)	f	A	ΔA	A%	LHE	Electronic transition
WS-51/Ti ₄₈ O ₉₆													
0	-6.653	-3.411	3.242	173.156	630	1.968	148750	2.047	1.91E+07			0.991	H-1->L+2 (32%), HOMO->L+17 (32%),
5	-6.024	-2.632	3.392	168.311	621	1.996	141250	1.953	1.77E+07	-1.40E+06	-7.322	0.989	H-1->L+8 (28%), HOMO->L+8 (31%)
10	-6.482	-2.700	3.782	166.436	620	1.999	133350	1.842	1.67E+07	-2.40E+06	-12.552	0.986	HOMO->LUMO (31%), HOMO->L+5 (30%)
15	-7.417	-3.624	3.794	164.736	627	1.977	125450	1.728	1.60E+07	-3.10E+06	-16.213	0.981	HOMO->LUMO (51%), HOMO->L+2 (31%)
WS-51/Ti ₄₈ O ₉₅ N													
0	-6.041	-3.664	2.377	179.020	638	1.943	154600	2.134	2.03E+07			0.993	HOMO->L+15 (34%), HOMO->L+16 (32%)
5	-6.590	-3.905	2.685	176.847	624	1.986	151250	2.089	1.92E+07	-1.10E+06	-5.424	0.992	H-1->LUMO (27%), HOMO->L+9 (30%)
10	-6.622	-3.565	3.057	174.850	619	2.002	142950	1.966	1.78E+07	-2.50E+06	-12.327	0.989	H-1->LUMO (21%), HOMO->L+5 (56%)
15	-7.276	-3.959	3.318	173.009	622	1.993	133350	1.839	1.68E+07	-3.50E+06	-17.258	0.986	H-4->LUMO (17%), HOMO->L+2 (71%)