Influence of the Auxiliary Acceptor on the Absorption Response and Photovoltaic Performance of Dye-Sensitized Solar Cells

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Abstract: Three new dyes with a 2-(1,1-dicyanomethylene)rhodanine (IDR-I, -III, -III) electron acceptor as anchor were synthesized and applied to dye-sensitized solar cells. We varied the bridging molecule to fine tune the electronic and optical properties of the dyes. It was demonstrated that incorporation of auxiliary acceptors effectively increased the molar extinction coefficient and extended the absorption spectra to the near-infrared (NIR) region. Introduction of 2,1,3-benzothiadiazole (BTD) improved the performance by nearly 50%. The best performance of the dye-sensitized solar cells (DSSCs) based on IDR-II reached 8.53% (short-circuit current density $(J_{\rm sc}) = 16.73 \text{ mA cm}^{-2}$, open-circuit voltage $(V_{\rm oc}) = 0.71 \text{ V}$, fill factor (FF) = 71.26%) at AM 1.5 simulated sunlight. However, substitution of BTD with a group that featured the more strongly electron-withdrawing thiadiazolo[3,4c]pyridine (PT) had a negative effect on the photovoltaic performance, in which IDR-III-based DSSCs showed the lowest efficiency of 4.02%. We speculate that the stronger auxiliary acceptor acts as an electron trap, which might result in fast combination or

Keywords: charge transfer • donoracceptor systems • dyes/pigments • electron trap • sensitizers hamper the electron transfer from donor to acceptor. This inference was confirmed by electrical impedance analysis and theoretical computations. Theoretical analysis indicates that the LUMO of IDR-III is mainly localized at the central acceptor group owing to its strong electron-withdrawing character, which might in turn trap the electron or hamper the electron transfer from donor to acceptor, thereby finally decreasing the efficiency of electron injection into a TiO₂ semiconductor. This result inspired us to select moderated auxiliary acceptors to improve the performance in our further study.

Introduction

Over the past decades, dye-sensitized solar cells (DSSCs) have been extensively investigated as an alternative to traditional solar cells based on silicon.^[1] To date, power-conversion efficiencies (PCE) have reached more than 11 % with ruthenium-based dyes.^[2] However, ruthenium-based dyes have some disadvantages such as high cost, use of noble metals, and difficulties in the synthesis and purification that limit their wider application. Recently, the most efficient of the DSSCs reached 13 %, which was reported by Grätzel et al.^[3] The main advantage of DSSCs that use metal-free organic dyes is that they have facile synthetic strategies and

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a high absorption coefficient. In addition to that, organic dyes have a versatile functional group for tuning electronic and optical properties.^[4] One successful strategy to improve the performance of DSSCs is by varying the components such as donor, bridge, and acceptor. Previously our group reported a highly efficient dye that incorporates the auxiliary acceptor 2,1,3-benzothiadiazole (BTD).^[5] The auxiliary electron acceptor significantly increased the molar extinction coefficient as well as short-circuit current density (J_{sc}) and redshifted the absorption, thereby resulting in an efficiency of 9.02%. Meanwhile, substitution of the traditional cyanoacetic acid with the stronger acceptor of 2-(1,1-dicyanomethylene)rhodanine (DCRD) displayed similar properties.^[6]

Because dyes with good planarity are vulnerable to form unfavorable π - π stacking, this aggregation might lead to back-electron transfer, thereby limiting electron accumulation in the TiO₂ conduction band and giving low open-circuit voltage (V_{oc}), whereas long-chain alkyls were widely used to disrupt the aggregation and improve the solubility of dye. Based on dye RD-II,^[6] we substituted the traditional triphenylamine-branching chromophore with a stronger donor indoline derivative and incorporated *n*-hexylthiophene into the bridge to construct dye IRD-I.

[1,2,5]Thiadiazolo[3,4-*c*]pyridine (PT) possesses a higher electron-withdrawing ability than BTD. PT-based polymers have been widely used in applications such as bulk hetero-

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junction (BHJ) solar cells.^[4i] Heeger reported the highest conversion efficiency of 6.7% for solution-processed small-molecule solar cells by incorporating PT into the small molecule.^[4o] Herein, based on the strategy that both a strong donor and acceptor can shift the absorption band toward the near-infrared (NIR) region and increase the molar extinction coefficient, which can ultimately improve the short-circuit current density (J_{sc}) ,^[6,7] we further introduced BDT or PT into the bridge to construct dyes IDR-II and IDR-III, respectively.



Scheme 1. Molecular structures of IDR-I-III.

Results and Discussion

Synthesis and Characterization

The molecular structures of dyes IDR-I-III and the synthetic routes to them are shown in Schemes 1 and 2. All of the dyes contain the same strong donor (indoline) and acceptor (DCRD). We varied the π bridge to tune the electronic and optical properties of IDR-I-III. 4,7-Dibromobenzothiadiazole (BTD) and 3-hexylthiophene are low cost and commercially available. The critical intermediate (7) was obtained by a selective Suzuki coupling reaction.^[8] In the Suzuki coupling reaction, preferential oxidative coupling occurs at the more electron-deficient 4carbon position of pyridine derivates, thus leading to the pyridyl N atoms proximal to the donor. It is important to highlight the regiochemistry of 7, in which the pyridal N atoms of the PT acceptor unit are oriented towards the 3-hexylthiophene moiety (proximal configuration). All the bromination products were used for the next step without further purification. The target products IDR-**I–III** were synthesized by means of Knoevenagel conden-



Scheme 2. Synthetic route to dyes IDR-I-III. Reagents and conditions: a) NBS, CH_2Cl_2 , and CH_3COOH , 6 h. b) 5-Formyl-2-thiopheneboronic acid, K_2CO_3 , $[Pd(dppf)Cl_2]$, THF, H_2O , and N_2 atmosphere. c) NBS, CH_2Cl_2 , and CH_3COOH , 6 h. d) 7-Bromo-1,2,3,3*a*,4,8*b*-hexahydro-4-(4-methylphenyl)cyclopent[*b*]indole, *n*BuLi, isopropyl borate, $[Pd(dppf)Cl_2]$, K_2CO_3 , THF, H_2O , and N_2 atmosphere. e) SOCl₂ (excess amount), reflux. f) 3-Hexylthiophene, *n*BuLi, isopropyl borate, K_2CO_3 , $[Pd(dppf)Cl_2]$, THF, H_2O , and N_2 atmosphere. e) NBS, CH_2Cl_2 , 6 h. h) 7-Bromo-1,2,3,3*a*,4,8*b*-hexahydro-4-(4-methylphenyl)cyclopent[*b*]indole, *n*BuLi, isopropyl borate, K_2CO_3 , $[Pd(dppf)Cl_2]$, THF, H_2O , and N_2 atmosphere. j) NBS, CH_2Cl_2 , 6 h. h) 7-Bromo-1,2,3,3*a*,4,8*b*-hexahydro-4-(4-methylphenyl)cyclopent[*b*]indole, *n*BuLi, isopropyl borate, K_2CO_3 , $[Pd(dppf)Cl_2]$, THF, H_2O , and N_2 atmosphere. i) NBS, CH_2Cl_2 , and CH_3COOH , 6 h. j) 5-Formyl-2-thiopheneboronic acid, K_2CO_3 , $[Pd(dppf)Cl_2]$, THF, H_2O , and N_2 atmosphere. i) NBS, CH_2Cl_2 , and CH_3COOH , 6 h. j) 5-Formyl-2-thiopheneboronic acid, K_2CO_3 , $[Pd(dppf)Cl_2]$, THF, H_2O , and N_2 atmosphere. k) DCRD, EtOH, NaOH, reflux.

sation reaction in the presence of a catalytic amount of piperidine in THF. All compounds were purified by means of column chromatography or recrystallization and characterized by standard ¹H and ¹³C NMR spectroscopy and HRMS. IDR-I–III are black powders, thus indicating great light-harvesting ability.

Optoelectronic Properties

The UV/Vis absorption spectra of the samples in CH_2Cl_2 are shown in Figure 1, and the data are summarized in Table 1. Generally, organic dyes show two main absorption bands: intramolecular charge transfer (ICT) absorption and a π – π * absorption band.^[9] In this paper, however, dyes IDR-**II** and IDR-**III** display three absorption bands. The absorption bands in the UV region for the three dyes originated from

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Figure 1. UV/Vis absorption spectra of solutions of IDR-I–III in CH_2Cl_2 .

Table 1. Optical and electrochemical properties of IDR-I-III.

Dye	$\lambda_{\max}^{[a]}$	$\varepsilon \times 10^4$	$E_{\rm HOMO}^{[b]}$	$E_{0-0}^{[c]}$	$E_{LUMO}^{[d]}$
	[nm]	$[M^{-1}cm^{-1}]$	(vs NHE)	[eV]	(vs NHE)
IDR-I	504	2.66	0.75	2.02	-1.37
IDR- II	538	3.53	0.70	1.94	-1.24
IDR- III	582	3.15	0.68	1.78	-1.10

[a] Absorption maximum in CH₂Cl₂ (1×10⁻⁵ M). [b] The ground-state oxidation potential of dyes was measured in a dichloromethane with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as electrolyte (Pt working electrode, saturated calomel electrode (SCE) reference electrode calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an external reference, Pt counter electrode). [c] E_{0-0} was estimated from the intersection of UV/Vis absorption and emission spectra of the dyes. [d] E_{LUMO} was calculated as $E_{HOMO}-E_{0-0}$.

local π - π * transitions and their peaks were located at 383, 333, and 333 nm, respectively. IDR-I and IDR-II showed the maximum absorption wavelength at 504 and 538 nm, respectively. The corresponding molar extinction coefficients were 26657 and $35365 \text{ m}^{-1} \text{ cm}^{-1}$, which could be ascribed to ICT. Clearly, the incorporation of the auxiliary acceptor redshifted the absorption spectra and increased the molar extinction coefficient. This phenomenon is consistent with previous reported results. We further substituted the BTD group with a stronger acceptor (PT) to construct IDR-III. IDR-III showed the maximum wavelength (λ_{max}) at 582 nm as well as a molar extinction coefficient of 31 573 M⁻¹ cm⁻¹ and realized a broad spectral response. Compared to IDR-I, the redshifts of the absorption band of IDR-II and IDR-III were 33 and 80 nm, respectively. The absorption spectra of IDR-II and IDR-III extended to 750 and 800 nm, respectively, thus indicating better light-harvesting ability. Therefore a high J_{sc} value could be expected. The origin of an additional band around 450 nm and higher absorption intensity for IDR-III relative to IDR-II in this band will be discussed below.

The absorption spectra of IDR-I-III on transparent film are shown in Figure 2; the maximum absorption peaks were located at 527, 539, and 578 nm, respectively. Compared to the absorption spectra of samples in solution, the redshift of 23 nm for IDR-I could be ascribed to the formation of J aggregation.^[10] However, the spectra of IDR-II and IDR-III



Figure 2. UV/Vis absorption spectra of IDR-I–III adsorbed on $\rm TiO_2$ films.

had no clear shift when adsorbed on film, which is possibly because strong electron-withdrawing units weaken the large blueshift in the ICT band caused by the deprotonation of the DCRD group (-CONH).^[5]

Cyclic voltammetry (CV) was carried out to determine the redox properties of dyes IDR-I-III (Figure 3). The oxidation potentials that correspond to the HOMO are determined exclusively by the donors. As shown in Table 1, the three dyes exhibited the same HOMO level; they are more positive than that of the electrolyte mediator, thus indicating that the oxidized dye could be regenerated effectively by I^{-1}/I^{3-} . E_{0-0} was estimated from the intersection of the UV/ Vis absorption and the emission spectra of the dyes; the values were 2.02, 1.94, and 1.78 eV, respectively. The decrease in the bandgap is consistent with the increase in the electron-withdrawing ability of the auxiliary acceptor and the redshift in the absorption spectra. The LUMO was estimated to be -1.37, -1.24, and -1.10 V versus the normal hydrogen electrode (NHE), respectively, thus indicating a sufficient driving force for electron injection from the oxidized dye into the conduction band. It is worth noting that all the three dyes are redox stable since their CV curves almost overlap after repeated scanning.



Figure 3. Cyclic voltammetry curves of solutions of IDR-I-III in CH2Cl2.

Photovoltaic Properties

Organic dyes tend to aggregate when anchored to TiO₂ film, so a coadsorption additive was used to disrupt aggregation and improve cell performance. Photocurrent density–voltage (I-V) data under different chenodeoxycholic acid (CDCA) concentrations are listed in Table 2. The devices were optimized using 10×10^{-3} M CDCA as a coadsorption additive, which was able to significantly improve the fill factor (FF).

Table 2. Photovoltaic performance of CDCA with different concentrations coadsorbed DSSCs based on dyes IDR-I–III.

Dye	CDCA [M]	$J_{ m SC}[m mAcm^{-2}]$	$V_{\rm OC}$ [V]	FF	η [%]
IDR-II	5×10^{-3}	15.54	0.67	64.89	6.83
IDR-II	10×10^{-3}	16.73	0.71	71.26	8.53
IDR-II	20×10^{-3}	15.25	0.68	64.77	6.74
IDR-I	10×10^{-3}	11.21	0.62	72.25	5.00
IDR-III	10×10^{-3}	11.01	0.54	67.13	4.02

The photocurrent density-voltage curves of the cells were measured under an irradiance of 100 mW cm⁻² simulated AM 1.5 sunlight. CDCA $(10 \times 10^{-3} \text{ M})$ was used as a coadsorption additive to construct the cells based on three dyes. As shown in Figure 4 and Table 2, DSSCs based on dye IDR-I displayed а short-circuit photocurrent $(J_{\rm sc})$ of 11.21 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.62 V, and a fill factor of 72.25%, thereby resulting in a power conversion efficiency (η) of 5.00%. After introducing BTD, a significant increase in $J_{\rm sc}$ was observed relative to dye IDR-I. The device based on dye IDR-II showed a J_{sc} of 16.73 mA cm⁻², a $V_{\rm oc}$ of 0.71 V, and a FF of 71.26%, thus giving a power conversion efficiency (η) of 8.53%. This improvement was ascribed to an increase in molar extinction coefficient and a redshift of the absorption band that extended beyond 700 nm. BTD also played a role in facilitating the electron transfer from donor to acceptor, and then electrons were injected into the conduction band.^[7a,11] As shown in Figure 5, over the whole simulated AM 1.5 spectra, IDR-II had a relatively high incident photon-to-electron conversion efficiency



Figure 4. I--V curves of devices based on dyes IDR-I-III.

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Figure 5. IPCE curve of DSSCs based on dyes IDR-I-III.

(IPCE) to that of IDR-I. The IPCE of IDR-II reached 65% from 450 to 650 nm, and nearly 45% at 700 nm. However, substitution of BTD with a group (PT) that featured a stronger electron-withdrawing ability had a negative effect on performance. DSSCs based on IDR-III showed a J_{sc} of 11.01 mA cm⁻², a $V_{\rm oc}$ of 0.54 V, and a FF of 67.13%, thus giving the lowest power conversion efficiency (η) of 4.02%. Interestingly, the previously reported dye that contained the PT group also gave a lower efficiency, which was ascribed to the low voltage of 0.43 V.^[12] Because molecular planarity facilitates dye aggregation, thereby resulting in fast recombination, we performed a theoretical analysis to calculate the dihedral angles between the auxiliary acceptor and the adjacent aromatic ring. As shown in Scheme 3 and Table 3, after incorporating an auxiliary acceptor, the dihedral angle (α) between the indoline donor and auxiliary acceptor increased from 22.9 to 31.6° for IDR-II, which partially contributed to decreased recombination. Relative to IDR-I, the increased dihedral angle of IDR-II is consistent with an increased



Scheme 3. Dihedral angles between auxiliary acceptors and the adjacent aromatic ring.

Table 3. Optimized dihedral angles in the three sensitizer dyes IDR-I-III.

Compound	α [°]	β [°]
IDR-I	22.9	_
IDR-II	31.6	0.2
IDR-III	30.9	0.2

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 $J_{\rm sc}^{[13a]}$ However, the dihedral angle α of IRD-III is almost the same as that of IRD-II. Furthermore, the dihedral angles β between the auxiliary acceptor and the adjacent hexylthiophene in IRD-II and IRD-III are both 0.2°. Thus, compounds IRD-II and IRD-III show a very similar degree of twisting, and we could therefore rule out the planarization effects of the pyridinothiadiazole unit upon fast recombination. Herein we attribute the decreased efficiency to the electron-withdrawing ability that is too strong, which results in fast combination of electrons in the conduction band of titanium dioxide with electron mediators.^[13] We also infer that the acceptor that is too strong behaves like an electron trap, which hinders the electron transfer from donor to acceptor.^[14] This speculation was confirmed by means of computational analysis, which will be discussed below. A decreased energy bandgap (0.33 eV) between the HOMO of the dye IDR-III and the electrolyte mediator (I^{-1}/I^{3-}) , which might fail to provide sufficient driving force for an electron-transfer reaction, might possibly lower the dye-regeneration efficiency. Both of these factors have a synergistic impact upon lowering J_{sc}. Although IDR-III displayed a better IPCE beyond 630 nm and a superior absorption performance, this superiority was offset by a lower IPCE in the region between 350 and 630 nm.

To gain insight into the lowest open-circuit voltage of IDR-III, which was ascribed to fast electron recombination, we performed electrochemical impedance spectroscopy. The Bode and Nyquist plots are shown in Figures 6 and 7. The radius of the large semicircle decreased in the order of IDR-III < IDR-I < IDR-II, thus indicating that electron-recombination resistance actually increased in the order of IDR-II > IDR-I < IDR-III, which was consistent with variation in the V_{oc} value. In the Bode phase plot, the peak of the middle frequency corresponds to long electron lifetime, which reflects slow recombination. The lifetime increased in the order of IDR-II > IDR-II > IDR-II > IDR-II. This result was also consistent with the increase in V_{oc} . The electron-combination resistance and electron lifetime could also explain the low



Figure 6. Nyquist-phase plots of impedance spectra that were all measured by applying a bias of 0.65 V in the dark.



Figure 7. Bode-phase plots of impedance spectra that were all measured by applying a bias of 0.65 V in the dark.

 J_{sc} of IDR-I and IDR-III relative to IDR-II. We were inspired that we could select an auxiliary acceptor with moderate electron-withdrawing ability to facilitate electron transfer without resulting in fast recombination.

The electron lifetime (τ_n) , which reflects the responsetime constant for recombination, is the product of recombination resistance and capacitance.^[15] The fitted relationship between the electron lifetime in DSSCs and the capacitance is shown in Figure 8, which was obtained from Nyquist plots



Figure 8. Electron lifetime as a function of capacitance in IDR-I-IIIbased DSSCs, which were obtained by EIS under various biases in the dark.

measured under different biases in the dark. According to Figure 8, the electron lifetime for IDR-III-based DSSCs was the longest, whereas IDR-III-based DSSCs had the shortest electron lifetime, which was one magnitude lower than IDR-II, thus indicating a fast recombination rate in IDR-III-based DSSCs.

Computational Analysis

We used theoretical computation to understand the differences in the absorption spectra and performance of the three dyes. The frontier molecular orbitals of compounds IDR-I,

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Table 4. Computed contour plots of frontier molecular orbitals at the B3LYP/6-31G* level of theory.



IDR-II, and IDR-III are presented in Table 4, in which one can see that the LUMO is mostly localized at the peripheral acceptor group of compound IDR-I. In compound IDR-II, the LUMO receives contribution from both the central and the peripheral acceptor groups, and the LUMO+1 is largely localized on the central acceptor group. This is similar to previously reported D-A- π -A-type sensitizer dyes for highperformance solar cells.^[16] On the contrary, the LUMO of compound IDR-III shows considerable localization on the central acceptor group, and the peripheral acceptor group contributes much less to the LUMO than the other two compounds. This may lead to inefficient electron injection into the TiO₂ semiconductor upon solar-light irradiation. We further analyzed the fragmental contribution to the frontier molecular orbitals of these sensitizer dyes from their D, A, π , and A groups, as shown in the Supporting Information. Here the contribution from the peripheral acceptor group to LUMO follows the order: IDR-I > IDR-II > IDR-III. In compound IDR-II, the peripheral acceptor group contributes more to the LUMO and the central acceptor group contributes more to the LUMO+1. However, in compound IDR-III this is reversed; the central acceptor group contributes more to the LUMO, whereas the peripheral acceptor group contributes more to the LUMO+1. This agrees with the inefficient electron injection from IDR-III and may thus hamper the efficiency of the sensitizing process.

From time-dependent (TD) DFT calculations we obtained the excitation wavelengths of compounds IDR-I, IDR-II, and IDR-III in the visible spectral region, in which the lowest singlet excitation energies are in excellent agreement with the experimentally observed spectra. As shown in the Supporting Information, all the S₁ states receive a large contribution from the HOMO \rightarrow LUMO transition corresponding to electron transfer from the donor to the terminal acceptor. The S₂ states arise from combined electronic transitions of HOMO-1→LUMO and HOMO→LUMO+1; however, the corresponding absorptions are at different spectral regions, that is, approximately 350 nm for IDR-I and approximately 440 nm for IDR-II and IDR-III, respectively. As shown in Figure 9, the oscillator strengths of the S₂ states are unfortunately underestimated by the TD-DFT calculations; nonetheless, the theoretical simulations provide explanations for the different absorption spectra of these sensitizer dyes. The absorption band around 450 nm, which is present in IDR-II and IDR-III and absent in IDR-I, originates from electronic transitions involving the central acceptor group. This absorption band exhibits stronger intensity in IDR-III than that in IDR-II, which reflects the stronger electron-withdrawing character of the central acceptor group in IDR-III.

Our theoretical calculations thus provide interpretation for several phenomena relevant to the performance of the sensitizers. First, compound IDR-I does not have an absorp-



Figure 9. Simulated absorption spectra of IDR-I-III.

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tion band at around 450 nm, since the central acceptor group is not present. Second, the central acceptor group of IDR-III has stronger electron-withdrawing character than that of IDR-III, which leads to a redshifted absorption maximum and an enhanced absorption band around 450 nm. Third, the LUMO of IDR-III is largely localized at the central acceptor group owing to its strong electron-withdrawing character, which may in turn hamper the efficiency of electron injection into the TiO₂ semiconductor. The frontier molecular orbitals and absorption spectrum of IDR-III show similar characters to previously reported D-A- π -A sensitizer dyes^[16] and are thus expected to be beneficial for photovoltaic efficiency.

Conclusion

In summary, a different auxiliary acceptor was introduced into the molecular design of organic sensitizers, and three dyes were synthesized. Among them, IDR-II-based DSSCs showed the highest overall conversion efficiency of 8.53% with $V_{\rm oc} = 710 \text{ mV}$, $J_{\rm sc} = 16.73 \text{ mA cm}^{-2}$, and a fill factor (FF)=0.71 after a 10 mM chenodeoxycholic acid (CDCA) treatment standard illumination under conditions (100 mW cm⁻² simulated AM 1.5 solar light). We illustrate that an auxiliary acceptor with appropriate electron-withdrawing ability increases the molar extinction coefficient, extends the absorption spectra, and facilitates electron transfer, which finally improve the $J_{\rm sc}$. In contrast, too strong an auxiliary acceptor facilitates the recombination between electrons in the conduction band with an electrolyte mediator and traps electrons resulting in hampering of the electron transfer from donor to acceptor. In our future work, we will further explore the effect of the auxiliary acceptor on the photovoltaic performance.

Experiment Section

Materials

Optically transparent fluorine-doped SnO₂ (FTO) conducting glass (transmission >90% in the visible region, sheet resistance 15 Ω square⁻¹) was obtained from the Geao Science and Educational Co. Ltd. of China and cleaned by a standard procedure. Methoxypropionitrile (MPN) was purchased from Aldrich. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆), 4-*tert*-butylpyridine (4-TBP), and lithium iodide were bought from Fluka, and iodine (99.999%) was purchased from Alfa Aesar. THF was pre-dried over 4 Å molecular sieves and distilled under an argon atmosphere from sodium benzophenone ketyl immediately prior to use. Dichloromethane was distilled under normal pressure and dried over calcium hydroxide. Compound **5** was synthesized according to reported literature.^[5] All other chemicals were purchased from Aldrich and used as received without further purification.

Instrumentation

NMR spectra were obtained by using a Brücker AM 400 spectrometer. The absorption spectra of the dyes in solution were measured with a Varian Cary 500 spectrophotometer. MS were recorded on an ESI mass spectrometer. The cyclic voltammograms of dyes were obtained with a Versastat II electrochemical workstation (Princeton applied research) using a normal three-electrode cell with a Pt working electrode, a Pt-wire counter electrode, and a regular calomel reference electrode in saturated KCl solution. The current density versus voltage (*J*–*V*) characteristics of the DSSCs were measured by recording *J*–*V* curves using a Keithley 2400 source meter under the illumination of AM 1.5 G simulated solar light (Newport-91160 equipped with a 300 W Xe lamp and an AM 1.5 G filter). The incident light intensity was calibrated to 100 mW cm⁻² with a standard silicon solar cell (Newport 91150 V). Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of the monochromatic light was measured with a Si detector (Newport-71640).

Synthesis of 2-Bromo-3-hexylthiophene (1)

3-Hexylthiophene (2.00 g, 11.9 mmol) was dissolved in a mixed solution of CH₂Cl₂ (20 mL) and CH₃COOH (20 mL), then *N*-bromosuccinimide (NBS; 2.22 g, 12.5 mmol, 1.05 equiv) was added. After the reaction was complete, the mixture was neutralized with saturated NaHCO₃, CH₂Cl₂ (100 mL) was added, and the organic layer was separated. The aqueous solution was washed with CH₂Cl₂ twice. After removing the solvent, the residue was used for the next step without further purification.

Synthesis of 3'-Hexyl-[2,2'-bithiophene]-5-carbaldehyde (2)

In a 100 mL round-bottomed flask with a condenser, compound **1** (1.90 g, 7.70 mmol), 5-formyl-2-thiopheneboronic acid (1.00 g, 6.40 mmol), K₂CO₃ (1.38 g, 100 mmol), and a catalytic amount of [Pd(dppf)Cl₂] (dppf =1,1'-bis(diphenylphosphino)ferrocene) was dissolved in a solution of THF (20 mL) and H₂O (4 mL). The mixture was heated at reflux overnight under an N₂ atmosphere. After the reaction was complete, CH₂Cl₂ (20 mL) was added and the organic layer was separated. Then, the aqueous solution was washed with CH₂Cl₂ twice. After removing the solvent by evaporation, the residue was purified by chromatography to afford compound **2** (1.40 g, 79%). ¹H NMR (400 MHz, CDCl₃): δ =9.79, (s, 1H),7.62 (d, *J*=3.9 Hz, 1H), 7.19 (d, *J*=5.1 Hz, 1H), 7.13 (d, *J*=3.9 Hz, 1H), 6.89 (d, *J*=5.2 Hz, 1H), 2.73 (dd, 2H), 1.50–1.52 (m, 6H), 1.31–1.21 (m, 2H), 0.80 ppm (t, *J*=6.6 Hz, 3H).

Synthesis of 5'-Bromo-3'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (3)

Compound 2 (1.10 g, 3.96 mmol) was dissolved in CH_2Cl_2 and cooled to 0°C, then NBS (0.70 g, 3.96 mmol) was added into the solution and the mixture was stirred for 6 h. After the reaction was complete, CH_2Cl_2 (20 mL) was added and the organic layer was separated. Then the aqueous solution was washed with CH_2Cl_2 twice. Removal of the solvent afforded the product, which was used for the next step without further purification.

Synthesis of 3'-Hexyl-5'-{4-(p-tolyl)-1,2,3,3a,4,8b-

hexahydrocyclopenta[b]in-dol-7-yl}-[2,2'-bithiophene]-5-carbaldehyde (4)

Compound **3** (300 mg, 0.84 mmol), compound **5** (an excess amount), a catalytic amount of [Pd(dppf)Cl₂], and K₂CO₃ (1.38 g, 10 mmol) were dissolved in a solution of THF (25 mL) and H₂O (5 mL) in a 50 mL roundbottomed flask. Then the mixture was heated at reflux overnight under an N₂ atmosphere. After the reaction was complete, CH₂Cl₂ (20 mL) was added and the organic layer was separated, then the aqueous solution was washed with CH₂Cl₂ twice. All of the organic solution was collected. After removal of the solvent, the residue was purified by chromatography to afford the desired compound **4** (250 mg, 56.5%). ¹H NMR (400 MHz, CDCl₃): δ = 9.79 (s, 1H), 7.62 (d, *J* = 3.8 Hz, 1H), 7.20 (s, 2H), 7.4–7.10 (m, 5H), 6.96 (s, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 4.75 (t, *J* = 7.2 Hz, 1H), 3.77 (t, *J* = 8.3 Hz, 1H), 2.76–2.73 (m, 2H), 2.27 (s, 3H), 2.00–1.95 (m, 1H), 1.84 (s, 2H), 1.67–1.59 (m, 4H), 1.40–1.30 (m, 3H), 1.28–1.22 (m, 4H), 0.86 ppm (t, *J* = 6.8 Hz, 3H).

Synthesis of 4,7-Dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (6)

Compound 3, 4-diaminopyridine (4 g, 4.98 mmol), and an excess amount of $SOCl_2$ were added to a 250 mL three-necked round-bottomed flask with a condenser, then the mixture was heated at reflux for 5 h and cooled to room temperature. The excess amount of thionyl chloride was

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evaporated and the residue was slowly neutralized with saturated NaHCO₃. Once the reaction was quenched, CH₂Cl₂ (150 mL) was added, then the organic layer was separated. The aqueous solution was washed twice with CH₂Cl₂ and dried with MgSO₄. After removing the solvent, the crude product was purified by recrystallization from methanol to afford compound **6** (2.71 g, 73%). ¹H NMR (400 MHz, CDCl₃): δ = 8.56 ppm (s, 1 H).

Synthesis of 7-Bromo-4-(4-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]-pyridine (7)

3-Hexylthiophene (0.48 mL) was dissolved in freshly distilled THF (10 mL) and then cooled down to -78°C for 10 min, then nBuLi (1.60 mL, 4.02 mmol) was added dropwise to the mixture. After 30 min of stirring at the same temperature, isopropyl borate (0.93 mL, 4.02 mmol) was slowly injected into the reaction solution. After stirring for a further 2 h, the solution was warmed to room temperature and the mixture was stirred overnight. The crude mixture was used without further purification. The solution was mixed with compound 6 (1.00 g, 4.02 mmol, 1.50 equiv), a catalytic amount of [Pd(dppf)Cl₂], K₃PO₄ (1.70 g, 3 equiv), H₂O (2 mL), and then heated at reflux overnight under an N2 atmosphere. After the reaction was complete, CH2Cl2 (20 mL) was added. The organic layer was separated and the aqueous solution was washed with CH22Cl2 twice. All of the organic solution was collected and dried with Na₂SO₄. After removal of the solvent solvent by evaporation, the crude product was purified by chromatography to afford the desired product 7 (760 mg, 75.2%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.66$ (s, 1H), 8.52 (s, 1H), 7.24 (s, 1H), 2.73-2.69 (m, 2H), 1.73-1.67 (m, 2H), 1.38-1.30 (m, 6H), 0.90 ppm (t, J=7.0 Hz, 3H).

Synthesis of 7-Bromo-4-(5-bromo-4-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (8)

Compound 7 (484 mg, 1.27 mmol) was dissolved in CH_2Cl_2 and cooled to 0°C, then NBS (248 mg, 1.39 mmol) was added into the solution and the mixture was stirred for 6 h. After the reaction was complete, CH_2Cl_2 (20 mL) was added and the organic layer was removed by separation. Then the aqueous solution was washed with CH_2Cl_2 twice. Removal of the solvent afforded product **8**, which was used for the next step without further purification.

Synthesis of 4-(5-Bromo-4-hexylthiophen-2-yl)-7-{4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl}-[1,2,5]thiadiazolo[3,4-c]pyridine (9)

Compound 8 (490 mg, 1.07 mmol), compound 5 (an excess amount), a catalytic amount of [Pd(dppf)Cl₂], K₂CO₃ (1.38 g, 10 mmol), and solution of THF (25 mL) and H₂O (5 mL) were added to a 50 mL round-bottomed flask. Then the mixture was heated at reflux overnight under an N2 atmosphere. After the reaction was complete, CH2Cl2 (20 mL) was added and the organic layer was removed by separation, and then the aqueous solution was washed with CH2Cl2 twice. All of the organic solution was collected. After removing the solvent, the residue was purified by chromatography to afford desired compound 9 (420 mg, 62.6%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.61$ (s, 1H), 8.34 (s, 1H), 7.80 (s, 1H), 7.74 (d, J = 8.3 Hz, 1 H), 7.25–7.17 (m, 4 H), 7.02 (d, J = 8.4 Hz, 1 H), 6.82 (d, J =8.4 Hz, 1H), 4.90–4.87 (m, 1H), 3.94 (t, J=8.3 Hz, 1H), 2.66 (t, J= 7.7 Hz, 2H), 2.36 (s, 3H), 2.10-2.06 (m, 2H), 1.94 (s, 2H), 1.84-1.76 (m, 1 H), 1.72–1.66 (m, 3 H), 1.37 (m, 6 H), 0.91 ppm (t, J = 6.9 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz): $\delta = 155.32$, 147.88, 147.07, 143.41, 142.97, 140.35, 140.35, 138.83, 134.67, 130.97, 130.70, 128.82, 127.74, 126.02, 124.26, 123.14, 119.50, 114.15, 106.53, 68.29, 44.34, 34.22, 32.62, 30.62, 28.82, 28.68, 27.93, 23.40, 21.60, 19.82, 13.10 ppm; HRMS: m/z: calcd for C₃₃H₃₄BrN₄S₂: 629.1408; found: 629.1403 [*M*+H]⁺.

Synthesis of 3'-Hexyl-5'-(7-{4-(p-tolyl)-1,2,3,3a,4,8b-

hexahydrocyclopenta[*b*]-indol-7-yl}-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)-[2,2'-bithiophene]-5-carbaldehyde (**10**)

Compound **9** (380 mg, 0.605 mmol), 5-formyl-2-thiopheneboronic acid (122.7 mg, 0.786 mmol, 1.3 equiv), a catalytic amount of $[Pd(PPh_3)_4]$, and K_2CO_3 (1.38 g) were dissolved in a mixed solvent of THF (20 mL) and H_2O (5 mL). Then the mixture was heated at reflux overnight under an

N₂ atmosphere. After the reaction was complete, CH₂Cl₂ (20 mL) was added and the organic layer was removed by separation, and the aqueous layer was washed with CH₂Cl₂ twice. All of the organic layer was collected. After removing the solvent, the crude product **10** was purified by chromatography. ¹H NMR (400 MHz, CDCl₃): δ = 9.92 (s, 1H), 8.67 (s, 1H), 8.53 (s, 1H), 7.83 (s, 1H), 7.80–7.75, (m, 2H), 7.40 (d, 1H), 7.21 (q, 4H), 7.03 (d, 1H), 4.91–4.88 (m, 1H), 3.97–3.93 (m, 1H), 2.96–2.92 (m, 2H), 2.36 (s, 3H), 2.16–2.06 (m, 1H), 1.97 (d, 2H), 1.86–1.78 (m, 3H), 1.70–1.65 (m, 2H), 1.48 (m, 2H), 1.36–1.35 (m, 4H), 0.91 ppm (t, *J* = 6.8 Hz, 3H); HRMS: *m/z*: calcd for C₃₈H₃₇N₄OS₃: 661.2129; found: 661.2130 [*M*+H]⁺.

*Synthesis of 2-{5-[-(3'-hexyl-5'-{4-(p-tolyl)-1,2,3,3a,4,8b*hexahydrocyclopenta[*b*]indol-7-yl}-[2,2'-bithiophen]-5-yl)methylene]-4oxothiazolidin-2-ylidene}malononitrile (IDR-I).

Equimolar quantities of compound 4 (200 mg, 0.38 mmol) and DCRD (62 mg, 0.38 mmol) in EtOH (20 mL) were stirred under basic conditions (1 drop, 20% aqueous NaOH solution) and heated at reflux overnight. After the reaction was complete, the solvent was removed and the mixture was purified by chromatography to afford the desired product as a black powder (120 mg, 47 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.90$ (s, 1H), 7.71 (s, 1H), 7.53 (d, J=3.9 Hz, 1H), 7.46 (s, 1H), 7.31 (d, J= 8.2 Hz, 1H), 7.28-7.26 (m, 2H), 7.19 (s, 4H), 6.82 (s, 1H), 4.87 (s, 1H), 3.83 (s, 1H), 2.77 (s, 2H), 2.28 (s, 3H), 2.10-1.98 (m, 1H), 1.88-1.72 (m, 3H), 1.71-1.56 (m, 3H), 1.48-1.37 (m, 3H), 1.36-1.27 (m, 4H), 0.86 ppm (t, J = 6.8 Hz, 3 H); ¹³C NMR ([D₆]DMSO, 100 MHz): $\delta = 180.39$, 178.35, 147.75, 147.72, 143.81, 142.00, 140.63, 139.88, 139.78, 133.86, 127.80, 126.70, 126.50, 125.41, 125.25, 123.67, 122.31, 121.18, 120.18, 118.36, 117.00, 68.75, 48.09, 45.95, 45.02, 35.27, 33.57, 31.14, 30.28, 29.62, 28.94, 24.46, 22.45, 20.87, 14.45, 14.32 ppm; HRMS: m/z: calcd for C₃₉H₃₅N₄OS₃: 671.1973; found: 671.1974 [*M*-H]⁻.

*Synthesis of 2-[5-([3'-hexyl-5'-(7-[4-(p-tolyl)-1,2,3,3a,4,8b*hexahydrocyclopenta[*b*]indol-7-yl}benzo[*c*][1,2,5]thiadiazol-4-yl)-[2,2'-

hexanydrocyclopenta[*b*]indol-7-yijbenzo[*c*][1,2,3]thiadiazol-4-yi]-[2,2 bithiophen]-5-yi}methylene)-4-oxothiazolidin-2-ylidene]malononitrile (IDR-II).

Equimolar quantities of compound **5** and DCRD in EtOH (20 mL) were stirred under basic conditions (1 drop, 20% aqueous NaOH solution) and heated at reflux overnight. After the reaction was complete, the solvent was removed and the mixture was purified by chromatography to afford the desired product as a black powder. ¹H NMR (400 MHz, $[D_6]DMSO)$: δ =8.01 (d, J=7.6 Hz, 1H), 7.96 (s, 1H), 7.81 (s, 1H), 7.72–7.70 (m, 3H), 7.53 (d, J=4.0 Hz, 1H), 7.96 (s, 1H), 7.81 (s, 1H), 7.20 (q, J=8.5 Hz, 1H), 6.91 (d, J=8.4 Hz, 1H), 4.86 (s, 1H), 3.84 (s, 1H), 2.81 (s, 2H), 2.29 (s, 3H), 2.13–1.98 (m, 1H), 1.90–1.72 (m, 3H), 1.72–1.56 (m, 3H), 1.36–1.27 (m, 4H), 0.86 ppm (t, 3H); ¹³C NMR (100 MHz, $[D_6]DMSO)$: δ =180.12, 178.20, 152.97, 151.86, 147.50, 140.71, 139.50, 139.43, 134.96, 130.79, 129.73, 128.71, 127.91, 126.42, 125.85, 125.20, 122.70, 119.48, 106.73, 68.28, 47.72, 44.55, 33.08, 31.00, 30.94, 29.84, 28.72, 23.96, 22.06, 20.37, 13.94 ppm; HRMS: *m/z* calcd for C₄₅H₃₀N₆OS₄: 807.2068; found: 807.2068 [*M*+H]⁺.

Synthesis of 2-[5-(/3'-Hexyl-5'-(7-{4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl]-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)-[2,2'-bithiophen]-5-yl}methylene)-4-oxothiazolidin-2-ylidene]malononitrile (IDR-III).

Equimolar quantities of compound **10** (196 mg, 0.297 mmol) and DCRD (48.7 mg, 0.297 mmol) in EtOH (20 mL) were stirred under basic conditions (1 drop, 20% aqueous NaOH solution) and heated at reflux overnight. After the reaction was complete, the solvent was removed and the mixture was purified by chromatography to afford the desired product as a black powder. ¹H NMR (400 MHz, CDCl₃): δ =8.64 (s, 1H), 8.49 (s, 1H), 7.81 (s, 1H), 7.74 (d, *J*=8.2 Hz, 1H), 7.71 (s, 1H), 7.32 (s, 2H), 7.23–7.17 (m, 4H), 7.03 (d, *J*=8.6 Hz, 1H), 4.89 (s, 1H), 3.95 (s, 1H), 2.93 (s, 2H), 2.35 (s, 3H), 2.16–2.04 (m, 1H), 2.02–1.90 (m, 3H), 1.83–1.77 (m, 6H), 1.55–1.45 (m, 4H), 0.89 ppm (t, *J*=6.8 Hz, 3H); ¹³C NMR (100 MHz, [D₈]THF): δ =179.08, 176.53, 154.16, 146.7, 146.20, 142.17, 139.92, 139.01, 138.87, 138.20, 137.83, 133.55, 132.50, 131.95, 130.18

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129.58, 127.70, 126.76, 125.19, 124.84, 123.32, 122.69, 119.03, 118.34,105.35, 113.99, 113.64, 67.26, 44.12, 43.51, 33.30, 31.62, 29.85, 28.56, 28.06, 27.46, 20.71, 18.07 11.69 ppm; HRMS: m/z: calcd for C₄₄H₃₆N₇OS₄: 806.1864; found: 806.1864 [M-H]⁻.

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FULL PAPER

Solar Cells

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Influence of the Auxiliary Acceptor on the Absorption Response and Photovoltaic Performance of Dye-Sensitized Solar Cells

Bring me sunshine: New sensitizers with indoline as donor and a 2,1,3-benzothiadiazole (BTD)/[1,2,5]thiadiazolo-[3,4-*c*]pyridine (PT) moiety as the auxiliary acceptor were synthesized. By fine-tuning the auxiliary acceptor, we obtained a photoelectric conversion



efficiency of 8.53% for a 2-(1,1-dicyanomethylene)rhodanine-based dyesensitized solar cell (DSSC; see figure). The results indicate that the incorporation of BTD can improve the DSSC performance.