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Molecular engineering of organic sensitizers containing indole moiety for dye-sensitized solar cells

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ABSTRACT

Three organic dyes, **JK-77**, **JK-78**, and **JK-79** containing indole unit are designed and synthesized. Nanocrystalline TiO_2 dye-sensitized solar cells were fabricated using these dyes. Under standard global AM 1.5 solar condition, the **JK-79** sensitized solar cell gave a short circuit photocurrent density of 13.62 mA cm^{-2}, open-circuit voltage of 0.705 V, and a fill factor of 0.74, corresponding to an overall conversion efficiency η of 7.18%. We found that the η of **JK-79** was higher than those of other two cells due to the higher V_{oc}. The improved V_{oc} value is attributed to the suppression of dark current owing to the blocking effect of a long alkyl chain.

1. Introduction

Global warming and depletion of fossil fuels urge the development of efficient solar energy conversion technology that fulfills the green energy demands. Dye-sensitized nanocrystalline TiO_2 solar cells (DSSCs) based on Ru complex photosensitizers have been intensively studied as an alternative to the conventional solar cells because of their low-cost production and high performance.[1] Organic dyes have been also utilized as photosensitizers in DSSCs. Recently, the solar cell performance of DSSCs based on organic dyes has been remarkably improved. Impressive photovoltaic performance has been obtained with some organic coumarin,[2] oligoene,[3] merocyanine,[4] hemicyanine,[5] and indoline dyes[6] having efficiencies in the range of 6–9%. An important approach on the design of organic sensitizers has been the structural variation of the compounds in order to obtain sensitizers showing high power conversion efficiency and long-term stability. Modification of the dye is one of the strategies to improve the performance of DSSCs. Recently, we have reported efficient and stable organic sensitizers containing bis-dimethylfluorenyl amino unit. In the previous studies, we adapted the (9,9-dimethylfluoren-2-yl)aminophenyl,[7] benzo[*b*]furan,[8] benzo[*b*]thiophene,[9] and *N*-aryl carbazole units[10] as the donor moieties. In order to improve the photovoltaic performance of DSSCs, a successful approach would be the replacement of the above units with an indole group included advantage of expanded π-conjugation as well as electron donor ability. Even such structural changes of dyes result in significant changes in redox energies, absorption spectra, and the energy gaps between the highest occupied molecular orbital and lowest unoccupied molecular orbital of the dyes, affecting dramatically the performance of DSSCs.

In this article, as part of our efforts to develop more efficient organic dyes, we report three new organic sensitizers containing an indole unit as electron donor and a cyanoacrylic acid as electron acceptor bridged by thiophene unit (Fig. 1).

2. Results and discussion

The three dyes **JK-77**, **JK-78**, and **JK-79** were synthesized by the stepwise synthetic protocol (Scheme 1). Bromination of 2-phenylindole was performed using NBS to give **1**. The X-ray structure analysis of **1** confirmed the bromo substituted structure at C10 (see Supplementary data). Disappearance of H10 resonance at 6.90 ppm was evident in the ^1H NMR spectrum. Suzuki coupling reaction of **1** with 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane **2**[11] in the presence of $Pd(PPh_3)_4$ led to **3**. N-Phenylation of **3** was carried out under Ullmann coupling reaction.[12] Subsequent cleavage of 1,3-dioxalane protecting group in aqueous acid produced the aldehyde 5-(5-(1-(9,9-dimethylfluoren-7-yl)-2-phenylindol-3-yl)thio-phen-2-yl)thiophene-2-carbaldehyde **5**. The aldehyde reacted with

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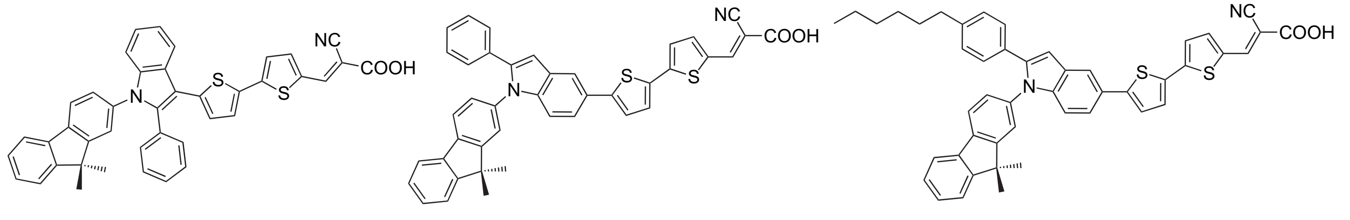


JK-77 **JK-78** **JK-79**

Figure 1. Structure of **JK-77**, **JK-78**, and **JK-79**.

cyanoacetic acid in the presence of a catalytic amount of piperidine in acetonitrile to give the **JK-77**. Fischer indole synthesis[13] of acetonitrile and bromophenylhydrazine led to 5-bromo-2-phenylindole. Suzuki coupling reaction of **6** with **2**, followed by N-phenylation of **7** gave **8**. The thiophene derivative was converted into its corresponding thiophene aldehyde **9** by dedioxanylation with trifluoroacetic acid (TFA), which yielded the dye **JK-78** on treatment of cyanoacetic acid. We have also designed to introduce the long alkyl group on **JK-78** in order to prevent the recombination reaction. The synthetic methodology of **JK-79** is essentially same as that of **JK-78**.

The UV–vis and emission spectra of **JK-77** and **JK-79** in ethanol are shown in Figure 2 and listed in Table 1, together with the UV–vis spectra of the corresponding dyes absorbed on TiO_2 film. The absorption spectra of **JK-78** and **JK-79** exhibit visible band at 429 and 431 nm, respectively, which is due to the π–π^* transition of the conjugated molecule. On the other hand, the absorption spectrum of **JK-77** caused a slightly red shift to 433 nm relative to the **JK-78** and **JK-79** due to a relatively weak electron donating ability of the indole moiety in **JK-77**, indicating that a ring structure in the indole framework is important for a red shift in the absorption spectrum. Adsorption of dyes **JK-77**–**JK-79** onto a TiO_2 electrode was observed to broaden the absorption spectrum and to red shift the absorption threshold up to 650 nm. Similar broadening and red shifts have been reported in other organic dyes on TiO_2 electrodes.[2b,14] Such wide absorption and red shift of absorption maximum in the visible region is desirable for harvesting the solar spectrum and leads to a large photocurrent. We also observed that the dyes **JK-77**–**JK-79** exhibited strong luminescence maxima at 566–603 nm when they are excited within their π–π^* bands in EtOH at 298 K. The fluorescence emission peaks in the visible region disappear when the dyes are adsorbed onto a nanocrystalline TiO_2 film, demonstrating that the electron injection from an excited state to TiO_2 occurs efficiently.

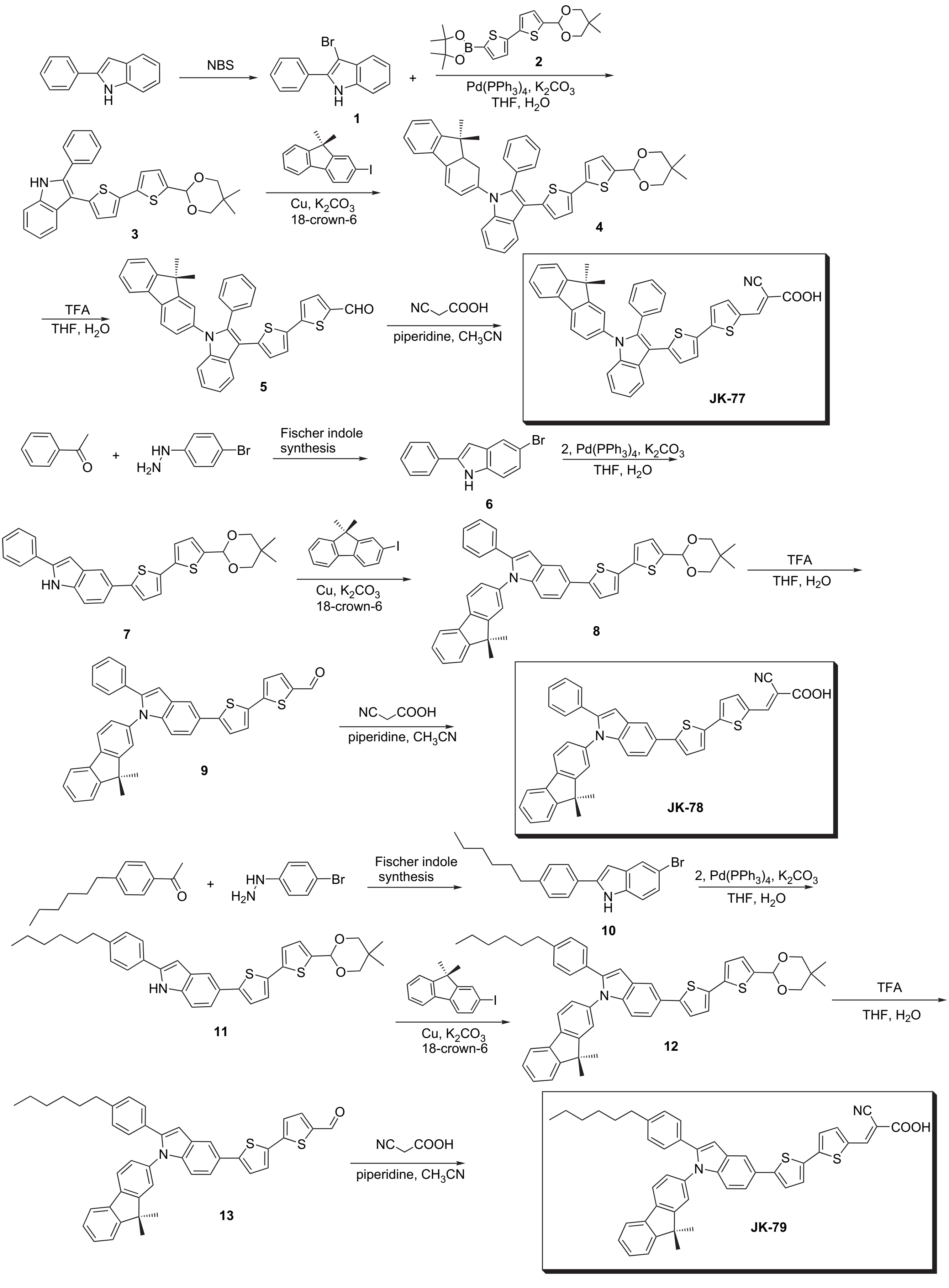
To thermodynamically evaluate the possibility of electron transfer from the excited state of the dye to the conduction band of TiO_2 electrode and the photophysical property of the dyes, cyclic voltammogram was carried out to determine the redox potential (Table 1). The redox potentials of three dyes **JK-77**–**JK-79** were measured in CH_3CN with 0.1 M tetrabutylammonium hexafluorophosphate. TiO_2 films coated with the sensitizers were used as working electrodes. Redox potential of the dyes was quite sensitive to the substitution of the functional groups. The **JK-77** and **JK-78** absorbed on TiO_2 film show a quasi-reversible couple at 1.42 and 1.40 V versus NHE with a separation of 0.20 and 0.18 V, which is assigned to the oxidation of the 1-(9,9-dimethylfluoren-7-yl)-2-phenylindole. The reduction potentials of 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-77**: −0.85 V; **JK-78**: −0.96 V; **JK-79**: −0.93 V vs NHE) are much negative than the conduction band of TiO_2 at −0.5 V vs NHE, allowing the electron injection from the LUMO of dye to the conduction band of TiO_2.

To gain insight into the geometrical configuration and characteristic features of the electronic structure, molecular orbital calculations of three dyes were performed with the TD-DFT on B3LYP/3-21G*. The calculation indicates that the HOMO of **JK-77** is delocalized over the π-conjugated system through the phenylamino group and the thienyl unit next to the phenyl group (Fig. 3). On the other hand, the HOMO of **JK-78** and **JK-79** is delocalized over the conduit channel through an entire bridging unit.

The LUMO of the three dyes is delocalized over the cyanoacrylic unit through thiophene. Examination of the HOMO and LUMO of these dyes indicates that HOMO–LUMO excitation moves the electron distribution from the phenylamino unit to the cyanoacrylic acid moiety. The change in electron distribution induced by photoexcitation results in an efficient charge separation.

For the preparation of DSSC, a washed FTO (Pilkington, $8\ \Omega\ s\ q^{-1}$) glass plate was immersed in 40 mM $TiCl_4$ aqueous solution as reported by the Grätzel group.[15] The first TiO_2 layer of 12 μm thickness was prepared by screen printing TiO_2 paste (13 nm anatase), and the second layer of 4 μm thickness (400 nm) was coated. The TiO_2 electrodes were immersed into the dyes solution in the presence of 10 mM 3a,7a-dihydroxy-5b-cholic acid solution in ethanol and kept at room temperature for 18 h. Cholic acid derivative has been employed as co-adsorbates in DSSCs to suppress dye aggregation on the TiO_2 surface. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg Pt in 1 mL ethanol) on a FTO plate. The electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2-dimethylimidazolium iodide, 0.05 M iodide, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile. The active area was 0.25 cm^2 with employing a mask.

Figure 4 shows action spectra of monochromatic incident-to-current conversion efficiencies (IPCEs) for DSSCs based on **JK-77**–**JK-79**. The onset of IPCE spectra for DSSCs based on **JK-78** and **JK-79** was 680 nm. IPCE values higher than 80% were observed in the range from 420 to 545 nm with a maximum value of 82% at 463 and 492 nm for the DSSC based on **JK-78** and **JK-79**, respectively. The IPCE spectrum of **JK-77** sensitizer is red shifted by about 25 nm compared to those of **JK-78** and **JK-79** as a result of positive shift in the reduction potential of **JK-77**. However, the maximum IPCE value of **JK-77** is much lower than those of both dyes. A plausible reason for this is that electron transfer from the excited dye to TiO_2 would be suppressed due to a small energy gap between the LUMO of the dye and the conduction band edge of TiO_2. The J–V curve for the cells based on the **JK-77**, **JK-78**, and **JK-79** is presented in Figure 4. Under standard global AM 1.5 solar condition, the **JK-77** cell gave the short circuit photocurrent density (J_{sc}) of 12.89 mA cm^{-2}, open-circuit voltage (V_{oc}) of 0.679 V, and a fill factor of 0.73, corresponding to an overall conversion efficiency of 6.43%. In the same condition, the **JK-79** sensitized cell gave J_{sc} of 13.62 mA cm^{-2}, V_{oc} of 0.705 V, and *ff* of 0.74, corresponding to η of 7.18%. From these results (Table 1), we have observed that the η of **JK-79** was higher than those of other cells. Of particular importance is the 10–25 mV increase in V_{oc} of **JK-79** cell under illumination. This improved V_{oc} value is attributed to suppression of dark current owing to the



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-77**, **JK-78**, and **JK-79**.

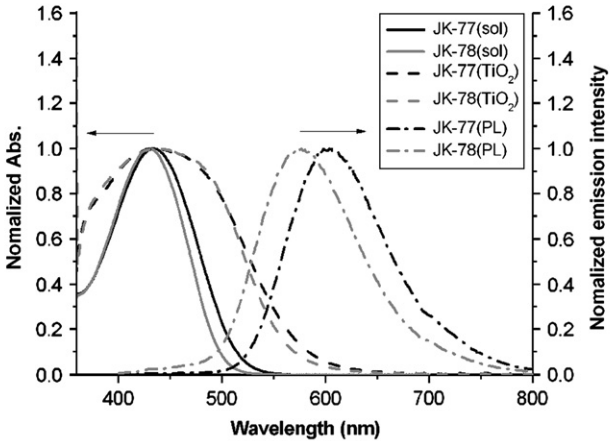


Figure 2. Absorption and emission spectra of **JK-77** (black solid line) and **JK-78** (gray solid line) in EtOH and absorption spectra of **JK-77** (black dashed line) and **JK-78** (gray dashed line) adsorbed on a TiO_2 film. The emission spectra were obtained using the same solution by exciting at 430 nm at 298 K.

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

Dye	λ_{abs}[a]/nm (ε/M^{-1} cm^{-1})	E_{ox}[b]/V	E_{0-0}[c]/V	E_{LUMO}[d]/V	J_{sc} (mA cm^{-2})	V_{oc} (V)	*ff*	η (%)
JK-77	433 (20,369)	1.42	2.27	−0.85	12.89	0.679	0.73	6.43
JK-78	429 (28,075)	1.40	2.36	−0.96	13.68	0.694	0.73	6.96
JK-79	431 (29,370)	1.46	2.39	−0.93	13.62	0.705	0.74	7.18

[a] Absorption spectra were measured in ethanol.
[b] Redox potential of dyes on TiO_2 were measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 50 mV s^{-1} (vs F_c/F_c^+).
[c] E_{0-0} was determined from intersection of absorption and emission spectra in ethanol.
[d] E_{LUMO} was calculated by $E_{ox}-E_{0-0}$.

blocking effect of a long alkyl chain. Minimization of interfacial charge recombination losses in the device is also evident from the dark current data for the cells.

Figure 5 shows the electron diffusion coefficient (D_e) and lifetime (τ_e) of the DSSCs employing different dyes (i.e., **JK-77**, **JK-78**, and **JK-79**) as a function of the J_{sc} and the V_{oc}, respectively. The D_e and τ_e values were determined by the photocurrent and photovoltage transients induced by a stepwise change in the laser light intensity controlled with a function generator.[16–18] The D_e value was obtained by a time constant (τ_c) determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_c)$ and the TiO_2 film thickness (ω) using the equation, $D_e=\omega^2/(2.77\tau_c)$.[16] The τ_e value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau_e)$.[16] The D_e values of the photoanodes adsorbing the organic dyes are shown to be similar to each other at the identical short circuit current condition, showing the similar trend to those of coumarin dyes.[19] Meanwhile, the difference in the τ_e values was clearly observed among the cells employing different dyes. The increasing order of the τ_e values was **JK-77**<**JK-78**<**JK-79** at the identical open-circuit voltage condition, demonstrating that the electron recombination process was effectively controllable by the modification of dye molecular structure (such as the introduction of hydrophobic alkyl chain in **JK-79**). The results of the electron lifetime are also well consistent with those of the V_{oc} shown in Table 1.

The ac impedances of the cells were measured at the dark and illumination conditions. Figure 6 shows the ac impedance spectra of the DSSCs measured in dark and illumination (inset) conditions. In the dark under forward bias (−0.67 V), the semicircle in intermediate frequency regime demonstrates the dark reaction impedance caused by the electron transport from the conduction band of TiO_2 to I_3^- ions in electrolyte.[20] The increased radius of the semicircle in intermediate frequency regime means the reduced electron recombination rate at the dyed TiO_2/electrolyte interface. In dark, the radius of the intermediate frequency semicircle showed the increasing order of **JK-77** (70.9 Ω)<**JK-78** (71.7 Ω)<**JK-79** (96.2 Ω), in accord with the trends of the V_{oc} and τ_e values.

Under the illumination (100 mW cm^{-2}, open-circuit voltage (OCV) condition), the radius of the intermediate frequency

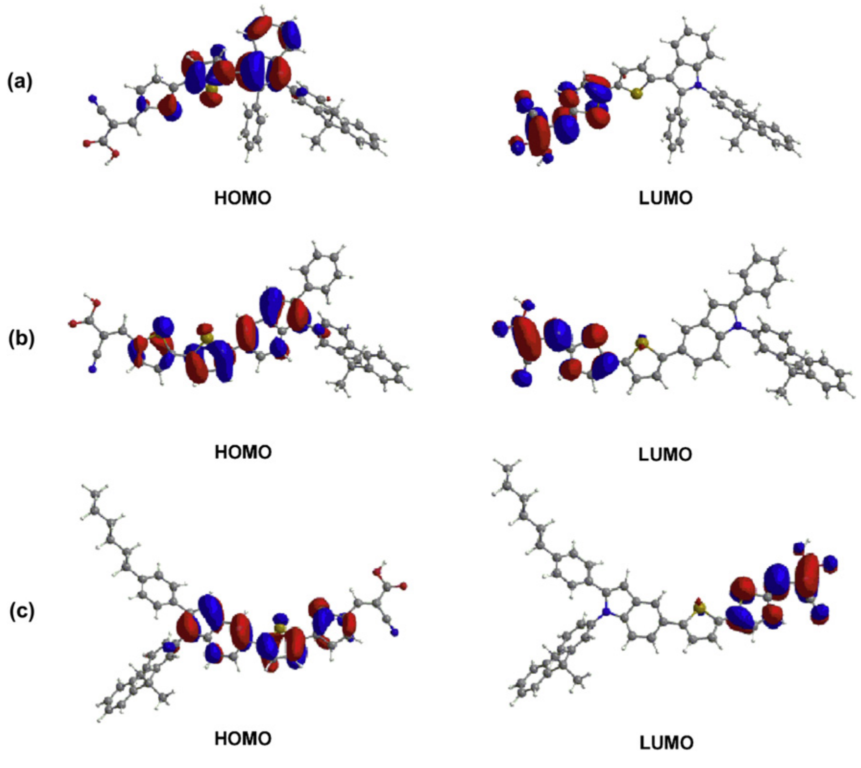


Figure 3. Isodensity surface plots of the HOMO and LUMO of (a) **JK-77**, (b) **JK-78**, and (c) **JK-79**.

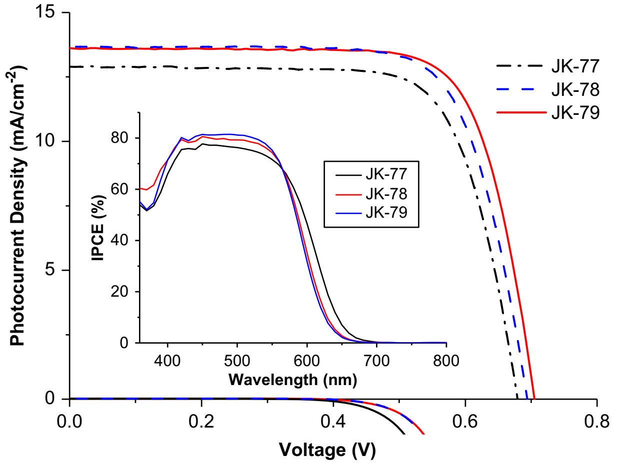


Figure 4. J–V curve and IPCE spectra of **JK-77** (dashed dot line), **JK-78** (dashed line), and **JK-79** (solid line).

semicircle in the Nyquist plot decreased in the order of **JK-77** (85.2 Ω)>**JK-78** (54.6 Ω)>**JK-79** (49.8 Ω), indicating the improved electron generation and transport. This result also well corresponds to that of the overall efficiency.

In conclusion, we have designed and synthesized three novel organic dyes (**JK-77**, **JK-78**, and **JK-79**). We obtained a maximum solar energy to electricity conversion efficiency (η) of 7.18% under AM 1.5 irradiation with a DSSC based on **JK-79**. The power conversion efficiency was shown to be sensitive to the structural modifications. A large increase in V_{oc} of **JK-79** with a long alkyl chain results in a lengthening of the lifetime by preventing the approach of acceptors to the TiO_2 surface. The improved V_{oc} value is attributed to suppression of dark current. Our results suggest that the development of highly efficient organic sensitizers can be possible through the more sophisticated structural modifications.

3. Experimental

3.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich. 2-Iodo-9,9-dimethylfluorene[21] and 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (**2**)[11] 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 performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. The absorption and photoluminescence spectra were recorded on a Perkin–Elmer Lambda 2S UV–visible spectrometer and a Perkin LS fluorescence spectrometer, respectively.

3.2. Cyclovoltagram

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 were 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. Characterization of DSSC

The cells were measured using 1000 W xenon light source, whose power of an AM 1.5 Oriel solar simulator was calibrated by using KG5 filtered Si reference solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV measurements).

3.4. Electron transport measurements

Electron diffusion coefficients and lifetimes were measured by the stepped light-induced transient measurements of photocurrent and voltages (SLIM-PCV).[16–18] The transients were induced by a stepwise change in the laser intensity. A diode laser (λ=635 nm) as a light source was modulated using a function generator (UDP-303, PNCYS Co. Ltd., Korea). 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 (0.04 cm^2). The laser was operated at the voltage of 3.0 V and stepped down to 2.9 V for 5 s. Then the single shot of the time-profiles of the photocurrent and photovoltage was obtained from an oscilloscope (TDS 3052B, Tektronix) through a current amplifier (SR570, Stanford Research Systems) and a voltage amplifier (5307, NF electronic Instruments), respectively. For the measurement of SLIM-PCV, the TiO_2 thickness of the photoelectrode was controlled as approximately 10 μm.

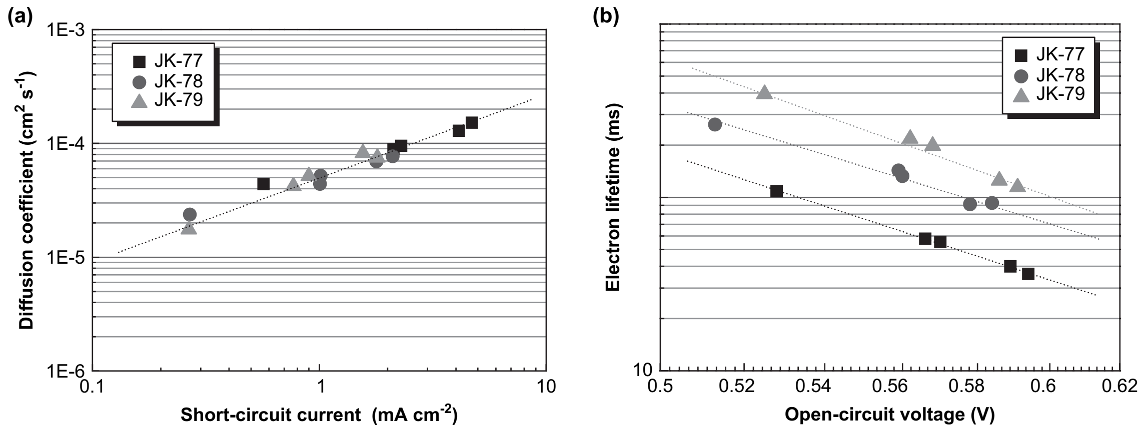


Figure 5. Electron diffusion coefficients (a) and lifetimes (b) in the photoelectrodes adsorbing different dyes (i.e., **JK-77**, **JK-78**, and **JK-79**).

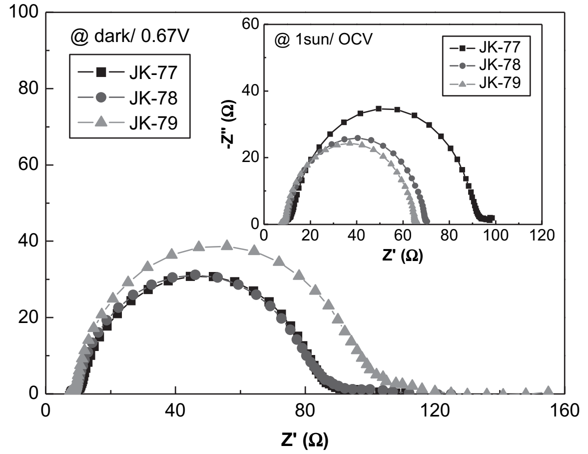


Figure 6. Electrochemical impedance spectra measured in the dark and under the illumination (1 sun, inset) for the cells employing different dyes (i.e., **JK-77**, **JK-78**, and **JK-79**).

3.5. The ac impedance measurements

The ac impedance measurements were carried out under illumination (1 sun) and dark conditions using an impedance analyzer (1260A, Solartron, UK).

3.6. 3-Bromo-2-phenylindole (1)

To a solution of 2-phenylindole (1.0 g, 5.17 mmol) in $CHCl_3$ (120 mL) at 0 °C was added *N*-bromosuccinimide (0.92 g, 5.17 mmol) over 5 min as a small potion. The mixture was stirred at same temperature for 3 h. 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 **1** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:3) as an eluent (yield 91%). Mp: 108 °C. ^1H NMR ($CDCl_3$): δ 8.29 (s, 1H), 7.82 (d, 2H, *J*=7.5 Hz), 7.63 (d, 1H, *J*=7.5 Hz), 7.51 (t, 2H, *J*=7.5 Hz), 7.42 (t, 1H, *J*=7.5 Hz), 7.38 (d, 1H, *J*=6.9 Hz), 7.27 (t, 1H, *J*=7.5 Hz), 7.23 (t, 1H, *J*=6.9 Hz). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 135.2, 129.5, 129.3, 129.0, 128.8, 128.6, 128.4, 123.9, 121.2, 119.5, 112.5, 88.9. MS: *m*/*z* 271 [M^+]. Anal. Calcd for $C_{14}H_{10}BrN$: C, 61.79; H, 3.70. Found: C, 61.66; H, 3.64.

3.7. 3-(5-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-2-phenylindole (3)

To a stirred solution of **1** (0.59 g, 2.19 mmol) and $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol) in tetrahydrofuran (15 mL) were added 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-thiophen-2-yl)-1,3,2-dioxaborolane (**2**) (0.89 g, 2.19 mmol), potassium carbonate (2.76 g, 20 mmol) in THF (15 mL), and H_2O (10 mL). The mixture was refluxed for 18 h. After cooling the solution, H_2O (30 mL) was added to the solution and extracted by dichloromethane (30 mL×3). The organic layer was separated and dried in $MgSO_4$. The solvent was removed in vacuo. The pure product **3** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:1) as an eluent (yield 81%). Mp: 137 °C. ^1H NMR (CD_3COCD_3): δ 10.83 (s, 1H), 7.77 (d, 1H, *J*=8.1 Hz), 7.65 (d, 2H, *J*=8.1 Hz), 7.48 (t, 1H, *J*=8.1 Hz), 7.42 (d, 1H, *J*=7.2 Hz), 7.41 (t, 2H, *J*=8.1 Hz), 7.26 (d, 1H, *J*=3.9 Hz), 7.22 (t, 1H, *J*=8.1 Hz), 7.15 (t, 1H, *J*=7.2 Hz), 7.09 (d, 1H, *J*=3.9 Hz), 7.03 (d, 1H, *J*=3.9 Hz), 6.98 (d, 1H, *J*=3.9 Hz), 5.67 (s, 1H), 3.69 (m, 4H), 1.23 (s, 3H), 0.79 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 141.6, 138.2, 137.4, 137.2, 136.7, 136.6, 133.2, 129.5, 129.4, 129.0, 127.7, 126.6, 124.9, 123.4, 123.1, 121.2, 120.0, 112.3, 107.8, 98.7, 77.7, 30.6, 23.1, 21.8. MS: *m*/*z* 471 [M^+]. Anal. Calcd for $C_{23}H_{25}NO_2S_2$: C, 71.31; H, 5.34. Found: C, 71.21; H, 5.27.

3.8. 3-(5-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1-(9,9-dimethylfluoren-7-yl)-2-phenylindole (4)

A stirred mixture of **3** (0.64 g, 1.35 mmol), 2-iodo-9,9-dimethylfluorene (0.44 g, 1.35 mmol), powdered anhydrous potassium carbonate (0.37 g, 2.70 mmol), copper bronze (0.074 g, 0.41 mmol), and 18-crown-6 (0.054 g, 0.20 mmol) in 1,2-dichlorobenzene (40 mL) was refluxed for 36 h. After cooling, the insoluble inorganic material was filtered off and washed with dichloromethane (3×30 mL). The combined filtrate and organic phase were washed with dilute aqueous ammonia and water and dried with magnesium sulfate. The solvent was removed under reduced pressure. The pure product **3** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:3) as an eluent (yield 86%). Mp: 133 °C. ^1H NMR ($CDCl_3$): δ 8.04 (d, 1H, *J*=8.1 Hz), 7.73 (d, 1H, *J*=8.1 Hz), 7.71 (d, 1H, *J*=8.1 Hz), 7.45–7.18 (m, 12H), 7.07 (d, 1H, *J*=3.9 Hz), 7.05 (s, 1H), 6.99 (d, 1H, *J*=3.9 Hz), 6.98 (t, 1H, *J*=6.9 Hz), 6.87 (d, 1H, *J*=3.9 Hz), 5.61 (s, 1H), 3.70 (m, 4H), 1.29 (s, 3H), 0.80 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.6, 153.9, 139.5, 138.4, 138.3, 138.1, 137.6, 136.5, 136.3, 135.6, 131.4, 128.2, 128.1, 127.6, 127.2, 127.1, 126.7, 126.6, 126.4, 125.8, 124.0, 123.1, 123.0, 122.8, 122.5, 121.3, 120.3, 120.2, 120.0, 111.0, 109.6, 98.3, 77.6, 46.9, 30.3, 26.8, 23.1, 21.9. MS: *m*/*z* 663 [M^+]. Anal. Calcd for $C_{43}H_{37}NO_2S_2$: C, 77.79; H, 5.62. Found: C, 77.64; H, 5.54.

3.9. 5-(5-(1-(9,9-Dimethylfluoren-7-yl)-2-phenylindol-3-yl)thiophen-2-yl)thiophene-2-carbaldehyde (5)

THF (30 mL) and water (30 mL) were added to a flask containing acetal **4** (0.77 g, 1.16 mmol). Then, TFA (0.1 mL) was added to the solution. The resulting reaction mixture was stirred for 3 h at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined organic phases were washed with aqueous sodium bicarbonate (2% w/v), dried (Na_2SO_4), and evaporated in vacuo. The pure product **5** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:1) as an eluent (yield 95%). Mp: 171 °C. ^1H NMR ($CDCl_3$): δ 9.84 (s, 1H), 8.03 (d, 1H, *J*=8.2 Hz), 7.73 (d, 1H, *J*=8.1 Hz), 7.71 (d, 1H, *J*=8.1 Hz), 7.64 (d, 1H, *J*=3.9 Hz), 7.45–7.21 (m, 13H), 7.17 (d, 1H, *J*=3.9 Hz), 7.05 (s, 1H), 6.93 (d, 1H, *J*=3.6 Hz), 1.28 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 182.6, 154.6, 153.8, 148.0, 140.9, 139.6, 138.7, 138.4, 138.3, 138.0, 137.8, 137.7, 136.2, 134.0, 131.4, 131.2, 128.4, 128.3, 127.7, 127.2, 126.8, 126.7, 126.6, 123.5, 123.3, 122.9, 122.8, 121.6, 120.4, 120.2, 119.8, 111.2, 109.2, 46.9, 26.8. MS: *m*/*z* 577 [M^+]. Anal. Calcd for $C_{38}H_{27}NOS_2$: C, 79.00; H, 4.71. Found: C, 78.89; H, 4.68.

3.10. 2-Cyano-3-(5-(5-(1-(9,9-dimethylfluoren-7-yl)-2-phenylindol-3-yl)thiophen-2-yl)thiophen-2-yl)-acrylic acid (JK-77)

In a vacuum-dried flask cyanoacetic acid (0.051 g, 0.060 mmol) and **5** (0.26 g, 0.40 mmol) were placed under argon. Then acetonitrile (30 mL) and piperidine (0.04 mL) were added. The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed in vacuo. The pure product was obtained by silica gel chromatography using a mixture of methylene chloride and methanol (10:1) as an eluent (yield 91%). Mp: 254 °C. ^1H NMR (DMSO-d_6): δ 8.08 (s, 1H), 7.98 (d, 1H, *J*=8.1 Hz), 7.87 (d, 1H, *J*=8.1 Hz), 7.84 (d, 1H, *J*=8.1 Hz), 7.62 (d, 1H, *J*=3.9 Hz), 7.51 (d, 1H, *J*=7.8 Hz), 7.40 (d, 1H, *J*=3.9 Hz), 7.39–7.28 (m, 13H), 6.99 (d, 1H,

J=3.6 Hz), 1.26 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 164.7, 163.5, 154.2, 153.5, 141.4, 140.2, 138.5, 137.8, 137.6, 137.4, 137.2, 136.2, 135.7, 135.3, 133.6, 131.3, 130.8, 128.6, 128.2, 127.7, 127.2, 126.7, 126.5, 125.9, 123.9, 123.4, 123.1, 122.8, 121.6, 120.7, 120.5, 119.3, 118.8, 110.9, 109.1, 108.4, 46.4, 26.4. MS: m/z 644 [M$^+$]. Anal. Calcd for $C_{41}H_{23}N_2O_2S_2$: C, 76.37; H, 4.38. Found: C, 76.30; H, 4.29.

3.11. 5-Bromo-2-phenylindole (6)

To a suspension of acetophenone (1.03 g, 5.0 mmol) and 4-bromophenylhydrazine hydrochloride (1.12 g, 5.0 mmol) in ethanol (5 mL) was added a few drops of glacial acetic acid. The reaction was stirred at 80 °C for 2 h. Solvent was evaporated to yield the phenylhydrazone intermediate, which was added to polyphosphoric acid (20 g). The reaction mixture was stirred at 120 °C for 2 h. The mixture was poured into crashed ice and then neutralized with 1 M NaOH and extracted with CH_2Cl_2. The combined organic extracts were washed with water, dried over anhydrous Na_2SO_4, and evaporated to give the desired 5-bromo-2-phenylindole (**6**) (0.92 g, 68%) as a pale yellow solid. Mp: 132 °C. ^{1}H NMR (CD_3COCD_3): δ 10.89 (br s, 1H), 7.86 (d, 2H, J=7.8 Hz), 7.73 (s, 1H), 7.46 (t, 2H, J=7.8 Hz), 7.38 (d, 1H, J=9.0 Hz), 7.35 (t, 1H, J=7.8 Hz), 7.21 (d, 1H, J=9.0 Hz), 6.90 (s, 1H). ^{13}C{^{1}H} NMR (CD_3COCD_3): δ 133.3, 129.8, 125.8, 124.8, 122.7, 121.6, 118.9, 118.0, 116.2, 106.7, 106.1, 92.3. MS: m/z 271 [M$^+$]. Anal. Calcd for $C_{14}H_{10}BrN$: C, 61.79; H, 3.70. Found: C, 61.68; H, 3.67.

3.12. 5-(5-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-2-phenylindole (7)

The product was synthesized according to the procedure as described above for synthesis of **2**, giving a yellow solid of the product **7** in 73% yield. Mp: 131 °C. ^{1}H NMR (CD_3COCD_3): δ 10.97 (br s, 1H), 7.95 (d, 2H, J=7.5 Hz), 7.57 (d, 1H, J=3.9 Hz), 7.48 (t, 2H, J=7.5 Hz), 7.46 (s, 1H), 7.41 (d, 1H, J=7.5 Hz), 7.35 (d, 1H, J=3.6 Hz), 7.34 (d, 1H, J=7.5 Hz), 7.22 (d, 1H, J=3.6 Hz), 7.19 (t, 1H, J=7.5 Hz), 7.08 (d, 1H, J=3.9 Hz), 5.69 (s, 1H), 3.71 (m, 4H), 1.25 (s, 3H), 0.80 (s, 3H). ^{13}C{^{1}H} NMR (CD_3COCD_3): δ 143.9, 141.9, 139.8, 139.1, 138.1, 136.7, 133.2, 129.8, 128.6, 127.0, 126.8, 126.4, 126.1, 125.4, 123.5, 122.9, 119.5, 112.0, 99.5, 98.7, 77.7, 30.6, 23.1, 21.8. MS: m/z 471 [M$^+$]. Anal. Calcd for $C_{23}H_{25}NO_2S_2$: C, 71.31; H, 5.34. Found: C, 71.16; H, 5.31.

3.13. 5-(5-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1-(9,9-dimethylfluoren-2-yl)-2-phenylindole (8)

The product was synthesized according to the procedure as described above for synthesis of **3**, giving a yellow solid of the product **8** in 89% yield. Mp: 153 °C. ^{1}H NMR ($CDCl_3$): δ 7.93 (s, 1H), 7.79 (d, 1H, J=8.1 Hz), 7.76 (d, 1H, J=8.1 Hz), 7.47–7.04 (m, 16H), 6.85 (s, 1H), 5.64 (s, 1H), 3.72 (m, 4H), 1.35 (s, 3H), 1.31 (s, 6H), 0.82 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.9, 153.9, 142.9, 141.6, 140.1, 139.5, 138.4, 138.3, 138.0, 137.1, 136.6, 132.4, 129.2, 129.1, 128.2, 127.6, 127.5, 127.2, 126.6, 125.9, 125.7, 125.6, 124.5, 122.9, 122.8, 122.6, 120.6, 120.2, 120.1, 110.5, 103.2, 98.3, 77.5, 46.9, 30.3, 26.9, 23.1, 21.9. MS: m/z 663 [M$^+$]. Anal. Calcd for $C_{43}H_{37}NO_2S_2$: C, 77.79; H, 5.62. Found: C, 77.63; H, 5.57.

3.14. 5-(5-(1-(9,9-Dimethylfluoren-2-yl)-2-phenylindol-5-yl)thiophen-2-yl)thiophene-2-carbaldehyde (9)

The product was synthesized according to the procedure as described above for synthesis of **4**, giving an orange solid of the product **9** in 94% yield. Mp: 184 °C. ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 7.96 (s, 1H), 7.79 (d, 1H, J=8.1 Hz), 7.76 (d, 1H, J=8.1 Hz), 7.69 (d, 1H, J=3.9 Hz), 7.51–7.15 (m, 15H), 6.86 (s, 1H), 1.36 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.6, 154.9, 153.9, 147.6, 145.8, 142.0, 141.4, 139.5, 138.5, 138.3, 137.7, 136.9, 135.0, 132.2, 129.2, 129.1, 128.3, 127.7, 127.3, 127.0, 126.6, 126.0, 125.9, 125.6, 124.0, 123.7, 122.8, 122.6, 120.7, 120.4, 120.3, 111.2, 102.9, 46.9, 26.9. MS: m/z 577 [M$^+$]. Anal. Calcd for $C_{38}H_{27}NOS_2$: C, 79.00; H, 4.71. Found: C, 78.91; H, 4.66.

3.15. 2-Cyano-3-(5-(5-(1-(9,9-dimethylfluoren-2-yl)-2-phenylindol-5-yl)thiophen-2-yl)thiophen-2-yl)-acrylic acid (JK-78)

The product was synthesized according to the procedure as described above for synthesis of **JK-77**, giving a red solid of the product **JK-78** in 91% yield. Mp: 264 °C. ^{1}H NMR (DMSO-d_6): δ 8.08 (s, 1H), 8.01 (s, 1H), 7.93 (d, 1H, J=7.2 Hz), 7.85 (d, 1H, J=7.2 Hz), 7.70–7.63 (m, 2H), 7.58–7.43 (m, 4H), 7.39–7.22 (m, 10H), 6.94 (s, 1H), 1.30 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 163.3, 154.6, 153.6, 145.6, 143.3, 141.6, 141.3, 141.0, 140.0, 139.3, 137.9, 137.8, 137.7, 136.5, 136.2, 135.9, 135.6, 134.7, 131.6, 128.9, 128.7, 128.4, 128.3, 127.8, 127.2, 126.6, 125.2, 124.6, 122.9, 121.0, 120.5, 119.7, 119.4, 110.8, 109.7, 102.6, 46.5, 26.4. MS: m/z 644 [M$^+$]. Anal. Calcd for $C_{41}H_{28}N_2O_2S_2$: C, 76.37; H, 4.38. Found: C, 76.24; H, 4.33.

3.16. 5-Bromo-2-(4-hexylphenyl)indole (10)

The product was synthesized according to the procedure as described above for synthesis of **6**, giving a white solid of the product **10** in 70% yield. Mp: 131 °C. ^{1}H NMR (CD_3COCD_3): δ 10.83 (s, 1H), 7,76 (d, 2H, J=8.4 Hz), 7.71 (s, 1H), 7.36 (d, 1H, J=8.4 Hz), 7.29 (d, 2H, J=8.4 Hz), 7.19 (d, 1H, J=8.4 Hz), 6.83 (s, 1H), 2.64 (t, 2H, J=7.8 Hz), 1.62 (m, 2H), 1.32 (m, 6H), 0.88 (m, 3H). ^{13}C{^{1}H} NMR (CD_3COCD_3): δ 143.6, 140.6, 136.8, 132.0, 130.4, 129.8, 126.0, 124.9, 123.2, 113.6, 113.1, 98,8, 36.2, 32.4, 32.1, 29.6, 23.2, 14.3. MS: m/z 355 [M$^+$]. Anal. Calcd for $C_{20}H_{22}BrN$: C, 67.42; H, 6.22. Found: C, 67.29; H, 6.18.

3.17. 2-(4-Hexylphenyl)-5-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)indole (11)

The product was synthesized according to the procedure as described above for synthesis of **2**, giving a white solid of the product **11** in 75% yield. Mp: 105 °C. ^{1}H NMR (CD_3COCD_3): δ 10.79 (s, 1H), 7.68 (s, 1H), 7.79 (d, 2H, J=8.1 Hz), 7.45 (m, 2H), 7.33 (d, 1H, J=3.9 Hz), 7.31 (d, 2H, J=8.1 Hz), 7.25 (d, 1H, J=3.9 Hz), 7.15 (d, 1H, J=3.9 Hz), 7.06 (d, 1H, J=3.9 Hz), 6.91 (s, 1H), 5.68 (s, 1H), 3.71 (m, 4H), 2.65 (t, 2H, J=7.8 Hz), 1.65 (m, 2H), 1.33 (m, 6H), 1.24 (s, 3H), 0.88 (m, 3H), 0.80 (s, 3H). ^{13}C{^{1}H} NMR (CD_3COCD_3): δ 143.4, 141.9, 140.9, 138.5, 138.2, 135.7, 130.7, 129.8, 128.1, 126.7, 125.9, 125.7, 125.6, 123.4, 123.2, 120.8, 117.9, 112.8, 112.5, 98.7, 77.7, 36.2, 32.4, 32.2, 30.6, 29.6, 23.2, 23.1, 21.8, 14.3. MS: m/z 555 [M$^+$]. Anal. Calcd for $C_{34}H_{37}NO_2S_2$: C, 73.47; H, 6.71. Found: C, 73.45; H, 6.59.

3.18. 2-(4-Hexylphenyl)-5-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1-(9,9-dimethylfluoren-2-yl)indole (12)

The product was synthesized according to the procedure as described above for synthesis of **3**, giving a yellow solid of the product **12** in 80% yield. Mp: 125 °C. ^{1}H NMR ($CDCl_3$): δ 7.91 (s, 1H), 7.79 (d, 1H, J=8.1 Hz), 7.75 (d, 1H, J=8.1 Hz), 7.48–7.35 (m, 6H), 7.23–7.14 (m, 5H), 7.11 (s, 1H), 7.05 (d, 2H, J=8.1 Hz), 7.03 (d, 2H, J=8.1 Hz), 6.81 (s, 1H), 5.63 (s, 1H), 3.71 (m, 4H), 2.53 (t, 2H, J=7.8 Hz), 1.53 (m, 2H), 1.34 (s, 6H), 1.30 (s, 3H), 1.26 (m, 6H), 0.86 (m, 3H), 0.81 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.8, 154.8, 153.9, 145.3, 142.5, 142.1, 139.7, 138.9, 138.5, 138.4, 138.1, 137.2, 135.5, 129.7, 129.0, 128.9, 128.3, 127.6, 127.3, 127.1, 126.3, 125.9, 124.8, 122.8, 120.8, 120.6, 120.2, 117.7, 111.1, 104.3, 103.3, 98.3, 77.5, 46.9, 35.7, 31.8, 31.4, 30.3, 29.0, 26.9, 23.1, 22.7, 21.9, 14.2. MS: *m*/*z* 747 [M$^+$]. Anal. Calcd for $C_{49}H_{49}NO_2S_2$: C, 78.67; H, 6.60. Found: C, 78.61; H, 6.52.

3.19. 5-(5-(2-(4-Hexylphenyl)-1-(9,9-dimethylfluoren-2-yl)indol-5-yl)thiophen-2-yl)thiophene-2-carbaldehyde (13)

The product was synthesized according to the procedure as described above for synthesis of **4**, giving an orange solid of the product **13** in 95% yield. Mp: 161 °C. ^{1}H NMR (CDCl$_3$): δ 9.86 (s, 1H), 7.94 (s, 1H), 7.79 (d, 1H, *J*=7.5 Hz), 7.75 (d, 1H, *J*=7.5 Hz), 7.68 (d, 1H, *J*=3.9 Hz), 7.49–7.31 (m, 6H), 7.28–7.24 (m, 3H), 7.18 (d, 2H, *J*=8.1 Hz), 7.11 (s, 1H), 7.04 (d, 2H, *J*=8.1 Hz), 6.83 (s, 1H), 2.53 (t, 2H, *J*=7.5 Hz), 1.55 (m, 2H), 1.34 (s. 6H), 1.26 (m, 6H), 0.87 (m, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 182.6, 154.8, 153.9, 148.3, 147.9, 142.7, 142.4, 141.1, 138.7, 138.4, 138.3, 137.7, 137.1, 133.9, 129.5, 129.0, 128.9, 128.3, 127.7, 127.4, 127.3, 126.4, 126.3, 123.7, 123.2, 122.8, 122.7, 120.7, 120.6, 120.3, 118.0, 111.3, 103.4, 47.0, 35.7, 31.8, 31.4, 29.0, 26.9, 22.7, 14.2. MS: *m*/*z* 661 [M$^+$]. Anal. Calcd for $C_{44}H_{39}NOS_2$: C, 79.84; H, 5.94. Found: C, 79.75; H, 5.88.

3.20. 2-Cyano-3-(5-(5-(2-(4-hexylphenyl)-1-(9,9-dimethyl-fluoren-2-yl)indol-5-yl)thiophen-2-yl)thiophen-2-yl)acrylic acid (JK-79)

The product was synthesized according to the procedure as described above for synthesis of **JK-77**, giving a red solid of the product **JK-79** in 85% yield. Mp: 260 °C. ^{1}H NMR (DMSO-d_6): δ 8.05 (s, 1H), 8.01 (s, 1H), 7.95 (d, 1H, *J*=7.2 Hz), 7.87 (d, 1H, *J*=7.2 Hz), 7.65 (d, 1H, *J*=3.9 Hz), 7.53–7.45 (m, 3H), 7.48 (d, 1H, *J*=3.9 Hz), 7.42 (d, 1H, *J*=3.9 Hz), 7.40–7.25 (m, 5H), 7.17 (d, 2H, *J*=7.8 Hz), 7.07 (d, 2H, *J*=7.8 Hz), 6.90 (s, 1H), 2.47 (m, 2H), 1.46 (m, 2H), 1.29 (s, 6H), 1.19 (m, 6H), 0.80 (m, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 162.9, 154.4, 153.5, 145.5, 142.0, 141.7, 141.1, 139.6, 138.1, 137.7, 136.5, 135.9, 135.6, 133.5, 129.0, 128.7, 128.5, 128.4, 128.3, 128.1, 127.6, 127.2, 126.7, 126.2, 125.9, 123.9, 123.7, 122.8, 122.6, 120.9, 120.4, 119.5, 117.2, 111.1, 110.0, 103.2, 46.4, 34.7, 31.0, 30.7, 28.1, 26.3, 22.0, 13.9. MS: *m*/*z* 728 [M$^+$]. Anal. Calcd for $C_{47}H_{40}N_2O_2S_2$: C, 77.44; H, 5.53. Found: C, 77.28; H, 5.50.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.045.

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