Tetrahedron 65 (2009) 6236–6243

Contents lists available at ScienceDirect

Tetrahedron

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

Novel organic sensitizers containing a bulky spirobifluorene unit for solar cell

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ARTICLE INFO

Article history:
Received 6 April 2009
Received in revised form 8 May 2009
Accepted 12 May 2009
Available online 18 May 2009

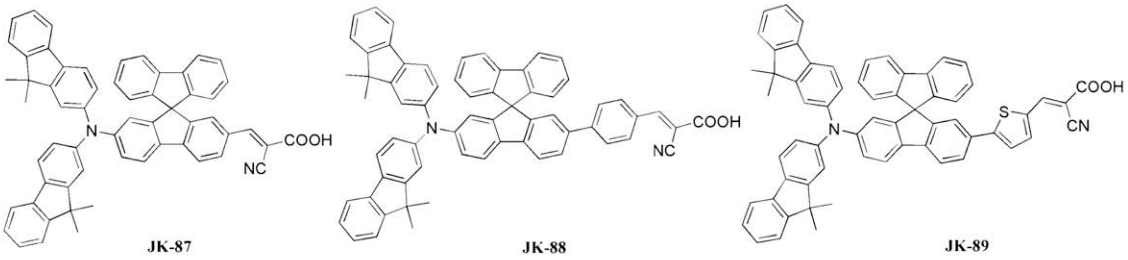
ABSTRACT

Three organic sensitizers **JK-87**, **JK-88**, and **JK-89** containing a bulky spirobifluorene unit in the bridged group are designed and synthesized. Under standard global A.M. 1.5 solar condition, the **JK-89** sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 13.02 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.75 V, and a fill factor of 0.70, corresponding to an overall conversion efficiency η of 6.83%. The η of **JK-89** is higher than those of other two cells due to the larger J_{sc}. The improved J_{sc} value is mainly attributed to the broad and red-shifted absorption band.

1. Introduction

Increasing energy demands and concerns over global warming urge the development of renewable energy sources in recent years.[1] Dye-sensitized solar cells (DSSCs) have attracted significant attention as low-cost alternatives to conventional solid-state photovoltaic devices.[2] Several Ru polypyridyl complexes have achieved power conversion efficiencies of 10–11%.[3] Recently, several groups have developed metal free organic sensitizers to overcome the cost and synthetic difficulty of ruthenium metal complexes and the solar cell performance of DSSCs based on organic sensitizers has been remarkably improved.[4] Nevertheless, many organic dyes have still presented the low conversion efficiency and low stability. A major factor for the low conversion efficiency of organic sensitizers in the DSSCs is the formation of dye aggregates on the TiO_2 surface.[5] Therefore, aggregation of organic dyes must be avoided through appropriate structural modification. Several strategies have been employed for controlling the aggregation behavior of dyes on TiO_2 surfaces. One of the approaches to prevent aggregation would be to employ some additives as a co-adsorbant.[6] Other methods have included the structural modification of the dye molecule.

Recently, we[7,19] and others[8] have reported the novel organic dyes containing dimethylfluorenyl unit. The amorphous non-planar fluorenyl moiety was adapted to prevent aggregation via molecular stacking and ensure greater resistance to degradation when exposed to light and high temperature. We already introduced the (9,9-dimethylfluoren-2-yl)amino phenyl,[9] benzo[*b*]furan,[10] and benzo[*b*]thiophene[11] as the donor moiety. As part of our efforts to investigate the structural modifications of phenylamine derivatives that can prevent the aggregation, 9,9-spirobifluorenyl amino unit has been introduced. Changing such electron donor unit would not only suppress aggregation formation but also affect the absorption properties. In this paper, we report three new organic sensitizers (**JK-87**, **JK-88**, and **JK-89**) containing spirobifluorenyl amino unit as electron donor. The photovoltaic properties, electronic, and optical properties of the three sensitizers are described.



JK-87 **JK-88** **JK-89**

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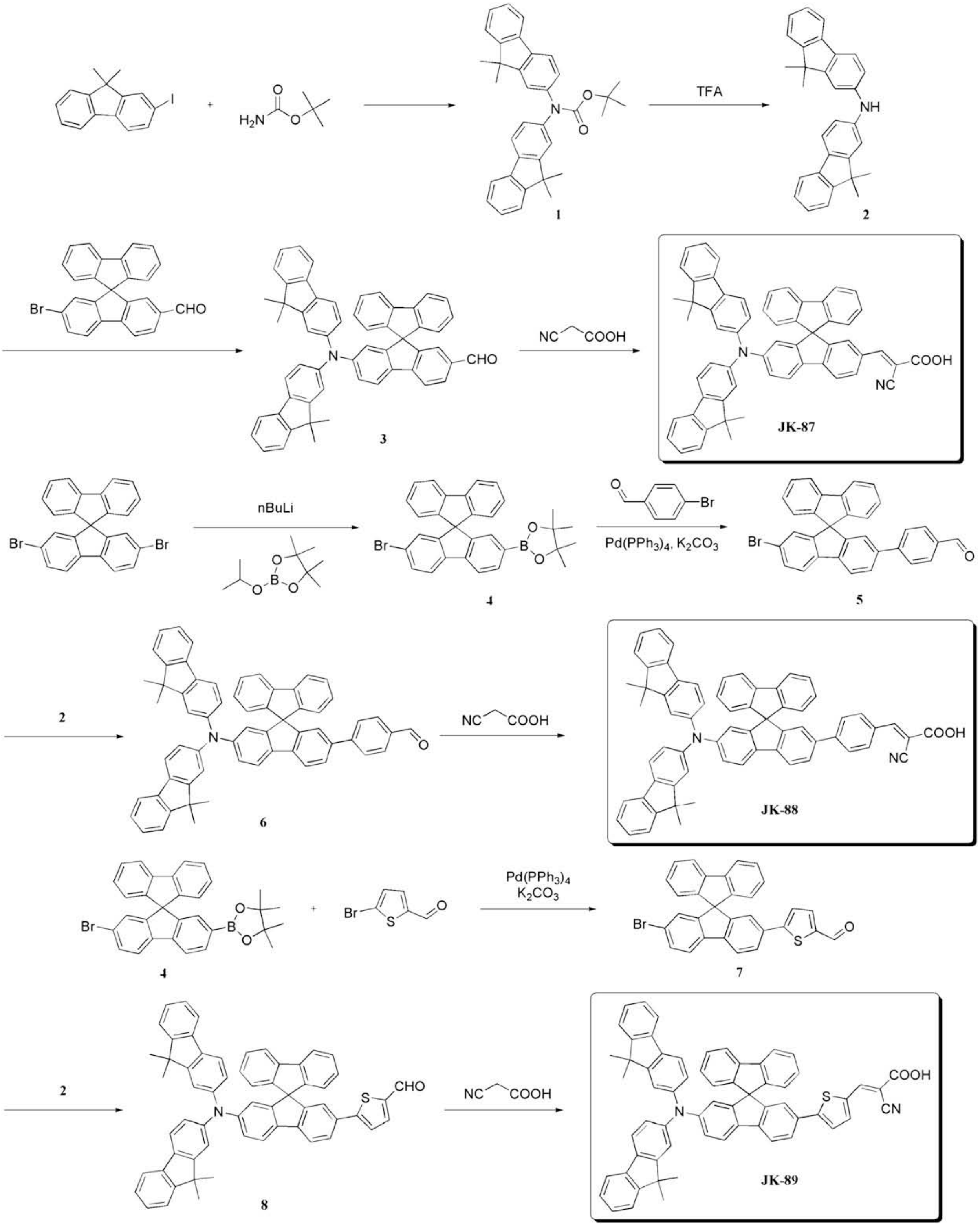
doi:10.1016/j.tet.2009.05.028

2. Results and discussion

The three organic dyes **JK-87**, **JK-88**, and **JK-89** were synthesized by the stepwise synthetic protocol (Scheme 1). For the synthesis of a variety of (9,9-dimethylfluoren-2-yl) amino phenyl derivatives, we first synthesized the (9,9-dimethylfluoren-2-yl) amine **2**. Recently, Buchwald[12] developed a highly efficient Cu-catalyzed tandem C–N bond formation. Using this methodology, the amine **2** was conveniently prepared. The Cu-catalyzed reaction of 2-iodo-9,9-dimethylfluorene with *tert*-butyl carbamate[13] afforded compound **1** in 60% yield. Although numerous methods have been reported for the deprotonation of *tert*-butoxycarbonyl group,[14] trifluoroacetic acid is shown to be an efficient and mild reagent. The arylamination of the 2-bromo-7-formyl-9,9-spirobifluorene[15,23] was readily performed in the presence of a palladium catalyst. The aldehyde **3** reacted with cyanoacetic acid to give the **JK-87**. The dioxaborolane derivative **4** was prepared from 2,7-dibromo-9,9-spirobifluorene with 1.2 equiv *n*-butyllithium and subsequent quenching with



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-87**, **JK-88**, and **JK-89**.

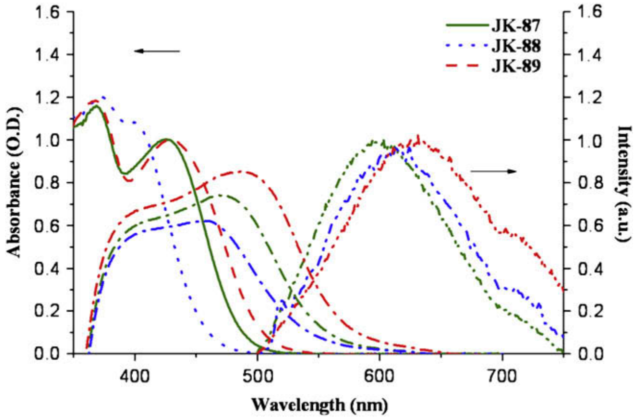
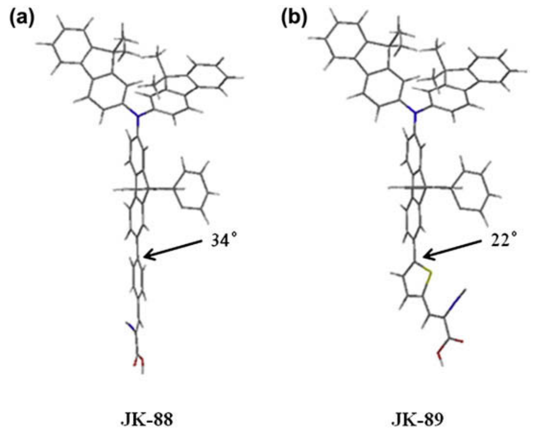


Figure 1. Absorption spectra of **JK-87** (olive solid line), **JK-88** (blue dot line), and **JK-89** (red dash line) in 10^{-5} M ethanol solution, emission spectra of **JK-87** (olive dash–dot–dot line), **JK-88** (blue dash–dot–dot line), and **JK-89** (red dash–dot–dot line) in 10^{-5} M ethanol solution, and absorption spectra of **JK-87** (olive dash–dot), **JK-88** (blue dash–dot line), and **JK-89** (red dash–dot line) adsorbed on nanocrystalline TiO_2 film.

2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[16] Suzuki coupling reaction[17] of **4** with 4-bromobenzaldehyde, followed by N-phenylation of **2** gave **6**. The corresponding aldehyde **6** afforded the dye **JK-88** on treatment of cyanoacetic acid. Dye **JK-89** was conveniently synthesized in three steps. The Suzuki coupling of **4** with 5-bromothiophene-2-carbaldehyde, followed by N-phenylation of **7** with **2** gave **8**. The condensation reaction of **8** with cyanoacetic acid yielded the dye **JK-89**.

The UV–vis and emission spectra of **JK-87**, **JK-88**, and **JK-89** in ethanol are shown in Figure 1, together with the UV–vis spectra of the corresponding sensitizers absorbed on TiO_2 film. The absorption spectrum of **JK-89** exhibits visible bands at 368 and 428 nm, which is due to the π–π^* transition of the conjugate molecule. Under the same conditions the **JK-88** sensitizer that contains the phenyl group instead of thienyl group causes a blue shift to 410 nm relative to the **JK-89**. A blue shift of **JK-88** can be readily understood from molecular modeling studies of the two sensitizers (Fig. 2). The ground state structure of **JK-88** possess a 34° twist between 9,9-spirobifluorene and the phenyl unit. For **JK-89**, the dihedral angle between 9,9-spirobifluorene and the thiophenyl unit is 22°.

Accordingly, a red shift of **JK-89** relative to **JK-88** derives from more delocalization over an entire conjugated system. Absorption of sensitizers **JK-87**–**JK-89** absorbed on a TiO_2 electrode was observed to broaden the absorption spectrum and to red shift the absorption threshold up to 660 nm. Such broadening and red shifts have been observed in other organic sensitizers on TiO_2 electrode.[18]



JK-88 JK-89

Figure 2. The optimized structure calculated with TD-DFT on B3LYP/3-21G* of (a) **JK-88** and (b) **JK-89**.

Table 1
Optical, redox and DSSC performance parameters of dyes

Dye	λ_{abs}[a]/nm (ε/M^{-1} cm^{-1})	E_{ox}[b] (V)	E_{0-0}[c] (V)	E_{LUMO}[d]/V	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
JK-87	369 (22,000) 427 (19,000)	1.14	2.469	−1.33	11.31	0.78	0.75	6.58
JK-88	371 (32,000) 410 (28,000)	1.12	2.474	−1.36	9.28	0.76	0.75	5.28
JK-89	368 (40,000) 428 (34,000)	1.13	2.431	−1.31	13.02	0.75	0.70	6.83

[a] Absorption spectra were measured in ethanol.
[b] Redox potential of dyes on TiO_2 were measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 100 mV s^{-1} (vs Fc/Fc^+).
[c] E_{0-0} was determined from intersection of absorption and emission spectra in ethanol.
[d] E_{LUMO} was calculated by E_{ox}–E_{0-0}.

We also observed that the sensitizers **JK-87**–**JK-89** exhibited strong luminescence maxima at 596–642 nm when they are excited with their π–π^* bands in EtOH at 298 K.

To judge the feasibility of electron transfer from the excited dye molecule to the conduction band of TiO_2 electrode, redox potentials of the three dyes were investigated by cyclic voltammetry. The redox potentials of **JK-87**–**JK-89** were measured in MeCN with 0.1 M tetra-butylammonium hexafluorophosphate. The three organic sensitizers absorbed on TiO_2 film show quasi-reversible couples. The oxidation potentials of **JK-87**, **JK-88**, and **JK-89** were measured to be 1.14, 1.12, and 1.13 V versus NHE, respectively, energetically favorable for iodide oxidation (Table 1). The reduction potentials of the three dyes calculated from the oxidation potentials and the E_{0-0} determined from the intersection of absorption and emission spectra were tabulated (Table 1). The excited state oxidation potentials (E_{ox}^{*}) of the dyes (**JK-87**: −1.33 V vs NHE; **JK-88**: −1.36 V vs NHE; **JK-89**: −1.31 V vs NHE) are much negative than the conduction band of TiO_2 at −0.5 V versus NHE. A slight positive shift of the reduction potential in **JK-89** relative to that of **JK-88** is due to more delocalization of the π-conjugation system.

To gain insight into the geometrical configuration and photophysical properties, molecular orbital calculations of **JK-87**–**JK-89** were performed with the TD-DFT on B3LYP/3-21G* (Fig. 3). The calculation illustrates that the HOMO of three sensitizers is delocalized over the π-conjugated system through the phenyl amino group. The LUMO is localized over the twisted fluorine unit. On the other hand, the LUMO+1 of **JK-87**–**JK-89** is delocalized over the cyanoacrylic unit through the next conduit channel. 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 in three sensitizers indicates that HOMO–LUMO excitation moves the electron distribution from the phenyl amino unit to the twisted fluorine unit and the photo-induced electron transfer from the dyes to TiO_2 electrode cannot be efficiently occurred by the HOMO–LUMO transition. A relatively low efficiency in three sensitizers can be explained as a mismatch of vectorial electron flow from the HOMO to the LUMO.

Figure 4 shows the photocurrent action spectra for DSSCs based on **JK-87**–**JK-89** using an acetonitrile based electrolyte (electrolyte: 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05 M I_2, 0.1 M LiI, and 0.5 M 4-*tert*-butylpyridine). The incident photon-to-current conversion efficiency (IPCE) of **JK-87** and **JK-89** shows a plateau of over 75% from 420 to 530 nm, reaching the maximum of 81% at 464 nm. These two sensitizers show a relatively large photocurrent due to large IPCEs. The IPCE spectrum of **JK-88** is due to blue shift by about 90 nm compared to those of **JK-87** and **JK-89** as a result of distortion of bridging unit, which is consistent with the absorption spectrum of **JK-88**. Photovoltaic performances of the three sensitized cells are listed in Table 1.

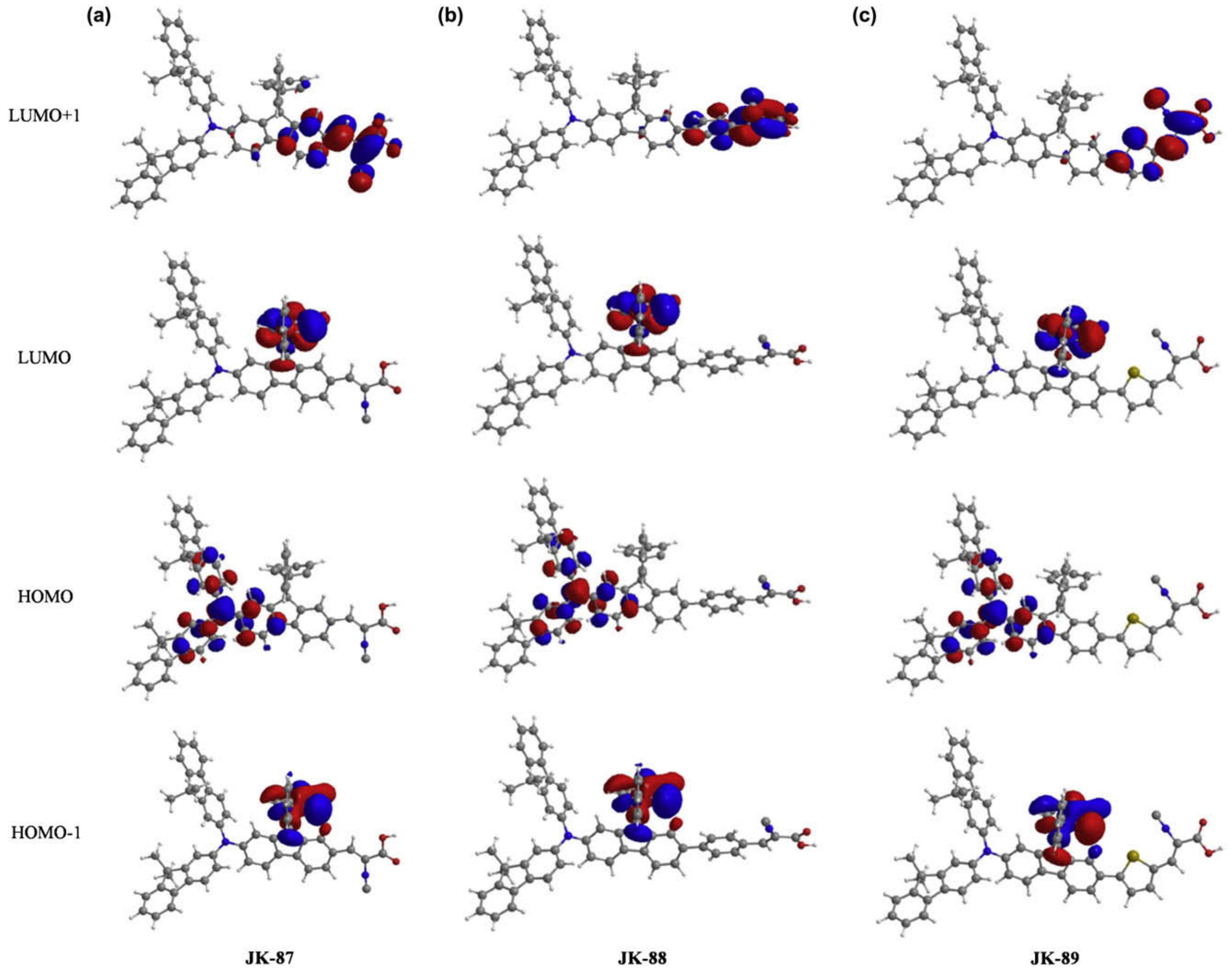


Figure 3. Isodensity surface plots of the HOMO, HOMO-1, LUMO, and LUMO+1 of (a) **JK-87**, (b) **JK-88**, and (c) **JK-89**.

Under standard global A.M. 1.5 solar condition, the **JK-89** sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 13.02 mA cm^{-2}, as an open-circuit voltage (V_{oc}) of 0.75 V, and a fill factor of 0.70, corresponding to η of 6.83% (Fig. 5). Under the same condition, the **JK-88** sensitized cell gave a J_{sc} of 9.28 mA cm^{-2}, V_{oc} of 0.76 V, and a fill factor of 0.75, corresponding to η of 5.28%. The power conversion efficiency of **JK-88** is relatively low compared to those of **JK-87** and **JK-89**. To clarify the above result, we have measured the amount of dyes adsorbed TiO$_2$ film to explain the higher efficiency of **JK-87** and **JK-89** sensitized cells compared to the **JK-88** sensitized cell. The adsorbed amounts of 2.26×10^{-6} mmol cm^{-2} for **JK-87**, 2.58×10^{-6} mmol cm^{-2} for **JK-88**,

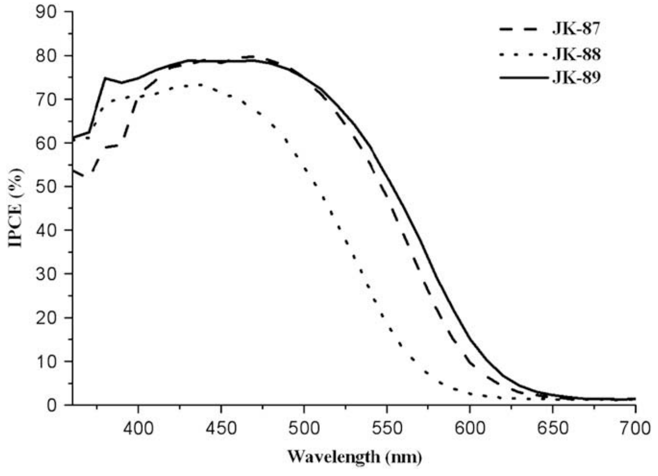


Figure 4. Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSC based on **JK-87** (dashed line), **JK-88** (dotted line), and **JK-89** (solid line).

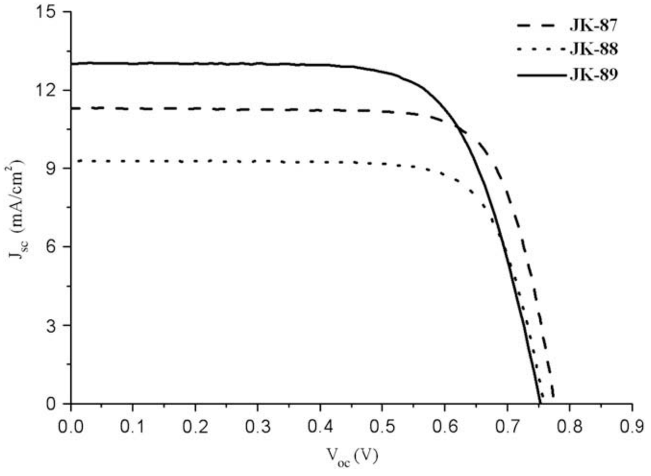


Figure 5. A photocurrent–voltage curve obtained with a DSSC based on **JK-87** (dashed line), **JK-88** (dotted line), and **JK-89** (solid line) under A.M. 1.5 radiation (100 mW cm^{-2}).

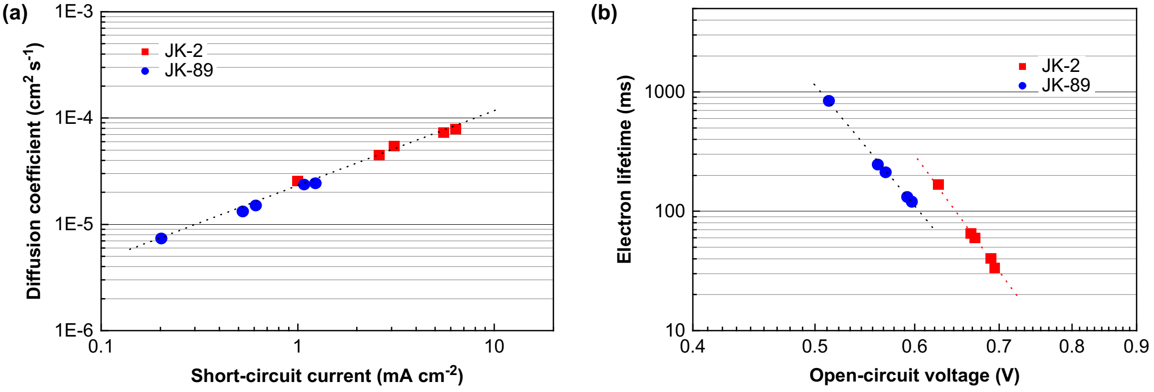


Figure 6. (a) Electron diffusion coefficients and (b) lifetimes of the photovoltaic cells employing **JK2** and **JK-89**.

and 2.71×10^{-6} mmol cm^{-2} for **JK-89** are observed. Therefore, the higher efficiencies of **JK-87** and **JK-89** compared to that of **JK-88** may be attributable to the broad and red-shifted absorption bands rather than the absorbed quantity, resulting in the large IPCE.

Figure 6 shows the electron diffusion coefficients and lifetimes of the DSSCs (employing **JK2** and **JK-89**, respectively) displayed as a function of the J_{sc} and V_{oc}, respectively. Note that we selected **JK-2** dye for the comparison because this dye has not only the backbone structure similar to that of **JK-89** but also the reliable performances as we reported previously.[19] There is no significant difference among the D_e values at the identical short-circuit current conditions. This result indicates that the D_e values are hardly affected by the kind of dye molecules, showing the similar trend to those of coumarin dyes.[20] On the other hand, the τ_e values show a significant gap between the dyes. The τ_e values of **JK-89** were somewhat smaller than those of **JK-2** due to the relatively poor dye adsorption onto the TiO_2 surface.[21] The amounts of the dye molecules adsorbed on the TiO_2 electrodes (film thickness=ca. 6 μm) were shown to be 1.27×10^{-7} and 0.98×10^{-7} mol cm^{-2} for **JK-2** and **JK-89**, respectively. The electron recombination can be facilitated along with the insufficient coverage on the TiO_2 surface, resulting in the decrease in the τ_e values.[20] This result might be owing to the relatively bulky structure of **JK-89** compared to that of **JK-2**.

The ac impedances of the cells were measured under the illumination conditions. Figure 7 shows the ac impedance spectra measured under open-circuit conditions and under illumination of 100 mW cm^{-2}. The radius of the intermediate-frequency semicircle in the Nyquist plot decreased in the order of **JK-88** (30.64 Ω)>**JK-87** (25.67 Ω)>**JK-89** (21.61 Ω), indicating the improved charge generation and transport, which correspond to the overall device efficiency.

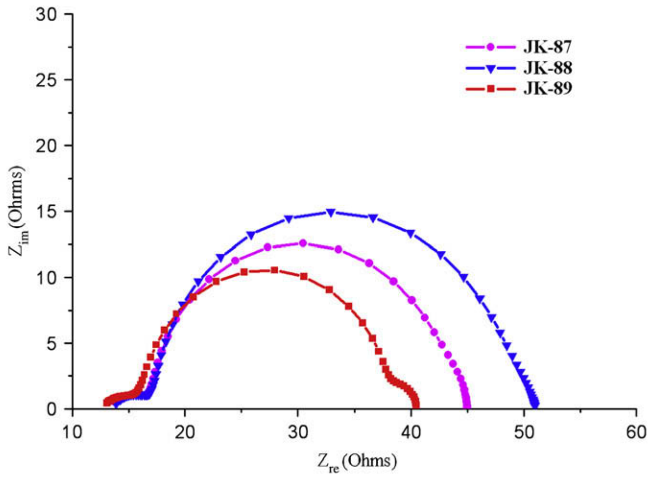


Figure 7. Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) for the devices employing different dyes (● **JK-87**, ▼ **JK-88**, ■ **JK-89**).

In summary, we have designed and synthesized three organic sensitizers containing *N*,*N*-bis(9,9-dimethylfluoren-2-yl) amine unit bridged by sterically bulky spirobifluorenyl unit. The power conversion efficiency of the DSSCs based on the **JK-89** sensitizer reached 6.83%. The power conversion efficiency was demonstrated to be quite sensitive to the bridging group and its molecular configuration. This work also proved that the development of highly efficient organic sensitizers is possible through molecular engineering, and these works are now in progress.

3. Experimental section

3.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich, TCI, and Acros Organics. 2-Iodo-9,9-dimethylfluorene[22] and 2-bromo-7-formyl-9,9-spirobifluorene[15,23] were synthesized using a modified procedure of previous references.

3.1.1. Spectroscopic measurements

^1H NMR 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.

3.1.2. Electrochemical measurements

Cyclic voltammogram was carried out with a BAS 100B (Bioanalytical System, Inc.). A three-electrode system was used and consisted of a gold disk, working electrode, and a platinum wire electrode. Redox potential of dyes on TiO_2 was measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate between 100 mV s^{-1} (vs Fc/Fc$^+$).

3.1.3. Fabrication of DSSC

For the preparation of DSSC, a washed FTO (Pilkington, 8 Ω sq^{-1}) glass plate was immerged in 40 mM $TiCl_4$ aqueous solution as reported by the Grätzel group.[19] The first TiO_2 layer of 12 μm thickness was prepared by screen printing with transparent mesoporous TiO_2 paste (13 nm anatase, solaronix), and the second opaque layer of 4 μm thickness (400 nm, CCIC) was coated for the purpose of light scattering. The TiO_2 electrodes were immersed into the dyes (**JK-87**, **JK-88**, and **JK-89**) solution (0.3 mM in ethanol containing 10 mM 3a,7a-dihydroxy-5b-cholic acid) and kept at room temperature for 18 h. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg Pt in 1 ml ethanol) on an FTO plate. The electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M 4-*tert*-butylpyridine in acetonitrile.

3.1.4. 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).

3.1.5. 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).[24–27] 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 less than 10% of the light intensity was turned down using an ND filter. The laser beam was positioned at the front side of the fabricated samples (TiO_2 film thickness=ca. 6 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, $D_e=\omega^2/(2.77\tau_c)$.[24] The τ_e value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau_e)$.[24] All experiments were conducted at room temperature.

*3.1.6. tert-Butyl bis(9,9-dimethyl-9H-fluoren-7-yl)carbamate (**1**)*

An oven-dried flask was charged with CuI (0.014 g, 0.074 mmol), 2-iodo-9,9-dimethylfluorene (1 g, 3.12 mmol), *tert*-butyl carbamate (0.174 g, 1.48 mmol), and Cs_2CO_3 (1.45 g, 4.45 mmol). The flask was evacuated and backfilled with nitrogen gas. Under a positive pressure of nitrogen gas, *N*,*N*′-dimethylethylenediamine (0.031 ml, 0.29 mmol) was added via syringe, followed by the addition of dry tetrahydrofuran (THF) (5 ml). The flask was refluxed at 80 °C in oil bath for 36 h. The reaction mixture was cooled to room temperature. The solution was extracted with dichloromethane, dried over $MgSO_4$, and subjected to column chromatography (silica gel, ethyl acetate/hexanes=1:10, R_f=0.4). A white sponge solid was obtained. Yield: 60% (0.45 g). Mp: 156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69–7.62 (m, 4H), 7.42–7.40 (m, 2H), 7.32 (m, 6H), 7.2–7.17 (m, 2H), 1.48 (s, 12H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.27, 154.07, 153.9, 142.62, 138.79, 136.61, 127.13, 125.75, 122.65, 121.42, 120.06, 119.98, 81.174, 46.99, 28.44, 27.19. Anal. Calcd for $C_{35}H_{35}NO_2$: C, 83.80; H, 7.03. Found: C, 83.52; H, 6.96.

*3.1.7. Bis(9,9-dimethyl-9H-fluoren-7-yl)amine (**2**)*

tert-Butoxycarbonyl (BOC)-protected arylamine **1** (0.4 g, 0.8 mmol) was dissolved in tetrahydrofuran(THF) (1 ml) and trifluoroacetic acid (TFA) (8 ml). And then, the reaction mixture was stirred at room temperature for 10 min. The resulting mixture was changed into an intense deep-green color. After evaporation of TFA, dichloromethane was added to the residue, then the mixture was neutralized with saturated aqueous solution of NaOH. The organic layer was extracted with dichloromethane, dried over $MgSO_4$, and subjected to flash column chromatography (silica gel, ethyl acetate/hexanes=1:10, R_f=0.3). A white-yellow solid was obtained. Yield: 95% (0.3 g). Mp: 178 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.70–7.67 (m, 4H), 7.48 (d, *J*=6.9 Hz), 7.36 (s, 2H), 7.31–7.22 (m, 4H), 7.18 (d, 2H, *J*=7.2 Hz), 1.46 (s, 12H). ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ 155.97, 153.83, 144.45, 140.29, 132.48, 127.79, 126.73, 123.27, 121.67, 119.69, 117.32, 112.46, 47.28, 27.53. Anal. Calcd for $C_{30}H_{27}N$: C, 89.73; H, 6.78. Found: C, 89.57; H, 6.68.

*3.1.8. 7-(Bis(9,9-dimethyl-9H-fluoren-7-yl)amino)-9,9-spirobifluorene-2-carbaldehyde (**3**)*

Under nitrogen atmosphere, a mixture of 2-bromo-7-formyl-9,9-spirobifluorene (0.3 g, 0.7 mmol), **2** (0.44 g, 1.05 mmol), $Pd(OAc)_2$ (0.023 g, 0.1 mmol), P(*t*Bu)$_3$ (0.04 g, 0.2 mmol), and Cs_2CO_3 (1.4 g, 4.3 mmol) in dry toluene (15 ml) was stirred and heated at 130 °C for overnight. After cooling to room temperature, saturated ammonium chloride solution was added to the reaction solution. The solution was extracted with dichloromethane, dried over $MgSO_4$, and subjected to column chromatography (silica gel, dichloromethane/hexanes=3:1). A yellow solid was obtained. Yield: 50% (0.26 g). Mp: 180 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 9.85 (s, 1H), 8.12 (d, 1H, *J*=8.4 Hz), 8.03 (d, 1H, *J*=8.4 Hz), 7.97 (d, 1H, *J*=7.8 Hz), 7.86 (d, 2H, *J*=7.2 Hz), 7.70 (d, 2H, *J*=7.2 Hz), 7.64 (d, 2H, *J*=8.1 Hz), 7.45 (d, 2H, *J*=7.2 Hz), 7.35 (m, 12H), 6.96 (dd, 2H, *J*=8.1, 1.2 Hz), 6.84 (d, 2H, *J*=7.5 Hz), 6.56 (s, 1H), 1.28 (s, 12H). ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ 191.91, 155.95, 154.39, 152.44, 150.41, 148.7, 148.53, 147.5, 142.55, 139.48, 136.41, 135.76, 135, 131.49, 129.01, 127.9, 127.66, 124.74, 124.65, 124.49, 123.41, 123.29, 121.75, 121.25, 120.74, 120.43, 119.99, 117.87, 66.52, 54.93, 47.42, 27.56. Anal. Calcd for $C_{56}H_{41}NO$: C, 90.41; H, 5.56. Found: C, 90.24; H, 5.48.

*3.1.9. 3-(2-(Bis(9,9-dimethyl-9H-fluoren-7-yl)amino)-9,9-spirobifluoren-7-yl)-2-cyanoacrylic acid (**JK-87**)*

A mixture of **3** (0.14 g, 0.188 mmol) and cyanoacetic acid (0.025 g, 0.3 mmol) in dry toluene (15 ml) and piperidine (0.028 ml, 0.29 mmol) were added. The solution was refluxed for 10 h. After cooling the solution was extracted with dichloromethane and 0.1 M aqueous solution of HCl. Then, the organic layer was dried over $MgSO_4$. The pure product **JK-87** was obtained by column chromatography (silica gel, ethyl acetate, R_f=0.1). Yield: 45% (0.068 g). Mp: 243 °C. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 8.02(m, 3H), 7.83 (d, 2H, *J*=7.5 Hz), 7.75 (s, 1H), 7.67 (m, 4H), 7.46 (d, 2H, *J*=7.5 Hz), 7.33 (m, 6H), 7.16 (m, 4H), 7.02 (m, 2H), 6.85 (dd, 2H, *J*=8.1, 1.5 Hz), 6.76 (d, 2H, *J*=7.8 Hz), 6.3 (s, 1H), 1.18 (s, 12H). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 163.32, 154.76, 153.21, 150.68, 148.83, 148.28, 147.65, 147.07, 146.1, 143.82, 141.1, 138.08, 134.31, 131.87, 129.76, 128.24, 128.11, 127.14, 126.89, 124.26, 123.6, 123.48, 122.72, 122.37, 122, 121.22, 120.6, 120.25, 119.71, 119.27, 118.8, 116.21, 111.99, 110.99, 65.31, 46.41, 26.72. MS: *m*/*z* 810.53 [M^+]. Anal. Calcd for $C_{59}H_{42}N_2O_2$: C, 87.38; H, 5.22. Found: C, 87.30; H, 5.17.

*3.1.10. 2-(2-Bromo-9,9-spirobifluoren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**)*

Under nitrogen atmosphere and at −78 °C, *n*-BuLi (5.1 ml, 1.6 M in hexane) was added dropwise to a dry THF solution containing 2,7-dibromo-9,9-spirobifluorene (3.50 g, 7.38 mmol). After 30 min stirring at −78 °C, 1.7 ml (8.33 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added slowly to the reaction solution at −78 °C. The solution was warmed to room temperature and the reaction mixture was stirred for 8 h. Then, the reaction was quenched with water. The solution was extracted with dichloromethane, dried over $MgSO_4$, and subjected to column chromatography (silica gel, ethyl acetate/hexane=1:10, R_f=0.45). A white solid was obtained. Yield: 85% (3.26 g). Mp: 305 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, 4H, *J*=7.2 Hz), 7.73 (d, 1H, *J*=7.2 Hz), 7.48 (d, 1H, *J*=7.2 Hz), 7.38 (dd, 2H, *J*=7.2, 1.2 Hz), 7.16 (s, 1H), 7.11 (dd, 2H, *J*=7.2, 1.2 Hz), 6.79 (s, 1H), 6.71 (d, 2H, *J*=7.2 Hz), 1.25 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8, 147.8, 147.61, 143.8, 142, 140.4, 135.08, 134.93, 131.01, 130.41, 128.08, 128.04, 127.34, 124.29, 122.11, 121.84, 120.29, 119.51, 83.9, 65.9, 48.2, 24.9. Anal. Calcd for $C_{31}H_{26}BBrO_2$: C, 71.43; H, 5.03. Found: C, 71.24; H, 4.98.

3.1.11. 4-(2-Bromo-9,9-spirobifluoren-7-yl)benzaldehyde (**5**)

Under nitrogen atmosphere, a mixture of **4** (1.52 g, 2.92 mmol), 4-bromobenzaldehyde (0.54 g, 2.92 mmol), $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol), K_2CO_3 (4.04 g, 29.2 mmol), and degassed water (2 M) in dry THF (60 ml) was refluxed overnight. After cooling to room temperature, the solution was extracted with dichloromethane, dried over $MgSO_4$, and subjected to column chromatography (silica gel, dichloromethane/hexane=3:1, R_f=0.37). A light yellow solid was obtained. Yield: 85% (1.23 g). Mp: 186 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.93 (m, 3H), 7.83 (d, 2H, J=8.4 Hz), 7.77 (d, 1H, J=8.7 Hz), 7.69 (dd, 1H, J=8.4, 1.5 Hz), 7.58 (d, 2H, J=8.7 Hz), 7.54 (dd, 1H, J=8.1, 1.3 Hz), 7.44 (m, 2H), 7.18 (m, 2H), 7.1 (s, 1H), 6.89 (s, 1H), 6.8 (d, 2H, J=7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.87, 151.41, 149.67, 147.72, 146.76, 141.9, 141.25, 140.07, 139.87, 135.21, 131.24, 130.2, 128.31, 127.68, 124.22, 123, 122.09, 121.71, 120.73, 120.4, 66, 48.2. Anal. Calcd for $C_{32}H_{19}BrO$: C, 76.96; H, 3.83. Found: C, 76.74; H, 3.72.

3.1.12. 4-(2-(Bis(9,9-dimethyl-9H-fluoren-7-yl)amino)-9,9-spirobifluoren-7-yl)benzaldehyde (**6**)

Under nitrogen atmosphere, a mixture of **2** (0.5 g, 1.25 mmol), **5** (0.4 g, 0.8 mmol), $Pd(OAc)_2$ (0.023 g, 0.1 mmol), P(t-Bu)$_3$ (0.04 g, 0.2 mmol), and Cs_2CO_3 (1.4 g, 4.3 mmol) in dry toluene (15 ml) was stirred and heated at 130 °C overnight. After cooling to room temperature, saturated ammonium chloride solution was added to the reaction solution. The solution was extracted with dichloromethane, dried over $MgSO_4$, and subjected to column chromatography (silica gel, dichloromethane/hexanes=3:1). A yellow solid was obtained. Yield: 50% (0.33 g). Mp: 185 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.9 (m, 6H), 7.69 (m, 8H), 7.41 (m, 9H), 7.2 (m, 4H), 7.03 (m, 4H), 6.75 (s, 1H), 1.33 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.85, 155.03, 153.6, 150.7, 149.96, 148.59, 148.41, 147.04, 142.26, 141.8, 138.97, 138.29, 135.42, 134.95, 134.35, 130.15, 128.03, 127.33, 127.07, 126.6, 124.29, 123.45, 122.7, 122.54, 121.05, 120.63, 120.29, 119.87, 119.5, 118.65, 66.09, 46.83, 27.13. Anal. Calcd for $C_{62}H_{45}NO$: C, 90.81; H, 5.53. Found: C, 90.68; H, 5.42.

3.1.13. 3-(4-(2-(Bis(9,9-dimethyl-9H-fluoren-7-yl)amino)-9,9-spirobifluoren-7-yl)phenyl)-2-cyanoacrylic acid (**JK-88**)

A mixture of **6** (0.27 g, 0.33 mmol) and cyanoacetic acid (0.056 g 0.66 mmol) in dry chloroform (8 ml) and piperidine (0.0652 ml, 0.66 mmol) were added. The solution was refluxed for 10 h. After cooling the solution was extracted with dichloromethane and 0.1 M aqueous solution of HCl. Then, the organic layer was dried over $MgSO_4$. The pure product **JK-88** was obtained by column chromatography (silica gel, ethyl acetate, R_f=0.1). Yield: 55% (0.32 g). Mp: 263 °C. ^1H NMR (300 MHz, $(CD_3)_2SO$): δ 7.99 (m, 3H), 7.82 (m, 4H), 7.65 (d, 2H, J=6.9 Hz), 7.59 (d, 2H, J=8.1 Hz), 7.51 (d, 2H, J=7.2 Hz), 7.43 (d, 2H, J=6.3 Hz), 7.28 (m, 9H), 7.12 (m, 4H), 6.82 (m, 4H), 6.31 (s, 1H), 1.15 (s, 12H). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 163.69, 154.77, 153.21, 150.29, 149.27, 148.06, 147.75, 147.4, 146.3, 141.89, 141.42, 141.16, 138.15, 137.73, 134.93, 134.15, 131.97, 130.17, 128.27, 128.11, 127.18, 126.84, 123.56, 123.42, 122.75, 122.34, 121.93, 121.22, 120.63, 119.71, 119.03, 118.61, 116.75, 112.43, 46.42, 26.75. MS: m/z 866.62 [M^+]. Anal. Calcd for $C_{65}H_{46}N_2O_2$: C, 88.01; H, 5.23. Found: C, 87.88; H, 5.17.

3.1.14. 5-(2-Bromo-9,9-spirobifluoren-7-yl)thiophene-2-carbaldehyde (**7**)

Under nitrogen atmosphere, a mixture of **4** (0.45 g, 0.86 mmol), 5-bromothiophene-2-carbaldehyde (0.15 ml, 1.3 mmol), $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol), K_2CO_3 (1.19 g, 8.61 mmol), and degassed water (4.3 ml) in dry THF (20 ml) was refluxed overnight. After cooling to room temperature, the solution was extracted with dichloromethane, dried over $MgSO_4$, and subjected to column chromatography (silica gel, dichloromethane/hexane=3:1, R_f=0.45). A light yellow solid was obtained. Yield: 80% (0.34 g). Mp: 225 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.89 (m, 3H), 7.74 (dd, 2H, J=8.1, 1.5 Hz), 7.60 (d, 1H, J=4.8 Hz), 7.53 (dd, 1H, J=8.1, 1.4 Hz), 7.42 (m, 2H), 7.19 (d, 1H, J=4.2 Hz), 7.14 (m, 2H), 6.99 (dd, 1H, J=7.4, 1.3 Hz), 6.86 (s, 1H), 6.76 (dd, 2H, J=7.5, 1.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.64, 153.8, 151.31, 149.74, 148.13, 147.31, 142.23, 142.02, 141.79, 139.73, 137.29, 136.65, 134.68, 133.04, 131.52, 131.25, 130.48, 128.36, 127.38, 126.66, 124.07, 122.3, 121.8, 121.79, 120.87, 120.4, 83.29, 48.24. Anal. Calcd for $C_{30}H_{17}BrOS$: C, 71.29; H, 3.39. Found: C, 71.08; H, 3.31.

3.1.15. 5-(2-(Bis(9,9-dimethyl-9H-fluoren-7-yl)amino)-9,9-spirobifluoren-7-yl)thiophene-2-carbaldehyde (**8**)

Under nitrogen atmosphere, a mixture of **2** (1.05 g, 2.61 mmol), **7** (0.88 g, 1.74 mmol), $Pd(OAc)_2$ (0.016 g, 0.071 mmol), P(t-Bu)$_3$ (0.03 g, 0.148 mmol), and Cs_2CO_3 (1.25 g, 3.84 mmol) in dry toluene (30 ml) was stirred and heated at 130 °C overnight. After cooling to room temperature, saturated ammonium chloride solution was added to the reaction solution. The solution was extracted with dichloromethane, dried over $MgSO_4$, and subjected to column chromatography (silica gel, dichloromethane/hexanes=3:1). An orange-yellow solid was obtained. Yield: 60% (1.15 g). Mp: 197 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.98 (m, 6H), 7.77 (dd, 3H, J=8.1, 1.4 Hz), 7.68 (d, 2H, J=7.5 Hz), 7.55 (m, 8H), 7.31 (dd, 6H, J=7.8, 1.5 Hz), 7.11 (m, 4H), 6.85 (s, 1H), 1.46 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.69, 155.06, 154.64, 154.64, 150.74, 150.12, 148.28, 146.97, 143.22, 141.89, 141.8, 138.97, 137.35, 135.08, 134.46, 131.63, 128.07, 127.08, 126.64, 124.16, 124.01, 123.91, 123.55, 123.28, 122.57, 121.68, 121.14, 120.65, 120.36, 119.97, 119.52, 118.74, 118.47, 65.99, 46.86, 27.14. Anal. Calcd for $C_{60}H_{43}NOS$: C, 87.24; H, 5.25. Found: C, 87.02; H, 5.18.

3.1.16. 3-(5-(2-(Bis(9,9-dimethyl-9H-fluoren-7-yl)amino)-9,9-spirobifluoren-7-yl)thiophen-2-yl)-2-cyanoacrylic acid (**JK-89**)

A mixture of **8** (0.19 g, 0.23 mmol) and cyanoacetic acid (0.04 g, 0.43 mmol) in dry chloroform (12 ml) and piperidine (0.047 ml, 0.47 mmol) were added. The solution was refluxed for 10 h. After cooling the solution was extracted with dichloromethane and 0.1 M aqueous solution of HCl. Then, the organic layer was dried over $MgSO_4$. The pure product **JK-89** was obtained by column chromatography (silica gel, ethyl acetate, R_f=0.1). Yield: 50% (0.1 g). Mp: 285 °C. ^1H NMR (300 MHz, $(CD_3)_2SO$): δ 8.06 (s, 1H), 7.98 (m, 2H), 7.86 (d, 2H, J=7.2 Hz), 7.79 (d, 1H, J=8.1 Hz), 7.67 (d, 2H, J=7.2 Hz), 7.62 (d, 2H,, J=8.4 Hz), 7.45 (m, 3H), 7.34 (d, 1H, J=7.8 Hz), 7.28 (m, 7H), 7.14 (m, 4H), 7.04 (d, 1H, J=8.4 Hz), 6.84 (m, 4H), 6.3 (s, 1H), 1.18 (s, 12H). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 189.11, 163.51, 154.67, 153.12, 150.24, 149.19, 148.46, 147.7, 147.84, 146.13, 142.08, 141.29, 141.01, 138.04, 135.62, 134.43, 134.11, 131.41, 128.24, 128.11, 127.04, 126.76, 126.24, 124.48, 123.47, 123.36, 122.62, 122.2, 121.92, 121.1, 120.67, 119.91, 119.91, 119.6, 118.57, 118.82, 65.34, 46.33, 26.64. MS: m/z 892.6 [M^+]. Anal. Calcd for $C_{63}H_{44}N_2O_2S$: C, 84.72; H, 4.97. Found: C, 84.58; H, 4.92.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation through the ERC program (no. R11-2008-088-02001-0), the Ministry of Information & Communication, Korea, under the Information Technology Research Center (ITRC, no. IITA 2008 C1090 0904 0013) program, NRL program (No. R0A-2005-000-10034-0) and BK21.

References and notes

1. Robertson, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 2338.
2. (a) Asbury, J. B.; Ellingson, R. J.; Gosh, H. N.; Ferrere, S.; Notzig, A. J.; Lian, T. *J. Phys. Chem. B* **1999**, *103*, 3110; (b) Heimer, T. A.; Heilweil, E. J.; Bifnozzi, C. A.; Meyer, G. J. *J. Phys. Chem. A* **2000**, *104*, 4256; (c) Lee, J.-J.; Coia, G. M.; Lewis, N. S.

J. Phys. Chem. B **2004**, *108*, 5269; (d) Saito, Y.; Fukuri, N.; Senadeera, R.; Kitamura, T.; Wada, Y.; Yanagida, S. *Electrochem. Commun.* **2004**, *6*, 71.

3. (a) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Bessho, T.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835; (b) Grätzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145; (c) Grätzel, M. *Prog. Photovoltaics Res. Appl.* **2006**, *14*, 429.
4. (a) Ito, S.; Miura, H.; Uchida, S.; Takata, M.; Sumioka, K.; Liska, P.; Comte, P.; Péchy, P.; Grätzel, M. *Chem. Commun.* **2008**, 5194; (b) Wang, Z. S.; Cui, Y.; Hara, K.; Dan-oh, Y.; Kasada, C.; Shinpo, A. *Adv. Mater.* **2007**, *19*, 1138; (c) Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256; (d) Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806.
5. (a) Ehret, A.; Stuhl, L.; Spitler, M. T. *Electrochim. Acta* **2000**, *45*, 4553; (b) Ehret, A.; Stuhl, L.; Spiltler, M. T. *J. Phys. Chem. B* **2001**, *105*, 9960.
6. (a) Khazraji, A. C.; Hotchandani, S.; Das, S.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 4693; (b) Das, S.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 209.
7. Kim, S.; Kim, D.; Choi, H.; Kang, M.-S.; Kang, S. O.; Ko, J. *Chem. Commun.* **2008**, 4951.
8. Qin, H.; Wenger, S.; Xu, M.; Gao, F.; Jing, X.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 9202.
9. (a) Chio, H.; Baik, C.; Kang, S. O.; Ko, J.; Kang, M. S.; Nazeeruddin, M. K.; Grätzel, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 327; (b) Kim, J.-J.; Choi, H.; Lee, J.-W.; Kang, M.-S.; Song, K.; Kang, S. O.; Ko, J. *J. Mater. Chem.* **2008**, *18*, 5223; (c) Kim, C.; Choi, H.; Kim, S.; Baik, C.; Song, K.; Kang, M.-S.; Kang, S. O.; Ko, J. *J. Org. Chem.* **2008**, *73*, 7072; (d) Kim, S.; Choi, H.; Kim, D.; Song, K.; Kang, S. O.; Ko, J. *Tetrahedron* **2007**, *63*, 9206.
10. Jung, I.; Lee, J. K.; Song, K. H.; Song, K.; Kang, S. O.; Ko, J. *J. Org. Chem.* **2007**, *72*, 3652.
11. Choi, H.; Lee, J. K.; Song, K.; Kang, S. O.; Ko, J. *Tetrahedron* **2007**, *63*, 3115.
12. Martin, R.; Larsen, C. H.; Cuenca, A.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 3379.
13. Jiang, L.; Job, G. E.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 3667.
14. Li, B.; Bemish, R.; Buzon, R. A.; Chiu, C. K.-F.; Colgan, S. T.; Kissel, W.; Le, Tung; Leeman, K. R.; Newell, L.; Roth, J. *Tetrahedron Lett.* **2003**, *44*, 8113.
15. Chiang, C.-L.; Wu, M.-F.; Dai, D.-C.; Wen, Y.-S.; Wang, J. K.; Chen, C.-T. *Adv. Funct. Mater.* **2005**, *15*, 231.
16. Park, Y.-I.; Son, J.-H.; Kang, J.-S.; Kim, S.-K.; Lee, J.-H.; Park, J.-W. *Chem. Commun.* **2008**, 2143.
17. Zhang, X.; Gorohmaru, H.; Kadowaki, M.; Kobayashi, T.; Ishi-I, T.; Thiemann, T.; Mataka, S. *J. Mater. Chem.* **2004**, *14*, 1901.
18. (a) Nuesch, F.; Moser, J. E.; Shklover, V.; Grätzel, M. *J. Am. Chem. Soc.* **1996**, *118*, 5420; (b) Iriyama, K.; Mizutani, F.; Yoshiura, M. *Chem. Lett.* **1980**, 1399; (c) Sayama, K.; Hara, K.; Mori, N.; Satsuki, M.; Suga, S.; Tsukagoshi, S.; Abe, Y.; Sugihara, H.; Arakawa, H. *Chem. Commun.* **2000**, 1173.
19. Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J.-H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701.
20. Hara, K.; Miyamoto, K.; Abe, Y.; Yanagida, M. *J. Phys. Chem. B* **2005**, *109*, 23776.
21. Yum, J.-H.; Jang, S.-R.; Walter, P.; Geiger, T.; Nüesch, F.; Kim, S.; Ko, J.; Grätzel, M.; Nazeeruddin, M. K. *Chem. Commun.* **2007**, 4680.
22. Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11.
23. Faming Zhuanli Shenqing Gongkai Shuomingshu, CN1634839, 2005.
24. Nakade, S.; Kanzaki, T.; Wada, Y.; Yanagida, S. *Langmuir* **2005**, *21*, 10803.
25. Kang, M.-S.; Ahn, K.-S.; Lee, J.-W.; Kang, Y. S. *J. Photochem. Photobiol., A* **2008**, *195*, 198.
26. Ahn, K.-S.; Kang, M.-S.; Lee, J.-K.; Shin, B.-C.; Lee, J.-W. *Appl. Phys. Lett.* **2006**, *89*, 013103.
27. Ahn, K.-S.; Kang, M.-S.; Lee, J.-W.; Kang, Y. S. *J. Appl. Phys.* **2007**, *101*, 084312.