Effects of Internal Electron-Withdrawing Moieties in D−A−π−A Organic Sensitizers on Photophysical Properties for DSSCs: A Computational Study

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ABSTRACT: D−A−π−A dyes differ from the traditional D−π−A framework having several merits in dye-sensitized solar cell (DSSC) applications. With regard to D−π−A dyes, D−A−π−A dyes red-shift absorption spectra and show particular photostability. Nevertheless, the effects of internal acceptor on the charge transfer (CT) probability are unclear. We employed density functional theory (DFT), time-dependent DFT (TD-DFT), and TD-DFT molecular dynamics (MD) simulations to investigate the effects of internal acceptor on the photophysical properties of D−A−π−A dyes on DSSCs. Our calculations show the absorption bands of D−A−π−A dyes with strong electron-withdrawing internal acceptors exhibiting significant characteristics of dual CT; the excited electron density is transferred to the internal and terminal acceptors simultaneously. Particularly, the internal acceptor traps a significant amount of electron density upon photoexcitation. The TD-DFT MD simulations at 300 K show that only a small amount of excited electron density is pushing and pulling between the internal acceptor and terminal acceptor moieties; the thermal energy is not high enough to drive the electron density from the internal acceptor to the terminal acceptor. Our study reveals the nature of CT bands of D−A−π−A dyes providing a theoretical basis for further rational engineering.

INTRODUCTION

The Sun has been considered as a promising sustainable energy source. Photovoltaic devices are regarded as optimal methods to directly convert solar energy into electricity. Various technologies, such as crystalline Si, semiconductors (e.g., GaAs-based cells), organic bulk heterojunction, and dye-sensitized solar cells (DSSCs), can be used. DSSCs have the advantage of being lightweight in comparison to inorganic semiconductor solar cells and have a higher conversion efficiency than polymer-based bulky heterojunction cells.

In DSSC devices, the dye sensitizers play the first and crucial step in light harvesting. For higher light-harvesting efficiency, the absorption spectra of dye sensitizers should be optimally matched with the solar spectra and also have a larger extinction coefficient. In addition, the transition characters of absorption spectra of dye sensitizers influence and determine the efficiency of electron injection. Moreover, the stability of photoexcited dye sensitizers will determine the lifetime of DSSCs. To enhance the efficiency of DSSCs, researchers are dedicated to engineering configurations of dye sensitizers to optimize various entangled parameters as mentioned above.

DSSCs based on organic dyes have several advantages. Metal-free organic dyes are easily prepared and relatively less expensive. Moreover, the more interesting feature of metal-free organic dyes is that their absorption (wavelength range and extinction coefficients) and photoelectrical properties (related to frontier molecular orbital energy level) are adjustable through molecular engineering. Most metal-free organic sensitizers are typically designed to have a donor−π−acceptor (D−π−A) framework. D−π−A dyes with dipolar features are designed with the aim of performing efficient photoinduced charge transfer (CT). Previous studies have designed the dyes based on the D−π−A framework in terms of engineering the donors (e.g., triphenylamine (TPA), indoline, etc.) and π-spacer (e.g., benzene, thiophene, etc.). Probably due to its simple structure, the achievement of D−π−A DSSC is more limited. Nevertheless, variation of the D−π−A framework can lead to other frameworks of dyes. Recently, novel organic dyes with a D−A−π−A configuration made by introducing an internal acceptor into the traditional D−π−A structure have efficiencies up to 10%. D−A−π−A sensitizers employ an auxiliary electron-withdrawing group, known as internal acceptors A; commonly used internal acceptors are quinoxaline, diketopyrrolopyrrole, isindigo, bithiazole, benzo-thiadiazole (BT), benzo[2,1-b]thiazole (BT), and pyrido[3,4-b]pyrazine (PP). Previous comprehensive studies showed that the internal electron-withdrawing acceptor can be regarded as an “electron trap” and exhibits some distinguishing characteristics: (i) Incorporation of an electron-withdrawing...
acceptor into the D−π−A configuration tunes the molecular energy gap; an acceptor owning a low-lying lowest unoccupied molecular orbital (LUMO) is expected to reduce the LUMO of the whole molecule red-shifting the absorption spectra when the highest occupied molecular orbital (HOMO) of the whole molecule remains the same. Wang and co-workers introduced a BTD group into one D−π−A dye, generating a new dye of D−A−π−A configuration; the new D−A−π−A dye (D2 in the original literature) performed a red-shifted absorption of 556 nm relative to that of the original D−π−A dye (λ_{max} = 512 nm; D1 in the original literature). (ii) Furthermore, it may result in a new absorption band in the UV−vis region expanding the range of the light-harvesting response. In the work of Wang et al.,10 the D2 molecule has an extra absorption band at 466 nm and a prominent extinction coefficient of up to 30 500 M^{-1} cm^{-1}, whereas the D1 molecule shows a blue-shifted band at 363 nm with a smaller extinction coefficient of 9300 M^{-1} cm^{-1}. (iii) More importantly, it can significantly improve the photostability.16 (iv) The structural features of most internal acceptor units allow for facile structural modification. In addition, their N-containing heterocycles are considered to improve the Voc.22

The internal acceptor, no doubt having electron-withdrawing ability, is also expected to alter the electronic transition characteristics of the absorption band, which is crucial for electron injection for photo-to-current conversion. In particular, whether the internal acceptor promotes or retards the electron transfer (ET) is still unclear.21 Conceptually, it is anticipated that the internal acceptor can potentially trap a certain amount of photoexcited electron density at the initial stage. However, it is not known whether the D−A−π−A dye follows a two-step CT process driven by thermal energy. In a two-step CT process, the internal acceptor receives electron density from the donor upon photoexcitation. Thereafter, thermal energy drives the photoexcited electron density on the internal acceptor toward the terminal acceptor for electron injection. Moreover, introduction of an internal acceptor into a D−π−A dye is not assured to give a red-shifted spectra and a better performance of J_{sc}. In the work of Zhu et al.,23 the LS-1 molecule (in the original literature) with a D−π−A framework has a λ_{max} of 483 nm and gives a J_{sc} value of 11.25 mA cm^{-2}; retaining the same D and A moieties, the LS-2 with a D−A−π−A framework has a blue-shifted λ_{max} of 442 nm and gives a lower J_{sc} value of 10.06 mA cm^{-2}. Therefore, theoretical investigation of the effects of the internal acceptor in the D−A−π−A dyes on the photophysical properties, in particular the features of absorption spectra, as well as electron-transfer characters, is needed for rational engineering of novel D−A−π−A dyes for better DSSC applications.

To elucidate the effects of the internal acceptor underlying the complex D−A−π−A configurations, we employed density functional theory (DFT), time-dependent DFT (TD-DFT), and TD-DFT nonadiabatic (NA) molecular dynamics (MD) to investigate four D−A−π−A molecules and one D−π−A molecule, as displayed in Figure 1. The D−π−A molecule (Figure 1e) is used for parallel comparison. These five molecules were carefully selected from published literature containing rich experimental data. In particular, they share several common features, providing us with suitable systems to comparatively elucidate the effects of the internal acceptor on the photophysical properties from the complex interrelated experimental data. The five molecules studied have the same electron-donating group (triphenylamine, TPA), π-spacer (Th), and acceptor/anchor (cyanoacrylic acid, CAA). The only structural variation between the four D−A−π−A molecules is the internal acceptor located between the donor and the π-spacer. In addition, the internal acceptors have similar molecular structure but with different physical properties.

Figure 1. Chemical structures of studied dye sensitizers with the D−A−π−A framework: (a) TPA-BTD-Th-CAA, (b) TPA-BT-Th-CAA, (c) TPA-DBT-Th-CAA, (d) TPA-PP-Th-CAA, and (e) TPA-Ph-Th-CAA.
(e.g., HOMO−LUMO (H−L) gap). Moreover, our calculations in this study (vide infra) show that they own a planar A−π−A moiety and thus have similar molecular length. Nevertheless, they have distinct UV−vis spectra and photo-to-current conversion efficiency. Experimentally, the TPA-DBT-Th-CAA molecule (Figure 1c) has λmax at 423 nm, which is close to that of the D−π−A molecule (Figure 1e, λmax = 417 nm). Replacement of DBT by BTD gives the TPA-BTD-Th-CAA molecule having a significantly red-shifted spectrum of 497 nm. Our theoretical calculations reveal that the primary absorption of D−A−π−A molecules has electron density transferred to the internal acceptor and terminal acceptor moieties at the same time upon photoexcitation, which is significantly different from the commonly observed D-to-A transition in the D−π−A molecules. Moreover, we show that the thermal energy at 300 K has limited effect in further promoting the excited electron density on the internal acceptor to the terminal acceptor side.

RESULTS AND DISCUSSION

Studied Molecules. The sensitizers displayed in Figure 1 have similar molecular configuration having a triphenylamine (TPA) moiety as the electron-donating group, a thiophene (Th) unit as the π-spacer, and cyanoacrylic acid (CAA) as the terminal acceptor/anchor. These units were chosen mainly because they are frequently used in dye sensitizers. TPA-PP-Th-CAA (Figure 1d) to avoid the aggregation of the dyes and thus increases the efficiency of charge separation. TPA-Ph-Th-CAA sensitizers (Figure 1b) have benzotriazole (BT) introduced into the sensitizer as an internal acceptor developed by Hua et al. In particular, BT is a close analogue of BTD; however, BT is electron-rich, leading to a higher LUMO energy level. TPA-DBT-Th-CAA (Figure 1c) was developed by Yu, Ma, and co-workers. 2-methylbenzo[d]thiazole (DBT) has a nonplanar structure, which is expected to avoid the aggregation of the dyes and thus increases the lifetime of the excited state. TPA-PP-Th-CAA (Figure 1d) has a pyrido[3,4-b]pyrazine (PP) unit as the internal acceptor. PP is well known to have electron-withdrawing ability due to its unsaturated nitrogen atoms. It has shown promising photovoltaic properties in polymer structures for near-infrared light-emitting diodes.

Energy Level of Building Blocks. Figure 2 displays the HOMO and LUMO energy levels and HOMO−LUMO (H−L) energy gap of the “building blocks” of studied molecules, including TPA, Th, Ph, CAA, as well as four internal acceptors, BT, BT, PP, and BTD, calculated at the CAM-B3LYP/6-31G(d,p) level based on their optimized structures by B3LYP/6-31G(d,p). The TPA moiety has the highest HOMO energy level, facilitating the donation of electrons. The CAA moiety has the lowest LUMO level and thus the largest driving force to accept electron density. The Ph and Th groups designed as π-spacers have relatively high-energy LUMO, which is less
capable of trapping electrons, instead assisting the electron transportation and also extending the π-conjugation length.

Four internal acceptors exploited in this study have low-lying LUMO levels and a smaller H−L energy gap. Nevertheless, they have distinct LUMO energy levels and an H−L energy gap, providing us suitable models to understand their effects on the photophysical properties of D−A−π−A organic sensitizers. Among them, BTD has the lowest-energy LUMO and a smaller H−L gap and DBT has the highest-energy LUMO and the largest H−L gap. The order of LUMO energy level of the four internal acceptors is DBT > BT > PP > BTD. The magnitude of the H−L gap of these four internal acceptors is correlated with their LUMO energy levels.

Ground-State Molecular Geometries. Figure 3 shows the lengths of C−C bonds connecting two neighboring building blocks and their associated dihedral angles. As the building blocks are aromatic rings, in which their structures are less sensitive to the chemical environments, instead, the dihedral angles and bond lengths between two neighboring aromatic rings can determine their photophysical properties.

The bond lengths between two neighboring aromatic rings of studied molecules are between 1.34 Å (standard carbon−carbon double-bond length) and 1.54 Å (standard carbon−carbon single-bond length). This indicates that these bonds are partially conjugated within the molecule. We define four dihedral angles (depicted in Figure 3a), $\phi_1$ (between the Ph ring on TPA and internal acceptor ring), $\phi_2$ (between internal acceptor ring and Th ring), $\phi_3$ (between Th ring and C=C double bond), and $\phi_4$ (between CN and C=O groups), which may potentially change with different internal acceptors. As expected, the TPA moiety has a propeller-like nonplanar geometry. The Ph ring on TPA forms a certain twisted angle ($\phi_1$) with its neighboring ring; such a twisted angle may retard the electron back donation after photoexcitation. The $\phi_2$, $\phi_3$, and $\phi_4$ angles of TPA-BTD-Th-CAA, TPA-BT-Th-CAA, TPA-DBT-Th-CAA, and TPA-PP-Th-CAA are close to 0°, having a nearly planar A−π−A motif. Therefore, TPA-BTD-Th-CAA, TPA-BT-Th-CAA, TPA-DBT-Th-CAA, and TPA-PP-Th-CAA have similar molecular structures. The planar A−π−A motif can extend the π-conjugation length. On the other hand, $\phi_2$ of...
Table 2. Transition Characters and Absorption Bands of Studied Dyes at Protonated State in Solution

| dye                     | absorption/oscillator strength | transitions                      |
|-------------------------|--------------------------------|----------------------------------|
|                         | \( \lambda_{\text{max}} \) |                                     |
|                         | state | \( f^0 \) | absorption (nm) |                                     |
| TPA-BTD-Th-CAA \(^a\)   | \( \lambda_{\text{max}} \) | 499 | 1.35 | \( H \rightarrow L \) (72%)          |
|                         | #2    | 378 | 0.12 | \( H \rightarrow L + 1 \) (21%)     |
|                         |       |     |      | \( H \rightarrow L \) (60%)         |
|                         |       |     |      | \( H \rightarrow L + 1 \) (16%)     |
|                         |       |     |      | \( H \rightarrow L \) (11%)         |
| TPA-BT-Th-CAA \(^b\)    | \( \lambda_{\text{max}} \) | 466 | 1.70 | \( H \rightarrow L \) (66%)         |
|                         | #2    | 354 | 0.04 | \( H \rightarrow L \) (27%)         |
|                         |       |     |      | \( H \rightarrow L \) (56%)         |
|                         |       |     |      | \( H \rightarrow L + 1 \) (16%)     |
| TPA-DBT-Th-CAA \(^c\)   | \( \lambda_{\text{max}} \) | 425 | 1.51 | \( H \rightarrow L \) (49%)         |
|                         | #2    | 337 | 0.04 | \( H \rightarrow L \) (39%)         |
|                         |       |     |      | \( H \rightarrow L \) (37%)         |
|                         |       |     |      | \( H \rightarrow L + 1 \) (10%)     |
| TPA-PP-Th-CAA \(^d\)    | \( \lambda_{\text{max}} \) | 475 | 1.57 | \( H \rightarrow L \) (72%)         |
|                         | #2    | 370 | 0.08 | \( H \rightarrow L \) (19%)         |
|                         |       |     |      | \( H \rightarrow L \) (59%)         |
|                         |       |     |      | \( H \rightarrow L + 1 \) (18%)     |
|                         |       |     |      | \( H \rightarrow L \) (9%)          |
|                         |       |     |      | \( H \rightarrow L \) (48%)         |
|                         |       |     |      | \( H \rightarrow L \) (44%)         |
|                         |       |     |      | \( H \rightarrow L \) (43%)         |
|                         |       |     |      | \( H \rightarrow L \) (32%)         |
|                         |       |     |      | \( H \rightarrow L + 1 \) (12%)     |
| TPA-Ph-Th-CAA \(^e\)    | \( \lambda_{\text{max}} \) | 410 | 1.56 | \( H \rightarrow L \) (66%)         |
|                         | #2    | 330 | 0.10 | \( H \rightarrow L \) (21%)         |

In dichloromethane. \(^b\)In CH\(_2\)Cl\(_2\). \(^c\)In THF. \(^d\)Oscillator strength. \(^e\)H = HOMO; L = LUMO; \( H = HOMO - 1 \) and \( L + 1 = LUMO + 1 \).

TPA-Ph-Th-CAA, due to the Th–Ph steric repulsion, is 20.7°, having a nonplanar Ph–Th motif, which reduces the effective \( \pi \)-conjugation length of the whole molecule.

UV–Vis Spectra of Dye in Solution. Table 1 lists the optical data of studied dyes in solution obtained from both experimental observations and TD-DFT calculations. Experimentally, the studied molecules have the \( \lambda_{\text{max}} \) bands located at 417–500 nm. The \( \lambda_{\text{max}} \) bands of TPA-BTD-Th-CAA, TPA-BT-Th-CAA, TPA-DBT-Th-CAA, TPA-PP-Th-CAA, and TPA-Ph-Th-CAA appear at 497, 454, 423, 500, and 417 nm, respectively. In particular, TPA-Ph-Th-CAA has the most blue-shifted band. These results reveal that replacement of the Ph by an internal acceptor, while maintaining the planarity of A-Th-CAA moiety, red-shifts the spectra. Furthermore, the magnitude of red shift in the spectra after introducing an internal acceptor moiety is correlated with the \( H \rightarrow L \) gap and LUMO energy level of the internal acceptor. The calculated \( \lambda_{\text{max}} \) bands of dyes are in good agreement with the experimental observations. The average absolute deviation between the calculated \( \lambda_{\text{max}} \) values for these molecules in solution and those observed experimentally is 10.8 nm. The smallest deviation from the experimental value is only +2 nm (in TPA-BTD-Th-CAA), and the largest deviation from the experimental value is −25 nm (in TPA-PP-Th-CAA). Experimentally, TPA-BTD-Th-CAA (\( \epsilon_{\text{max}} = 13\,000\, \text{M}^{-1}\, \text{cm}^{-1} \)) and TPA-PP-Th-CAA (\( \epsilon_{\text{max}} = 16\,700\, \text{M}^{-1}\, \text{cm}^{-1} \)) have the smallest \( \epsilon_{\text{max}} \) values of the \( \lambda_{\text{max}} \) bands. These results indicate that introduction of strong electron-withdrawing moieties, such as BTD and PP, reduces the absorption coefficients of the \( \lambda_{\text{max}} \) bands. Similar results are also observed in other studies of D–A–π–A molecule. WS-2 (\( \epsilon_{\text{max}} = 16\,700\, \text{M}^{-1}\, \text{cm}^{-1} \)) has a D–A–π–A framework using the BTD moiety, as internal acceptor has a smaller \( \epsilon_{\text{max}} \) value than its D–π–A analogue (LS-1 in the original literature; \( \epsilon_{\text{max}} = 21\,000\, \text{M}^{-1}\, \text{cm}^{-1} \)). Computationally, TPA-BTD-Th-CAA gives the smallest oscillator strength, whereas the CAM-B3LYP/6-31G(d,p) method predicts that TPA-PP-Th-CAA has a similar oscillator strength to TPA-Ph-Th-CAA.

The D–A–π–A molecules exhibit second higher-energy absorption bands. Experimentally, the second bands for TPA-BTD-Th-CAA and TPA-PP-Th-CAA appear at 395 and 423 nm, respectively. More importantly, the second bands for TPA-BTD-Th-CAA and TPA-PP-Th-CAA appear in the visible (vis)-light region, which can potentially contribute to the photo-to-current conversion. Experimentally, the second absorption band of the TPA-Ph-Th-CAA molecule is located at ~310 nm, which is poorly spectrally matched with solar spectra. Molecules with the introduction of larger H–L acceptors, such as TPA-BT-Th-CAA and TPA-DBT-Th-CAA, do not have red-shifted second absorption band. Except for TPA-PP-Th-CAA, other molecules have weaker second absorption band than the corresponding \( \lambda_{\text{max}} \) bands. The calculated second absorption bands of dyes have larger deviations from the experimental observations than those of the \( \lambda_{\text{max}} \) bands. The average absolute deviation between the calculated second absorption bands for these molecules in solution and those observed experimentally is 36.2 nm. These results indicate that the CAM-B3LYP method has better performance in reproducing the visible absorption than near UV absorption.

Table 2 lists the transition characters of the absorption bands. The major contribution of the electronic density transition of \( \lambda_{\text{max}} \) bands is from HOMO to LUMO transition, and the minor contribution is from low-lying HOMO − 1 to LUMO transition. On the other hand, the major contribution...
of the electronic density transition of the second bands is from low-lying HOMO − 1 to LUMO transition, and the minor contribution is from HOMO to LUMO and from HOMO to higher-energy LUMO + 1 transitions. Table 3 lists the electron density difference map (EDDM) (where the excited electron density is coming from and going to) of absorption bands upon photoexcitation. The EDDM shows that the λ max and second bands of studied molecules have electron density mainly coming from the electron-donating TPA moiety; however, the character of excited electron density is distinctly different. The λ max bands of TPA-BTD-Th-CAA and TPA-PP-Th-CAA exhibit a dual charge-transfer character; the electron density is significantly transferred from the TPA moiety to both the internal acceptor and CAA moieties simultaneously upon photoexcitation. Upon excitation, TPA-BTD-Th-CAA has the electron density of the BTD and CAA moieties increased by 31 and 18%, respectively. For TPA-PP-Th-CAA, the electron density of the PP and CAA moieties is increased by 29 and 20%, respectively, upon excitation. Particularly, the internal acceptor moieties of TPA-BTD-Th-CAA and TPA-PP-Th-CAA receive more electron density than their corresponding CAA moieties. The short-range CT (to internal acceptor) has a higher probability than the long-range CT (to CAA). Similar EDDM results are also observed for the second absorption bands of TPA-BTD-Th-CAA and TPA-PP-Th-CAA; the second absorption bands of TPA-BTD-Th-CAA and TPA-PP-Th-CAA are dual CT bands. Interestingly, for the second absorption bands of TPA-BTD-Th-CAA and TPA-PP-Th-CAA,

Table 3. EDDMs of Studied Dyes in Solution^c

| dye          | absorption oscillator strength | percent contribution (%) | EDDM before (where the excited electron density is coming from) | EDDM after (where the excited electron density is going to) |
|--------------|--------------------------------|--------------------------|---------------------------------------------------------------|----------------------------------------------------------|
|              | absorption change              | TPA | A  | Th | CAA | TPA | A  | Th | CAA |
| TPA-BTD-Th-CAAa | λmax = 499 nm, f = 1.35 | Before  | 68  | 16  | 11  | 6   | After | 6  | 47  | 23  | 24  |
|               |                                | Net  | -62 | +31 | +12 | +18 |        | 44 | 23  | 22  | 12  |
| TPA-BT-Th-CAAb | λmax = 466 nm, f = 1.70 | Before  | 63  | 19  | 12  | 6   | After | 6  | 27  | 32  | 35  |
|               |                                | Net  | -57 | +8  | +20 | +29 |        | 47 | 23  | 19  | 10  |
| TPA-DBT-Th-CAAc | λmax = 425 nm, f = 1.51 | Before  | 51  | 21  | 19  | 9   | After | 4  | 20  | 35  | 42  |
|               |                                | Net  | -47 | -1  | +16 | +33 |        | 55 | 21  | 16  | 8   |
| TPA-PP-Th-CAAc | λmax = 475 nm, f = 1.57 | Before  | 70  | 13  | 11  | 6   | After | 7  | 42  | 25  | 26  |
|               |                                | Net  | -63 | +29 | +14 | +20 |        | 43 | 19  | 25  | 13  |
| TPA-Ph-Th-CAAc | λmax = 410 nm, f = 1.56 | Before  | 57  | 16  | 18  | 9   | After | 5  | 13  | 37  | 45  |
|               |                                | Net  | -52 | -3  | +19 | +36 |        | 56 | 16  | 18  | 9   |
|               |                                |        |     |     |     |     |        |     |     |     |     |

^a^ In dichloroethane. ^b^ In CH₂Cl₂. ^c^ In THF. ^d^ Oscillator strength. ^e^ Before (where the excited electron density is coming from) and after (where the excited electron density is going to) transition.
the electron density of Th moiety is nearly unchanged before and after excitation. On the other hand, the excited electron density of the $\lambda_{\text{max}}$ and second absorption bands of TPA-BTD-Th-CAA and TPA-Ph-Th-CAA is mainly transferred to the CAA moiety, and the electron density of the internal acceptor moiety is slightly decreased upon photoexcitation. These results indicate that the $\lambda_{\text{max}}$ and second absorption bands of TPA-BTD-Th-CAA and TPA-Ph-Th-CAA are single CT bands. For TPA-BT-Th-CAA, upon excitation on the $\lambda_{\text{max}}$ band, the excited electron density of the Th and CAA moieties is increased by 20 and 29%, respectively, and that of the BT is slightly increased by 8%. Similarly, upon excitation on the second absorption band of TPA-BT-Th-CAA, the excited electron density is mainly transferred to Th (increased by 10%) and CAA (increased by 23%) moieties.

**UV–Visible Spectra of Dye Adsorbed on TiO$_2$** Table 4 lists the calculated transition characters and absorption bands of studied dyes adsorbed on TiO$_2$ obtained from CAM-B3LYP/6-31G(d,p) calculations and their experimental absorption bands. The calculated $\lambda_{\text{max}}$ bands for TPA-BTD-Th-CAA, TPA-BT-Th-CAA, TPA-BT-Th-CAA, TPA-Ph-Th-CAA, and TPA-Ph-Th-CAA adsorbed on (TiO$_2$)$_{38}$ clusters in acetonitrile are 503, 479, 436, 486, and 417 nm, respectively. The root-mean-square deviation of calculated $\lambda_{\text{max}}$ values from the experimental values is 33 nm. TPA-BTD-Th-CAA is the red-shifted molecule, and TPA-Ph-Th-CAA is the blue-shifted molecule. Except for TPA-Ph-Th-CAA, the transition of the $\lambda_{\text{max}}$ band is mainly from HOMO to LUMO and partly from HOMO $\rightarrow$ LUMO (increased by 23%) moieties.

Table 4. Experimental Absorption, Calculated Absorption, and Transition Characters of the Bands of Studied Dyes Adsorbed on a (TiO$_2$)$_{38}$ Cluster in Acetonitrile

| dye                  | experiment absorption (nm) | $\lambda_{\text{max}}$ | state absorption (nm) | $f^{\text{osc}}$ | transitions$^6$ |
|----------------------|-----------------------------|-------------------------|------------------------|-----------------|-----------------|
| TPA-BT-Th-CAA        | 426$^{17}$                  | $\lambda_{\text{max}}$  | 479                    | 2.115           | H $\rightarrow$ L (63%) H $\rightarrow$ L + 1 (27%) |
|                      |                             | #2                      | 359                    | 0.035           | H $\rightarrow$ L (53%) |
| TPA-DBT-Th-CAA       | 436$^{18}$                  | $\lambda_{\text{max}}$  | 436                    | 1.924           | H $\rightarrow$ L (47%) |
|                      |                             | #2                      | 342                    | 0.016           | H $\rightarrow$ L (37%) |
| TPA-PP-Th-CAA        | 486$^{20}$                  | $\lambda_{\text{max}}$  | 486                    | 1.970           | H $\rightarrow$ L (70%) H $\rightarrow$ L + 1 (20%) |
|                      |                             | #2                      | 376                    | 0.138           | H $\rightarrow$ L (55%) |
| TPA-Ph-Th-CAA        | 417$^{20}$                  | $\lambda_{\text{max}}$  | 417                    | 1.970           | H $\rightarrow$ L (8%) H $\rightarrow$ L + 1 (24%) |
|                      |                             | #2                      | 335                    | 0.057           | H $\rightarrow$ L (16%) H $\rightarrow$ L + 1 (16%) |

$^4$Oscillator strength. $^5$H = HOMO; L = LUMO.

For the first band ($\lambda_{\text{max}}$), the transition characters of four D–A–π–A molecules adsorbed on a (TiO$_2$)$_{38}$ cluster are mainly from the HOMO and HOMO $\rightarrow$ LUMO, which are similar to those in solution. On the other hand, the transition character of the TPA-Ph-Th-CAA dye mixes more higher-energy LUMO + 1 orbitals, whose electron densities are mainly localized on TiO$_2$.

**Table 5** lists the EDDM (before and after photoexcitation) for dyes adsorbed on a (TiO$_2$)$_{38}$ cluster. TPA-BTD-Th-CAA, after photoexcitation, has the electron density redistributed onto the BTD and CAA/(TiO$_2$)$_{38}$ moieties, increasing by the same amount of 25%. For TPA-PP-Th-CAA, the electron density on the PP and CAA/(TiO$_2$)$_{38}$ moieties is increased by 23 and 28%, respectively, after excitation. These results indicate that the $\lambda_{\text{max}}$ bands of TPA-BTD-Th-CAA and TPA-PP-Th-CAA are apparently dual-charge-transfer bands. These two dyes adsorbed on TiO$_2$ have minor electron density delocalized onto TiO$_2$ (61%), showing the $\lambda_{\text{max}}$ a strong single CT band. Upon adsorption on TiO$_2$ and after photoexcitation, the electron density of DGT on TPA-BTD-Th-CAA is slightly decreased and moderate electron density is redistributed onto TiO$_2$. $\lambda_{\text{max}}$ of TPA-BTD-Th-CAA is a single CT band. For TPA-BT-Th-CAA, the electron density on CAA/(TiO$_2$)$_{38}$ is significantly increased, a character of a single CT band. In general, upon adsorption onto TiO$_2$ (a sink for electron acceptor), the capacity of the internal acceptor in receiving electron density is decreased relative to that in solution. For the blue-shifted band of a given dye, TiO$_2$ decreases more electron density than the $\lambda_{\text{max}}$ band. These results may be due to that the higher-energy transition of dyes (mainly LUMO) is better hybridized with the interfacial orbitals in the
Table 5. EDDM of Dyes on a (TiO$_2$)$_{38}$ Cluster$^b$

| Dye                        | $\lambda_{max}$ (nm) | Oscillator strength ($f$) | Percent contribution (%) | EDDM before (where the excited electron density is coming from) | EDDM after (where the excited electron density is going to) |
|----------------------------|-----------------------|---------------------------|--------------------------|---------------------------------------------------------------|------------------------------------------------------------|
| TPA-BTD-Th-CAA             | 382 nm ($f = 0.20$)   | 46                        | 46                       | 0                                                             | 20                                                         |
| TPA-BT-Th-CAA              | 359 nm ($f = 0.03$)   | 49                        | 49                       | 9                                                             | 0                                                          |
| TPA-DBT-Th-CAA             | 342 nm ($f = 0.02$)   | 57                        | 57                       | 15                                                            | 7                                                          |
| TPA-PP-Th-CAA              | 376 nm ($f = 0.14$)   | 46                        | 46                       | 19                                                            | 0                                                          |
| TPA-Ph-Th-CAA              | 417 nm ($f = 1.97$)   | 53                        | 53                       | 17                                                            | 0                                                          |

$^a$Oscillator strength. $^b$Before (where the excited electron density is coming from) and after (where the excited electron density is going to) transition.
Figure 4. Energy alignment of dyes adsorbed on TiO₂. The bottom bars represent the GSOP; the top bars represent the aligned ESOP. The experimental CB energy of TiO₂ (−3.94 eV) is shown on the left.

conduction band (CB) region of TiO₂ with high density of states.

TPA-BTD-Th-CAA and TPA-PP-Th-CAA with strong internal acceptors have red-shifted absorption spectra and additional bands in the UV−vis region. Therefore, their absorption bands are better matched with solar spectra than other studied dyes, and in principle, they should have higher absorption bands are better matched with solar spectra than other studied dyes, and in principle, they should have higher absorption.

The later calculated the ground-state oxidation potential (GSOP) (ESOP) aligned by the method proposed by De Angelis and colleagues. The aligned excited-state energy also represents the driving force as well as a weak coupling with TiO₂. The fast photoinduced ET process from the donor to the acceptor was investigated by TD-DFT nonadiabatic (NA) molecular dynamics (MD) simulations on the femtosecond scale with atomistic details. These NAMD simulations address the CT mechanism of D−A−π−A dyes adsorbed on a (TiO₂)₃₈ cluster in its neutral and cation states based on the B3LYP/6-31G(d,p) method. The ESOP can be calculated approximated by ESOP = GSOP − E₀−e, where GSOP is the ground-state oxidation potential (GSOP) calculated by (G − G')_GS and E₀−e is the energy difference between optimized excited and ground states. For large systems, such as dye adsorbed on TiO₂, it is not feasible to optimize the excited-state geometry. The E₀−e is approximated by vertical excitation energy. We first calculated the ground-state oxidation potential (GSOP) by computing the energy difference of dyes adsorbed on a (TiO₂)₃₈ cluster in its neutral and cation states based on the B3LYP/6-31G(d,p) method. The ESOP is calculated by adding the absorption energy (Eₐb) calculated at CAM-B3LYP/6-31G(d,p) level to the GSOP. In conjunction with the EDDM analysis above, it is seen that TPA-Ph-Th-CAA has a large driving force for electron injection as well as strong coupling with TiO₂. On the other hand, the D−A−π−A dyes have a smaller driving force for electron injection to TiO₂; moreover, the coupling of their excited state with the TiO₂ is relatively weaker. In particular, introduction of a strong electron-withdrawing BTD group results in a small driving force as well as a weak coupling with TiO₂.

The photostability of dyes will directly affect the duration time of DSSC devices. In principle, a photoexcited dye with lower energy is expected to be less active in undergoing photochemical reactions and vice versa. The calculated ESOP values (Figure 4) of TPA-BTD-Th-CAA, TPA-BT-Th-CAA, TPA-BT-Th-CAA, TPA-PP-Th-CAA, and TPA-Ph-Th-CAA adsorbed on a (TiO₂)₃₈ cluster are −2.72, −2.56, −2.36, −2.66, and −2.19 eV, respectively. The four studied D−A−π−A dyes adsorbed on TiO₂ have lower ESOP values than the D−π−A framework can potentially improve the photostability. In particular, TPA-BTD-Th-CAA has 0.53 eV lower ESOP than TPA-Ph-Th-CAA. Previous study has shown that the introduction of the electron-deficient BTD moiety can significantly improve the photostability of indoline-based organic sensitizers. Our calculations suggest that the insertion of an internal acceptor into a D−π−A framework can potentially improve the photostability. In conjunction with the EDDM analysis above, it is seen that TPA-Ph-Th-CAA has a large driving force for electron injection as well as strong coupling with TiO₂. On the other hand, the D−A−π−A dyes have a smaller driving force for electron injection to TiO₂; moreover, the coupling of their excited state with the TiO₂ is relatively weaker.
corresponding to the inhomogeneous broadening of the absorption spectra that thus influences the energies of the donor and acceptor. On the other hand, the chemical bonds of photoexcited molecules are considered to be weaker than those in the ground state. Therefore, how thermal fluctuations of the atoms at the photoexcited state affect the energies of donor and acceptor and the CT character need to be investigated. Photoexcitation creates the initial charge separation. The EDDM analysis of the zero-temperature UV−vis spectra discussed above shows that the electron density of the photoexcited state is partially delocalized onto the acceptor moiety at the Franck−Condon state. In particular, the excited electron density of photoexcited TPA-BTD-Th-CAA is mainly delocalized onto the BTD and CAA moieties at the same time.

One interesting question is whether the thermal energy promotes the second CT process from the internal to the terminal acceptor. Figure 5 shows the EDDM (where the excited electron density is going to) of four building units of first singlet excited TPA-BTD-Th-CAA molecule as a function of simulation time. After photoexcitation, the excited electron has several possible pathways; it can delocalize more electron density to the acceptor or the electron density on the acceptor can move back to the internal acceptor and even to the donor. It is seen that the electron density on the TPA moiety remains in a steady state with low and stable electron population with a small variance of 0.0002. The electron population on the BTD unit has a large value and a relatively large fluctuation with a

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Figure 5. EDDM (where the electron density is going to) of four building units (TPA, BTD, Th, and CAA) of TPA-BTD-Th-CAA molecule at the S1 state as a function of simulation time.

Figure 6. First excited-state energy of TPA-BTD-Th-CAA as a function of simulation time. The thick line represents the average energy every 25 fs. The thin line shows the original energy every 0.5 fs.
variance of 0.0017. On the CAA moiety, the electron population has a variance of 0.0006. No significant amount of electron density populated on CAA moiety is observed. These results indicate that only a small amount of electron density has been pushed and pulled between the internal BTD acceptor and the terminal CAA acceptor. The excited electron density redistribution is less sensitive to thermal motions.

Figure 6 shows that the first excited-state energy of TPA-BTD-Th-CAA molecule evolves with time. The variance of energy is 0.12 eV, which is approximately equal to eight atoms that contribute to change in the electronic energies at 300 K. As shown in Figure 2, the BTD unit has a lower LUMO energy than the CAA moiety by 0.31 eV, which is larger than the variance of excited energy. One of the possible reasons that the excited electron density is rarely pushed to the CAA moiety by thermal energy is the thermal energy lower than the electronic energy difference between the BTD and CAA moieties. That is, the BTD unit traps a significant amount of excited electron density.

**CONCLUSIONS AND SUMMARY**

In this study, we employed DFT, TD-DFT, and TD-DFT nonadiabatic MD simulations to investigate the photophysical properties of four D–A–π–A dyes and one D–π–A dye in solution and adsorbed on a (TiO$_2$)$_{38}$ cluster. Our main conclusions are summarized as follows:

1. Introduction of a strong electron-withdrawing group into the D–π–A framework effectively induces red shifts in absorption due to the small band gap and low-lying LUMO of internal acceptor A.
2. In addition, a strong electron-withdrawing group A, such as the BTD and PP moieties, generates a new band in the UV–visible region, which potentially contributes to the photo-to-current conversion.
3. D–A–π–A dyes exhibit distinct transition characters of absorption. Strong electron-withdrawing groups, such as BTD and PP, induce dual CT bands. The excited electron density is transferred from the TPA donor to the internal and terminal acceptors simultaneously, whereas weaker electron-withdrawing group does not. The strong electron-withdrawing groups trap the electron density and hamper the electron density transferred to the terminal acceptor upon photoexcitation.
4. TiO$_2$ serving as the electron acceptor can assist in delocalizing the excited electron density from the internal acceptor to the CAA/TiO$_2$ side upon photoexcitation.
5. Thermal energy of 300 K, applied in TD-DFT nonadiabatic MD simulations, drives the excited electron density fluctuation between the internal and terminal acceptors, whereas it has limited effect in pushing significant electron density toward the terminal acceptor. It seems that the thermal energy is not populated high enough on proper vibrational modes to drive a significant amount of photoexcited electron density on internal acceptor to the terminal acceptor.
6. Introduction of an internal acceptor with small band gap results in the D–A–π–A dye a lower ESOP relative to the analogous D–π–A dyes, giving significant features of photostability. These results support experimental observations.

Our study provides new insights into the nature of the absorption bands of D–A–π–A dyes, giving pointers about how to improve the performance of newly designed D–A–π–A dyes.

**COMPUTATIONAL METHODS**

The density functional theory (DFT) implemented within Gaussian 09 program$^{37}$ was exploited in our static ground-state calculations. The ground-state molecular geometries of the studied molecules displayed in Figure 1 were optimized by the Becke, three-parameter, Lee–Yang–Parr (B3LYP) functional$^{38,39}$ with 6-31G(d,p) basis set. The solvation effect was implemented using conductor-like polarizable continuum model (C-PCM).$^{40}$ Different solvents were used to match with experimental conditions. The long alky group of the moiety of benzotriazole (RT) was replaced with a methyl group to reduce the computing resource because the long alky chain has less effect on the electronic structure of the backbone. The time-dependent DFT (TD-DFT) was exploited for UV–vis spectra calculations. To investigate the charge-transfer excitation properties, Coulomb-attenuating method (CAM) was applied (at CAM-B3LYP/6-31G(d,p) level) to calculate the UV–vis spectra of the studied molecules based on the optimized geometries by B3LYP/6-31G(d,p) methods.

To model the photophysical properties of dye sensitizers adsorbed on TiO$_2$ thin films, a dye molecule adsorbed on a (TiO$_2$)$_{38}$ cluster was calculated. The geometries of the (TiO$_2$)$_{38}$ cluster were optimized at the B3LYP/6-31G(d,p) level. Deprotonated dyes are adsorbed on a (TiO$_2$)$_{38}$ supercluster with an anatase (101) surface in a bidentate mode,$^{44}$ one proton is transferred to a nearby two-coordinated oxygen atom. The two oxygen atoms of the carboxylate are bound to the two neighboring five-coordinated Ti atoms on the (TiO$_2$)$_{38}$ cluster surface. The geometries of dye–(TiO$_2$)$_{38}$ complexes were optimized by the B3LYP/6-31G(d,p) method in the gas phase. All of the atoms of the dye–(TiO$_2$)$_{38}$ complexes are free for optimization. This model was used as a compromise between computational resources and the stated purpose of predictions. The UV–vis spectra of the optimized dye–(TiO$_2$)$_{38}$ complexes were performed at the CAM-B3LYP/6-31G(d,p) level using acetoneitrile as solvent (C-PCM model) within the Gaussian 09 program. The acetoneitrile was chosen to match with experimental conditions. The electron density difference maps (EDDMs), which indicate the electron density before and after excitation, were generated using GaussSum (version 3.0).

The TD-DFT nonadiabatic molecular dynamics (MD) simulations of free molecules were performed in terms of the Newton-X program$^{45–48}$ (version 1.4.0-2) interfaced to Gaussian 09. The molecule we studied was first optimized using the Gaussian 09 program. Thereafter, we calculated vibrational frequencies for the studied molecule. The optimized structures and calculated frequencies were used to generate the initial conditions. A 1 ps adiabatic ground-state MD simulation (B3LYP/6-31G(d,p)) based on one of the initial conditions was performed to reach thermal equilibrium prior to the excited-state simulation (CAM-B3LYP/6-31G(d,p)). The simulation temperature was controlled at 300 K through Andersen thermostat.$^{49,50}$ The thermostat was applied every 1 fs. The simulation time step was set to 0.5 fs. The final trajectory from the 1 ps adiabatic MD simulation at S$_0$ was used as the initial condition for the following nonadiabatic MD simulations. We performed the nonadiabatic MD simulations at the first singlet excited state (S$_1$) using time-derivative coupling method$^{51}$ and fewest switching algorithm.$^{52}$ The method to compute the global phase was set to overlap the $h$ vectors. And
hopping from one state to another surface was computed and is allowed at any time step. Butcher’s\textsuperscript{53} fifth-order method was used for the integration of time-dependent Schrödinger equation. Nonconsecutive states (e.g., S\textsubscript{0} and S\textsubscript{2}) are all included in computing the nonadiabatic coupling. The output trajectories were saved every 5 fs. To maintain the stability of the system, the job was terminated when the energy difference between two neighboring steps or between the current step and the initial step was higher than 0.5 eV.

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**Notes**

The authors declare no competing financial interest.

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