

Novel Organic Sensitizers with a Quinoline Unit for Efficient Dye-sensitized Solar Cells

Hyeju Choi, Hyunbong Choi, Sanghyun Paek, Kihyung Song,[†] Moon-sung Kang,[‡] and Jaejung Ko^{*}

Department of Advanced Material Chemistry, Korea University, Jochiwon, Chungnam 339-700, Korea

^{*}E-mail: jko@korea.ac.kr[†]Department of Chemical Education, Korea National University of Education, Cheongwon, Chungbuk 363-791, Korea[‡]Energy Lab, Samsung SDI Corporate R&D Center, Yongin, Gyeonggi-do 449-577, Korea

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Three organic sensitizers, **JK-128**, **JK-129**, and **JK-130** containing quinoline unit are designed and synthesized. Under standard global AM 1.5 solar condition, the **JK-130** sensitized solar cell gave a short circuit photocurrent density of 11.52 mA cm⁻², an open circuit voltage of 0.70 V, and a fill factor of 0.75, corresponding to an overall conversion efficiency of 6.07%. We found that the η of **JK-130** was higher than those of other two cells due to the higher photocurrent. The higher J_{sc} value is attributed to the broad and intense absorption spectrum of **JK-130**.

Key Words: Quinoline, Dye, Bithiophene, Dye-sensitized solar cell

Introduction

Increasing energy demands and environmental issues such as fossil fuel shortage and global warming have lead to the need for clean renewable energy.¹ Dye-sensitized solar cells are attracting widespread interest for a renewable energy source as a cost-effective alternative to conventional solid-state solar cells.² In this cell, the sensitizer is a crucial element in DSSCs, exerting significant influence on the power conversion efficiency as well as the stability of the devices. Some polypyridyl ruthenium sensitizers have reached power conversion efficiencies over 11%.³ Due to their precious metal and limited quantity, cheap metal-free organic sensitizers need to be developed for commercial applications. Recently impressive photovoltaic performance has been obtained with some organic indoline⁴ and triarylamine dyes⁵ having efficiencies in the range of 8 ~ 9.7%. The efficient organic dyes contained a donor and acceptor moiety bridged by π -conjugation. In order to improve the photovoltaic performance and stability of DSSCs, an important strategy on organic sensitizers has been the structural modification of the compounds. The absorption spectra of organic sensitizers have to be red-shifted and broadened by expansion of the π -conjugation in the dyes. To obtain organic sensitizers with both red-shift absorption and high stability, introduction of new π -conjugation units into organic framework is necessary.

Recently, a successful approach was introduced by incorporating a π -conjugation linker such as thiophene,⁶ thienothiophene,⁷ 3,4-ethylenedioxy-thiophene,⁸ benzo[1,2,5]-thiadiazole⁹ and *p*-phenylene vinylene derivatives.¹⁰ As part of our efforts to investigate the structural modifications that can enhance the efficiency and stability, organic dyes containing quinoline moiety have been synthesized for DSSCs (Fig. 1).

It is well documented that molecules and polymers containing quinoxaline,¹¹ oxadiazole,¹² and quinoline¹³ offer highly efficient electron-transport material. Jenekle and co-workers¹⁴ reported that a new n-type conjugated copolymer containing 3,3'-dialkylthiophene and bis(phenylquinoline) moiety was shown to be a good electron-transport material. One challenge is to develop more efficient and robust electron-transport organic sensitizers which can be utilized as an efficient dye-sensitized solar cell. In this paper, we report three organic dyes containing quinoline as bridged group. We also investigated the effect of bridged structural modifications on the power conversion efficiency.

Results and Discussion

The novel organic sensitizers **JK-128**, **JK-129**, and **JK-130** were prepared by the synthetic protocol depicted in Scheme 1. 1-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)ethan-

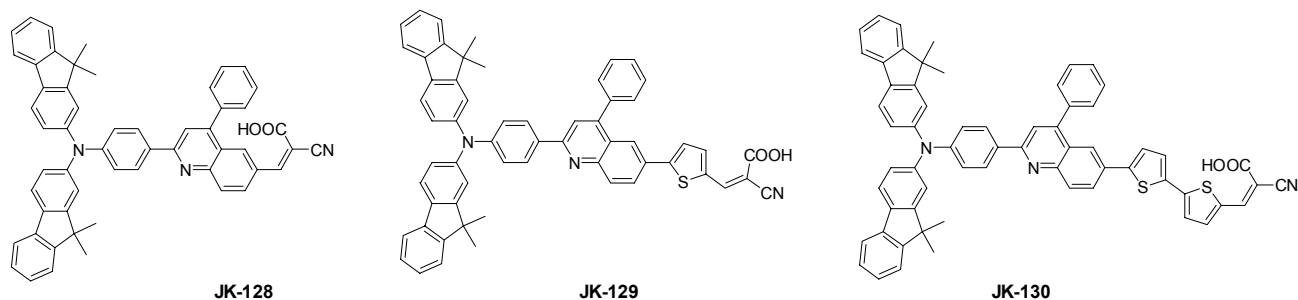
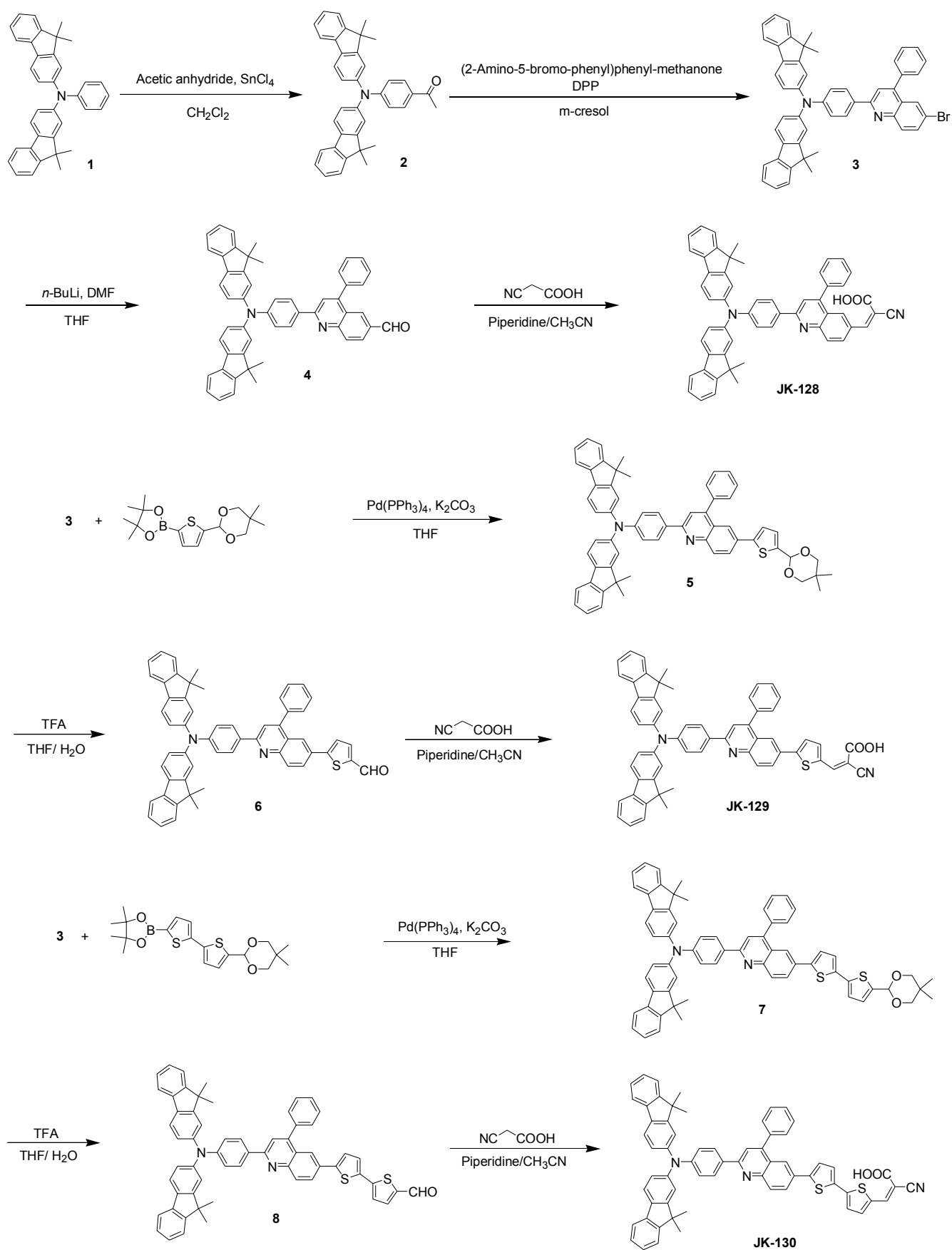


Figure 1. Structure of the dyes of **JK-128**, **JK-129** and **JK-130**.

**Scheme 1.** Schematic diagram for the synthesis of **JK-128**, **JK-129** and **JK-130**

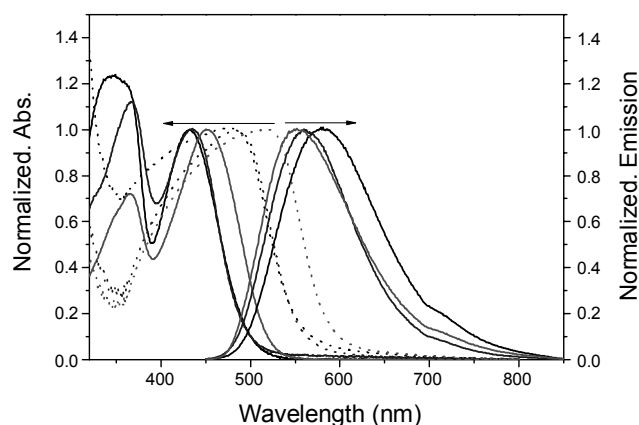


Figure 2. Absorption and emission spectra of **JK-128** (black solid line), **JK-129** (blue solid line) and **JK-130** (red solid line) in THF and absorption spectra of **JK-128** (black dash line), **JK-129** (blue dash line) and **JK-130** (red dash line) adsorbed on TiO₂ film.

one (**2**) was readily synthesized *via* a Friedel-Craft acylation reaction. The Friedlander condensation reaction¹⁵ of **2** with (2-amino-5-bromo-phenyl)phenyl-methanone in the presence of diphenyl phosphate yielded **3**. Compound **4** was prepared from **3** by a lithiation with 1.2 equiv of *n*-butyllithium and subsequent quenching with DMF. The aldehyde **4**, on reaction with cyanoacetic acid in the presence of piperidine in CH₃CN gave the **JK-128** dye. The **JK-129** and **JK-130** dyes were synthesized by Suzuki coupling reaction¹⁶ of 6-bromo-phenylquinoline derivatives with 1.2 equiv of 2-(5-thiophen-2-yl)-1,3,2-dioxaborolane or 2-(2,2'-bithiophen-5-yl)-1,3,2-dioxaborolane, followed by dedioxanylation of **5** and **7** with trifluoroacetic acid.

Fig. 2 shows the absorption and emission spectra of the **JK-128**, **JK-129**, and **JK-130** sensitizers measured in THF and the data are listed in Table 1. The absorption spectrum of **JK-128** displays two absorption maxima at 431 nm ($\epsilon = 22,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 352 nm ($\epsilon = 27,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), which are due to the π - π^* transitions of the conjugated system. Under the same conditions the **JK-129** sensitizer that contains the thiophene unit exhibits absorption bands at 435 nm ($\epsilon = 28,100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 367 nm ($\epsilon = 31,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) that are red-shifted about 4 and 15 nm when compared with those of **JK-128**. On the other hand, the introduction of bithiophene unit, giving **JK-130**, causes a further red shift to 453 nm ($\epsilon = 51,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) compared to the **JK-128** and **JK-129** sensitizers.⁶ Such a high molar extinction coefficient and red

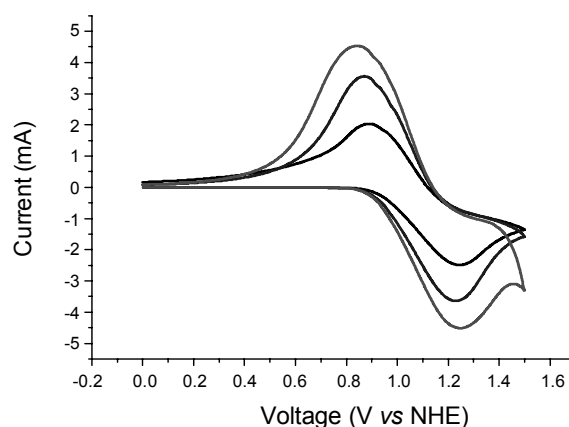


Figure 3. Cyclic voltammograms of **JK-128** (black solid line), **JK-129** (blue solid line), and **JK-130** (red solid line).

shift result from the extension of the π -conjugation in the sensitizer due to the introduction of bithiophene unit in the bridged framework. When the **JK-128**, **JK-129**, and **JK-130** sensitizers were adsorbed on TiO₂ electrode, a large red shift of 44 ~ 72 nm was found due to the *J*-aggregation.¹⁷ The absorption spectra of the three dyes on TiO₂ are much broadened due to an interaction between the dyes and TiO₂.⁶ Such broadening and red shift of the absorption spectra are desirable for harvesting the solar spectrum and lead to large photocurrent. When the **JK-128**, **JK-129**, and **JK-130** sensitizers are excited within their π - π^* bands in an air-equilibrated solution and at 298 K, they exhibit strong luminescence maxima at 556, 564, and 594 nm, respectively.

Electrochemical properties of the dyes **JK-128** ~ **JK-130** were scrutinized by cyclic voltammetry in acetonitrile containing 0.1 M tetrabutyl ammonium hexafluoro-phosphate. TiO₂ films stained with the sensitizers were used as working electrodes. The three organic dyes adsorbed on TiO₂ film show quasi-reversible couples (Fig. 3). The oxidation potential of **JK-128** was measured to be 1.16 V *versus* NHE with a separation of 0.36 V between anodic-to-cathodic peak. Under similar conditions the **JK-129** and **JK-130** dyes exhibit the redox couples at 1.14 and 1.13 V *versus* NHE, respectively. The redox potentials of the three dyes were calculated from the oxidation potential and the E_{0-0} determined from the intersection of absorption and emission spectra (Table 1). The excited state oxidation potentials (E_{OX}^*) of the sensitizers (**JK-128**: -1.33 V; **JK-129**: -1.38 V; **JK-130**:

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

Dye	$\lambda_{\text{abs}}^a/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	$E_{\text{redox}}^b/\text{V}$	E_{0-0}^c/V	$E_{\text{LUMO}}^d/\text{V}$	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF	η^e (%)
JK-128	352 (27 500), 431 (22 500)	1.16	2.49	-1.33	7.568	0.7671	78.34	4.55
JK-129	367 (31 000), 435 (28 100)	1.14	2.52	-1.38	8.289	0.7059	77.50	4.53
JK-130	320 (36 800), 453 (51 000)	1.13	2.48	-1.35	11.519	0.6998	75.29	6.07

^aAbsorption spectra measured in THF solution. ^bRedox potential of dyes on TiO₂ were measured in CH₃CN with 0.1 M (*n*-C₄H₉)₄NPF₆ with a scan rate of 50 mVs⁻¹ (vs. NHE). ^c E_{0-0} was determined from intersection of absorption and emission spectra in THF. ^d E_{LUMO} was calculated by $E_{\text{OX}} - E_{0-0}$. ^ePerformances of DSSCs were measured with 0.18 cm² working area. Electrolyte 0.6 M DMOImI, 0.05 M I₂, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile.

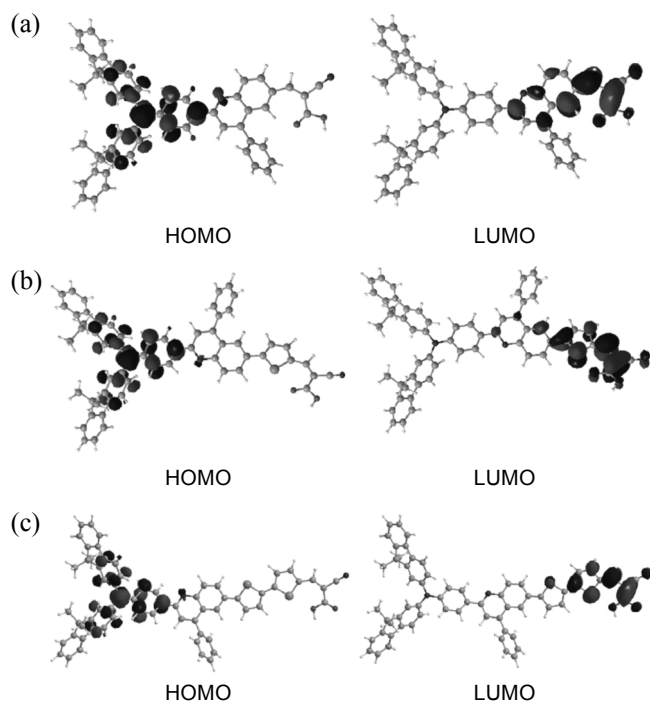


Figure 4. Isodensity surface plots of the HOMO and LUMO of (a) JK-128, (b) JK-129 and (c) JK-130.

−1.35 V vs. NHE) are much negative than the conduction band level of TiO₂ at approximately −0.5 V *versus* NHE, indicating that the electron injection should be thermodynamically favourable.¹⁸

To gain insight into the characteristic features of the electronic structure, molecular orbital calculations of three sensitizers were performed with the TD-DFT on B3LYP/3-21G*. The calculations indicate that the HOMO of three dyes is localized over the fluorenylamino unit over phenyl and the LUMO of JK-128 is localized over the cyanoacrylic unit through the extension of the quinoline unit (Fig. 4). On the other hand, the LUMO of JK-129 and JK-130 is localized through the cyanoacrylic and thiophene moieties. Examination of the HOMO and LUMO of the three dyes indicates that the excitation of the dyes moved the electron distribution from the amino unit to the cyanoacrylic acid unit. Therefore the change in electron distribution induced by photoexcitation results in an efficient charge separation.

Fig. 5 shows action spectra of monochromatic incident-to-current conversion efficiencies (IPCEs) for DSSCs based on JK-128 ~ JK-130. The onset of IPCE spectra for DSSCs based on JK-128 and JK-129 is 650 nm. On the other hand, the onset of JK-130 tails off toward 690 nm, contributing to the broad spectral light harvesting. Furthermore, the enhanced light harvesting of JK-130 in the 550 ~ 650 nm due to the introduction of bithiophene can be clearly seen from Figure 5. The IPCE of JK-130 sensitizer exceeds 80% in the spectral region from 400 to 550 nm, reaching its maximum of 85% at 435 nm. Integrating the IPCE curve of JK-130 over the solar spectrum results in a short circuit current of 11.31 mA cm^{−2} in agreement with the measured device photocurrent. In addition, we find

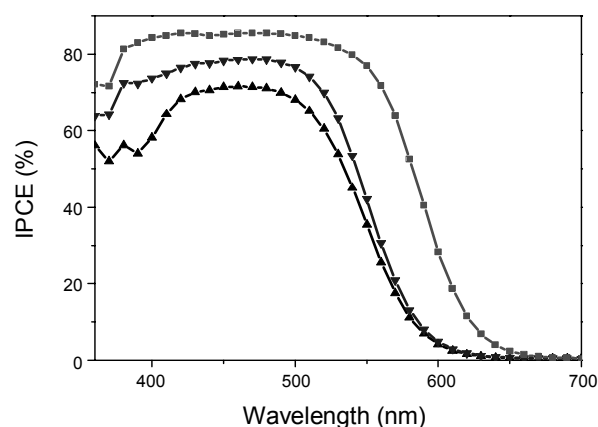


Figure 5. Spectra of incident photon-to-current conversion efficiencies (IPCEs) for DSSC based on JK-128 (black line), JK-129 (blue line), and JK-130 (red line).

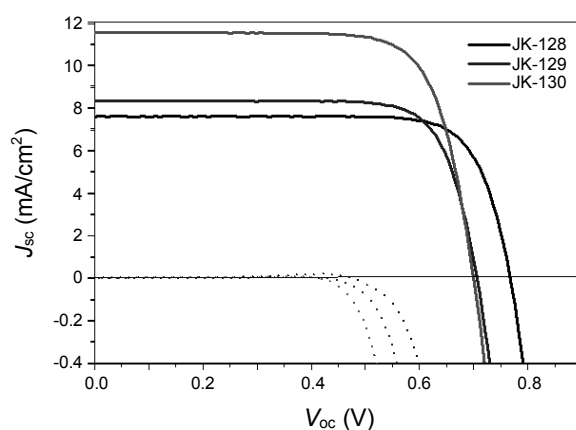


Figure 6. J-V curve of JK-128 (black solid line), JK-129 (blue solid line) and JK-130 (red solid line). Dark current-bias potential relationship is shown as dotted curves.

that the device based on JK-130 exhibits a significant increase in the short circuit current density (J_{sc}). This observation most probably stems from the high molar extinction coefficient and the red shift in the absorption spectrum of JK-130 relative to JK-128 and JK-129. The J-V curve for the cells based on the JK-128 ~ JK-130 is presented in Figure 6. Under standard global AM 1.5 solar condition, the JK-128 and JK-129 sensitized cell gave a short circuit photocurrent density (J_{sc}) of 7.57 and 8.29 mA cm^{−2}, an open circuit voltage (V_{oc}) of 0.77 and 0.71 V and a fill factor of 0.78 and 0.77, corresponding to an overall conversion efficiency η of 4.55 and 4.53%, respectively. Under the same condition, the JK-130 sensitized cell gave a J_{sc} of 11.52 mA cm^{−2}, V_{oc} of 0.70 V and a fill factor of 0.75 corresponding to η of 6.07%. Of particular importance is the 3.23–3.95 mA cm^{−2} increase in J_{sc} of the JK-130 cell. In order to explain the high photocurrent of JK-130, we have measured the amount of dyes absorbed on TiO₂ film. The absorbed amount of 1.98×10^{-6} mmol cm^{−2} for JK-128, 2.64×10^{-6} mmol cm^{−2} for JK-129, and 2.54×10^{-6} mmol cm^{−2} for JK-130 are observed. Therefore, the large photocurrent in JK-130 is attributable to a broad and intense absorption spectrum rather than their absorbed amounts.

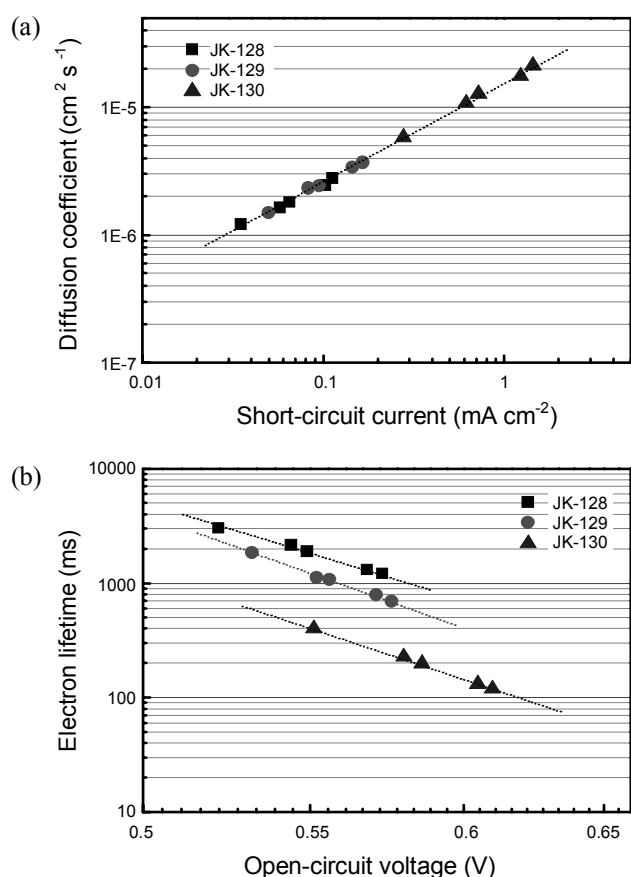


Figure 7. Electron diffusion coefficients (a) and lifetimes (b) of the DSSCs employing **JK-128**, **JK-129**, and **JK-130**, respectively.

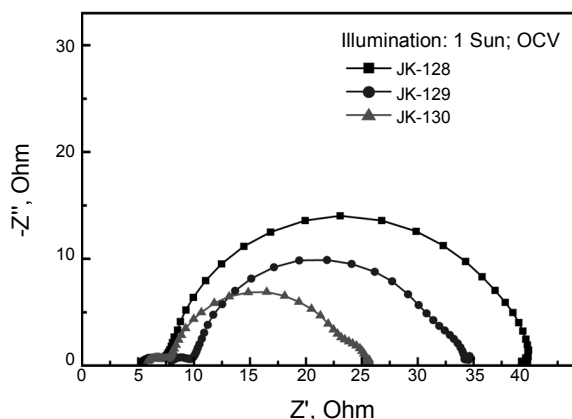


Figure 8. Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) for the devices employing different dyes (\blacksquare **JK-128**, \bullet **JK-129**, \blacktriangle **JK-130**).

To understand the electron injection property and the change in V_{oc} of **JK-128**, **JK-129**, and **JK-130**, we measured electron diffusion coefficients and lifetimes in the photoelectrode. Fig. 7 shows the electron diffusion coefficients and lifetimes of the DSSCs employing different dyes (*i.e.* **JK-128**, **JK-129**, and **JK-130**) displayed as a function of the J_{sc} and V_{oc} , respectively. No significant differences among the D_e values were seen at the identical short-circuit current conditions, showing the similar

trend to those of coumarin dyes.^{6b} On the other hand, the τ_e values show a significant gap among the dyes, resulting in the increasing order of **JK-128** > **JK-129** > **JK-130**. The increase in the number of thiophene unit enhances the light absorption of long wavelength, and therefore the J_{sc} significantly increases but the V_{oc} decreases simultaneously as shown in Table 1. The results of the electron lifetime are also well consistent with those of the V_{oc} .

Fig. 8 shows the ac impedance spectra of the DSSCs measured under the illumination conditions. Under the illumination (100 mW cm^{-2} , open-circuit voltage (OCV) condition), the radius of the intermediate-frequency semicircle in the Nyquist plot decreased in the order of **JK-128** (32.1Ω) > **JK-129** (17.7Ω) > **JK-130** (10.5Ω), indicating the improved electron generation and transport. This result also well corresponds to that of the overall efficiency.

In summary, We have designed and synthesized three organic sensitizers containing a quinoline unit. We obtained a maximum solar energy to electricity conversion efficiency (η) of 6.07% under AM 1.5 irradiation with a DSSC based on **JK-130**. Our results suggest that the development of efficient sensitizers comparable to ruthenium dyes can be possible through the structural modifications of bridging units and these works are now in progress.

Experimental Section

General methods. All reactions were carried out under argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma-Aldrich and TCI. 9,9-Dimethyl-*N*-(9,9-dimethyl-9*H*-fluoren-7-yl)-*N*-phenyl-9*H*-fluoren-2-amine¹⁰ and (2-amino-5-bromophenyl)phenyl-methanone¹⁹ were synthesized using a modified procedure of previous references. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were recorded on a JEOL JMS-SX102A instruments CHNS-OEA 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.

Cyclovoltamogram: Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.). A three-electrode system was used and consisted of a gold disk, working electrode, a platinum wire electrode. Redox potential of dyes on TiO_2 were measured in CH_3CN with $0.1 \text{ M } (n\text{-C}_4\text{H}_9)_4\text{N-PF}_6$ with a scan rate of 50 mV s^{-1} (vs. Fc/Fc^+).

Dye-sensitized solar cell Fabrication: FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min, rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM TiCl_4 (aqueous) at 70°C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by doctor blade printing TiO_2 paste (Solaronix, Ti-Nanoxide T/SP) and then dried for 2 h at 25°C . The TiO_2 electrodes were gradually heated under an air flow at 325°C for 5 min, at 375°C for 5 min, at 450°C for 15 min, and at 500°C for 15 min. The thickness of the transparent layer was measured by using an Alpha-

step 250 surface profilometer (Tencor Instruments, San Jose, CA), a paste for the scattering layer containing 400 nm sized anatase particles (CCIC, PST-400C) was deposited by doctor blade printing and then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The resulting layer was composed of 20 µm thickness of transparent layer and 4 µm thickness of scattering layer. The TiO₂ electrodes were treated again by TiCl₄ at 70 °C for 30 min and sintered at 500 °C for 30 min. The TiO₂ electrodes were immersed into the **JK-128**, **JK-129** and **JK-130** (0.3 mM in THF) containing 10 mM 3a,7a-dihydroxy-5b-cholic acid (Cheno)) and kept at room temperature for 24 h. The FTO plate (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) for counter electrodes cleaned with ultrasonic bath in H₂O, acetone and 0.1 M HCl aq., subsequently. Counter electrodes were prepared by coating with a drop of H₂PtCl₆ solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate and heating at 400 °C for 15 min. The dye adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell by heating at 80 °C with a hot-melt ionomer film (Surlyn SX 1170-25, Solaronix) as a spacer between the electrodes. A drop of electrolyte solution (electrolyte of 0.6 M 1-hexyl-2,3-dimethylimidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile) was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell *via* vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness).

Electron transport measurements: The electron diffusion coefficient (D_e) and lifetimes (τ_e) in TiO₂ photoelectrode were measured by the stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV).²⁰⁻²⁴ The transients were induced by a stepwise change in the laser intensity. A diode laser ($\lambda = 635$ nm) as a light source was modulated using a function generator. The initial laser intensity was a constant 90 mW cm⁻² and was attenuated up to approximately 10 mW cm⁻² using a ND filter which was positioned at the front side of the fabricated samples (TiO₂ film thickness = *ca.* 10 µm; active area = 0.04 cm²). 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 TiO₂ film thickness (ω) using the equation, $D_e = \omega^2 / (2.77 \tau_c)$.¹⁷ The τ_e value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau_e)$.¹⁷ All experiments were conducted at room temperature.

1-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)ethanone (2): To a stirred solution of the compound **1** (0.615 g, 1.3 mmol) in CH₂Cl₂ was added a solution of acetic anhydride in dry CH₂Cl₂ (1.1 equiv) and a solution of SnCl₄ (1.1 equiv) in dry CH₃CN. The mixture was refluxed for 24 h and then poured over ice containing glacial acetic acid. The organic layer was separated and dried in MgSO₄. The product **2** was obtained by silica gel column chromatography (eluent EA : Hx = 1 : 3). ¹H NMR (CDCl₃) δ 7.84 (d, $J = 9.0$ Hz, 2H), 7.66 (t, $J = 7.2$ Hz, 4H), 7.41 (d, $J = 6.3$ Hz, 2H), 7.31 (t, $J = 5.7$ Hz, 4H), 7.25 (d, $J = 2.1$ Hz, 2H), 7.16–7.11 (m, 4H), 2.56 (s, 3H), 1.42 (s, 12H). ¹³C NMR (CDCl₃) δ 196.7, 155.4, 153.7, 152.5, 146.1, 141.9,

138.7, 135.8, 130.2, 130.0, 127.1, 125.2, 124.3, 122.8, 121.0, 120.3, 120.0, 47.1, 27.3, 27.0. MS: m/z 519 [M⁺]. Anal. Calc. for C₃₈H₃₃NO: C, 87.83; H, 6.40. Found: C, 87.61; H, 6.19.

N-(4-(6-Bromo-4-phenylquinolin-2-yl)phenyl)-9,9-dimethyl-N-(9,9-dimethyl-9H-fluoren-7-yl)-9H-fluoren-2-amine (3): A mixture of compound **2** (0.412 g, 0.79 mmol), diphenyl phosphate (DPP, 0.422 g, 1.68 mmol) and (2-amino-5-bromophenyl)phenyl-methanone (0.24 g, 0.87 mmol) in *m*-cresol (2 mL) was stirred at room temperature for 20 min and then refluxed at 140 °C for 12 h. The solution was extracted with CH₂Cl₂, and dried with MgSO₄. The yellow product **3** was obtained by silica gel column chromatography (eluent EA : Hx = 1 : 10). ¹H NMR (CDCl₃) δ 8.08 (t, $J = 8.7$ Hz, 3H), 8.02 (d, $J = 1.5$ Hz, 1H), 7.81 (s, 1H), 7.78 (d, $J = 8.7$ Hz, 1H), 7.72 (d, $J = 1.8$ Hz, 1H), 7.68–7.53 (m, 10H), 7.42 (d, $J = 14.7$ Hz, 2H), 7.37–7.28 (m, 6H), 7.16 (d, $J = 8.1$ Hz, 2H), 1.43 (s, 12H). ¹³C NMR (CDCl₃) δ 156.9, 155.3, 153.7, 149.6, 148.3, 147.6, 147.0, 139.0, 137.9, 134.8, 133.1, 132.7, 131.8, 129.6, 129.4, 128.9, 128.8, 128.6, 126.9, 126.8, 123.9, 123.5, 122.7, 120.8, 120.1, 119.8, 119.6, 119.3, 47.0, 27.2. MS: m/z 758 [M⁺]. Anal. Calc. for C₅₁H₃₉BrN₂: C, 80.62; H, 5.17. Found: C, 80.41; H, 4.95.

3-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4-phenylquinoline-6-carbaldehyde (4): Under a nitrogen atmosphere, *n*-BuLi (0.143 mL, 2.5 M solution in hexane) was dropwise added into compound **3** (0.247 g, 0.33 mmol) solution in dry tetrahydrofuran (THF) and the mixture was stirred at -10 °C for 1 h. After dimethylformamide (0.027 mL, 0.34 mmol) was added to the reaction mixture, the solution was then left under stirring overnight at room temperature. After solvent was evaporated, the organic layer was separated and dried in MgSO₄. The product **4** was obtained by silica gel column chromatography (eluent EA : Hx = 1 : 5). ¹H NMR (CDCl₃) δ 10.10 (s, 1H), 8.38 (s, 1H), 8.30 (d, $J = 8.7$ Hz, 1H), 8.20 (t, $J = 8.4$ Hz, 3H), 7.90 (s, 1H), 7.69–7.25 (m, 19H), 7.17 (d, $J = 8.1$ Hz, 2H), 1.44 (s, 12H). ¹³C NMR (CDCl₃) δ 191.8, 159.0, 155.3, 153.7, 151.9, 150.6, 150.1, 146.8, 138.9, 137.7, 136.2, 135.6, 135.1, 133.8, 133.2, 132.2, 132.1, 131.2, 129.6, 129.1, 128.9, 127.2, 126.8, 125.2, 124.0, 122.9, 122.6, 121.5, 120.8, 119.8, 119.7, 119.4, 48.2, 27.2. MS: m/z 708 [M⁺]. Anal. Calc. for C₅₂H₄₀N₂O: C, 88.10; H, 5.69. Found: C, 87.89; H, 5.48.

(Z)-3-(3-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4-phenylquinolin-6-yl)-2-cyanoacrylic acid (JK-128): A mixture of compound **4** (0.09 g, 0.13 mmol) and cyanoacetic acid (0.02 g, 0.25 mmol) were added CH₃CN (30 mL) and piperidine (0.02 g, 0.23 mmol). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed *in vacuo*. The crude product was extracted with CH₂Cl₂ and water. The pure product **JK-128** was obtained by silica gel column chromatography (eluent MC : MeOH = 9 : 1). ¹H NMR (DMSO-*d*₆) δ 8.30 (d, $J = 15.3$ Hz), 8.23 (s, 1H), 8.17 (s, 1H), 8.06 (s, 1H), 7.97 (s, 1H), 7.79 (t, $J = 10.8$ Hz, 4H), 7.68–7.28 (m, 14H), 7.19 (d, $J = 6.3$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 1.40 (s, 12H). ¹³C NMR (DMSO-*d*₆) δ 163.3, 162.7, 156.4, 154.9, 153.3, 149.2, 149.0, 148.9, 146.8, 146.2, 139.5, 138.2, 137.0, 134.5, 134.5, 131.4, 131.1, 130.3, 129.7, 129.4, 128.9, 127.2, 126.9, 125.7, 124.7, 123.7, 122.8, 121.9, 121.3, 119.8, 119.1, 114.5, 46.5, 26.7. MS: m/z 775 [M⁺]. Anal. Calc. for C₅₅H₄₁N₃O₂: C, 85.13; H, 5.33. Found: C, 84.92; H, 5.12.

9,9-Dimethyl-N-(4-(6-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-4-phenylquinolin-2-yl)phenyl)-N-(9,9-dimethyl-9H-fluoren-7-yl)-9H-fluoren-2-amine (5): A mixture of compound **3** (0.213 g, 0.28 mmol), 4,4,5,5-tetramethyl-2-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (0.11 g, 0.34 mmol), 2 M solution of K_2CO_3 (0.581 g, 4.2 mmol) in H_2O (2.1 mL), and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) in dry THF was refluxed at 80 °C for 24 h. After cooling the solution, the organic layer was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried in $MgSO_4$. The product **5** was obtained by silica gel column chromatography (eluent EA : Hx = 1 : 5). 1H NMR ($CDCl_3$) δ 8.21 (d, J = 9.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 1.5 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.81 (s, 1H), 7.69-7.54 (m, 9H), 7.41 (d, J = 6.9 Hz, 2H), 7.36-7.23 (m, 10H), 7.17 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 3.6 Hz, 1H), 5.36 (s, 1H), 3.72 (d, J = 11.1 Hz, 4H), 1.45 (s, 12H), 1.30 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 156.4, 155.2, 153.7, 149.4, 149.1, 148.6, 147.1, 144.4, 141.3, 140.4, 139.0, 138.4, 137.7, 134.7, 133.1, 132.1, 129.6, 128.9, 128.6, 128.0, 127.1, 126.7, 126.3, 125.9, 123.7, 123.4, 122.6, 122.0, 120.8, 119.8, 119.6, 119.2, 98.4, 98.2, 77.6, 47.0, 30.4, 27.2, 23.0, 21.9. MS: m/z 876 [M^+]. Anal. Calc. for $C_{61}H_{52}N_2O_2S$: C, 83.53; H, 5.98. Found: C, 83.32; H, 5.77.

5-(3-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4-phenylquinolin-6-yl)thiophene-2-carbaldehyde (6): To the compound **5** (0.174 g, 0.2 mmol) in THF was added water. Then trifluoroacetic acid (TFA, 1.075 mL) was added to the solution. The mixture was refluxed for 2 h. The solution was quenched with saturated aqueous sodium bicarbonate and extracted with CH_2Cl_2 and dried with $MgSO_4$. The product **6** was obtained by silica gel column chromatography (eluent EA : Hx = 1 : 5). 1H NMR ($CDCl_3$) δ 9.89 (s, 1H), 8.24 (d, J = 9.3 Hz, 1H), 8.19 (s, 1H), 8.13 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.85 (s, 1H), 7.74-7.59 (m, 9H), 7.40 (d, J = 7.2 Hz, 4H), 7.33-7.31 (m, 9H), 7.17 (d, J = 7.8 Hz, 2H), 1.43 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 182.8, 157.2, 155.3, 153.9, 153.6, 149.7, 149.4, 149.3, 146.9, 142.8, 138.9, 138.0, 137.7, 137.4, 134.9, 132.6, 131.2, 130.9, 130.5, 129.7, 129.1, 128.5, 127.7, 127.5, 126.7, 125.8, 124.5, 123.9, 123.3, 122.6, 120.8, 120.1, 119.8, 119.5, 119.2, 118.7, 47.0, 27.1. MS: m/z 790 [M^+]. Anal. Calc. for $C_{56}H_{42}N_2OS$: C, 85.03; H, 5.35; Found: C, 84.82; H, 5.14.

(Z)-3-(5-(3-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4-phenylquinolin-6-yl)thiophen-2-yl)-2-cyanoacrylic acid (JK-129): A mixture of compound **6** (0.14 g, 0.2 mmol) and cyanoacetic acid (0.034 g, 0.4 mmol) were added CH_3CN (30 mL) and piperidine (0.03 g, 0.35 mmol). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and water. The pure product **JK-129** was obtained by silica gel column chromatography (eluent MC : MeOH = 9 : 1). 1H NMR ($DMSO-d_6$) δ 8.32 (d, J = 8.7 Hz, 2H), 8.18 (s, 1H), 8.06 (t, J = 8.1 Hz, 3H), 7.82-7.62 (m, 12H), 7.52 (d, J = 6.9 Hz, 2H), 7.37-7.28 (m, 6H), 7.20 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 1.40 (s, 12H). ^{13}C NMR ($DMSO-d_6$) δ 164.2, 163.0, 155.6, 155.0, 153.9, 153.3, 149.1, 148.5, 148.2, 147.2, 146.3, 140.3, 139.8, 138.2, 137.3, 137.2, 136.2, 134.5, 131.6, 130.7, 129.7, 128.9, 127.8, 127.0, 126.8, 125.6, 125.1, 123.9, 123.6, 122.9, 122.7, 122.4, 122.2, 121.4, 119.8, 119.3, 112.0, 110.5,

46.6, 26.8. MS: m/z 857 [M^+]. Anal. Calc. for $C_{59}H_{43}N_3O_2S$: C, 82.59; H, 5.05; Found: C, 82.38; H, 4.94.

9,9-Dimethyl-N-(4-(6-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-4-phenylquinolin-2-yl)phenyl)-N-(9,9-dimethyl-9H-fluoren-7-yl)-9H-fluoren-2-amine (7): A mixture of compound **3** (0.233 g, 0.31 mmol), 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (0.15 g, 0.37 mmol), 2 M solution of K_2CO_3 (0.638 g, 4.6 mmol) in H_2O (2.3 mL), and $Pd(PPh_3)_4$ (0.018 g, 0.015 mmol) in dry THF was refluxed at 80 °C for 24 h. After cooling the solution, the organic layer was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried in $MgSO_4$. The product **7** was obtained by silica gel column chromatography (eluent EA : Hx = 1 : 3). 1H NMR ($CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 1H), 8.12 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 1.5 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.80 (s, 1H), 7.68-7.57 (m, 8H), 7.40 (d, J = 7.8 Hz, 2H), 7.35-7.13 (m, 13H), 7.05 (d, J = 10.5 Hz, 2H), 5.62 (s, 1H), 3.70 (d, J = 11.1 Hz, 4H), 1.44 (s, 12H), 1.30 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 156.4, 155.2, 153.7, 149.4, 149.0, 148.6, 147.0, 143.9, 140.4, 139.0, 138.3, 137.7, 137.4, 134.7, 133.1, 131.7, 130.5, 129.7, 128.9, 128.7, 128.6, 128.4, 127.7, 127.0, 126.3, 125.9, 125.6, 125.2, 124.9, 124.5, 123.6, 123.0, 122.7, 122.5, 121.6, 120.8, 119.6, 119.2, 98.2, 77.4, 47.0, 30.4, 27.2, 23.1, 21.9. MS: m/z 958 [M^+]. Anal. Calc. for $C_{65}H_{54}N_2O_2S_2$: C, 81.38; H, 5.67; Found: C, 81.17; H, 5.46.

5'-(3-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4-phenylquinolin-6-yl)-2,2'-bithiophene-5-carbaldehyde (8): To the compound **7** (0.208 g, 0.217 mmol) in THF was added water. Then TFA (4.5 mL) was added to the solution. The mixture was refluxed for 2 h. The solution was quenched with saturated aqueous sodium bicarbonate and extracted with CH_2Cl_2 and dried with $MgSO_4$. The product **8** was obtained by silica gel column chromatography (eluent EA : Hx = 1 : 3). 1H NMR ($CDCl_3$) δ 8.22 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 9.0 Hz, 1H), 8.10 (d, J = 2.1 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.83 (s, 1H), 7.68-7.26 (m, 24H), 7.16 (d, J = 8.1 Hz, 2H), 1.44 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 182.6, 174.5, 156.8, 155.3, 153.7, 149.6, 149.1, 148.8, 147.1, 147.0, 145.9, 141.8, 139.0, 138.3, 137.5, 135.8, 134.8, 132.9, 131.1, 130.9, 129.7, 128.9, 128.8, 127.6, 127.4, 127.1, 126.8, 126.2, 125.9, 125.0, 124.3, 123.8, 123.3, 122.7, 122.2, 120.8, 119.9, 119.6, 119.3, 48.2, 27.2. MS: m/z 872 [M^+]. Anal. Calc. for $C_{60}H_{44}N_2O_2S_2$: C, 82.54; H, 5.08; Found: C, 82.32; H, 4.87.

(Z)-3-(5'-(3-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4-phenylquinolin-6-yl)-2,2'-bithiophen-5-yl)-2-cyanoacrylic acid (JK-130): A mixture of compound **8** (0.19 g, 0.21 mmol) and cyanoacetic acid (0.04 g, 0.42 mmol) were added CH_3CN (30 mL) and piperidine (0.04 g, 0.57 mmol). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and water. The pure product **JK-130** was obtained by silica gel column chromatography (eluent MC : MeOH = 9 : 1). 1H NMR ($DMSO-d_6$) δ 8.30 (d, J = 7.8 Hz, 2H), 8.16 (s, 1H), 8.03 (t, J = 10.2 Hz, 3H), 7.82-7.28 (m, 22H), 7.20 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 1.20 (s, 12H). ^{13}C NMR ($DMSO-d_6$) δ 165.1, 164.6, 163.2, 155.8, 155.3, 154.2, 153.9, 153.4, 150.1, 148.7, 148.4, 147.4, 146.5, 140.5, 140.0, 138.4, 137.5, 137.4,

136.8, 136.4, 134.9, 134.7, 131.8, 130.9, 129.9, 128.9, 128.0, 127.2, 127.0, 125.8, 125.3, 124.1, 123.8, 123.1, 122.9, 122.6, 122.4, 121.6, 120.0, 119.5, 112.5, 110.7, 46.7, 26.9. MS: m/z 939 [M^+]. Anal. Calc. for $C_{63}H_{45}N_3O_2S_2$: C, 80.48; H, 4.82; Found: C, 80.27; H, 4.61.

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