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# Synthesis and photovoltaic properties of novel organic sensitizers containing indolo[1,2-*f*]phenanthridine for solar cell

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ABSTRACT

Organic dyes containing indolo[1,2-*f*]phenanthridine unit are a promising new class of sensitizers for dye-sensitized solar cells, as a result of their broad and intense visible absorptions. Under standard global AM 1.5 solar condition, the **JK-61** sensitized cell gave a short circuit photocurrent density ($J_{sc}$) of 15.81 mA $cm^{-2}$, an open circuit voltage ($V_{oc}$) of 0.73 V, a fill factor of 0.72, corresponding to an overall conversion efficiency of 8.34%.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) using photosensitization of mesoporous $TiO_2$ films by adsorbed sensitizers have been intensively investigated as a cost-effective alternative to conventional solid-state solar cells.[1] Several $Ru^{II}$ polypyridyl complexes have achieved power conversion efficiencies above 11% in standard global air mass 1.5.[2] Recently, impressive photovoltaic performance has been reported with some organic coumarin,[3] indoline,[4] oligoene,[5] merocyanine,[6] and fluorenyl amino dyes[7] having efficiencies in the range of 6–9%. The disadvantage of organic dyes is the low conversion efficiency and stability compared to metal-complexed sensitizers. The absorption coefficients of organic sensitizers are much higher than those of metal pyridyl complexes. However, the sharp and narrow absorption peak of organic sensitizers is one of serious disadvantage. An important goal on organic dyes has been the development of new organic dyes having a wide and strong absorption band. The advantage of organic dyes is the ease of tuning their photophysical properties through the structural modification. The absorption spectra of organic sensitizers can be tuned by careful consideration of the HOMO and LUMO energy levels. Systematic tuning of the energy levels can be easily achieved through the length of the conjugated system[8] and the electron-donating ability of the donar moiety.[9] Among these approaches, we are especially interested in the structural modification of the organic dye donor unit and concerned about its structures and related efficiencies for DSSC. To obtain a panchromatic absorption band, a planarization around nitrogen atom will induce a red shift of the absorption spectrum due to the expansion of π-electron systems conjugated with aromatic units.

In this article, as part of our efforts to develop more efficient organic dyes, we report new organic dyes (**JK-60** and **JK-61**) containing indolo[1,2-*f*]phenanthridine as the electron donor and cyanoacrylic acid as the electron acceptor bridged by a thiophene unit.

## 2. Results and discussion

The synthetic procedures of organic sensitizers **JK-60** and **JK-61** are outlined in Scheme 1. As illustrated in Scheme 1, compound **1** was synthesized according to the method described in the previous literature.[10] The bromoindolo[1,2-*f*]phenanthridine **2** was synthesized by bromination of **1** with NBS (*N*-bromosuccinimide) in $CHCl_3$. The Suzuki coupling reaction[11] of **2** with 2-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophenyl-2-yl)-5-trimethyltin and 2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-5-trimethyltin yielded **JK-60** and **JK-61**, respectively. Subsequent cleavage of 1,3-dioxalane protecting group in TFA produced the aldehydes **4** and **5**. The aldehydes **4** and **5** reacted with cyanoacetic acid in the presence of a catalytic amount of piperidine in chloroform and acetonitrile to give the **JK-60** and **JK-61**, respectively.

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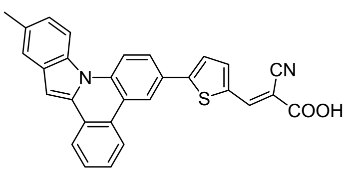
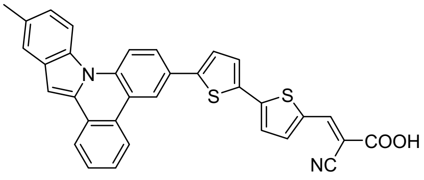
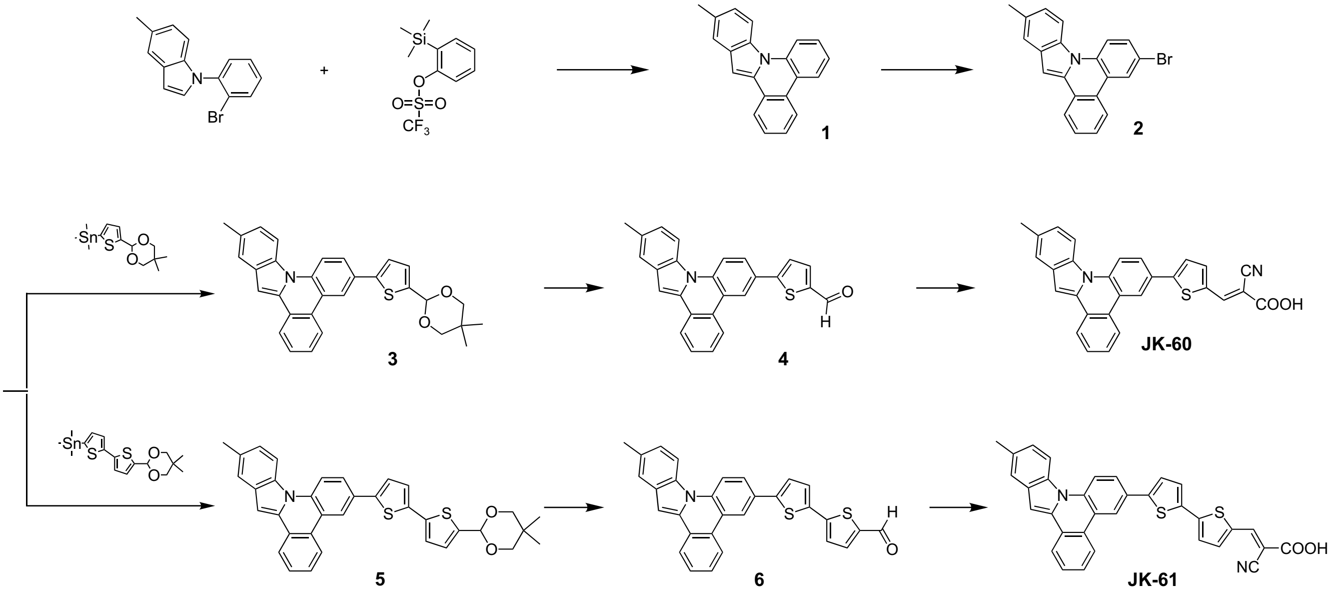


**JK-60**



**JK-61**



**Scheme 1.** Schematic diagram for the synthesis of organic dyes **JK-60** and **JK-61**.

The absorption and emission spectra of sensitizers **JK-60** and **JK-61** measured in THF are shown in Figure 1 and listed in Table 1, together with the UV–vis spectra of the corresponding dyes absorbed on $TiO_2$ film. The absorption and emission spectra in Figure 1 were normalized to same intensity. The absorption spectrum of **JK-60** displays absorption bands at 453 nm ($\varepsilon$=22,600 dm$^3$ mol$^{-1}$ cm$^{-1}$) and 339 nm ($\varepsilon$=39,400 dm$^3$ mol$^{-1}$ cm$^{-1}$), which are assigned as the $\pi$–$\pi$* transitions of the conjugated system. On the other hand, the absorption spectrum of **JK-61** exhibits an intense and broad peak at 411 nm. Two thiophene moieties in **JK-61** seem to contribute to the broadening of the absorption spectrum of the dye.[12] Adsorption of dye **JK-61** onto a $TiO_2$ electrode was observed to broaden the absorption spectrum and to red shift the absorption threshold up to 680 nm. Similar broadening and red shift have been observed in other organic dyes on $TiO_2$ electrodes.[13] We also observed that the dyes **JK-60** and **JK-61** exhibited strong luminescence maxima of 622–724 nm when they are excited within their $\pi$–$\pi$* bands in an air-equilibrated solution at 298 K.

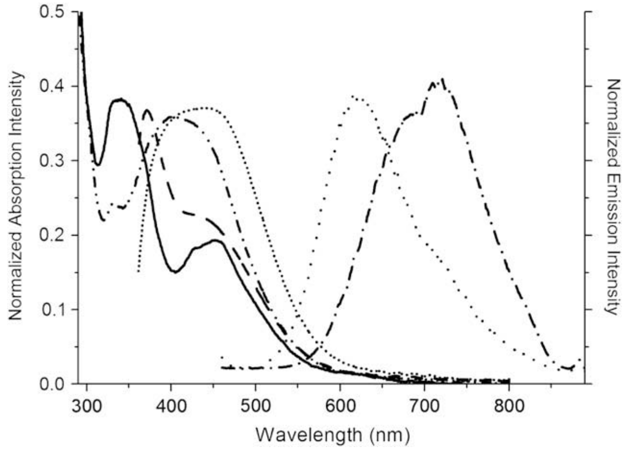


**Figure 1.** Absorption and emission spectra of **JK-60** (solid lind) and **JK-61** (dashed dot line) in THF compared with the absorption spectra of **JK-60** (dashed line) and **JK-61** (dotted line) anchored to $TiO_2$, and their emission spectra of **JK-60** (dotted line) and **JK-61** (dashed dot line).

Electrochemical properties of the dyes **JK-60** and **JK-61** were scrutinized by cyclovoltametry in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate using $TiO_2$ film with absorbed dyes as working electrode. The results are listed in Table 1. The two organic dyes absorbed on $TiO_2$ film showed quasi-reversible couples. The oxidation potentials of **JK-60** and **JK-61** were measured to be 1.01 V and 1.09 V versus NHE with a separation of 0.14 V and 0.16 V between anodic and cathodic peaks, respectively, oxidation potentials energetically favorable for iodide oxidation. The

**Table 1**
Optical, redox, and DSSC performance parameters of **JK-60** and **JK-61**

| Dye | $\lambda_{abs}$,[a] nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) | $E_{ox}$,[b] V | $E_{0-0}$,[c] V | $E_{LUMO}$,[d] V | $J_{sc}$, mA cm$^{-2}$ | $V_{oc}$, V | FF | $\eta$[e] (%) |
|---|---|---|---|---|---|---|---|---|
| **JK-60** | 339 (39,400)<br>453 (22,600) | 1.01 | 2.33 | −1.32 | 12.17 | 0.69 | 0.73 | 6.22 |
| **JK-61** | 411 (37,600) | 1.09 | 2.19 | −1.12 | 15.81 | 0.73 | 0.72 | 8.34 |

[a] Absorption spectra were measured in THF.

[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 in THF.

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

[e] Performances of DSSCs were measured with 0.25 cm$^2$ working area.

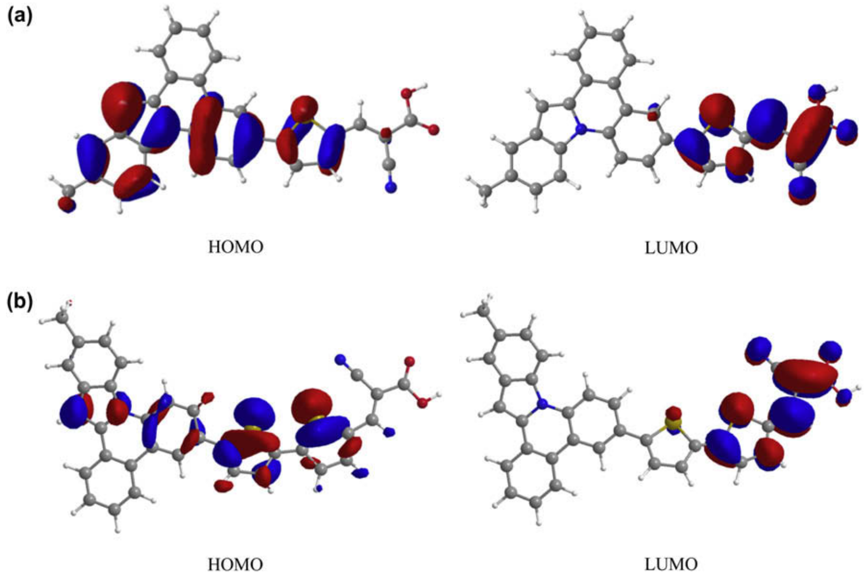


**Figure 2.** Isodensity surface plots of the HOMO and LUMO of (a) **JK-60** and (b) **JK-61**.

reduction potentials of two dyes calculated from the oxidation potentials and the $E_{0-0}$ determined from the intersection of normalized absorption and emission spectra is listed in Figure 1 and Table 1. The excited state oxidation potentials ($E^*_{ox}$) of the dyes (**JK-60**: −1.32 V vs NHE; **JK-61**: −1.12 V vs NHE) are much more negative than the conduction band of $TiO_2$ at approximately −0.5 V versus NHE.[14] A positive shift in the reduction potential in **JK-61** compared to **JK-60** is due to more delocalization of the π-conjugated system by two thiophene groups.

To further understand the photophysical properties, molecular orbital calculations of the two dyes were performed using B3LYP/3-21G*. The calculations illustrates that the HOMO of **JK-60** is delocalized over the π-conjugated system through the phenyl indole and thiophenyl units and the LUMO is delocalized over the cyanoacrylic unit through thiophene (Fig. 2a). On the other hand, the HOMO of **JK-61** is heavily delocalized over the bridging unit from phenyl amino unit to thiophene groups. Examination of the HOMO and LUMO of these dyes indicates that HOMO–LUMO excitation moves the electron distribution from the phenyl amino unit to the cyanoacrylic acid moiety. Accordingly, the change in electron distribution induced by photoexcitation results in an efficient charge separation.

The photocurrent action spectra of the devices based on the two dyes are presented and compared with **N719** in Figure 3. The onset of IPCE spectra for DSSCs based on **JK-60** and **JK-61** was ca. 710 and 760 nm, respectively. The IPCE spectrum of **JK-61** is much broader and red shifted by about 40 nm compared to **JK-60** as a result of extended π-conjugation. The incident photon-to-current conversion efficiency (IPCE) of **JK-61** exceeds 70% in a broad spectral range from 400 to 580 nm, reaching its maximum of 73% at 490 nm. On the other hand, the IPCE spectrum of **JK-60** exceeds 70% in a narrow region from 460 to 505 nm, which is consistent with the absorption spectrum of **JK-60**. The photovoltaic parameters of the devices are summarized in Table 1. Under standard global AM 1.5 solar condition, the **JK-60** and **JK-61** sensitized cell gave a short circuit photocurrent density ($J_{sc}$) of 12.17 and 15.81 mA cm$^{-2}$, an open circuit voltage ($V_{oc}$) of 0.69 and 0.73 V and a fill factor of 0.73 and 0.72, corresponding to an overall conversion efficiencies $\eta$ of 6.22 and 8.34%, respectively (Fig. 4). Under the same condition, the **N719** sensitized cell gave a $J_{sc}$ of 17.06 mA cm$^{-2}$, $V_{oc}$ of 0.80 V and a fill factor of 0.69, corresponding to $\eta$ of 9.41%. From this result (Table 1), of particular importance is the 40 mV increase in $V_{oc}$ and 0.64 mA cm$^{-2}$ increase in $J_{sc}$ of the **JK-61** cell. The increase of $V_{oc}$ in

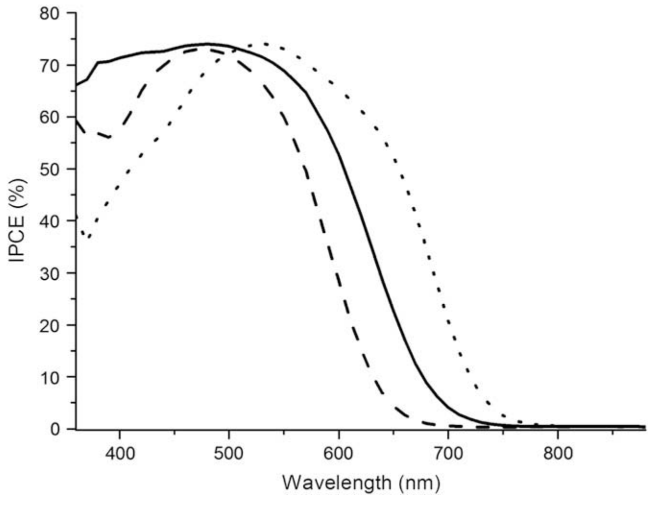


**Figure 3.** Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSCs based on **JK-60** (dashed line), **JK-61** (solid line), and **N719** (dotted line).

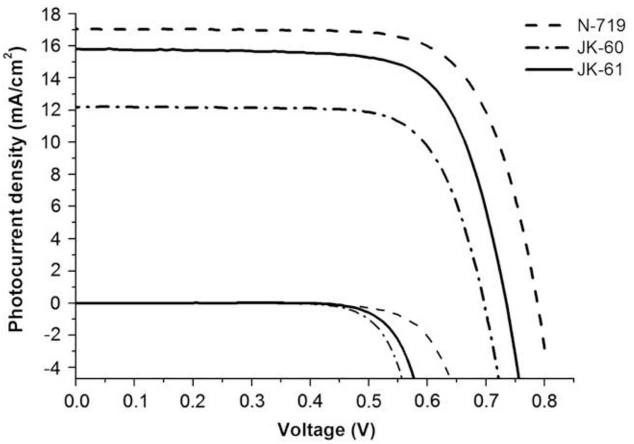


**Figure 4.** A photocurrent voltage curve obtained with a DSSC based on **JK-60** (dashed dot line), **JK-61** (solid line), and **N719** (dashed line) under AM 1.5 radiation.

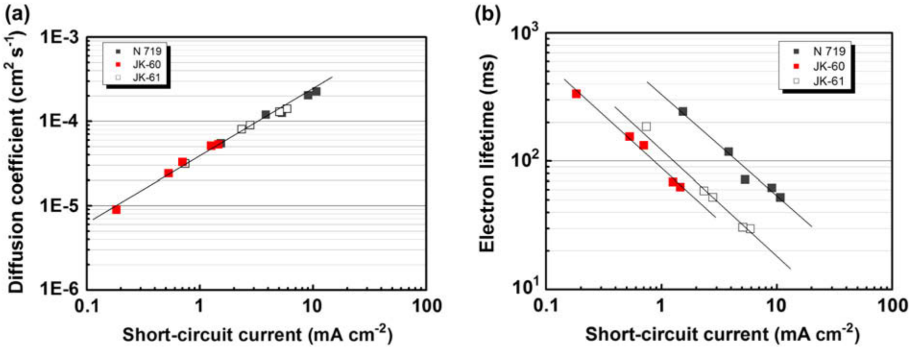


**Figure 5.** Electron diffusion coefficients (a) and lifetimes (b) in the photoelectrodes adsorbing different dyes (i.e., **N719**, **JK-60**, and **JK-61**).

**JK-61** can be interpreted as the suppression of the charge recombination reaction. Minimization of interfacial charge recombination losses in the device is evident from the dark-current data for the cells (Fig. 4). We have also measured the amount of dyes absorbed on $TiO_2$ film to explain the high photocurrent of **JK-61** sensitized cells compared to the **JK-60** sensitizer. The absorbed amounts of $2.96\times10^{-6}$ mmol cm$^{-2}$ for **JK-60** and $2.84\times10^{-6}$ mmol cm$^{-2}$ for **JK-61** are observed. Therefore, it is assumed that the large photocurrent in **JK-61** is originated from a broad and intense absorption spectrum rather than their absorbed amounts.

To understand the electron injection property and the change in $V_{oc}$ of **JK-60** and **JK-61** more clearly, we measured electron diffusion coefficients and lifetimes in the photoelectrode. Figure 5 shows the electron diffusion coefficient ($D_e$) and lifetime ($\tau_e$) of the DSSCs employing different dyes (i.e., **N719**, **JK-60**, and **JK-61**) as a function of the $J_{sc}$. The $D_e$ value was obtained by a time constant ($\tau_c$) determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_c)$ and the $TiO_2$ film thickness ($\omega$) using the equation, $D_e=\omega^2/(2.77\tau_c)$. The $\tau$ value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau)$. The $J_{sc}$ values in the X-axis increased with an increase in the initial laser intensity controlled by ND filters with different optical densities. The $D_e$ values of the photoanodes adsorbing the **JK-60** and **JK-61** dyes are shown to be very similar to those of **N719** at the identical short-circuit current conditions. It demonstrates that the electron injection property of the **JK-60** and **JK-61** is excellent enough for the application in DSSCs. Meanwhile, the difference in the $\tau_e$ values was observed among the cells employing different dyes. It seems that the electron recombination rates were determined by the molecular structures of the dyes due to the different coverage on the $TiO_2$ surface. The results of the electron lifetime are well consistent with those of the $V_{oc}$ shown in Table 1.

In summary, we have designed and synthesized two organic sensitizers containing a planar indolo[1,2-*f*]phenanthridine unit. The power conversion efficiency of the DSSCs based on the **JK-60** and **JK-61** reaches 6.22–8.34%. The power conversion efficiency was shown to be sensitive to the bridging thiophene group. We believe that the development of efficient dyes will be possible through the structural modifications of electron-donating units and bridging groups.

## 3. Experimental section

### 3.1. General methods

#### 3.1.1. Spectroscopic measurements

$^1H$ 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. ATR-FTIR spectra were measured using a Nicolet 5700 spectrometer. The data reported here were taken with the smart orbit diamond ATR accessory. The samples were measured under the same mechanical force pushing the samples in contact with the diamond windows. No ATR correction has been applied to the data.

#### 3.1.2. Electrochemical measurements

Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.). A three electrode system was used and consisted of a gold disk, working electrode, and a platinum wire electrode. Redox potential of dyes on $TiO_2$ was measured in $CH_3CN$ with 0.1 M $(n\text{-}C_4H_9)_4N\cdot PF_6$ with a scan rate of 50 mV s$^{-1}$ (vs Fc/Fc$^+$).

#### 3.1.3. Device fabrication

Fluorine doped tin oxide (FTO) glass plates (Pilkington, 8 Ω sq$^{-1}$, 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 15 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 $TiO_2$ paste (Solaronix, Ti-Nanoxide T/SP) and a scattering layer paste (CCIC, PST-400C) were deposited by doctor blade printing. The sintered layer was composed of 10 μm thickness of transparent layer and 4 μm thickness of scattering layer. The $TiO_2$ electrodes were treated again by $TiCl_4$ and sintered at 500 °C for 30 min. The $TiO_2$ electrodes were immersed into the dye solution (0.5 mM in THF), and then kept at room temperature for 24 h under nitrogen in the dark. 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 (Pilkington, 8 Ω sq$^{-1}$, 2.3 mm thickness) and heating at 400 °C for 15 min. The dye adsorbed $TiO_2$ electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell by heating with a hot-melt ionomer film (Surlyn 1702, 100 μm thickness, Du-Pont) as a spacer between the electrodes. A drop of electrolyte solution (electrolyte of 0.6 M 1-Hexyl-2,3-dimethyl-imidiazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in a 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 film and a cover glass (0.1 mm thickness).

#### 3.1.4. Photovoltaic measurements 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 KG-5 filtered Si reference solar cell. The measurement delay time of photo *I–V* characteristics of DSSCs was fixed to 40 ms. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV Measurements).

## 3.2. Synthesis

### *3.2.1. 11-Methylindolo[1,2-f]phenanthridine (**1**)*

Compound **1** was synthesized using a modified procedure of previous Ref. 8. To a solution of 1-(2-bromophenyl)indole (1 g, 3.49 mmol), CsF (1.5 g, 1.5 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.09 g, 0.087 mmol) and dppp (0.071 g, 0.174 mmol) in $CH_3CN$ (3 mL) and toluene (20 mL) was added *o*-(trimethylsilyl)phenyl triflate (1.04 g, 3.49 mmol) in toluene (7 mL). After reflux for 24 h, the reaction mixture was filtered. The pure product was isolated by chromatography. Yield: 73%.

### *3.2.2. 3-Bromo-11-methylindolo[1,2-f]phenanthridine (**2**)*

To a solution of 11-methylindolo[1,2-*f*]phenanthridine **1** (0.716 g, 2.54 mmol) in $CHCl_3$ (60 mL) at −78 °C was added *N*-bromosuccinimide (0.453 g, 2.54 mmol). The mixture was stirred at same temperature for 30 min and slowly warmed up to room temperature. After evaporating the solvent, the residue was extracted by dichloromethane and washed by $H_2O$. The organic layer was separated and dried in $MgSO_4$. The solvent was removed in vacuo. The pure product **2** was isolated by recrystallization. Yield: 84%. $^{1}$H NMR ($CHCl_3$): δ 9.32 (m, 1H), 8.42 (d, 1H, *J*=8.4 Hz), 8.29 (m, 2H), 8.23 (d, 1H, *J*=8.4 Hz), 7.63 (s, 1H), 7.56 (m, 3H), 7.36 (t, 1H, *J*=7.8 Hz), 7.26 (d, 1H, *J*=2.4 Hz), 2.57 (s, 3H). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): δ 138.5, 134.4, 134.2, 131.2, 130.8, 129.9, 129.8, 128.6, 127.9, 128.0, 128.1, 127.6, 126.2, 125.2, 124.6, 122.0, 119.2, 114.0, 110.7, 95.2, 22.8. MS: *m*/*z* 359. [$M^+$]. Anal. Calcd for $C_{21}H_{14}BrN$: C, 70.01; H, 3.92. Found: C, 69.89; H, 3.78.

### *3.2.3. 3-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-11-methylindolo[1,2-f]phenanthridine (**3**)*

A mixture of 3-bromo-11-methylindolo[1,2-*f*]phenanthridine **2** (0.15 g, 0.41 mmol), trimethyl(5-(5,5-dimethyl-1,3-dioxan-2-yl)-thiophen-2-yl)stannane (0.20 g, 0.41 mmol), and $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol) in dimethylformamide (30 mL) was stirred at 100 °C for overnight. After cooling the solution, $H_2O$ (50 mL) was added to the solution and extracted with dichloromethane. The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo. The pure product **3** was obtained by silica gel chromatography as a yellow solid in 81% yield. $^{1}$H NMR ($CHCl_3$): δ 8.55 (d, 1H, *J*=8.1 Hz), 8.34 (d, 1H, *J*=8.4 Hz), 8.27 (d, 1H, *J*=7.5 Hz), 8.25 (d, 1H, *J*=7.5 Hz), 7.99 (d, 1H, *J*=8.1 Hz), 7.60 (t, 1H, *J*=7.8 Hz), 7.47–7.28 (m, 6H), 7.08 (d, 1H, *J*=2.4 Hz), 5.78 (s, 1H), 3.85 (d, 2H, *J*=10.8 Hz), 3.73 (d, 2H, *J*=10.8 Hz), 2.49 (s, 3H), 1.35 (s, 3H), 0.84 (s, 3H). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): δ 142.5, 137.6, 135.8, 132.6, 132.0, 131.9, 131.1, 128.9, 128.2, 128.1, 127.9, 127.8, 126.5, 126.0, 125.8, 124.7, 124.2, 123.3, 122.5, 122.4, 119.8, 116.6, 113.8, 98.8, 77.9, 30.4, 23.2, 22.0, 21.47. MS: *m*/*z* 477. [$M^+$]. Anal. Calcd for $C_{31}H_{27}NO_2S$: C, 77.96; H, 5.70. Found: C, 77.81; H, 5.53.

### *3.2.4. 5-(11-Methylindolo[1,2-f]phenanthridin-3-yl)thiophene-2-carbaldehyde (**4**)*

THF (30 mL) and water (10 mL) were added to a flask containing 3-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-11-methylindolo-[1,2-*f*]phenanthridine **3** (0.15 g, 0.314 mmol). Then, TFA (3 mL) was added to the solution. The resulting reaction mixture was stirred for 50 min at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with ether. The combined ether phases were then washed with aqueous sodium bicarbonate (2% w/v), dried ($Na_2SO_4$), and evaporated in vacuo. The pure product **4** was obtained by silica gel chromatography as a yellow solid in 94% yield. $^{1}$H NMR ($CHCl_3$): δ 10.03 (s, 1H), 8.51 (d, 1H. *J*=8.4 Hz), 8.31 (d, 1H, *J*=8.1 Hz), 8.24 (m, 2H), 7.95 (d, 1H, *J*=2.4 Hz), 7.87 (d, 1H, *J*=7.5 Hz), 7.58 (t, 1H, *J*=7.8 Hz), 7.48–7.23 (m, 6H), 2.50 (s, 3H). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): δ 183.0, 148.5, 144.5, 137.6, 135.4, 132.4, 1322, 131.5, 131.3, 129.9, 129.1, 128.3, 128.1, 128.0, 125.7, 125.6, 125.0, 124.2, 123.7, 122.8, 122.3, 119.0, 116.6, 114.1, 103.7, 21.5. MS: *m*/*z* 391. [$M^+$]. Anal. Calcd for $C_{26}H_{17}NOS$: C, 77.77; H, 4.38. Found: C, 77.63; H, 4.20.

### *3.2.5. (E)-2-Cyano-3-(5-(11-methylindolo[1,2-f]phenanthridin-3-yl)thiophen-2-yl)acrylic acid (**JK-60**)*

A mixture of 5-(11-methylindolo[1,2-*f*]phenanthridin-3-yl) thiophene-2-carbaldehyde **4** (0.11 g, 0.29 mmol) and cyanoacetic acid (0.05 g, 0.60 mmol) was vacuum-dried and chloroform (40 mL), acetonitrile (20 mL) and piperidine (0.029 mL, 0.30 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. The pure product **4** was obtained by silica gel chromatography as a red orange solid in 61% yield. $^{1}$H NMR (DMSO-$d_6$): δ 8.67 (d, 1H, *J*=9 Hz), 8.58 (d, 1H, *J*=7.2 Hz), 8.50 (d, 1H, *J*=8.7 Hz), 8.47 (d, 1H, *J*=8.7 Hz), 8.25 (s, 1H), 7.92 (d, 1H, *J*=3 Hz), 7.84 (d, 1H, 8.1 Hz), 7.72 (t, 1H, *J*=7.8 Hz), 7.55–7.46 (m, 2H), 7.41–7.35 (m, 3H), 7.28 (d, 1H, *J*=9.0 Hz), 2.44 (s, 3H). MS: *m*/*z* 458. [$M^+$]. Anal. Calcd for $C_{29}H_{18}N_2O_2S$: C, 75.96; H, 3.96. Found: C, 75.81; H, 3.79.

### *3.2.6. 3-(5′-(5,5-Dimethyl-1,3-dioxan-2-yl)-2,2′-bithiophen-5-yl)-11-methylindolo[1,2-f]-phenanthridine (**5**)*

A mixture of 3-bromo-11-methylindolo[1,2-*f*]phenanthridine **2** (0.20 g, 0.55 mmol), (5′-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2′-bithiophen-5-yl)trimethyl-stannane (0.27 g, 0.55 mmol), and $Pd(PPh_3)_4$(0.027 g, 0.025 mmol) in dimethylformamide (30 mL) was stirred at 100 °C for overnight. After cooling the solution, $H_2O$ (50 mL) was added to the solution and extracted with dichloromethane. The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo. The pure product **5** was obtained by silica gel chromatography as a yellow solid in 80% yield. $^{1}$H NMR ($CHCl_3$): δ 8.55 (d, 1H, *J*=8.1 Hz), 8.34 (d, 1H, *J*=8.4 Hz), 8.27 (d, 1H, *J*=7.5 Hz), 8.25 (d, 1H, *J*=7.5 Hz), 7.99 (d, 1H, *J*=8.1 Hz), 7.60 (t, 1H, *J*=7.8 Hz), 7.51–7.26 (m, 6H), 7.12–7.07 (m, 3H), 5.65 (s, 1H), 3.79 (d, 2H, *J*=12 Hz), 3.67 (d, 2H, *J*=12 Hz), 2.52 (s, 3H), 1.31 (s, 3H), 0.82 (s, 3H). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): MS: *m*/*z* 559. [$M^+$]. Anal. Calcd for $C_{35}H_{29}NO_2S_2$: C, 75.10; H, 5.22. Found: C, 74.98; H, 5.04.

### *3.2.7. 5′-(11-Methylindolo[1,2-f]phenanthridin-3-yl)-2,2′-bithiophene-5-carbaldehyde (**6**)*

THF (30 mL) and water (10 mL) were added to a flask containing 3-(5′-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2′-bithiophen-5-yl)-11-methylindolo[1,2-*f*]phenanthridine **5** (0.22 g, 0.40 mmol). Then, TFA (3 mL) was added to the solution. The resulting reaction mixture was stirred for 50 min at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with ether. The combined ether phases were then washed with aqueous sodium bicarbonate (2% w/v), dried ($Na_2SO_4$), and evaporated in vacuo. The pure product **4** was obtained by silica gel chromatography as an orange solid in 91% yield. $^{1}$H NMR ($CHCl_3$): δ 9.90 (s, 1H), 8.57 (d, 1H, *J*=8.4 Hz), 8.36 (d, 1H, *J*=8.1 Hz), 8.28 (m, 2H), 8.05 (d, 1H, *J*=7.5 Hz), 7.71 (d, 1H, *J*=3.3 Hz), 7.62 (t, 1H, *J*=7.5 Hz), 7.56 (d, 1H *J*=2.4 Hz), 8.49 (m, 2H), 7.40 (t, 1H, *J*=7.5 Hz), 7.30 (m, 3H), 7.18 (d, 1H, *J*=2.4 Hz), 2.52 (s, 3H). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): δ 182.7, 147.6, 141.6, 138.6, 137.6, 137.2, 135.6, 132.2, 132.2, 131.2, 130.0, 129.9, 127.1, 128.2, 128.1, 127.1, 129.2, 126.1, 125.6, 124.9, 124.3, 124.2, 123.6, 122.7, 122.3, 119.3, 116.6, 114.1, 103.8, 21.6. MS: *m*/*z* 473. [$M^+$]. Anal. Calcd for $C_{30}H_{19}NOS_2$: C, 64.53; H, 4.95. Found: C, 64.36; H, 4.79.

### *3.2.8. (E)-2-Cyano-3-(5′-(11-methylindolo[1,2-f]phenanthridin-3-yl)-2,2′-bithiophen-5-yl)acrylic acid (**JK-61**)*

A mixture of 5′-(11-methylindolo[1,2-*f*]phenanthridin-3-yl)-2,2′-bithiophene-5-carbaldehyde **6** (0.16 g, 0.34 mmol) and cyanoacetic acid (0.057 g, 0.68 mmol) was vacuum-dried and chloroform (40 mL), acetonitrile (20 mL) and piperidine (0.033 mL, 0.34 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. The pure product was obtained by silica gel chromatography as a red solid in 53% yield. $^{1}$H NMR (DMSO-$d_6$): $\delta$ 8.56 (d, 1H, $J$=8.1 Hz), 8.47 (d, 1H, $J$=6.6 Hz), 8.38 (d, 1H, $J$=9.0 Hz), 8.34 (d, 1H, $J$=9.0 Hz), 8.21 (s, 1H), 7.90 (d, 1H, $J$=7.5 Hz), 7.66 (m, 3H), 7.43 (m, 3H), 7.33 (m, 2H), 7.19 (m, 2H), 2.37 (s, 3H). $^{13}$C{$^{1}$H} NMR (DMSO-$d_6$): $\delta$ 164.1, 141.5, 141.0, 137.1, 136.7, 136.4, 135.7, 134.5, 131.7, 131.2, 131.0, 130.4, 130.2, 129.6, 128.9, 128.4, 128.2 127.3, 126.6, 125.3, 124.7, 124.4, 123.8, 123.1, 121.3, 119.1, 118.5, 116.4, 114.3, 108.6, 103.3, 27.1. MS: $m/z$ 540. [M$^{+}$]. Anal. Calcd for $C_{33}H_{20}N_2O_2S_2$: C, 73.31; H, 3.73. Found: C, 73.19; H, 3.59.

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