

Synthesis of conjugated organic dyes containing alkyl substituted thiophene for solar cell

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Abstract—Three organic dyes, **JK-41**, **JK-42**, and **JK-43** containing bis-dimethylfluoreneaniline and alkyl substituted thiophene unit are designed and synthesized. Under standard global AM 1.5 solar condition, the **JK-41** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 15.23 mA cm⁻², open circuit voltage (V_{oc}) of 0.67 V, and a fill factor of 0.67, corresponding to an overall conversion efficiency η of 7.69%. Molecular-orbital calculations of the three dyes suggest that the electron distribution moves from the aniline derivative to the cyanoacrylic acid moiety. We found that the power conversion efficiency was shown to be quite sensitive to the structural variations of alkyl substituted thiophene moiety.

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1. Introduction

Increasing energy demands and concerns over global warming have led to a greater focus on renewable energy sources in recent years.¹ The conversion of solar energy to electricity appears as one of the substitutes that can replace fossil fuels. Dye-sensitized nanocrystalline TiO₂ solar cells (DSSCs) based on Ru complex photosensitizers² have been intensively studied because of both their high performance as unconventional solar cells and the possibility for low-cost production of such devices. Organic dyes have been also utilized as photosensitizers in DSSCs. Recently, the solar cell performance of DSSCs based on organic dye photosensitizers has been remarkably improved and obtained efficiencies in the range of 6–9%.^{3–8,13} However, organic dyes have several disadvantages as photosensitizers. First, organic sensitizers have relatively sharp absorption bands in the visible region. The absorption spectra of organic dyes must be broadened and red shifted for harvesting the entire solar spectrum. Second, the emission lifetimes of their excited states are generally shorter than those of metal complexes.⁹ One of the approaches to extend the absorption region of dyes is to introduce the methine unit in order to increase the π -conjugation. Such an extended π -conjugation with a methine chain often results in instability of organic dyes due to the possibility of isomer formation. In the excited state

the dye not only rotates but also undergoes trans–cis isomerization about the central methine bond (CH=CH).¹⁰ Such trans–cis photoisomerization is one of the major nonradiative deactivations for the excited singlet.¹¹ Accordingly, a restriction on the excited state makes the photoisomerization less feasible.¹² One of the approaches for the rigid configuration of the excited state would be to introduce the long alkyl chain in order to prevent isomerization by the restriction of rotation around the methine chain.¹³

Recently, Sun and co-workers¹⁵ reported an efficient polyene-diphenylaniline dye containing an extended π -conjugation with a methine chain. We envisioned that if the thiophene unit conjugated with a methine unit has a long alkyl group, we could make the photoisomerization less efficient by the restriction of rotation, resulting in increasing the power conversion efficiency η . In this article, we have designed and synthesized the novel unsymmetrical organic sensitizers **JK-41**, **JK-42**, and **JK-43** (Fig. 1) that consist of the bis-dimethylfluoreneaniline moiety acting as electron donor and cyanoacrylic acid moiety acting as acceptor, the two functions being connected by thiophene-ethylene unit. We also investigated the effect of bridged structural modifications on the power conversion efficiency.

2. Results and discussion

The unsymmetrical organic sensitizers **JK-41**, **JK-42**, and **JK-43** were synthesized by the stepwise synthetic protocol

Keywords: Organic dye; Alkyl substituted thiophene; Solar cell.

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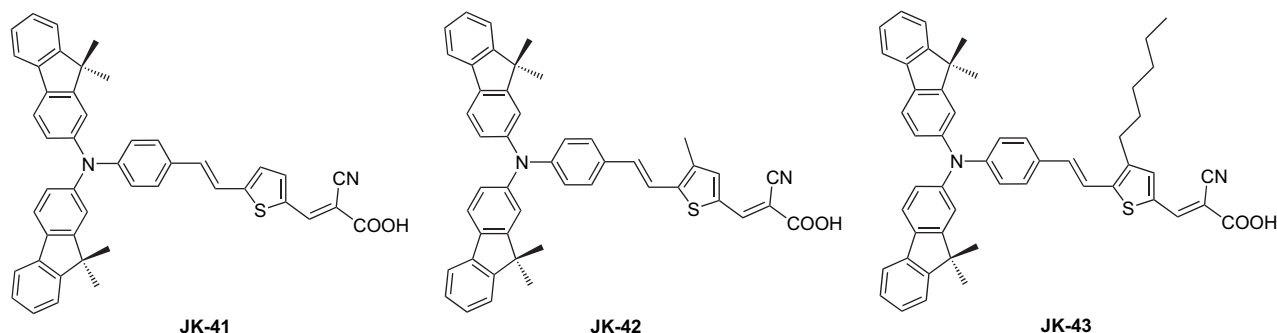


Figure 1. Structures of the dyes **JK-41**, **JK-42**, and **JK-43**.

illustrated in Scheme 1. Organic dye **JK-41** is readily prepared in four steps starting from the *N,N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline.¹⁶

Carbaldehyde **2** was prepared from **1** by lithiation with 1.2 equiv *n*-butyllithium and subsequent quenching with dimethylformamide. Coupling reaction of carbaldehyde **2** with diethyl [5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl]methylphosphonate under Horner–Emmons–Wittig reaction¹⁷ led to intermediate **3**. The thiophene derivative **3** was converted into its corresponding thiophene aldehyde **4** by dedioxanylation with trifluoroacetic acid (TFA). An acetonitrile solution of **4** and cyanoacetic acid were refluxed in the presence of piperidine for 6 h. Solvent removal followed by purification using chromatography yielded **JK-41**. We have also designed similar organic dyes to **JK-41** with alkyl substituted thiophene group. It is well established that introduction of alkyl chain of thiophene unit probably prevents photoisomerization by rather rigid configuration of the excited state, improving the solar cell efficiency.¹³ The synthetic strategy for the alkyl substituted dyes **JK-42** and **JK-43** is quite different from that of **JK-41**. Coupling reaction of carbaldehyde **2** with [(3-alkylthiophen-2-yl)methyl]triphenylphosphonium bromide under Horner–Emmons–Wittig coupling condition led to **5/6**. These were then converted to the aldehydes **7/8**, which yielded the dyes **JK-42** and **JK-43** on treatment with cyanoacetic acid.

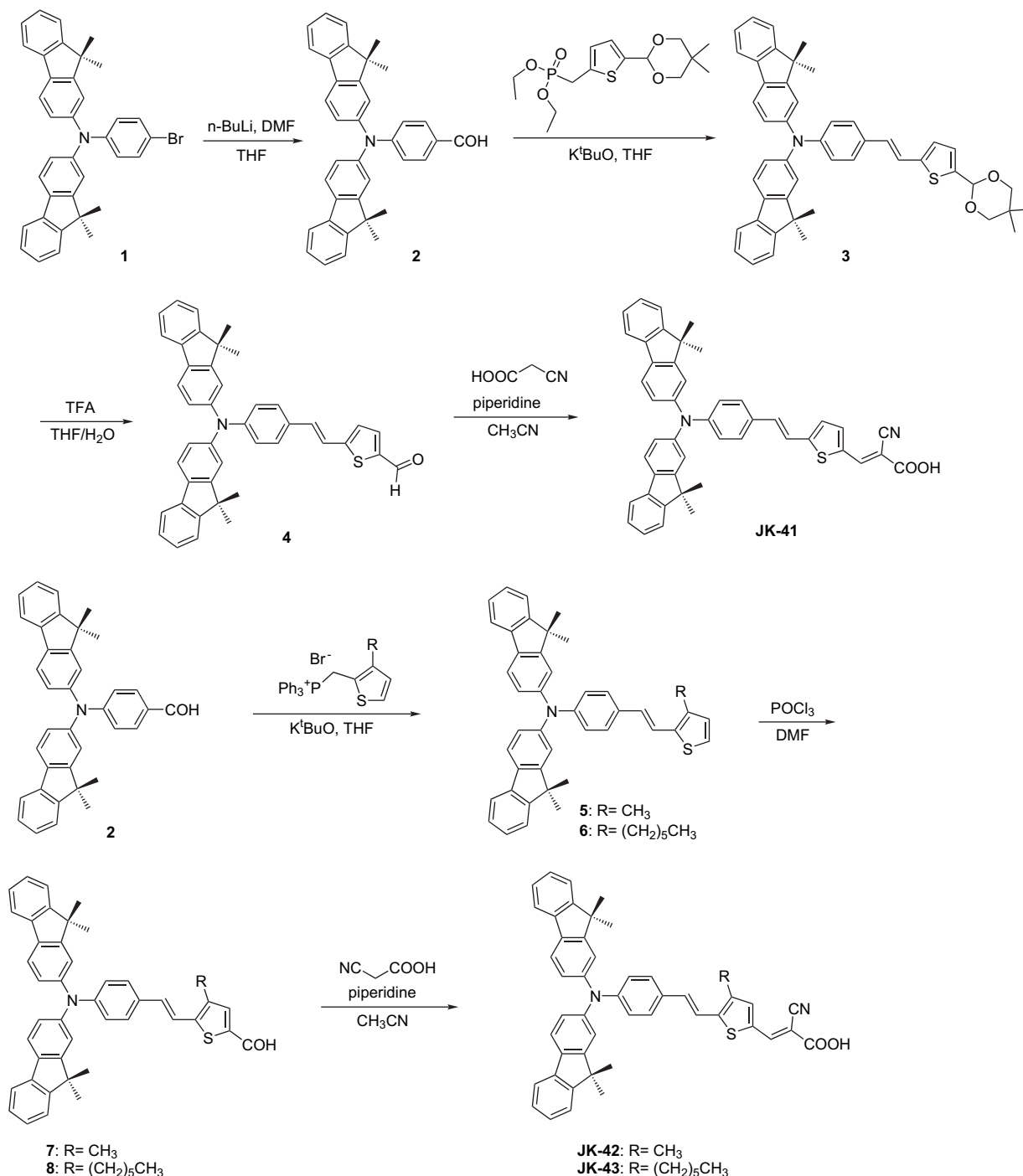
Figure 2 shows the absorption and emission spectra of the **JK-41**, **JK-42**, and **JK-43** sensitizers measured in ethanol and the data are listed in Table 1. The absorption spectrum of **JK-41** displays two absorption maxima at 461 nm ($\epsilon=55,890 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 368 nm ($\epsilon=70,330 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), which are due to the π – π^* transitions of the conjugated system. Under the same conditions the **JK-42** sensitizer that contains the methyl group on thiophene unit exhibits absorption peaks at 463 nm ($\epsilon=28,730 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 366 nm ($\epsilon=40,960 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) that are almost the same as the peaks of **JK-41**. On the other hand, the introduction of hexyl group on thiophene unit in **JK-41**, giving **JK-43**, caused a blue shift to 456 nm compared to the **JK-41** and **JK-42** sensitizers. A blue shift of **JK-43** can be readily understood from molecular modeling studies of the three dyes. The ground state structure of **JK-43** possesses an 8.15° twist between *N,N*-bis(9,9-dimethylfluoren-2-yl)aniline and the methine units (Fig. 3). The dihedral angle of the methine and thienyl units is 7.35°. For **JK-41**, the dihedral angles

between the phenyl and the methine unit and methine-thienyl unit are 1.18° and 0.65°, respectively. Accordingly, a red shift of **JK-41** relative to **JK-43** derives from more delocalization over an entire conjugated system.

When the **JK-41**, **JK-42**, and **JK-43** sensitizers were adsorbed on TiO₂ electrode, a slight blue shift of 4–6 nm was found due to the H-aggregation (Fig. 2b).¹² The absorption spectra of the three dyes on TiO₂ are broadened. Such a broadening of the absorption spectra is due to an interaction between the dyes and TiO₂.¹⁸ This broadening of the absorption spectrum is desirable for harvesting the solar spectrum and leads to a large photocurrent. When the **JK-41**, **JK-42**, and **JK-43** sensitizers are excited within their π – π^* bands in an air-equilibrated solution and at 298 K, they exhibit strong luminescence maxima at 582, 589, 587 nm, respectively. No emission signal was observed for the three dyes on TiO₂ films, suggesting that the interaction of the excited electron from the excited dye to the TiO₂ electrodes is efficient.

The electrochemical data for the dyes **JK-41**, **JK-42**, and **JK-43** are listed in Table 1. The cyclic voltammogram of the three dyes on TiO₂ measured in CH₃CN solvent containing 0.1 M tetrabutylammonium tetrafluoroborate shows a quasi-reversible behavior. The oxidation potential of **JK-41** dye was measured to be 1.09 V versus NHE with a separation of 0.13 V between anodic to cathodic peaks. Under similar conditions the **JK-42** and **JK-43** dyes show the redox couple at 1.08 V and 1.07 V versus NHE, respectively. 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 are listed in Table 1. The excited state oxidation potentials (E_{ox}^*) of the dyes (**JK-41**: –1.27 V vs NHE; **JK-42**: –1.27 V vs NHE; **JK-43**: –1.29 V vs NHE) are all higher than the energy level of TiO₂ conduction band edge (–0.5 V vs NHE), showing that the energy injection should be possible thermodynamically. A slight positive shift of the reduction potentials in **JK-41** and **JK-42** is due to more delocalization of the π -conjugation system, in keeping with the theoretical analysis presented above.

To gain insight into the geometrical and electronic properties of the **JK-41**, **JK-42**, and **JK-43** sensitizers, we performed DFT calculations on the three organic sensitizers using the Gaussian 03 program package. In particular we used B3LYP as exchange-correlation functional and 3-21G* as



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-41**, **JK-42**, and **JK-43**.

basis set. We optimized the molecular structure of **JK-41**, **JK-42**, and **JK-43** in the gas phase without any symmetry constraints, obtaining the geometries shown in Figure 4. The HOMO of the three organic dyes is delocalized over the π -conjugated system via the aniline and the methine units (Fig. 4) and the LUMO is delocalized over the cyanoacrylic unit through thiophene. Molecular-orbital calculations of these dyes strongly suggest that the electron distribution moves from the aniline derivative to the cyanoacrylic acid moiety by means of photoexcitation of the dye and is injected to the conduction band of TiO₂ via the anchoring

carboxyl group. Therefore, the change in electron distribution induced by photoexcitation results in an efficient separation.

The J - V curve for the DSSCs based on the **JK-41**, **JK-42**, and **JK-43** dyes is presented in Figure 5. Under standard global AM 1.5 solar conditions, the **JK-41**, **JK-42**, and **JK-43** sensitized cells gave the short circuit photocurrent density (J_{sc}) of 15.23, 12.72, and 10.56 mA cm⁻², open circuit voltage (V_{oc}) of 0.67, 0.64, and 0.66 V and a fill factor of 75.8, 76.7, and 77.4, corresponding to an overall conversion

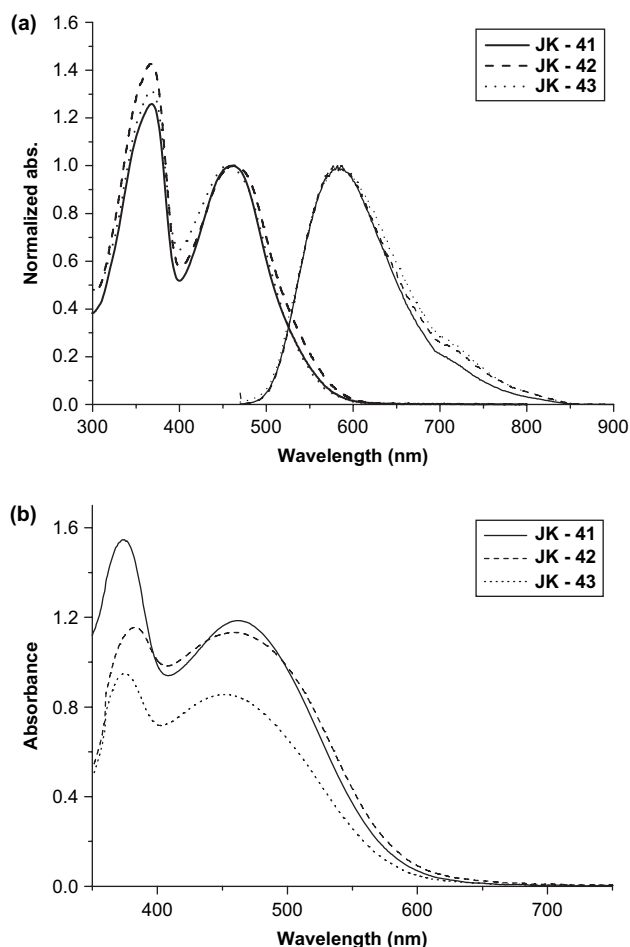


Figure 2. (a) Absorption and emission spectra of **JK-41** (solid line), **JK-42** (dashed line), and **JK-43** (dot line) in ethanol solution. (b) Absorption spectra of **JK-41** (solid line), **JK-42** (dashed line), and **JK-43** (dot line) adsorbed on TiO₂ film.

efficiency η of 7.69, 6.23, and 5.42%, respectively. **Figure 6** shows the incident monochromatic photon-to-current conversion efficiency (IPCE) for the DSSCs based on the three dyes. The IPCE data of **JK-41** sensitizer in the maximum region is about 77% at 496 nm. When the reflection and absorption losses in the transparent conducting oxide substrate are considered, the net photon-to-current conversion efficiency exceeds 90%, indicating the highly efficient performance of this solar cell. The **JK-41** sensitizer IPCE

spectrum is red shifted by about 25 nm compared to **JK-43** as a result of extended π -conjugation, which is consistent with the absorption spectrum of the **JK-41** sensitizer. From the above results, we have observed that the J_{sc} and η of **JK-41** were higher than those of **JK-43**. To understand the high J_{sc} observed with **JK-41**, we calculated the light-harvesting efficiency (LHE(λ)) and the absorbed photon-to-current conversion efficiency (APCE(λ)) at 500 nm based on the following equation.^{14a,b}

$$\text{IPCE} = \text{LHE}(\lambda) \times \Phi_{\text{inj}}(\lambda) \times \eta_c(\lambda) = \text{LHE}(\lambda) \times \text{APCE}(\lambda)$$

IPCE is the product of light-harvesting efficiency (LHE(λ)), the quantum yield of electron injection ($\Phi_{\text{inj}}(\lambda)$), and the efficiency of collecting the injected charge ($\eta_c(\lambda)$) at the back contact. The LHE(λ) is defined as $\text{LHE}(\lambda) = 1 - 10^{-\text{ABS}(\lambda)}$ where ABS(λ) is absorbance of the dye adsorbed on nanocrystalline TiO₂.^{14b} It is noteworthy that the LHE for DSSCs based on **JK-41** (0.893) was higher than that for **JK-43** (0.780) in the same condition (**Table 2**). Increased adsorbed amount cannot be responsible for the increased IPCE completely,^{14a} but this result indicated that the increased adsorbed amount contributes to IPCE. To clarify the above results, we have measured the amount of dyes adsorbed on TiO₂ film. The adsorbed amounts of 2.66×10^{-6} mmol cm⁻² for **JK-41**, 2.38×10^{-6} mmol cm⁻² for **JK-42**, and 2.14×10^{-6} mmol cm⁻² for **JK-43** are observed. One of the main reasons for the low efficiency of **JK-43** with the hexyl group was attributed to the difficulty of the dye absorption because of the steric reason. It is also documented that the electron injection process from the excited state of the dye to the TiO₂ electrode generally competes with other undesirable processes and photoisomerization is one of the major decay pathways for the nonradiative deactivation of the singlet excited state.¹¹ Initially, we expected that the solar conversion efficiency of organic dyes with long alkyl chain is higher than that of organic dyes without any alkyl chain because the presence of long alkyl chain prevents isomerization by the restriction of rotation. Therefore, the low efficiency of **JK-43** with a hexyl group demonstrates that the electron injection from the photo-excited state to TiO₂ electrode is more faster than nonradiative deactivation.

In summary, we have designed and synthesized three organic dyes containing *N,N*-bis(9,9-dimethylfluoren-2-yl)aniline unit bridged by three different methine thiophene units.

Table 1. Optical, redox, and DSSC performance data of **JK-41**, **JK-42**, and **JK-43**

Dye	$\lambda_{\text{abs}},^a$ nm (ϵ , dm ³ mol ⁻¹ cm ⁻¹)	$\lambda_{\text{em}},^a$ nm	$E_{\text{ox}},^b$ V	$E_{0-0},^c$ V	$E_{\text{LUMO}},^d$ V	$J_{sc},$ mA cm ⁻²	$V_{oc},$ V	ff	$\eta,^e$ %
JK-41	368 (70,330)	582	1.09	2.36	-1.27	15.23	0.67	75.8	7.69
	461 (55,890)								
JK-42	366 (40,960)	589	1.08	2.35	-1.27	12.72	0.64	76.7	6.23
	463 (28,730)								
JK-43	368 (26,600)	587	1.07	2.36	-1.29	10.56	0.66	77.4	5.42
	456 (20,270)								

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 TiO₂ was measured in CH₃CN with 0.1 M (*n*-C₄H₉)₄NPF₆ 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 $E_{\text{ox}} - E_{0-0}$.

^e Performances of DSSCs were measured with 0.18 cm² working area.

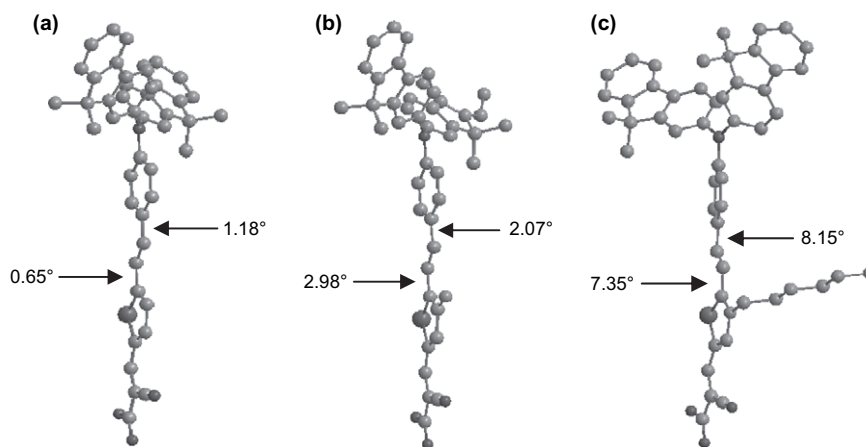


Figure 3. The optimized structure calculated with TD-DFT on B3LYP/3-21G* of (a) **JK-41**, (b) **JK-42**, and (c) **JK-43**.

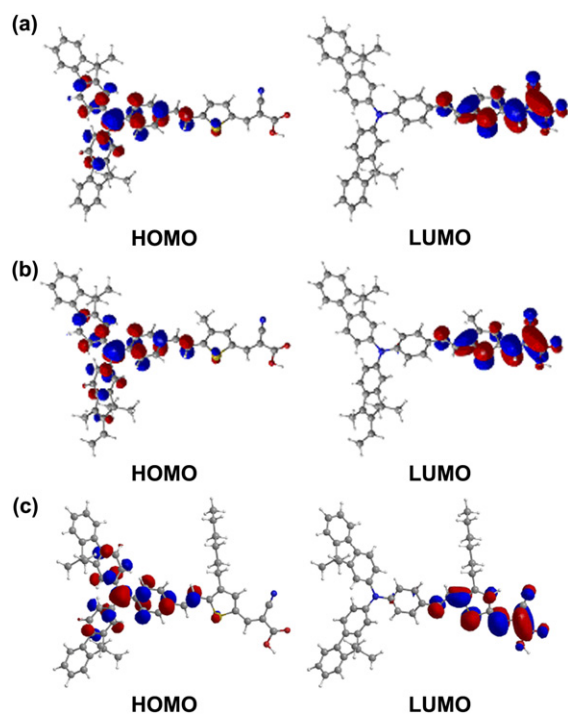


Figure 4. Isodensity surface plots of the HOMO and LUMO of (a) **JK-41**, (b) **JK-42**, and (c) **JK-43**.

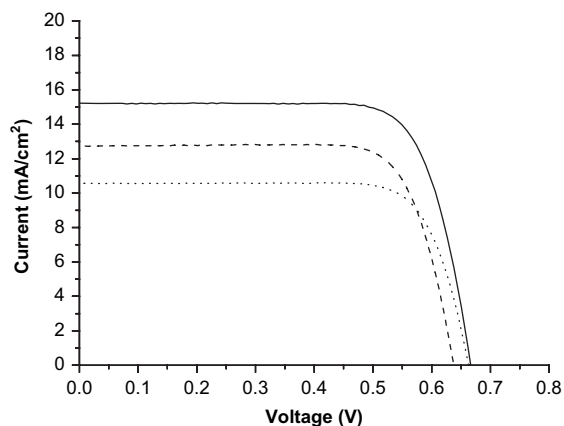


Figure 5. A photocurrent–voltage curve obtained with a DSSC based on **JK-41** (solid line), **JK-42** (dashed line), and **JK-43** (dotted line) under AM 1.5 radiation (100 mW cm^{-2}).

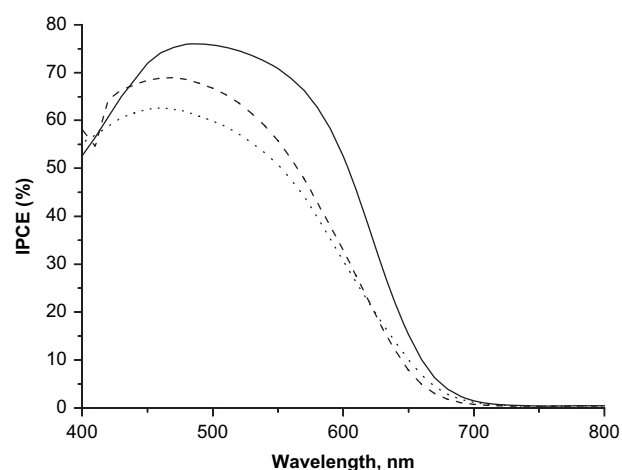


Figure 6. Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSC based on spectra of **JK-41** (solid line), **JK-42** (dashed line), and **JK-43** (dotted line).

The power conversion efficiency of the DSSCs based on the **JK-41** sensitizer reaches 7.69%. The power conversion efficiency was shown to be sensitive to the structural modifications of bridging thiophene groups. We believe that the development of highly efficient organic dyes comparable to ruthenium dyes is possible through more sophisticated structural modifications, and these works are now in progress.

Table 2. IPCE, LHE, and APCE of **JK-41**, **JK-42**, and **JK-43** at 500 nm

Dye	IPCE	LHE	APCE
JK-41	0.757	0.893	0.848
JK-42	0.667	0.895	0.745
JK-43	0.599	0.780	0.768

3. Experimental section

3.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini

300 spectrometer operating at 300.00 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. *N,N*-Bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline,¹⁶ diethyl [5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl]methylphosphonate¹⁷ were synthesized according to procedures reported in the literature.

3.2. Cyclic voltammogram

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 TiO₂ was measured in CH₃CN with 0.1 M (*n*-C₄H₉)₄NPF₆ 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 immersed in 40 mM TiCl₄ (aqueous) at 70 °C for 30 min and washed with water and ethanol. The first TiO₂ layer of 13 μm thickness was prepared by screen printing TiO₂ paste (Solaronix, 13 nm anatase), and the second scattering layer containing 400 nm sized anatase particles (Catalysis & Chemicals Ind. Co. Ltd.) was coated. The TiO₂ electrodes were immersed into the **JK-41**, **JK-42**, and **JK-43** solutions (0.3 mM in ethanol containing 3α,7α-dihydroxy-5β-cholic acid (10 mM)) and kept at room temperature for 18 h. The stained TiO₂ electrode and Pt-counter electrode were assembled into a sealed sandwich cell by heating with a hot-melt film (Surlyn 1702, 25 μm thickness) as a spacer between the electrodes. The electrolyte 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 *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).

3.4. 4-[*N,N*-Bis(9,9-dimethylfluoren-2-yl)amino]-benzaldehyde (**2**)

N,N-Bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (2.23 g, 4.0 mmol) dissolved in tetrahydrofuran (30 mL) was cooled to -78 °C under N₂. *n*-Butyllithium (3 mL, 1.6 M solution in hexane, 4.8 mmol) was added dropwise with stirring. It was warmed to 0 °C and kept at this temperature for additional 1 h. Again the solution was cooled to -78 °C and dry dimethylformamide (0.93 mL, 12 mmol) was added. Stirring at ambient temperature was continued for 2 h to complete the reaction, and water (15 mL) was added. The solvents were removed in vacuum, and the residue was taken up in methylene chloride. The combined organic extract was dried over anhydrous MgSO₄ and filtered. The pure product **2** was obtained by silica gel chromatography (eluent EA/Hx=1:5) in 73%

yield. ¹H NMR (CDCl₃, 300 MHz): δ 9.84 (s, 1H), 7.73 (d, *J*=8.7 Hz, 2H), 7.68 (d, *J*=7.5 Hz, 2H), 7.67 (d, *J*=8.1 Hz, 2H), 7.42 (d, *J*=8.1 Hz, 2H), 7.33 (d, *J*=6.9 Hz, 2H), 7.32 (d, *J*=6.6 Hz, 2H), 7.27 (s, 2H), 7.18 (d, *J*=7.8 Hz, 2H), 7.17 (d, *J*=7.8 Hz, 2H), 1.43 (s, 12H). ¹³C{¹H} NMR (CDCl₃, 75.44 MHz): δ 190.5, 155.6, 153.8, 153.7, 145.8, 138.7, 136.3, 131.5, 129.4, 127.3, 127.2, 124.9, 122.7, 121.1, 120.5, 120.1, 119.9, 47.1, 27.1. MS: *m/z* 505.17 [M⁺]. Anal. Calcd for C₃₇H₃₁NO: C, 87.89; H, 6.18. Found: C, 87.66; H, 6.11.

3.5. 5-{4-[*N,N*-Bis(9,9-dimethylfluoren-2-yl)amino]-styryl}thiophene-2-carbaldehyde (**4**)

A mixture of **2** (0.30 g, 0.59 mmol), diethyl [5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl]methylphosphonate (0.25 g, 0.71 mmol), and potassium *tert*-butoxide (0.09 g, 0.77 mmol) was vacuum-dried and THF (15 mL) was added. The solution was refluxed for 6 h. THF was removed under reduced pressure. The crude mixture was redissolved in methylene chloride, washed with water, and dried with MgSO₄. The organic layer was removed in vacuo. To the compound **3** (0.34 g) in THF was added water. Then TFA (2.1 mL) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate and extracted with methylene chloride. The combined methylene chloride phases were then washed with aqueous sodium bicarbonate and dried with MgSO₄. The organic layer was removed in vacuo. The crude product was purified by column chromatography using a mixture of ethyl acetate and *n*-hexane (1:5) as an eluent (yield: 82%). ¹H NMR (CDCl₃, 300 MHz): δ 9.85 (s, 1H), 7.66 (d, *J*=7.2 Hz, 2H), 7.62 (d, *J*=8.1 Hz, 2H), 7.40 (d, *J*=6.9 Hz, 2H), 7.38 (d, *J*=7.5 Hz, 2H), 7.32 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.7 Hz, 2H), 7.24 (d, *J*=8.1 Hz, 4H), 7.17 (d, *J*=8.4 Hz, 2H), 7.14–7.11 (m, 4H), 1.42 (s, 12H). ¹³C{¹H} NMR (CDCl₃, 75.44 MHz): δ 182.6, 155.3, 153.7, 153.3, 148.8, 146.8, 141.1, 138.9, 137.6, 134.9, 132.7, 129.6, 128.1, 127.2, 126.8, 126.1, 123.8, 123.1, 122.7, 120.8, 119.6, 119.3, 118.9, 47.0, 27.2. MS: *m/z* 613.19 [M⁺]. Anal. Calcd for C₃₇H₃₁NO: C, 84.14; H, 5.75. Found: C, 83.82; H, 5.61.

3.6. 3-(5-{4-[*N,N*-Bis(9,9-dimethylfluoren-2-yl)amino]-styryl}thiophen-2-yl)-2-cyanoacrylic acid (**JK-41**)

The resulting thiophene aldehyde **4** (0.25 g, 0.40 mmol) and cyanoacetic acid (0.06 g, 0.60 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.04 mL, 0.40 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 chromatography using methanol as an eluent to give a red solid product **JK-41** (0.21 g, 0.31 mmol, yield: 78%). Mp: 201 °C. ¹H NMR (DMSO-*d*₆, 300 MHz): δ 8.03 (s, 1H), 7.75 (d, *J*=7.5 Hz, 2H), 7.72 (d, *J*=6.6 Hz, 2H), 7.59 (d, *J*=8.1 Hz, 2H), 7.56 (d, *J*=8.7 Hz, 2H), 7.49 (d, *J*=6.9 Hz, 2H), 7.39 (d, *J*=15.9 Hz, 1H), 7.32 (d, *J*=7.2 Hz, 2H), 7.28 (m, 5H), 7.06 (d, *J*=8.1 Hz, 2H), 7.03 (d, *J*=7.5 Hz, 2H), 1.35 (s, 12H). ¹³C{¹H} NMR (DMSO-*d*₆, 75.44 MHz): δ 163.2, 154.9, 153.2, 147.6, 147.5, 146.4, 139.9, 138.3, 135.9, 135.6, 134.2, 130.3, 129.9, 128.0, 127.2, 126.8, 126.6,

123.4, 122.8, 121.3, 119.9, 119.7, 119.6, 119.5, 118.7, 109.7, 46.5, 26.7. MS: m/z 680.19 [M⁺]. Anal. Calcd for C₄₆H₃₆N₂O₂S: C, 81.15; H, 5.33. Found: C, 81.46; H, 5.28.

3.7. 5-(4-[N,N-Bis(9,9-dimethylfluoren-2-yl)amino]-styryl)-4-methylthiophene-2-carbaldehyde (7)

To a mixture of **2** (0.80 g, 1.58 mmol) and [(3-methylthiophen-2-yl)methyl] triphenylphosphonium bromide (0.79 g, 1.74 mmol) in THF (30 mL) was added potassium *tert*-butoxide (0.25 g, 2.21 mmol) in THF (10 mL) dropwise at 0 °C. The mixture was stirred at room temperature for 20 h, and then poured into distilled water (100 mL). The pH value was adjusted to 7.0 by 0.1 M HCl. The product was extracted twice with methylene chloride and the organic layer was dried with MgSO₄. The organic layer was removed in vacuo. To the compound **5** (0.82 g) in *N,N*-dimethylformamide (DMF) was added phosphorus oxychloride (0.15 mL, 1.64 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 (1:5) as an eluent (yield: 77%). ¹H NMR (CDCl₃, 300 MHz): δ 9.79 (s, 1H), 7.67 (d, *J*=7.2 Hz, 2H), 7.62 (d, *J*=8.1 Hz, 2H), 7.45 (s, 1H), 7.42 (d, *J*=8.7 Hz, 2H), 7.40 (d, *J*=7.2 Hz, 2H), 7.32 (d, *J*=7.8 Hz, 2H), 7.28 (d, *J*=7.5 Hz, 2H), 7.25 (d, *J*=6.9 Hz, 2H), 7.24 (d, *J*=7.5 Hz, 1H), 7.17 (d, *J*=8.4 Hz, 2H), 7.12 (d, *J*=8.1 Hz, 2H), 7.10 (s, 1H), 2.35 (s, 3H), 1.43 (s, 12H). ¹³C{¹H} NMR (CDCl₃, 75.44 MHz): δ 182.5, 155.3, 153.7, 148.6, 147.8, 146.9, 139.9, 139.1, 138.9, 135.9, 134.9, 132.2, 130.1, 128.0, 127.1, 126.8, 123.7, 123.2, 122.6, 120.8, 119.6, 119.2, 117.5, 47.0, 27.1, 14.1. MS: m/z 627.18 [M⁺]. Anal. Calcd for C₄₄H₃₇NOS: C, 84.17; H, 5.94. Found: C, 84.04; H, 5.788.

3.8. 5-(4-[N,N-Bis(9,9-dimethylfluoren-2-yl)amino]-styryl)-4-hexylthiophene-2-carbaldehyde (8)

The product was synthesized according to the procedure as described above for the synthesis of **7**, in 69% yield. ¹H NMR (CDCl₃, 300 MHz): δ 9.80 (s, 1H), 7.66 (d, *J*=7.2 Hz, 2H), 7.62 (d, *J*=8.4 Hz, 2H), 7.52 (s, 1H), 7.41 (d, *J*=8.4 Hz, 2H), 7.40 (d, *J*=7.5 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=7.5 Hz, 2H), 7.25 (d, *J*=7.2 Hz, 2H), 7.24 (d, *J*=7.2 Hz, 1H), 7.17 (d, *J*=8.1 Hz, 2H), 7.13 (d, *J*=7.8 Hz, 2H), 7.11 (s, 1H), 2.69 (t, 2H), 1.62 (q, 2H), 1.42 (s, 12H), 1.33 (m, 6H), 0.88 (t, 3H). ¹³C{¹H} NMR (CDCl₃, 75.44 MHz): δ 182.6, 155.3, 153.7, 148.6, 147.6, 146.9, 141.5, 139.3, 139.1, 138.9, 134.9, 132.1, 130.1, 128.0, 127.2, 126.8, 123.7, 123.2, 122.7, 120.8, 119.6, 119.2, 117.4, 47.0, 31.8, 30.8, 29.1, 28.5, 27.2, 22.7, 14.2. MS: m/z 697.30 [M⁺]. Anal. Calcd for C₄₉H₄₇NOS: C, 84.32; H, 6.79. Found: C, 84.03; H, 6.57.

3.9. 3-(5-(4-[N,N-Bis(9,9-dimethylfluoren-2-yl)amino]-styryl)-4-methylthiophen-2-yl)-2-cyanoacrylic acid (JK-42)

The resulting 4-methylthiophene aldehyde **7** (0.2 g, 0.32 mmol) and cyanoacetic acid (0.04 g, 0.48 mmol) were allowed to react in acetonitrile in the presence of piperidine

(0.03 mL, 0.32 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 chromatography using methanol as an eluent to give a red solid product **JK-42** (0.16 g, 0.23 mmol, yield: 72%). Mp: 193 °C. ¹H NMR (DMSO-*d*₆, 300 MHz): δ 7.95 (s, 1H), 7.75 (d, *J*=7.8 Hz, 2H), 7.73 (d, *J*=6.9 Hz, 2H), 7.62 (d, *J*=8.7 Hz, 2H), 7.49 (d, *J*=6.9 Hz, 2H), 7.43 (s, 1H), 7.36 (d, *J*=8.4 Hz, 2H), 7.29 (d, *J*=8.7 Hz, 2H), 7.28 (s, 1H), 7.25 (d, *J*=7.2 Hz, 2H), 7.04 (d, *J*=6.9 Hz, 2H), 7.03 (d, *J*=6.9 Hz, 2H), 6.93 (d, *J*=16.2 Hz, 1H), 2.29 (s, 3H), 1.36 (s, 12H). ¹³C{¹H} NMR (DMSO-*d*₆, 75.44 MHz): δ 163.2, 154.9, 153.2, 147.3, 146.4, 141.7, 139.6, 138.2, 135.9, 135.7, 134.1, 133.7, 130.6, 129.4, 128.1, 127.1, 126.8, 123.3, 122.8, 122.7, 121.2, 119.6, 119.5, 118.6, 118.3, 109.7, 46.5, 30.7, 26.7. MS: m/z 694.88 [M⁺]. Anal. Calcd for C₄₇H₃₈N₂O₂S: C, 81.24; H, 5.51. Found: C, 81.19; H, 5.48.

3.10. 3-(5-(4-[N,N-Bis(9,9-dimethylfluoren-2-yl)amino]-styryl)-4-hexylthiophen-2-yl)-2-cyanoacrylic acid (JK-43)

The resulting 4-hexylthiophene aldehyde **8** (0.2 g, 0.29 mmol) and cyanoacetic acid (0.04 g, 0.43 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.03 mL, 0.29 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 chromatography using methanol as an eluent to give a red solid product **JK-43** (0.17 g, 0.22 mmol, yield: 76%). Mp: 197 °C. ¹H NMR (DMSO-*d*₆, 300 MHz): δ 7.95 (s, 1H), 7.76 (d, *J*=7.5 Hz, 2H), 7.74 (d, *J*=6.9 Hz, 2H), 7.62 (d, *J*=8.1 Hz, 2H), 7.50 (d, *J*=7.2 Hz, 2H), 7.46 (s, 1H), 7.37 (d, *J*=7.8 Hz, 2H), 7.33 (d, *J*=8.1 Hz, 2H), 7.29 (s, 1H), 7.27 (d, *J*=7.5 Hz, 2H), 7.04 (d, *J*=7.2 Hz, 2H), 7.03 (d, *J*=6.9 Hz, 2H), 6.94 (d, *J*=16.2 Hz, 1H), 2.68 (t, 2H), 1.49 (q, 2H), 1.34 (s, 12H), 1.25 (m, 6H), 0.81 (t, 3H). ¹³C{¹H} NMR (DMSO-*d*₆, 75.44 MHz): δ 163.8, 154.9, 153.3, 146.4, 145.9, 142.0, 141.7, 138.1, 137.6, 135.0, 134.1, 133.8, 130.8, 130.2, 128.0, 127.1, 126.8, 123.3, 122.9, 122.7, 121.2, 119.7, 119.1, 118.6, 118.3, 109.6, 46.5, 31.0, 30.3, 28.2, 26.7, 24.2, 22.1, 13.9. MS: m/z 764.31 [M⁺]. Anal. Calcd for C₅₂H₄₈N₂O₂S: C, 81.64; H, 6.32. Found: C, 81.60; H, 6.29.

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