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Tetrahedron 63 (2007) 9206–9212
Tetrahedron

Novel conjugated organic dyes containing bis-dimethylfluorenyl amino phenyl thiophene for efficient solar cell

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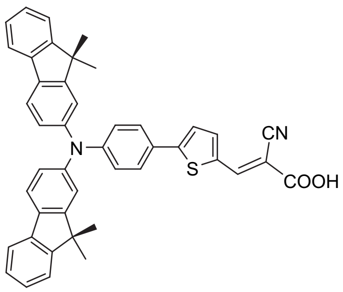
Received 23 April 2007; revised 14 June 2007; accepted 18 June 2007
Available online 23 June 2007

Abstract—Two novel organic dyes (**JK-5** and **JK-6**) containing bis-dimethylfluorenyl amino phenyl thiophene and additional methine unit are synthesized. Nanocrystalline TiO_2 dye-sensitized solar cell was fabricated using these dyes. A solar-to-electric conversion efficiency of 5.12% and 4.78% is achieved with **JK-5** and **JK-6**, respectively.

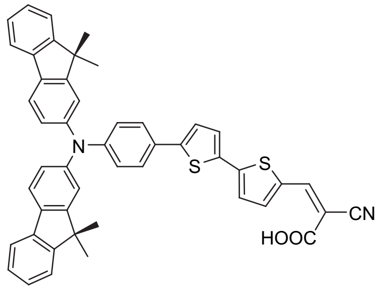
1. Introduction

Dye-sensitized solar cells (DSSCs) present an important alternative to current solar technology.[1–4] These cells employ mostly ruthenium polypyridyl complexes as charge-transfer sensitizers. Until now only three polypyridyl ruthenium complexes have achieved power conversion efficiencies over 10% in standard air mass 1.5 sunlight.[5] Some organic dyes with rich photophysical properties are shown to be promising sensitizers for nanocrystalline solar cells. Recently, the solar-cell performance of DSSCs based on organic dye photosensitizers has been remarkably improved, and an impressive photovoltaic performance has been obtained with some organic coumarin,[6] indoline,[7] oligoene,[8] merocyanine,[9] and hemicyanine[10] dyes having efficiencies in the range of 5–9%. Nevertheless, many organic dyes have still presented the low conversion efficiency. The major factor for the low conversion efficiency of many organic dyes in the DSSCs is due to the sharp and narrow absorption band of organic dyes. Therefore, the absorption spectra of organic dyes must be broadened and red-shifted for efficient solar-cell performance. One of the approaches to improve performance of organic dyes would be to increase π-conjugation by extending the methine unit into the framework of organic dyes. Arakawa and co-workers[11] reported that the introduction of methine unit into the coumarin framework (**NKX-2388**) expanded the π-conjugation in the dye and resulted in wide absorption in the visible region. These novel dyes performed as efficient photosensitizers for DSSCs. Recently, we[12] reported the highly efficient and stable organic dyes (**JK-1** and **JK-2**) having bis-dimethylfluorenyl amino phenyl donor unit with an overall conversion efficiency of 8.01%.

In order to improve the efficiency of such dyes, a wide absorption range in the visible region for the sensitizers is required. Accordingly, we envisioned that if we could



JK-1



JK-2

Keywords: Organic dye; Dimethylfluorenyl amino unit; Methine unit; Solar cell.

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doi:10.1016/j.tet.2007.06.061

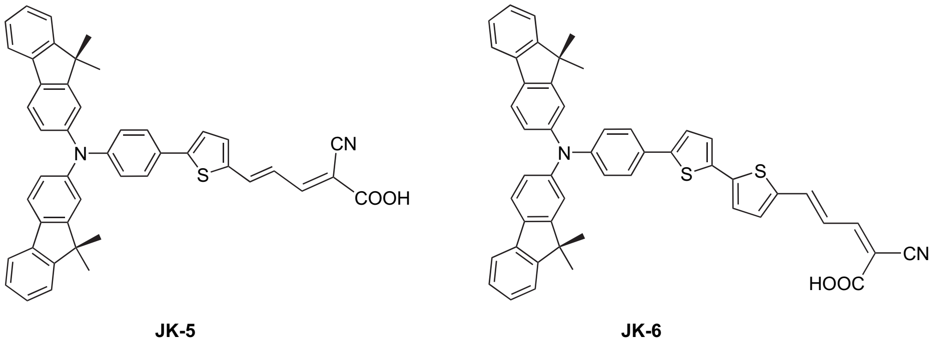


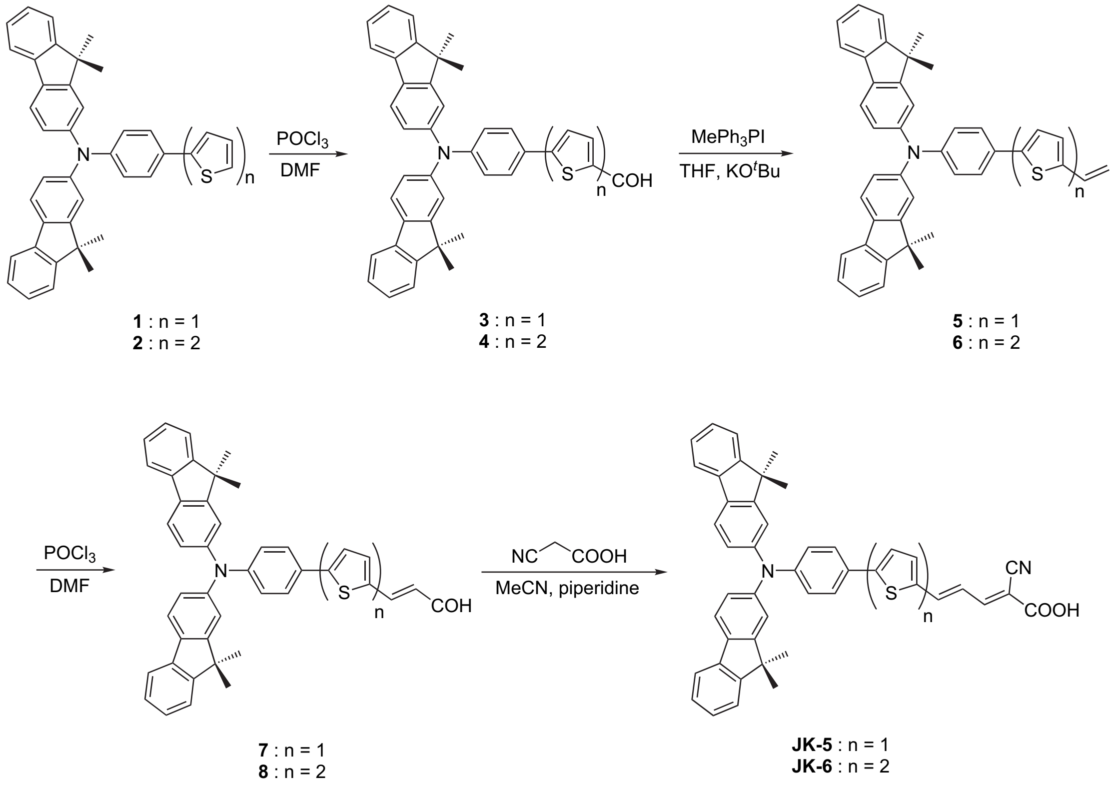
Figure 1. Structure of the dyes **JK-5** and **JK-6**.

introduce the –CH=CH– unit into the **JK-1** and **JK-2** framework, the sensitizers would expand the conjugation in the dyes resulting in a wide absorption in the visible region. Here we report two new organic dyes (**JK-5** and **JK-6**) containing [bis(9,9-dimethylfluorene-2-yl)amino]benzene as electron donor and cyano acrylic acid as electron acceptor bridged by thiophene-vinylene units. The photovoltaic properties, electronic and optical properties of the two sensitizers **JK-5** and **JK-6** are described (Fig. 1).

2. Results and discussion

The novel organic dyes **JK-5** and **JK-6** were prepared by the stepwise synthetic protocol illustrated in Scheme 1. New dyes are readily synthesized in four steps according to modified procedures reported in the literature.[13] Carbaldehydes **3** and **4** were prepared from **1** and **2** by a Vilsmeier–Haack reaction.[14] Coupling reaction of carbaldehydes **3** and **4** with methyltriphenylphosphonium iodide under Horner–Emmons–Wittig reaction[15] using potassium *tert*-butoxide in THF led to intermediates **5** and **6**. Subsequent Vilsmeier–Haack reaction of **5** and **6** produced the aldehydes 3-{5-[*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene-2-yl}acrylaldehyde **7** and 3-{5′-[*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl]-2,2′-bisthiophene-5-yl}acrylaldehyde **8**. The aldehydes **7** and **8**, on reaction with cyanoacetic acid in the presence of a catalytic amount of piperidine in acetonitrile, produced the **JK-5** and **JK-6** dyes.

Figure 2 shows the absorption and emission spectra of the **JK-5** and **JK-6** sensitizers measured in ethanol and the data are listed in Table 1. The absorption spectrum of **JK-5** displays two absorption maxima at 438 nm (ε=38,000 dm^3 mol^{-1} cm^{-1}) and 362 (ε=84,000 dm^3 mol^{-1} cm^{-1}), which are due to the π–π* transitions of the conjugated molecule. Under similar conditions the **JK-6** sensitizer that contains two thiophene units exhibits absorption peaks at 459 nm (ε=38,000 dm^3



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-5** and **JK-6**.

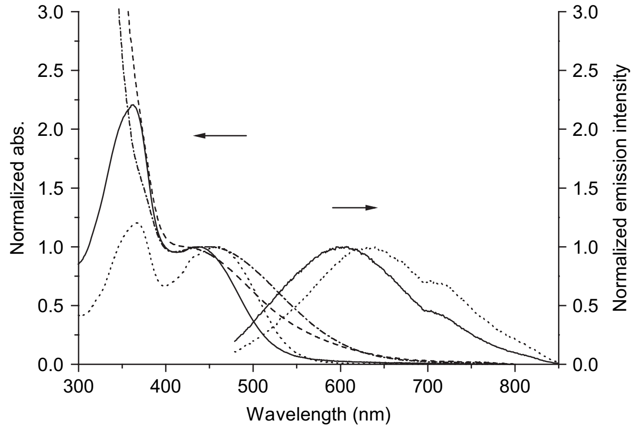


Figure 2. Absorption and emission spectra of **JK-5** (solid line) and **JK-6** (dotted line) in ethanol and absorption spectra of **JK-5** (dashed line) and **JK-6** (dot-dashed line) absorbed on TiO_2 film.

mol^{-1} cm^{-1}) and 367 nm (ε=46,000 dm^3 mol^{-1} cm^{-1}) that are red-shifted relative to the absorptions of **JK-5**. The sensitizers **JK-5** and **JK-6** induced bathochromatic shifts of the absorption spectra compared to the peaks of **JK-1** and **JK-2** due to the introduction of methine unit conjugated with thiophene group. The absorption spectrum of **JK-6** on TiO_2 film is relatively broadened. Such broadening has been reported in several organic dyes on TiO_2 electrodes.[16] When the **JK-5** sensitizer was absorbed on TiO_2 electrode, a slight blue shift from 438 nm to 432 nm was observed probably due to the H-aggregation.[17] We observed that the sensitizers **JK-5** and **JK-6** exhibited strong luminescence maxima at 605 nm and 631 nm, respectively, when they are excited within their π–π* bands in an air-equilibrated solution at 298 K.

The cyclic voltammogram of **JK-5** on TiO_2 film measured in acetonitile containing 0.1 M tetrabutylammonium hexafluorophosphate shows a quasi-reversible couple at 1.01 V versus NHE, which is assigned to the oxidation of the 3-{5-[*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl]. The separation between the cathodic and anodic wave is 0.18 V. Under identical experimental conditions **JK-6** shows a quasi-reversible wave at 0.99 V versus NHE with a separation of 0.20 V. The E_{LUMO} of **JK-5** and **JK-6** calculated from the redox potential and the energy at the intersection point of absorption and emission spectra observed in solution are −1.04 V and −0.98 V. The positive shift of the reduction potential in **JK-6** compared to that of **JK-5** is attributable to the extention of the π-conjugation. The LUMO values of **JK-5** and **JK-6** are much positively shifted compared to those of **JK-1** and **JK-2**. This result suggests that the red shift in the absorption owing to the introduction of the methine unit can be attributed to positive shifts in the reduction potentials of **JK-5** and **JK-6** rather than negative shifts in the oxidation potentials.

In order to obtain the geometrical configuration and characteristic features of the electronic structure, molecular orbital calculations of **JK-5** and **JK-6** were performed with the TD-DFT on B3LYP/3-21G*. The HOMO is delocalized over the π-conjugated system via the amino phenyl unit, and LUMO is delocalized over the cyanoacrylic unit through methine units (Fig. 3). Examination of the HOMO and LUMO of **JK-5** and **JK-6** indicates that HOMO–LUMO excitation moved the electron distribution from the bis-dimethylfluorenyl amino phenyl unit to the vinylene cyanoacrylic acid group. The change in electron distribution induced by photoexcitation results in an efficient charge separation.

Figure 4 shows the incident monochromatic photon-to-current conversion efficiency (IPCE) obtained with a sandwich cell using 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate, and 0.28 M *tert*-butylpyridine in acetonitirle. The IPCE for **JK-5** reached about 70% at 480 nm, and **JK-6** reached about 58% at 450 nm. The IPCE spectrum of **JK-6** is red-shifted by about 20 nm compared to the **JK-6** as a result of extended π-conjugation, which is consistent with the absorption spectrum of **JK-6**. Photovoltaic performance of the **JK-5** and **JK-6** sensitized cells is summarized in Table 1. Under standard global AM 1.5 solar condition, an overall conversion efficiency (η) of 5.12% for **JK-5** and 4.78% for **JK-6** sensitized cells (for **JK-5**: short-circuit photocurrent density, J_{sc}=10.47 mA cm^{-2}; open-circuit voltage, V_{oc}= 0.69 V; fill factor, ff=0.71. For **JK-6**: J_{sc}=10.52 mA cm^{-2}; V_{oc}=0.64 V; ff=0.70) was obtained (Fig. 5). In the same condition, the **N719** sensitized cell gave a J_{sc} of 16.79 mA cm^{-2}, V_{oc} of 0.75 V, and a fill factor of 0.63 corresponding to η of 7.98%. A slightly higher V_{oc} of **JK-5** compared to **JK-6** suggests that the V_{oc} and different dark currents are caused by changing the band gap between the conduction band of TiO_2 electrode and redox couple of I^-/I_3^-, resulting in reduced dark current. Of particular note is that the efficiencies of **JK-5** and **JK-6** with more conjugation system are lower than those of **JK-1** and **JK-2**. One of the reasons for that is the photoisomerization, which is one of the major decay pathways for methine dyes available for the excited singlet in solvent such as acetonitrile. Another reason is that because the more conjugated organic dyes with additional methine unit are more flexible on TiO_2 surface than that of rigid conjugated dyes, the flexible

Table 1. Optical, redox, and DSSC performance data of **JK-5** and **JK-6**

Dye	λ_{abs},[a] nm (ε, M^{-1} cm^{-1})	λ_{em},[a] nm	E_{ox},[b] V (ΔE_p)	E_{0-0},[c] V	E_{LUMO},[d] V	J_{sc}, mA cm^{-2}	V_{oc}, V	ff	η,[e] %
JK-5	438 (38,000); 362 (84,000)	605	1.01 (0.18)	2.05	−1.04	10.47	0.69	0.71	5.12
JK-6	459 (38,000); 367 (46,000)	631	0.99 (0.20)	1.97	−0.98	10.52	0.64	0.70	4.78
N719						16.79	0.75	0.63	7.98

ε: absorption coefficient; E_{ox}: oxidation potential; E_{0-0}: 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.

[a] Absorption spectra were measured in ethanol solution.

[b] Oxidation 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 50 mV s^{-1} (vs NHE).

[c] E_{0-0} was determined from intersection of absorption and emission spectra in ethanol.

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

[e] Performances of DSSCs were measured with 0.18 cm^2 working area.

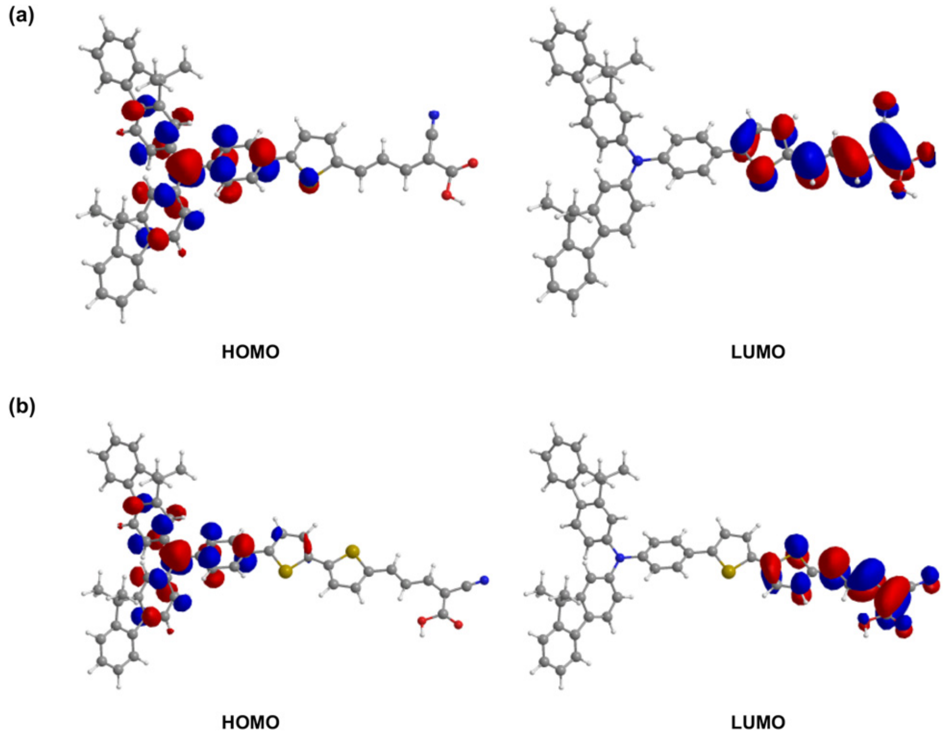


Figure 3. Isodensity surface plots of the HOMO and LUMO of (a) **JK-5** and (b) **JK-6**.

conjugated organic dyes can lie on the neighboring TiO_2 surface and can affect the electronic state of band potential of TiO_2 conduction band, and these effects can reduce the electron injection efficiency from the excited state to TiO_2 by filtering effect. Thus J_{sc} and V_{oc} of **JK-5** and **JK-6** may be lower than those of **JK-1** and **JK-2** because of these reasons.

In summary, we have designed and synthesized two novel organic dyes (**JK-5** and **JK-6**) containing bis-dimethylfluorenyl amino phenyl thiophene moiety with methine unit in order to understand the role of more conjugated system. The power conversion efficiency of the DSSCs based on **JK-5** and **JK-6** sensitizers reaches 5.12% and 4.78%, respectively. The lower power conversion efficiency of **JK-5** and **JK-6** compared to those of **JK-1** and **JK-2** may be attributable to the photoisomerization and dye aggregation. We believe that the development of highly efficient organic dyes over 8% power conversion efficiency can be possible through the more sophisticated structural modifications, and these works are now in progress.

3. Experimental section

3.1. General methods

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard

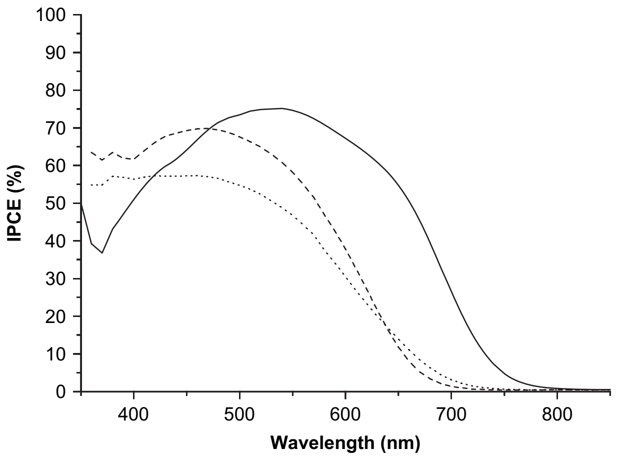


Figure 4. Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSC based on spectra of **JK-5** (dashed line), **JK-6** (dotted line), and **N719** (solid line).

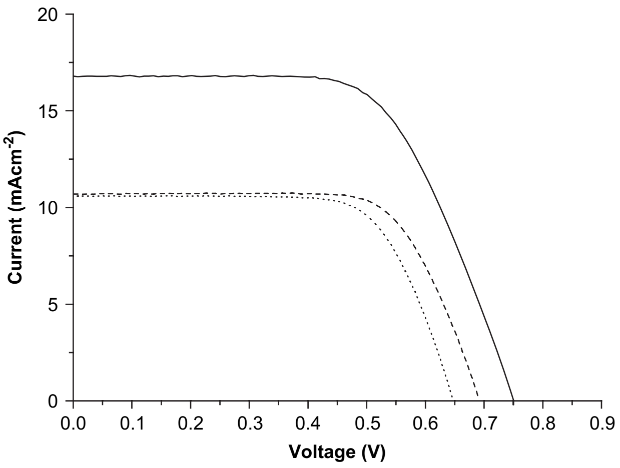


Figure 5. A photocurrent voltage curve obtained with a DSSC based on **JK-5** (dashed line), **JK-6** (dotted line), and **N719** (solid line) under AM 1.5 radiation (100 mW cm^{-2}).

Schlenk techniques. THF and toluene were distilled from sodium benzophenone. *N*,*N*-Dimethylformamide (DMF) and acetonitrile were dried and distilled from CaH_2. The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.00 MHz and 75.44 MHz, respectively. The IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. The absorption and photoluminescence spectra were recorded on a Perkin–Elmer Lambda 2S UV–visible spectrometer and a Perkin LS fluorescence spectrometer, respectively. 2-[*N*,*N*-Bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene,[18] and 5-[*N*,*N*-bis(9,9-dimethylfluorene-2-yl)-phenyl]-2,2′-bithiophene[18] were synthesized according to procedures reported in the literature.

3.2. Cyclovoltagram

Cyclic voltammetry 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 the dyes on TiO_2 was measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4N\text{–}PF_6$ with a scan rate of 50 mV s^{-1}.

3.3. Fabrication and characterization 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) at 70 °C for 30 min and washed with water and ethanol. The first TiO_2 layer of 13 μm thickness was prepared by screen printing TiO_2 paste (Solaronix, 13 nm anatase), and the second scattering layer containing 400 nm sized anatase particles (Catalysis & Chemicals Ind. Co. Ltd.) was deposited by twice screen printing. The TiO_2 electrodes were immersed into **JK-5** and **JK-6** solutions (0.3 mM in ethanol containing 3a,7a-dihydroxy-5b-cholic acid (10 mM) and kept at room temperature for 18 h. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate. The dye-absorbed TiO_2 electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell. A drop of electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate, and 0.28 M *tert*-butylpyridine in acetonitrile. The cells were measured using 1000 W xenon light source, whose power of an AM 1.5 Oirel 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).

3.3.1. 5-[*N*,*N*-Bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene-2-carbaldehyde (3). To 2-[*N*-,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene (0.85 g, 1.52 mmol) in *N*,*N*-dimethyl-formamide (DMF) was added phosphorous oxychloride (0.17 mL, 1.82 mmol) at 0 °C. The solution was warmed to room temperature and stirred for additional 2 h. After removal of DMF in vacuo, the reaction mixture was neutralized with sodium acetate and extracted with methylene chloride. The crude product was purified by column chromatography using a mixture of ethyl acetate and *n*-hexane (1:10) as an eluent (yield 81%). ^1H NMR ($CDCl_3$, 300 MHz): δ 9.87 (s, 1H), 7.72 (d, 1H), 7.67 (d, 2H), 7.64 (d, 2H), 7.57 (d, 2H), 7.41 (d, 2H), 7.36–7.33 (m, 3H), 7.31 (t, 2H), 7.28 (d, 1H), 7.25 (s, 1H), 7.20 (d, 2H), 7.15 (d, 2H), 1.43 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.44 MHz): δ 182.5, 155.4, 153.7, 149.4, 146.6, 141.3, 138.9, 137.9, 135.2, 134.7, 127.4, 127.2, 126.9, 123.9, 123.0, 122.9, 122.7, 120.9, 120.8, 119.7, 119.4, 47.0, 27.2. MS: *m/z* 587.16 [M^+]. Anal. Calcd for $C_{41}H_{33}NOS$: C, 83.78; H, 5.66. Found: C, 83.65; H, 5.52.

3.3.2. 5′-[*N*,*N*-Bis(9,9-dimethylfluorene-2-yl)phenyl]-2,2′-bithiophene-5-carbaldehyde (4). The product was synthesized according to the procedure as described above for the synthesis of **3**, giving product **4** in 82% yield. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.86 (s, 1H), 7.67 (d, 1H), 7.66 (d, 1H), 7.62 (d, 2H), 7.50 (d, 2H), 7.40 (d, 2H), 7.34–7.33 (m, 3H), 7.30 (t, 2H), 7.29 (d, 1H), 7.25 (d, 2H), 7.22–7.18 (m, 4H), 7.13 (d, 2H), 1.36 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.44 MHz): δ 182.6, 155.3, 153.7, 148.3, 147.6, 146.9, 146.4, 141.3, 138.9, 137.7, 134.8, 134.2, 127.4, 127.3, 127.2, 126.8, 126.7, 123.9, 123.6, 123.5, 123.3, 122.7, 120.8, 119.6, 119.1, 46.9, 27.1. MS: *m/z* 669.13 [M^+]. Anal. Calcd for $C_{45}H_{35}NOS_2$: C, 80.68; H, 5.27. Found: C, 80.59; H, 5.15.

3.3.3. 3-{5-[*N*,*N*-Bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene-2-yl}acrylaldehyde (7). A mixture of **3** (0.41 g, 0.7 mmol), methyltriphenylphosphonium iodide (0.35 g, 0.84 mmol), and potassium *tert*-butoxide (0.17 g, 0.84 mmol) in THF (20 mL) was stirred at 60 °C for 2 h. After extraction with methylene chloride (15 mL) and evaporation of the solvent, 0.5 g of oily product **5** was obtained. To the resulting 0.5 g of **5** in *N*,*N*-dimethylformamide (DMF) was added phosphorous oxychloride (0.5 g, 0.12 mmol) at 0 °C. The solution was warmed to room temperature and stirred for additional 2 h. After removal of DMF in vacuo, the reaction mixture was neutralized with sodium acetate and extracted with methylene chloride. The crude product was purified by column chromatography using a mixture of ethyl acetate and *n*-hexane (1:10) as an eluent (yield 72%). ^1H NMR ($CDCl_3$, 300 MHz): δ 9.63 (d, 1H), 7.67 (d, 2H), 7.63 (d, 2H), 7.54 (d, 1H), 7.52 (d, 2H), 7.41 (d, 2H), 7.32 (d, 2H), 7.30 (d, 2H), 7.28 (m, 3H), 7.19 (d, 2H), 7.14 (d, 2H), 6.50 (dd, 1H), 1.43 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.44 MHz): δ 192.8, 155.4, 153.7, 149.3, 148.8, 146. 8, 138.9, 137.4, 135.1, 134.0, 127.2, 127.0, 126.8, 126.5, 124.1, 123.8, 126.5, 124.1, 123.8, 123.4, 122.6, 120.9, 119.3, 47.0, 27.2. MS: *m/z* 613.17 [M^+]. Anal. Calcd for $C_{43}H_{35}NOS$: C, 84.14; H, 5.75. Found: C, 84.11; H, 5.69.

3.3.4. 3-{5′-[*N*,*N*-Bis(9,9-dimethylfluorene-2-yl)phenyl]-2,2′-bisthiophene-5-yl}acrylaldehyde (8). The product was synthesized according to the procedure as described above for the synthesis of **7**, giving product **8** in 69% yield. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.62 (d, 1H), 7.66 (d, 2H), 7.62 (d, 2H), 7.53 (d, 1H), 7.50 (d, 2H), 7.39 (d, 2H), 7.31 (d, 2H), 7.29 (d, 2H), 7.27–7.24 (m, 4H), 7.19 (d, 2H), 7.18 (d, 2H), 7.12 (d, 2H), 6.47 (dd, 1H), 1.42 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.44 MHz): δ 192.8, 155.4, 153.7, 149.9, 148.9, 146.8, 144.6, 141.9, 138.9, 137.5, 135.1, 133.9, 130.2, 127.2, 127.1, 126.9, 126.5, 124.2, 123.9, 123.4, 123.2, 122.7, 122.4, 120.9, 119.7, 119.3, 119.1, 47.0, 27.1. MS: *m/z* 695.19 [M$^+$]. Anal. Calcd for $C_{47}H_{37}NOS_2$: C, 81.11; H, 5.36. Found: C, 81.01; H, 5.29.

3.3.5. 5-{5-[*N*,*N*-Bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene-2-yl}-2-cyanopenta-2,4-dienoic acid (JK-5). The resulting acrylaldehyde thiophene (0.25 g, 0.41 mmol) and cyanoacetic acid (0.05 g, 0.61 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.02 mL, 0.21 mmol). The solution was refluxed for 6 h. After removal of acetonitrile in vacuo, the crude product was extracted with methylene chloride and water. The crude product was purified by column chromarography using methanol as an eluent to give a red solid product 5-{5-[*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene-2-yl}-2-cyanopenta-2,4-dienoic acid (0.19 g, 0.28 mmol, yield 68%). Mp: 203 °C. ^{1}H NMR (CD_3OD-d_4, 300 MHz): δ 8.15 (s, 1H), 7.76 (d, 1H), 7.69 (d, 2H), 7.66 (d, 2H), 7.59 (d, 2H), 7.42 (d, 2H), 7.32 (d, 2H), 7.30 (d, 2H), 7.16 (d, 2H), 7.11–7.07 (m, 2H), 6.99 (d, 1H), 1.39 (s, 12H). $^{13}C\{^1H\}$ NMR (CD_3OD-d_4, 75.44 MHz): δ 164.1, 154.9, 153.3, 148.5, 147.6, 146.3, 145.7, 139.0, 138.2, 136.8, 135.4, 134.4, 134.3, 132.5, 127.2, 126.9, 126.5, 124.1, 123.5, 122.8, 122.5, 121.3, 119.7, 119.5, 118.9, 118.2, 46.5, 26.7. MS: *m/z* 680.94 [M$^+$]. Anal. Calcd for $C_{46}H_{36}N_2O_2S$: C, 81.15; H, 5.33. Found: C, 80.88; H, 5.07.

3.3.6. 5-{5′-[*N*,*N*-Bis(9,9-dimethylfluorene-2-yl)phenyl]-2,2′-bisthiophene-5-yl}-2-cyanopenta-2,4-dienoic acid (JK-6). The resulting acrylaldehyde bithiophene (0.26 g, 0.38 mmol) and cyanoacetic acid (0.05 g, 0.56 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.02 mL, 0.19 mmol). The solution was refluxed for 6 h. After removal of acetonitrile in vacuo, the crude product was extracted with methylene chloride and water. The crude product was purified by column chromarography using methanol as an eluent to give a deep red solid product 5-{5′-[*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl]-2,2′-bisthiophene-5-yl}-2-cyanopenta-2,4-dienoic acid (0.16 g, 0.21 mmol, yield 55%). Mp: 207 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.09 (s, 1H), 7.76 (d, 2H), 7.74 (d, 2H), 7.67 (d, 2H), 7.62 (d, 2H), 7.49 (d, 2H), 7.46 (d, 2H), 7.33–7.29 (m, 3H), 7.27–7.24 (m, 4H), 7.09 (d, 2H), 7.05 (d, 2H), 6.74 (dd, 1H), 1.36 (s, 12H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75.44 MHz): δ 163.7, 154.9, 153.2, 149.5, 147.3, 146.4, 145.1, 143.5, 139.2, 138.3, 135.9, 134.2, 134.1, 132.6, 130.4, 130.2, 127.2, 126.9, 126.8, 126.5, 125.0, 124.2, 123.3, 123.1, 122.8, 121.3, 119.7, 118.7, 117.7, 116.3, 46.5, 26.7. MS: *m/z* 762.63 [M$^+$]. Anal. Calcd for $C_{50}H_{38}N_2O_2S_2$: C, 78.71; H, 5.02. Found: C, 78.38; H, 4.91.

Acknowledgements

We are grateful to the KOSEF through National Research Laboratory (No. M10500000034-06J0000-03410) program and BK21 (2006).

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