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High Molar Extinction Coefficient Organic Sensitizers for Efficient Dye-Sensitized Solar Cells

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Abstract: We have designed and synthesized highly efficient organic sensitizers with a planar thienothiophene–vinylene–thienothiophene linker. Under standard global AM 1.5 solar conditions, the **JK-113**-sensitized cell gave a short circuit photocurrent density (J_{sc}) of 17.61 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.71 V, and a fill factor (FF) of 72%, corresponding to an overall conversion efficiency (η) of 9.1%. The incident monochromatic photo-to-current conversion efficiency (IPCE) of **JK-113** exceeds 80% over the spectral region from 400 to 640 nm, reaching its maximum of 93% at 475 nm. The band tails off toward 770 nm, contributing to the broad spectral light harvesting. Solar-cell devices based on the sensitizer **JK-113** in conjunction with a volatile electrolyte and a solvent-free ionic liquid electrolyte gave high conversion efficiencies of 9.1% and 7.9%, respectively. The **JK-113**-based solar cell fabricated using a solvent-free ionic liquid electrolyte showed excellent stability under light soaking at 60 °C for 1000 h.

Keywords: dyes/pigments · sensitizers · solar cells · solid-state electrolytes · thienothiopenes

Introduction

Energy demands and environmental issues such as global warming have led to the search for clean renewable energy sources in recent years.[1] In this context, dye-sensitized solar cells (DSSCs) are attracting widespread interest due to their low cost and high performance.[2] Some polypyridyl ruthenium sensitizers achieve power conversion efficiencies in excess of 11%[3] and show good stability. However, due to the precious metal and its rarity, metal-free organic dyes have attracted considerable attention for practical applications. Recently, the solar-cell performances of DSSCs based on organic dyes have been remarkably improved and impressive efficiencies in the range 8–9.7% have been achieved.[4] The main factors responsible for the low efficiencies of organic dyes compared to the ruthenium sensitizers are narrow absorption bands in the visible region and the formation of dye aggregates on the semiconductor surface.[5] Therefore, many attempts have been made to design and construct organic dye molecules with higher molar extinction coefficients and broader spectral responses. Most of the efficient organic dyes contain a donor and acceptor bridged by a π-conjugated linker (D-π-A). To enhance the molar extinction coefficient as well as to realize panchromatic light-harvesting, tuning of the length and torsion angle of the conjugated linker is important. Recently, a successful approach was introduced in which a π-conjugated linker such as a thiophene[6] or thienothiophene[7] derivative was incorporated into an organic framework, thereby enhancing the efficiency and stability. Herein, we report highly efficient organic sensitizers, coded as **JK-112** and **JK-113** (Scheme 1), which consist of a dimethylfluorenylamino-appended thienothiophene–vinylene–thienothiophene unit with aliphatic chains that maintain the planar geometry of the conjugated linker. This not only increases the extinction coefficient of the sensitizer by extending the π-conjugation of the bridging linker, but also augments its hydrophobicity, increasing the stability under long-term light soaking and thermal stress.

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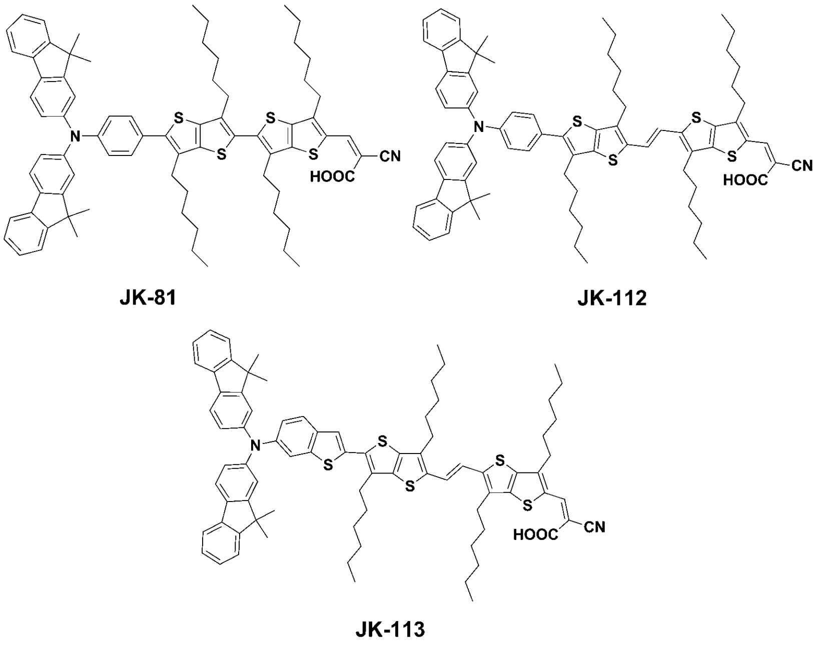


Scheme 1. The structures of **JK-81**, **JK-112**, and **JK-113**.

Results and Discussion

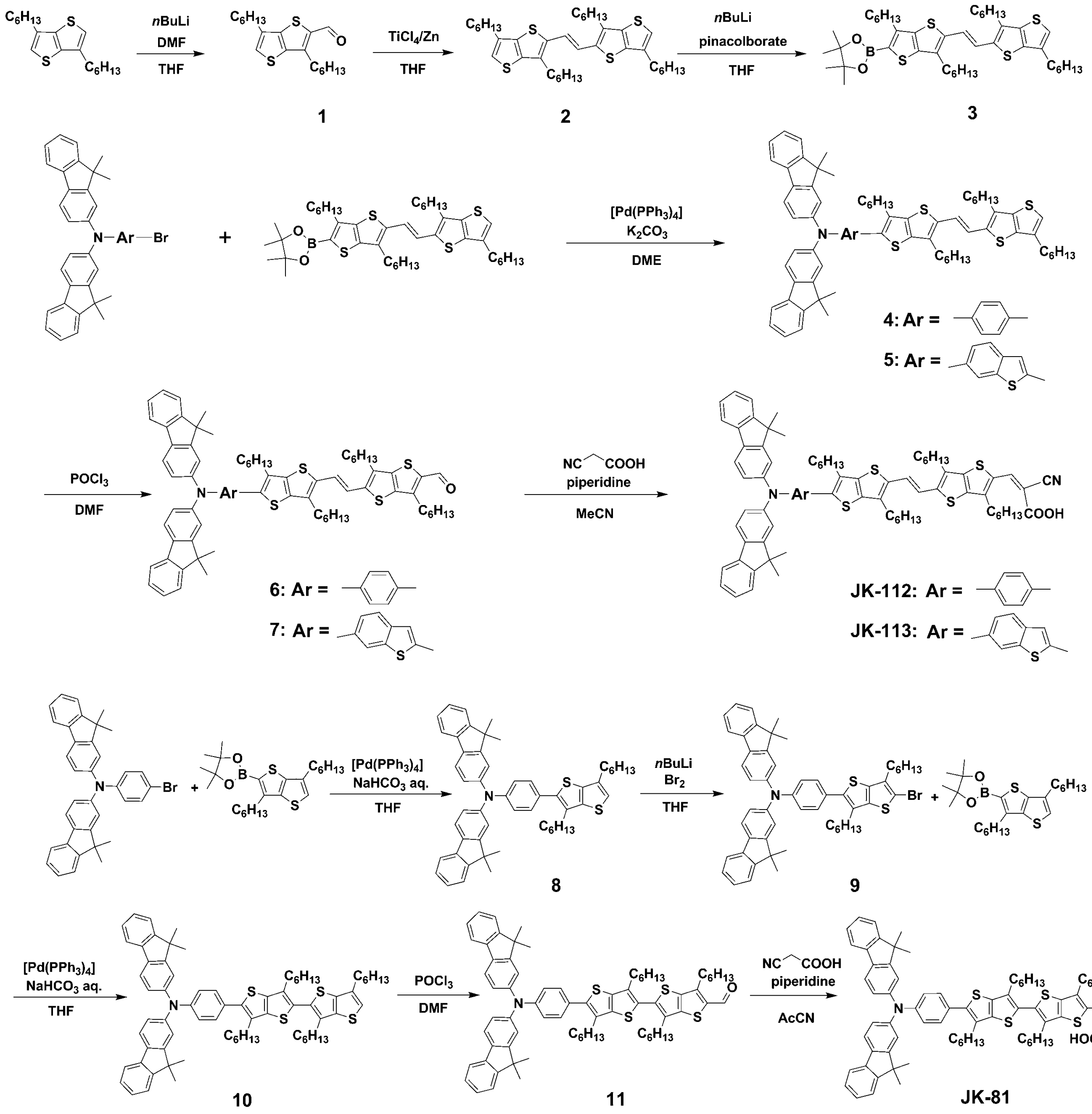
The organic sensitizers have been efficiently synthesized by the stepwise synthetic protocol illustrated in Scheme 2. Compound **2** was prepared from **1** by a McMurry reaction and was then converted into **3** by lithiation with *n*-butyllithium and subsequent quenching with pinacol borate. Suzuki coupling reactions of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline[11] and 6-[bis(9,9-dimethylfluoren-2-yl)amino]-2-bromobenzo[*b*]thiophene[12] with 1.2 equivalents of **3** yielded **4** and **5**, respectively. Suzuki coupling reaction of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline with 2-(3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane led to **8**. Bromination of **8** with Br_2 gave **9**. Compound **10** was prepared from **9** with 2-(3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane by a Suzuki reaction. The thienothiophene–vinylene–thienothiophene derivatives **4** and **5** and the dithienothiophene derivative **10** were converted into their corresponding carbaldehydes **6**, **7**, and **11** by Vilsmeier–Haack reactions. Reactions of the aldehyde derivatives with cyanoacetic acid in the presence of piperidine in acetonitrile produced the dyes **JK-81**, **JK-112**, and **JK-113**, respectively.

The visible absorption spectrum of **JK-112** displays two absorption maxima at 480 nm ($\varepsilon = 73\,800\,\text{M}^{-1}\text{cm}^{-1}$) and 365 nm ($\varepsilon = 51\,800\,\text{M}^{-1}\text{cm}^{-1}$), which are due to the π–π* transitions of the conjugated system. Under the same conditions, the dye **JK-113** exhibits absorption bands at 490 nm ($\varepsilon = 85\,000\,\text{M}^{-1}\text{cm}^{-1}$) and 365 nm ($\varepsilon = 50\,400\,\text{M}^{-1}\text{cm}^{-1}$), as shown in Figure 1. Such high coefficients can be expected to permit a reduction in film thickness in solar-cell applications, which should increase the open-circuit voltage and overall efficiency. The slight blueshift in the absorptions of **JK-112** compared to those of **JK-113** can be readily understood from molecular modeling studies (Figure 2). The ground-state structures of **JK-112** and **JK-113** have twist angles of 51.0° and 46.6°, respectively, between the aminophenyl or -benzo[*b*]thiophenyl moieties and the thienothiophene units, indicating that the latter has a more planar geometry due to a smaller torsion angle. On the other hand, the dye **JK-81** exhibits a further blue shift to 372 nm due to the wide dihedral angle (64.7°) of the two thienothiophene units, which gives rise to a twisted nonplanar geometry. For **JK-112** and **JK-113**, the dihedral angles of the thienothiophene–vinylene–thienothiophene bridged units are 1.8° and 0.8°, respectively. Accordingly, the higher extinction coefficients of **JK-112** and **JK-113** relative to that of **JK-81** and the associated redshifts derive from increased electron delocalization over the conjugated system. Similar distortions have been reported for other organic dyes.[7b,8]

When **JK-112** and **JK-113** are excited within their π–π* bands, they exhibit strong luminescence maxima at 632 nm, with $E_{0\text{-}0}$ transition energies of 2.28 and 2.24 eV, respectively (Table 1). The excited-state oxidation potentials (E^*_{ox}) of the dyes (**JK-112**: −1.15 V; **JK-113**: −1.18 V vs. NHE) are much more negative than the conduction band of TiO_2, located at −0.5 V versus NHE, allowing efficient electron injection from the LUMO of the dye to the conduction band of TiO_2.

Molecular-orbital calculations have indicated that the HOMOs of **JK-112** and **JK-113** are spread over the fluorenylamino unit through the phenyl or benzo[*b*]thiophene groups and that the LUMOs are located on the cyanoacrylic units and extend to the thienothiophene moieties (Figure 3). Examination of the HOMOs and LUMOs of these dyes indicates that HOMO–LUMO excitation moves the electron from the phenyl- or benzo[*b*]thiophene unit to the cyanoacrylic acid moiety. The change in local electron density distribution induced by photoexcitation results in efficient charge separation.

The incident monochromatic photo-to-current conversion efficiency (IPCE) of **JK-113** exceeds 80 % over the spectral region from 400 to 640 nm, reaching its maximum of 93 % at 475 nm (Figure 4, top). The band tails off toward 770 nm, contributing to the broad spectral light harvesting. Under standard global AM 1.5 solar conditions, the **JK-113**-sensitized cell gave a short circuit photocurrent density (J_{sc}) of 17.61 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.71 V, and a



Scheme 2. Synthetic routes to **JK-112**, **JK-113**, and **JK-81**.

fill factor (*FF*) of 72 %, corresponding to an overall conversion efficiency (η) of 9.1 %. Integrating the IPCE curve for **JK-113** over the standard AM 1.5 global solar spectrum results in a short circuit current of 17.4 mA cm^{-2}, in good agreement with the measured photocurrent of the device. To the best of our knowledge, this is the highest efficiency ever reported for a DSSC based on an organic sensitizer without using 3α,7α-dihydroxy-5β-cholic acid as a co-adsorbent. Using a TiO_2 electrode stained with 0.15 mM **JK-113** in the presence of 1 mM tetrabutylammonium deoxycholic acid salt (DCA·TBA) in THF, the cell displayed a J_{sc} of 14.9 mA cm^{-2}, a V_{oc} of 810 mV, and an *FF* of 79 %, corresponding to an η of 9.5 % when the spectra were measured two days after cell fabrication (Figure 5). Reproducible efficiencies of 9.2–9.5 % were obtained with the solar cell based on **JK-113**. Using a solvent-free ionic-liquid electrolyte composed of 0.2 M I_2, 0.5 M N-methyl benzimidazole (NMBI), and 0.1 M guanidinium thiocyanate (GuNCS) in 1-methyl-3-propylimidazolium iodide (PMII)/1-methyl-3-ethylimidazolium thiocyanate (EMINCS) (13:7), the **JK-113** sensitizer displayed a strikingly high conversion efficiency of 7.9 %, which is comparable to the highest values hitherto achieved for solvent-free DSSCs based on ruthenium sensitizers.[3c,d,9] Devices based on **JK-113** using ionic liquid electrolytes showed excellent long-term stability under accelerated light soaking at 60 °C. Figure 6 shows stability data for **JK-112**

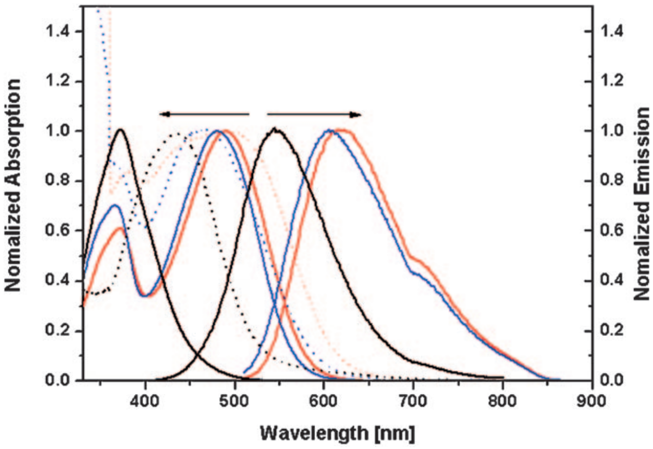


Figure 1. Absorption (left scale) and emission (right scale) spectra of **JK-81** (black solid line), **JK-112** (blue solid line), and **JK-113** (red solid line) in THF. The absorption spectra as anchored sensitizers on TiO_2 film of **JK-81** (black dotted line), **JK-112** (blue dotted line), and **JK-113** (red dotted line) are also included. The emission spectra were obtained using the same solutions by exciting at 370, 480, and 490 nm for **JK- 81**, **JK-112**, and **JK-113**, respectively, at 298 K.

and **JK-113** during long-term accelerated aging. After 1000 h of light soaking, the V_{oc} of **JK-113** had decreased by 54 mV, but the loss was compensated by a slight increase in the short-circuit current density from 16.5 to 16.7 mA cm^{-2} and in the fill factor from 68 % to 69 %. The initial efficiency of 7.9 % slightly decreased to 7.4 % during the 1000 h light-soaking test.

An all-solid-state dye-sensitized solar cell (ssDSSC) was constructed, employing **JK-112** as a sensitizer and 2,2′,7,7′-tetrakis(*N*,*N*-dimethoxyphenylamine)-9,9′-spiro-bifluorene (Spiro-OMeTAD) as a hole conductor. This device gave a J_{sc} of 8.0 mA cm^{-2}, a V_{oc} of 900 mV, and an *FF* of 60 %, corresponding to an overall conversion efficiency η of 4.3 % under standard global AM 1.5 solar conditions (Table 2). At lower light intensity, the power conversion efficiency increased to 4.8 %, which is a remarkable value for an ssDSSC based on an organic sensitizer. Of particular note are the high V_{oc} values of the cells (both with **JK-112** (900 mV) and **JK-113** (920 mV)). This stems from the thinner TiO_2 film, which retards the charge recombination dynamics due to the higher absorption coefficient arising from extended conjugation.

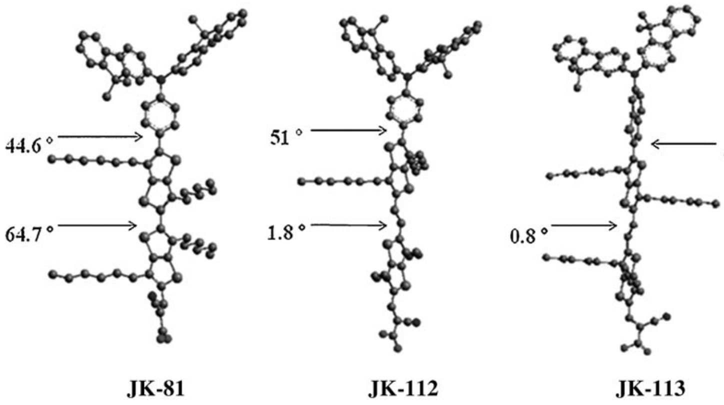


Figure 2. Optimized structures calculated by TD-DFT using the B3LYP functional and the 3-21G* basis set for **JK-81**, **JK-112**, and **JK-113**.

Table 1. Optical, redox, and DSSC performance parameters of **JK-81**, **JK-112**, and **JK-113**.

	JK-81	JK-112	JK-113
λ_{abs}[a][nm] (ε [M^{-1}cm^{-1}])	372 (55800)	365 (51800), 480 (73800)	365 (50400), 490 (85000)
E_{redox}[b] [V]	1.06	1.13	1.06
E_{0-0}[c] [V]	2.71	2.28	2.24
E^*_{ox}[d] [V]	−1.65	−1.15	−1.18
J_{sc} [mA cm^{-2}]	9.4	15.7	17.6
V_{oc} [mV]	710	690	710
FF [%]	75	74	72
η [%]	5.1	8.0	9.1

[a] Absorption spectra were measured in THF solution. [b] Redox potentials of the dyes on TiO_2 were measured in CH_3CN with 0.1 M [(n-$C_4H_9)_4N][PF_6]$ as supporting electrolyte at a scan rate of 50 mV s^{-1} (vs. NHE). [c] E_{0-0} was determined from the intersection of the absorption and emission spectra in ethanol. [d] E^*_{ox} was calculated as $E^*_{redox} - E_{0-0}$. [e] Performances of the DSSCs were measured with 0.18 cm^2 working area. Electrolyte 1: 0.6 M DMPImI, 0.05 M I_2, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile.

AC impedance spectra of the cells were measured to check for any changes in the electric circuit elements of the DSSC during aging. Figure 7 shows the AC impedance spectra of the DSSCs measured in the dark and under illumination (bottom). In the dark under forward bias (−0.68 V), the semicircle in the intermediate frequency regime reflects mainly the recombination impedance caused by electron loss from the conduction band of TiO_2 to I_3^- ions in the electrolyte.[10] A larger radius of the semicircle in this intermediate frequency regime implies a lower rate of electron recombination at the TiO_2/dye/electrolyte interface. In the dark at 0.68 V forward bias, the radius of this semicircle increases in the order **JK-112** (50.0 Ω) < **JK-113** (60.7 Ω) < **JK-81** (68.51 Ω), in accord with the trends in the values of V_{oc}. Upon illumination under open-circuit conditions (100 mW cm^{-2}), the radius of the intermediate-frequency semicircle in the Nyquist plot decreased in the order **JK-81** (24.1 Ω) > **JK-112** (12.0 Ω) > **JK-113** (11.7 Ω), indicating improved electron generation and transport. These results are in good agreement with the trends observed in the overall efficiency.

Conclusions

In summary, we have designed and synthesized three highly efficient organic sensitizers with a planar thienothiophene–

vinylene–thienothiophene linker. Solar-cell devices based on the sensitizer **JK-113** in conjunction with a volatile electrolyte without the tetrabutylammonium salt of deoxycholic acid DCA·TBA, with DCA·TBA, and a solvent-free ionic liquid electrolyte gave high conversion efficiencies of 9.1 %, 9.5 %, and 7.9 %, respectively. A **JK-113**-based solar cell fabricated using a solvent-free ionic liquid electrolyte showed excellent stability under light soaking at 60 °C for 1000 h. We believe that the development of highly efficient organic dyes comparable to ruthenium dyes is possible through meticulous molecular engineering of organic dyes, and work directed towards this aim is now in progress.

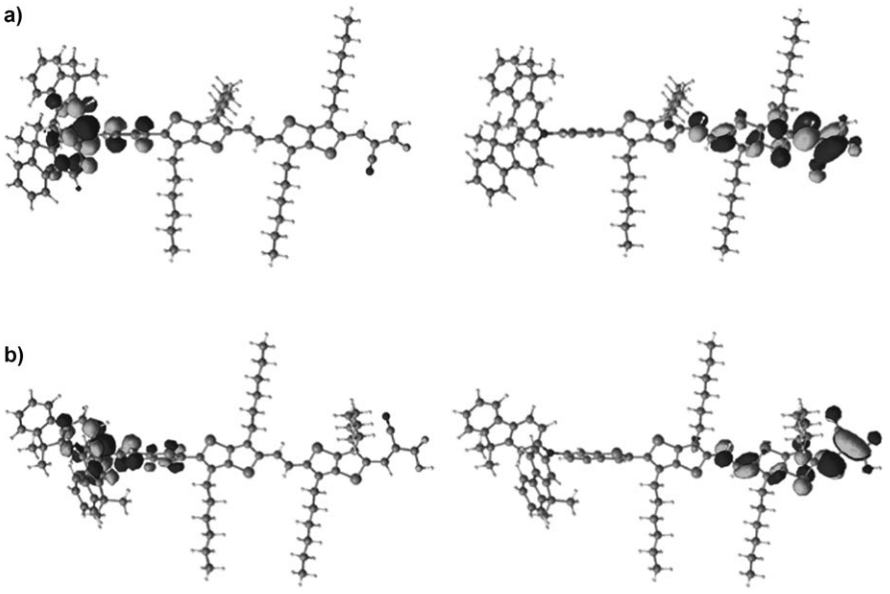


Figure 3. Isodensity surface plots of the HOMO and LUMO of (a) **JK-112** and (b) **JK-113**.

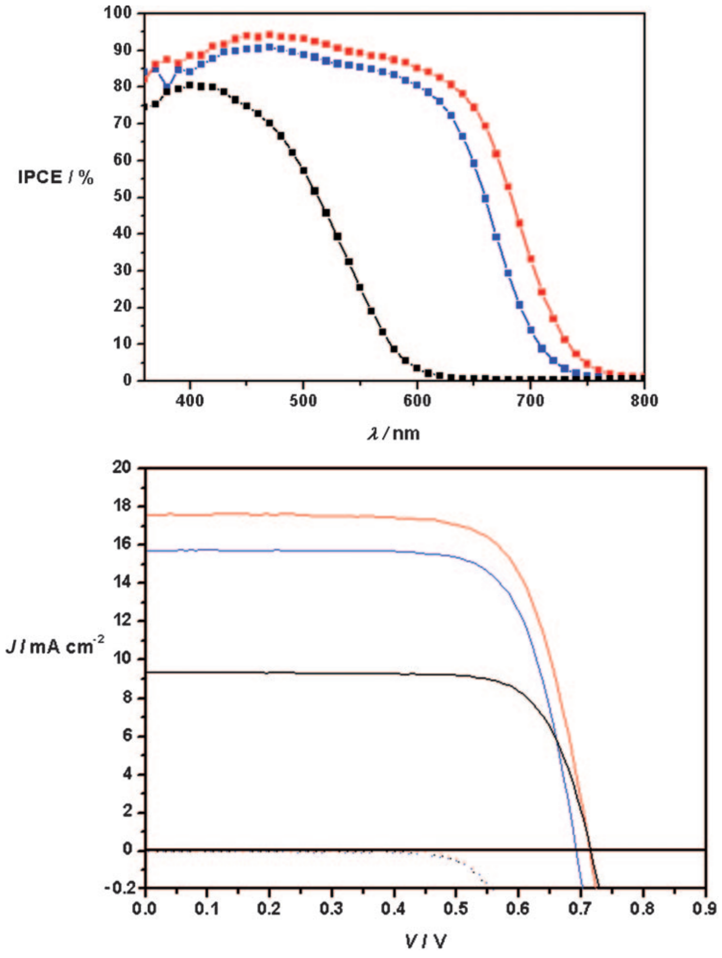


Figure 4. IPCE spectra (top) and *J*–*V* curves (bottom) of **JK-81** (black lines), **JK-112** (blue lines), and **JK-113** (red lines). Dark current–bias potential relationships are shown as dotted curves.

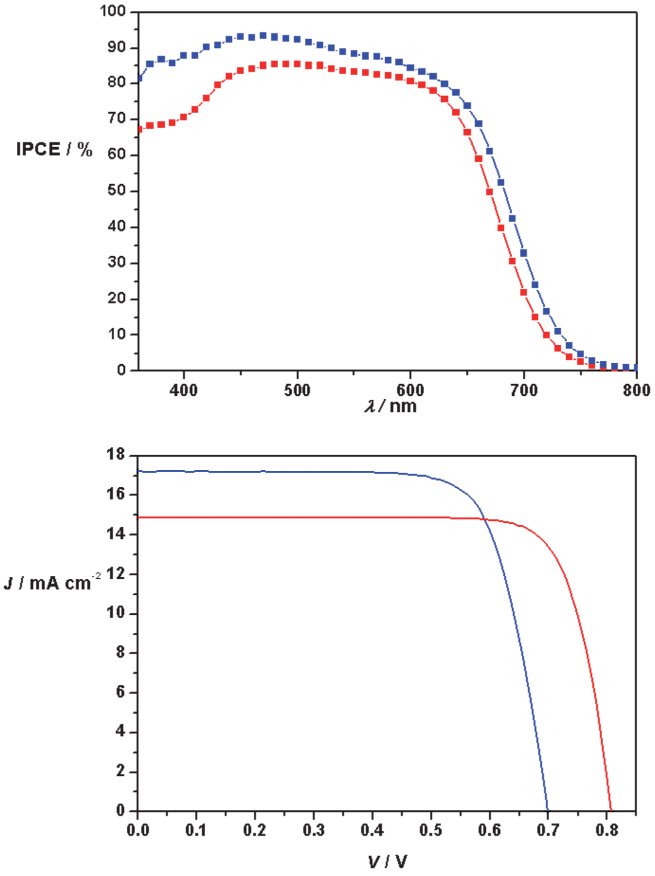


Figure 5. IPCE spectra (top) and *J*–*V* curves (bottom) of **JK-113**+DCA·TBA (blue lines) and **JK-113**+DCA·TBA after two days (red lines).

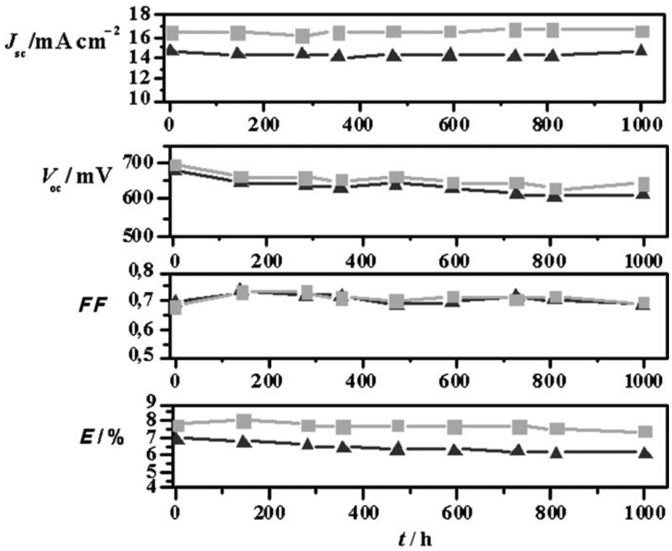


Figure 6. Evolution of solar-cell parameters with **JK-112** (▲) and **JK-113** (■) during visible-light soaking (AM 1.5 G, 100 mW cm^{-2}) at 60 °C. A 420 nm cut-off filter was placed on the cell surface during illumination. Ionic liquid electrolyte 2: 0.2 M iodine, 0.5 M NMBI, 0.1 M GuNCS in PMII/EMINCS (13:7).

Table 2. *J–V* characteristics of **JK-112**- and **JK-113**-sensitized solar cells with solid-state electrolytes under different light intensities.

Dye	Intensity [% sun]	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	*FF* [%]	η [%]
JK-112	10	0.8	780	73	4.8
	100	8.0	900	60	4.3
JK-113	10	0.7	810	70	4.2
	100	8.3	920	57	4.3

Experimental Section

General: All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich. *N*,*N*-Bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline,[11] 6-[bis(9,9-dimethylfluoren-2-yl)amino]-2-bromobenzo[*b*]thiophene,[12] and 3,6-dihexylthieno[3,2-*b*]thiophene[13] were synthesized using modified procedures based on those in the previous references. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102 A instrument. Absorption and photoluminescence spectra were recorded on a Perkin–Elmer Lambda 2S UV/visible spectrophotometer and a Perkin LS fluorescence spectrometer, respectively.

3,6-Dihexylthieno[3,2-*b*]thiophene-2-carbaldehyde (1): *n*BuLi (2.85 mL, 2.5 M solution in hexane) was added to a solution of 3,6-dihexylthieno[3,2-*b*]thiophene (2 g, 6.48 mmol) in dry THF (50 mL) at 0 °C under argon. After 1 h, DMF (1 g, 6.48 mmol) was added dropwise at 0 °C under argon. The solution was washed with 5 % HCl and dried with $MgSO_4$. The solvent was evaporated. The pure product **1** was obtained in 90 % yield by silica gel chromatography (eluent CH_2Cl_2/hexane, 1:1, R_f = 0.5). M.p. 140 °C; ^{1}H NMR ($CDCl_3$): δ = 10.09 (s, 1 H), 7.26 (s, 1 H), 3.09 (t, J = 7.8 Hz, 2 H), 2.72 (t, J = 7.2 Hz, 2 H), 1.72 (br, 4 H), 1.36 (m, 12 H), 0.89 (t, J = 6.8 Hz, 3 H), 0.86 ppm (t, J = 6.8 Hz, 3 H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 182.1, 142.1, 141.5, 137.5, 135.6, 131.1, 121.3, 31.7, 31.6, 30.5, 30.0, 29.4, 29.2, 28.9, 28.5, 28.0, 22.7, 14.3, 14.2 ppm; MS: *m*/*z*: 336 [M^+]; elemental analysis calcd (%) for $C_{19}H_{28}OS_2$: C 67.81, H 8.39; found: C 67.21, H 8.19.

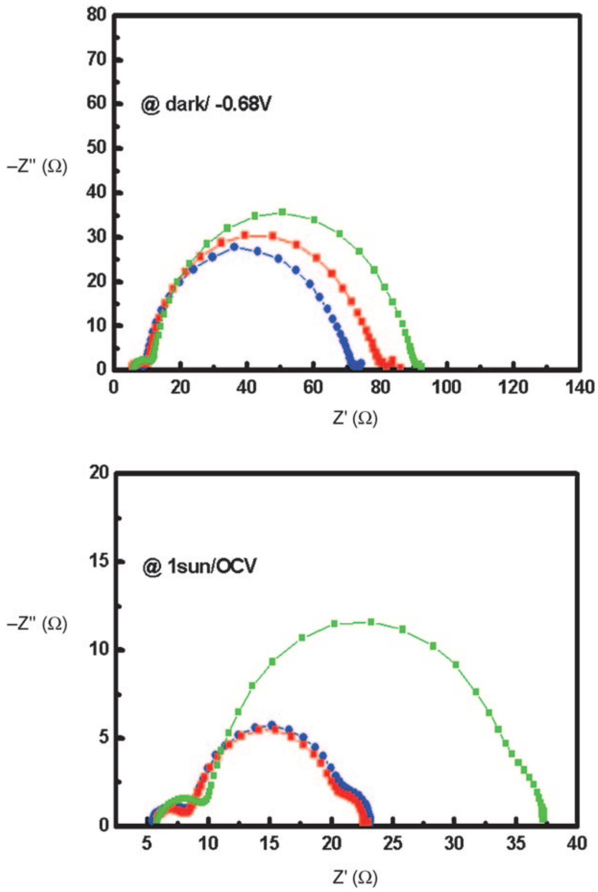


Figure 7. Electrochemical impedance spectra measured in the dark and under illumination (1 sun, bottom) for cells with different adsorbed dyes (i.e. **JK-112** (blue line), **JK-113** (red line), and **JK-81** (green line)).

(*E*)-1,2-Bis(3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)ethene (2): $TiCl_4$ (1.95 mL, 17.82 mmol) was added to a suspension of Zn powder (1.165 g, 17.82 mmol) in dry THF (50 mL) at 0 °C under argon. After 1 h, a solution of compound **1** (2 g, 5.94 mmol) in THF (10 mL) was added dropwise at 0 °C under argon. The mixture was stirred at 70 °C for 10 h, then cooled to room temperature, quenched with H_2O (30 mL), and extracted with EtOAc (3 × 30 mL). The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo. The pure product **2** was obtained by chromatographic work-up (eluent CH_2Cl_2/hexane, 1:3, R_f = 0.4) as a yellow solid in 60 % yield. M.p. 182 °C; ^{1}H NMR ($CDCl_3$): δ = 7.06 (s, 1 H), 6.95 (s, 1 H), 2.80 (t, J = 7.2 Hz, 4 H), 2.70 (t, J = 7.2 Hz, 4 H), 1.72 (br, 8 H), 1.34 (m, 24 H), 0.89 ppm (m, 12 H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 137.7, 135.6, 134.5, 133.6, 121.5, 119.8, 31.7, 31.6, 30.5, 30.0, 29.9, 29.4, 28.8, 28.5, 28.1, 22.7, 14.3, 14.2 ppm; MS: *m*/*z*: 640 [M^+]; elemental analysis calcd (%) for $C_{38}H_{56}S_4$: C 71.19, H 8.80; found: C 70.98, H 8.69.

(*E*)-2-{5-[2-(3,6-Dihexylthieno[3,2-*b*]thiophen-2-yl)vinyl]-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3): *n*BuLi (0.24 mL, 2.5 M solution in hexane) was added to a solution of compound **2** (0.35 g, 0.55 mmol) in dry THF (30 mL) at −78 °C under argon. After 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.121 g, 0.655 mmol) was added dropwise at −78 °C under argon. The mixture was stirred at 20 °C for 1 h, then quenched with H_2O (30 mL) and extracted with EtOAc (3 × 30 mL). The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo. The pure product **3** was obtained by chromatographic work-up (eluent CH_2Cl_2/hexane, 1:1, R_f = 0.4) as a yellow solid in 60 % yield. M.p. 162 °C; ^{1}H NMR ($CDCl_3$): δ = 9.82 (s, 1 H), 7.65 (t, J = 6.3 Hz, 2 H), 7.09 (s, 1 H), 7.08 (s, 1 H), 6.95 (s, 1 H), 2.97 (t, J = 7.8 Hz, 2 H), 2.81 (m, 4 H), 2.70 (t,

$J=7.8$ Hz, 2H), 1.73 (m, 8H), 1.35 (m, 24H), 0.89 ppm (m, 12H); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta=146.2$, 146.0, 140.9, 140.2, 138.4, 138.2, 137.7, 136.4, 135.6, 133.6, 133.2, 125.9, 122.0, 121.3, 83.9, 31.7, 31.6, 30.5, 30.0, 29.9, 29.4, 28.8, 28.5, 28.1, 22.9, 22.7, 14.2, 14.1 ppm; MS: m/z: 766 [M^+]; elemental analysis calcd (%) for $C_{44}H_{67}BO_2S_4$: C 68.89, H 8.80; found: C 68.12, H 8.32.

(*E*)-*N*-(4-{5-[2-(3,6-Dihexylthieno[3,2-*b*]thiophen-2-yl)vinyl]-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl}phenyl)-*N*-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine (4): A stirred mixture of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (0.138 g, 0.25 mmol), **3** (0.191 g, 0.25 mmol), K_2CO_3 (0.20 g, 1.5 mmol), and Pd(PPh$_3$)$_4$ (0.029 g, 0.025 mmol) in THF (50 mL) and H_2O (5 mL) was refluxed for 12 h. After cooling the solution, H_2O (10 mL) and brine (10 mL) were added. The organic layer was separated and dried over MgSO$_4$. The solvent was removed in vacuo. The pure product **4** was obtained by chromatographic work-up (eluent CH$_2$Cl$_2$/hexane, 1:3, $R_f=0.4$) as a green solid in 70% yield. M.p. 178 °C; ^{1}H NMR (CDCl$_3$): $\delta=7.65$ (t, $J=7.8$ Hz, 2H), 7.63 (d, $J=8.2$ Hz, 2H), 7.40 (d, $J=8.2$ Hz, 2H), 7.35 (t, $J=7.8$ Hz, 2H), 7.33–7.25 (m, 6H), 7.24 (s, 2H), 7.16 (d, $J=7.6$ Hz, 2H), 7.13 (s, 1H), 7.10 (s, 1H), 7.00 (s, 1H), 2.82 (t, $J=7.8$ Hz, 2H), 2.81–2.71 (m, 6H), 1.85–1.71 (m, 8H), 1.43 (s, 12H), 1.34–1.24 (m, 24H), 0.89 (t, $J=6.8$ Hz, 3H), 0.88–0.86 (m, 6H), 0.85 ppm (t, $J=6.8$ Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta=155.2$, 153.6, 147.6, 147.2, 140.4, 139.3, 139.0, 136.8, 135.5, 135.3, 134.6, 132.3, 132.1, 132.0, 131.3, 130.8, 130.1, 129.7, 128.8, 128.7, 128.5, 127.1, 126.7, 125.6, 123.6, 123.3, 122.6, 120.8, 119.6, 119.0, 47.0, 31.8, 31.7, 31.6, 31.5, 30.5, 30.4, 30.0, 29.8, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.7, 14.3, 14.2, 14.1 ppm; MS: m/z: 1115 [M^+]; elemental analysis calcd (%) for $C_{74}H_{85}NS_4$: C 79.59, H 7.67; found: C 79.18, H 7.43.

(*E*)-2-{5-[2-(3,6-Dihexylthieno[3,2-*b*]thiophen-2-yl)vinyl]-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl}-*N*,*N*-bis(9,9-dimethyl-9*H*-fluoren-2-yl)benzo[*b*]thiophen-6-amine (5): Compound **5** was synthesized by a similar procedure to that described for **4**, except that 6-[bis(9,9-dimethylfluoren-2-yl)amino]-2-bromobenzo[*b*]thiophene (0.16 g, 0.261 mmol) was used in place of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline. Yield: 51%. M.p. 187 °C; ^{1}H NMR (CDCl$_3$): $\delta=7.64$ (d, $J=9.0$ Hz, 1H), 7.59 (d, $J=8.1$ Hz, 2H), 7.58 (t, $J=8.1$ Hz, 2H), 7.56 (s, 1H), 7.39 (t, $J=8.1$ Hz, 2H), 7.36 (d, $J=9.0$ Hz, 1H), 7.32–7.28 (m, 4H), 7.25 (s, 2H), 7.19 (s, 1H), 7.13 (s, 1H), 7.11 (s, 1H), 7.10 (d, $J=8.1$ Hz, 2H), 2.82 (t, $J=7.8$ Hz, 2H), 2.81–2.71 (m, 6H), 1.85–1.71 (m, 8H), 1.43 (s, 12H), 1.34–1.24 (m, 24H), 0.89 (t, $J=6.8$ Hz, 3H), 0.88–0.86 (m, 6H), 0.85 ppm (t, $J=6.8$ Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta=155.3$, 153.7, 147.5, 146.5, 145.4, 143.7, 142.2, 141.1, 139.0, 138.4, 137.5, 136.5, 135.2, 134.8, 134.4, 134.1, 133.9, 133.8, 132.8, 132.3, 131.2, 130.9, 129.8, 128.7, 127.1, 126.7, 126.5, 126.3, 123.2, 122.7, 120.8, 119.5, 118.6, 116.7, 47.0, 31.8, 31.7, 31.6, 31.5, 30.5, 30.4, 30.0, 29.8, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.7, 14.3, 14.2, 14.1 ppm; MS: m/z: 1117 [M^+]; elemental analysis calcd (%) for $C_{76}H_{85}NS_5$: C 77.83, H 7.31; found: C 77.38, H 7.23.

(*E*)-5-[2-(5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]phenyl}-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)vinyl]-3,6-dihexylthieno[3,2-*b*]thiophene-2-carbaldehyde (6): The Vilsmeier reagent, which was prepared from POCl$_3$ (0.06 mL) in DMF (0.1 mL), was added to a cold solution of **4** (0.37 g, 0.33 mmol) in dry DMF (10 mL) at 0 °C. The mixture was stirred at 70 °C for 4 h, then cooled to room temperature, quenched with 10% aqueous NaOAc solution (30 mL), and extracted with EtOAc (3× 30 mL). The organic layer was separated and dried over MgSO$_4$. The solvent was removed in vacuo. The pure product **6** was obtained by chromatographic work-up (eluent CH$_2$Cl$_2$/hexane, 1:1, $R_f=0.4$) as an orange solid in 85% yield. M.p. 176 °C; ^{1}H NMR (CDCl$_3$): $\delta=10.05$ (s, 1H), 7.65 (t, $J=7.2$ Hz, 2H), 7.62 (d, $J=8.2$ Hz, 2H), 7.36 (d, $J=8.2$ Hz, 2H), 7.35 (t, $J=7.2$ Hz, 2H), 7.33–7.25 (m, 5H), 7.24 (s, 2H), 7.19 (d, $J=15.6$ Hz, 1H), 7.13 (d, $J=8.1$ Hz, 2H), 7.06 (d, $J=15.6$ Hz, 1H), 6.98 (s, 1H), 3.08 (t, $J=7.8$ Hz, 2H), 2.82–2.81 (m, 4H), 2.71 (t, $J=7.8$ Hz, 2H), 1.85–1.71 (m, 8H), 1.43 (s, 12H), 1.34–1.24 (m, 24H), 0.89 (t, $J=6.8$ Hz, 3H), 0.88–0.86 (m, 6H), 0.85 ppm (t, $J=6.8$ Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta=181.2$, 155.4, 153.2, 147.3, 147.1, 140.4, 139.3, 139.0, 136.8, 135.7, 135.3, 134.6, 133.4, 132.3, 132.1, 132.0, 130.8, 130.3, 130.1, 129.7, 128.8, 128.7, 128.5, 128.1, 127.7, 126.6, 124.6, 123.4, 122.6, 120.8, 120.6, 47.0, 31.8, 31.7, 31.6, 31.5, 30.5, 30.4, 30.0, 29.8, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.7, 14.3, 14.2, 14.1 ppm; MS: m/z: 1143 [M^+]; elemental analysis calcd (%) for $C_{75}H_{85}NOS_4$: C 78.69, H 7.48; found: C 78.28, H 7.13.

(*E*)-5-[2-(5-{6-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]benzo[*b*]thiophen-2-yl}-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)vinyl]-3,6-dihexylthieno[3,2-*b*]thiophene-2-carbaldehyde (7): Compound **7** was synthesized by a procedure similar to that described for **6**, except that **4** (0.3 g, 0.249 mmol) was used in place of **5**. Yield: 51%. M.p. 186 °C; ^{1}H NMR (CDCl$_3$): $\delta=10.05$ (s, 1H), 7.64 (d, $J=9.0$ Hz, 1H), 7.59 (d, $J=8.1$ Hz, 2H), 7.58 (t, $J=8.1$ Hz, 2H), 7.61 (s, 1H), 7.39 (t, $J=8.1$ Hz, 2H), 7.36 (d, $J=9.0$ Hz, 1H), 7.32–7.28 (m, 4H), 7.25 (s, 2H), 7.19 (d, $J=15.6$ Hz, 1H), 7.10 (d, $J=8.1$ Hz, 2H), 7.06 (d, $J=15.6$ Hz, 1H), 6.98 (s, 1H), 3.07 (t, $J=7.8$ Hz, 2H), 2.96 (t, $J=7.8$ Hz, 2H), 2.82 (t, $J=7.8$ Hz, 4H), 1.85–1.71 (m, 8H), 1.43 (s, 12H), 1.34–1.24 (m, 24H), 0.89 (t, $J=6.8$ Hz, 3H), 0.88–0.86 (m, 6H), 0.85 ppm (t, $J=6.8$ Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta=180.8$, 155.6, 154.7, 148.5, 147.5, 145.3, 143.7, 142.2, 141.1, 139.0, 138.4, 137.5, 136.5, 136.2, 134.8, 134.4, 134.1, 133.9, 133.8, 133.4, 132.8, 132.3, 131.8, 131.2, 130.8, 129.5, 128.5, 127.1, 126.7, 126.5, 126.3, 123.2, 122.7, 120.8, 119.5, 47.0, 31.8, 31.7, 31.6, 31.5, 30.5, 30.4, 30.0, 29.8, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.7, 14.3, 14.2, 14.1 ppm; MS: m/z: 1199 [M^+]; elemental analysis calcd (%) for $C_{77}H_{85}NOS_5$: C 77.02, H 7.13; found: C 76.98, H 7.03.

***N*-[4-(3,6-Dihexylthieno[3,2-*b*]thiophen-2-yl)phenyl]-*N*-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine (8)**: *n*BuLi (1.78 mL, 1.6 M solution in hexane) was added to a solution of 3,6-dihexylthieno[3,2-*b*]thiophene (0.8 g, 2.59 mmol) in dry THF at −78 °C under argon. After 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.578 g, 3.108 mmol) was added dropwise at −78 °C under argon. The mixture was stirred at 20 °C for 1 h, then quenched with H_2O (30 mL) and extracted with EtOAc (3×30 mL). The organic layers were combined and dried over MgSO$_4$. The solvent was removed in vacuo. The pure product 2-(3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained by chromatographic work-up (eluent CH$_2$Cl$_2$/hexane, 1:3, $R_f=0.4$). A stirred mixture of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (0.5 g, 0.89 mmol), 2-(3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.39 g, 0.89 mmol), NaHCO$_3$ (0.23 g, 2.69 mmol), and Pd(PPh$_3$)$_4$ (0.051 g, 0.045 mmol) in THF (50 mL) and H_2O (5 mL) was refluxed for 12 h. After cooling the solution, H_2O (10 mL) and brine (10 mL) were added. The organic layer was separated and dried over MgSO$_4$. The solvent was removed in vacuo. The pure product **8** was obtained by chromatographic work-up (eluent CH$_2$Cl$_2$/hexane, 1:3, $R_f=0.4$) as a yellow solid in 70% yield. M.p. 178 °C; ^{1}H NMR (CDCl$_3$): $\delta=7.65$ (t, $J=7.5$ Hz, 2H), 7.63 (d, $J=8.7$ Hz, 2H), 7.40 (d, $J=8.7$ Hz, 2H), 7.35 (t, $J=7.5$ Hz, 2H), 7.29–7.25 (m, 6H), 7.24 (s, 2H), 7.15 (d, $J=7.2$ Hz, 2H), 6.94 (s, 1H), 2.82 (t, $J=7.8$ Hz, 2H), 2.73 (d, $J=7.8$ Hz, 2H), 1.72 (br, 4H), 1.43 (s, 12H), 1.34–1.24 (m, 12H), 0.89 (t, $J=6.8$ Hz, 3H), 0.86 ppm (t, $J=6.8$ Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta=155.2$, 153.7, 147.5, 147.2, 140.7, 139.0, 138.9, 136.8, 135.5, 134.5, 130.9, 130.1, 129.1, 127.1, 126.7, 123.5, 123.3, 122.6, 120.8, 120.2, 119.6, 119.0, 47.0, 31.7, 31.6, 30.5, 30.0, 29.4, 29.2, 28.9, 28.5, 28.0, 27.2, 22.7, 14.3, 14.2 ppm; MS: m/z: 783 [M^+]; elemental analysis calcd (%) for $C_{54}H_{57}NS_2$: C 82.71, H 7.33; found: C 82.10, H 7.28.

***N*-[4-(5-Bromo-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)phenyl]-*N*-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine (9)**: *n*BuLi (0.50 mL, 1.6 M solution in hexane) was added to a solution of **8** (0.53 g, 0.67 mmol) in dry Et$_2$O under argon. After 3 h, bromine (0.12 g, 0.74 mmol) was added dropwise at 0 °C under argon. The mixture was washed with 5% aqueous KOH solution and dried with MgSO$_4$. The solvent was evaporated. The pure product **9** was obtained in 80% yield by silica gel chromatography (eluent CH$_2$Cl$_2$/hexane, 1:3, $R_f=0.5$). M.p. 181 °C; ^{1}H NMR (CDCl$_3$): $\delta=7.64$ (t, $J=8.1$ Hz, 2H), 7.62 (d, $J=8.7$ Hz, 2H), 7.39 (d, $J=8.7$ Hz, 2H), 7.33 (t, $J=8.1$ Hz, 2H), 7.30–7.23 (m, 6H), 7.20 (s, 2H), 7.14 (d, $J=7.8$ Hz, 2H), 2.92 (t, $J=7.8$ Hz, 2H), 2.72 (d, $J=7.8$ Hz, 2H), 1.72 (br, 4H), 1.42 (s, 12H), 1.34–1.24 (m, 12H), 0.89 (t, $J=6.8$ Hz, 3H), 0.86 ppm (t, $J=6.8$ Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta=155.2$, 153.6, 147.6, 147.1, 140.5, 139.0, 138.7, 136.8, 135.5, 134.6, 130.9, 130.0, 129.1, 128.4, 127.1, 126.7, 123.6, 123.2, 122.6, 120.8, 119.6, 119.1, 47.0, 31.7, 31.6, 30.5, 30.1, 29.5, 29.2, 28.9, 28.5, 28.0, 27.2, 22.7, 14.3, 14.2 ppm; MS: *m*/*z*: 863 [M^+]; elemental analysis calcd (%) for $C_{54}H_{56}BrNS_2$: C 75.15, H 6.54; found: C 74.98, H 6.48.

N-(9,9-Dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-*N*-[4-(3,3′,6,6′-tetrahexyl-2,2′-bithieno[3,2-*b*]thiophen-5-yl)phenyl]-9*H*-fluoren-2-amine (10): Compound **10** was synthesized by a similar procedure to that described for **8**, except that **9** (0.5 g, 0.58 mmol) was used in place of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline. Yield: 67%. M.p. 182°C; ^{1}H NMR ($CDCl_3$): δ=7.65 (t, J=7.8 Hz, 2H), 7.63 (d, J=8.2 Hz, 2H), 7.40 (d, J=8.2 Hz, 2H), 7.35 (t, J=7.8 Hz, 2H), 7.33–7.25 (m, 6H), 7.24 (s, 2H), 7.16 (d, J=7.6 Hz, 2H), 7.00 (s, 1H), 2.82 (t, J=7.8 Hz, 2H), 2.81–2.71 (m, 6H), 1.81–1.71 (m, 8H), 1.43 (s, 12H), 1.34–1.24 (m, 24H), 0.89 (t, J=6.8 Hz, 3H), 0.88–0.86 (m, 6H), 0.85 ppm (t, J=6.8 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=155.2, 153.6, 147.6, 147.2, 140.4, 139.3, 139.0, 136.8, 135.5, 135.3, 134.6, 132.3, 132.1, 132.0, 130.8, 130.1, 128.8, 128.7, 128.5, 127.1, 126.7, 125.6, 123.6, 123.3, 122.6, 120.8, 119.6, 119.0, 47.0, 31.8, 31.7, 31.6, 31.5, 30.5, 30.4, 30.0, 29.8, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.7, 14.3, 14.2, 14.1 ppm; MS: *m*/*z*: 1090 [M^+]; elemental analysis calcd (%) for $C_{72}H_{83}NS_4$: C 79.29, H 7.67; found: C 78.98, H 7.43.

5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]phenyl}-3,3′,6,6′-tetrahexyl-2,2′-bithieno[3,2-*b*]thiophene-5′-carbaldehyde (11): Compound **11** was synthesized by a procedure similar to that described for **6**, except that **10** (0.5 g, 0.58 mmol) was used in place of **4**. Yield: 83%. M.p. 172°C; ^{1}H NMR ($CDCl_3$): δ=10.1 (s, 1H), 7.65 (t, J=8.1 Hz, 2H), 7.64 (d, J=8.7 Hz, 2H), 7.40 (d, J=8.7 Hz, 2H), 7.33 (t, J=8.1 Hz, 2H), 7.30–7.25 (m, 6H), 7.22 (s, 2H), 7.16 (d, J=8.1 Hz, 2H), 3.11 (t, J=7.8 Hz, 2H), 2.83 (t, J=7.8 Hz, 2H), 2.71–2.68 (m, 4H), 1.81–1.71 (m, 8H), 1.43 (s, 12H), 1.34–1.24 (m, 24H), 0.88 (t, J=6.7 Hz, 3H), 0.88–0.86 (m, 6H), 0.83 ppm (t, J=6.7 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=182.6, 155.3, 153.6, 147.7, 147.1, 145.5, 145.3, 140.8, 139.3, 139.0, 138.2, 137.2, 137.0, 135.7, 134.6, 130.7, 130.1, 129.2, 128.5, 127.9, 127.1, 126.7, 123.6, 123.2, 122.6, 120.8, 119.6, 119.1, 47.0, 31.8, 31.7, 31.6, 31.4, 30.5, 30.4, 30.1, 29.9, 29.7, 29.5, 29.3, 29.2, 29.0, 28.8, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.6, 14.3, 14.2, 14.1 ppm; MS: *m*/*z*: 1118 [M^+]; elemental analysis calcd (%) for $C_{73}H_{83}NOS_4$: C 78.37, H 7.48; found: C 78.18, H 7.33.

(*Z*)-3-{5-[(*E*)-2-(5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]phenyl}-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)vinyl]-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl}-2-cyanoacrylic acid (JK-112): A mixture of **6** (0.16 g, 0.140 mmol) and cyanoacetic acid (0.024 g, 0.28 mmol) was vacuum-dried and then dissolved in MeCN (60 mL) containing piperidine (0.012 g, 0.140 mmol). The solution was refluxed for 6 h. After cooling, the volatiles were removed in vacuo. The pure product **JK-112** was obtained in 51% yield by silica gel chromatography (eluent CH_2Cl_2/MeOH, 2:1, R_f=0.6). M.p. 221°C; ^{1}H NMR ([D_6]DMSO): δ=8.20 (s, 1H), 7.77 (t, J=8.1 Hz, 2H), 7.50 (d, J=8.7 Hz, 2H), 7.42 (d, J=8.7 Hz, 2H), 7.32 (t, J=8.1 Hz, 2H), 7.30–7.25 (m, 6H), 7.24 (s, 2H), 7.21 (d, J=15.6 Hz, 1H), 7.13 (d, J=8.4 Hz, 2H), 7.10 (d, J=15.6 Hz, 1H), 7.08 (d, J=8.4 Hz, 2H), 3.19 (t, J=7.8 Hz, 2H), 2.93 (t, J=7.8 Hz, 2H), 2.71–2.68 (m, 4H), 1.81–1.71 (m, 8H), 1.37 (s, 12H), 1.34–1.24 (m, 24H), 0.82–0.79 ppm (m, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=166.1, 155.8, 154.9, 153.2, 152.1, 150.1, 147.7, 146.4, 145.5, 145.3, 140.8, 139.8, 139.0, 138.4, 137.2, 137.0, 135.7, 134.6, 133.4, 132.1, 130.7, 130.1, 129.4, 128.5, 127.8, 127.1, 126.8, 123.6, 123.4, 122.6, 120.3, 119.5, 119.1, 46.4, 31.8, 31.7, 31.6, 31.4, 30.5, 30.4, 30.1, 29.9, 29.7, 29.5, 29.3, 29.2, 29.0, 28.8, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.6, 14.3, 14.2, 14.1 ppm; MS: *m*/*z*: 1210 [M^+]; elemental analysis calcd (%) for $C_{78}H_{86}N_2O_2S_4$: C 77.31, H 7.15; found: C 77.14, H 7.01.

(*Z*)-3-{5-[(*E*)-2-(5-{6-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]benzo[*b*]thiophen-2-yl}-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl)vinyl]-3,6-dihexylthieno[3,2-*b*]thiophen-2-yl}-2-cyanoacrylic acid (JK-113): Compound **JK-113** was synthesized by a procedure similar to that described for **JK-112**, except that **7** (0.21 g, 0.175 mmol) was used in place of **6**. Yield: 53%. M.p. 197°C; ^{1}H NMR ($CDCl_3$): δ=8.19 (s, 1H), 7.77 (d, J=9.0 Hz, 1H), 7.69 (d, J=8.1 Hz, 2H), 7.61 (t, J=8.1 Hz, 2H), 7.58 (s, 1H), 7.39 (t, J=8.1 Hz, 2H), 7.36 (d, J=9.0 Hz, 1H), 7.32–7.28 (m, 4H), 7.25 (s, 2H), 7.22 (d, J=15.6 Hz, 1H), 7.16 (d, J=15.6 Hz, 1H), 7.13 (d, J=8.1 Hz, 2H), 7.10 (s, 1H), 3.07 (t, J=7.8 Hz, 2H), 2.96 (t, J=7.8 Hz, 2H), 2.82 (t, J=7.8 Hz, 4H), 1.85–1.71 (m, 8H), 1.43 (s, 12H), 1.34–1.24 (m, 24H), 0.89 (t, J=6.8 Hz, 3H), 0.88–0.86 (m, 6H), 0.85 ppm (t, J=6.8 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=166.2, 156.2, 155.6, 154.7, 148.5, 147.5, 146.5, 145.3, 143.7, 142.2, 141.1, 139.0, 138.4, 137.5, 136.5, 136.2, 134.8, 134.4, 134.1, 133.9, 133.8, 133.4, 132.8, 132.3, 131.8, 131.2, 130.8, 129.5, 128.5, 127.1, 126.7, 126.5, 126.3, 123.2, 122.7, 120.8, 119.5, 47.0, 31.8, 31.7, 31.6, 31.5, 30.5, 30.4, 30.0, 29.8, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.7, 14.3, 14.2, 14.1 ppm; MS: *m*/*z*: 1266 [M^+]; elemental analysis calcd (%) for $C_{80}H_{86}N_2O_2S_5$: C 75.78, H 6.84; found: C 75.34, H 6.67.

(*Z*)-3-(5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]phenyl}-3,3′,6,6′-tetrahexyl-2,2′-bithieno[3,2-*b*]thiophen-5′-yl)-2-cyanoacrylic acid (JK-81): Compound **JK-81** was synthesized by a procedure similar to that described for **JK-112**, except that **11** (0.04 g, 0.036 mmol) was used in place of **6**. Yield: 83%. M.p. 172°C; ^{1}H NMR ([D_6]DMSO): δ=8.20 (s, 1H), 7.77 (t, J=8.1 Hz, 2H), 7.50 (d, J=8.7 Hz, 2H), 7.42 (d, J=8.7 Hz, 2H), 7.32 (t, J=8.1 Hz, 2H), 7.30–7.25 (m, 6H), 7.24 (s, 2H), 7.13 (d, J=8.4 Hz, 2H), 7.08 (d, J=8.4 Hz, 2H), 3.21 (t, J=7.8 Hz, 2H), 2.93 (t, J=7.8 Hz, 2H), 2.71–2.68 (m, 4H), 1.81–1.71 (m, 8H), 1.37 (s, 12H), 1.34–1.24 (m, 24H), 0.82–0.79 ppm (m, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=166.1, 154.9, 153.2, 147.7, 146.4, 145.5, 145.3, 140.8, 139.8, 139.0, 138.4, 137.2, 137.0, 135.7, 134.6, 130.7, 130.1, 129.4, 128.5, 127.8, 127.1, 126.8, 123.6, 123.4, 122.6, 120.3, 119.5, 119.1, 46.4, 31.8, 31.7, 31.6, 31.4, 30.5, 30.4, 30.1, 29.9, 29.7, 29.5, 29.3, 29.2, 29.0, 28.8, 28.7, 28.5, 28.3, 28.0, 27.8, 27.6, 27.1, 22.6, 14.3, 14.2, 14.1 ppm; MS: *m*/*z*: 1184 [M^+]; elemental analysis calcd (%) for $C_{76}H_{84}N_2O_2S_4$: C 76.98, H 7.14; found: C 76.54, H 7.03.

Device preparation (DSSC using liquid electrolyte): Photoanodes composed of nanocrystalline TiO_2 were prepared according to a previously reported procedure.[14] A paste composed of 20 nm anatase TiO_2 particles for the transparent nanocrystalline layer was coated onto fluorine-doped tin oxide (FTO) glass plates (Nippon Sheet Glass, 4 mm thickness) pretreated with $TiCl_4$ (40 mM) by repetitive screen printing to obtain a thickness of 8 μm. Then, a paste for the scattering layer containing 400 nm anatase particles (CCIC, HPW-400) was deposited onto the transparent nanocrystalline layer. The resulting layer had a thickness of around 5 μm. The TiO_2 electrodes were gradually sintered according to a programmed sequence: at 325°C for 5 min, at 375°C for 5 min, at 450°C for 15 min, and finally at 500°C for 15 min. The TiO_2 electrodes were further treated with $TiCl_4$ at below 70°C for 30 min and then sintered once more at 500°C for 30 min. Thereafter, they were immersed in dye solutions (0.3 mM in THF) at room temperature for 16–18 h. The dye-adsorbed TiO_2 electrode and a thermally platinized counter electrode were assembled into a sealed sandwich-type cell with a gap of a hot-melt ionomer film (Surlyn, thickness 25 μm, DuPont). Two different electrolyte solutions were used for the redox couple: electrolyte 1: 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI), 0.05 M I_2, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile; electrolyte 2: 0.2 M iodine, 0.5 M NMBI, 0.1 M GuNCS in PMII/EMINCS (13:7). An anti-reflection and UV cut-off film ($\lambda < 380$ nm, ARKTOP, Asahi Glass) was attached to the DSSC surface. To reduce scattered light from the edge of the dyed TiO_2 layer of the glass electrodes, a light-shading mask was placed on the DSSCs so that their active area was fixed at 0.159 cm^2.

Device preparation (ssDSSC): Details of the construction process for the solid-state solar cell have been described previously.[15] The cell consisted of an FTO glass substrate (15 Ω cm^{-2}, Pilkington) onto which a compact layer of approximately 100 nm TiO_2 had been deposited by spray pyrolysis. A nanoporous layer (film thickness ~2.1 μm) of 20 nm diameter TiO_2[16] was coated by screen printing. After the TiO_2 layer had been gradually sintered according to a programmed sequence (at 100°C for 10 min, at 150°C for 5 min, at 325°C for 10 min, at 450°C for 10 min, and finally at 500°C for 30 min), the film was treated with 40 mM aqueous $TiCl_4$ solution for 30 min at 70°C. The TiO_2 electrodes were immersed in the dye solutions (unless mentioned otherwise, 3 mM in THF) at room temperature in the dark for 3 h. After rinsing the electrodes, a hole-conducting matrix (see below) was applied by spin-coating (72 μL per 2.5 × 3 cm^2 area, spinning for 30 s at 2000 rpm). Fabrication of the device was completed by evaporating a 100 nm gold electrode on the top surface. The active area of each ssDSSC was about 0.2 cm^2.

Preparation of the hole-conducting matrix: 2,2′,7,7′-Tetrakis(*N*,*N*-dimethoxyphenylamine)-9,9′-spiro-bifluorene (spiro-OMeTAD) (72 mg) was dissolved in C_6H_5Cl (420 μL) at 60 °C. Distilled 4-*tert*-butylpyridine (TBP) (7 μL) and 15 μL of a solution of $Li[(CF_3SO_2)_2N]$ (17 mg) in MeCN (100 μL) were then added to the solution.

Device measurements: For photovoltaic measurements of the DSSCs, the irradiation source was a 450 W xenon lamp (Osram XBO 450, USA), the power of which as an AM 1.5 solar simulator was calibrated using a Tempax 113 solar filter (Schott). The output power of an AM 1.5 solar simulator was calibrated using a reference Si photodiode equipped with a colour-matched IR cut-off filter (KG-3, Schott) to reduce the mismatch in the region 350–750 nm between the simulated light and AM 1.5. The measured IPCE values were plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.).

Impedance measurements: AC impedance measurements were made under illumination (1 sun) and in dark conditions using an impedance analyzer (1260 A, Solartron, UK).

Cyclic voltammetry: Cyclic voltammetry was carried out with a BAS 100 B apparatus (Bioanalytical Systems, Inc.). A three-electrode system was used, which consisted of a gold disk, a working electrode, and a platinum wire electrode. The redox potentials of the dyes on TiO_2 were measured in CH_3CN with 0.1 M $(nC_4H_9)_4N{\cdot}PF_6$ as supporting electrolyte at a scan rate of 50 $mV\,s^{-1}$ (vs. Fc/Fc^+).

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