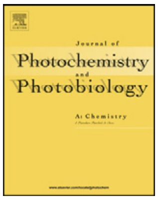
Journal of Photochemistry and Photobiology A: Chemistry 219 (2011) 122–131

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



A new class of organic sensitizers with fused planar triphenylamine for nanocrystalline dye sensitized solar cells

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ARTICLE INFO

Article history:
Received 2 August 2010
Received in revised form 4 January 2011
Accepted 1 February 2011
Available online 2 March 2011

Keywords:
Fused triphenylamine
Organic dye
Dye-sensitized solar cell
DSSCs

ABSTRACT

Five novel organic sensitizers that contain a fused-planar triphenylamine as electron donor have been synthesized and their photophysical properties, theoretical calculation and photovoltaic performances as well as stability test have been studied. Under standard AM 1.5 sunlight, the sensitizer **JK-164** yielded a short-circuit photocurrent density of 15.32 mA cm^{-2}, an open-circuit voltage of 0.70 V, and a fill factor of 0.74, corresponding to an overall conversion efficiency of 7.86%. The **JK-164** cell exhibits an excellent stability, revealing a slight change after 1000 h of light soaking at 60 °C using a solvent free ionic liquid. The cell shows a higher open-circuit voltage (V_{oc}) compared to that of **JK-163** due to an increased electron life time (τ_c) in the conduction band of TiO_2.

1. Introduction

The growing demands of a sustainable and renewable alternative to fossil fuels have aroused interest in photovoltaic devices [1]. Among several new energy technologies, dye-sensitized solar cells (DSSCs) have shown a significant promise as a cost-effective, efficient, and an environmentally friendly alternative to conventional solid photovoltaic devices [2,3]. For example, DSSCs based on polypyridyl ruthenium sensitizers were recently shown to demonstrate power conversion efficiencies of up to 11% [4–7]. However, the increasing costs and limited supplies of ruthenium place the long-term feasibility of the metal as sensitizer into question. Therefore, there is a need to develop new types of sensitizers that are composed of earth-abundant elements. Recently, metal-free organic sensitizers have garnered interest as their low-cost and environmentally benign component. Some organic dyes have been utilized as promising sensitizers, and impressive photovoltaic performance has been reported with coumarin [8–10], indoline [11–14], oligoene [15–17], merocyanine [18–21], triphenyl amine [22–24], and fluorenyl amino dyes [25–30], having efficiencies in the range of 7–9%. The main drawbacks of organic sensitizers compared to the ruthenium sensitizers are the sharp and narrow bands in the visible region [31–33], the formation of dye aggregate on the semiconductor surface [34–40], and the interfacial recombination dynamics [41–43]. Our strategy toward the high photovoltaic performance of organic dye sensitized solar cell is based on the molecular engineering to diminish the charge recombination between the electrons and acceptors and to prevent the aggregation of dye. A successful approach was achieved by incorporating a fused planar amine unit as the electron donor, which not only lengthened the lifetime of the charge-separated state by the delocalization of the generated cation through a planar amine ring, but also exhibited the decreased electronic coupling between the surface and the hole, leading to an increase of open-circuit voltage (V_{oc}). A planarization around nitrogen atom will induce a red shift of the absorption spectrum due to the expansion of π-electron systems conjugated with aromatic units [44,45]. A bulky substituent attached on the fused amine ring prevents dye-aggregation as well as increases electron lifetime (τ_c) of the dye in the conduction band of TiO_2.

In this article, as part of our efforts to develop novel organic dyes, we report new type of organic dyes (**JK-160**, **JK-161**, **JK-162**, and **JK-163**, **JK-164**) containing a planar triphenylamine as the electron donor and cyanoacrylic acid as the electron acceptor bridged by a variety of linkers (Fig. 1).

2. Experimental

2.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All

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doi:10.1016/j.jphotochem.2011.02.001

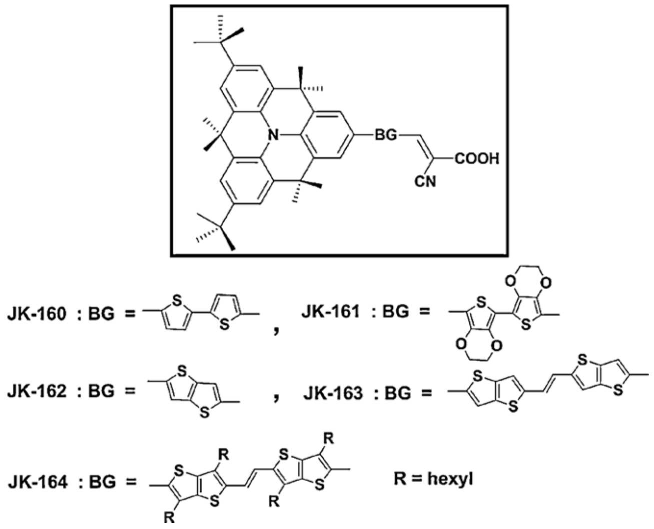


Fig. 1. The structure of **JK-160**, **JK-161**, **JK-162**, **JK-163**, and **JK-164**.

reagents were purchased from Sigma–Aldrich. 2-Bromo-DHBQA (DHBQA = 6,10-di-*tert*-butyl-4,4,8,8,12,12-hexamethyl-4*H*,8*H*,12 *H*-benzo-[1,9]quinolizino[3,4,5,6,7,-*defg*]acridine) (**1**) [46,47], 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dime-thyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (**2**) [48], Pt $(PEt_3)_4$ [49], 2-(2,3-dihydro-5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) thieno[3,4-b][1,4]dioxin-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) [50], 4,4,5,5-tetramethyl-2-(2-(5,5-dimeth-yl-1,3-dioxan-2-yl)thieno[3,2-b]thiophen-5-yl)-1,3,2-dioxaborolane (**8**) [51], 4,4,5,5-tetram-ethyl-2-(2-(2-(thieno[3,2-b]thiophen-2-yl)vinyl)thieno[3,2-b]thiophen-5-yl)-1,3,2-diox-aborolane (**11**) [51,52], 2-(3,6-dihexyl-2-(2-(3,6-dihexylthieno[3,2-b]thiophen-2-yl)vinyl)thi-eno[3,2-b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**) [52], were synthesized using a modified procedure of previous references. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively.

2.2. Cyclovoltagram

Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.). A three-electrode system was used and consisted of a gold disk working electrode and a platinum counter electrode. The redox potential of dyes measured under the conditions deposited on the TiO_2 surface in THF with 0.1 M $(n\text{-}C_4H_9)_4N\text{-}PF_6$ with a scan rate of 50 mV s^{-1}.

2.3. Electron transport measurements

The electron diffusion coefficient (D_e) and lifetimes (τ_e) in TiO_2 photoelectrode were measured by the stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV) [66–69]. The transients were induced by a stepwise change in the laser intensity. A diode laser (λ = 635 nm) as a light source was modulated using a function generator. The initial laser intensity was a constant 90 mW cm^{-2} and was attenuated up to approximately 10 mW cm^{-2} using a ND filter which was positioned at the front side of the fabricated samples (TiO_2 film thickness = ca. 10 μm; active area = 0.04 cm^2). The photocurrent and photovoltage transients were monitored using a digital oscilloscope through an amplifier. The D_e value was obtained by a time constant (τ_c) determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_c)$ and the TiO_2 film thickness (ω) using the equation, $D_e = \omega^2/(2.77\tau_c)$ [66]. The τ_e value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau_e)$ [66]. All experiments were carried out at room temperature.

2.4. Characterization of DSSC

The cells were measured using 1000 W xenon light source, whose power of an AM 1.5 Oriel solar simulator was calibrated by using KG5 filtered Si reference solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV Measurements).

2.5. Synthesis

2.5.1. 2-(5-(5-(DHBQA-2-yl)thiophen-2-yl) thiophen-2-yl)-5,5-dimethyl-1,3-dioxane (**3**)

To a stirred solution of 1 (0.23 g, 0.41 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) in tetrahydrofuran (10 mL) was added 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (**2**) (0.25 g, 0.61 mmol), potassium carbonate (0.22 g, 1.62 mmol) in THF (15 mL) and H_2O (5 mL). The mixture was refluxed for 18 h. After cooling the solution, H_2O (30 ml) was added to the solution and extracted by dichloromethane (30 mL × 3). The organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo*. The pure product **3** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:3) as an eluent (yield: 90%). Mp: 163 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (s, 2H), 7.38 (s, 4H), 7.40 (d, 1H, J = 3.6 Hz), 7.14 (d, 1H, J = 3.6 Hz), 7.07 (d, 1H, J = 3.6 Hz), 7.05 (d, 1H, J = 3.6 Hz), 5.64 (s, 1H), 3.71 (m, 4H), 1.68 (s, 6H), 1.66 (s, 12H), 1.37 (s, 18H), 1.31 (s, 3H), 0.81 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.8, 147.2, 145.3, 141.2, 139.9, 137.6, 133.7, 130.3, 129.7, 129.1, 127.4, 125.9, 123.7, 122.8, 121.3, 121.1, 120.4, 98.3, 77.6, 35.9, 34.6, 33.2, 31.5, 30.3, 29.8, 23.1, 21.9, 21.4. MS: m/z 755 [M$^+$]. Anal. Calcd. for $C_{49}H_{57}NO_2S_2$: C, 77.84; H, 7.60. Found: C, 77.62; H, 7.43.

2.5.2. 5-(5-(DHBQA-2-yl)thiophen-2-yl) thiophen-2-carbaldehyde (**4**)

THF (20 mL) and water (10 mL) were added to a flask containing acetal **2** (0.29 g, 0.38 mmol). Then, TFA (0.5 mL) was added to the solution. The resulting reaction mixture was stirred for 6 h at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined organic phases were washed with aqueous sodium bicarbonate (2% w/v), dried (Na_2SO_4), and evaporated *in vacuo*. The pure product **4** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:1) as an eluent (yield: 91%). Mp: 188 °C. ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 7.69 (d, 1H, J = 3.6 Hz), 7.57 (s, 2H), 7.40 (s, 4H), 7.36 (d, 1H, J = 3.6 Hz), 7.27 (d, 1H, J = 3.6 Hz), 7.24 (d, 1H, J = 3.6 Hz), 1.69 (s, 6H), 1.68 (s, 12H), 1.38 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.42, 147.8, 147.2, 145.3, 141.2, 139.9, 137.6, 133.7, 130.3, 129.7, 129.1, 127.4, 125.9, 123.7, 122.8, 121.3, 121.1, 120.4, 35.9, 34.6, 33.2, 31.5, 30.3, 29.8, 23.1. MS: m/z 669 [M$^+$]. Anal. Calcd. for $C_{44}H_{47}NOS_2$: C, 78.88; H, 7.07. Found: C, 78.59; H, 6.94.

2.5.3. 2-Cyano-3-(5-(5-(DHBQA-2-yl)thiophen-2-yl) thiophen-2-yl)acrylic acid (***JK-160***)

A mixture of **4** (0.10 g, 0.15 mmol) and cyanoacetic acid (0.019 g, 0.22 mmol) were vacuum-dried and added acetonitrile (20 ml), chloroform (15 ml) and piperidine (0.02 ml). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed *in vacuo*. The pure product was obtained by silica gel chromatography using a mixture of methylene chloride and methanol (10:1) as an eluent (yield: 87%). Mp: 254 °C. ^{1}H NMR (DMSO): δ 7.97 (s, 1H), 7.88 (d, 1H, J = 3.6 Hz), 7.60 (s, 2H), 7.57 (s, 4H), 7.45 (d, 1H, J = 3.6 Hz), 7.41 (d, 1H, J = 3.6 Hz), 7.34 (d, 1H, J = 3.6 Hz), 1.67 (s, 6H), 1.66 (s, 12H), 1.27 (s, 18H). ^{13}C{^{1}H} NMR (DMSO): δ 163.32, 145.6, 145.1, 143.1, 140.2, 138.1, 136.4, 132.1,131.5, 128.9, 128.1, 127.7, 125.9, 124.2, 122.1, 121.5, 120.0, 119.6, 118.4, 35.1, 33.9, 32.5, 30.3, 29.1, 28.6, 22.2. MS: m/z 736 $[M^+]$. Anal. Calcd. for $C_{47}H_{48}N_2O_2S_2$: C, 76.59; H, 6.56. Found: C, 76.33; H, 6.41.

*2.5.4. 2-(2,3-Dihydro-5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thieno[3,4-b][1,4]dioxin-7-yl)-DHBQA (**6**)*

The product was synthesized according to the procedure as described above for synthesis of **3**, giving a yellow solid of the product **6** in 85% yield. Mp: 193 °C. ^{1}H NMR ($CDCl_3$): δ 7.73 (s, 2H), 7.39 (s, 4H), 6.29 (s, 1H), 4.41 (m, 6H), 4.29 (m, 2H), 1.69 (s, 18H), 1.38 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.8, 141.4, 137.7, 136.9, 130.8, 129.8, 129.4, 129.2, 127.0, 121.7, 121.5, 121.4, 121.0, 120.6, 120.4, 115.9, 110.4, 106.8, 65.2, 65.0, 64.9, 64.7, 36.0, 35.9, 34.5, 33.4, 31.6, 31.5. MS: m/z 757 $[M^+]$. Anal. Calcd. for $C_{47}H_{51}NO_4S_2$: C, 74.47; H, 6.78. Found: C, 74.25; H, 6.59.

*2.5.5. 2,3-Dihydro-7-(2,3-dihydro-5-(DHBQA-2-yl)thieno[3,4-b][1,4]dioxin-7-yl)thieno-[3,4-b][1,4]dioxine-5-carbaldehyde (**7**)*

The Vilsmeier reagent, which was prepared from $POCl_3$ (0.02 ml) in DMF (0.1 ml), was added to a cold solution of **6** (0.13 g, 0.17 mmol) in dry DMF (20 ml) at 0 °C. The mixture was stirred at room temperature for 8 h, then 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 **7** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:1) as an eluent (yield: 86%). Mp: 225 °C. ^{1}H NMR ($CDCl_3$): δ 9.90 (s, 1H), 7.73 (s, 2H), 7.38 (s, 4H), 4.44 (m, 8H), 1.67 (s, 6H), 1.66 (s, 12H), 1.37 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.40, 145.5, 142.1, 138.2, 137.5, 131.3, 130.4, 130.2, 130.1, 128.1, 122.8, 122.6, 122.3, 122.0, 121.4, 121.1, 116.8, 111.3, 107.3, 66.3, 66.1, 65.7, 65.4, 37.1, 36.7, 35.3, 34.3, 32.3, 32.6. MS: m/z 785 $[M^+]$. Anal. Calcd. for $C_{48}H_{51}NO_5S_2$: C, 73.34; H, 6.54. Found: C, 73.15; H, 6.42.

*2.5.6. 2-Cyano-3-(2,3-dihydro-5-(2,3-dihydro-5-(DHBQA-2-yl)thieno[3,4-b][1,4]dioxin-7-yl)thieno-[3,4-b][1,4]dioxin-7-yl)acrylic acid (**JK-161**)*

The product was synthesized according to the procedure as described above for synthesis of **JK-160**, giving a dark red solid of the product **JK-161** in 84% yield. Mp: 331 °C. ^{1}H NMR (DMSO): δ 8.07 (s, 1H), 7.72 (s, 2H), 7.40 (s, 4H), 4.45 (m, 8H), 1.63 (s, 6H), 1.61 (s, 12H), 1.34 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.34, 144.8, 141.8, 137.7, 137.0, 131.1, 130.6, 129.8, 129.4, 129.1, 127.6, 122.1, 121.8, 121.4, 120.9, 120.4, 120.1, 116.1, 110.6, 106.8, 65.8, 65.5, 64.9, 64.6, 36.7, 35.8, 34.8, 33.9, 31.8, 31.1. MS: m/z 852 $[M^+]$. Anal. Calcd. for $C_{51}H_{52}N_2O_6S_2$: C, 71.80; H, 6.14. Found: C, 71.61; H, 6.02.

*2.5.7. 2-(2-(5,5-Dimethyl-1,3-dioxan-2-yl)thieno[3,2-b]thiophen-5-yl)-DHBQA (**9**)*

The product was synthesized according to the procedure as described above for synthesis of **3**, giving a yellow solid of the product **9** in 88% yield. Mp: 211 °C. ^{1}H NMR ($CDCl_3$): δ 7.61 (s, 2H), 7.48 (s, 1H), 7.41 (s, 4H), 7.33 (s, 1H), 5.72 (s, 1H), 3.75 (m, 4H), 1.71 (s, 6H), 1.70 (s, 12H), 1.40 (s, 18H), 1.33 (s, 3H), 0.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.2, 145.0, 141.9, 140.2, 136.6, 132.2, 130.2, 129.5, 129.1, 129.0, 128.6, 121.1, 120.4, 117.9, 114.0, 98.5, 77.6, 35.9, 34.5, 34.2, 33.2, 31.7, 31.6, 30.3, 23.1, 21.9. MS: m/z 729 $[M^+]$. Anal. Calcd. for $C_{47}H_{55}NO_2S_2$: C, 77.32; H, 7.59. Found: C, 77.09; H, 7.42.

*2.5.8. 5-(DHBQA-2-yl)thieno[3,2-b]thiophene-2-carbaldehyde (**10**)*

The product was synthesized according to the procedure as described above for synthesis of **4**, giving a orange solid of the product **10** in 90% yield. Mp: 238 °C. ^{1}H NMR ($CDCl_3$): δ 9.94 (s, 1H), 7.91 (s, 1H), 7.64 (s, 2H), 7.54 (s, 1H), 7.43 (s, 4H), 1.72 (s, 6H), 1.70 (s, 12H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.42, 147.2, 145.0, 141.9, 140.2, 136.6, 132.2, 130.2, 129.5, 129.1, 129.0, 128.6, 121.1, 120.4, 117.9, 114.0, 35.9, 34.5, 34.2, 33.2, 31.7, 31.6, 30.3. MS: m/z 643 $[M^+]$. Anal. Calcd. for $C_{42}H_{45}NOS_2$: C, 78.34; H, 7.04. Found: C, 78.18; H, 6.92.

*2.5.9. 2-Cyano-3-(2-(DHBQA-2-yl)thieno[3,2-b]thiophen-5-yl)acrylic acid (**JK-162**)*

The product was synthesized according to the procedure as described above for synthesis of **JK-160**, giving a dark red solid of the product **JK-162** in 88% yield. Mp: 298 °C. ^{1}H NMR ($CDCl_3$): δ 8.11 (s, 1H), 7.83 (s, 1H), 7.57 (s, 2H), 7.47 (s, 1H), 7.35 (s, 4H), 1.66 (s, 6H), 1.63 (s, 12H), 1.34 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.34, 146.4, 144.6, 141.1, 139.6, 135.8, 132.3, 131.9, 129.7, 129.1, 128.6, 128.0, 127.4, 120.6, 119.7, 117.1, 113.4, 34.5, 34.1, 33.9, 33.2, 31.1, 30.9, 29.8. MS: m/z 710 $[M^+]$. Anal. Calcd. for $C_{45}H_{46}N_2O_2S_2$: C, 76.02; H, 6.52. Found: C, 75.86; H, 6.38.

*2.5.10. 2-(2-(2-(Thieno[3,2-b]thiophen-2-yl)vinyl)thieno[3,2-b]thiophen-5-yl)-DHBQA (**12**)*

The product was synthesized according to the procedure as described above for synthesis of **3**, giving a yellow solid of the product **12** in 79% yield. Mp: 165 °C. ^{1}H NMR ($CDCl_3$): δ 7.58 (s, 1H), 7.41 (d, 1H, J = 15.3 Hz), 7.39 (s, 2H), 7.37 (d, 1H, 5.1 Hz), 7.24 (d, 1H, 5.1 Hz), 7.23 (d, 1H, J = 15.3 Hz), 7.22 (s, 4H), 7.09 (s, 1H), 7.07 (s, 1H), 1.68 (s, 6H), 1.54 (s, 12H), 1.37 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.0, 144.4, 143.8, 143.1, 140.2, 138.1, 137.0, 134.9, 134.7, 134.1, 133.9, 131.7, 130.7, 129.9, 129.1, 128.9, 128.5, 128.3, 127.7, 123.3, 122.0, 120.5, 119.8, 117.3, 36.7, 36.2, 34.9, 33.6, 31.8, 31.7. MS: m/z 755 $[M^+]$. Anal. Calcd. for $C_{47}H_{49}NS_4$: C, 74.65; H, 6.53. Found: C, 74.34; H, 6.42.

*2.5.11. 5-(2-(2-(DHBQA-2-yl)thieno[3,2-b]thiophen-5-yl)vinyl)thieno[3,2-b]thiophene-2-carbaldehyde (**13**)*

The product was synthesized according to the procedure as described above for synthesis of **7**, giving an orange solid of the product **13** in 82% yield. Mp: 194 °C. ^{1}H NMR ($CDCl_3$): δ 9.93 (s, 1H), 7.86 (s, 1H), 7.58 (s, 2H), 7.40 (s, 4H), 7.38 (d, 1H, J = 15.3 Hz), 7.25 (s, 1H), 7.23 (s, 1H), 7.20 (d, 1H, J = 15.3 Hz), 7.08 (s, 1H), 1.68 (s, 6H), 1.56 (s, 12H), 1.38 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 181.9, 147.1, 145.2, 144.9, 144.3, 141.3, 138.8, 137.9, 135.9, 135.7, 134.9,134.7, 132.9, 131.8, 130.5, 129.6, 129.4, 129.0, 128.9, 128.4, 124.1, 122.9, 121.1, 120.3, 118.1, 36.7, 36.2, 34.9, 33.6, 31.8, 31.7. MS: m/z 783 $[M^+]$. Anal. Calcd. for $C_{48}H_{49}NOS_4$: C, 73.52; H, 6.30. Found: C, 73.31; H, 6.18.

*2.5.12. 2-Cyano-3-(2-(2-(2-(DHBQA-2-yl)thieno[3,2-b]thiophen-5-yl)vinyl)thieno[3,2-b]th-iophen-5-yl)acrylic acid (**JK-163**)*

The product was synthesized according to the procedure as described above for synthesis of **JK-160**, giving a dark red solid of the product **JK-163** in 90% yield. Mp: 275 °C. ^{1}H NMR ($CDCl_3$): δ 8.27 (s, 1H), 7.74 (s, 1H), 7.51 (s, 2H), 7.33 (s, 4H), 7.30 (d, 1H, J = 15.3 Hz), 7.19 (s, 1H), 7.14 (s, 1H), 7.11 (d, 1H, J = 15.3 Hz), 7.03 (s, 1H), 1.61 (s, 6H), 1.52 (s, 12H), 1.31 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.4, 146.2, 144.6, 144.3, 144.0, 140.8, 137.9, 137.0, 135.1, 134.9, 134.7, 134.2, 132.7, 132.1, 131.2, 129.8, 129.2, 128.8, 128.2, 127.7, 127.3, 123.6, 122.2, 120.3, 119.5, 117.3, 36.4, 35.9, 34.6, 33.1, 31.2, 30.9.

MS: *m*/*z* 850 [M$^+$]. Anal. Calcd. for $C_{51}H_{50}N_2O_2S_4$: C, 71.96; H, 5.92. Found: C, 71.79; H, 5.77.

*2.5.13. 2-(3,6-Dihexyl-2-(2-(3,6-dihexylthieno[3,2-b]thiophen-2-yl)vinyl)thieno[3,2-b]thiophen-5-yl)-DHBQA (**15**)*

The product was synthesized according to the procedure as described above for synthesis of **3**, giving a dark yellow solid of the product **15** in 81% yield. Mp: 203 °C. ^{1}H NMR ($CDCl_3$): δ 7.45 (s, 2H), 7.39 (s, 4H), 7.09 (m, 2H), 6.95 (s, 1H), 2.81 (m, 6H), 2.71 (m, 2H), 1.75 (m, 8H), 1.69 (s, 6H), 1.66 (s, 12H), 1.40–1.27 (m, 24H), 1.38 (s, 18H), 0.89 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.1, 145.3, 144.5, 144.0, 141.1, 139.0, 138.1, 135.7, 135.9, 135.2, 134.8, 132.5, 131.8, 130.6, 130.1, 129.6, 129.0, 128.9, 128.4, 124.1, 123.0, 121.1, 120.3, 119.0, 36.0, 35.9, 34.5, 33.4, 32.0, 31.9, 31.6, 31.5, 31.4, 31.3,30.2, 30.1, 29.9, 29.8, 29.6, 29.4, 29.2, 29.1, 29.0, 28.8, 28.6, 28.4, 28.1, 27.9, 27.8, 27.6, 22.4, 14.1, 14.0, 13.9. MS: *m*/*z* 1091 [M$^+$]. Anal. Calcd. for $C_{71}H_{97}NS_4$: C, 78.03; H, 8.95. Found: C, 77.87; H, 8.81.

*2.5.14. 3,6-Dihexyl-5-(2-(3,6-dihexyl-2-(DHBQA-2-yl)thieno[3,2-b]thiophen-5-yl)vinyl)thieno[3,2-b]thiophene-2-carbaldehyde (**16**)*

The product was synthesized according to the procedure as described above for synthesis of **7**, giving a orange solid of the product **16** in 81% yield. Mp: 223 °C. ^{1}H NMR ($CDCl_3$): δ 10.06 (s, 1H), 7.46 (s, 2H), 7.43 (s, 4H), 7.23 (d, 1H, J = 15.3 Hz), 7.05 (d, 1H, J = 15.3 Hz), 3.08 (m, 2H), 2.83 (m, 6H), 1.80 (m, 8H), 1.70 (s, 6H), 1.67 (s, 12H), 1.45–1.23 (m, 24H), 1.38 (s, 18H), 0.89 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 181.5, 149.0, 147.1, 146.1, 145.7, 142.4, 139.9, 139.1, 136.7, 137.0, 136.4, 135.7, 133.8, 132.9, 131.5, 131.0, 130.3, 129.8, 129.2, 128.9, 125.2, 124.0, 122.2, 121.3, 120.0, 37.1, 36.4, 35.3, 34.2, 33.0, 32.5, 32.1, 32.0, 31.9, 31.6, 31.1, 30.9, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.8, 29.6, 29.3, 29.1, 29.0, 28.7, 28.5, 28.4, 23.2, 15.0, 14.9, 14.5 MS: *m*/*z* 1120 [M$^+$]. Anal. Calcd. for $C_{72}H_{97}NOS_4$: C, 77.16; H, 8.72. Found: C, 77.01; H, 8.58.

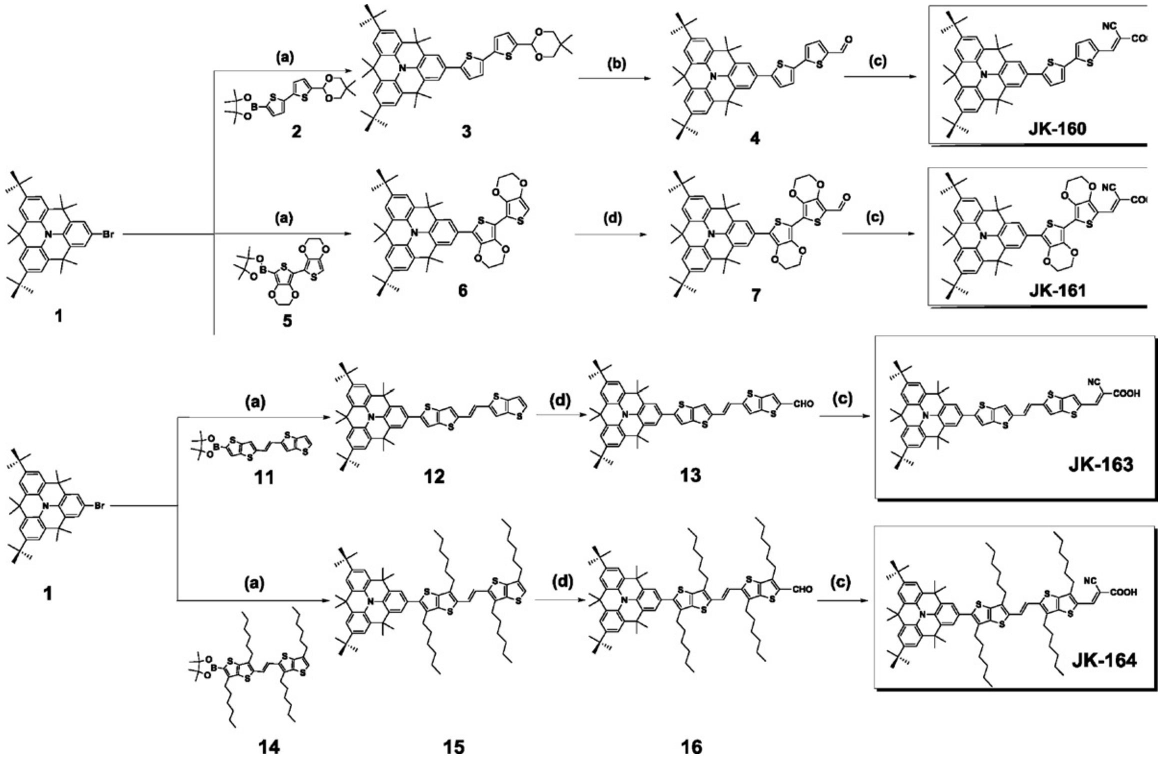
*2.5.15. 2-Cyano-3-(3,6-dihexyl-2-(2-(3,6-dihexyl-2-(DHBQA-2-yl)thieno[3,2-b]thiophen-5-yl)vinyl)thieno[3,2-b]thiophen-5-yl)acrylic acid (**JK-164**)*

The product was synthesized according to the procedure as described above for synthesis of **JK-160**, giving a dark red solid of the product **JK-164** in 77% yield. ^{1}H NMR ($CDCl_3$): δ 8.12 (s, 1H), 7.38 (s, 2H), 7.36 (s, 4H), 7.14 (d, 1H, J = 15.3 Hz), 6.97 (d, 1H, J = 15.3 Hz), 2.96 (m, 2H), 2.73 (m, 6H), 1.73 (m, 8H), 1.66 (s, 6H), 1.62 (s, 12H), 1.40–1.19 (m, 24H), 1.31 (s, 18H), 0.87 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.5, 147.8, 146.3, 145.2, 144.6, 141.1, 139.0, 138.3, 135.8, 135.9, 135.4, 135.1, 134.4, 134.0, 130.7, 130.3, 130.1, 129.1, 128.8, 128.2, 124.5, 123.7, 121.2, 120.7, 119.4, 36.2, 35.8, 35.4, 33.6, 32.5, 32.1, 31.8, 31.7, 31.5, 31.3, 31.0, 30.6, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.8, 29.5, 29.4, 29.2, 29.0, 28.7, 28.5, 28.3, 28.1, 22.8, 14.8, 14.5, 14.1. Mp: 267 °C. MS: *m*/*z* 1187 [M$^+$]. Anal. Calcd. for $C_{75}H_{98}N_2O_2S_4$: C, 75.83; H, 8.32. Found: C, 75.68; H, 8.06.

3. Results and discussion

3.1. Synthesis

The novel organic sensitizers **JK-160**, **JK-161**, **JK-162**, **JK-163**, and **JK-164** were prepared by the stepwise synthetic protocol illustrated in Scheme 1. New dyes are readily synthesized in three steps starting from the 6,10-di-*tert*-butyl-4,4,8,8,12,12-hexamethyl-4*H*,8*H*,12*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine (2-bromo-DHB-QA) **1**. The bromoacridine **1** was synthesized by bromination of DHBQA with NBS in $CHCl_3$ [47]. The Suzuki coupling [53,54] of **1** with 1.5 equiv. of **2** or **8** yielded **3** or **9**, respectively. Subsequent cleavage of the 1,3-dioxalane protecting group in aqueous acid produced the aldehydes **4** and **10**. The aldehydes **4** and **10**, upon reaction with cyanoaceticacid in the presence of a catalytic amount of piperidine in CH_3CN, produced the **JK-160** and **JK-162** sensitizers. Compounds **6**, **12**, and **15** were synthesized by Suzuki coupling reaction of **1** with **5**, **11**, and **14**. The thiophene



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-160**, **JK-161**, **JK-162**, **JK-163** and **JK-164**. Reagents and reaction condition: (a) $Pd(PPh_3)_4$, K_2CO_3, THF, H_2O; (b) TFA, THF, H_2O; (c) cyanoacetic acid, piperidine, $CH_3CN/CDCl_3$ = 1:1; (d) $POCl_3$, DMF.

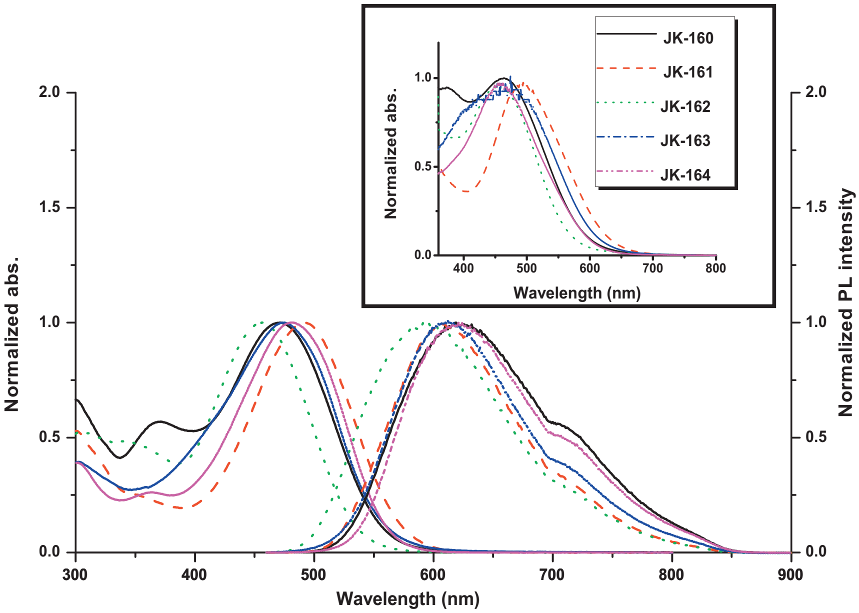
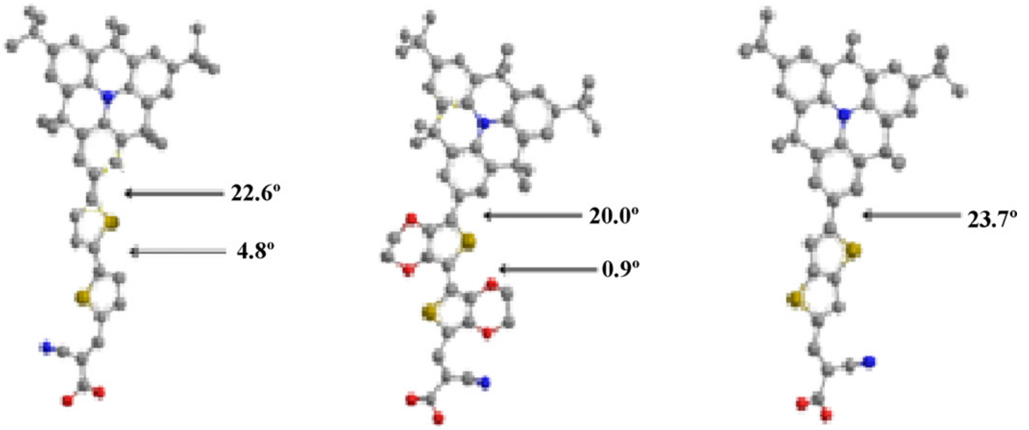


Fig. 2. Absorption (left) and emission (right) spectra of **JK-160** (solid line), **JK-161** (dash line), and **JK-162** (dot line), **JK-163** (dash-dot line), and **JK-164** (dash-dot-dot line) in THF. The inset shows absorption spectra adsorbed on a nanocrystalline TiO_2 film.

derivatives were converted to their corresponding carbaldehydes **7**, **13**, and **16** according to the Vilsmeier–Haack reaction [55,56]. The aldehydes **7**, **13**, and **16**, upon reaction with cyanoacetic acid in the presence of piperidine, yielded the sensitizers **JK-161**, **JK-163**, and **JK-164**. Details of some compound preparation (compound **3**, **4**, **6**, **7**, **9**, **10**, **12**, **13**, **15**, **16**) are provided in Section 2.

3.2. Spectroscopic studies

Fig. 2 shows the absorption and emission spectra of **JK-160**, **JK-161**, and **JK-162** in THF. The absorption spectrum of the **JK-160** sensitizer exhibits two absorption maxima at 471 nm ($\varepsilon = 30{,}040\,dm^3\,mol^{-1}\,cm^{-1}$) and 371 nm ($\varepsilon = 16{,}100\,dm^3\,mol^{-1}\,cm^{-1}$), which are assigned to the π–π* transitions of the conjugated molecule. Under similar condition the **JK-162** sensitizer exhibits its maximum at 456 nm ($\varepsilon = 27{,}476\,dm^3\,mol^{-1}\,cm^{-1}$) and 352 nm ($\varepsilon = 17{,}638\,dm^3\,mol^{-1}\,cm^{-1}$) that are 15 nm blue-shifted with respect to its bithiophene counterpart. On the other hand, the adaptation of a bis-3,4-ethylenedi-oxythiophene (EDOT) as a linker, giving **JK-161**, caused a further red shift to 491 nm. A significant red shift of **JK-161** relative to **JK-160** and **JK-162** derived from the delocalization over an entire conjugated system because the oxygen atoms of the EDOT unit decrease the aromatic character of thiophene unit, extending the conjugation length [57,58,22]. This red-shift can be further supported from molecular modeling studies of the dye. The molecular modeling studies were performed using the B3LYP functional and the 3-21G* basis set. The ground state structure of **JK-160** possesses a 22.6° twist between the acridine and thienyl unit (Fig. 3). The dihedral angle of two thienyl units in **JK-160** is 4.8°. For the thienothiophene case in **JK-162**, the dihedral angle between the acridine and thienothiophene unit is 23.7°, giving more twisted than that of **JK-160**. On the other hand, the dihedral angles of acridine and EDOT and bis-EDOT in **JK-161** are 20.0° and 0.9°, respectively, indicating that the latter has a more planar geometry due to a smaller torsion angle. Accordingly, the red-shift and higher extinction coefficient of **JK-161** relative to those of **JK-160** and **JK-162** derive from the increased electron delocalization over the conjugated system. Similar distortions have been observed for other organic sensitizers [59,60].



JK-160 **JK-161** **JK-162**

Fig. 3. The optimized structure calculated with B3LYP/3-21G* basis set of **JK-160**, **JK-161**, and **JK-162**.

Table 1
Optical, redox, and DSSC performance parameters of dyes.

Dye	$\lambda_{abs}{}^{a}$/nm(ε/M^{-1} cm^{-1})	$E_{ox}{}^{b}$/V	$E_{0\text{-}0}{}^{c}$/V	$E_{LUMO}{}^{d}$/V	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η^{e}/%
JK-160	471(30,040)	1.01	2.29	−1.28	13.53	0.742	73.29	7.37
JK-161	491(31,907)	0.93	2.27	−1.34	15.83	0.676	65.61	7.06
JK-162	456(27,476)	1.06	2.39	−1.33	13.74	0.679	75.41	7.04
JK-163	474(31,800)	0.99	2.28	−1.29	12.45	0.601	70.10	5.25
JK-164	481(57,040)	1.02	2.26	−1.24	15.32	0.696	73.66	7.86

[a] Absorption spectra were measured in THF solution.

[b] Oxidation potentials of dyes on TiO_2 were measured in THF with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 50 mV s^{-1} (vs NHE).

[c] $E_{0\text{-}0}$ was determined from intersection of absorption and emission spectra in THF (value of $E_{0\text{-}0}$ (eV) = 1240 (eV/nm)/intersection point (nm)).

[d] E_{LUMO} was calculated by $E_{ox} - E_{0\text{-}0}$.

[e] Performances of DSSCs were measured with 0.18 cm^2 working area. ε: absorption coefficient; E_{ox}: oxidation potential; $E_{0\text{-}0}$: voltage of intersection point between absorption and emission spectra; J_{sc}: short circuit photocurrent density; V_{oc}: open circuit photovoltage; FF: fill factor; η: total power conversion efficiency.

3.3. Redox behavior of dyes

To thermodynamically evaluate the energy match of electron transfer from the excited state of the dye to the conduction band of the TiO_2 electrode as well as charge generation electron transfer from the iodide to oxidize sensitizer, redox potentials of the five dyes were scrutinized by cyclic voltammetry. The two organic dyes adsorbed on TiO_2 films showed a double quasi-reversible oxidation potentials (**JK-160**: 1.01, 1.62 V; **JK-161**: 0.93, 1.26 V vs NHE) (Fig. 4). The first oxidation potentials of three (**JK-160** and **161** have two oxidation potentials, according to Table 1) dyes at low potential is similar to that of **JK-2** [25], thus it can be assigned to the oxidation of the same triphenylamino unit. Based on previous results on the electrochemical behaviors of bithiophene derivatives [12], the second oxidation of **JK-160** and **JK-161** is likely due to the dithiophene linker unit. The oxidation potentials of the three sensitizers are decreased in the order **JK-162** > **JK-160** > **JK-161**. The trend is expected on the basis of the strong electron donating character of the employed EDOT unit in **JK-161** that destabilize HOMO orbital. The reduction potential of each dye was calculated using the oxidation potential and the $E_{0\text{-}0}$ energy, the latter of which was determined from the intersection of the absorption and emission spectra. The excited-state oxidation potentials (E^*_{ox}) of the dyes (**JK-160**; −1.28 V; **JK-161**: −1.34 V; **JK-162**: −1.33 V vs NHE) are much more negative than the conduction band potential of the TiO_2 at −0.5 V vs NHE. Therefore, the introduction of EDOT unit in the bridged group does not have a big influence on the LUMO level (summarized in Table 1).

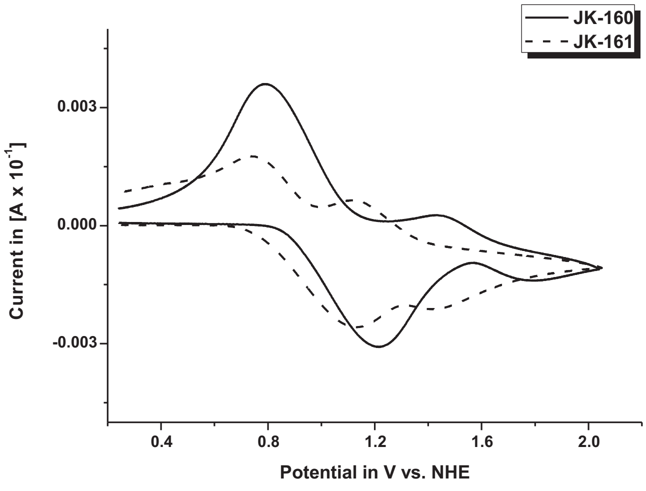


Fig. 4. Cyclic voltammogram of **JK-160** (solid line), **JK-161** (dash line) measured in THF solution containing 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ using a glassy carbon as a working and a Pt counter electrode at a scan rate of 50 mV s^{-1}.

3.4. Theoretical calculations of electronic properties

We performed the molecular orbital calculation of five sensitizers to gain insight into the photophysical properties using both DFT for the ground-state geometries and TD-DFT for the excited-state energies and properties. Fig. 5 presents the electron density plots of the frontier molecular orbital of five sensitizers. The calculation illustrates that the HOMO of five sensitizers is delocalized over the π-conjugated system through the fused phenyl amino group. The LUMO is delocalized over the cyanoacrylic unit with a sizable population on the next thiophene derivative. As light excitation should be associated with vectorial electron flow from the HOMO to the LUMO for efficient electron transfer, the examination of HOMO–LUMO of five sensitizers indicates that HOMO–LUMO excitation moved the electron distribution from the fused phenyl amino unit to the cyanoacrylic acid group. Therefore, the photo-induced electron transfer from the dyes to TiO_2 electrode can be efficiently occurred by the HOMO–LUMO transition. Excited-state TD-DFT calculated that the lowest transition of **JK-160** at 442 nm (f = 1.089) is mainly characterized by a mixture of HOMO-1 → LUMO (66%) and HOMO → LUMO + 1 excitation (23%), **JK-161** at 444 nm (f = 0.932) is HOMO-1 → LUMO (87%) and HOMO → LUMO + 1 excitation (15%), and **JK-162** at 398 nm (f = 1.101) is HOMO-1 → LUMO (64%) and HOMO → LUMO + 1 excitation (28%), affording a charge flow from the amino core (HOMO) to the anchoring unit (LUMO) (Table 2).

3.5. Photovoltaic performance

The photocurrent action spectra of the five sensitizers are presented in the inset of Fig. 6(b). The incident-photon-to-current conversion (IPCE) of **JK-164** exceeds 70% in a broad spectral range from 400 to 618 nm, reaching its maximum of 80% at 468 nm. The onset wavelengths of IPCE spectra for the devices based on **JK-160**, **JK-162**, **JK-163**, and **JK-164** are 760 nm. However, the spectrum of **JK-161** tails off toward 805 nm, contributing to the broad spectral light harvesting. The IPCE spectrum of **JK-161** is significantly red-shifted by 45 nm relative to that of other four sensitizers, which is consistent with its absorption spectrum. The *J*–*V* curve for the devices based on five sensitizers is presented in Fig. 6(a). The **JK-161** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 15.83 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.68 V, and a fill factor (*ff*) of 0.66, corresponding to an overall conversion efficiency (η) of 7.06%. Under the same condition, the **JK-160** sensitized cell gave J_{sc} of 13.53 mA cm^{-2}, V_{oc} of 0.74 V, and *ff* of 0.73, corresponding to η of 7.37%. A large J_{sc} of **JK-161** relative to **JK-160** and **JK-162** can be related to the delocalization over an entire conjugated system and its broad UV spectrum of **JK-161**. The V_{oc} and *ff* of **JK-161** are much lower than for **JK-160** cell, although its J_{sc} is increased, resulting in a reduced efficiency. This is likely due to a high series resistance, which suggests that thinner donor layer is necessary for good device performance.

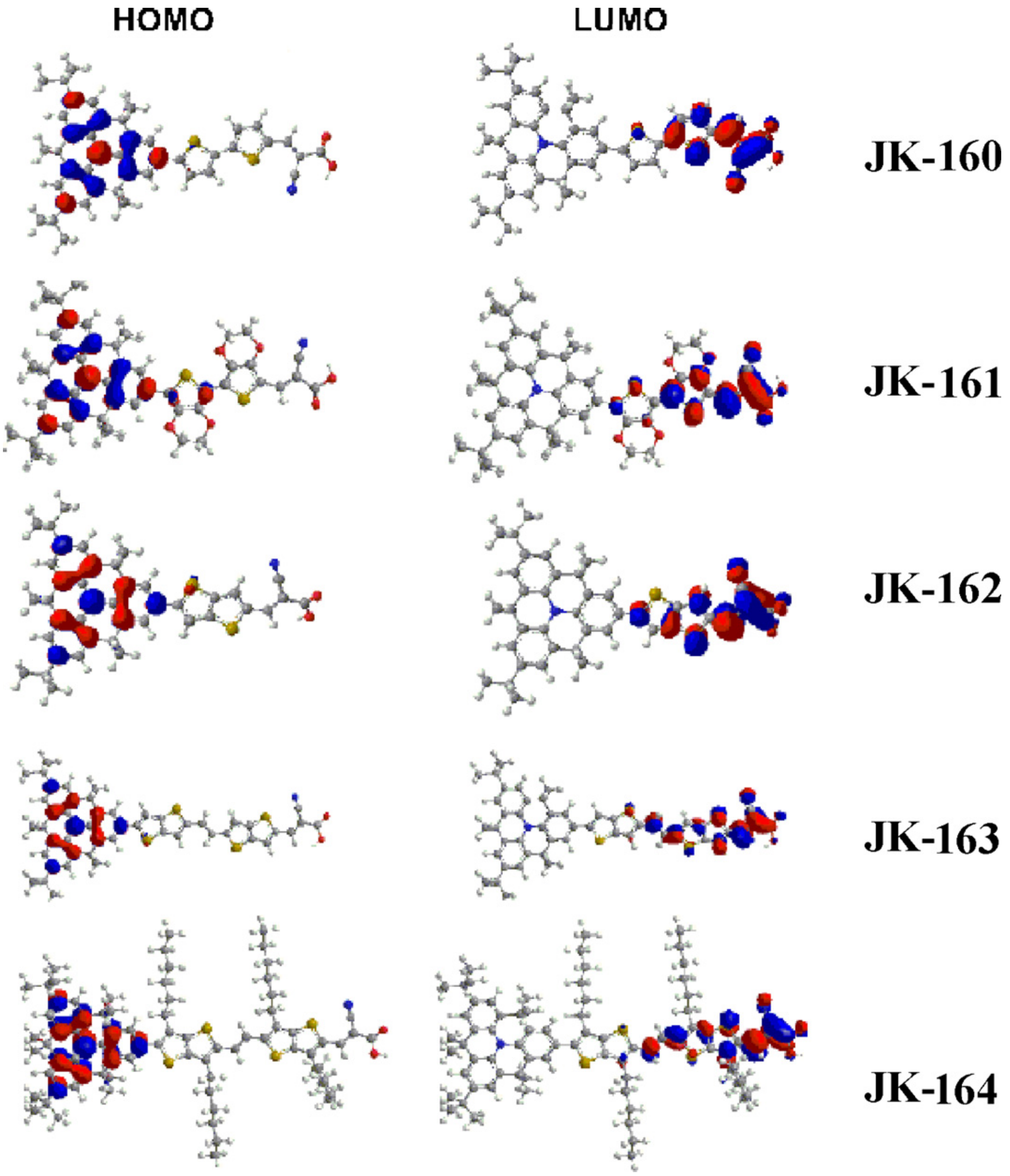


Fig. 5. The molecular structures and the frontier molecular orbitals of the HOMO and LUMO calculated with B3LYP/3-21G* of **JK-160**, **JK-161**, **JK-162**, **JK-163**, and **JK-164**.

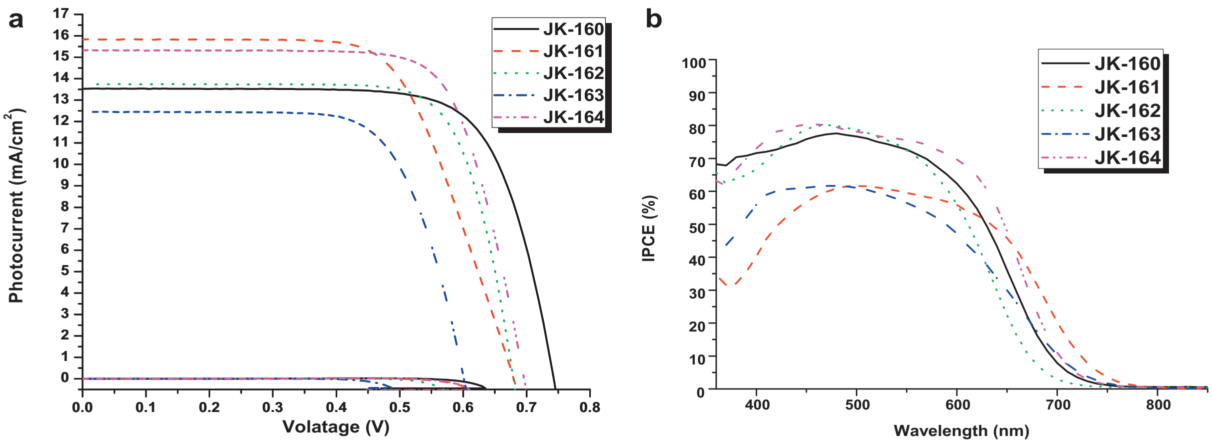


Fig. 6. (a) Photocurrent–voltage characteristics of representative TiO_2 electrodes sensitized with dye: **JK-160** (solid line), **JK-161** (dash line), and **JK-162** (dot line), **JK-163** (dash-dot line), **JK-164** (dash-dot-dot line). (b) The spectra shows the IPCE spectra of the DSSCs as a function of the wavelength of the light.

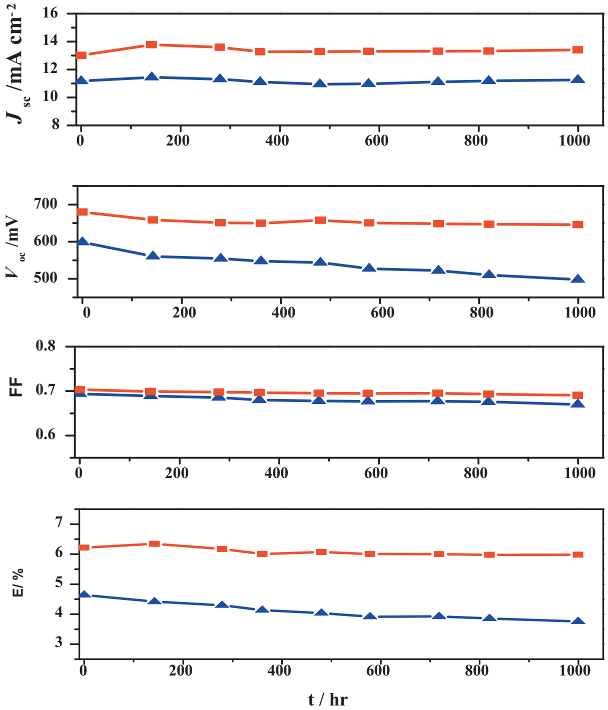


Fig. 7. Evolution of solar-cell parameters with **JK-163** (▲) and **JK-164** (■) during visible-light soaking (AM 1.5 G, 100 mW cm^{-2}) at 60 °C. A 420 nm cut-off filter was placed on the cell surface during illumination. Ionic liquid electrolyte 2: 0.2 M iodine, 0.5 M NMBI, 0.1 M GuNCS in PMII/EMINCS (13:7).

Kroeze et al. [61–65] showed that alkyl substitution of dye improved the V_{oc}, due to the blocking effect of the charge recombination between I_3^- and electrons injected in the nanocrystalline TiO_2 films. The hexyl substituents on the linker in **JK-164** have been introduced to evaluate the effect of substituent on the photovoltaic parameters. The efficiency, η, of 7.86% in **JK-164** was obtained with J_{sc} of 15.32 mA cm^{-2}, V_{oc} of 0.70 V, and *ff* of 0.74. Under the same condition we obtained η of 5.25% for the **JK-163** solar cell with J_{sc} of 12.45 mA cm^{-2}, V_{oc} of 0.60 V, and *ff* of 0.70, indicating that η for the **JK-163** solar cell is about 2.6% inferior to that of the **JK-164** solar cell. In particular, the open circuit voltage for the DSSCs of **JK-164** is higher than that for **JK-163** under the same conditions. A significant increase of V_{oc} in **JK-164** is closely related to the incorporation of hexyl groups substituted at the thienothiophene units by the suppression of dark current.

3.6. Stability of dyes

Fig. 7 shows the photovoltaic performance during long-term accelerated aging of **JK-163** and **JK-164** using an 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 device of **JK-164** showed an excellent long-term stability. The initial efficiency of 6.22% slightly decreased to 5.98% during the 1000 h light-soaking test at 60 °C. After 1000 h of light soaking test, the V_{oc} of **JK-164** decreased by 34 mV, but the loss was compensated by a slight increase in the short-circuit current density. On the other hand, the initial efficiency of 4.64% in **JK-163** sharply decreased to 3.76% after 1000 h of light soaking at 60 °C. In particular, the enhanced long stability of **JK-164** relative to **JK-163** can be related to the substituted hexyl units on the bridged group by preventing the approach of acceptors to the TiO_2 films, resulting in preventing the dark current.

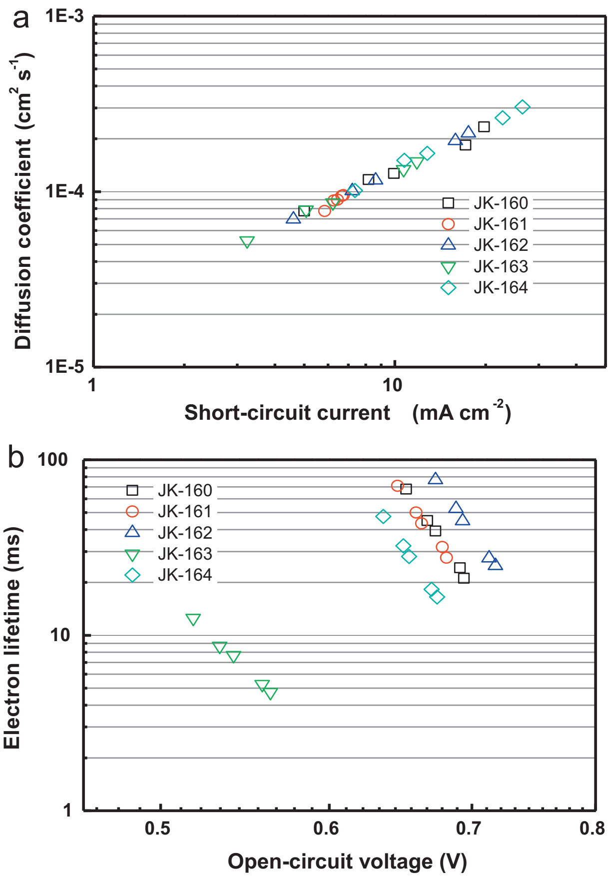


Fig. 8. Electron diffusion coefficients (a) and lifetimes (b) of DSSCs employing different organic dyes.

3.7. Laser-induced transient photocurrent and photovoltage measurements

Fig. 8 shows the electron diffusion coefficients and lifetimes of the DSSCs employing different dyes displayed as a function of the

Table 2
Theoretical excited-state TD-DFT calculation of **JK-160**, **161**, and **162**.

Sensitizers	Wavelength	*f*	Characters		
			Occupied orbitals	Empty orbitals	Contributions (%)
JK-160	442	1.089	HOMO-1 HOMO	LUMO LUMO-1	66 23
JK-161	444	0.932	HOMO-1 HOMO	LUMO LUMO-1	87 15
JK-162	398	1.101	HOMO-1 HOMO	LUMO LUMO-1	64 28

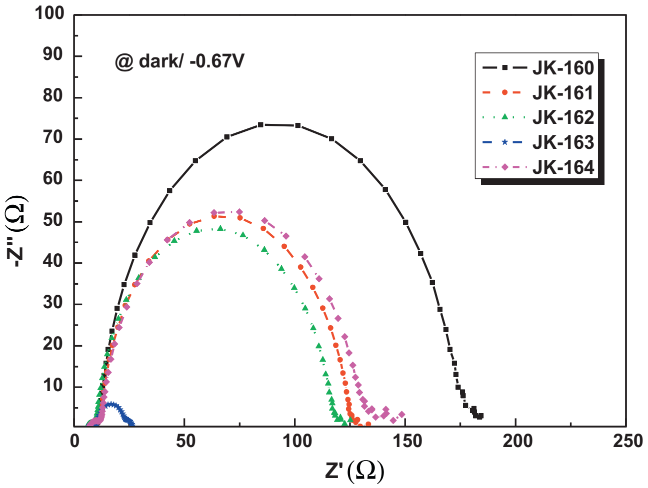


Fig. 9. Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) and at the dark for the cells employing different dyes (*i.e.* **JK-160**, **JK-161**, **JK-162**, **JK-163**, and **JK-164**).

J_{sc} and V_{oc}, respectively. No significant differences among the D_e values were seen at the identical short-circuit current conditions as shown in Fig. 8a. On the other hand, the order of magnitude of the τ_e values was largely varied with the structure of dyes as shown in Fig. 8b. Especially, **JK-163** showed much shorter electron lifetimes compared with those of other dyes. However, the introduction of alkyl chains into thiophen units (*i.e.* **JK-164**) could largely enhance the electron lifetimes by retarding the aggregation among the dye molecules during the adsorption onto TiO_2 surface and the electron recombination originated from the direct contact between the electrons on TiO_2 surface and $I_3{}^-$ ions in electrolyte.

3.8. Electrochemical impedance study

Fig. 9 shows the ac impedance spectra of the DSSCs measured in the dark. In the dark under forward bias (−0.67 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. 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 −0.67 V forward bias, the radius of this semicircle increases in the order **JK-163** (28.35 Ω) < **JK-162** (102.5 Ω) < **JK-161** (104.8 Ω) < **JK-164** (119.1 Ω) < **JK-160** (151.2 Ω), in accord with the trends in the values of V_{oc}. These results are in good agreement with the trends observed in the overall efficiency.

4. Conclusion

In conclusion, we have synthesized five efficient organic sensitizers containing a sterically hindered acridine unit. A photovoltaic performance is quite sensitive to the bridged group. A solar-cell device based on the **JK-164** in conjunction with a volatile and an ionic-liquid electrolyte yielded an overall conversion efficiency of 7.86% and 6.22%, respectively. Moreover, the **JK-164** based device showed an excellent stability under light soaking at 60 °C for 1000 h. The initial efficiency of 7.86% in **JK-164** revealed a slight change to 7.45% after 1000 h of light soaking. The open circuit voltage for the device of **JK-164** is higher than that for **JK-163** due to the incorporation of hexyl groups into the space unit, resulting in the suppression of dark current. We believe that the molecular design and synthesis of highly efficient organic sensitizers are possible through structural modifications, and work on these is now in progress.

Acknowledgments

This work was supported by the WCU (the Ministry of Education and Science) program (No. R31-2008-000-10035-0), the Ministry of Information & Communication, Korea under ITRC (No. IITA 2008 C 10900904 0013).

References

[1] N. Robertson, Angew. Chem. Int. Ed. 45 (2006) 2338.
[2] B. O'Ragen, M. Grtäzel, Nature 363 (1991) 737.
[3] M. Grtäzel, Nature 414 (2001) 338.
[4] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L.Y. Han, Jpn. J. Appl. Phys. Part 2 45 (2006) L638.
[5] M.K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, T. Bessho, M. Grtäzel, J. Am. Chem. Soc. 127 (2005) 16835.
[6] Y. Cao, Y. Bai, Q. Yu, Y. Cheng, S. Liu, D. Shi, F. Gao, P. Wang, J. Phys. Chem. C 113 (2009) 6290.
[7] F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S.M. Zakeeruddin, M. Grtäzel, J. Am. Chem. Soc. 130 (2008) 10720.
[8] K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, J. Phys. Chem. B 107 (2003) 597.
[9] K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, New J. Chem. 27 (2003) 783.
[10] K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, H. Arakawa, Chem. Commun. (2001) 569.
[11] T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, Chem. Commun. (2003) 3036.
[12] T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, J. Am. Chem. Soc. 126 (2004) 12218.
[13] L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, S. Ito, S. Uchida, M. Grätzel, Adv. Mater. 17 (2005) 813.
[14] S. Ito, S.M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M.K. Nazeeruddin, P. Péchy, M. Takada, H. Miura, S. Uchida, M. Grätzel, Adv. Mater. 18 (2006) 1202.
[15] K. Hara, M. Kurashige, S. Ito, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, Chem. Commun. (2003) 252.
[16] T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N.A. Anderson, X. Ai, T. Lian, S. Yanagida, Chem. Mater. 16 (2004) 1806.
[17] K. Hara, T. Sato, R. Katoh, A. Furube, T. Yoshihara, M. Murai, M. Kurashige, S. Ito, A. Shinpo, S. Suga, H. Arakawa, Adv. Funct. Mater. 15 (2005) 246.
[18] K. Sayama, S. Tsukagoshi, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, H. Arakawa, J. Phys. Chem. B 106 (2002) 1363.
[19] K. Sayama, K. Hara, N. Mori, M. Satsuki, S. Suga, S. Tsukagoshi, Y. Abe, H. Sugihara, H. Arakawa, Chem. Commun. (2000) 1173.
[20] Q.-H. Yao, L. Shan, F.-Y. Li, D.-D. Yin, C.-H. Huang, New J. Chem. 27 (2003) 1277.
[21] J.-S. Wang, F.-Y. Li, C.-H. Huang, Chem. Commun. (2000) 2063.
[22] G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, Chem. Commun. (2009) 2198.
[23] W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan, P. Wang, Chem. Mater. 22 (2010) 1915.
[24] C.-H. Yang, H.-L. Chen, C.-P. Chen, S.-H. Liao, H.-A. Hsiao, Y.-Y. Chuang, H.-S. Hsu, T.-L. Wang, Y.-T. Shieh, L.-Y. Lin, Y.-C. Tsai, J. Electroanal. Chem. 631 (2009) 43.
[25] 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. 128 (2006) 16701.
[26] H. Choi, J.K. Lee, K. Song, S.O. Kang, J. Ko, Tetrahedron 63 (2007) 3115.
[27] I. Jung, J.K. Lee, K.-H. Song, K. Song, S.O. Kang, J. Ko, Tetrahedron 63 (2007) 1553.
[28] D. Kim, J.K. Lee, S.O. Kang, J. Ko, Tetrahedron 63 (2007) 1913.
[29] H. Choi, C. Baik, S.O. Kang, J. Ko, M.-S. Kang, M.K. Nazeeruddin, M. Grätzel, Angew. Chem. Int. Ed. 47 (2008) 327.
[30] H. Choi, S. Kim, S.O. Kang, J. Ko, M.-S. Kang, J.N. Clifford, A. Forneli, E. Palomares, M.K. Nazeeruddin, M. Grätzel, Angew. Chem. Int. Ed. 47 (2008) 8259.
[31] Y. Liang, B. Peng, J. Liang, Z.J. Tao, Chen, Org. Lett. 12 (2010) 1204.
[32] H.-Y. Yang, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou, J.T. Lin, Org. Lett. 12 (2010) 16.
[33] C. Kim, H. Choi, S. Kim, C. Baik, K. Song, M.-S. Kang, S.O. Kang, J. Ko, J. Org. Chem. 73 (2008) 7072.
[34] M.K. Nazeeruddin, R. Humphry-Baker, M. Grtäzel, B.A. Nurrer, Chem. Commun. (1998) 719.
[35] M.K. Nazeeruddin, R. Humphry-Baker, M. Grtäzel, D. Wöhrle, G. Schnurpfeil, G. Schneider, A. Hirth, N. Trombach, J. Porphyrins Phthalocyanines 3 (1999) 230.
[36] J. He, G. Benkö, F. Korodi, T. Polívka, R. Lomoth, B. Åkermark, L. Sun, A. Hagfeldt, V. Sundström, J. Am. Chem. Soc. 124 (2002) 4922.
[37] L. Giribabu, Ch.V. Kumar, V.G. Reddy, P.Y. Reddy, Ch.S. Rao, S.-R. Jang, J.-H. Yum, M.K. Nazeeruddin, M. Grätzel, Sol. Energy Mater. Sol. Cells 91 (2007) 1611.
[38] S. Eu, T. Katoh, T. Umeyama, Y. Matano, H. Imahori, Dalton Trans. 40 (2008) 5476.
[39] S. Mori, M. Nagata, Y. Nakahata, K. Yasuta, T. Goto, M. Kimura, M. Taya, J. Am. Chem. Soc. 132 (2010) 4054.
[40] K. Liu, R.W. Fessenden, G.L. Hug, P.V. Kamat, J. Phys. Chem. B 101 (1997) 2583.
[41] H. Choi, S. Kim, S.O. Kang, J. Ko, M.-S. Kang, J.N. Clifford, A. Forneli, E. Palomares, M.K. Nazeeruddin, M. Grätzel, Angew. Chem. Int. Ed. 47 (2008) 8259.

[42] M. Miyashita, K. Sunahara, T. Nishikawa, Y. Uemura, N. Koumura, K. Hara, A. Mori, T. Abe, E. Suzuki, S. Mori, J. Am. Chem. Soc. 130 (2008) 17874.
[43] B.C. O'Regen, I. López-Duarte, M.V. Martinez-Diaz, A. Forneli, J. Albero, A. Morandeira, E. Palomares, T. Torres, J.R. Durrant, J. Am. Chem. Soc. 130 (2008) 2906.
[44] C. Baik, D. Kim, M.-S. Kang, K. Song, S.O. Kang, J. Ko, Tetrahedron 65 (2009) 5302.
[45] K.L. Mutolo, E.I. Mayo, B.P. Rand, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 128 (2006) 8108.
[46] D. Hellwinkel, M. Melan, Chem. Ber. 107 (1974) 616.
[47] Z. Fang, T.-L. Teo, L. Cai, Y.-H. Lai, A. Samoc, M. Samoc, Org. Lett. 11 (2009) 1.
[48] A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake, M. Irie, J. Org. Chem. 66 (2001) 3913.
[49] T. Yoshida, T. Matsuda, S. Otsuka, Inorg. Synth. 28 (1990) 122.
[50] B. Jousselme, P. Blanchard, M. Allain, E. Levillain, E. Dias, J. Roncali, J. Phys. Chem. A 110 (2006) 3488.
[51] L.S. Fuller, B. Iddon, K.A. Smith, J. Chem. Soc., Perkin Trans. 1 (1997) 3465.
[52] H. Choi, I. Raabe, D. Kim, F. Teocoli, C. Kim, K. Song, J.-H. Yum, J. Ko, M.K. Nazeeruddin, M. Grätzel, Chem. Eur. J. 16 (2010) 1193.
[53] C.-H. Huang, N.D. McClenaghan, A. Kuhn, J.W. Hofstaat, D.M. Bassan, Org. Lett. 7 (2005) 3409.
[54] K.J. Hoffmann, E. Bakken, E.J. Samuelsen, P.H.J. Carlsen, Synth. Met. 113 (2000) 39.
[55] V.J. Majo, P.T. Perumal, J. Org. Chem. 61 (1996) 6523.
[56] O. Meth-Cohn, M. Ashton, Tetrahedron Lett. 41 (2000) 2749.
[57] H. Choi, J.K. Lee, K.H. Song, K. Song, S.O. Kang, J. Ko, Tetrahedron 63 (2007) 1553.
[58] M. Xu, S. Wenger, H. Bala, D. Shi, R. Li, Y. Zhou, S.M. Zakeeruddin, M. Grtäzel, P. Wang, J. Phys. Chem. C 113 (2009) 2966.
[59] J.-J. Kim, H. Choi, J.-W. Lee, M.-S. Kang, K. Song, S.O. Kang, J. Ko, J. Mater. Chem. 18 (2008) 5223.
[60] N. Cho, H. Choi, D. Kim, K. Song, M.-S. Kang, S.O. Kang, J. Ko, Tetrahedron 65 (2009) 6236.
[61] K.-J. Jiang, N. Masaki, J.-B. Xia, S. Noda, S. Yanagida, Chem. Commun. (2006) 2460.
[62] F. Gao, Y. Wang, J. Zhang, D. Shi, M. Wang, R. Humphry-Baker, P. Wang, S.M. Zakeeruddin, M. Grtäzel, Chem. Commun. (2008) 2635.
[63] C.-Y. Chen, S.-J. Wu, C.-G. Wu, J.-G. Chen, K.-C. Ho, Angew. Chem. Int. Ed. 45 (2006) 5822.
[64] N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, J. Am. Chem. Soc. 128 (2006) 14256.
[65] S. Kim, D. Kim, H. Choi, M.-S. Kang, K. Song, S.O. Kang, J. Ko, Chem. Commun. (2008) 4951.
[66] S. Nakade, T. Kanzaki, Y. Wada, S. Yanagida, Langmuir 21 (2005) 10803.
[67] M.-S. Kang, K.-S. Ahn, J.-W. Lee, Y.S. Kang, J. Photochem. Photobiol. A: Chem. 195 (2008) 198.
[68] K.-S. Ahn, M.-S. Kang, J.-K. Lee, B.-C. Shin, J.-W. Lee, Appl. Phys. Lett. 89 (2006) 013103.
[69] K.-S. Ahn, M.-S. Kang, J.-W. Lee, Y.S. Kang, J. Appl. Phys. 101 (2007) 084312.