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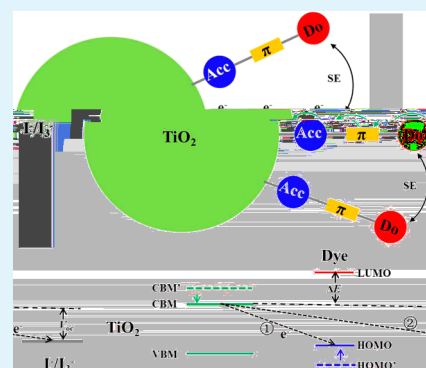
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S Supporting Information

ABSTRACT: In this work, the interfacial properties of a series of metal-free organic naphthodithienothiophene (NDTT)-based photosensitizers adsorbed on TiO₂ surfaces were investigated by a combination of ab initio calculations and experimental measurements. The calculations and experiments reveal that because of the efficient charge transfer from the adsorbed dyes to TiO₂ nanocrystal surface there is an upward shift for the energy levels of dyes and a downward shift for the conduction band of surface TiO₂ and that the band gaps for both of them are also reduced. Such electronic level alignments at the interface would lead to increased light absorption range by adsorbed dyes and increased driving force for charge injection but reduced open-circuit potential (V_{oc}). More interestingly, we found that molecule engineering of the donor group and introducing additional electron-withdrawing unit have little effect on the electronic level alignments at the interface (because band gaps of the dyes adsorbed on TiO₂ surfaces become approximately identical when compared with those of the dyes measured in solution) but that they can affect the steric effect and the charge separation at the interface to tune V_{oc} and the short-circuit current density (J_{sc}) effectively. All these findings suggest that optimizing the interfacial properties of dyes adsorbed on TiO₂ surfaces by synchronously modifying steric effects of dye molecules anchored on TiO₂ and charge-transfer and separation properties at the interfaces is important to construct efficient dye-sensitized solar cells.

KEYWORDS: DSSCs, metal-free photosensitizer, interface, steric effect, electronic structure, ab initio calculations



INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted considerable interest as an alternative renewable energy source in the decades since the seminal works by O'Regan and Grätzel.¹ Because of their intriguing advantages of low-cost fabrication, high molar extinction coefficient, and flexible tailor-making,² metal-free organic photosensitizers have recently drawn increasing attention in DSSC applications. Such organic photosensitizers generally possess a donor- π -acceptor (D- π -A) structure motif with strong intramolecular charge transfer (ICT) characteristics. To date, a record PCE of 13% has been reported by Grätzel and co-workers, using porphyrin-Zn(II)-based D- π -A photosensitizers.³

After absorption of light, charge separation is generally initiated at the interface between the dye bound to the TiO₂ surface and the hole-transporting material. The performance of DSSCs generally depends on not only the lowest unoccupied

molecular orbital (LUMO), the highest occupied molecular orbital (HOMO), and their distributions of the photosensitizers but also the kinetics of the electron-transfer processes at the interface between the dye bound to the semiconductor surface and the hole-transporting material.⁴ As a result, it is important that the microscopic interfacial properties of these all-organic metal-free dyes on TiO₂ photoanodes be investigated and understood including the anchoring state and charge transfer at the interface, band gap offset for the anchored dyes, HOMO and LUMO shift, and their redistributions. Meanwhile, the steric effect of the adsorbed dye molecules at the interface also plays an important role on the DSSC efficiency because the aggregation of the dye molecules on the TiO₂ surface may lead

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to nonradiative decay of the excited state to the ground state, fast charge recombination, and low open-circuit voltage (V_{oc}).^{5,6} In contrast, low dye-loading content on the TiO_2 surface would reduce the short-circuit current density (J_{sc}).

To construct an efficient all-organic dye for efficient DSSCs, lots of experimental studies have been focused on molecular engineering of photosensitizer molecules by modifying the structural component(s), including electron-donating groups,
 π

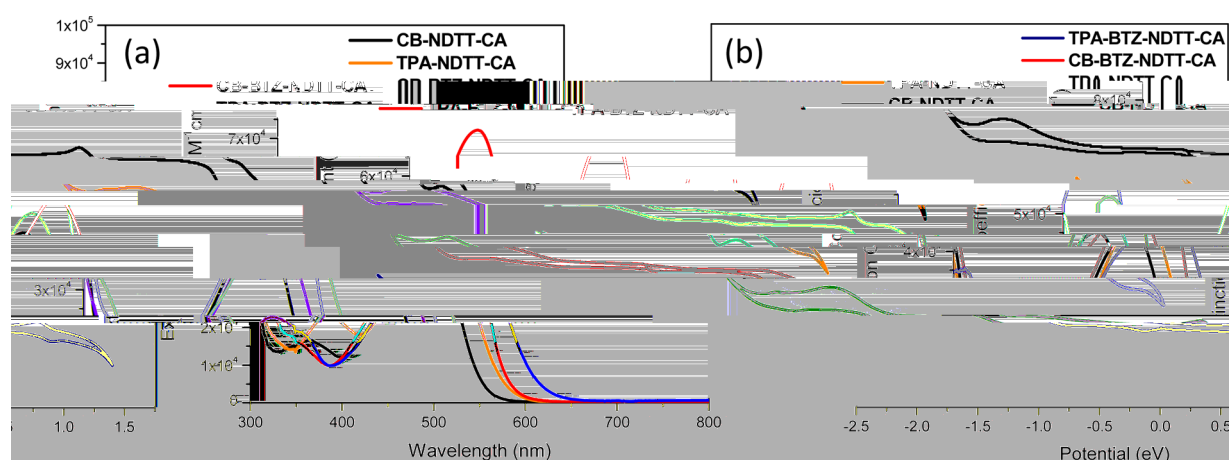


Figure 2. (a) Absorption spectra of CB-NDTT-CA, TPA-NDTT-CA, CB-BTZ-NDTT-CA, and TPA-BTZ-NDTT-CA in THF. (b) CV traces of CB-NDTT-CA, TPA-NDTT-CA, CB-BTZ-NDTT-CA, and TPA-BTZ-NDTT-CA.

Table 1. Results of Optical and Electrochemical Measurements of CB-NDTT-CA, TPA-NDTT-CA, CB-BTZ-NDTT-CA, and TPA-BTZ-NDTT-CA

compound	$\lambda_{\text{max}}^{\text{abs}}$ (nm) ^a	optical gap (eV) ^{a,b}	$E_{\text{p}}^{\text{oxd}}$ (eV) ^c	$E_{\text{p}}^{\text{red}}$ (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^d	EG ^e
CB-NDTT-CA	486 (4.93)	2.24	0.87	−0.89	−5.11	−3.35	1.76
TPA-NDTT-CA	498 (5.50)	2.15	0.76	−0.87	−5.00	−3.37	1.63
CB-BTZ-NDTT-CA	513 (6.46)	2.13	0.89	−0.70	−5.13	−3.52	1.61
TPA-BTZ-NDTT-CA	531 (6.95)	2.02	0.77	−0.78	−5.01	−3.46	1.55

^a $\lambda_{\text{max}}^{\text{abs}}$ given in nanometers. Measured in THF ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ^bEstimated from the absorption edge in THF; optical band gap = $1240/\lambda_{\text{onset}}^{\text{abs}}$ eV.

^cDetermined by the CV method using a platinum disc electrode as the working electrode, platinum wire as the counter electrode, and SCE as the reference electrode with an agar salt bridge connecting to the solution of oligomers in THF. Ferrocene was used as the external standard, $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.56 \text{ eV}$ vs SCE. ^dCalculated from the first oxidation potential with ferrocene (4.8 eV vs vacuum). ^eEG = LUMO − HOMO.

light harvesting, and photostability of the resulting photosensitizer molecule.^{17–19}

The molecular structures of novel naphthodithienylthiophene-based photosensitizers are shown in Figure 1, and their synthesis are outlined in Schemes S1 and S2. The starting substrates 1–4 are synthesized according to procedures reported previously.^{15,20–22} Triarylamine or carbazole was used as an electron-donating group, benzothiadiazole acted as an auxiliary electron-accepting unit, and cyanoacrylic acid played the role of an electron-accepting and anchoring group. In addition, to improve the solubility and reduce the π – π aggregation of photosensitizer molecules on the TiO_2 surface that could decrease charge recombination and thus enhance the open circuit voltage (V_{oc}),²³ the branched alkoxy chains were incorporated onto the naphthalenedithienylthiophene moiety.

For the carbazole-donor series, the palladium-catalyzed Suzuki coupling of carbazole-based boronate ester 1 with 1,4-dibromobenzothiadiazole afforded the intermediate 5 in an excellent yield, followed by the Miyaura borylation with bis(pinacolato)diboron catalyzed by $\text{Pd}(\text{dppf})_2\text{Cl}_2$ using KOAc as a base, affording carbazole-substituted benzothiadiazoleboronate ester 6. In contrast, double Suzuki cross-coupling of dibromobenzene derivative 2 with boronate ester 3 gave bis-thienylthiophene intermediate 7 in good yield, followed by FeCl_3 -catalyzed ring-closure reaction, yielding naphthodithienylthiophene 8. Monobromination of 8 by means of NBS in THF yielded bromonaphthodithienylthiophene 9. Subsequent Vilsmeier–Haack reaction of 9 gave bromonaphthodithienylthiophenealdehyde 10 in good yield. The palladium-catalyzed Suzuki cross coupling of 10 with the corresponding donor boronate esters, 1 or 6, yielded the carbazole-substituted

naphthodithienylthiophene intermediate, 11 or 12, respectively. The condensation reaction of aldehyde 11 or 12 with 2-cyanoacetic acid catalyzed by NH_4OAc in AcOH afforded the desired CB-NDTT-CA and CB-BTZ-NDTT-CA, respectively, in good yield.

For the triarylamine-donor series, diarylaminophenylboronate ester 13 was prepared by Miyaura borylation of bromide 4 with bis(pinacolato)diboron. The palladium-catalyzed Suzuki coupling of 13 with 1,4-dibromobenzothiadiazole yielded the intermediate 14, followed by a facile Miyaura borylation affording triarylamine-substituted benzothiadiazoleboronate ester 15. Then, the palladium-catalyzed Suzuki coupling of bromo-naphthodithienylthiophenealdehyde 10 with the corresponding boronate ester, 13 or 15, gave the coupled aldehyde, 16 or 17, respectively, in good yield. Condensation of aldehyde 16 or 17 with 2-cyanoacetic acid afforded the desired dye TPA-NDTT-CA or TPA-BTZ-NDTT-CA, respectively, in excellent yield.

The thermal properties of the newly synthesized naphthodithienylthiophene-based photosensitizers were first examined by thermogravimetric analysis (TGA). All these photosensitizers exhibit good thermal stability with decomposition temperatures above 250 °C under inert atmosphere (Figure S1).

The absorption spectra of CB-NDTT-CA, CB-BTZ-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA measured in THF solution are shown in Figure 2a. These photosensitizing dyes exhibit distinct strong and broad absorptions peaked at 475–550 nm, corresponding to intramolecular charge-transfer transition, and a moderate absorption around 300 nm,

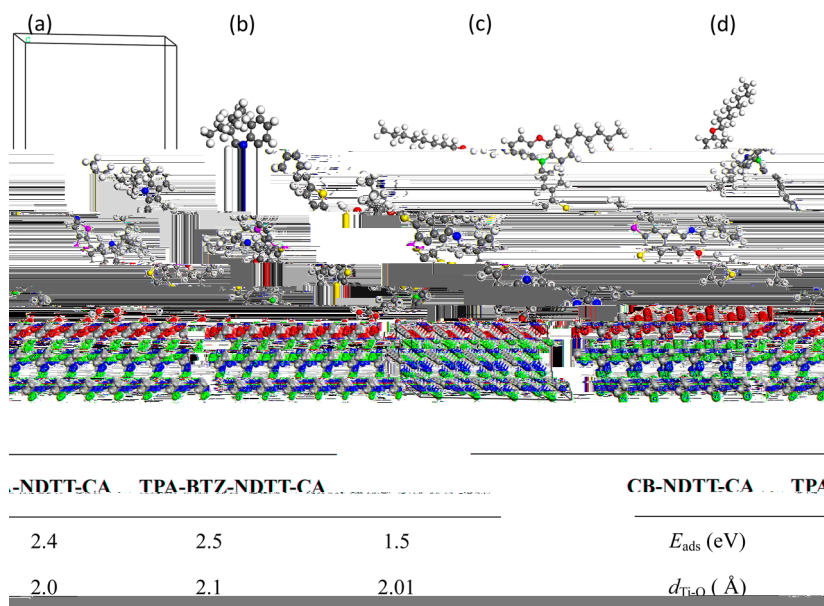


Figure 3. Ab initio calculations for the dye molecules/TiO₂ interfaces. (a) Unit cell with CB-NDTT-CA molecule adsorbed on TiO₂ anatase (101) surface. (b–d) Most energy stable adsorption structures of CB-NDTT-CA (b), TPA-NDTT-CA (c), and TPA-BTZ-NDTT-CA (d) on TiO₂ (101) surface. The table shows adsorption energies (E_{ads}) and geometry parameters for all adsorption configurations on TiO₂.

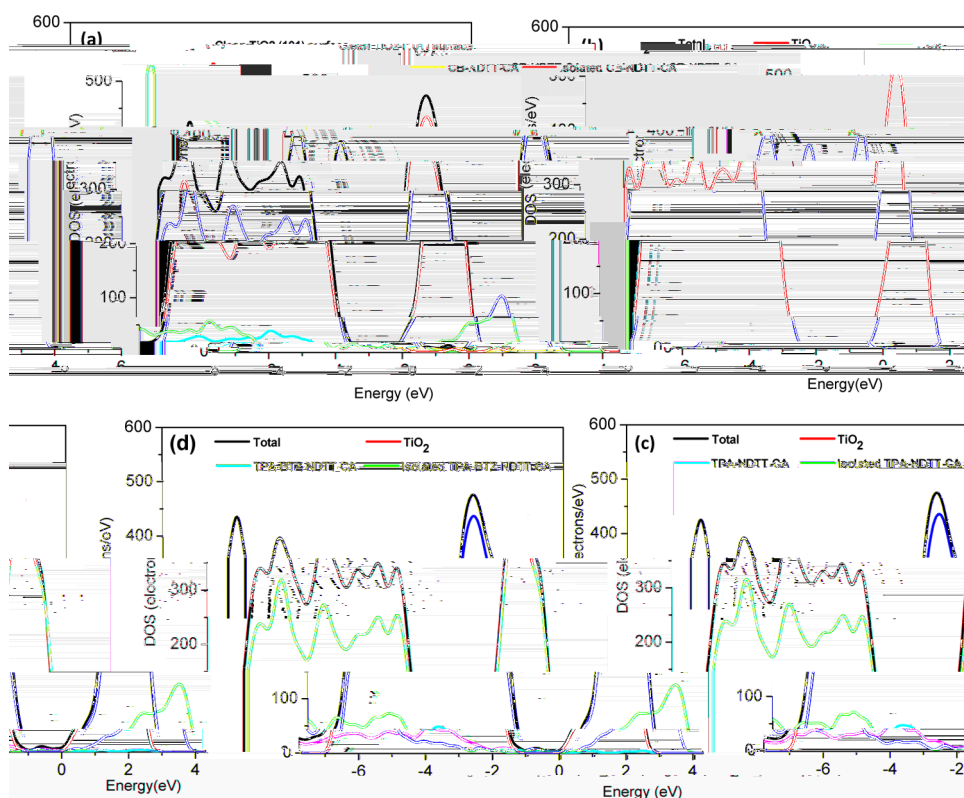


Figure 4. Calculated total density of states (DOS) and projected density of states (PDOS) for (a) clean TiO₂ surface and interfaces of TiO₂ adsorbed with CB-NDTT-CA (b), TPA-NDTT-CA (c), and TPA-BTZ-NDTT-CA (d).

corresponding to $n-\pi^*$ transition, which are typical absorption characteristics of donor–acceptor-type π -conjugated molecules. There is a significant bathochromic shift of the absorption maximum concomitant with an increase in molar absorptivity upon an incorporation of electron-deficient benzothiadiazole (BTA) unit into the π -conjugated backbone. This is attributed to the increased conjugation length and enhanced intermo-

lecular charge transfer along the π -conjugated backbone. In addition, the strong donating triarylamine group induces a larger bathochromic shift of the absorption spectrum relative to those of carbazole-based counterparts. The optical band gaps of these photosensitizers deduced from the onset of their absorption spectra measured in THF solution are in the range of 2.02–2.24 eV (Table 1), which are also consistent with

the results of the excitation spectra and the room-temperature photoluminescence (PL) spectra (Figure S2).

The electrochemical characteristics of these photosensitizers were determined by cyclic voltammetry (CV) in THF using a platinum disc electrode as the working electrode, platinum wire as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode in 0.1 M of Bu₄NPF₆ with a scan rate of 100 mV/s. The resulting CV traces are shown in Figure 2b. The energy levels of HOMO and LUMO were estimated from the onset of the oxidation and reduction waves, respectively (Table 1). The HOMO energy levels of CB-NDTT-CA and TPA-NDTT-CA were estimated to be −5.11 and −5.00 eV, respectively. Because of an incorporation of electron-deficient BTZ unit, the HOMO energy levels of CB-BTZ-NDTT-CA and TPA-BTZ-NDTT-CA are slightly stabilized and lowered to −5.13 and −5.01 eV, respectively. However, the band gaps of these photosensitizers estimated from the onset of the oxidation and reduction waves are in the range of 1.55–1.76 eV, which is smaller than the optical band gaps measured in THF solution by ~0.5 eV. The smaller band gaps measured by CV method compared with the optical band gaps measured in THF solution are most probably attributed to the charge transfer between the dye molecules and the electrode surfaces, as indicated in the following *ab initio* calculations.

To get an in-depth picture of the NDTT-based dye/TiO₂ interface, we carried out *ab initio* calculations to study the adsorption structures of three representative kinds of NDTT-type dyes (CB-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA) on TiO₂. Figure 3a shows a representative supercell model for CB-NDTT-CA adsorption. A 9 layer (4 × 4) TiO₂ slab (total 144 atoms) is used to model the anatase (101) surface, and the bottom six layers are fixed to simulate the bulk geometry. This model gives a reliable description of surface electronic structure, and the calculated lattice constants of $a = b = 3.82$ Å and $c = 9.66$ Å also agree well with experimental values of 3.79 and 9.51 Å.²⁴ We have estimated the stability of different adsorption model from total energy calculation, discovering that the bridging model is the most stable binding form and is more stable than the esterlike model in contrast to previous studies on other organic dye adsorbed on TiO₂ surface.^{25,26} Figure 3b–d shows the most energy stable adsorption structures for all-NDTT-type dyes on anatase (101). All structures except Figure 3d show a bidentate adsorption conformer with two interface Ti–O bonds via the carboxylic groups, and the binding energies for CB-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA are 2.4, 2.5, and 1.5 eV, respectively. This bidentate configuration was also always thought to be the most stable in previous works,²⁷ and the strong chemical bonding maintains the interface stability of NDTT-type dyes solar cells.

We next examined the electronic structures for clean and dye-adsorbed anatase (101) surfaces. Figure 4 shows the density of states (DOS) and projected density of states (PDOS) for all the adsorption configurations. Compared with the clean (101) surface, the conduction band of surface TiO₂ is shifted downward, and the band gaps of surface TiO₂ for all samples are reduced after the dye adsorption (from 1.8 eV for clean surface to around 1.25 eV after dye adsorption). This can be attributed to the charge transfer between the TiO₂ and dye molecules, which would build a favorable dipolar field

at the interface to tune the band energy levels of the surface TiO₂.²⁷ This band gap reduction for the TiO₂ surface would facilitate the electron transport and increase the gap between the LUMO of dyes and CBM of TiO₂, thus increasing the driving force for charge injection at the interface. However, the downward shift of the conduction band of the surface TiO₂ would also lead to reduced V_{oc} . Furthermore, we can see that the DOS of dye molecules shift to higher energy after adsorption (compared with isolated dye molecules), indicating a significant charge (electron) transfer from dye molecules to TiO₂ surface. The HOMOs of molecules have shifted into the band gap region of TiO₂, and LUMOs moved 0.5–0.9 eV higher than the conduction band minimum (CBM) of the TiO₂ surface, providing sufficient driving force for charge injection, which is critical for solar cell applications.

The band gaps (the energy gap between the HOMO and LUMO) of isolated CB-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA dye molecules are 1.50, 1.15, and 0.98 eV, with LUMO changing only slightly around −3 eV (Table 2). Interestingly, band gaps are narrowed into 0.97, 0.87, and

Table 2. *Ab Initio* (VASP) Calculated Band Gaps Before (E_{g1}) and After Adsorption (E_{g2}) for Dye Molecules^a

	CB-NDTT-CA	TPA-NDTT-CA	TPA-BTZ-NDTT-CA
E_{g1} (eV)	1.50	1.15	0.98
E_{g2} (eV)	0.97	0.87	0.91
Q	0.24	0.30	0.25

^a Q denotes the electrons transferred from dye molecules to TiO₂ surfaces.

0.91 eV after being adsorbed on TiO₂ surface for CB-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA molecules (Table 2), indicating that the absorption range for the dyes is increased and that the band gap differences for these molecules are reduced. Thus, these results suggest that molecular engineering of the donor group or introducing an additional electron-withdrawing unit (BTZ) has little effect on the electronic level alignments at the interface with the dyes loading on TiO₂ surfaces. The Bader charge analysis^{28,29} of the VASP results reveals the similar charge transfer from the dye molecules to TiO₂ surface (Table 2), which can be attributed to the same electron-accepting and anchoring group of CA for all dye molecules.

To clarify the mechanisms behind the above phenomenon, we additionally calculated the molecular orbitals of the three kinds of dyes using the Gaussian09 package³⁰ for comparison. A BLYP functional was adopted, and the 6-31G* is set as Gaussian basis with polarization functions.^{31,32} We also calculated the molecular orbitals of the three kinds of dyes with one added positive charge, which simulates the case of electrons being transferred from dye molecules to TiO₂ surface. Figures 5 and 6 presented the calculated HOMOs and LUMOs for the three kinds of dye molecules. Though the band gaps calculated from Gaussian09 (Table 3) are close to the optical band gaps of these photosensitizers deduced from the onset of their absorption spectra measured in THF solution and are larger than those calculated from VASP package (based on the plane wave basis) by nearly 60%, both methods show the same trend that the band gap differences for these molecules are reduced when the electrons are transferred out or positive charge is added. In these three dye molecules, the LUMOs are largely populated along the acceptor groups and π bridge, and

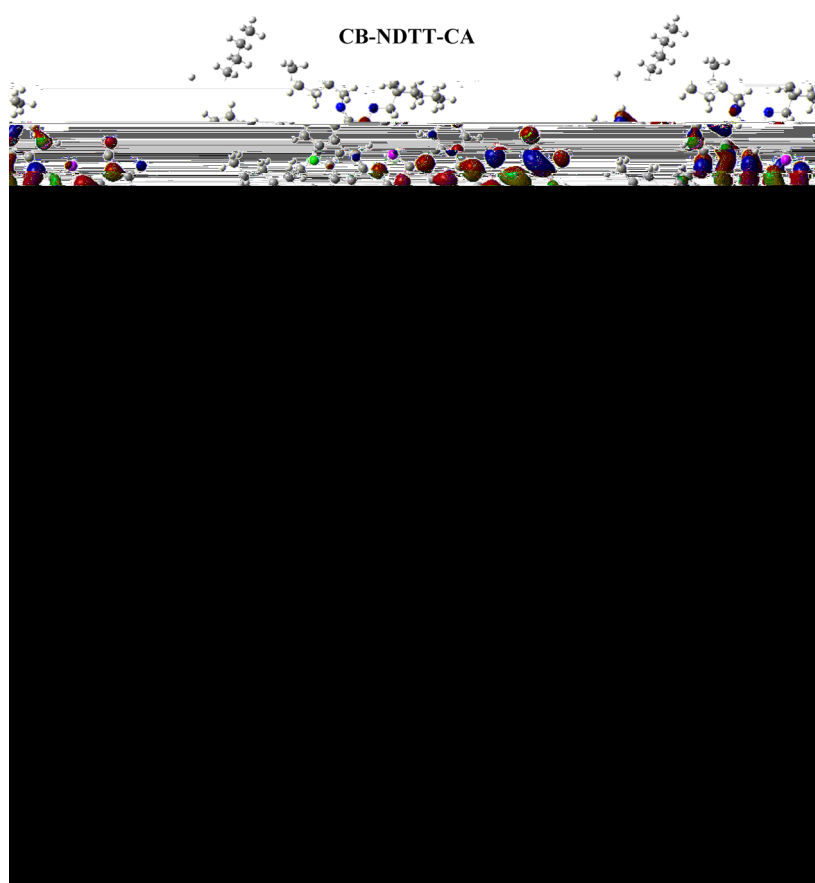


Figure 5. Frontier orbitals of CB-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA.

the HOMOs are mainly localized in donor units for TPA-NDTT-CA and TPA-BTZ-NDTT-CA but spread to π bridge for CB-NDTT-CA, providing evidence for weak intramolecular charge transfer for CB-NDTT-CA and leading to the largest band gap. However, when adsorbed on the TiO_2 surface, both HOMOs and LUMOs become delocalized for all these dye molecules, and the capability of intramolecular charge transfer becomes identical, thus leading to the narrowed band gaps and little band gap differences for these molecules.

Characterization of the electronic structure of the dyes was performed by soft X-ray emission spectroscopy (XES) and soft X-ray absorption spectroscopy (XAS) are used to detect the electronic structure variation of the TiO_2 surface with and without dye loading (Figure 7). It can be observed that the valence band remains nearly unchanged and the conduction band shifts downward after dye absorption (Figure 7, clearly for CB-TPA-NDTT-CA and TPA-BTZ-NDTT-CA absorption) which confirmed our ab initio calculations. Next, we recorded the UV-vis diffuse reflectance spectra of the dyes anchored on TiO_2 films at different dye concentrations after 5 h adsorption (Figure 8). It was found that there was minor difference among different concentrations suggesting that aggregation of dye molecules on the surface of TiO_2 films was negligible. More interestingly, compared with the optical band gaps of these photosensitizers measured in THF solution, the band gaps of these photosensitizers adsorbed on TiO_2 films have become smaller and approximately identical, estimated to be 1.80–1.78 eV (around 686 nm ~695 nm) from the onset of

the diffuse reflectance spectra (Figure 8), which is very consistent with the ab initio calculation predictions.

Finally, we fabricated DSSCs using these NDTT-based photosensitizers and investigated their photovoltaic properties. The typical current–voltage (I – V) characteristics at AM 1.5 simulated sunlight are shown in Figure 9 with the corresponding performance parameters summarized in Table S1. The solar cell based on CB-NDTT-CA shows an efficiency of 7.29%, with a short-circuit photocurrent density (J_{sc}) of 14.48 mA cm^{-2} , an open-circuit photovoltage (V_{oc}) of 695 mV, and a fill factor (FF) of 0.724. The solar cell based on TPA-NDTT-CA only shows an efficiency of 5.33%, with a J_{sc} of 11.0 mA cm^{-2} , a V_{oc} of 718 mV, and a FF of 0.675. The lower efficiency of TPA-NDTT-CA based device can be attributed to the decreased J_{sc} and FF after replacing carbazole-donor with triarylamino donor. Because of the large and bulky triarylamino donor, the dye-loading content of TPA-NDTT-CA on TiO_2 is less than that of carbazole-donor analog, CB-NDTT-CA, which accounts for the reduced J_{sc} . The lower dye-loading content of TPA-NDTT-CA is reflected by the absorption spectra of TiO_2 films sensitized with one layer of dye molecules (Figure S4). The thickness of the adsorbed dyes is kept to 3 μm for all the samples. We can see that the absorption degree of TPA-NDTT-CA is weaker than that of CB-NDTT-CA, indicating a lower dye-loading content on TiO_2 films for TPA-NDTT-CA. In contrast, this large and bulky triarylamino donor can limit aggregation between the dye molecules, which is a recurrent problem during device fabrication and operation, and prevents the charge recombination between the TiO_2 surface and I^-/I_3^- in

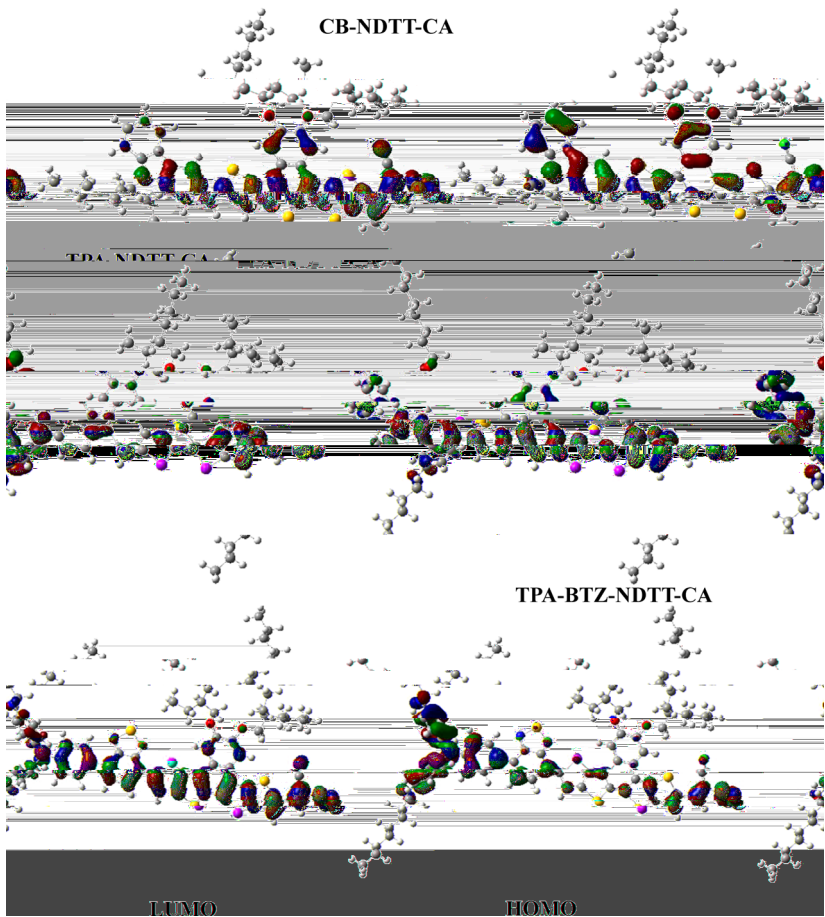


Figure 6. Frontier orbitals of CB-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA with one added positive charge.

Table 3. Calculated Band Gaps for Neutral (E_{g1}) and Positively Charged (E_{g2}) Dye Molecules by Gaussian09 Package

	CB-NDTT-CA	TPA-NDTT-CA	TPA-BTZ-NDTT-CA
E_{g1} (eV)	2.38	2.02	1.84
E_{g2} (eV)	0.92	0.96	1.01
reduction (eV)	1.46	1.06	0.83

the electrolyte. Moreover, the strong electron-rich triaryl amino donor also induces a HOMO more localized on the donor part

(Figure 5) to suppress the charge recombination between TiO_2 and dyes.⁴ All the above reasons lead to the increased V_{oc} . This is further confirmed by the Nyquist plots of electrochemical impedance spectroscopy (EIS) and intensity-modulated photovoltage spectroscopy (IMVS) measurements of the DSSCs (Figure S5, S6 and Table S2). The larger semicircles in lower-frequency in EIS reflect the recombination resistance (R_{ct2}) at TiO_2 /electrolyte interface. The radius of the semicircle for TPA-NDTT-CA is larger than that of CB-NDTT-CA, indicating a smaller charge recombination rate for TPA-NDTT-CA and consistent with its increased V_{oc} . The electron

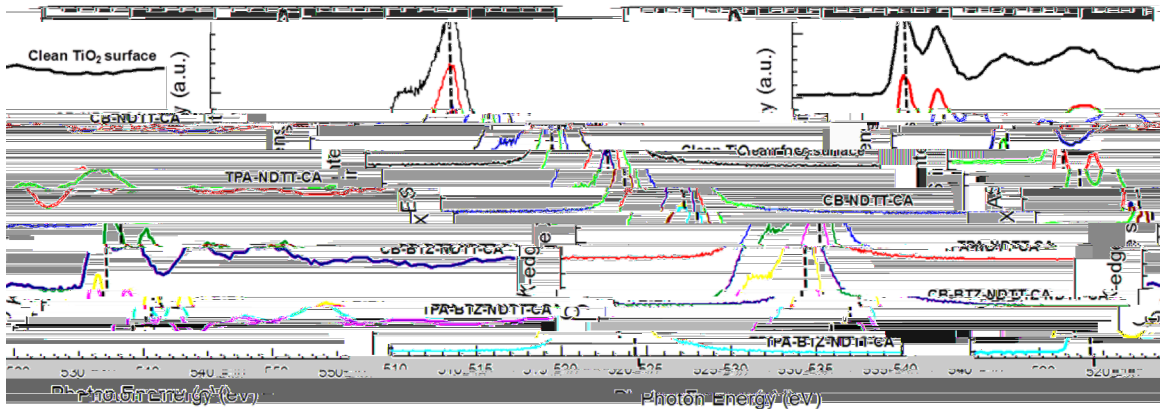


Figure 7. Soft X-ray emission spectroscopy (XES) (left) and soft X-ray absorption spectroscopy (XAS) (right) of clean TiO_2 surfaces and TiO_2 surfaces adsorbed with CB-NDTT-CA, TPA-NDTT-CA, CB-BTZ-NDTT-CA, and TPA-BTZ-NDTT-CA.

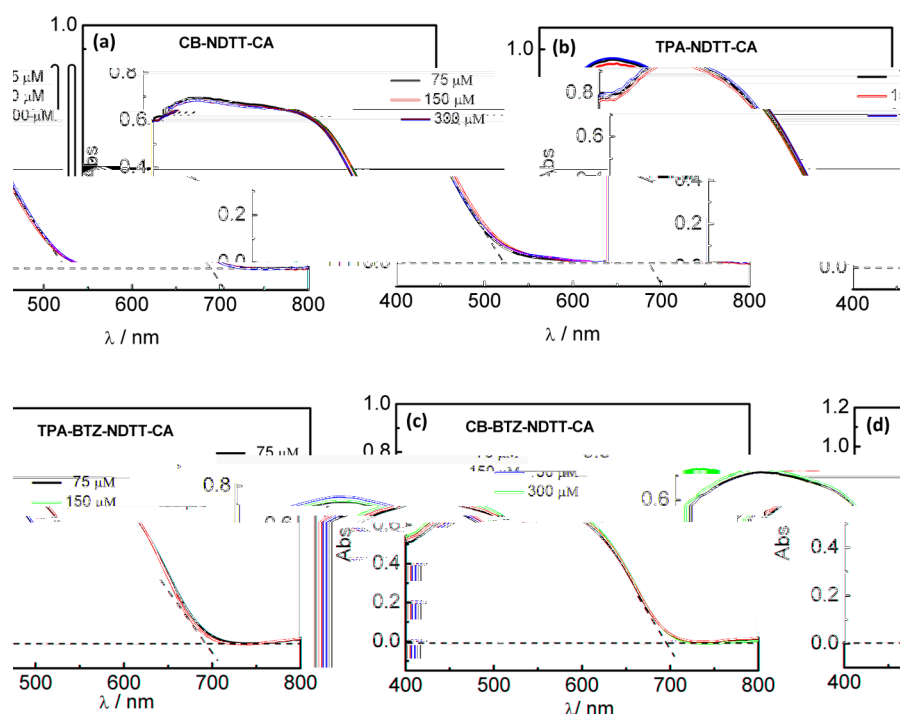


Figure 8. UV-vis diffuse reflectance spectra for TiO₂ films sensitized with different concentration of CB-NDTT-CA (a), TPA-NDTT-CA (b), CB-BTZ-NDTT-CA (c), and TPA-BTZ-NDTT-CA (d).

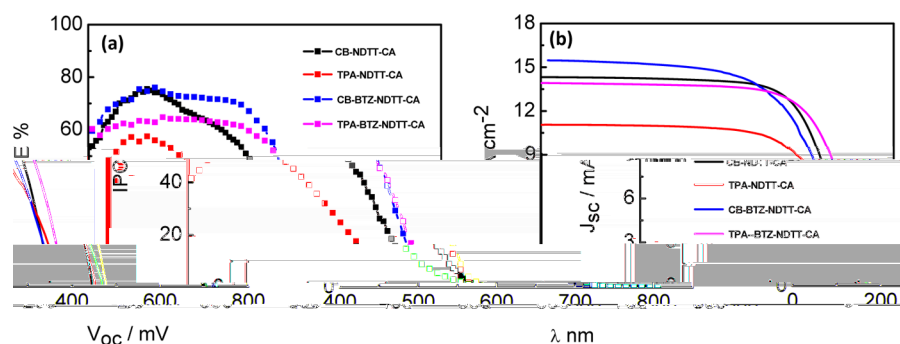


Figure 9. IPCE spectra (a) and J - V curves (b) of DSSCs with CB-NDTT-CA, TPA-NDTT-CA, CB-BTZ-NDTT-CA, and TPA-BTZ-NDTT-CA.

lifetime (τ_n) can be estimated by the equation $\tau = (2\pi f_{\min})^{-1}$, where $f_{\min}$ is the frequency of the minimum of the IMVS imaginary component. The electron lifetime of TPA-NDTT-CA (159.2 ms) is larger than that of CB-NDTT-CA (126.5 ms), also indicating a suppressed charge recombination for TPA-NDTT-CA.

Once a BTZ unit is introduced as an additional electron-withdrawing unit into the π bridge of CB-NDTT-CA, affording CB-BTZ-NDTT-CA, the improved J_{sc} (15.47 mA cm⁻²) and V_{oc} (700 mV) are observed. Such enhancement in device performance is also observed when a BTZ unit is introduced into TPA-NDTT-CA to construct TPA-BTZ-NDTT-CA (J_{sc} = 13.91 mA cm⁻²; V_{oc} = 725 mV). The density functional theory (DFT) simulation indicates that the distributions of both HOMO and LUMO orbitals for sensitizers TPA-BTZ-NDTT-CA are overlapped with those of the BTZ unit (Figure 5), indicating the preferably facilitated electron transfer from HOMO to LUMO orbitals. Convincingly, the cascaded electron withdrawal from donor (D) to internal acceptor (A), then to terminal A in the D-A- π -A configuration may benefit charge separation in organic sensitizers, thus leading to the

increased J_{sc} and V_{oc} . This is also confirmed by the IMVS measurements (Figure S6 and Table S2), which show that the electron lifetime of TPA-BTZ-NDTT-CA (503.9 ms) is larger than that of TPA-NDTT-CA (224.9 ms) indicating that the BTZ unit introduced into the π bridge can enhance the charge separation in organic sensitizers. As a result, compared with TPA-NDTT-CA, the efficiency of TPA-BTZ-NDTT-CA is improved from 5.33 to 7.22%. In contrast, despite the improved J_{sc} and V_{oc} , the final efficiency of CB-BTZ-NDTT-CA is decreased from 7.29 to 6.85% compared with that of CB-NDTT-CA, which is mainly due to the greatly decreased FF from 0.724 for CB-NDTT-CA to 0.632 for CB-BTZ-NDTT-CA. This is mainly attributed to the large J_{sc} for the sample of CB-BTZ-NDTT-CA, which would reduce FF and is also usually observed in other DSSCs.^{33–35} The above photovoltaic properties demonstrated that though molecular engineering of the donor group and introduction of an additional electron-withdrawing unit (BTZ) have little effect on the electronic level alignments and the absorption range for the dyes at the interface with dyes loading on TiO₂ surfaces they still affect the

steric effect and the charge separation at the interface effectively.

All the theoretical and experimental findings in this work can be summarized in Figure 10, which proposes how to optimize

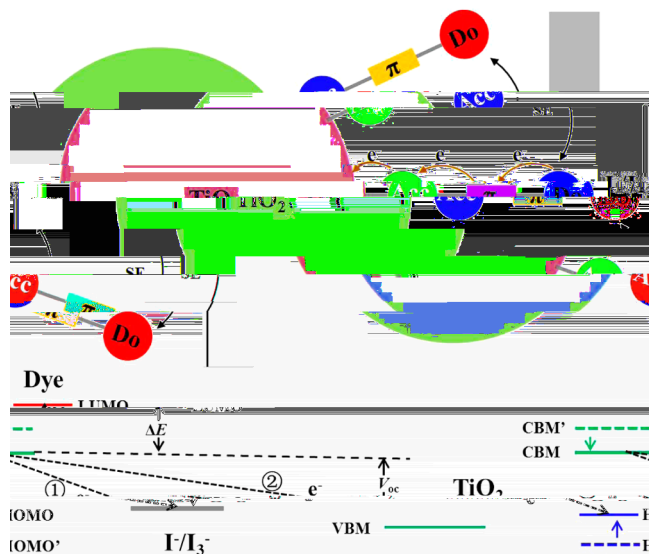


Figure 10. Schematic model of the dye/TiO₂ interface and energy-level diagram of a DSSC. SE denotes the steric effect among the dye molecules adsorbed on the TiO₂ surfaces. ΔE is defined as the difference between the energy level of the dye's LUMO and the CBM of the TiO₂. CBM' denotes the original valence band maximum of surface TiO₂ before dye adsorption, and HOMO' denotes the original HOMO level of dye molecules before adsorption on TiO₂. Process 1 (①) denotes the charge recombination between electrons at TiO₂ surface and holes of the dyes; process 2 (②) denotes the charge recombination between electrons at TiO₂ surface and the redox mediator (I^-/I_3^-).

the interface between photosensitizers and TiO₂ nanocrystals with molecular engineering to enhance performances of dye-sensitized solar cells. When the dyes are anchored on TiO₂ films, there is an efficient charge transfer from the dyes to TiO₂, thus leading to the energy level alignment at the interface: an upward shift for the energy levels of dyes (only showing the shift of HOMO relative to LUMO) and a downward shift for the conduction band of surface TiO₂, accompanied by reduced band gaps for both of them. The downward shift of CBM means an increased driving force for charge injection with the disadvantage of reduced V_{oc} , and the reduced band gap for dyes means increased absorption range. Compared with the band gaps obtained in THF solution, the band gaps of photosensitizers absorbed on TiO₂ films become approximately identical, which is found and systematically studied for the first time, indicating that molecular engineering of the donor group and introduction of an additional electron-withdrawing unit (BTZ) have little effect on the electronic level alignments and the absorption range for the dyes at the dye/TiO₂ interface. The more efficient way to tune the electronic level alignments at the interface is molecular engineering of the anchoring group of dyes, e.g., cyano group anchoring could induce different electronic level alignments at the interface from carboxylic/carboxylate groups.¹⁰ However, molecular engineering of the donor group and introduction of an additional electron-withdrawing unit can affect the steric effect and the charge separation at the interface to tune J_{sc} and V_{oc} effectively. The

steric effect at the interface could tune the dye-loading content and the charge recombination between the TiO₂ and redox mediator in the electrolyte (Figure 10, process 2). Molecular engineering of the donor group and introduction of an additional electron-withdrawing unit can also make the positive charge resulting after electron injection be more localized on the donor part and enhance the charge separation in dyes to minimize charge recombination between the injected electrons and the resulting oxidized dye (Figure 10, process 1).

CONCLUSIONS

Using ab initio calculations and experimental measurements, we systematically studied the interfacial properties of a series of metal-free organic NDTT-based photosensitizers adsorbed on TiO₂ surfaces. We first found that because of the efficient charge transfer from the dyes to the TiO₂ there is an upward shift for the energy levels of dyes and a downward shift for the conduction band of surface TiO₂ and that the band gaps for both of them are also reduced. We next found that molecular engineering of the donor group and introduction of an additional electron-withdrawing unit have little effect on the electronic level alignments and the absorption range for the dyes at the dye/TiO₂ interface because band gaps of the dyes adsorbed on TiO₂ surfaces become approximately identical when compared with those of the dyes measured in solution. However, they can affect the steric effect and the charge separation at the interface effectively. Hence, the interfacial properties of dyes adsorbed on TiO₂ surfaces with molecular engineering can be optimized for high-performance DSSC by synchronously modifying steric effects of dye molecules anchored on specifically orientated surfaces of nanocrystals and charge-transfer properties in a dye and at the interface between dyes and nanocrystals. We believe that such a fundamental understanding of the photosensitizers/TiO₂ interface would share microscopic mechanisms for further dye design and interface optimization for practical DSSC applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07591.

Details about materials and methods; schemes of synthesis of CB-NDTT-CA, CB-BTZ-NDTT-CA, TPA-NDTT-CA, and TPA-BTZ-NDTT-CA; their TGA traces; their room temperature photoluminescence (PL) excitation and emission spectra in THF; IPCE spectra of DSSCs; J-V curves for DSSCs; detailed photovoltaic parameters of DSSCs with four dyes; absorption spectra of TiO₂ films sensitized with one layer of CB-NDTT-CA, TPA-NDTT-CA, CB-BTZ-NDTT-CA, and TPA-BTZ-NDTT-CA; Nyquist plots from impedance spectra, IMVS and IMPS spectra of the DSSCs based on four dyes. (PDF)

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