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Improving the Photovoltage of Dithienopyrrole Dye-Sensitized Solar Cells via Attaching the Bulky Bis(octyloxy) biphenyl Moiety to the Conjugated π -Linker

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The judicious design of 3D giant organic dye molecules to enable the formation of a porous photoactive layer on the surface of titania is one of the viable tactics to abate the adverse interfacial charge recombination in dyesensitized solar cells (DSCs) employing outer-sphere redox couples. Here 2',6'-bis(octyloxy)-biphenyl substituted dithieno[3,2-b:2',3'-d]pyrrole segment is constructed and employed as the π -linker of a high molar absorption coefficient organic push-pull dye. With respect to its congener possessing the hexyl substituted dithieno[3,2-b:2',3'-d]pyrrole linker, the new dye can self-assemble on the surface of titania to afford a porous organic coating, which effectively slow down the kinetics of charge recombination of titania electrons with both outer-sphere tris(1,10-phenanthroline)cobalt(III) ions and photooxidized dye molecules, improving the cell photovoltage. In addition, the diminishments of charge recombination via modulating the microstructure of interfacial functional zone can also overcompensate the disadvantageous impact of reduced light-harvesting and evoke an enhanced photocurrent output, bringing forth an efficiency improvement from 7.5% to 9.3% at the 100 mW cm⁻², simulated AM1.5 conditions.

1. Introduction

During the past two decades, substantial research passions have been fascinated by dye-sensitized solar cells (DSCs)^[1,2] in the light of their grand potential to achieve the solar-to-electricity transformation at a low cost, based upon resource-abundant and less energy-intensive materials as well as simple manufacture technologies. The energy gap and energy offsets of a dye molecule, the light-harvesting component of this nanostructured device, with respect to other materials jointly impact the photocarrier generation. In addition, the free energy of output electrons could be considerably modulated by an organic layer mainly composed of dye molecules, lying between titania nanocrystals and redox shuttles. The cutting-edge DSC dyes are ruthenium polypyridyl and zinc porphyrin complexes, exhibiting ≈12% power conversion efficiencies at the air mass 1.5 conditions.^[3,4]

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devoted to metal-free organic D- π -A dyes, primarily owing to the flexibility of molecular design.^[5,6] The elaborate option of conjugated π -linkers is one of the executable tactics towards energy-level engineering of organic D-π-A dyes,^[7] apart from electron donors and acceptors. In this respect, a great amount of organic dyes involving thiophene and its numerous derivative segments have been exploited^[8-14] since the work by Arakawa et al.^[15] on the coumarin-thiophene DSC chromophores. Amongst all metal-free dyes, so far only a few dyes featuring either dithienosilole (DTS) or cyclopentadithiophene (CPDT) have been demonstrated to exhibit over 10% efficiencies.^[16–18] However the preparations of DTS and CPDT typically involve cryogenic temperatures and hazardous organolithium reagents.

On the other side, much effort has been

Thereby the dithieno[3,2-b:2',3'-d]pyrrole (DTP) unit pioneered by Rasmussen

et al.^[19] as a promising building block of electronic materials has been exploited as the electron-donor or π -linker of metalfree organic dyes.^[12,20] It is valuable to note that the triphenylamine-cyanoacrylic acid dye with the DTP linker displays a higher molar extinction coefficient than its counterparts with DTS and CPDT, ensuring a comparable photocurrent generation. Unfortunately, an inferior photovoltage was observed for the **C241** dye with the 4-hexyl-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole linker (Figure 1A).^[12] Recent studies on DSCs with outersphere electron mediators have suggested that the extraordinary merit of devising bulky organic dyes for high open-circuit photovoltage cells.^[4,18,21-24] In this work, we will synthesize the 4-(2',6'-bis(octyloxy)biphenyl-4-yl)-4*H*-dithieno[3,2-b:2',3'-d]pyrrole segment and employ it as the π -conjugated linker of a new dye coded C251 (Figure 1A), and further compare its electrochemical, photophysical, and photovoltaic characteristics with respect to the reference DTP dye C241.

2. Results and Discussion

As depicted in Scheme 1, C251 was prepared according to a previously reported procedure of the Suzuki-Miyaura cross-coupling of a pinacol bisarylaminophenyl boronate with



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www.afm-iournal.de A) n-C₆H₁₃O CN **C241** соон n-C₆H₁₃ n-C₆H₁₃C n-C₆H₁₃C CN C251 соон n-C6H13C n-C8H17O On-C8H17 80 C) B) - C241 - C241 12 C251 - C251 60 10 ε [10³ M⁻¹ cm⁻¹] 8 *a* [10³ cm⁻ 40 6 4 20 2 0 0 400 500 600 700 400 500 600 700



λ [nm]

λ [nm]



a bromine substituted aromatic aldehvde.^[12] and the widelv deployed Knoevenagel condensation to produce a cyanoacrylic acid DSC dye.^[25,26] Bisoctyloxy substituted iodobenzene 2 was almost quantitatively obtained by alkylation of 2-iodobenzene-1,3-bis(olate) in the polar aprotic solvent of acetone. By virtue of a highly active phosphine ligand of 2-(2',6'-dimethoxybiphenyl) dicyclohexylphosphine (SPhos),^[27] the hindered iodide 2 was successfully cross-coupled at a moderate temperature with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine in excellent yield to afford amine 3, which further underwent the Buchwald-Hartwig amination of 3,3'-dibromo-2,2'-bithiophene to give the key intermediate 4 in excellent yield. Aldehyde 5 was obtained in excellent yield by the selective monoformylation of 4 via the Vilsmeier-Haack reaction, and further brominated with N-bromosuccinimide (NBS) to generate the key intermediates 6. Note that the bromination must be carried out at a low temperature of ≈ 0 °C to avoid the side reaction on the bis(octyloxy) phenvl moietv.

The electronic absorption spectra of diluted THF solutions of C241 and C251 were first recorded to evaluate the molecular-level capacity of solar radiation capture. As depicted in Figure 1B, a slightly lower maximum molar absorption coefficient (ε^{abs}_{max}) of 61×10^3 M⁻¹ cm⁻¹ at 506 nm was measured for the C251 dye, compared to that of 65×10^3 M⁻¹ cm⁻¹ at 511 nm for C241. The experimentally measured blue-shifting of absorption peak and the decrease of absorption coefficient from C241 to C251 can be nicely reproduced by the TDDFT calculations on the maximum absorption wavelength (λ_{max}) and the corresponding oscillator strengths (f) listed in Table S1 of the Supporting Information. Less intense and blue-shifted absorption of C251 in comparison to C241 is mainly related to the small increase from 18 to 20° of the torsion angle between the phenyl and DTP moieties. Further analyses on the molecular orbital topologies (Figure 2) involving the $S_0 \rightarrow S_1$ transitions disclose that the low-energy absorption bands of C241 and C251 are mainly assigned to the intramolecular charge transfer transitions from the triphenylamine donor to the cyanoacrylic acid acceptor. It is also worthy of noting that



Scheme 1. Synthetic route of the **C251** dye. Reagents and conditions: i) 1-bromooctane, K_2CO_3 , acetone, reflux; ii) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine, Pd(OAc)₂, SPhos, K_3PO_4 , dioxane/H₂O (ν/ν , 5/1), rt; iii) 3,3'-dibromo-2,2'-bithiophene, Pd₂(dba)₃, BINAP, NaOt-Bu, toluene, reflux; iv) DMF, POCl₃, 1,2-dichloroethane, rt; v) NBS, THF, 0 °C; vi) 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2dioxaborolane, Pd(OAc)₂, SPhos, K_3PO_4 , dioxane/H₂O (ν/ν , 5/1), rt; vii) cyanoacetic acid, piperidine, CHCl₃, reflux.

HOMO-1 HO

Figure 2. Distribution of frontier molecular orbitals involving the $S_0 \rightarrow S_1$ transitions of **C241** and **C251** in THF. All the iodensity surface values are fixed at 0.03.

there is nearly no distribution of these frontier orbitals on the 2',6'-bis(octyloxy)-biphenyl moiety, which could be considered as an insulating spacer to reduce the intermolecular exciton annihilation in the assembly of dye molecules grafted on the surface of titania.

The attenuation of intermolecular interaction in the assembly of DTP dve molecules via attaching the 2',6'-bis(octyloxy)biphenyl group was further supported by recording the progressive blue-shifting of absorption peaks (Figure S1, Supporting Information) during the dyeing of titania. The shift of absorption peak is less evident for C251 during the dying process than C241, suggesting that C241 is prone to aggregate on the surface of titania. We also measured the electronic absorption of a stained titania film reaching the stage of adsorption-desorption equilibrium, which is more closely related to the DSC light-harvesting capacity. As presented in Figure 1C, lower absorption coefficients (a) in the whole visible region are noted for a dyed film with C251 than C241. The measured dye load amounts of C241 and C251 are 2.8 \times 10^{-8} and 1.4 \times 10^{-8} mol $\text{cm}^{-2} \ \mu\text{m}^{-1}$, respectively, which could be rationalized in terms of the geometries (Figure S2, Supporting Information) of C241 and C251.

The substituent related intermolecular interaction was further assessed by measuring the cyclic voltammograms of dye-coated titania films at various scan rates, to probe the diffusive lateral charge transfer characteristics^[28–30] in the electroactive dye layer on titania. The ground-state redox potentials E_{D/D^+} of **C241** and **C251** grafted on titania can be precisely derived through averaging the anodic and cathodic peak potentials shown in **Figure 3**A, being 0.28 and 0.32 V versus the ferrocene/ferrocenium (Fc/Fc⁺) reference, respectively. Furthermore, the peak current of anodic wave (i_{pa}) can be nicely correlated with the

scan rate (v) in terms of the following equation of $i_{pa} = (2.69 \times 10^5) A_s c_m n^{3/2} D_{app}^{1/2} \nu^{1/2} .$ ^[31] At a given film geometry with invariant electrode area (A_s) , film thickness, and porosity, the dye concentration (c_m) is proportional to the dye load amount. Herein, n is the transferred electron number and D_{app} refers to the apparent charge diffusion coefficient. Through comparing the fitting slopes of data shown in Figure 3B, the D_{app} in the molecular layer composed of the hexyl substituted DTP dye is ~4 times higher than that of the 2',6'-bis(octyloxy)-biphenyl substituted DTP counterpart, proving a stronger intermolecular electronic interaction for C241 with respect to C251.

We further carried out the incident photon-to-collected electron conversion efficiency (IPCE) measurement of a dyecoated titania film in conjunction with an acetonitrile (MeCN) electrolyte containing the tris(1,10-phenanthroline)cobalt(II)/(III) redox couple. The cell details are described in the experimental section. As shown in **Figure 4**A, the **C251** cell exhibits a broad plateau with similar IPCE summit compared



Figure 3. A) Cyclic voltammograms of the dye-coated titania films in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. Scan rate: 60 mV s⁻¹. B) Plots of anodic peak current (i_{pa}) as a function of the square root of scan rate ($v^{1/2}$). The solid lines are fitting in terms of equation $i_{pa} = (2.69 \times 10^5) A_s c_m n^{3/2} D_{app}^{1/2} v^{1/2}$.

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Figure 4. A) Photocurrent action spectra. B) *j*–V characteristics measured at an irradiation of 100 mW cm⁻² AM1.5 sunlight. C) Plots of open-circuit photovoltage as a function of short-circuit photocurrent density. Cells were tested using a metal mask with an aperture area of 0.158 cm². An antireflection film was adhered to the testing cell during measurements.

to the **C241** counterpart. However, it is valuable to notice that the **C241** confers relatively lower IPCEs from 550 to 630 nm, in spite of higher absorptions of the **C241** dye-coated titania film in this spectral region (Figure S3, Supporting Information), suggesting that the **C251** dye can endow a titania film to display an improved charge collection efficiency compared to **C241**.

The solar-to-electricity conversion efficiencies of DSCs made with **C241** and **C251** as the photosensitizers were examined by recording the photocurrent density–voltage (*j*–V) characteristics at the 100 mW cm⁻², simulated AM1.5 conditions, and the detailed photovoltaic parameters were compiled in **Table 1**. As Figure 4B presents, the short-circuit photocurrent density (*j*_{sc}), open-circuit photovoltage (*V*_{oc}), and fill factor (FF) of the **C241** cell are 12.53 mA cm⁻², 0.82 V, and 0.73, respectively, affording a power conversion efficiency (η) of 7.5%. Furthermore, a notably improved *V*_{oc} of 0.96 V concomitant with an increased *j*_{sc} of 13.53 mA cm⁻² was achieved with the **C251** dye, contributing to a higher η of 9.3%. Note that the efficiency of the **N719** dye under the same device condition is only ≈3%. It is known that



Table 1. Photovoltaic parameters obtained at the simulated AM1.5 conditions. $^{\mathrm{a})}$

dye	calculated j _{sc} [mA cm ⁻²]	j _{sc} [mA cm ⁻²]	V _{oc} [V]	FF	η [%]
C241	12.33	12.53	0.82	0.73	7.5
C251	13.40	13.53	0.96	0.72	9.3

^{a)} The validity of our photovoltaic data is confirmed by comparing the calculated j_{sc} via wavelength integration of the product of the standard AM1.5 emission spectrum (ASTM G173-03) and measured IPCE spectrum with the experimental j_{sc} , showing a less than 5% error. Also note that all our cells show a linear dependence of photocurrent on light intensity as shown in Figure S4, Supporting Information.

the j_{sc} of DSCs is measured at the condition of a considerable low electron density in the mesoporous titania film, which can significantly reduce the charge recombination flux, thereby it is roughly proportional to the photocarrier generation flux. This estimation has motivated us to compare the dye structure correlated V_{oc} variation at a certain j_{sc} by measuring j-V curves under various metal-mesh attenuated lights and plotting V_{oc} as a function of j_{sc} , as presented in Figure 4C. It is noted that at a given j_{sc} , the **C251** cell exhibits an obviously higher V_{oc} than **C241**.

For an invariable redox electrolyte in DSCs, the rise or fall of V_{oc} originates from an upward or downward displacement of electron quasi-Fermi-level $(E_{F,n})$ in titania, which intrinsically stems from a change of titania conduction band edge (E_c) and/ or a fluctuation of electron density.^[32-35] At a given photocarrier generation flux, the electron density is determined by the interfacial recombination rate of titania electrons with electron accepting species in electrolytes and/or dye cations. We further performed charge extraction and transient photovoltage decay measurements to scrutinize the origins of Voc variation. As depicted in Figure 5A, two type of cells made with C241 and **C251** display a similar extracted electron density (d_n) at the same potential bias, indicative of a fixed conduction-band edge of titania with respect to the electrolyte Fermi-level. As Figure 5B presents, an over one order of magnitude longer charge recombination lifetime (τ_n) for the C251 cell is however measured compared to the C241 congener at a given d_n , accounting for the aforementioned superior photovoltage at a given j_{sc} .

Obviously, albeit an evident reduction of dye load amount, the replacement of the linear hexyl group with the bulky 2',6'-bis(octyloxy)-biphenyl moiety must endow dye molecules to form a more favorite organic layer to inhibit the charge recombination, at the interface between the redox shuttle and titania. To further picture the microstructure of the dye molecule layers, we first measured their damping effect on the escape of photoelectrons from titania to vacuum. Note that in some previous work^[18,36,37] the intensity (*I*) of Ti2p_{3/2} signal in X-ray photoelectron spectroscopy (XPS) measurements has been correlated to the charge recombination at the titania/electrolyte interface. Herein evident reductions of both Ti2p_{3/2} and Ti2p_{1/2} signal intensities (**Figure 6**) can also be perceived for the **C241** or **C251** dye-coated titania film in comparison with the bare substrate.

If the dye coating on titania is compact and vertically homogeneous, the $Ti2p_{3/2}$ intensity from a dye-coated titania film can be quantitatively described with a two-layer model

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Figure 5. Plots of A) extracted electron density in titania against opencircuit photovoltage and B) electron lifetime as a function of extracted electron density.

 $I = I_0 \exp(-d/\lambda \sin \alpha)$,^[38] where I_0 is the intensity of a titania substrate without dye coating, α is the electron take-off angle of 90°, λ is the inelastic mean free path (IMFP) of electrons in a compact organic solid composed of dye molecules, and *d* is the mean thickness of a compressed dye layer. The λ values of **C241** and **C251** calculated by means of semi-empirical equations and parameters^[39] are 31.3 and 31.2 Å, respectively. On the basis of Ti2p_{3/2} intensities compiled in Table S2, Supporting Information, the compressed mean thicknesses of dye coatings on titania are calculated to be 25.9 and 21.2 Å for **C241** and **C251**. Note that there is not a positive correlation between the thickness estimated by XPS and the electron lifetime evaluated by transient photovoltage decay. This scenario suggests that



Figure 6. $Ti2p_{3/2}$ and $Ti2p_{1/2}$ photoelectron signals of titania films uncoated (a) and coated by (b) C241 and (c) C251.



Figure 7. ATR-FTIR spectra of C241 (a), C241Na (b), C251 (d), and C251Na (e) spin-coated on flat quartz as well as C241 (c) and C251 (f) grafted on mesoporous titania.

with respect to **C241**, the three-dimensional giant **C251** dye molecules should form a larger porosity organic coating on the surface of titania, however the diameter of resultant micropores should be still smaller than that of tris(1,10-phenanthroline) cobalt(III) ions. This finding has highlighted the necessity of constructing an efficient porous dye layer on the surface of titania through judicious molecular engineering to restrain the adverse interfacial charge recombination with outer-sphere redox shuttles.^[35]

The chemical bonding behaviors^[40,41] of C241 and C251 on titania were further investigated with the aid of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrum measurements. In contrast to dye films spin-coated on a flat quartz showing the characteristic absorption bands of carboxylic acid (1677 cm⁻¹ for C241; 1679 cm⁻¹ for C251, Figure 7), both the corresponding deprotonated sodium salt forms on quartz and dye-coated titania films present two new absorption bands (1603 and 1361 cm⁻¹ for C241Na; 1602 and 1360 $\rm cm^{-1}$ for C251Na; 1592 and 1367 $\rm cm^{-1}$ for C241/titania; 1589 and 1372 cm⁻¹ for C251/titania), which can be assigned to the asymmetric and symmetric stretching of carboxylate group.^[42] The carboxylic acid absorption bands are not observed for two dye-coated titania films, which can rule out the possibility of dye multilayer formation however still can not confirm a monolayer.

The relative mean tilt angles of dye molecules with respect to the titania surface were analyzed by measuring the charge recombination kinetics of photoinjected electrons in titania and oxidized dye molecules. The validity of this analysis was based on the similar electronic backbone of these two photosensitizers as well as the comparable distribution of titania surface states in our cells. In our experiments, we selected the probe light of 765 nm in joint consideration of strong absorptions in the near-infrared region of these oxidized dye molecules^[12] and the signal sensitivity of our photomultiplier tube detector. To ensure a similar charge carrier distribution profile in the testing samples, the excitation wavelengths were carefully chosen according to an optical density of ~0.2 for the FULL PAPER

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Figure 8. Absorption decay traces recorded at 765 nm of 13-µm-thick, **C241** (a) and **C251** (b) coated titania films in contact with an inert electrolyte upon pulsed laser excitation. Laser pulse fluence: 11 µJ cm⁻²; excitation wavelength: 663 nm (**C241**) and 652 nm (**C251**). Smooth lines are stretched exponential fittings over raw data obtained by averaging 500 laser shots.

dye-coated titania films infiltrated with an inert electrolyte consisting of 0.5 M 4-tert-butylpyridine (TBP) and 0.1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in MeCN. The absorption traces (Figure 8) can be fitted to a stretched exponential decay function $\Delta A \propto A_0 \exp[-(t/\tau)^{\alpha}]$, where A_0 is the pre-exponential factor, α is the stretching parameter, and τ is the characteristic time. By use of the gamma function $\Gamma(x)$, the mean times of these charge recombination reaction ($\langle \tau \rangle_{rec}$) were derived through $\langle \tau \rangle = (\tau/\alpha)\Gamma(1/\alpha)$,^[43] being 2.7 and 5.7 ms for C241 and C251, respectively. It is obvious that replacing the hexyl unit with 2',6'-bis(octyloxy)-biphenyl brings forth an evident deceleration of charge recombination, although the C251 dye has a 40 meV larger Gibbs free energy for this electron transfer reaction, which is estimated based on the aforementioned E_{D/D^+} in Figure 3. By correlating the reduced electron transfer rate to a longer tunneling distance between titania electrons and triphenylamine holes,^[44,45] we image that with respect to **C241** there is a smaller tilt angle of the **C251** dye molecules anchored on the surface of titania probably due to its 3D steric encumbrance, as pictorially illustrated in **Scheme 2**, which comes up based upon the preceding theoretical and experimental information.

3. Conclusions

To summarize, we have synthesized a new push-pull dye featuring the 4-(2',6'-bis(octyloxy)biphenyl-4-yl)-4H-dithieno[3,2*b*:2',3'-*d*]pyrrole π -linker, which presents a power conversion efficiency 9.3% at the 100 mW cm⁻², simulated AM1.5 conditions. The attachment of this insulating three-dimensional branched moiety to the conjugated electronic backbone of dve molecules brings forth enhanced photocurrent and photovoltage in comparison with the linear hexyl group. Transient absorption and photovoltage decay measurements have disclosed that the new dye can form a powerful porous photoactive layer on the surface of TiO₂ nanocrystals to decelerate the charge recombination kinetics involving photoinjected titania electrons. The strategy presented here on the construction of a three-dimensional dithienopyrrole dye could be extended to the design of other infrared absorption DSC dyes for more efficient cells employing the single-electron redox shuttles or solid holetransporters, on account that the significant control of charge recombination in these devices is a big challenge.

4. Experimental Section

Materials: MeCN, tert-butanol (t-BuOH), phosphorus oxychloride (POCl₃), and DMF were distilled before use. Pd(OAc)₂, SPhos, NBS tris(dibenzylideneacetone)dipalladium $(Pd_2(dba)_3),$ and (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (BINAP) were purchased from Sigma-Aldrich and used without any purification. C241,^[12] 4,4,5,5-tetramethyl-2-{4-[N,N-bis(4-hexyloxyphenyl)amino] phenyl}-1,3,2-dioxaborolane,[46] 2-iodobenzene-1,3-diol (**1**),^[47] 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine,[48] and 3,3'-dibromo-2,2'-bithiophene^[49] were synthesized according to the corresponding literature methods. The synthetic details of C251 are described as follows.

2-Iodo-1, 3-bis(octyloxy)benzene (2): To a stirred solution of 1 (10.000 g,

42.371 mmol) and K₂CO₃ (29.280 g, 211.855 mmol) in acetone (200 mL) was added 1-bromooctane (32.730 g, 169.484 mmol). The mixture was refluxed under argon overnight and then cooled to room temperature before filtering and washing with dichloromethane. After evaporation of the filtrate under reduced pressure, the crude product was purified by column chromatography over silica gel with petroleum ether as eluent to obtain a colorless oil as the desired product 2 (18.729 g, 96% yield). ¹H NMR (600 MHz, DMSO-*d*₆, δ): 7.24 (t, J = 8.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 4.00 (t, J = 6.3 Hz, 4H), 1.71 (m, 4H), 1.47 (m, 4H), 1.26 (m, 16H), 0.86 (t, J = 6.9 Hz, 6H). ¹³C NMR (150 MHz, DMSO-d₆, δ): 158.42, 129.93, 105.26, 78.67, 68.62, 31.16, 28.62, 28.56, 25.52, 22.03, 13.91. MS (ESI) m/z calcd. for C₂₂H₃₇IO₂: 460.2. Found: 461.1 ([M+H]⁺). Anal. calcd. for C₂₂H₃₇IO₂: C, 57.39; H, 8.10. Found: C, 57.31; H, 8.14.

4-Amino-2',6'-bis(octyloxy)-biphenyl (3): To a stirred solution of **2** (2.000 g, 4.343 mmol),



Scheme 2. Pictorial adsorptions of **C241** and **C251** on the surface of titania proposed on the basis of joint experimental and theoretical data. The tunneling distances of two charge transfer channels of photoinjected electrons in titania with the tris(1,10-phenanthroline)cobalt(III) ions (d_1) and dye cations (d_2) are both longer for **C251** than **C241**.



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4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine (0.793 3.620 mmol), and K₃PO₄ (3.842 g, 18.100 mmol) in dioxane/H₂O (106 mL, v/v, 5/1) was added Pd(OAc)₂ (0.016 g, 0.072 mmol) and SPhos (0.030 g, 0.072 mmol). The resulting mixture was stirred at 45 °C under argon for 24 h and then cooled to room temperature. The solution was extracted with ethyl acetate before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether $(\nu/\nu, 2/1)$ as eluent to obtain a colorless oil as the desired product **3** (1.418 g, 92% yield). ¹H NMR (600 MHz, DMSO- d_6 , δ): 7.12 (t, J =8.4 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 8.4 Hz, 2H), 4.94 (s, 2H), 3.83 (t, J = 6.3 Hz, 4H), 1.52 (m, 4H), 1.27 (m, 8H), 1.22 (m, 12H), 0.86 (t, J = 7.2 Hz, 6H). ¹³C NMR (150 MHz, DMSO-*d*₆, *δ*): 156.69, 146.79, 131.34, 127.50, 120.91, 120.00, 112.70, 105.56, 67.73, 31.14, 28.63, 28.47, 25.35, 22.04, 13.92. MS (ESI) m/z calcd. for (C₂₈H₄₃NO₂): 425.3. Found: 426.4 ([M+H]⁺). Anal. calcd. for C₂₈H₄₃NO₂: C, 79.01; H, 10.18; N, 3.29. Found: C, 79.11; H, 10.24; N, 3.17.

4-(2',6'-Bis(octyloxy)biphenyl-4-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (4): To a solution of 3,3'-dibromo-2,2'-bithiophene (0.326 g, 1.006 mmol) in toluene (9 mL) was added NaOt-Bu (0.230 g, 2.414 mmol), Pd₂(dba)₃ (0.022 g, 0.025 mmol), and BINAP (0.062 g, 0.101 mmol) under argon. The resulting mixture was stirred for 30 min before 3 (0.430 g, 1.011 mmol) was added. The reaction was refluxed for 20 h and then cooled to room temperature. Water (10 mL) was added to quench the reaction and the solution was extracted with ethyl acetate before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (ν/ν , 1/2) as eluent to obtain a colorless oil as the desired product 4 (0.561 g, 95% yield). ¹H NMR (600 MHz, DMSO- d_6 , δ): 7.63 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 4.8 Hz, 2H), 7.46 (d, J= 8.4 Hz, 2H), 7.30 (d, J = 5.4 Hz, 2H), 7.27 (t, J = 8.4 Hz, 1H), 6.74 (d, J = 8.4 Hz, 2H), 3.92 (t, J = 6.6 Hz, 4H), 1.56 (m, 4H), 1.25 (m, 4H), 1.13 (m, 16H), 0.72 (t, J = 6.6 Hz, 6H). ¹³C NMR (150 MHz, DMSO- d_6 , δ): 156.59, 143.26, 137.13, 132.48, 131.76, 129.02, 124.58, 120.43, 118.44, 116.22, 112.43, 105.62, 68.05, 31.09, 28.65, 28.56, 25.44, 21.97, 13.74. MS (ESI) m/z calcd. for (C₃₆H₄₅NO₂S₂): 587.3. Found: 588.4 ([M+H]⁺). Anal. calcd. for C₃₆H₄₅NO₂S₂: C, 73.55; H, 7.72; N, 2.38. Found: C, 73.39; H. 7.80: N. 2.29.

4-(2',6'-Bis(octyloxy)biphenyl-4-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2-carbaldehyde (5): To a solution of 4 (0.470 g, 0.799 mmol) and DMF (0.174 mL, 2.237 mmol) in 1,2-dichloroethane (10 mL) was added POCl₃ (0.087 mL, 0.945 mmol). The resulting mixture was stirred at room temperature under argon for 10 h and then saturated sodium acetate aqueous solution (20 mL) was added. After stirred overnight at room temperature, the solution was extracted with dichloromethane before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (ν/ν , 2/1) as eluent to afford a yellow solid as the desired product 5 (0.448 g, 91% yield). ¹H NMR (600 MHz, DMSO- d_6 , δ): 9.92 (s, 1H), 8.26 (s, 1H), 7.78 (d, J = 5.4 Hz, 1H), 7.69 (d, / = 8.4 Hz, 2H), 7.50 (d, / = 8.4 Hz, 2H), 7.37 (d, / = 5.4 Hz, 1H), 7.28 (t, J = 8.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 2H), 3.93 (t, J = 6.3 Hz, 4H), 1.56 (m, 4H), 1.24 (m, 4H), 1.10 (m, 16H), 0.69 (t, J = 7.2 Hz, 6H). ¹³C NMR (150 MHz, DMSO-*d*₆, δ): 184.16, 156.58, 147.22, 142.51, 140.32, 136.24, 132.58, 130.40, 129.13, 123.71, 122.97, 120.88, 118.38, 116.43, 112.32, 105.68, 68.12, 31.07, 28.62, 28.56, 25.41, 21.94, 13.68. MS (ESI) m/z calcd. for $C_{37}H_{45}NO_3S_2$: 615.3. Found: 616.2 ([M+H]⁺). Anal. calcd. for C37H45NO3S2: C, 72.16; H, 7.36; N, 2.27. Found: C, 72.28; H. 7.45: N. 2.13.

4-(2', 6'-Bis(octyloxy)biphenyl-4-yl)-6-bromo-4H-dithieno[3,2-b:2',3'-d]pyrrole-2-carbaldehyde (6): To a stirred solution of 5 (0.200 g, 0.325 mmol) in THF (15 mL) at 0°C was added NBS (0.058 g, 0.325 mmol). The resulting mixture was stirred at the same temperature under argon for 24 h and then acetone (20 mL) was added to quench the reaction. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (ν/ν , 2/1) as eluent to obtain a yellow solid as the desired product **6** (0.192 g, 85% yield). ¹H NMR (400 MHz, DMSO- d_6 , δ): 9.92 (s, 1H), 8.23 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.54 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 8.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 2H), 3.93 (t, J = 6.0 Hz, 4H), 1.55 (m, 4H), 1.24 (m, 8H), 1.17 (m, 12H), 0.68 (t, J = 6.8 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃, δ): 182.94, 157.13, 145.68, 142.58, 140.88, 136.38, 133.67, 133.00, 129.05, 124.35, 121.57, 120.90, 118.69, 116.64, 115.75, 115.66, 105.34, 68.64, 31.75, 29.26, 29.17, 29.10, 26.00, 22.59, 14.01. MS (ESI) *m*/*z* calcd. for C₃₇H₄₄BrNO₃S₂: C 63.96; H, 6.38; N, 2.02. Found: C, 64.05; H, 6.47; N, 1.99.

6-{4-[N, N-Bis(4-hexyloxyphenyl)amino]phenyl}-4-(2', 6'-bis(octyloxy) biphenyl-4-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2-carbaldehyde (7): To a stirred solution of 6 (0.146 g, 0.210 mmol), 4,4,5,5-tetramethyl-2-{4-[N,N-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (0.144 g, 0.252 mmol), and K₃PO₄ (0.233 g, 1.050 mmol) in dioxane/ H₂O (6 mL, v/v, 5/1) was added Pd(OAc)₂ (1 mg, 0.004 mmol) and SPhos (2 mg, 0.004 mmol). The resulting mixture was stirred overnight at room temperature under argon and then the solution was extracted with ethyl acetate before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with ethyl acetate/petroleum ether (v/v, 1/10) as eluent to obtain an orange solid as the desired product 7 (0.220 g, 99% yield). ¹H NMR (400 MHz, DMSO-*d*₆, δ): 9.89 (s, 1H), 8.21 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.56 (s, 1H), 7.49 (d, / = 8.4 Hz, 2H), 7.28 (t, / = 8.4 Hz, 1H), 7.04 (d, / = 8.8 Hz, 4H), 6.91 (d, J = 8.8 Hz, 4H), 6.76 (m, 4H), 3.93 (m, 8H), 1.70 (m, 4H), 1.55 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 1.18, (m, 12H), 1.08 (m, 8H), 0.88 (t, J = 6.8 Hz, 6H), 0.66 (t, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 182.72, 157.15, 155.84, 149.05, 148.76, 148.39, 142.88, 140.08, 139.92, 136.87, 133.13, 132.88, 128.97, 126.90, 126.39, 126.24, 125.44, 121.60, 120.81, 119.88, 118.82, 115.34, 114.81, 106.32, 105.35, 68.64, 68.26, 31.73, 31.59, 29.70, 29.30, 29.24, 29.15, 29.08, 25.97, 25.75, 22.59, 14.01. MS (ESI) m/z calcd. for C₆₇H₈₂N₂O₅S₂: 1058.6. Found: 1059.7 ($[M+H]^+$). Anal. calcd. for $C_{67}H_{82}N_2O_5S_2$: C, 75.95; H, 7.80; N, 2.64. Found: C, 75.87; H, 7.91; N, 2.60.

2-Cyano-3-{6-{4-[N, N-bis(4-hexyloxyphenyl)amino]phenyl}-4-(2', 6'bis(octyloxy)biphenyl-4-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2-yl}acrylic acid (C251): To a stirred solution of 7 (0.200 g, 0.189 mmol) and cyanoacetic acid (0.048 g, 0.566 mmol) in chloroform (10 mL) was added piperidine (0.130 mL, 1.323 mmol). The resulting mixture was refluxed for 12 h under argon and then cooled to room temperature before acidified with 2 M hydrochloric acid aqueous solution. The solution was extracted with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with methanol/chloroform (v/v, 1/50) as eluent to afford a purple-black powder as the desired product C251. (0.190 g, 89% yield) ¹H NMR (400 MHz, DMSO-*d*₆, δ): 13.38 (s, 1H), 8.51 (s, 1H), 8.22 (s, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.55 (m, 3H), 7.49 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 8.4 Hz, 1H), 7.04 (d, J = 8.8 Hz, 4H), 6.91 (d, J = 9.2 Hz, 4H), 6.76 (m, 4H), 3.93, (m, 8H), 1.70 (m, 4H), 1.55 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 1.15, (m, 20H), 0.88 (t, J = 6.8 Hz, 6H), 0.66 (t, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 168.99, 157.12, 155.91, 150.51, 150.22, 149.29, 148.54, 143.63, 139.91, 136.54, 133.34, 133.03, 132.76, 128.96, 128.42, 126.97, 126.44, 125.82, 122.03, 121.49, 119.61, 118.69, 116.78, 115.35, 115.01, 106.02, 105.30, 91.98, 68.63, 68.26, 31.73, 31.59, 29.69, 29.30, 29.24, 29.15, 29.06, 25.96, 25.74, 22.58, 14.01. HR-MS (ESI) m/z calcd. for $C_{70}H_{83}N_3O_6S_2$: 1125.57233. Found: 1124.56597 ([M-H]⁻). Anal. calcd. for C₇₀H₈₃N₃O₆S₂: C, 74.63; H, 7.43; N, 3.73. Found: C, 74.52; H, 7.49; N, 3.66. IR-FTIR (KBr): 1677 cm⁻¹ (COOH), 2214 cm⁻¹ (CN).

Spectral, Electrochemical, and XPS Measurements: Static electronic absorption and vibration spectra were measured with an Agilent G1103A spectrometer and a BRUKER Vertex 70 FTIR spectrometer, respectively.



Transient absorption decay traces were recorded with a LP920 laser flash photolysis spectrometer using a tunable OPOLett 35511 laser to supply the nanosecond excitation pulse. The ground-state redox potentials of dyes grafted on titania were measured on a CHI660C electrochemical workstation in conjunction with a three-electrode electrochemical cell having a platinum gauze, a silver wire, and a dye-coated titania film on FTO. All potentials were reported with Fc/Fc⁺ as the internal reference. XPS spectra were recorded with an ESCALAB 250 spectrometer equipped with a hemispherical electron energy analyzer using the Al K α radiation (hv = 1486.6 eV) and an energy step of 0.1 eV. The electron take-off angle was 90°.

Computational Details: The ground state geometries were optimized employing the hybrid B3LYP^[50] function and 6-31G** basis set. The solvent effect of THF on geometry has been simulated by the C-PCM method.^[51] Frequency analysis was also performed during the structure optimization to ensure that there is no imaginary frequency. Vertical excitation energies were calculated by TDDFT at the MPW1K/6-31G** levels.^[52–54] All calculations were carried out with Gaussian 09 program packages.^[55]

Cell Fabrication and Characterization: A double layer titania film made via screen-printing on a pre-cleaned fluorine-doped tin oxide (FTO) conducting glass (Nippon Sheet Glass, Solar, 4 mm thick) was deployed as the negative electrode of DSCs presented in this paper. A 4.2- μ m-thick translucent layer of 25 nm sized titania particles was first deposited on a FTO glass and further covered with a 5-µm-thick lightscattering layer of 350-450 nm sized titania particles (WER4-O, Dyesol). Preparation procedures of titania nanocrystals, screen-printing pastes, and nanostructured titania films were very similar to those described in a previous paper.^[56] A circular titania electrode (≈0.28 cm²) was dyeloaded by immersing it into a 150 μ M dye solution in the mixed solvent of MeCN and t-BuOH. The dye-coated titania electrode was assembled with a thermally platinized FTO electrode by use of a $25-\mu$ m-thick Surlyn ring to produce a thin-layer electrochemical cell. The infiltrated electrolyte is composed of 0.25 M tris(1,10-phenanthroline)cobalt(II) di[bis(trifluoromethanesulfonyl)imide], 0.05 M tris(1,10-phenanthroline) cobalt(III) tris[bis(trifluoromethanesulfonyl)imide], 0.5 M TBP, and 0.1 M LiTFSI in MeCN. Details on IPCE, j-V, charge extraction and photovoltage decay measurements can be found in our previous publication.[37]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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