Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 1913–1922

Molecular engineering of organic dyes containing *N*-aryl carbazole moiety for solar cell

Duckhyun Kim, Jae Kwan Lee, Sang Ook Kang* and Jaejung Ko*

Department of Chemistry, Korea University, Jochiwon, Chungnam 339-700, Republic of Korea

Received 31 October 2006; revised 22 December 2006; accepted 25 December 2006
Available online 4 January 2007

Abstract—Organic dyes containing *N*-aryl carbazole moiety are designed and synthesized. Under standard global AM 1.5 solar condition, the **JK-25** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 11.50 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.68 V, a fill factor of 0.66, corresponding to an overall conversion efficiency η of 5.15%, and the maximum incident monochromatic photon-to-current conversion efficiency (IPCE) of 77% at 430 nm.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention over the last 15 years owing to their prospect of high energy conversion efficiency and low production cost.[1] Until now, however, only few photosensitizers based on ruthenium metal complexes have achieved solar-to-electric power conversion over 10% under AM 1.5.[2] Recently, several groups have developed metal free organic sensitizers to overcome the prohibitive cost of ruthenium metal complexes, and the impressive photovoltaic performance has been obtained with some organic coumarin,[3] indoline,[4] oligoene,[5] merocyanine,[6] and hemicyanine[7] dyes having efficiencies in the range of 5~8%. However, many organic dyes have often presented the low conversion efficiency and low operation stability compared to metal complexes. The major factor for the low conversion efficiency of many organic dyes in the DSSCs is due to the formation of dye aggregates on the semiconductor surface. Another issue of organic dyes is the stability due to the formation of unstable radical species during redox reaction cycles.

Very recently, we have designed and synthesized the novel organic dyes containing dimethylfluorenyl unit to overcome the low conversion efficiency and low operational stability. The amorphous non-planar dimethylfluorenyl moiety was introduced to prevent aggregation via molecular stacking and to ensure greater resistance to degradation when exposed to light and high-temperature.[8] Also, we have been interested in an excellent hole-transporting material such as carbazole moiety, which has been widely drawn interest in organic light-emitting diodes (OLEDs) and solid-state DSSCs.[9] In this paper, we report six new organic dyes containing *N*-(9,9-dimethylfluoren-2-yl)carbazole or *N*-(4-(2,2-diphenylvinyl)phenyl)carbazole as electron donor and cyanoacrylic acid or rhodanine-3-acetic acid as electron acceptor bridged by thiophene or vinylene thiophene units (Fig. 1). Although many structure frameworks such as coumarin, aniline, and indoline have been employed as good electron donor unit, the small molecular organic dyes containing the *N*-substituted carbazole structural motif have been little explored for DSSCs.

2. Results and discussion

The novel organic dyes **JK-24**–**JK-27** were constructed by the stepwise synthetic protocol illustrated in Scheme 1. For the synthesis of well-defined model compounds a monofunctional carbazole unit substituted in the 3-position is required. The monohalogenated carbazole **1** was synthesized by iodination with periodic acid dihydrate and iodine. Due to two possibilities of N-arylation in 3-iodocarbazole, firstly we introduced thiophene moieties. The carbazolyl mono- and bithiophenes **2** and **3** were obtained by coupling 3-iodocarbazole **1** with tetrakis(triphenylphosphine)palladium(0), dimethylformamide, and stannylthiophene units according to the Stille reaction conditions.[10] Fluorene substituted carbazolyl thiophene derivatives **4** and **5** were obtained by Ullmann coupling reactions[11] involving copper bronze, potassium carbonate, and 18-crown-6. These thiophene derivatives were converted into their corresponding thiophene aldehydes **6** and **7** by lithiation with 2.5 equiv *n*-butyl lithium and subsequent quenching with dimethylformamide in 89% and 86% excellent yield, respectively. An acetonitrile solution of thiophene aldehyde derivatives and cyanoacetic

Keywords: Carbazole; Organic dye; Dye-sensitized solar cell.
* Corresponding authors. Tel.: +82 41 860 1337; fax: +82 41 867 5396; e-mail: jko@korea.ac.kr

0040–4020/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.tet.2006.12.082

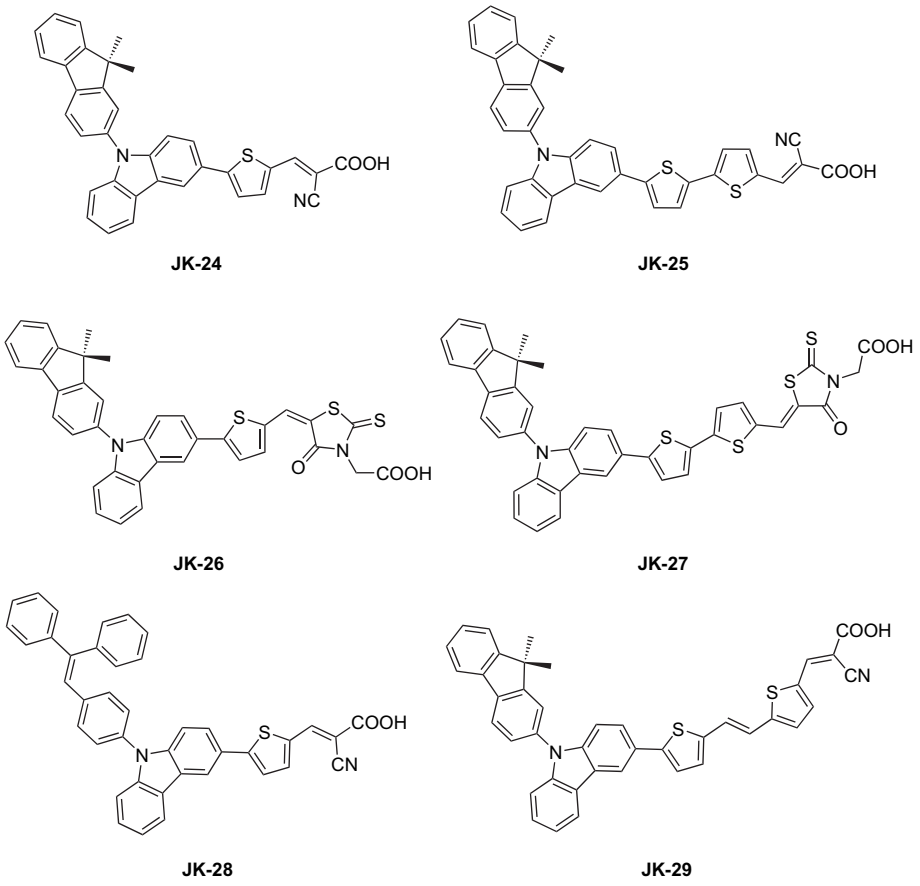
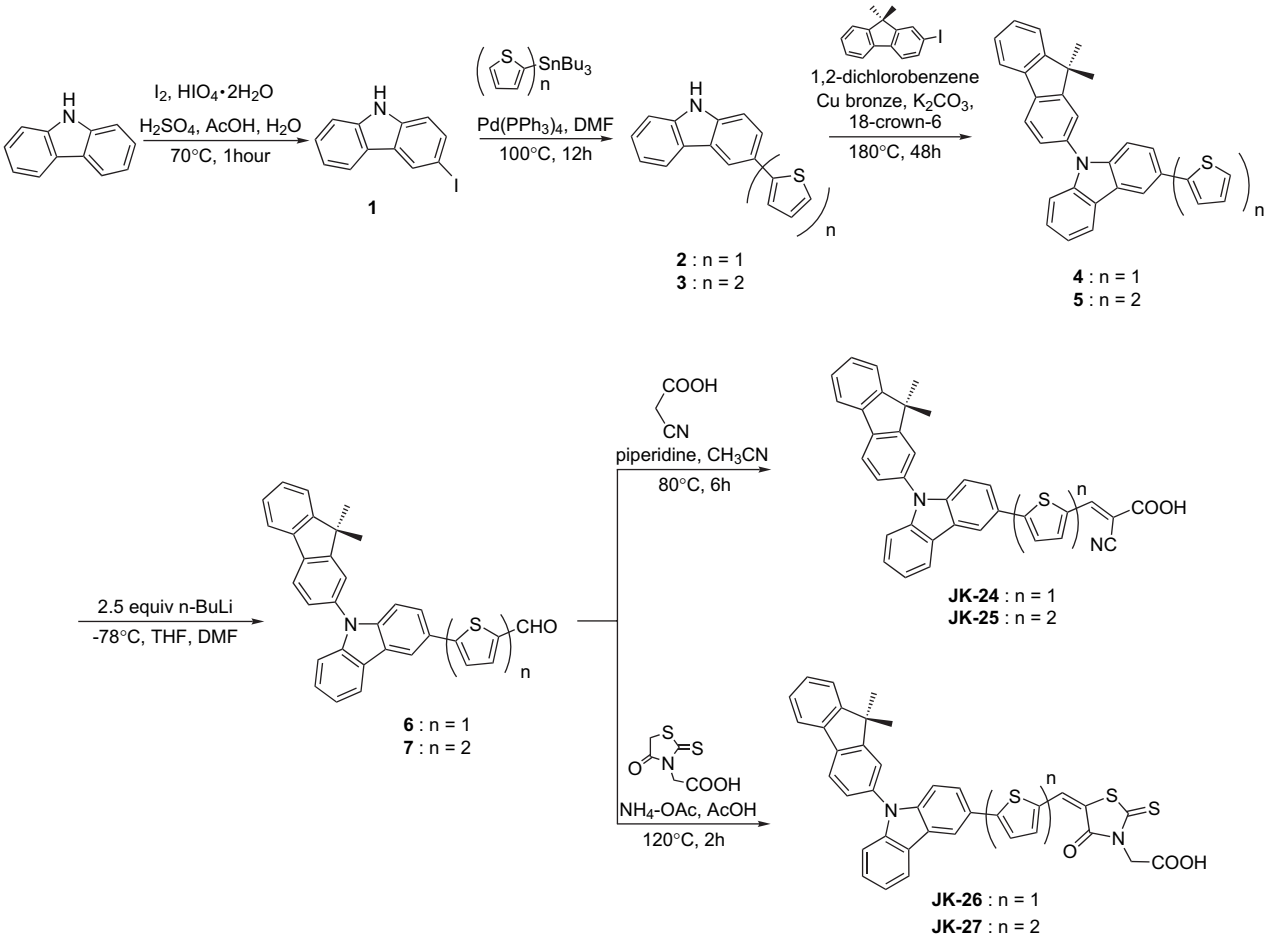


Figure 1. Structure of **JK-24**–**JK-29**.

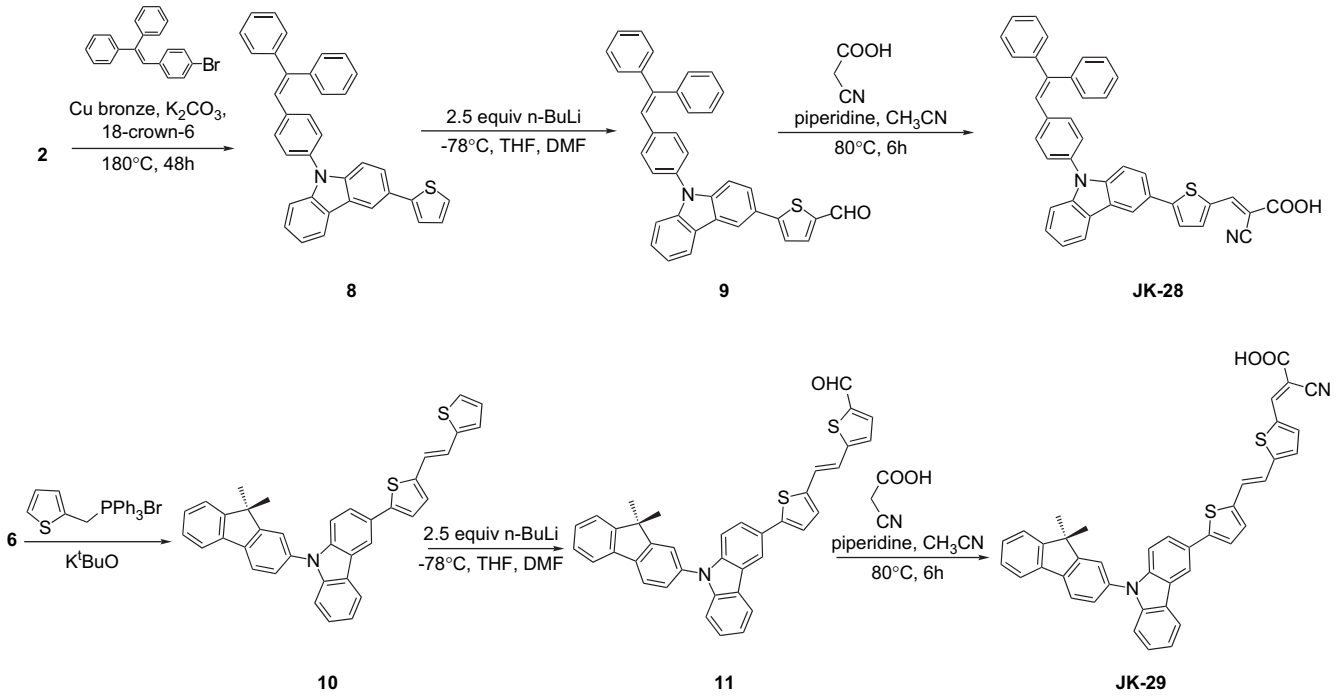
acid was refluxed in the presence of piperidine for 6 h. Solvent removal followed by purification by silica gel column chromatography yielded **JK-24** and **JK-25** dyes as a red solid. Similarly, condensation of thiophene aldehydes **6** and **7** with rhodanine-3-acetic acid and ammonium acetate in acetic acid produced organic dyes **JK-26** and **JK-27**.

The route to compounds **JK-28** and **JK-29** is shown in Scheme 2. N-Arylation of 3-(thiophen-2-yl)carbazole **2** with 1-(2-(4-bromophenyl)-1-phenylvinyl)benzene under Ullmann conditions produced the new carbazolyl thiophene **8**. A formylation reaction with 2.5 equiv of *n*-butyl lithium and dimethylformamide gave the aldehyde **9** in 82% yield. Aldehyde, on reaction with cyanoacetic acid in the presence of a catalytic amount of piperidine in acetonitrile, produced the **JK-28** dye. We have designed to insert the ethylene group between two thiophenes. Coupling reaction of aldehyde **6** with (2-thienylmethyl)triphenylphosphonium bromide under Horner–Emmons–Wittig coupling condition[12] using potassium-*tert*-butoxide in THF led to 9-(9,9-dimethyl-9*H*-fluoren-2-yl)-3-(5-(2-(thiophen-2-yl)vinyl)thiophen-2-yl)-9*H*-carbazole **10**. This was then converted to the aldehyde **11**, which produced the dye **JK-29** on treatment with cyanoacetic acid.

UV–vis and fluorescence spectra of dyes 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-24** and **JK-25** display visible band at 411 and 435 nm, respectively, which is due to the π–π^* transition of the conjugated molecule. The red-shifted band at about 20 nm of **JK-24** compared to **JK-25** is due to the increase of the π-conjugation system by thiophene. The result was also observed in the absorption band of **JK-26** and **JK-27**. The introduction of ethylene unit also induced the red-shifted band at about 15 nm (**JK-26** and **JK-29**). On the other hand, the absorption band of **JK-28** having a (4-(2,2-diphenylvinyl)phenyl moiety presented slightly blue-shift compared to that of **JK-24** having a fluorenyl moiety. The absorption band of **JK-26** and **JK-27** having the rhodanine-3-acetic acid as acceptor exhibited red-shift at about 50 nm compared to that of **JK-24** and **JK-25** having the cyanoacetic acid. From these results, we can interpret that the rhodanine-3-acetic acid extends the π-conjugation system of dye through the 4-oxo-2-thioxothiazolidine ring. The absorption spectra of all the dyes **JK-24**–**JK-29** on TiO_2 film are broadened due to the interaction of the anchoring group with the surface titanium ions. Similar broadening has been reported in several organic dyes on TiO_2 electrodes.[13] Absorption band of **JK-24**, **JK-25**, and **JK-28** on TiO_2 film is similar to that of the corresponding solution spectra. However, the **JK-27** and **JK-29** on TiO_2 film have blue-shifted band and **JK-26** on TiO_2 film has red-shifted band compared to those of the corresponding solution spectra. From these results, we can explain that the *N*-substituted carbazole unit of dyes can induce the non-planar structure by preventing aggregation via molecular stacking but the ability of prevention may be reduced in the larger conjugated dyes. We observed that the dyes **JK-24**–**JK-29** exhibited strong luminescence



Scheme 1. Synthesis of **JK-24**–**JK-27**.



Scheme 2. Synthesis of **JK-28** and **JK-29**.

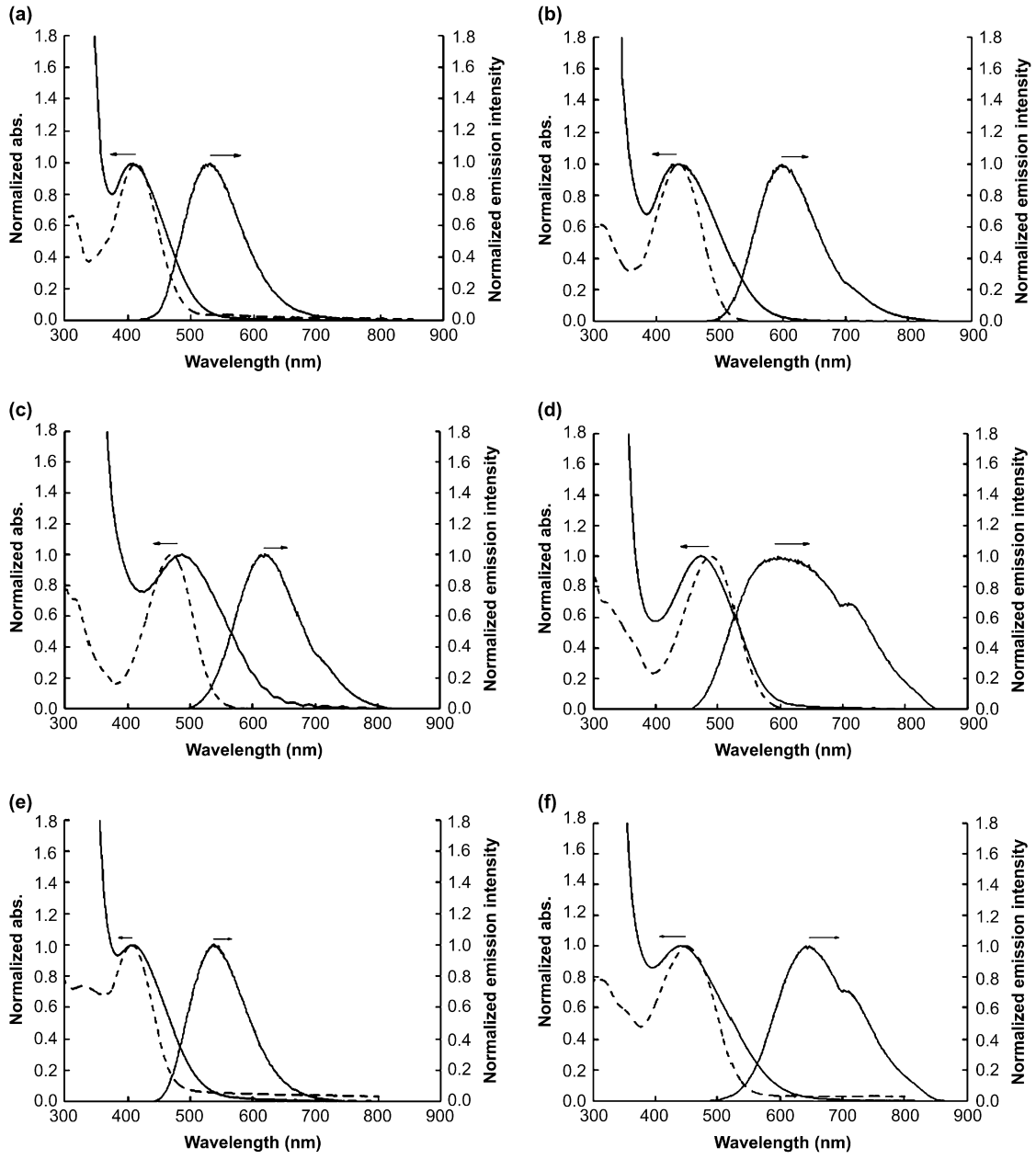


Figure 2. Absorption spectra in ethanol (dashed line) and on TiO_2 film (straight line), and emission spectra (straight line) of **JK-24** (a), **JK-25** (b), **JK-26** (c), **JK-27** (d), **JK-28** (e), and **JK-29** (f).

Table 1. Optical and electrochemical properties of **JK-24**–**JK-29**

Dye	λ_{abs}[a]/nm (ε/M^{-1} cm^{-1})	λ_{abs}[b]/nm	λ_{em}[c]/nm	E_{ox}[d] (ΔE_p)/V	E_{0-0}[e]/V	E_{LUMO}[f]/V	E_{LUMO}/V versus NHE
JK-24	411 (27,000)	408	528	0.89 (0.38)	2.65	−1.76	−1.13
JK-25	435 (30,060)	435	595	0.66 (0.58)	2.42	−1.76	−1.13
JK-26	469 (12,300)	486	619	0.91 (0.23)	2.33	−1.42	−0.79
JK-27	489 (6012)	472	600	1.01 (0.14)	2.35	−1.34	−0.71
JK-28	406 (21,500)	408	538	0.95 (0.34)	2.63	−1.68	−1.05
JK-29	451 (29,500)	440	643	0.91 (0.26)	2.44	−1.53	−0.90

[a] Absorption spectra were measured in ethanol.
[b] Absorption spectra were measured on TiO_2 film.
[c] Emission spectra were measured in ethanol.
[d] Redox potential of dyes on TiO_2 was 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 Ag/Ag^+).
[e] E_{0-0} was determined from intersection of absorption and emission spectra in ethanol.
[f] E_{LUMO} was calculated by $E_{ox}-E_{0-0}$.

maxima of 528–619 nm when they are excited within their π–π* bands in an air-equilibrated solution at 298 K.

Electrochemical properties of the dyes **JK-24**–**JK-29** were scrutinized by cyclovoltammetry in acetonitrile with 0.1 M tetrabutyl ammonium hexafluorophosphate using TiO_2 film with adsorbed dyes as working electrode. The results are listed in Table 1. All dyes adsorbed on TiO_2 film showed the quasi-reversible coupling between 0.66 and 1.01 V versus Ag/Ag^+ with separation within 0.58 V between anodic and cathodic peaks. The E_{LUMO} of dyes was calculated from the redox potential and the energy at the crossing section of absorption and emission spectra was observed in solution. We observed that the E_{ox} of **JK-25** is the highest than those of other dyes and the E_{LUMO} of **JK-27** is the lowest than those of other dyes. The excited state oxidation potential (E^*_{ox}) of the dyes (−0.71 to −1.13 V vs NHE) is much negative than the conduction band level of TiO_2 of approximately −0.5 V versus NHE.

In order to gain insight into the geometrical configuration and photophysical properties, molecular orbital calculations of the **JK-24**–**JK-29** sensitizers were performed with the TD-DFT on B3LYP/3-21G* (Fig. 3). The calculation illustrates that the HOMO is delocalized over the π-conjugated system via fluorenyl or 4-(2,2-diphenylvinyl)phenyl group through carbazole and the LUMO is delocalized over the cyanoacrylic unit through thiophene (**JK-24**, **JK-25**, **JK-28**, and **JK-29**). Examination of the HOMO and LUMO of these dyes indicates that HOMO–LUMO excitation moved the electron distribution from the carbazole unit to the cyanoacrylic acid moiety and the photo-induced electron transfer from the dyes to TiO_2 electrode can be efficiently occurred by the HOMO–LUMO transition. Interestingly, we could observe that the LUMO of dyes containing the rhodanine-3-acetic acid is delocalized over 4-oxo-2-thioxothiazolidine ring but the delocalization is broken between 4-oxo-2-thioxothiazolidine ring and acetic acid (**JK-26** and **JK-27**). From these results, we induce that the efficiencies of **JK-26** and **JK-27** may be affected by these discontinuous electron distributions to acetic acid.

Figure 4 shows action spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSCs based on **JK-24**–**JK-29** (electrolyte: 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.04 M I_2, 0.025 M LiI, 0.05 M guanidium thiocyanate, and 0.28 M *tert*-butylpyridine in acetonitrile). The IPCE for carbazole dye **JK-24** reached about 78% at 408 nm, and carbazole dye **JK-25** reached about 77% at 435 nm. These two dyes show a relatively large photocurrent due to large IPCEs. The IPCE spectrum of **JK-27** sensitizer is red shifted by about 60 nm compared to that of **JK-25** as a result of π-conjugation. However, the maximum IPCE value (8%) of **JK-27** is much lower than that of **JK-25**. A likely reason for this is that electron injection from the dye to TiO_2 would be suppressed due to a small energy gap between the LUMO level of the dye and the conduction band edge of TiO_2 decreased in particular by the addition of TBP. Photovoltaic performances of the **JK-24**–**JK-29** sensitized cells are summarized in Table 2. Under standard global AM 1.5 solar condition, the **JK-24** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 9.83 mA cm^{-2}, open circuit voltage (V_{oc}) of 0.74 V, and

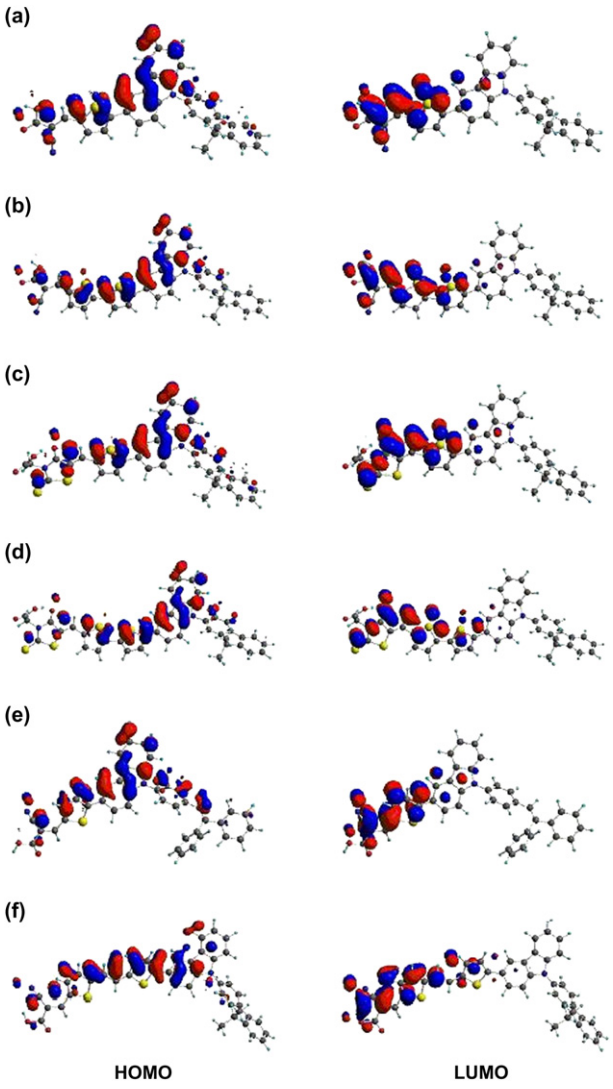


Figure 3. The frontier molecular orbitals of the HOMO and LUMO calculated with TD-DFT on B3LYP/3-21G* of **JK-24** (a), **JK-25** (b), **JK-26** (c), **JK-27** (d), **JK-28** (e), and **JK-29** (f).

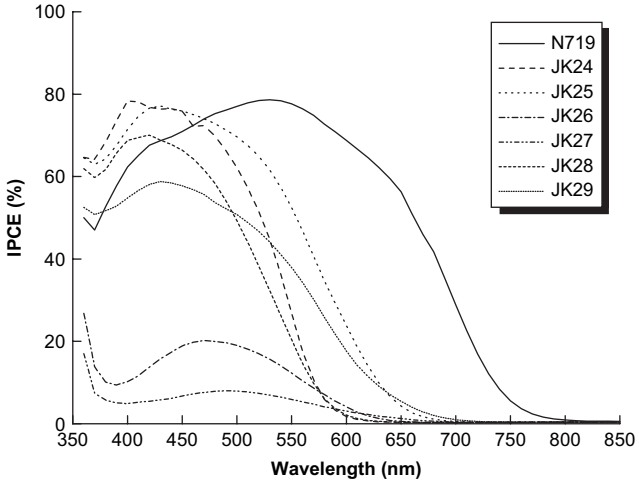


Figure 4. Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSC based on carbazole dyes: **N719** (straight line), **JK-24** (dashed line), **JK-25** (dotted line), **JK-26** (dash dotted line), **JK-27** (dash dot dotted line), **JK-28** (short dashed line), and **JK-29** (short dotted line).

Table 2. DSSC performance parameters of dyes[a]

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)	λ_{max} (nm) (IPCE (%))
N719	16.29	0.75	0.64	7.84	530 (79)
JK-24	9.83	0.74	0.70	5.02	400 (78)
JK-25	11.50	0.68	0.66	5.15	430 (77)
JK-26	3.76	0.62	0.77	1.79	470 (20)
JK-27	1.39	0.55	0.73	0.55	490 (8)
JK-28	7.85	0.69	0.71	3.87	420 (70)
JK-29	9.11	0.61	0.68	3.76	430 (59)

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

a fill factor of 0.70, corresponding to an overall conversion efficiency (η) of 5.02%. On the other hand, the **JK-27** sensitized cell gave a poor overall efficiency (η) of 0.55%. The lower efficiency of the **JK-27** sensitized cell compared to the **JK-24** and **JK-25** may be attributable to the difficulty in the photo-induced electron transfer from the LUMO of dye to the conduction band of TiO_2 because of a small energy gap (0.21 V) between the two energy levels.

In summary, we have designed and synthesized six novel organic dyes containing *N*-aryl carbazole bridged by thiophene units. We obtained a maximum solar energy to electricity conversion efficiency (η) of 5.15% under AM 1.5 irradiation with a DSSC based on **JK-25**. Our results suggest that the development of alternative highly efficient organic dyes comparable to ruthenium complexes can be possible through the more sophisticated structural modifications, and these works are now in progress.

3. Experimental section

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,[8a] 3-iodocarbazole,[14] 1-bromo-4-(2,2-diphenylvinyl)benzene,[15] and (2-thienylmethyl)triphenylphosphonium bromide[16] were synthesized using a modified procedure of previous references. ^{1}H 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 was measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ a scan rate between 50 mV s^{-1} (vs Fc/Fc$^+$).

3.3. Fabrication of DSSC

For the preparation of DSSC, a washed FTO (Pilkington, 8 Ω sq^{-1}) glass plate was immerged in 40 mM $TiCl_4$ aqueous solution as reported by the Grätzel group.[17] The first TiO_2 layer of 13 μm thickness was prepared by screen printing TiO_2 paste (Solaronix, 13 nm anatase), and the second scattering layer of 10 μm thickness (CCIC, HWP-400) was coated. The TiO_2 electrodes were immersed into the sample (**JK-24**–**JK-29**) solution (0.3 mM in ethanol containing 10 mM 3a,7a-dihydroxy-5b-cholic acid (Cheno)) and kept at room temperature for 18 h. 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-dimethyl imidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidium thiocyanate, and 0.28 M *tert*-butylpyridine in acetonitrile. For photovoltaic measurement of the DSSCs, the cell was measured using 1000 W xenon light source.

3.4. Characterization of DSSC

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

3.5. 3-(Thiophen-2-yl)carbazole (2)

A stirred mixture of **1** (1.0 g, 3.41 mmol), tributyl(thiophen-2-yl)stannane (1.27 g, 3.41 mmol), and $Pd(PPh_3)_4$ (0.197 g, 0.17 mmol) in dimethylformamide (30 mL) was stirred at 100 °C for 12 h. After cooling the solution, H_2O (50 mL) was added to the solution and extracted with dichloromethane (50×5). 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 (eluant MC/Hx=1:2, R_f=0.4) as a white solid in 82% yield. Mp: 197 °C. ^{1}H NMR (acetone-d_6): δ 10.45 (br, 1H), 8.43 (s, 1H), 8.20 (d, 1H, J=8.1 Hz), 7.72 (d, 1H, J=8.1 Hz), 7.55 (d, 1H, J=8.1 Hz), 7.53 (d, 1H, J=8.1 Hz), 7.44 (d, 1H, J=3.6 Hz), 7.41 (t, 1H, J=8.1 Hz), 7.38 (d, 1H, J=5.1 Hz), 7.21 (t, 1H, J=8.1 Hz), 7.12 (dd, 1H, J=3.6, 5.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$/acetone-d_6): δ 145.8, 140.4, 139.4, 127.8, 125.9, 125.8, 124.2, 123.6, 123.0, 121.9, 120.2, 119.6, 119.1, 117.5, 111.1, 110.9. MS: m/z 249 [M$^+$]. Anal. Calcd for $C_{16}H_{11}NS$: C, 77.07; H, 4.45. Found: C, 76.88; H, 4.28.

3.6. 3-(5-(Thiophen-2-yl)thiophen-2-yl)carbazole (3)

The product was synthesized according to the procedure as described above for the synthesis of **2**, giving a white solid of the product **3** in 78% yield. Mp: 201 °C. ^{1}H NMR (acetone-d_6): δ 10.47 (br, 1H), 8.46 (s, 1H), 8.23 (d, 1H, J=7.2 Hz), 7.74 (d, 1H, J=8.1 Hz), 7.59 (d, 1H, J=7.2 Hz), 7.54 (d, 1H, J=8.1 Hz), 7.43 (d, 1H, J=3.6 Hz), 7.42 (t, 1H, J=7.5 Hz), 7.41 (d, 1H, J=3.6 Hz), 7.32 (d, 1H, J=5.1 Hz), 7.27 (d, 1H, J=3.6 Hz), 7.22 (t, 1H, J=7.5 Hz), 7.10 (dd, 1H, J=5.1, 3.6 Hz). ^{13}C{^{1}H} NMR (acetone-d_6): δ 145.6, 141.6, 140.7, 138.3, 135.9, 128.9, 126.9, 126.1, 125.7, 125.3, 124.6, 124.2, 123.8, 123.7, 121.3, 120.9, 118.4, 118.0, 112.3, 112.0. MS: m/z 359 [M$^+$]. Anal. Calcd for $C_{20}H_{13}NS_2$: C, 72.47; H, 3.95. Found: C, 72.18; H, 3.85.

3.7. 9-(9,9-Dimethylfluoren-2-yl)-3-(thiophen-2-yl)-carbazole (4)

A stirred mixture of **2** (1.40 g, 5.61 mmol), 2-iodo-9,9-dimethylfluorene (1.97 g, 6.17 mmol), powdered anhydrous potassium carbonate (1.55 g, 11.22 mmol), copper bronze (0.36 g, 5.61 mmol), 18-crown-6 (0.22 g, 0.84 mmol), and 1,2-dichlorobenzene (50 mL) was refluxed for 48 h. After cooling, the insoluble inorganic material was filtered off under suction and the dark brown filtrate was collected. The insoluble material was washed with dichloromethane (3×30 mL). The combined filtrate and organic phase were washed with dilute aqueous ammonia and water, and dried over magnesium sulfate. The solvent was removed under reduced pressure. The pure product **4** was obtained by silica gel chromatography (eluant MC/Hx=1:3, R_f=0.4) to afford **4** (1.96 g) in 79% yield. Mp: 207 °C. ^{1}H NMR ($CDCl_3$): δ 8.39 (s, 1H), 8.21 (d, 1H, J=7.5 Hz), 7.94 (d, 1H, J=8.1 Hz), 7.82 (s, 1H, J=8.1 Hz), 7.71 (d, 1H, J=8.4 Hz), 7.64 (s, 1H), 7.55 (d, 1H, J=8.1 Hz), 7.50 (t, 1H, J=7.5 Hz), 7.48 (d, 1H, J=8.4 Hz), 7.46 (d, 1H, J=8.1 Hz), 7.42 (d, 1H, J=8.1 Hz), 7.41 (t, 1H, J=7.5 Hz), 7.39 (t, 1H, J=7.5 Hz), 7.38 (d, 1H, J=3.6 Hz), 7.33 (t, 1H, J=7.5 Hz), 7.28 (d, 1H, J=5.1 Hz), 7.13 (dd, 1H, J=5.1, 3.6 Hz), 1.58 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.6, 153.9, 145.7, 141.6, 140.7, 138.7, 138.5, 136.5, 131.2, 130.9, 130.0, 128.1, 127.8, 127.4, 126.9, 126.4, 126.9, 124.7, 123.9, 123.4, 122.9, 122.4, 121.5, 121.3, 120.6, 120.3, 117.9, 110.3, 47.3, 27.3. MS: m/z 441 [M$^+$]. Anal. Calcd for $C_{31}H_{23}NS$: C, 84.32; H, 5.25. Found: C, 84.04; H, 5.14.

3.8. 9-(9,9-Dimethylfluoren-2-yl)-3-(5-(thiophen-2-yl)-thiophen-2-yl)carbazole (5)

The product was synthesized according to the procedure as described above for the synthesis of **4**, giving a white solid of the product **5** in 76% yield. Mp: 211 °C. ^{1}H NMR ($CDCl_3$): δ 8.38 (s, 1H), 8.21 (d, 1H, J=7.5 Hz), 7.94 (d, 1H, J=8.1 Hz), 7.81 (d, 1H, J=8.1 Hz), 7.69 (d, 1H, J=8.7 Hz), 7.63 (s, 1H), 7.54 (d, 1H, J=8.1 Hz), 7.52 (t, 1H, J=7.5 Hz), 7.48 (d, 1H, J=8.4 Hz), 7.45 (d, 1H, J=8.7 Hz), 7.41 (t, 1H, J=7.5 Hz), 7.39 (t, 1H, J=7.5 Hz), 7.35 (d, 1H, J=8.4 Hz), 7.33 (t, 1H, J=7.5 Hz), 7.28 (d, 1H, J=3.9 Hz), 7.23 (d, 1H, J=3.9 Hz), 7.22 (d, 1H, J=5.1 Hz), 7.20 (d, 1H, J=3.6 Hz), 7.05 (dd, 1H, J=3.6, 5.1 Hz), 1.57 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.6, 153.9, 144.6, 141.7, 140.7, 138.8, 138.5, 137.9, 136.5, 135.8, 127.9, 127.8, 127.4, 126.5, 125.9, 124.8, 124.4, 124.2, 124.1, 124.0, 123.5, 123.4, 122.9, 122.8, 121.5, 121.3, 120.7, 120.4, 120.3, 117.6, 110.4, 110.2, 47.3, 27.3. MS: m/z 523 [M$^+$]. Anal. Calcd for $C_{35}H_{25}NS_2$: C, 80.27; H, 4.81. Found: C, 79.96; H, 4.73.

3.9. 5-(9-(9,9-Dimethylfluoren-2-yl)carbazol-6-yl)-thiophene-2-carbaldehyde (6)

Compound **4** (0.26 g, 0.59 mmol) dissolved in tetrahydrofuran (20 mL) was cooled to −78 °C under N_2. n-Butyl lithium (0.92 mL, 1.6 M solution in hexane, 1.47 mmol) was added dropwise over 10 min with vigorous stirring. It was brought to 0 °C for 1 h and kept at this temperature for additional 1 h. Again the solution was cooled to −78 °C and dry dimethylformamide (1 mL) was added at once. The solution was warmed to room temperature and stirred overnight. The reaction was quenched by the addition of dilute HCl (1 mL) in 20 mL water and extracted with diethyl ether (3×20 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The pure product **6** was obtained by silica gel chromatography (eluant MC/Hx=1:2, R_f=0.3) to afford **6** in 89% yield. Mp: 226 °C. ^{1}H NMR ($CDCl_3$): δ 9.95 (s, 1H), 8.74 (s, 1H), 8.38 (d, 1H, J=7.5 Hz), 8.14 (d, 1H, J=7.5 Hz), 7.99 (d, 1H, J=3.9 Hz), 7.96 (d, 1H, J=8.1 Hz), 7.90 (d, 1H, J=8.4 Hz), 7.86 (s, 1H), 7.74 (d, 1H, J=4.5 Hz), 7.64 (d, 1H, J=8.1 Hz), 7.63 (t, 1H, J=7.5 Hz), 7.55 (d, 1H, J=8.4 Hz), 7.49 (t, 1H, J=7.5 Hz), 7.43 (d, 1H, J=6.9 Hz), 7.42 (t, 1H, J=7.5 Hz), 7.38 (d, 1H, J=6.9 Hz), 7.35 (t, 1H, J=7.5 Hz), 1.61 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.7, 156.1, 155.7, 153.9, 141.8, 141.7, 141.6, 139.1, 138.4, 137.9, 136.1, 127.9, 127.4, 126.9, 125.9, 125.3, 124.8, 124.1, 123.2, 123.0, 122.9, 121.4, 121.3, 120.7, 120.6, 120.4, 118.6, 110.6, 110.4, 47.3, 27.2. MS: m/z 469 [M$^+$]. Anal. Calcd for $C_{32}H_{23}NOS$: C, 81.85; H, 4.94. Found: C, 81.58; H, 4.79.

3.10. 5-(5-(9-(9,9-Dimethylfluoren-2-yl)carbazol-6-yl)-thiophen-2-yl)thiophene-2-carbaldehyde (7)

The product was synthesized according to the procedure as described above for the synthesis of **6**, giving a yellow solid of the product **7** in 86% yield. Mp: 234 °C. ^{1}H NMR ($CDCl_3$): δ 9.84 (s, 1H), 8.37 (s, 1H), 8.21 (d, 1H, J=7.8 Hz), 7.92 (d, 1H, J=8.1 Hz), 7.81 (d, 1H, J=8.1 Hz), 7.66 (d, 1H, J=8.4 Hz), 7.63 (d, 1H, J=3.9 Hz), 7.62 (s, 1H), 7.51 (d, 1H, J=8.1 Hz), 7.50 (t, 1H, J=7.5 Hz), 7.47 (d, 1H, J=8.1 Hz), 7.46 (t, 1H, J=7.5 Hz), 7.42 (d, 1H, J=8.4 Hz), 7.41 (t, 1H, J=7.5 Hz), 7.36 (d, 1H, J=8.1 Hz), 7.34 (t, 1H, J=7.5 Hz), 7.34 (d, 1H, J=3.6 Hz), 7.29 (d, 1H, J=3.6 Hz), 7.23 (d, 1H, J=3.9 Hz), 1.58 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.5, 155.6, 153.9, 147.7, 141.7, 141.2, 141.0, 138.9, 138.4, 137.7, 136.2, 134.0, 127.8, 127.4, 127.3, 126.7, 125.8, 125.7, 124.3, 124.0, 123.9, 123.7, 123.3, 123.2, 122.9, 121.4, 121.3, 120.6, 120.5, 120.3, 117.8, 110.5, 110.3, 47.3, 27.2. MS: m/z 551 [M$^+$]. Anal. Calcd for $C_{36}H_{25}NOS_2$: C, 78.27; H, 4.57. Found: C, 78.01; H, 4.51.

3.11. 2-Cyano-3-(5-(9-(9,9-dimethylfluoren-2-yl)-carbazol-6-yl)thiophen-2-yl)acrylic acid (JK-24)

A mixture of **6** (0.3 g, 0.64 mmol) and cyanoacetic acid (0.082 g, 0.96 mmol) was vacuum-dried and added acetonitrile (20 mL) and piperidine (0.063 mL). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed in vacuo. The pure product **JK-24** was obtained by silica gel chromatography (eluant EA/MeOH=10:1, R_f=0.2) to afford **JK-24** (0.19 g) in 89% yield. Mp: 251 °C. ^{1}H NMR (DMSO-d_6): δ 8.77 (s, 1H), 8.49 (s, 1H), 8.43 (d, 1H, J=7.8 Hz), 8.13 (d, 1H, J=8.1 Hz), 8.04 (d, 1H, J=3.9 Hz), 7.96 (d, 1H, J=8.1 Hz), 7.90 (s, 1H), 7.89 (d, 1H, J=8.7 Hz), 7.84 (d, 1H, J=3.9 Hz), 7.62 (d, 1H, J=8.1 Hz), 7.61 (d, 1H, J=7.8 Hz), 7.52 (t, 1H, J=7.5 Hz), 7.51 (d, 1H, J=8.7 Hz), 7.47 (t, 1H, J=7.5 Hz), 7.41 (t, 1H, J=7.8 Hz), 7.40 (d, 1H, J=8.7 Hz), 7.36 (t, 1H, J=7.5 Hz), 1.54 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 163.8, 155.4, 154.5, 153.7, 146.5, 141.6, 141.0, 138.3,

137.7, 135.3, 134.1, 133.7, 127.8, 127.3, 127.1, 125.6, 125.1, 124.6, 124.1, 123.5, 122.9, 122.5, 121.6, 121.4, 121.2, 120.6, 120.5, 119.1, 118.6, 116.8, 110.8, 110.1, 46.9, 26.6. MS: *m/z* 536 [M^+]. Anal. Calcd for $C_{35}H_{24}N_2O_2S$: C, 78.33; H, 4.51. Found: C, 78.05; H, 4.44.

3.12. 2-Cyano-3-(5-(5-(9-(9,9-dimethylfluoren-2-yl)carbazol-6-yl)thiophen-2-yl)-thiophen-2-yl)acrylic acid (JK-25)

The product was synthesized according to the procedure as described above for the synthesis of **JK-24**, giving a red solid of the product **JK-25** in 86% yield. Mp: 258 °C. ^{1}H NMR (DMSO-d_6): δ 8.66 (s, 1H), 8.40 (d, 1H, J=8.1 Hz), 8.11 (d, 1H, J=7.8 Hz), 8.07 (s, 1H), 7.94 (d, 1H, J=8.1 Hz), 7.88 (s, 1H), 7.81 (d, 1H, J=7.8 Hz), 7.66 (d, 1H, J=3.9 Hz), 7.61 (m, 3H), 7.53 (d, 1H, J=3.9 Hz), 7.49–7.32 (m, 7H), 1.53 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 162.8, 155.4, 154.5, 153.7, 145.2, 141.2, 140.8, 140.0, 139.9, 138.1, 137.8, 136.5, 136.2, 135.7, 135.6, 133.7, 127.8, 127.3, 127.1, 126.9, 125.9, 125.5, 125.4, 124.2, 124.0, 123.4, 122.9, 122.7, 121.6, 121.3, 121.11, 120.5, 119.5, 117.6, 110.5, 110.0, 49.9, 26.7. MS: *m/z* 618 [M^+]. Anal. Calcd for $C_{39}H_{26}N_2O_2S_2$: C, 75.70; H, 4.24. Found: C, 75.42; H, 4.13.

3.13. 2-(5-((5-(9-(9,9-Dimethylfluoren-2-yl)carbazol-6-yl)thiophen-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (JK-26)

To a stirred **6** (0.3 g, 0.64 mmol) in CH_3COOH (30 mL) were added rhodanine-3-acetic acid (0.13 g, 0.67 mmol) and ammonium acetate (0.02 g, 0.26 mmol). Then the mixture was heated to 120 °C. The reaction was continued for 2 h at the temperature. Then the reaction mixture was allowed to cool to room temperature. The solid was collected by filtration and washed with water thoroughly. After drying in air, the crude product was purified by column chromatography on silica gel with CH_2Cl_2/methanol (10:1, v/v) as eluant to give a black solid **JK-26** in 74% yield. Mp: 261 °C. ^{1}H NMR (DMSO-d_6): δ 8.78 (s, 1H), 8.45 (d, 1H, J=7.5 Hz), 8.13 (d, 1H, J=8.1 Hz), 8.06 (s, 1H), 7.95 (d, 1H, J=8.1 Hz), 7.92 (d, 1H, J=7.5 Hz), 7.90 (s, 1H), 7.82 (m, 2H), 7.62 (d, 1H, J=8.1 Hz), 7.61 (d, 1H, J=8.4 Hz), 7.52–7.33 (m, 6H), 4.34 (s, 2H), 1.54 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 191.9, 175.2, 167.1, 166.6, 155.4, 153.7, 153.1, 140.9, 140.6, 138.2, 137.8, 137.6, 135.6, 135.4, 127.8, 127.3, 127.0, 125.5, 124.9, 124.6, 124.5, 123.5, 122.9, 122.6, 121.6, 121.3, 121.2, 120.6, 120.5, 119.1, 118.2, 110.6, 110.1, 46.9, 26.7, 23.5. MS: *m/z* 642 [M^+]. Anal. Calcd for $C_{41}H_{28}N_2O_3S_4$: C, 67.93; H, 3.89. Found: C, 68.90; H, 3.80.

3.14. 2-(5-((5-(5-(9-(9,9-Dimethylfluoren-2-yl)carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (JK-27)

The product was synthesized according to the procedure as described above for the synthesis of **JK-26**, giving a black solid of the product **JK-27** in 71% yield. Mp: 305 °C. ^{1}H NMR (DMSO-d_6): δ 8.64 (s, 1H), 8.38 (d, 1H, J=7.8 Hz), 8.09 (d, 1H, J=8.1 Hz), 8.02 (s, 1H), 7.94 (d, 1H, J=8.1 Hz), 7.87 (s, 1H), 7.79 (d, 1H, J=8.7 Hz), 7.73 (d, 1H, J=3.9 Hz), 7.53 (d, 1H, J=3.9 Hz), 7.63–7.30 (m, 10H), 4.37 (s, 2H), 1.52 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 191.6, 189.5, 179.1, 176.1, 171.5, 166.5, 160.0, 156.4, 155.4, 153.7, 145.8, 144.6, 143.7, 140.9, 140.1, 138.1, 137.8, 135.8, 135.5, 133.3, 125.5, 125.3, 124.2, 123.9, 123.4, 122.9, 122.6, 122.5, 121.6, 121.2, 120.5, 119.6, 115.1, 112.4, 110.5, 110.3, 105.1, 46.9, 26.6, 23.8. MS: *m/z* 724 [M^+]. Anal. Calcd for $C_{37}H_{26}N_2O_3S_3$: C, 69.13; H, 4.08. Found: C, 69.01; H, 4.02.

3.15. 9-(4-(2,2-Diphenylvinyl)phenyl)-3-(thiophen-2-yl)-carbazole (8)

The product was synthesized according to the procedure as described above for the synthesis of **4**, giving a white solid of the product **8** in 68% yield. Mp: 214 °C. ^{1}H NMR ($CDCl_3$): δ 8.45 (s, 1H), 8.24 (d, 1H, J=7.5 Hz), 7.74 (d, 1H, J=8.4 Hz), 7.54–7.32 (m, 20H), 7.19 (dd, 1H, J=5.1, 3.9 Hz), 7.15 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.9, 145.3, 143.9, 143.2, 142.5, 141.5, 141.0, 140.2, 137.2, 135.5, 131.2, 130.4, 130.1, 129.0, 128.5, 128.2, 127.8, 127.5, 127.0, 126.7, 126.4, 125.8, 125.4, 124.5, 123.7, 123.6, 123.2, 122.3, 120.6, 120.1, 119.6, 118.0, 111.4, 110.8. MS: *m/z* 503 [M^+]. Anal. Calcd for $C_{36}H_{25}NS$: C, 85.85; H, 5.00. Found: C, 85.64; H, 4.86.

3.16. 5-(9-(4-(2,2-Diphenylvinyl)phenyl)carbazol-6-yl)-thiophene-2-carbaldehyde (9)

The product was synthesized according to the procedure as described above for the synthesis of **6**, giving a yellow solid of the product **9** in 82% yield. Mp: 222 °C. ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1H), 8.41 (s, 1H), 8.15 (d, 1H, J=7.5 Hz), 7.75 (d, 1H, J=3.6 Hz), 7.69 (d, 1H, J=8.4 Hz), 7.44 (d, 1H, J=3.9 Hz), 7.42–7.27 (m, 17H), 7.25 (d, 1H, J=3.9 Hz), 7.08 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.7, 156.1, 143.9, 143.2, 141.6, 141.5, 141.4, 141.0, 140.2, 139.2, 137.9, 137.1, 136.7, 135.5, 131.1, 130.4, 129.0, 128.5, 128.0, 127.9, 127.8, 127.0, 126.8, 126.4, 125.9, 125.3, 124.7, 124.5, 124.1, 123.2, 120.8, 120.6, 118.5, 110.6, 110.4. MS: *m/z* 531 [M^+]. Anal. Calcd for $C_{37}H_{25}NOS$: C, 83.59; H, 4.74. Found: C, 83.36; H, 4.66.

3.17. 2-Cyano-3-(5-(9-(4-(2,2-diphenylvinyl)phenyl)carbazol-6-yl)thiophen-2-yl)-acrylic acid (JK-28)

The product was synthesized according to the procedure as described above for the synthesis of **JK-24**, giving a red solid of the product **JK-28** in 78% yield. Mp: 255 °C. ^{1}H NMR (DMSO-d_6): δ 8.62 (s, 1H), 8.34 (d, 1H, J=7.5 Hz), 8.13 (s, 1H), 7.75 (d, 1H, J=7.5 Hz), 7.73 (d, 1H, J=3.9 Hz), 7.66 (d, 1H, J=3.9 Hz), 7.51–7.24 (m, 19H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 163.9, 152.5, 150.3, 149.8, 145.9, 143.7, 142.6, 142.4, 140.8, 140.6, 140.1, 139.8, 136.6, 136.4, 135.8, 135.3, 134.9, 130.9, 129.7, 129.2, 128.5, 127.9, 127.8, 127.2, 126.9, 126.8, 126.1, 125.4, 124.6, 123.5, 122.6, 121.1, 120.6, 119.3, 118.0, 110.5, 109.9, 108.3. MS: *m/z* 598 [M^+]. Anal. Calcd for $C_{40}H_{26}N_2O_2S$: C, 80.24; H, 4.38. Found: C, 79.94; H, 4.27.

3.18. 9-(9,9-Dimethylfluoren-2-yl)-3-(5-(2-(thiophen-2-yl)vinyl)thiophen-2-yl)carbazole (10)

To a suspension of (2-thienylmethyl)triphenylphosphonium bromide (0.65 g, 1.48 mmol) in THF (20 mL) at room

temperature under N_2 atmosphere was added ^{t}BuOK (0.17 g, 1.49 mmol). After cooling to 0 °C, a solution of **6** (0.7 g, 1.48 mmol) with THF was added dropwise. The mixture was stirred at 0 °C for 1 h and at room temperature for another 8 h. After being diluted with CH_2Cl_2, the mixture was washed twice with water, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel with CH_2Cl_2/hexane (1:3, v/v) as eluant to give a white solid of the product **10** in 73% yield. Mp: 238 °C. ^{1}H NMR ($CDCl_3$): δ 8.44 (s, 1H), 8.26 (d, 1H, J=7.8 Hz), 7.95 (d, 1H, J=8.4 Hz), 7.84 (d, 1H, J=7.2 Hz), 7.73 (d, 1H, J=8.7 Hz), 7.68 (s, 1H), 7.57–7.33 (m, 9H), 7.29 (d, 1H, J=3.9 Hz), 7.23 (d, 1H, J=15.9 Hz), 7.22 (d, 1H, J=5.1 Hz), 7.13 (d, 1H, J=3.9 Hz), 7.11 (d, 1H, J=15.9 Hz), 7.05 (dd, 1H, J=3.9, 5.1 Hz), 1.62 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.7, 154.0, 144.5, 142.9, 141.7, 141.0, 140.8, 138.9, 138.6, 136.5, 128.3, 127.9, 127.5, 127.0, 126.8, 126.6, 126.3, 126.1, 125.9, 124.5, 124.4, 124.1, 123.5, 122.9, 122.5, 122.0, 121.5, 121.4, 121.0, 120.8, 120.5, 117.7, 110.5, 110.3, 47.4, 27.4. MS: m/z 549 [M$^+$]. Anal. Calcd for $C_{37}H_{27}NS_2$: C, 80.84; H, 4.95. Found: C, 80.59; H, 4.85.

3.19. 5-(2-(5-(9-(9,9-Dimethylfluoren-2-yl)carbazol-6-yl)thiophen-2-yl)vinyl)thiophene-2-carbaldehyde (11)

The product was synthesized according to the procedure as described above for the synthesis of **6**, giving a yellow solid of the product **11** in 73% yield. Mp: 247 °C. ^{1}H NMR ($CDCl_3$): δ 9.82 (s, 1H), 8.38 (s, 1H), 8.20 (d, 1H, J=7.5 Hz), 7.92 (d, 1H, J=8.1 Hz), 7.81 (d, 1H, J=7.8 Hz), 7.67 (d, 1H, J=8.7 Hz), 7.63 (s, 1H), 7.60 (d, 1H, J=3.9 Hz), 7.53–7.33 (m, 8H), 7.28 (d, 1H, J=3.9 Hz), 7.23 (d, 1H, J=15.9 Hz), 7.11 (d, 1H, J=3.9 Hz), 7.07 (d, 1H, J=3.3 Hz), 6.99 (d, 1H, J=15.9 Hz), 1.58 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.4, 155.7, 154.0, 152.4, 146.7, 141.7, 141.3, 141.0, 139.7, 138.9, 138.4, 137.4, 136.3, 129.9, 127.8, 127.4, 126.6, 126.2, 125.9, 124.4, 124.0, 123.3, 123.2, 123.0, 122.9, 121.4, 121.3, 120.7, 120.6, 120.5, 120.3, 119.4, 117.8, 110.5, 110.3, 47.3, 27.2. MS: m/z 577 [M$^+$]. Anal. Calcd for $C_{38}H_{27}NOS_2$: C, 79.00; H, 4.71. Found: C, 78.78; H, 4.57.

3.20. 2-Cyano-3-(5-(2-(5-(9-(9,9-dimethylfluoren-2-yl)-carbazol-6-yl)thiophen-2-yl)vinyl)thiophen-2-yl)acrylic acid (JK-29)

The product was synthesized according to the procedure as described above for the synthesis of **JK-24**, giving a red solid of the product **JK-29** in 85% yield. Mp: 284 °C. ^{1}H NMR (DMSO-d_6): δ 8.61 (s, 1H), 8.36 (d, 1H, J=7.8 Hz), 8.12 (d, 1H, J=8.1 Hz), 8.07 (s, 1H), 7.95 (d, 1H, J=7.8 Hz), 7.88 (s, 1H), 7.77 (t, 1H, J=8.4 Hz), 7.68 (d, 1H, J=7.5 Hz), 7.63–7.31 (m, 12H), 7.19 (d, 1H, J=15.9 Hz), 1.54 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 163.3, 162.6, 161.4, 159.4, 155.3, 153.7, 149.7, 146.9, 144.6, 141.2, 140.8, 140.0, 139.8, 138.1, 137.7, 135.7, 135.6, 132.2, 129.9, 127.7, 127.2, 126.8, 125.8, 125.5, 124.2, 123.9, 123.6, 123.3, 122.8, 122.6, 121.5, 121.2, 120.9, 120.4, 119.2, 117.3, 110.5, 109.9, 46.8, 26.6. MS: m/z 644 [M$^+$]. Anal. Calcd for $C_{41}H_{28}N_2O_2S_2$: C, 76.37; H, 4.38. Found: C, 76.14; H, 4.21.

Acknowledgements

We are grateful to the KOSEF through National Research Laboratory (NRL 2005) program and BK21 (2006).

References and notes

1. (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737; Grätzel, M. *Nature* **2001**, *414*, 338; (b) Yanagida, M.; Yamaguchi, T.; Kurashige, M.; Hara, K.; Katoh, R.; Sugihara, H.; Arakawa, H. *Inorg. Chem.* **2003**, *42*, 7921; (c) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 808.
2. (a) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835; (b) Nazeeriddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613.
3. (a) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597; (b) Hara, K.; Kurashige, M.; Danoh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *New J. Chem.* **2003**, *27*, 783; (c) Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. *Chem. Commun.* **2001**, 569.
4. (a) Horiuchi, T.; Miura, H.; Uchida, S. *Chem. Commun.* **2003**, 3036; (b) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, *126*, 12218; (c) Schmidt-Mende, L.; Bach, U.; Humphry-Baker, R.; Horiuchi, T.; Miura, H.; Ito, S.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2005**, *17*, 813; (d) Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Péchy, P.; Takada, M.; Miura, H.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2006**, *18*, 1202.
5. (a) Hara, K.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *Chem. Commun.* **2003**, 252; (b) Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806; (c) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Yoshihara, T.; Murai, M.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Arakawa, H. *Adv. Funct. Mater.* **2005**, *15*, 246.
6. (a) Sayama, K.; Tsukagoshi, S.; Hara, K.; Ohga, Y.; Shinpou, A.; Abe, Y.; Suga, S.; Arakawa, H. *J. Phys. Chem. B* **2002**, *106*, 1363; (b) Sayama, K.; Hara, K.; Mori, N.; Satsuki, M.; Suga, S.; Tsukagoshi, S.; Abe, Y.; Sugihara, H.; Arakawa, H. *Chem. Commun.* **2000**, 1173.
7. (a) Yao, Q.-H.; Shan, L.; Li, F.-Y.; Yin, D.-D.; Huang, C.-H. *New J. Chem.* **2003**, *27*, 1277; (b) Wang, J.-S.; Li, F.-Y.; Huang, C. H. *Chem. Commun.* **2000**, 2063.
8. (a) Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto, K.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11021; (b) Kim, S.; Song, K.-H.; Kang, S. O.; Ko, J. *Chem. Commun.* **2004**, 68.
9. (a) Li, M.; Tang, S.; Shen, F.; Liu, M.; Xie, W.; Xia, H.; Liu, L.; Tian, L.; Xie, Z.; Lu, P.; Hanif, M.; Lu, D.; Cheng, G.; Ma, Y. *Chem. Commun.* **2006**, 3393; (b) Ohkita, H.; Benten, H.; Anada, A.; Noguchi, H.; Kido, N.; Ito, S.; Yamamoto, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3977; (c) Ikeda, N.; Miyasaka, T. *Chem. Commun.* **2005**, 1886.
10. Raposo, M. M. M.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2004**, *60*, 4071.

11. Bushby, R. J.; Mcgill, D. R.; Ng, K. M.; Taylor, N. *J. Mater. Chem.* **1997**, *7*, 2343.
12. Zhang, C.; Harper, A. W.; Dalton, L. R. *Synth. Commun.* **2001**, *31*, 1361.
13. (a) Nüesch, F.; Moser, J. E.; Shklover, V.; Grätzel, M. *J. Am. Chem. Soc.* **1996**, *118*, 5420; (b) Li, S.-L.; Jiang, K.-J.; Shao, K.-F.; Yang, L.-M. *Chem. Commun.* **2006**, 2792.
14. Suzuki, H. *Org. Synth.* **1988**, *6*, 700.
15. Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695.
16. Chou, S.-S. P.; Yeh, Y.-H. *Tetrahedron Lett.* **2001**, *42*, 1309.
17. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.