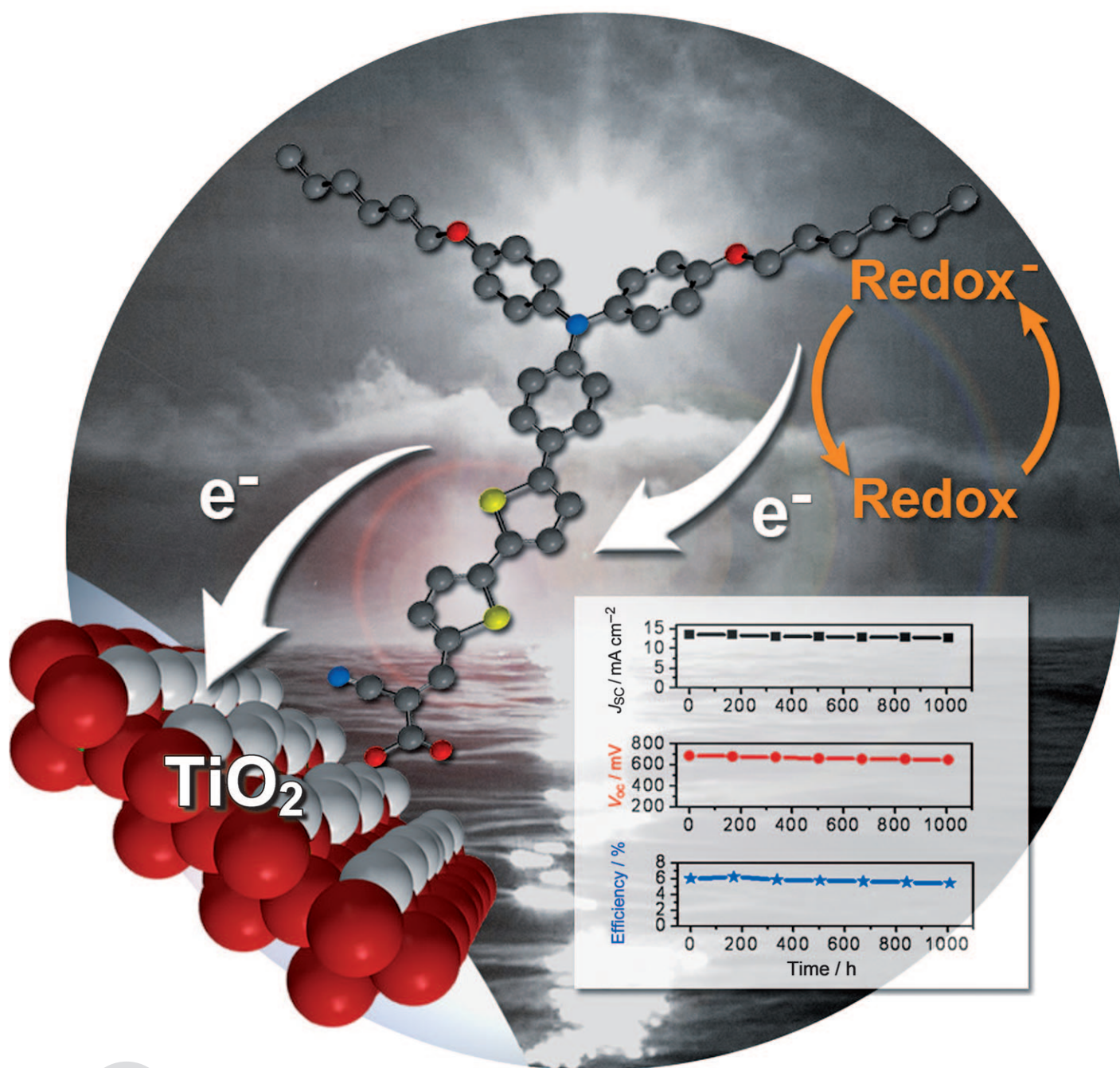


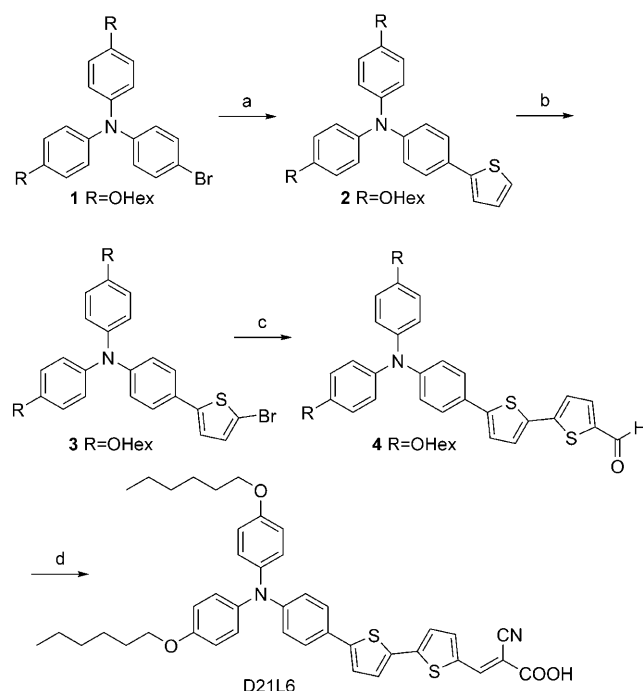
# A Light-Resistant Organic Sensitizer for Solar-Cell Applications\*\*

Jun-Ho Yum, Daniel P. Hagberg, Soo-Jin Moon, Karl Martin Karlsson, Tannia Marinado, Licheng Sun,\* Anders Hagfeldt, Mohammad K. Nazeeruddin,\* and Michael Grätzel



The conversion of sunlight to electricity by using dye-sensitized solar cells (DSCs) represents one of the most promising methods for future large-scale power production from renewable energy sources.<sup>[1]</sup> The sensitizer, which harvests the solar radiation and converts it to electric current, is one of the key components of these cells. Over the last 17 years, ruthenium complexes have exhibited remarkable efficiency and stability in DSCs. However, there are several challenges that limit their development for large-scale applications. Therefore, several research groups have developed metal-free organic sensitizers and obtained respectable efficiencies compared to the ruthenium sensitizers.<sup>[2]</sup> The main disadvantage of the organic sensitizers is their stability, which is generally lower than that of metal complexes, because of side reactions such as formation of excited triplet states and unstable radicals. Herein, we report a meticulously engineered organic sensitizer that exhibits not only an efficiency that is superior to that of ruthenium sensitizers in solid DSCs but also remarkable stability under light- and heat-soaking conditions with liquid electrolyte where the overall efficiency of the DSC remained at 90 % of the initial value after 1000 hrs.

The organic sensitizer 3-(5-(4-(bis(4-(hexyloxy)phenyl)thiophene-2-yl)thiophene-2-yl)-2-cyanoacrylic acid (D21L6) was synthesized by following the procedure reported by Plater and Jackson, in which aniline was functionalized by the Ullmann arylation.<sup>[3]</sup> In our case, a disubstituted triphenylamine **2** was utilized, which was then brominated by *N*-bromosuccinimide (NBS) to give the disubstituted triphenylamine bromide **3** (Scheme 1). The first Suzuki coupling reaction<sup>[4]</sup> was carried out with 2-thienylboronic acid and substituted triphenylamine bromide **1** under microwave irradiation. The thiophene moiety was brominated at the fifth position with NBS to provide **3**. The second Suzuki coupling reaction was carried out with unprotected 5-formyl-



**Scheme 1.** Synthesis of the D21L6 sensitizer. Reagents and conditions: a) 2-thienylboronic acid, [Pd(dppf)Cl<sub>2</sub>], K<sub>2</sub>CO<sub>3</sub>, toluene/MeOH (3:2), 75 °C, mw, 64 %; b) NBS, THF, 0 °C, 77 %; c) 5-formyl-2-thiopheneboronic acid, [Pd(dppf)Cl<sub>2</sub>], K<sub>2</sub>CO<sub>3</sub>, toluene/MeOH (3:2), 75 °C, mw, 45 %; d) cyanoacetic acid, piperidine, MeCN, reflux, D21L6: 70 % (step d). mw = microwave irradiation.

2-thiopheneboronic acid under microwave irradiation to directly produce the aldehyde **4**, which was necessary for the following reaction.<sup>[5]</sup> The final reaction was condensation of the aldehyde with cyanoacetic acid by the Knoevenagel reaction in presence of piperidine. The bridging thiophene units are used to provide conjugation between the donor triphenylamine and the anchoring cyanoacetic acid group. The hydrophobic hexyloxy groups are attached to the donor group in order to reduce the aggregation and enhance the solubility of the sensitizer.

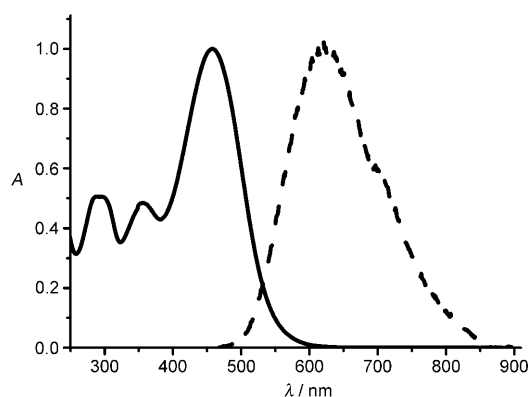
The D21L6 sensitizer shows an absorption maximum in the visible region at 458 nm, with a high molar extinction coefficient ( $\epsilon = 37\,000\text{ M}^{-1}\text{ cm}^{-1}$ ), which arises from  $\pi$ - $\pi^*$  charge transfer (CT) transitions (Figure 1). The cyclic voltammogram of the D21L6 sensitizer measured with a 0.1 V s<sup>-1</sup> scan rate in acetonitrile containing tetrabutylammonium tetrafluoroborate (0.1 M) shows a reversible couple that arises from oxidation of the substituted triphenylamine-bithiophene groups at 0.98 V versus the normal hydrogen electrode (NHE). The excited-state oxidation potential of the sensitizer, which is -1.35 V versus NHE, as obtained from the absorption and emission spectra of D21L6, plays an important role in the electron injection process. The excited state oxidation potential is notably more negative than the TiO<sub>2</sub> conduction band. On the other hand, the oxidation potential of D21L6 is more positive than the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple (ca. 0.4 V versus NHE), which ensures that there is a sufficient driving force for electron injection, and for the

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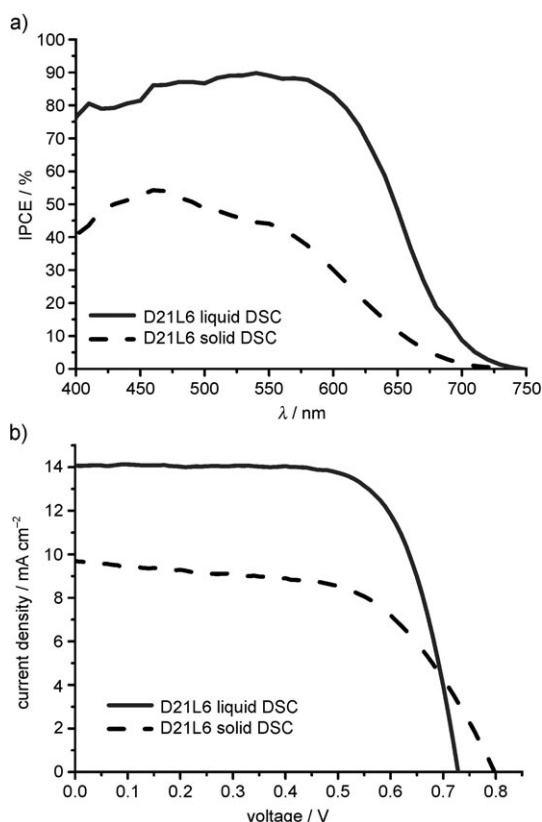
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**Figure 1.** Normalized UV/Vis absorption (solid line) and emission (dashed line) spectra of D21L6 in ethanol.

dye regeneration reaction to compete efficiently with recapture of the injected electrons by the dye cation radical.

The photovoltaic performance characteristics of D21L6-sensitized solar cells with liquid and solid-state electrolyte are shown in Figure 2a,b. The incident monochromatic photon-to-current conversion efficiency (IPCE) and current–voltage ( $J/V$ ) characteristics were obtained with a sandwich cell comprising *N*-methyl-*N*-butyl imidazolium iodide (0.6 M), iodine (0.04 M), LiI (0.02 M), guanidinium thiocyanate (GuNCS, 0.05 M), and *tert*-butylpyridine (0.28 M) in a valeronitrile/acetonitrile mixture (15:85 v/v) as the liquid electro-



**Figure 2.** a) Photocurrent action spectrum and b) current–voltage characteristics of D21L6-sensitized solar cells with volatile (solid lines) and solid-state electrolyte (dashed lines).

lyte. The IPCE data of D21L6 plotted as a function of excitation wavelength exhibit a high plateau value of 90%. Strikingly, the IPCE is still close to 90% at 600 nm where the light absorption of the sensitizer in solution is negligibly small. This important red shift in the photocurrent response is attributed to lateral interaction in the adsorbed monolayer of the sensitizer and warrants further analysis. Under standard global AM 1.5 solar conditions, the D21L6-sensitized cell gave a short-circuit photocurrent density value ( $J_{sc}$ ) of  $14.10 \text{ mA cm}^{-2}$ , an open-circuit voltage value ( $V_{oc}$ ) of 728 mV and a fill factor ( $ff$ ) of 0.71, which correspond to an overall conversion efficiency  $\eta$ , derived from the equation  $\eta = J_{sc} \times V_{oc} \times ff / \text{light intensity}$ , of 7.25%. The DSC demonstrated an almost-linear behavior under different light intensities (Table 1). The integrated current of IPCE is  $14.2 \text{ mA cm}^{-2}$  which is consistent with  $J_{sc}$  of  $14.1 \text{ mA cm}^{-2}$  under standard global AM1.5 solar conditions.

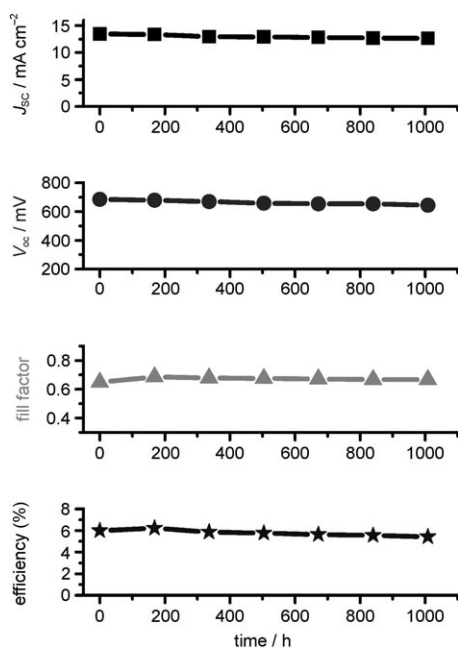
**Table 1:**  $J/V$  characteristics of D21L6-sensitized solar cells with either volatile or solid-state electrolytes under different light intensities.

	Intensity [% sun]	$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	$V_{oc}$ [mV]	$ff$	$\eta$ [%]
liquid	9.30	1.39	666	0.77	7.49
	51.62	7.50	712	0.74	7.45
	100.19	14.10	728	0.71	7.25
solid	9.32	0.78	740	0.73	4.51
	51.26	4.83	791	0.62	4.64
	99.52	9.64	798	0.57	4.44

For the solid-state dye-sensitized solar cells (SSDSCs), a 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD) hole conductor was used as a redox couple.<sup>[6]</sup> The SSDSC exhibited  $J_{sc} = 9.64 \text{ mA cm}^{-2}$ ,  $V_{oc} = 798 \text{ mV}$ , and  $ff = 0.57$ , which led to an overall conversion efficiency,  $\eta$ , of 4.44% under standard global AM 1.5 solar conditions, which is a high value for a SSDSC based on organic<sup>[6a]</sup> and ruthenium sensitizers reported to date.<sup>[7]</sup> After submission of this manuscript a D- $\pi$ -A sensitizer employing a fused thiophene dimer unit as a  $\pi$  bridge was reported that reached 4.8% conversion efficiency in a SSDSC.<sup>[2b]</sup> The IPCE value of the SSDSCs was 54% at 460 nm (Figure 2a), which is somewhat lower than the IPCE over 500–620 nm of liquid DSCs; this arises from a lower light-harvesting yield because of the use of a thinner  $\text{TiO}_2$  film. When the film thickness (1.7  $\mu\text{m}$ ) of  $\text{TiO}_2$  is considered, the results from D21L6 are promising with regards to applications in solid-state cells. A further advantage of the solid-state devices is the  $V_{oc}$  value obtained (798 mV), which is higher than that of the liquid-electrolyte cells (728 mV). This is not only due to the redox level of the hole conductor, which is more positive than the respective  $\text{I}^-/\text{I}_3^-$  couple used in the latter but also because of the thinner  $\text{TiO}_2$  film which helps to decrease the dark current.

Figure 3 shows the photovoltaic performance during a long-term accelerated aging of a D21L6-sensitized solar cell using an ionic liquid electrolyte in a solar simulator at full intensity ( $100 \text{ mW cm}^{-2}$ ) and 60°C. The  $J_{sc}$ ,  $V_{oc}$ ,  $ff$ , and  $\eta$  values were recorded over a period of 1000 h (Table 2). The overall efficiency remained at 90% of the initial value after 1000 h of light soaking at 60°C. This 10% decrease is caused





**Figure 3.** Variations of photovoltaic parameters ( $J_{sc}$ ,  $V_{oc}$ ,  $ff$ , and  $\eta$ ) with aging time for the device based on (7 + 5)  $\mu\text{m}$  film sensitized with D21L6 and ionic liquid electrolyte during successive 1 sun visible-light soaking at 60 °C.

**Table 2:**  $J/V$  characteristics of the D21L6-sensitized solar cell with ionic liquid electrolyte during continuous 1 sun visible-light soaking at 60 °C.

Aging time [h]	$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	$V_{oc}$ [mV]	$ff$	$\eta$ [%]
0	13.44	686	0.65	5.98
500	12.91	659	0.68	5.75
1008	12.63	644	0.67	5.44

by the slight drop of 42 mV in the  $V_{oc}$  and 0.8  $\text{mA cm}^{-2}$  in the  $J_{sc}$  values. An average of  $J_{sc} = 13.04 \text{ mA cm}^{-2}$  during 1000 h of light soaking means that the total charge passed through a surface area of 1  $\text{cm}^2$  is equal to 46944 coulombs. When a surface concentration of  $10^{-7} \text{ moles cm}^{-2}$  for the sensitizer is used, a turnover number of 4.69 million can be derived, which the D21L6 dye sustains without any noticeable decline in performance. This demonstrates that the amount of dye on the  $\text{TiO}_2$  surface remained intact after light soaking at 60 °C. To the best of our knowledge, this is the most remarkable stability for organic sensitizer.

In summary, we have demonstrated that meticulous engineering of organic sensitizer, D21L6, yielded very high incident monochromatic photon-to-current conversion efficiency and remarkable stability, which we believe is a breakthrough in the field of organic sensitizers useful for photovoltaic applications. We conclude that the organic sensitizer D21L6 is indeed a promising low-cost material for dye-sensitized solar cells.

## Experimental Section

Dichloromethane, dimethylformamide (DMF), hexane, and tetrahydrofuran (THF) were dried by passing through a solvent column composed of activated alumina.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were

recorded on Bruker 500 and 400 MHz instruments by using the residual signals  $\delta = 7.26 \text{ ppm}$  and  $77.0 \text{ ppm}$  from  $\text{CDCl}_3$ ,  $\delta = 2.50$  and  $39.4 \text{ ppm}$  from  $[\text{D}_6]\text{DMSO}$  and  $\delta = 2.05$ ,  $29.84$ , and  $206.26 \text{ ppm}$  from  $[\text{D}_6]\text{acetone}$ , as internal references for  $^1\text{H}$  and  $^{13}\text{C}$  respectively. HRMS were performed using a Q-ToF Micro (Micromass Inc., Manchester, England) mass spectrometer equipped with a Z-spray ionization source.

**4-Bromo-*N,N*-bis(4-hexyloxyphenyl)aniline (1):** Aniline (1.02 g, 10.4 mmol), copper powder (0.919 g, 10 mmol),  $\text{K}_2\text{CO}_3$  (16.36 g, 118 mmol), 18-crown-6 (50 mg), and 1-(hexyloxy)-4-iodobenzene (18.0 g, 303.9 mmol) was heated to reflux at 190 °C with stirring under a nitrogen atmosphere for 48 h. The reaction mixture was allowed to cool to ambient temperature and was dissolved in  $\text{CH}_2\text{Cl}_2$ . The solution was washed with distilled water the organic phase was dried with  $\text{MgSO}_4$  and concentrated by evaporation. Column chromatography using petroleum ether/DCM 9:1 gave *N,N*-bis(4-hexyloxyphenyl)aniline as a pale yellow oil (2.05 g, 46 %). A solution of *N,N*-bis(4-hexyloxyphenyl)aniline (1.485 g, 3.34 mmol) in THF (20 mL) was cooled to 0 °C. NBS (562 mg, 3.34 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 3 h. The reaction was quenched by addition of water and extracted with DCM. The combined organic extract was dried over anhydrous  $\text{MgSO}_4$  and filtered. Solvent removal by rotary evaporation followed by column chromatography over silica gel using petroleum ether/DCM 8:1 yielded **1** as a pale yellow oil (1.7 g, 96 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.22$  (d,  $J = 8.6 \text{ Hz}$ , 2H), 7.00 (d,  $J = 8.0 \text{ Hz}$ , 4H), 6.81 (d,  $J = 8.8 \text{ Hz}$ , 4H), 6.78 (d,  $J = 9.4 \text{ Hz}$ , 2H), 3.92 (t,  $J = 6.4 \text{ Hz}$ , 4H), 1.77 (m, 4H), 1.45 (m, 4H), 1.34 (m, 8H), 0.91 ppm (t,  $J = 7.0 \text{ Hz}$ , 6H).  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_6]\text{acetone}$ ):  $\delta = 157.5$ , 150.9, 142.7, 130.7, 128.3, 122.3, 122.2, 117.1, 69.7, 33.3, 31.1, 27.5, 24.3, 15.3 ppm.

**4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(thiophene-2-yl)phenyl)benzenamine (2):** A solution of 2-thienylboronic acid (122 mg, 0.95 mmol) and  $\text{K}_2\text{CO}_3$  (329 mg, 2.36 mmol) in dry methanol (2 mL) was added to a solution of **1** (250 mg 0.48 mmol) and  $[\text{Pd}(\text{dppf})\text{Cl}_2]$  (39 mg 0.048 mmol) in dry toluene (3 mL). The mixture was heated by microwave irradiation at 75 °C for 20 min. The reaction was quenched by the addition of water (30 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  30 mL). The combined organic extracts were dried over anhydrous  $\text{MgSO}_4$  and filtered. Solvent removal by rotary evaporation followed by column chromatography over silica gel using petroleum ether gave **2** as a pale yellow oil (168 mg, 64 %).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]\text{acetone}$ ):  $\delta = 7.45$  (d,  $J = 8.7 \text{ Hz}$ , 2H), 7.31 (d,  $J = 4.5 \text{ Hz}$ , 1H), 7.27 (d,  $J = 4.5 \text{ Hz}$ , 1H), 7.04 (d,  $J = 8.9 \text{ Hz}$ , 4H), 6.90 (d,  $J = 8.9 \text{ Hz}$ , 4H), 6.86 (d,  $J = 8.7 \text{ Hz}$ , 2H), 3.9 (t,  $J = 6.4 \text{ Hz}$ , 4H), 1.76 (m, 4H), 1.47 (m, 4H), 1.36 (m, 8H), 0.91 ppm (t,  $J = 7.0 \text{ Hz}$ , 6H);  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_6]\text{acetone}$ ):  $\delta = 157.8$ , 150.4, 142.2, 129.9, 128.7, 128.2, 128.1, 125.4, 123.6, 121.8, 117.2, 69.8, 33.6, 31.0, 27.8, 24.3, 15.3. HRMS (TOF-MS-ESI)  $m/z$ : 527.2847 [ $M^+$ ]; calcd for  $\text{C}_{34}\text{H}_{41}\text{NO}_2\text{S}$  [ $M^+$ ]: 527.2858.

***N*-(4-(5-bromothiophen-2-yl)phenyl)-4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)benzenamine (3):** NBS (144 mg, 0.81 mmol) was added in one portion to a solution of **2** (426 mg, 0.81 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h. The reaction was quenched by the addition of water and extracted with DCM. The combined organic extract was dried over anhydrous  $\text{MgSO}_4$  and filtered. Solvent removal by rotary evaporation followed by column chromatography over silica gel using petroleum ether/DCM 8:1 gave **3** as a pale yellow oil (375 mg, 77 %).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]\text{acetone}$ ):  $\delta = 7.39$  (d,  $J = 8.7 \text{ Hz}$ , 2H), 7.09 (m, 1H), 7.06 (d,  $J = 8.9 \text{ Hz}$ , 4H), 6.90 (d,  $J = 8.9 \text{ Hz}$ , 4H), 6.83 (d,  $J = 8.7 \text{ Hz}$ , 2H), 3.97 (t,  $J = 6.4 \text{ Hz}$ , 4H), 1.76 (m, 4H), 1.48 (m, 4H), 1.36 (m, 8H), 0.91 ppm (t,  $J = 7.0 \text{ Hz}$ , 6H);  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_6]\text{acetone}$ ):  $\delta = 158.0$ , 150.9, 148.2, 141.9, 133.2, 128.9, 128.0, 126.9, 123.9, 121.4, 117.3, 110.6, 69.8, 33.3, 31.1, 27.5, 24.3, 15.3 ppm; HRMS (TOF-MS-ESI)  $m/z$ : 605.2006 [ $M^+$ ]; calcd for  $\text{C}_{34}\text{H}_{40}\text{BrNO}_2\text{S}$  [ $M^+$ ]: 605.1958.

**5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophene-2-yl)thiophene-2-carbaldehyde (4):** Compound **3** (375 mg, 0.62 mmol),

5-formyl-2-thiopheneboronic acid (193 mg, 1.23 mmol), [Pd(dppf)Cl<sub>2</sub>] (50 mg, 0.06 mmol), and K<sub>2</sub>CO<sub>3</sub> (427 mg, 3.09 mmol) were dissolved in a mixture of toluene (3 mL) and methanol (2 mL). The mixture was heated by microwave irradiation at 75 °C for 15 min. The reaction was quenched by the addition of water (30 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic extracts were dried over anhydrous MgSO<sub>4</sub> and filtered. Solvent removal by rotary evaporation followed by column chromatography over silica gel using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> 4:1 gave **4** as an orange solid (178 mg, 45 %). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]acetone): δ = 9.90 (s, 1H), 7.90 (d, *J* = 4.0 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 3.9 Hz, 1H), 7.42 (d, *J* = 3.90 Hz, 1H), 7.32 (d, *J* = 3.9 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 4H), 6.85 (d, *J* = 8.9 Hz, 4H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 4H), 1.77 (m, 4H), 1.48 (m, 4H), 1.36 (m, 8H), 0.91 ppm (t, *J* = 6.9 Hz, 6H); <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]acetone): δ = 184.4, 158.1, 151.2, 148.3, 148.2, 143.5, 141.8, 140.1, 135.1, 129.5, 129.1, 128.3, 126.6, 125.9, 124.9, 121.1, 117.3, 69.8, 33.3, 31.1, 27.5, 24.3, 15.3 ppm; HRMS (TOF-MS-ESI) *m/z*: 637.2688 [*M*<sup>+</sup>]; calcd for C<sub>39</sub>H<sub>43</sub>NO<sub>3</sub>S<sub>2</sub> [*M*<sup>+</sup>]: 637.2679.

3-(5-(5-(4-(bis(4-(hexyloxy)phenyl)thiophene-2-yl)thiophene-2-yl)-2-cyanoacrylic acid (D21L6). Compound **4** (178 mg, 0.28 mmol), cyanoacetic acid (35 mg, 0.42 mmol), and piperidine (5 mg, 6.06 mmol) were dissolved in acetonitrile (10 mL) and heated under reflux for 3 h. The solvent was removed by rotary evaporation. Purification by extraction (petroleum ether and aqueous HCl (1 %)) gave the final compound D21L6 (137 mg, 70 %) as a dark red solid. m.p. 144.7–145.2 °C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO): δ = 8.25 (s, 1H), 7.78 (d, *J* = 4.0 Hz, 1H), 7.49 (m, 3H), 7.46 (d, *J* = 3.9 Hz, 1H), 7.36 (d, *J* = 3.8 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 4H), 6.90 (d, *J* = 8.8 Hz, 4H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.92 (t, *J* = 6.4 Hz, 4H), 1.68 (m, 4H), 1.41 (m, 4H), 1.29 (m, 8H), 0.86 ppm (t, *J* = 6.9 Hz, 6H); <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO): δ = 163.4, 155.5, 148.5, 145.2, 143.6, 139.3, 138.9, 134.4, 132.7, 128.8, 128.1, 127.5, 127.0, 126.3, 125.2, 124.1, 123.3, 118.6, 117.9, 115.5, 67.6, 30.9, 28.6, 25.1, 22.0, 13.8 ppm; HRMS (TOF-MS-ESI) *m/z*: 704.2707 [*M*<sup>+</sup>]; calcd. for C<sub>42</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> [*M*<sup>+</sup>]: 704.2737.

Solar-cell fabrication and characterization: The photoanodes composed of nanocrystalline TiO<sub>2</sub> were prepared according to a previously reported procedure.<sup>[8]</sup> The TiO<sub>2</sub> electrodes were immersed in a solution of D21L6 (0.3 mM in ethanol) and kept at room temperature for 15 h. An electrolyte solution (*N*-methyl-*N*-butyl imidazolium iodide (0.6 M), iodine (0.04 M), LiI (0.025 M), GuNCS (0.05 M), and *tert*-butylpyridine (0.28 M) in a mixture of valeronitrile and acetonitrile (15:85 v/v) was used for the redox couple. For stability tests, the binary ionic-liquid electrolyte consisted of iodine (0.2 M), *N*-butyl benzimidazole (NBB, 0.5 M), and GuNCS (0.1 M) in a mixture of 1-propyl-3-methylimidazolium iodide (PMII) and 1-ethyl-3-methyl-imidazolium tetracyanoborate (EMIB(CN)<sub>4</sub>, Merck; 65:35 v/v).<sup>[9a]</sup> NBB was synthesized according to a published procedure.<sup>[9b]</sup> The *J/V* characteristics and IPCE of the DSCs were measured by using previously reported techniques.<sup>[8]</sup> The measurement delay time of photo *J/V* characteristics of DSCs was fixed to 40 ms for volatile electrolyte and 200 ms for ionic-liquid electrolyte, respectively. The detailed procedure for solid-state solar cell fabrication was described previously.<sup>[6]</sup> A nanoporous layer (ca. 1.7 μm) of TiO<sub>2</sub> (20 nm) was prepared for photoanode and the hole-transporting materials used was Spiro-MeOTAD, which was dissolved in chlorobenzene. *tert*-Butylpyridine and Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N were added as additives. The device fabrication was completed by evaporating a 50 nm gold electrode over the top of the cell.

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- [1] a) B. O'Regan, M. Grätzel, *Nature* **1991**, 353, 737–740; b) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, 115, 6382; c) L. M. Peter, K. G. U. Wijayantha, *Electrochim. Acta* **2000**, 45, 4543; d) K. Hara, H. Sugihara, Y. Tachibana, A. Islam, M. Yanagida, K. Sayama, H. Arakawa, G. Fujihashi, T. Horiguchi, T. Kinoshita, *Langmuir* **2001**, 17, 5992; e) P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, *Nat. Mater.* **2003**, 2, 402; f) A. J. Frank, N. Kopidakis, J. van de Lagemaat, *Coord. Chem. Rev.* **2004**, 248, 1165; g) Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L. Y. Han, *Jpn. J. Appl. Phys. Part 2* **2006**, 45, L638; h) M. K. Nazeeruddin, M. Grätzel, *Struct. Bonding (Berlin)* **2007**, 123, 113.
- [2] a) K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, *J. Phys. Chem. B* **2003**, 107, 597; b) T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, *J. Am. Chem. Soc.* **2004**, 126, 12218; c) K. Hara, Z.-S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, *J. Phys. Chem. B* **2005**, 109, 15476; d) D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, *Chem. Commun.* **2006**, 2245; e) D. P. Hagberg, J. H. Yum, H. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. C. Sun, A. Hagfeldt, M. Grätzel, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2008**, 130, 6259; f) M. Xu, R. Li, N. Pootrakulchote, D. Shi, J. Guo, S. M. Zakeeruddin, M. Grätzel, P. Wang, *J. Phys. Chem. C* **2008**, 112, 19770; g) H. Qin, S. Wenger, M. Xu, F. Gao, X. Jing, P. Wang, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2008**, 130, 920; h) M. Wang, M. Xu, D. Shi, R. Li, F. Gao, H. Zhang, Z. Yi, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, *Adv. Mater.* **2008**, 20, 4460; i) C. Kim, H. Choi, S. Kim, C. Baik, K. Song, M.-S. Kang, S. O. Kang, J. Ko, *J. Org. Chem.* **2008**, 73, 7072; j) J. J. Kim, H. Choi, J.-W. Lee, M.-S. Kang, K. Song, S. O. Kang, J. Ko, *J. Mater. Chem.* **2008**, 18, 5223; k) H. Choi, C. Baik, S. O. Kang, J. Ko, M.-S. Kang, M. K. Nazeeruddin, M. Grätzel, *Angew. Chem.* **2008**, 120, 333; *Angew. Chem. Int. Ed.* **2008**, 47, 327; l) J.-J. Cid, J.-H. Yum, S.-R. Jang, M. K. Nazeeruddin, E. Martínez-Ferrero, E. Palomares, J. Ko, M. Grätzel, T. Torres, *Angew. Chem.* **2007**, 119, 8510; *Angew. Chem. Int. Ed.* **2007**, 46, 8358; m) H. Yum, S.-R. Jang, P. Walter, T. Geiger, F. Nüesch, S. Kim, J. Ko, M. Grätzel, M. K. Nazeeruddin, *Chem. Commun.* **2007**, 4680; n) S. Kim, J. K. Lee, S. O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, M. K. Nazeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2006**, 128, 16701.
- [3] M. J. Plater, T. Jackson, *Tetrahedron* **2003**, 59, 4673.
- [4] A. Suzuki, *J. Organomet. Chem.* **1999**, 576, 147.
- [5] M. Melucci, G. Barbarella, M. Zambianchi, P. Di Pietro, A. Bongini, *J. Org. Chem.* **2004**, 69, 4821.
- [6] a) L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida, M. Grätzel, *Adv. Mater.* **2005**, 17, 813; b) H. J. Snaith, L. Schmidt-Mende, M. Grätzel, M. Chiesa, *Phys. Rev. B* **2006**, 74, 045306.
- [7] a) L. Schmidt-Mende, S. M. Zakeeruddin, M. Grätzel, *Appl. Phys. Lett.* **2005**, 86, 013504; b) H. J. Snaith, A. J. Moule, C. Klein, K. Meerholz, R. H. Friend, M. Grätzel, *Nano Lett.* **2007**, 7, 3372; c) D. Kuang, C. Klein, H. J. Snaith, R. Humphry-Baker, S. M. Zakeeruddin, M. Grätzel, *Inorg. Chim. Acta* **2008**, 361, 699; d) J.-H. Yum, P. Chen, M. Grätzel, *ChemSusChem* **2008**, 1, 699.
- [8] M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, C. Le, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* **2001**, 123, 1613.
- [9] a) D. Kuang, P. Wang, S. Ito, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2006**, 128, 7732; b) D. Kuang, C. Klein, S. Ito, J. E. Moser, R. Humphry-Baker, N. Evans, F. Durrant, C. Grätzel, S. M. Zakeeruddin, M. Grätzel, *Adv. Mater.* **2007**, 19, 1133.