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Insight into D−A−π−A Structured Sensitizers: A Promising Route to Highly Efficient and Stable Dye-Sensitized Solar Cells

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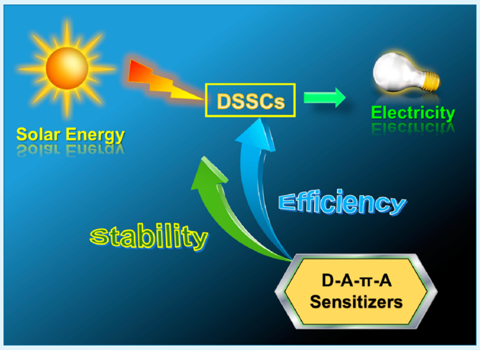
ABSTRACT: The dye-sensitized solar cell (DSSC) is one of the most promising photovoltaic technologies with potential of low cost, light weight, and good flexibility. The practical application of DSSCs requires further improvement in power conversion efficiency and long-term stability. Recently, significant progress has been witnessed in DSSC research owing to the novel concept of the D−A−π−A motif for the molecular engineering of organic photosensitizers. New organic and porphyrin dyes based on the D−A−π−A motif can not only enhance photovoltaic performance, but also improve durability in DSSC applications. This Spotlight on Applications highlights recent advances in the D−A−π−A-based photosensitizers, specifically focusing on the mechanism of efficiency and stability enhancements. Also, we find insight into the additional acceptor as well as the trade-off of long wavelength response. The basic principles are involved in molecular engineering of efficient D−A−π−A sensitizers, providing a clear road map showing how to modulate the energy bands, rationally extending the response wavelength, and optimizing photovoltaic efficiency step by step.



KEYWORDS: *solar cells, organic sensitizers, additional acceptor, photovoltaic performances, stability*

1. INTRODUCTION

The increasing demand for clean and renewable energy has aroused great enthusiasm on low-cost solar energy conversion on a global scale.[1] The dye-sensitized solar cell (DSSC) is one of the most promising photovoltaic technologies, and has attracted considerable attention owing to its potential for low-cost power production as well as its potential as a portable energy supply.[2,3] In DSSCs, sunlight is absorbed by molecular dyes that are attached onto the surface of a wide band gap semiconductor oxide (typically TiO_2). The dye molecules act as sensitizers, and inject electrons into the conduction band of metal oxides upon photoexcitation. The injected electrons are conducted through the nanostructured metal oxide to reach the external circuit, and the oxidized dyes are regenerated by a redox couple present in the electrolyte.[4]

The sensitized dye is probably one of the key elements in DSSCs since it governs the photon harvesting and the charge (electron−hole) generation as well as separation.[5−9] Generally, dyes fall into two broad categories: ruthenium (Ru)-polypyridyl complexes[2,10] and pure organic push−pull dyes.[11,12] For a long time, Ru-complexes were the "champion" dyes for DSSCs, with a power conversion efficiency higher than 11%.[13] However, ruthenium is not an "earth abundant element", which may limit widespread application. In contrast, organic sensitizers can be conveniently synthesized from a broad range of raw materials, ensuring a sustainable supply for terawatt deployment.

High-performance organic sensitizers usually feature a donor-π-bridge-acceptor (D−π−A) structure.[3,11] The electronic interaction between donor (D) and acceptor (A) results in strong charge-transfer absorption bands that harvest sunlight for photon-to-electron conversion. In 2011, Zhu et al. proposed a concept of a D−A−π−A motif for designing a new generation of efficient and stable organic sensitizers.[14] Specifically, an additional group of electron-withdrawing conjugated components has been introduced into the π-bridge of the D−π−A framework to function as an auxiliary electron acceptor. Interestingly, the additional acceptor in the D−A−π−A motif not only is instrumental to modulate the energy levels, absorption spectra, and photovoltaic performances, but also greatly improves the photostability of sensitizers.

Recently, several kinds of electron-withdrawing units [such as benzothiadiazole (BTD),[15−18] benzotriazole (BTZ),[19−21] quinoxaline (Qu),[22−25] phthalimide,[26] and diketo-pyrrolopyrrole (DPP)[27−29]] have been systematically exploited as the auxiliary acceptor for viable D−A−π−A structures. Along with a large effort into the molecular engineering of pure organic D−A−π−A sensitizers, we have demonstrated a significant increase in the photovoltaic efficiency from ~5% to greater than 10%, and a

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significant improvement in the stability of organic sensitizers as well as devices. At the same time, there are quite a number of D−A−π−A sensitizers, although sometimes they are not called as such, that have been developed and well-studied in other groups.[30−45] More recently, a record efficiency of 13.0% has been achieved with the D−A−π−A strategy to porphyrin sensitizers.[46] Besides, a benzothiadiazole-based D−A−π−A organic sensitizer has exhibited outstanding long-term stability under the aging test for 5000 h, continuously under light illumination of 1000 W cm^{-2} at 65 °C.[47] Obviously, the D−A−π−A motif is becoming a reliable route for designing photosensitizers toward highly efficient and stable DSSCs. In this Spotlight on Applications, we examine the D−A−π−A structured photosensitizers, especially with regards to molecular engineering and stability enhancements. It provides a clear road map describing how to rationally extend the wavelength response, enhance molecular extinction coefficients, and optimize photovoltaic efficiency step by step.

2. D−A−π−A MOTIF: EFFICIENTLY TUNING THE ENERGY BAND WITH ADDITIONAL ACCEPTOR UNIT

In organic molecules, oligomers, as well as polymeric systems,[48] the visible to NIR light absorption is accompanied by the covalently linked π-conjugated electron donor and electron acceptor groups (so-called D−A system, Figure 1). Here the donor HOMO orbital and the acceptor LUMO orbital are largely responsible for the location of the frontier orbitals in the D−A system, which in turn determines their light-absorption characteristics. In organic dyes based on traditional D−π−A motifs, the electron donors are usually aromatic amines, and the electron acceptors almost exclusively rely on the carboxyl acid derivatives, such as the cyanoacrylic acid group.[11,12] Their energy band and absorption characters are mainly modulated by tuning the structure of donor and π-spacer. In the case of the D−A−π−A motif, the additional auxiliary acceptor provides an alternative route for tuning the band energy as well as light-absorption profile.

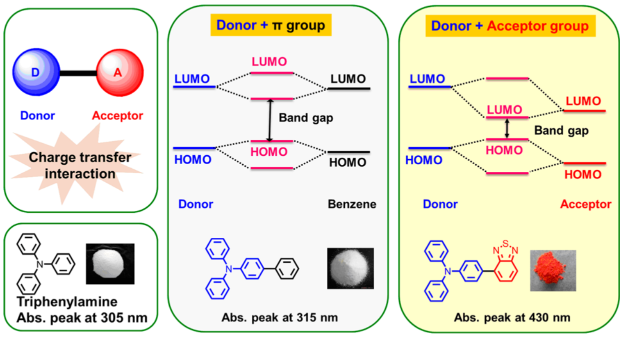


Figure 1. Energy level diagram of the donor−acceptor interaction in a D−A system. Efficient energy band modulation with a strong electron-withdrawing unit of benzothiadiazole, instead of increasing a simple conjugation bridge like benzene ring, results in a distinct color change.

2.1. Larger Electron Withdrawing in Additional Acceptor Unit, with the Larger Red Shift in Light Response.

Molecular engineering on the D−π−A system for broadening its absorption spectra always involves an enhancement in the electron-donating or electron-withdrawing ability, and increasing the effective conjugation length between the donor and acceptor. However, when using the anchoring group of cyanoacrylic acid as acceptor, the resulting absorption band is mostly shorter than 500 nm, despite much effort to improve the visible light harvesting of D−π−A structured organic dyes.[3,11] Compared to simply extending the conjugation by a bridge like the benzene ring, a more efficient way to modulate the absorption band is by introducing a strong electron-withdrawing unit of benzothiadiazole (Figure 1), resulting in a distinct color change from white (benzene-substituted triphenylamine) to fresh red (benzothiadiazole-substituted triphenylamine). With this in mind, since 2011 the Zhu group has proposed a novel structural design comprising the D−A−π−A motif, which adjusts the molecular frontier orbitals by incorporating the additional auxiliary electron-acceptor unit within the π-bridge. The first class of the auxiliary electron acceptors is a series of benzannulated structures, such as benzothiadiazole, benzotriazole, benzopyrazine (quinoxaline), and benzoxadiazole, which feature a benzoheterocyclic structure containing the electron-deficient C═N bonds. The additional acceptor groups in the D−A−π−A framework further decrease the HOMO−LUMO gap under the same principle depicted in Figure 1.

In a series of systematical studies, we consistently adopted an indoline derivative as the electron donor, and utilized a thiophene unit to connect the auxiliary acceptor and anchoring acceptor. Figure 2a shows the motif D−A−π−A framework as well as chemical structures of these dyes. Intriguingly, the different electron-withdrawing capability of additional acceptors in the framework has a significant impact on the frontier orbital

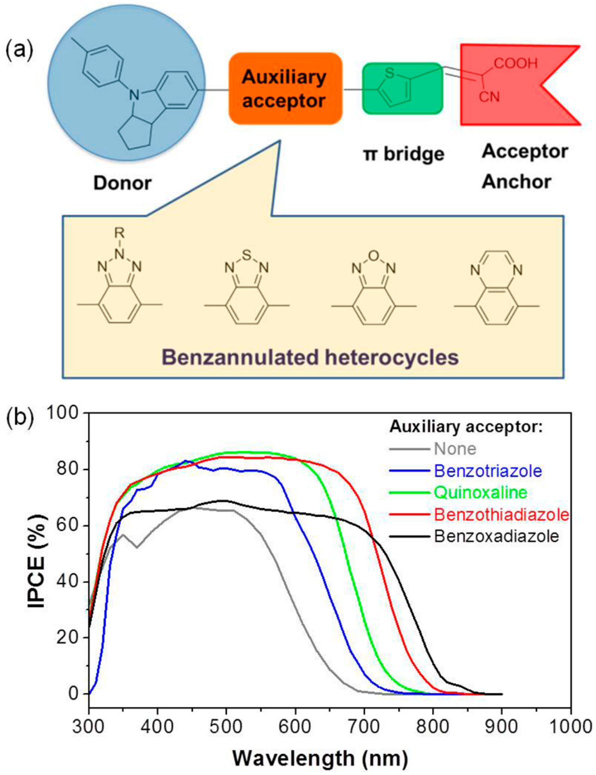


Figure 2. (a) D−A−π−A featured organic dyes with benzannulated heterocycles as the auxiliary acceptor. (b) IPCE curves of DSSCs based on D−A−π−A dyes containing benzothiadiazole, benzotriazole, benzopyrazine (quinoxaline), and benzoxadiazole as the auxiliary acceptor. “None” device is based on a reference dye without auxiliary acceptor.

energy levels, thus resulting in an efficient modulation in the absorption band with different light-harvesting response in DSSC devices (Figure 2b). Obviously, in a comparison with the reference typical D−π−A system in which no additional acceptor exists, the red-shift response in incident photon-to-current conversion efficiency (IPCE) follows the trend benzoxadiazole > benzothiadiazole > quinoxaline > benzotriazole. Thus, the nature of the auxiliary acceptor determines the spectral response of the photocurrent for these four dyes endowed with the same electron donor, π-bridge, and anchoring acceptor. Theoretical simulations as well as experimental evidence from organic polymer photovoltaics (OPVs) show the electron-withdrawing capability increases in the sequence benzotriazole < quinoxaline < benzothiadiazole < benzoxadiazole.[49,50] This indicates that the larger the electron-withdrawing nature of the additional acceptor unit, the larger the red shift in the photoresponse. Very impressively, the IPCE tail even reaches as far in the NIR as 860 nm upon incorporation of an additional benzoxadiazole unit (Figure 2b), which is very uncommon to pure organic sensitizers.

2.2. Why DPP Does Not Fit in a D−A−π−A Motif: Trade-Off of Long Wavelength Response in NIR Organic Dyes. Diketopyrrolopyrrole (DPP) is a commercially available industrial pigment which is widely applied, such as car-paint pigments and polymeric organic photovoltaics.[51] DPP-based materials generally possess several advantages such as strong fluorescence and high stability. Recently, utilization of a DPP unit as the building block in DSSCs sensitizers has become a hot topic.[52−55] Briefly, the very strong electron-withdrawing capability of the DPP unit renders it attractive for constructing D−A−π−A structured sensitizers. The early work was reviewed by Hua and Tian et al.[27] The incorporation of DPP into the traditional D−π−A framework indeed extends their absorption band to longer wavelengths, even the near-infrared (NIR) region.

However, it appears to be hard to achieve high-power conversion efficiencies with DPP-based sensitizers. As an example, although the absorption band of **DPP-II** is bathochromically shifted to 627 nm, it generates a short circuit current (J_{sc}) of only 2 mA cm^{-2} (Figure 3). Here the very strong electron-withdrawing property of the DPP lowers the LUMO level of the dye to such a low a value, i.e., −0.56 V, that there is insufficient driving force for electron injection to the TiO$_2$ conduction band from the D−A−π−A structured sensitizers. Nevertheless, the strong electron interaction between donor and DPP can be blocked to some extent. The conjugated bridge of a five-member-ring such as thiophene is known to keep the donor in better planarity than that of a six-member-ring like benzene.[14] As illustrated with the sensitizer **YCD01** (Figure 3), Han and Tian et al. inserted the thiophene moiety by benzene to decrease the electron interaction between the donor and DPP units. This increased the power conversion efficiency (PCE) to 7.43%,[29] showing that the judicious molecular engineering of the π-bridge between donor and acceptor can balance the red shift in the optical band, HOMO−LUMO levels, and IPCE. Moreover, Grätzel et al. improved the PCE of DPP-based sensitizers further to 8.74% by modifying the anchoring group.[56]

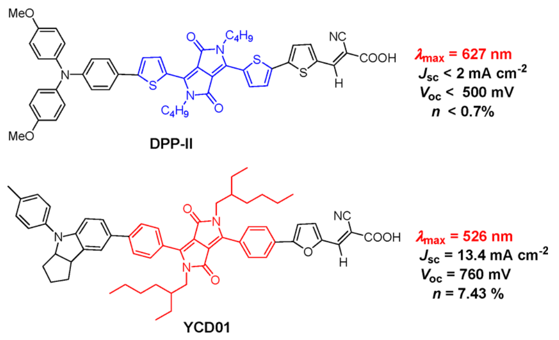


Figure 3. D−A−π−A featured organic sensitizers containing DPP unit as the additional acceptor.

Light harvesting from sun irradiation is the first step of solar energy conversion in photovoltaic devices. Specifically, a monolayer of dye molecules on the surface of nanocrystalline TiO$_2$ plays a central role in photon collection for DSSCs. In the classical photovoltaic theory, the light harvest for a single junction solar cell should have an optical band gap around 1.1 eV and absorb photons below 1100 nm as much as possible. However, molecular sensitizers in DSSCs need to spend some potential energy to drive the electron injection (from dye to TiO$_2$) and dye regeneration (receiving electrons from redox shuttles in the electrolyte). Thus, the optimal optical band gap for DSSCs is a little bit larger than that of traditional inorganic solar cells. The dyes for DSSCs are expected to endow an optical band gap of 1.5 eV, with shifting intensive absorption band below 950 nm. That is why the long wavelength absorption always becomes attractive, especially in NIR organic dyes.

While the DPP-based organic sensitizers can conveniently extend the light response to the NIR region, their photovoltaic efficiencies are generally low due to a mismatch in the energy levels for electron injection, but the situation for Ru complexes is quite different. The photocurrent response of the best performing Ru dye (black dye) starts at 950 nm while that for N3 starts at 800 (Figure 4).[57] Even though the light-harvesting efficiency of N719 (a salt form of N3) is similar to that of **DPP-II**, the PCE of the former reaches values over 11% which cannot be obtained with the latter dye,[58] mainly due to a lower open circuit voltage (V_{OC}).[59] The smaller V_{OC} reflects a shorter electron lifetime due to faster recombination with triiodide in the electrolyte for **DPP-II** loaded nanostructure TiO$_2$ films than for N719 ones. Thus, the nature of the adsorbed dye affects the rate of this unwanted interfacial back electron

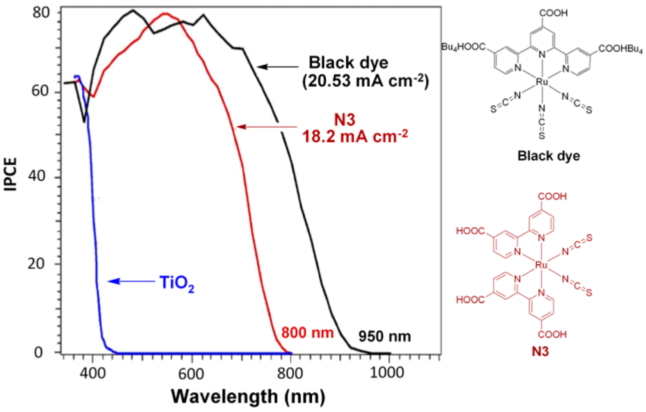
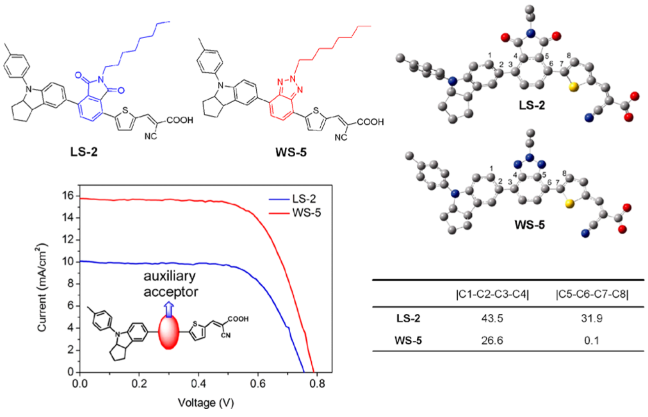


Figure 4. Efficient NIR light response of Ru dyes (**black dye** and **N3**), with the long triplet electron lifetime guaranteeing predominance to the overall performance.

transfer process. Careful design of the DPP structure can help to control the back reaction kinetics. For instance, Grätzel and co-workers have carefully modified the donor structure of DPP dyes to make it compatible to cobalt (II/III)-based electrolyte and realized a good efficiency.[60]

2.3. Negative Contribution: Twist Configuration from Steric Hindrance in Additional Acceptor. As demonstrated above, the introduction of a second additional acceptor affects strongly the DSSC performance. It is essential to choose the proper subsidiary withdrawing unit for constructing D−A−π−A sensitizers. Given the very similar five-member benzoheterocycles with benzotriazole, the electron-withdrawing unit of phthalimide was also incorporated as the auxiliary acceptor to construct D−A−π−A featured organic dyes (**LS-2**, as shown in Figure 5).[26] Unexpectedly, in contrast with **WS-5**, the phthalimide-containing sensitizer **LS-2** exhibits a low PCE. Thus, upon replacing benzotriazole by phthalimide maintaining the same D−A−π−A structural motif, the PCE of **LS-2** decreases to 5.1%, which is 39% lower than that of **WS-5** (8.38%, Figure 5). As both sensitizers give a relatively high V_{OC}, exceeding 750 mV, the low PCE of **LS-2**-based DSSCs is mainly caused by the small short circuit photocurrent (J_{SC}). In the optimized configuration of **WS-5**, the dihedral angle between the donor group and auxiliary acceptor benzotriazole group is calculated to be 26.6°, and the angle between benzotriazole group and thiophene moiety is about 0.1°, an exact coplanarity. Here the benzotriazole unit in **WS-5** promotes the overlap of HOMO and LUMO orbitals, consistent with the red shift of the intramolecular charge-transfer (ICT) absorption band. Conversely, the structure of **LS-2** shows the significant twist with the corresponding dihedral angles calculated to be 43.5° and 31.9°, respectively. The lower coplanarity in **LS-2** suggests that the incorporated phthalimide unit destroys electron delocalization between the donor and acceptor units, resulting in the observed distinct blue shift in the absorption. A similar phenomenon was observed in the previous work using fluorene as a conjugation bridge.[61] Generally, the aromatic rings linked by single bonds would undergo fast single bond rotation leading to a coplanar conformation. However, the presence of carbonyl groups in phthalimide may impair the rotation of the aryl groups, resulting in relatively larger dihedral angles and a highly twisted conformation. Accordingly, upon incorporation of the phthalimide unit, the resulting tilted conformation of **LS-2** disfavors the electron transition from the donor part to the acceptor in accordance with the observed large 41 nm blue shift in the absorption band and the more positive HOMO level. From electrochemical impedance spectroscopy (EIS), the benzotriazole unit in **WS-5** prolonged the photoinjected conduction band electron lifetime about 3.7 times over the phthalimide in **LS-2**. The distinct difference between **LS-2** and **WS-5** in absorption, energy levels, and photovoltaic performance illustrates well that, besides the electron-withdrawing capability, the steric hindrance must be taken into consideration in the selection of auxiliary acceptors.



	|C1-C2-C3-C4|	|C5-C6-C7-C8|
LS-2	43.5	31.9
WS-5	26.6	0.1

Figure 5. D−A−π−A featured sensitizers **LS-2** and **WS-5** bearing phthalimide and benzotriazole as auxiliary acceptor. The steric carbonyl hindrance from the neighboring phthalimide acceptor twists the molecular configuration, resulting in the distinct effect on absorption and charge recombination dynamics in DSSCs with negative contribution to photovoltaic performances.

3. D−A−π−A MOTIF: FACILITATING OR HAMPERING CHARGE TRANSFER WITH ADDITIONAL ACCEPTOR UNIT?

Generally for D−π−A featured organic sensitizers, the HOMO is mainly located on the donor group, while the LUMO is distributed on the acceptor part. Hence the absorbed photons excite the electron transition from HOMO to LUMO, which enables electrons to move spatially from donor to acceptor (anchor) with the specific charge separation. However, it may be changed when an additional electron-deficient group is introduced in the conjugated bridge. Especially, Lin and co-workers speculated that the electron-deficient benzothiadiazole (BTD) entity may cause partial charge-trapping and hamper electron injection from the dye to the TiO_2 conduction band, thus counteracting the performance of the DSSCs.[62] Thus, the issue regarding an additional acceptor in the D−A−π−A structured sensitizers needs to be addressed (Figure 6).

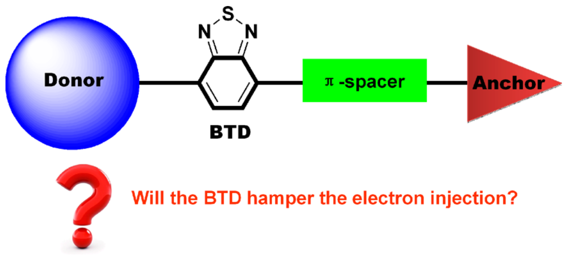


Figure 6. Does the additional acceptor hamper charge transfer within the D−A−π−A featured sensitizers?

As a matter of fact, upon incorporation of the auxiliary acceptor BTD unit, no discontinuity is observed in the DFT simulated HOMO and LUMO orbitals around the BTD unit (Figure 7). In contrast, the distribution of both HOMO and LUMO orbitals in **WS-2** and **WS-9** overlaps well with the BTD unit. Because there is a stronger overlap between HOMO and LUMO orbitals, enhancing charge transfer from donor to acceptor is expected.[14,16] That is, the BTD unit can actually facilitate electron transition from HOMO to LUMO orbitals, rather than block it. It appears that the sequential electron motion from D to the internal A, and then to terminal A in the D−A−π−A configuration, may benefit the charge separation in organic sensitizers. This is also apparent from their specific absorption characteristics, such as the appearance of additional absorption band and the red shift in the ICT band.[16]

Generally, the traditional D−π−A organic dye (such as the reference dye **LS-1** in Figure 7) contains two absorption bands:

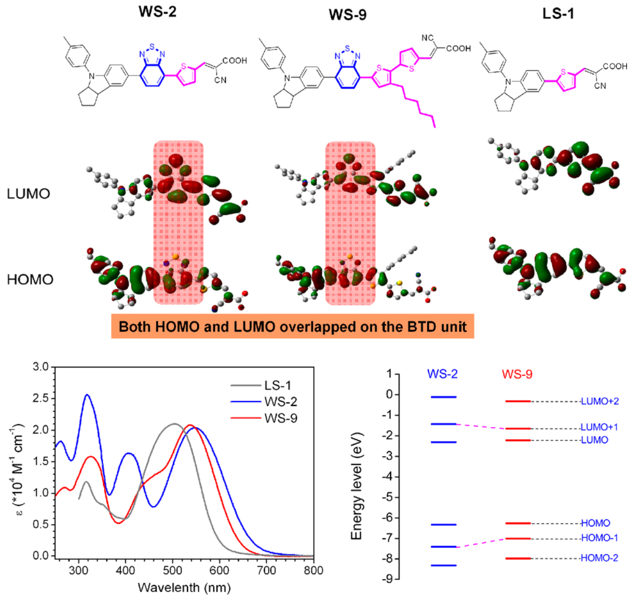


Figure 7. Efficient ICT facilitated with additional acceptor in D−A−π−A motif, not only resulting in a distinctly red-shifted absorption band, but also bringing forth an additional absorption band.

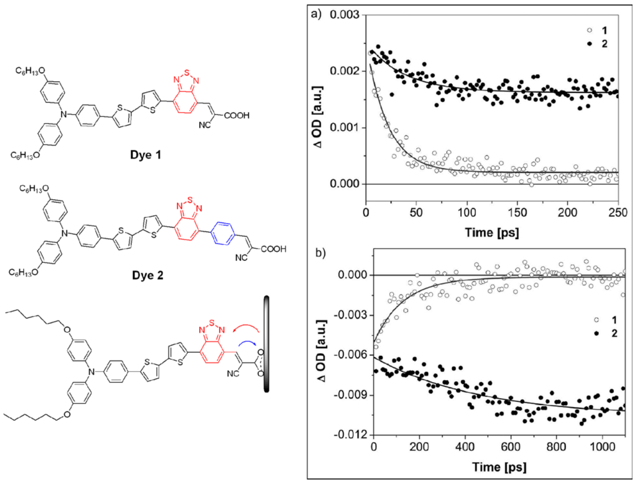


Figure 8. Chemical structures of dyes **1** and **2**, and schematic diagram showing the path for fast charge carrier recombination: (a) first-order-fits of the transient time-absorption profiles for the charge recombination dynamics of the radical cation signatures at 700 nm and (b) the ground state bleaching at 580 nm. Electron recapture by the oxidized sensitizer is much faster for the D−π−A−A dye **1** compared to that for dye 2 having a D−A−π−A motif.

one intramolecular charge-transfer (ICT) absorption in the visible region and one local π−π* absorption band in the UV.[63,64] In contrast, for the two D−A−π−A dyes (**WS-2** and **WS-9**), the incorporation of the auxiliary acceptor BTD results in a distinctly red-shifted absorption band. Moreover, an additional absorption band around 400 nm (Figure 7) is observed, which assists blue light harvesting. Compared with **WS-2**, **WS-9** contains one more thienyl unit in the π-conjugation; its ICT absorption peak is not red-shifted but blue-shifted by 10 nm. Obviously, for **WS-9**, extending the π-conjugation has little effect on the ICT band, but it red-shifts the absorption band around 400 nm. Actually, in the density functional theory (DFT) simulation, it is found that the HOMO and LUMO levels of both dyes are very similar, resulting in a nearly identical ICT absorption band at around 540 nm. However, since the HOMO − 1 and LUMO + 1 levels of **WS-9** drift significantly with respect to that of **WS-2**, it is easy to understand that the HOMO → LUMO + 1 and HOMO − 1 → LUMO transition energies become smaller, along with the red shift in absorption band at 458 nm. Moreover, the similar facilitation in charge transfer by the additional benzotriazole and quinoxaline acceptor unit is also observed.[19,22]

4. WHY D−A−π−A ARCHITECTURE, INSTEAD OF D−π−A−A

Bäuerle and Grätzel et al. compared the electron injection and recombination dynamics of two BTD-based sensitizers (**1** and **2**, Figure 8) with a delicate molecular engineering in the bridging framework.[65] From the chemical structure, dye **1** contains the electron-deficient BTD unit directly adjacent to the anchoring group (so-called D−π−A−A motif), whereas dye **2** contains a phenyl group between the two acceptor units (D−A−π−A motif). Strangely, upon incorporation of a BTD unit close to the anchoring acceptor, the resulting large red-shift absorption band by **1** did not translate into the improved cell performances. By measuring the excited state lifetimes in solution and when adsorbed on the TiO_2 surface, the electron injection yield can reach as high as 95% for both dyes, also indicating that the BTD unit does not hamper the electron injection. However, for the D−π−A−A fashioned dye **1**, the rapid recombination between injected electrons and oxidized dyes was observed. That is, dye-**1**-based solar cells exhibited high-injection efficiencies, but suffered from rapid charge recombination, which was well-demonstrated with transient laser photolysis experiments. From the femtosecond pump−probe studies of dyes **1** and **2**, the first-order-fits of time-absorption profiles showed the quite different charge recombination dynamics of the radical cation signatures at 700 nm (Figure 8a) and the ground state bleaching at 580 nm (Figure 8b). Compared with the behavior of dye **1**, the insertion of a phenyl group between BTD and cyanoacetic acid (in the case of D−A−π−A featured dye **2**) can greatly retard the back electron transfer, along with a vast improvement in the PCE which increased by 6.5 times, from 1.24% of dye **1** to 8.21% of dye **2** in devices using iodine-based liquid electrolyte.

More recently, Grätzel et al. have further developed a similar structural modification with D−π−A−A motif in the π-bridge for porphyrin dyes **GY21** and **GY50** (Figure 9), which also focused on the importance of inserting phenyl group as a spacer between the BTD and the zinc porphyrin to achieve high-power-conversion efficiencies.[66] Consistent with the theoretical predictions, the incorporation of a BTD moiety can efficiently fill the absorption gap between the Soret band and the Q band in porphyrin dyes, even being capable of avoiding the complementary cosensitization.[67] Several methods such as time-resolved fluorescence, transient-photocurrent decay, and transient-photovoltage decay measurements provided insight into the electron-injection dynamics and differences in the lifetime of the photogenerated charge carriers between porphyrin **GY21** and **GY50**. Although the insertion of the phenyl group in **GY50** brought forth a slight blue shift in the absorption band by 10 nm, it decreased the charge recombination rate by a factor of 100 in the case of a cobalt-based redox electrolyte and by a factor of 10 for an iodide-based redox electrolyte, thus resulting in a striking difference in J_{SC}

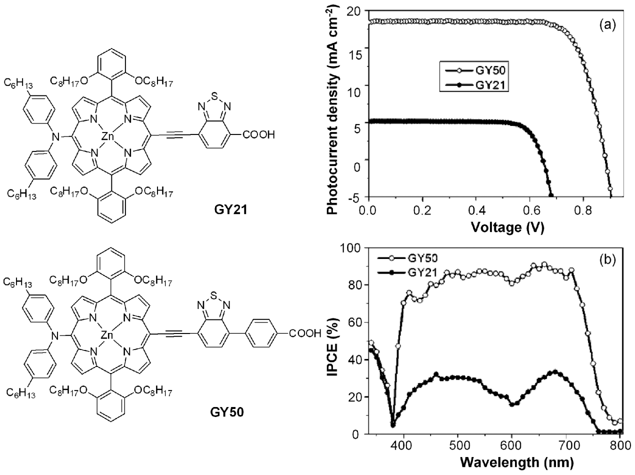


Figure 9. Chemical structures and photovoltaic behaviors of porphyrin dyes **GY21** and **GY50** for exploring the role of the inserting benzene spacer: (a) photocurrent density vs voltage (J−V) and (b) IPCE action spectra, illustrating that the D−A−π−A featured **GY50** is much more preferable to the D−π−A−A featured **GY21**, which mostly arises from the efficient blocking of the injected electron recombination.

and V_{OC} values and PCE obtained for **GY21** and **GY50** (Figure 9). Overall, a 5-fold increase in photovoltaic efficiency was observed from **GY21** (2.5%) to **GY50** (12.75%). Again, the D−A−π−A outperformed the D−π−A−A architecture predominantly blocking geminate recombination of photogenerated charge carriers. More recently, with a similar strategy, the Wang group has reported an N-annulated indenoperylene electron donor-based dye **C275**, achieving a high-power conversion efficiency of 12.5% under irradiance of 100 mW cm^{-2} AM1.5G sunlight with a Co-phen electrolyte.[42]

The laboratory development of highly efficient sensitizers utilized in DSSCs often invokes a trial-and-error approach, which often takes huge efforts involving extensive chemical synthesis and expensive materials processing. For the sake of avoiding such laborious and slow procedures, Geng et al. shed much light on how the π-spacer sequence influences the performance of organic sensitizers from the theoretical viewpoint.[68] In the density functional theory characterization and verification of high-performance indoline dyes, they also concluded that the D−A−π−A motif should be a more suitable structure with respect to D−π−A and D−π−A−A architectures. Nevertheless, how to design the optimal π-spacer order in organic sensitizers is still a key issue.[69,70]

5. DYE-STABILITY ENHANCEMENT BY D−A−π−A MOTIF

5.1. Stability Enhancement via Charge-Redistribution by Additional Acceptor.

For practical application, there are several degradation pathways within DSSCs, such as the aging of mesoporous photoelectrode, the leakage or component change of electrolyte, the deterioration of counter electrode, as well as the desorption/degradation of light-harvesting sensitizers. Among them, the intrinsic stability of organic dyes is a critical factor, especially under operation conditions.[71]

Upon considering the effect of organic sensitizers on the long-term stability of DSSCs, the heart of the matter is that organic sensitizers are subjected to illumination (i.e., by sunlight). Here the possible photolytic and photochemical reactions always lead to the degradation of device performance to a degree, which is closely correlated with the essential molecular units composing the sensitizer.

In organic sensitizers, oligoenes are always utilized as the π-bridge to link the electron donor and acceptor since their well-delocalized π orbitals can effectively facilitate electronic communications over the whole molecular framework.[11] However, the alternated single−double bonds of oligoenes are unfavorable for the dye photostability under light irradiation, especially in the presence of atmospheric oxygen. That is why the π-conjugated aromatic rings, especially oligothiophenes and fused-thiophene derivatives, become attractive in the development of organic sensitizers. Katoh et al. scrutinized the photostability of organic sensitizers with different chemical structures, and concluded that oligothiophene-based dye moieties are of great importance to obtain high durability under illumination.[72]

In spite of the good stability of oligothiophene-based organic sensitizers, extending their spectra to longer wavelength or NIR region encounters a bottleneck.[16] The red shift in absorption bands becomes negligible upon increasing the length of oligomers beyond tetrathiophene. Accordingly, a novel strategy on molecular design is highly desirable to enable both high stability and accessibility to NIR light response. In a comparison with the traditional D−π−A feature, the additional auxiliary acceptor in the D−A−π−A motif can exert a better charge delocalization, red-shift the charge-transfer absorption band to the low-energy region, decrease the reorganization energy, and suppress charge recombination. This molecular engineering rule is much different from previous ones. As shown above, the energy levels as well as absorption properties of D−A−π−A organic sensitizers can be conveniently modulated by varying the structure of auxiliary electron acceptors rather than extending the conjugation length. More importantly, the D−A−π−A motif has the potential for highly stable organic sensitizers.

For example, we found that the electron-withdrawing unit (such as BTD and quinoxaline units) can distinctly enhance the photostability of indoline-based organic dyes as well as related intermediates in synthesis. Actually, the bare indoline is extremely photosensitive, deteriorating in a very short time (Figure 10). Importantly, upon incorporating a quinoxaline unit, the corresponding intermediate becomes stable. Here the increase in photostability of indoline derivatives might arise from the decreased energy level of LUMO orbital, along with a beneficial electron distribution between the donor indoline and acceptor quinoxaline (Figure 10). Obviously, such an ability to

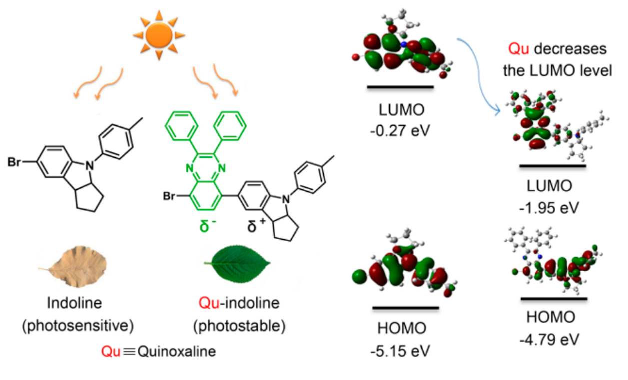


Figure 10. Mechanism of the quinoxaline unit for increasing the photostability of indoline derivatives.

improve the photostability of indoline derivatives is helpful to the synthetic process, as well as the long-living stability of DSSCs.

In this regard, we have carefully compared the photostability of aforementioned D−π−A dye **LS-1** and its analogue of D−A−π−A structured **WS-2** by using the method introduced by Katoh et al.[72] In short, we can measure the absorption spectra of dye loaded TiO_2 film before and after simulated sunlight irradiations, and observe the variation in the absorption curves during irradiation. As shown in Figure 11, the absorbance of **LS-1** (at 500 nm) decreased by 45% upon 30 min irradiation. In contrast, the absorbance of **WS-2** at 500 nm remained practically constant over the same time period. This indicates that the oxidized state of **WS-2** is much more stable than that of **LS-1**. It is well-demonstrated that the dye stability in its oxidized state is crucial to the long-term stability of DSSCs.[72] We speculate that the improved photostability of **WS-2** is attributed to the presence of a strong electron-withdrawing unit adjacent to the electron-rich indoline unit, resulting in a positive shift of the redox potential and decreased reaction activity of the oxidized indoline unit. Other kinds of auxiliary acceptors, such as quinoxaline and DPP, can also improve the stability of the indoline donor. Therefore, it is a universal and effective strategy for improving the photostability of the organic electron-rich functional group.

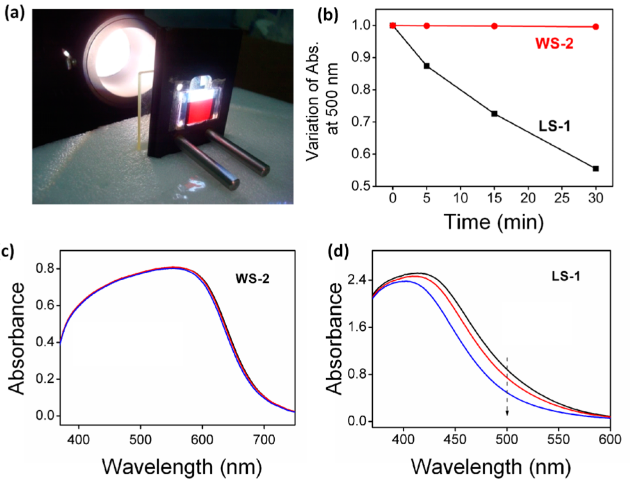


Figure 11. Dye **WS-2** with a distinctly improved photostability with respect to **LS-1** (their molecular structures are shown in Figure 7): (a) dye photostability measurement on the TiO_2 film, (b−d) absorption spectra of **LS-1** and **WS-2** adsorbed on nanocrystalline TiO_2 films before (black line) and after light irradiation for 5 min (red line) and 30 min (blue line).

Before the year 2011, there were few reports on the stability of indoline-dye-based DSSCs, though the photovoltaic performances of indoline dyes are among the best of all candidates. One of the most important reasons is that indoline is an unstable unit due to its high electron density and low oxidation potential. We developed the D−A−π−A motif and applied it in indoline dyes. For the first time, we have realized long-term stable and highly efficient DSSCs based on D−A−π−A fashioned indoline dyes. By using a similar acceptor and D−A−π−A structure, Joly and co-workers reported a simple dye **RK1**, impressively achieving a high efficiency of 10.2% with outstanding long-term stability.[47] After 5000 h of continuous irradiation at 65 °C, **RK1**-based ionic liquid electrolyte solar cells still show 75% of their initial power conversion efficiency. This further supports the notion that the incorporation of auxiliary acceptors, such as BTD into organic sensitizers, can greatly improve the photostability as well as thermal stability.

5.2. Stability Enhancement via Introducing Antiaggregation Unit on Additional Acceptor.

Organic sensitizers are easily aggregated on the TiO_2 surface, which is detrimental to the photovoltaic performances. In order to decrease the degree of dye aggregation, a useful strategy is to design some alkyl chains onto the structure of sensitizers. We also introduced an alkyl chain onto the thiophene unit of the aforementioned **WS-2**, resulting in the dye **WS-6** (Figure 12).[15] Indeed, the performance of **WS-6** is better than that of **WS-2** in the absence of coadsorbent (such as DCA). However, we found that photostability of **WS-6** is lower than that of **WS-2** (the photostability was evaluated by the experiment shown in Figure 11). Upon considering their very similar backbone structure, the low photostability of **WS-6** should be attributed to the introduced alkyl chain group on the thiophene unit. Another example is the dye **WS-9** (Figure 12), which contains one more hexylthiophene based on the structure of **WS-2**.[16] Photostability measurements indicated that the photostability of **WS-9** is also a little lower than that of **WS-2**. It is well-known that alkyl chains on the conjugated polymers greatly accelerate their photodegradation due to the side chain oxidation reactions.[73] Similar reactions may also occur on the alkyl chain containing organic sensitizers.

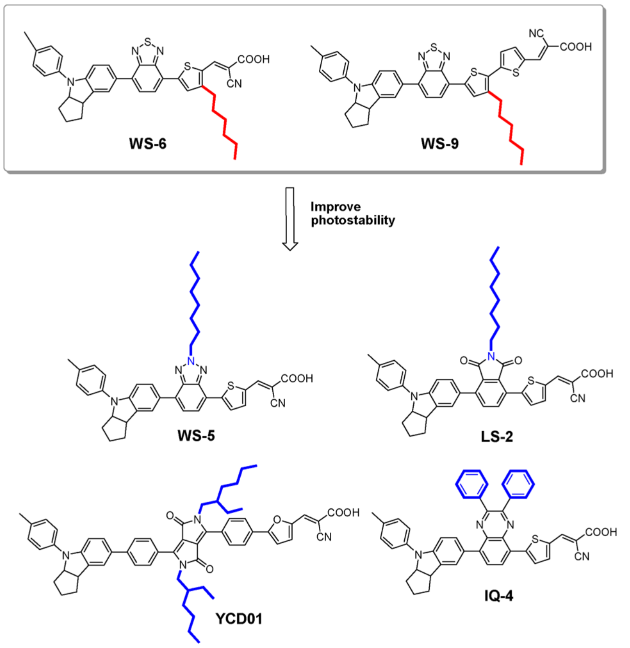


Figure 12. Improving the photostability of organic sensitizers by introducing alkyl chains onto electron-deficient auxiliary acceptors in D−A−π−A motif, or developing alkyl-chain free and steric hindrance building blocks, such as 2,3-diphenylquinoxaline in dye **IQ4**.

Given that the grafted alkyl chain on a π-bridge thiophene segment for preventing π aggregation can deteriorate its intrinsic photostability, it is desirable to develop highly stable new structures that can inhibit dye aggregation. Intriguingly, we found that, in specific D−A−π−A featured sensitizers, introduction of alkyl chains onto the auxiliary acceptors, such as benzotriazole, phthalimide, and DPP units that have secondary amine group for alkalization (Figure 12), does not decrease the photostability of sensitizers. Considering that the side chain oxidation occurs easily on the benzylic carbon site, the degradation of the alkyl chains on an electron-deficient unit may be suppressed to some extent. Accordingly, the D−A−π−A motif provides a convenient alkylation site on the additional acceptor improving their photostability.

On the other hand, developing alkyl-chain free sensitizer should be beneficial to the photostability of sensitizers once the unfavorable aggregation problem can be avoided. In this regard, we have developed a building block of 2,3-diphenylquinoxaline, which not only serves as an auxiliary acceptor, but also is capable of restraining the intermolecular aggregation due to the two twisted phenyl groups grafted onto the quinoxaline unit.[23] A new D−A−π−A-featured dye **IQ4** was developed with a good balance between the photocurrent and photovoltage as a result of the moderate electron-withdrawing acceptor. The coadsorbent-free dye-sensitized solar cell (DSSC) based on dye **IQ4** exhibits very promising conversion efficiency as high as 9.23%. More importantly, dye **IQ4** is highly stable under light irradiation, and **IQ4**-based DSSC devices can keep constant performance during a 1000 h aging test under 1 sun at 60 °C.[23] The strategy of designing an alkyl-free but sterically hindered building block, such as 2,3-diphenylquinoxaline, is a reliable way to highly efficient and stable organic sensitizers, thus realizing a facile structural modification for constructing organic coadsorbent-free D−A−π−A-featured sensitizers, and paving a route to replace the stability-deleterious method of grafting alkyl chains on the thiophene bridge.

6. EFFICIENCY ENHANCEMENT BY D−A−π−A MOTIF

Since we proposed the concept of D−A−π−A, we always focused on a specific structure, featuring an indoline as the electron donor, a thiophene as the π-spacer, and a cyanoacrylic acid as the anchor/acceptor, to illustrate the effect of an additional acceptor on the photophysical, photochemical, as well as photovoltaic properties. During the first research stage, the structure and electron-deficient character of the additional acceptor has been systematically modulated as summarized in Figure 13. According to theoretical simulation and experimental experience in polymer photovoltaics, the electron-withdrawing capability of these acceptor units are increased in the sequence BTZ < Qu < BTD < BOD.[49,50] The absorption bands of the series of sensitizers comprising **LS-1** (without additional acceptor), **WS-5**, **IQ4**, **WS-2**, and **WS-25** (not published) are gradually red-shifted as a result of the increase of electron-withdrawing capability of these acceptor units, corresponding to increased light-harvesting window for the solar spectrum (Figure 13b). State-of-the-art devices based on these sensitizers have been constructed (FF > 0.71 indicating good device quality),[14,19,23,61] allowing us to distinguish which acceptor unit is the most promising one. The J_{sc} values of these motif sensitizers significantly increase as the acceptor varied from NA (**LS-1** as a reference dye without auxiliary acceptor) to BTD (**WS-2**), but decreased in the case of BOD (**WS-25**), indicative of a trade-off between the light response range (optical band gap E_g) and HOMO−LUMO energy levels matching. In a comparison with dye **LS-1**, it is interesting to find that incorporation of BTZ (**WS-5**) and Qu (**IQ4**) greatly increases V_{OC}, although the E_g was decreased due to the additional acceptors. This can be rationalized by the existence of alkyl chain/2,3-diphenylquinoxaline in **WS-5**/**IQ4**, which effectively retards interfacial charge recombination as mentioned above. However, the V_{OC} of **WS-2** and **WS-25** decreased since the electron-withdrawing character of BTD and BOD greatly increased. Taking into account the tendency of J_{SC} and V_{OC} versus structure of additional acceptor units, the key photovoltaic metrics shed light on BTZ-, Qu-, and BTD-based sensitizers (Figure 13f).

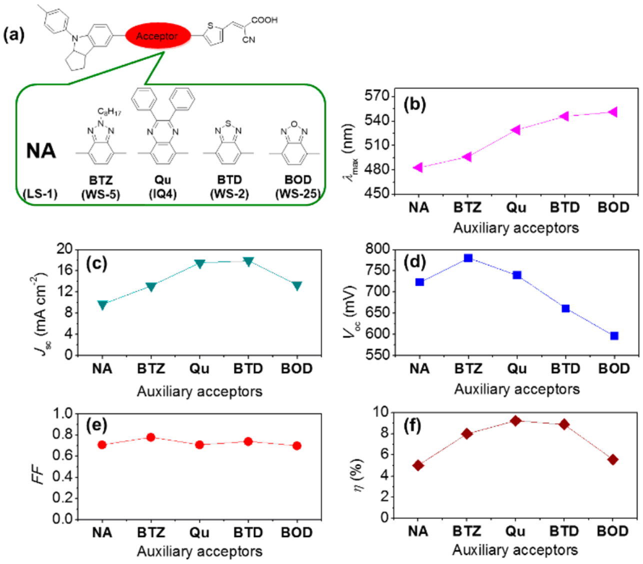


Figure 13. Efficiency enhancement of D−A−π−A sensitizers by modifying the structure of the auxiliary acceptors: (a) chemical structures, (b) absorption peaks, (c) photocurrent, (d) voltage, (e) fill factor, and (f) photovoltaic efficiency.

As shown in Figure 14, we illustrate the further molecular engineering and cosensitization strategy. In consideration of the weak electron-withdrawing capability of the BTZ unit, octyl-substituted 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT) was used instead of thiophene in **WS-5**, resulting in **WS-39**.[74] This molecular engineering not only extended the absorption of BTZ dyes to longer wavelength, but also realized dual protection to prevent binding of the iodide−triiodide redox couple and produce an efficient shielding effect to retard the charge recombination. A promising photovoltaic efficiency of 9.07% was achieved upon this structural optimization. For

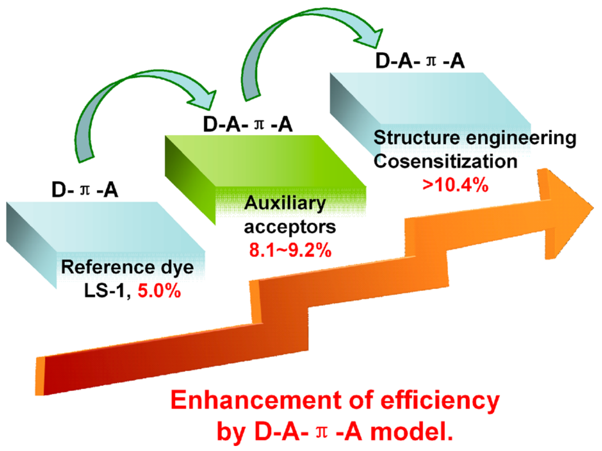
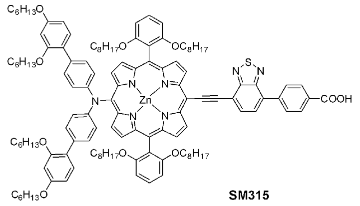


Figure 14. Photovoltaic efficiency enhancement by organic D−A−π−A sensitizers containing indoline donor unit, indicative of a reliable route to highly efficient and stable dye-sensitized solar cells.

quinoxaline-based sensitizers, the π-spacer and donor structure have been modified,[24] and a high efficiency of 10.65% has been achieved by using cobalt redox-based electrolyte.[75] Recently, the cosensitization strategy has been applied to the D−A−π−A sensitizers. Co-sensitizing a long wavelength responsive quinoxaline dye **IQ21** with a simple D−π−A dye resulted in a high efficiency of 10.41% in an iodide electrolyte system.[25] These achievements strongly suggest that the D−A−π−A motif is a promising way to high-performance pure organic sensitizers.

Porphyrin-based D−π−A dyes provide a highly flexible platform for developing panchromatic sensitizers.[67,76,77] The porphyrin chromophore has intrinsically strong light-absorption Soret band (λ = 400−450 nm) and moderately intense Q bands (λ = 550−650 nm) which cover the visible to the NIR region. To date, highly efficient porphyrin sensitizers have been typically functionalized with two bis(*ortho*-alkoxy)-wrapped *meso*-phenyl groups for eliminating dye aggregation, and an ethynyl benzoic acid group as the efficient acceptor.[78,79] However, the simultaneous filling of both absorption valleys in the Soret and Q bands of porphyrins is still attractive. Recently, on the basis of the similar D−A−π−A strategy, Grätzel et al. have re-engineered the prototypical structure of D−π−A porphyrins and inserted an additional electron-withdrawing group of the BTD unit (dye **SM315**, Figure 15), especially focused on electrolyte compatibility and light-harvesting improvements for panchromatic absorption.[46] Interestingly, the BTD-incorporated dye **SM315** distinctly broadens the absorbance features of Soret and Q bands, thus bringing forth an improved light response in both the green (500−600 nm) and red (up to 800 nm) regions. Upon the cobalt(II/III) redox shuttle, **SM315** achieved an impressive enhancement in green light absorption, along with a record photovoltaic efficiency of 13.0% at full sun illumination without the requirement of cosensitization (J_{SC} = 18.1 mA cm^{-2}, V_{OC} = 0.91 V, and FF = 0.78).



SM315

J_{sc} = 18.1 mA cm^{-2}
V_{oc} = 910 mV
FF = 0.78
η = 13%

Figure 15. D−A−π−A featured porphyrin dye **SM315** containing an additional electron-withdrawing group, a BTD unit.

7. CONCLUSIONS AND OUTLOOK

The light harvesting of most organic sensitizers is not broad enough to efficiently cover the solar photon-flux spectrum, to deliver panchromatic light harvesting[80] along with a high IPCE and PCE. In this Spotlight on Applications, we highlight recent advances in the D−A−π−A-based sensitizers for DSSCs, specifically focusing on the role of the incorporated additional acceptor for modulating the energy levels, extending light-harvesting wavelength, and as well as greatly improving photovoltaic performances and photostability. As demonstrated, the additional electron acceptor adjacent to the electron donor can enhance the intramolecular electronic push−pull effect, thus significantly affecting the energy levels and absorption properties of D−A−π−A sensitizers. The electron transfer cascade from D to internal A, then to terminal A in the D−A−π−A configuration, can facilitate charge transfer rather than hindering it with the additional acceptor unit. Upon screening the proper additional acceptors, the trade-off between light harvesting and suitable energy levels should be taken into account. On one hand, one should be cautious when employing those electron-deficient units with very strong electron-withdrawing capability, such as DPP. Also, those additional acceptors that can disturb the backbone conjugation should be avoided. Indeed, the π-spacer in the D−A−π−A motif is very crucial to the photovoltaic performance because a good π-spacer can not only enhance light harvesting, but also decrease recombination loss. Although the D−A−π−A motif is intensively studied for pure organic sensitizers, it can also extend to other categories of sensitizers, such as porphyrin dyes. Impressively, the D−A−π−A featured porphyrin dye **SM315** in combination with a cobalt(II/III) redox shuttle has achieved a record photovoltaic efficiency of 13.0%. The distinct stability-enhancement of dyes is established through both charge-redistribution by additional acceptor and the introduction of an antiaggregation unit on an additional acceptor in the D−A−π−A motif. The basic principles are well-analyzed in the delicate molecular engineering of organic indoline donor-containing sensitizers. These unique advantages of the D−A−π−A motif can provide a reliable route to develop highly efficient and stable sensitizers for future application of DSSCs.

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Notes

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