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Novel organic dyes containing bis-dimethylfluorenyl amino benzo[*b*]thiophene for highly efficient dye-sensitized solar cell

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Abstract—Novel organic dyes, **JK-16** and **JK-17** containing bis-dimethylfluorenyl amino benzo[*b*]thiophene are designed and synthesized. Under standard global AM 1.5 solar condition, the **JK-16** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 15.33 mA cm^{-2}, open circuit voltage (V_{oc}) of 0.74 V, and a fill factor of 0.66, corresponding to an overall conversion efficiency η of 7.43%, and the **JK-17** sensitized cell gave a J_{sc} of 12.66 mA cm^{-2}, V_{oc} of 0.67 V, and a fill factor of 0.65, corresponding to an overall conversion efficiency η of 5.49%.

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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 11% 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 5–9%. 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. And less stability of organic dyes is due to the formation of unstable radical species during redox reaction cycles. Very recently, we have interested in the structural modification for donor unit of push–pull organic dyes. And we have designed and synthesized the novel organic dyes containing dimethylfluorenyl unit to overcome the low conversion efficiency and low operational stability. We reported the highly efficient and stable organic dyes having bis-dimethylfluorenyl amino phenyl unit.[8] 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.[9]

In this paper, we report two new organic dyes containing [bis(9,9-dimethylfluoren-2-yl)amino]benzo[*b*]thiophene as electron donor and cyano acrylic acid as electron acceptor bridged by a thiophene or vinylene thiophene unit (Fig. 1). Although many structure frameworks such as coumarin, aniline, and indoline have been employed as good electron donor unit, the organic dye containing benzo[*b*]thiophene structural motif has never been explored for DSSCs.

2. Results and discussion

The dyes were prepared by the stepwise synthetic protocol. N-Phenylation of 6-amino benzo[*b*]thiophene was performed under Ullman's condition,[10] followed by *n*-butyllithium and Br_2 bromination to give 6-(bis(9,9-dimethylfluoren-2-yl)amino)-2-bromobenzo[*b*]thiophene **2**. 6-(Bis(9,9-dimethylfluoren-2-yl)amino)benzo[*b*]thiophene **1** was converted into 6-(bis(9,9-dimethylfluoren-2-yl)amino)-2-formylbenzo[*b*]thiophene **3** by lithiation with *n*-butyllithium and subsequent quenching with dimethylformamide. Stille cross coupling reaction with $Pd(PPh_3)_4$ led to 2-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl)aminobenzo[*b*]thiophene **4**.[11] Coupling reaction of aldehyde **3** with phosphonate under Horner–Emmons–Witting coupling[12] condition using potassium

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Keywords: Benzo[*b*]thiophene; Organic dye; Dimethylfluorenyl amino unit; Solar cell.

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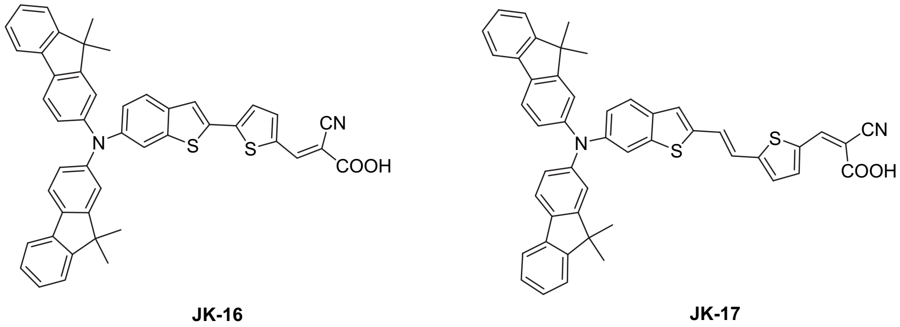
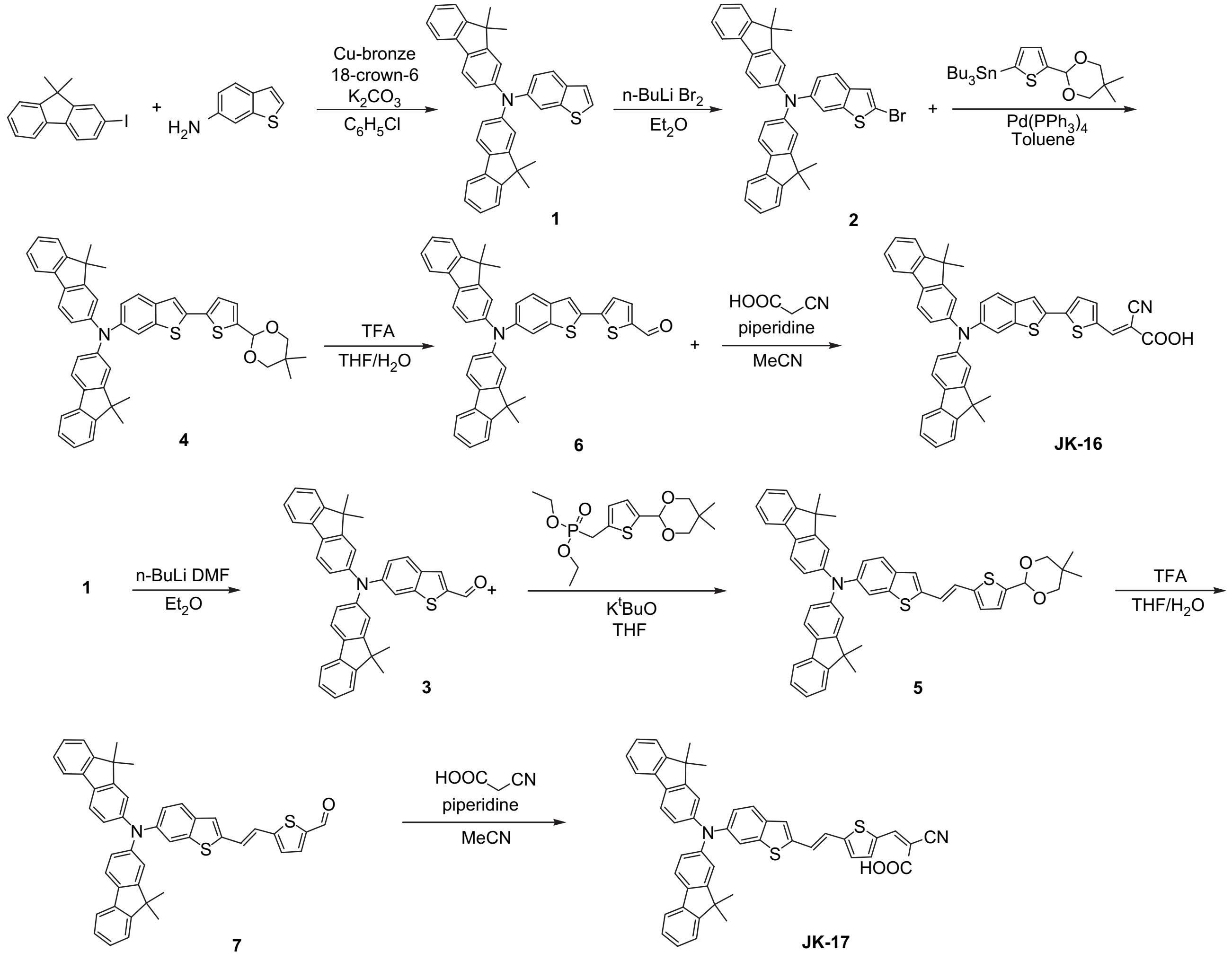


Figure 1. Structures of **JK-16** and **JK-17**.

tert-butoxide in THF led to (*E*)-2-(2-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)vinyl)-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl))amino benzo[*b*]thiophene **5**. Subsequent cleavage of 1,3-dioxalane protecting group in aqueous acid produced the aldehyde 2-(5-formylthiophen-2-yl)-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl)amino benzo[*b*]thiophene **6** and (*E*)-2-(2-formylthiophen-2-yl)vinyl)-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl))amino benzo[*b*]thiophene **7**. The aldehyde, on reaction with cyanoacetic acid in the presence of a catalytic amount of piperidine in acetonitrile, produced the **JK-16** and **JK-17** dyes (Scheme 1).

For the preparation of DSSC, the washed FTO (Pilkington, 8 Ω sq^{-1}, 2.3 mm thickness) glass plate was immersed in 40 mM $TiCl_4$ aqueous solution at 60 °C for 30 min and washed with water and ethanol as reported by Grätzel's group.[13] A transparent nanocrystalline layer on the FTO glass plate was prepared by screen printing TiO_2 paste (Solaronix, 13 nm anatase) and was sintered at 450 °C for 30 min. And then, a paste for the scattering layer (CCIC, HWP-400) was coated on transparent layer and was again sintered at 450 °C for 30 min. The resulting layer composed of 13 μm-thick transparent layer and 10 μm-thick scattering



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-16** and **JK-17**.

layer. The TiO_2 electrode was treated again with $NbCl_5$ followed by oxidation at 500 °C for 30 min. The TiO_2 electrodes were immersed into the **JK-16** and **JK-17** solution (0.3 mM dye in ethanol containing 10 mM 3a,7a-dihydroxy-5b-cholic acid (Cheno)) and kept at room temperature for 18 h. The chenodeoxycholic acid was added to the dye solution to prevent aggregation of dyes on the TiO_2 electrode.[14] 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 and heated 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 Surlyn film (25 μm thickness, Du-Pont) as a spacer between the electrodes. 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 acetonitirle. The photovoltaic measurements were recorded under the simulated AM 1.5 irradiation (1000 W xenon light).

The UV–vis and fluorescence spectra of dyes in ethanol are shown in Figure 2 and listed in Table 1, together with the UV–vis spectrum of the corresponding dye absorbed on TiO_2 film. The absorption spectra of the **JK-16** and **JK-17** display visible band at 456 nm and 476 nm, respectively. The red-shifted band of **JK-17** compared to **JK-16** is due to increasing the π-conjugation system. On the other hand, the absorption spectra of **JK-16** and **JK-17** on TiO_2 film are broadened. Similar broadening has been reported in several organic dyes on TiO_2 electrodes.[15] Absorption band of **JK-16** on TiO_2 film is similar to that of the corresponding solution spectra but **JK-17** on TiO_2 film has a slightly blue-shifted band compared to that of the corresponding solution spectra. From these results, we can know that the amorphous non-planar dimethylfluorenyl unit of dyes can prevent aggregation vis molecular stacking but the ability of prevention may be reduced in the larger conjugated dyes.

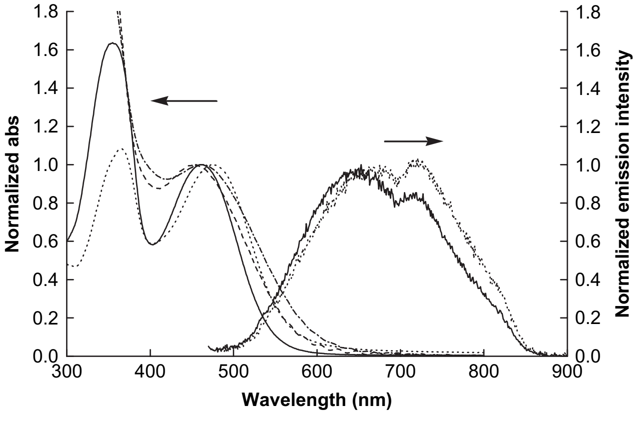


Figure 2. Absorption and emission spectra of **JK-16** (solid line) and **JK-17** (dotted line) in ethanol and absorption spectra of **JK-16** (dashed line) and **JK-17** (dot-dashed line) absorbed on TiO_2 film.

The highest-occupied molecular orbitals (HOMOs) and lowest-unoccupied molecular orbitals (LUMOs) of **JK-16** and **JK-17** were performed with the B3LYP/3-21G* (Fig. 3). The calculation illustrates that the HOMO is delocalized over the π-conjugated system via the dimethylfluorenyl amino group through benzo[*b*]thiophene and the LUMO is delocalized over the cyano acrylic unit through thiophene. From these results, we could induce that the photoinduced electron transfer from **JK-16** and **JK-17** dyes to TiO_2 electrode can efficiently occurr by the HOMO–LUMO transition as shown in Figure 3. Electrochemical properties of the **JK-16** and **JK-17** were scrutinized by cyclovoltametry in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate using TiO_2 film with adsorbed dyes as working electrode. The results are listed in Table 1. **JK-16** and **JK-17** adsorbed on TiO_2 film show a quasi-reversible couple at 1.48 V and 1.45 V versus NHE with a separation of 0.22 V and 0.19 V between anodic and cathodic peaks. The E_{LUMO} of **JK-16** and **JK-17** calculated from the redox potential and the energy at the intersection point of absorption and emission spectra observed in solution are −0.85 V and −0.80 V. These values are more negative than that of the nanocrystalline TiO_2 electrode (−0.5 V vs NHE), allowing the electron injection from the LUMO of dye to the conduction band of TiO_2.

The photovoltaic performances of the **JK-16** and **JK-17** sensitized cell are summarized in Table 1. Under standard global AM 1.5 solar condition, the **JK-16** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 15.33 mA cm^{-2}, open circuit voltage (V_{oc}) of 0.74 V, and a fill factor of 0.66, corresponding to an overall conversion efficiency η, derived from the equation: $\eta = J_{sc} \cdot V_{oc} \cdot \mathrm{FF}/\text{light intensity}$, of 7.43%. However, the **JK-17** sensitized cell gave a J_{sc} of 12.66 mA cm^{-2}, V_{oc} of 0.67 V, and a fill factor of 0.65, corresponding to an overall conversion efficiency η of 5.49%. We can explain that the low efficiency of **JK-17** compared to **JK-16** dye probably stems from the difference in the oxidation potentials of the dyes. The oxidation potential of **JK-16** is slightly higher than that of **JK-17**. This will

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

Dye	λ_{abs}[a]/nm (ε/M^{-1} cm^{-1})	E_{redox} [b](ΔE_p)/V	$E_{0\text{–}0}$[c]/V	E_{LUMO}[d]/V	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η[e] (%)
JK-16	456 (16,000)	1.48 (0.22)	2.33	−0.85	15.33	0.74	0.66	7.43
JK-17	476 (30,000)	1.45 (0.19)	2.25	−0.80	12.66	0.67	0.65	5.49
N719	535 (14,700)	0.95 (0.22)	1.60	−0.65	18.44	0.75	0.67	9.16

[a] Absorption spectra were measured in ethanol solution.

[b] Oxidation potentials 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] $E_{0\text{–}0}$ was determined from intersection of absorption and emission spectra in ethanol.

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

[e] Performances of DSSCs were measured with 0.18 cm^2 working area. ε: Absorption coefficient; E_{ox}: oxidation potential; $E_{0\text{–}0}$: voltage of intersection point between absorption and emission spectra; J_{sc}: short circuit photocurrent density; V_{oc}: open circuit photovoltage; FF: fill factor; η: total power conversion efficiency.

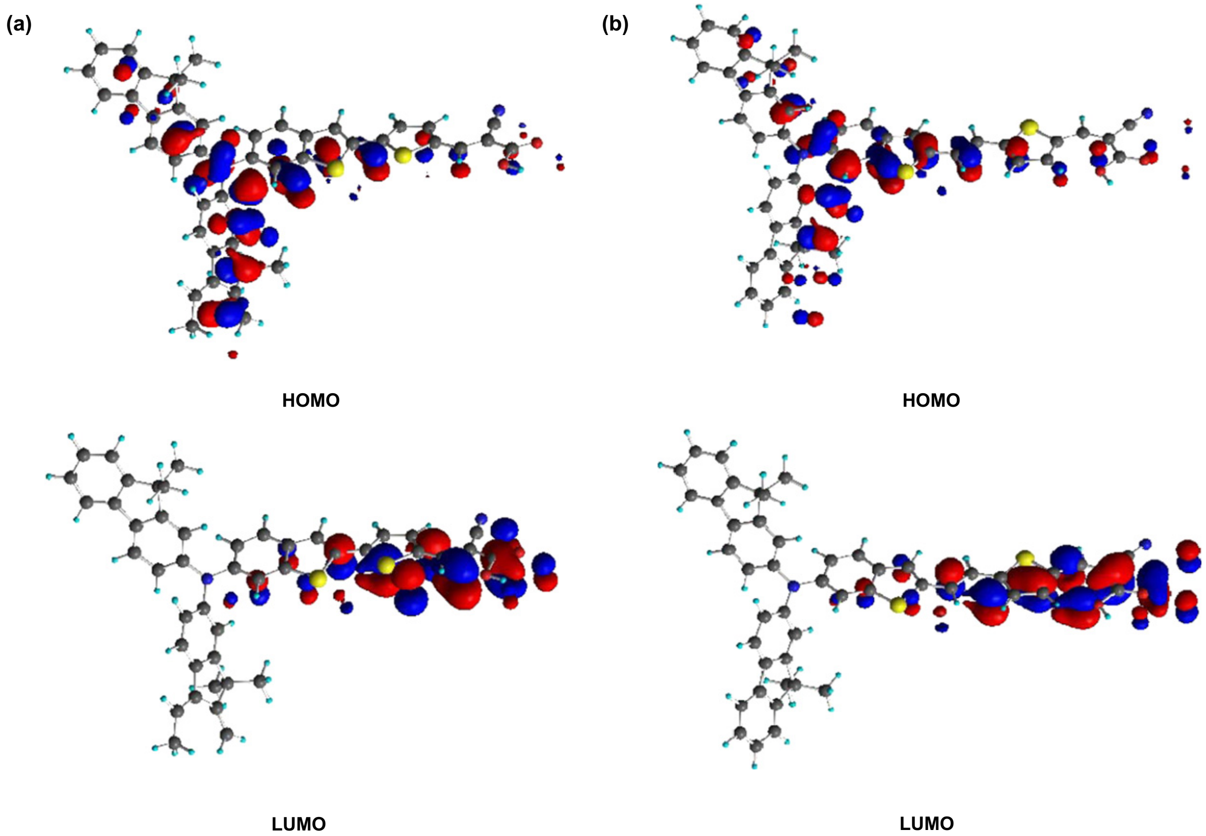


Figure 3. The molecular structures and the frontier molecular orbitals of the HOMO and LUMO calculated with B3LYP/3-21G* of **JK-16** (a) and **JK-17** (b).

increase the driving force for the reduction of the oxidized dye.[16] The incident monochromatic photon-to-current conversion efficiency (IPCE) of the **JK-16** and **JK-17** sensitized cells is shown in Figure 4. The onsets of the IPCE spectra of the **JK-16** and **JK-17** sensitized cells are 740 and 750 nm, and the maximum IPCE values of both **JK-16** and **JK-17** sensitized cells were observed at 470 and 480 nm and exhibited 76 and 64%.

In conclusion, this work has demonstrated that the organic dyes containing bis-dimethylfluorenyl amino benzo[*b*]thiophene moiety are very efficient dyes for dye-sensitized solar cells. We believe that the development of alternative highly efficient organic dyes to ruthenium complexes can be possible through the more sophisticated structural modifications, and these works are now in progress.

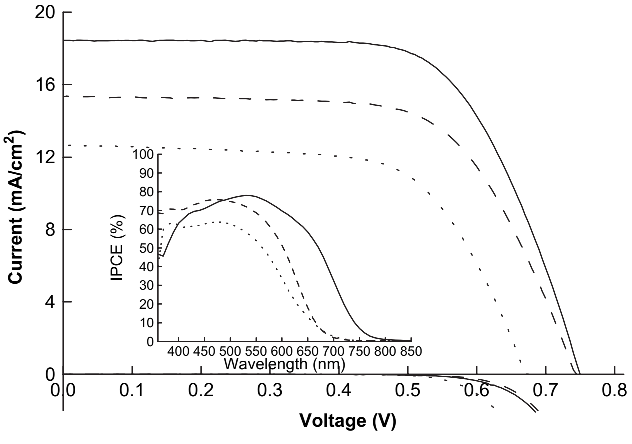


Figure 4. *J–V* curve and IPCE spectra of **N719** (solid line), **JK-16** (dashed line) and **JK-17** (dotted line).

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. 6-Amino benzo[*b*]thiophene[17] and 2-iodo-9,9-dimethylfluorene[9a] 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.

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

3.1.2. 6-(Bis(9,9-dimethylfluoren-2-yl)amino)benzo[*b*]thiophene (1). A stirred mixture of 6-amino benzo[*b*]thiophene (1.37 g, 9.23 mmol), 2-iodo-9,9-dimethylfluorene (6.5 g, 20.3 mmol), powdered anhydrous potassium carbonate (5.62 g, 40.6 mmol), copper bronze (1.93 g, 30.5 mmol), and 18-crown-6 (0.29 g, 1.11 mmol) in 1,2-dichlorobenzene (70 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 (3×50 ml). The combined filtrate and organic phase was washed with dilute aqueous ammonia and water and dried with magnesium sulfate. The solvent was removed under reduced pressure. The pure product **1** was obtained by silica gel chromatography (eluent MC/Hx=1:5, R_f=0.4) to afford **1** (3.69 g) in 75% yield. Mp: 179 °C. ^{1}H NMR (CDCl$_3$): δ 7.72 (d, *J*=9.0 Hz, 1H), 7.66 (t, *J*=7.2 Hz, 2H), 7.62 (d, *J*=8.1 Hz, 2H), 7.57 (s, 1H), 7.39 (d, *J*=7.2 Hz, 2H), 7.36 (d, *J*=9.0 Hz, 1H), 7.34–7.31 (m, 3H), 7.29–7.27 (m, 3H), 7.25 (s, 2H), 7.08 (d, *J*=8.1 Hz, 2H), 1.41 (s, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.2, 153.7, 147.8, 145.2, 141.1, 139.1, 135.6, 134.1, 132.0, 127.1, 126.6, 125.2, 124.1, 123.7, 123.3, 122.6, 120.7, 119.5, 118.4, 118.0, 47.0, 27.2. MS: *m/z* 533 [M$^+$]. Anal. Calcd for $C_{38}H_{31}NS$: C, 85.51; H, 5.85; N, 2.62. Found: C, 85.24; H, 5.84; N, 2.61.

3.1.3. 6-(Bis(9,9-dimethylfluoren-2-yl)amino)-2-bromobenzo[*b*]thiophene (2). *n*-BuLi (0.64 ml, 1.6 M solution in hexane) was added into **1** (0.5 g, 0.93 mmol) solution in dry Et$_2$O (50 ml), under argon. After 3 h bromine (0.16 g, 1.03 mmol) was added dropwise at 0 °C under argon. The solution was washed with 5% KOH and dried with MgSO$_4$. The solvent was evaporated. The pure product **2** was obtained by silica gel chromatography (eluent MC/Hx=1:5, R_f=0.6) to afford **2** in 69% yield. Mp: 191 °C. ^{1}H NMR (CDCl$_3$): δ 7.64 (d, *J*=9.0 Hz, 1H), 7.59 (d, *J*=8.1 Hz, 2H), 7.58 (t, *J*=8.1 Hz, 2H), 7.50 (s, 1H), 7.39 (d, *J*=8.1 Hz, 2H), 7.36 (d, *J*=9.0 Hz, 1H), 7.32–7.28 (m, 4H), 7.22 (s, 2H), 7.19 (s, 1H), 7.08 (d, *J*=8.1 Hz, 2H), 1.41 (s, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.3, 153.7, 147.5, 145.4, 142.2, 139.0, 135.2, 134.4, 133.8, 127.1, 126.7, 126.5, 126.3, 123.2, 122.7, 120.8, 119.5, 118.6, 116.7, 113.5, 47.0, 27.2. MS: *m/z* 613 [M$^+$]. Anal. Calcd for $C_{38}H_{30}BrNS$: C, 74.50; H, 4.94; N, 2.29. Found: C, 74.27; H, 4.93; N, 2.28.

3.1.4. 6-(Bis(9,9-dimethylfluoren-2-yl)amino)-2-formylbenzo[*b*]thiophene (3). *n*-BuLi (0.64 ml, 1.6 M solution in hexane) was added into **1** (0.5 g, 0.93 mmol) solution in dry Et$_2$O (50 ml), under argon. After 3 h DMF (0.075 g, 1.03 mmol) was added at 0 °C under argon. The reaction was continued for 2 h and washed with 5% KOH. The solution was dried with MgSO$_4$, and the solvent was evaporated. The pure product **3** was obtained by silica gel chromatography (eluent MC/Hx=1:1, R_f=0.3) to afford **3** in 75% yield. Mp: 187 °C. ^{1}H NMR (CDCl$_3$): δ 10.02 (s, 1H), 7.92 (s, 1H), 7.76 (d, *J*=9.0 Hz, 1H), 7.66 (t, *J*=7.2 Hz, 2H), 7.65 (d, *J*=8.1 Hz, 2H), 7.55 (s, 1H), 7.40 (d, *J*=7.2 Hz, 2H), 7.37 (d, *J*=9.0 Hz, 1H), 7.31 (t, *J*=8.1 Hz, 2H), 7.29 (d, *J*=8.0 Hz, 2H), 7.24 (s, 2H), 7.16 (d, *J*=8.0 Hz, 2H), 1.41 (s, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 184.1, 155.5, 153.7, 148.9, 146.6, 144.9, 141.5, 138.8, 135.5, 133.4, 127.2, 127.0, 126.7, 125.4, 124.1, 122.7, 121.9, 120.9, 119.7, 119.6, 115.1, 47.0, 27.1. MS: *m/z* 561 [M$^+$]. Anal. Calcd for $C_{39}H_{31}NOS$: C, 83.39; H, 5.56; N, 2.49. Found: C, 83.13; H, 5.55; N, 2.48.

3.1.5. 2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl)amino benzo[*b*]thiophene (4). A stirred mixture of **2** (0.4 g, 0.65 mmol), tributyl(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)stannane (0.47 g, 0.97 mmol), and Pd(PPh$_3$)$_4$ (0.075 g, 0.065 mmol) in toluene (50 ml) was refluxed for 12 h. After cooling the solution, H$_2$O (10 ml) and brine were added to the solution. The organic layer was separated and dried in MgSO$_4$. The solvent was removed in vacuo. The pure product **4** was obtained by chromatographic work-up (eluent MC/Hx=1:1, R_f=0.3) as a yellow solid in 70% yield. Mp: 198 °C. ^{1}H NMR (CDCl$_3$): δ 7.66 (d, *J*=9.0 Hz, 1H), 7.63 (t, *J*=7.2 Hz, 2H), 7.62 (d, *J*=9.0 Hz, 2H), 7.59 (s, 1H), 7.40 (d, *J*=7.2 Hz, 2H), 7.37 (d, *J*=9.0 Hz, 1H), 7.35–7.27 (m, 4H), 7.25 (s, 2H), 7.22 (s, 1H), 7.13 (d, *J*=3.3 Hz, 1H), 7.12 (d, *J*=9.0 Hz, 2H), 7.07 (d, *J*=3.3 Hz, 1H), 5.64 (s, 1H), 3.76 (d, *J*=11.1 Hz, 2H), 3.66 (d, *J*=11.1 Hz, 2H), 1.43 (s, 12H), 1.32 (s, 3H), 0.82 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.2, 153.6, 147.6, 145.4, 141.1, 140.6, 139.1, 137.9, 136.1, 134.2, 127.1, 126.6, 125.9, 125.7, 125.1, 124.1, 123.1, 122.6, 121.4, 120.7, 120.3, 119.6, 118.5, 117.3, 98.2, 77.6, 46.9, 30.3, 27.1, 23.1, 21.9. MS: *m/z* 729 [M$^+$]. Anal. Calcd for $C_{48}H_{43}NO_2S_2$: C, 78.98; H, 5.94; N, 1.92. Found: C, 78.74; H, 5.93; N, 1.91.

3.1.6. (*E*)-2-(2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)vinyl)-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl))-amino benzo[*b*]thiophene (5). A mixture of **3** (0.3 g, 0.53 mmol), 2-methylphophonate-5-thiophenecarboxyaldehyde 2,2-dimethylpropan-1,3-diyl acetal (0.28 g, 0.80 mmol), and potassium *tert*-butoxide (0.09 g, 0.80 mmol) was vacuum-dried and THF (30 ml) was added. The solution was refluxed for 6 h. THF was removed under reduced pressure. The crude mixture was redissolved in dichloromethane, washed with water, and dried with MgSO$_4$. The organic layer was removed in vacuo. The pure product **5** was obtained by silica gel chromatography (eluent MC/Hx=1:1, R_f=0.6) to afford **5** in 82% yield. Mp: 195 °C. ^{1}H NMR (CDCl$_3$): δ 7.67 (t, *J*=7.0 Hz, 2H), 7.63 (d, *J*=9.0 Hz, 1H), 7.59 (s, 1H), 7.58 (d, *J*=8.2 Hz, 2H), 7.42 (d, *J*=7.2 Hz, 2H), 7.39 (d, *J*=9.0 Hz, 1H), 7.35–7.27 (m, 4H), 7.23 (d, *J*=8.2 Hz, 2H), 7.16 (s, 2H), 7.14 (d, *J*=16.5 Hz, 1H), 7.13 (s, 1H), 7.12 (d, *J*=3.6 Hz, 1H), 7.00 (d, *J*=16.5 Hz, 1H), 6.95 (d, *J*=3.6 Hz, 1H), 5.62 (s, 1H), 3.76 (d, *J*=11.4 Hz, 2H), 3.65 (d, *J*=11.4 Hz, 2H), 1.45 (s, 12H), 1.33 (s, 3H), 0.83 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.2, 153.6, 151.8, 147.5, 145.6, 142.6, 141.2, 140.5, 140.3, 139.0, 135.9, 135.4, 134.3, 127.1, 126.7, 126.0, 123.9, 123.4, 123.2, 122.4, 122.3, 121.1, 120.7, 119.5, 118.6, 117.2, 98.2, 77.5, 46.9, 30.3, 27.1, 23.0, 21.9. MS: *m/z* 755 [M$^+$]. Anal. Calcd for $C_{50}H_{45}NO_2S_2$: C, 79.43; H, 6.00; N, 2.18. Found: C, 79.19; H, 5.99; N, 2.17.

3.1.7. 2-(5-Formylthiophen-2-yl)-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl)amino benzo[*b*]thiophene (6). THF (30 ml) and water (10 ml) were added to a flask containing **4** (0.3 g, 0.41 mmol). Then, TFA (3 ml) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried with $MgSO_4$. The organic layer was removed in vacuo. The pure product **6** was obtained by silica gel chromatography (eluent MC/Hx=1:1, R_f=0.3) to afford **6** in 95% yield. Mp: 189 °C. ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 7.68 (d, J=7.2 Hz, 1H), 7.64 (t, J=7.2 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H), 7.57 (d, J=3.9 Hz, 1H), 7.54 (s, 1H), 7.41 (d, J=7.2 Hz, 2H), 7.37 (d, J=7.2 Hz, 1H), 7.32 (d, J=3.9 Hz, 1H), 7.30–7.26 (m, 4H), 7.25 (s, 2H), 7.13 (s, 1H), 7.12 (d, J=8.4 Hz, 2H), 1.41 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 183.1, 155.3, 153.6, 147.2, 146.5, 142.2, 141.5, 138.9, 137.4, 136.4, 135.4, 134.7, 134.1, 129.3, 128.4, 127.1, 126.7, 125.6, 125.1, 124.2, 122.6, 120.8, 119.6, 118.9, 116.3, 46.9, 27.1. MS: *m/z* 643 [M$^+$]. Anal. Calcd for $C_{43}H_{33}NOS_2$: C, 80.21; H, 5.17; N, 2.18. Found: C, 79.96; H, 5.16; N, 2.17.

3.1.8. (*E*)-2-(2-Formylthiophen-2-yl)vinyl-6-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl))amino benzo[*b*]thiophene (7). THF (30 ml) and water (10 ml) were added to a flask containing **5** (0.27 g, 0.41 mmol). Then, TFA (3 ml) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried with $MgSO_4$. The organic layer was removed in vacuo. The pure product **7** was obtained by silica gel chromatography (eluent MC/Hx=1:1, R_f=0.3) to afford **7** in 95% yield. Mp: 195 °C. ^{1}H NMR ($CDCl_3$): δ 9.85 (s, 1H), 7.66 (d, J=7.2 Hz, 1H), 7.65 (t, J=7.3 Hz, 2H), 7.60 (s, 1H), 7.59 (d, J=9.0 Hz, 2H), 7.54 (d, J=3.9 Hz, 1H), 7.39 (d, J=7.2 Hz, 2H), 7.37 (d, J=15.6 Hz, 1H), 7.36 (d, J=7.2 Hz, 1H), 7.32 (d, J=3.9 Hz, 1H), 7.29 (d, J=7.2 Hz, 2H), 7.27 (t, J=9.0 Hz, 2H), 7.25 (s, 2H), 7.13 (s, 1H), 7.12 (d, J=8.1 Hz, 2H), 6.97 (d, J=15.6 Hz, 1H), 1.41 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 184.7, 156.9, 155.7, 154.1, 148.8, 147.7, 142.2, 141.4, 140.5, 140.3, 139.4, 135.8, 135.0, 131.3, 127.6, 127.1, 126.0, 123.9, 123.1, 122.8, 122.5, 121.9, 121.2, 120.9, 119.3, 117.0, 116.8, 46.9, 27.1. MS: *m/z* 669 [M$^+$]. Anal. Calcd for $C_{45}H_{35}NOS_2$: C, 80.68; H, 5.27; N, 2.09. Found: C, 80.43; H, 5.26; N, 2.08.

3.1.9. (*E*)-3-(5-(6-(Bis(9,9-dimethylfluoren-2-yl)amino)-benzothiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (JK-16). A mixture of **6** (0.26 g, 0.40 mmol) and cyanoacetic acid (0.07 g, 0.80 mmol) was vacuum-dried and MeCN (60 ml) and piperidine (0.039 ml, 0.40 mmol) were added. The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed in vacuo. The pure product **JK-16** was obtained by silica gel chromatography (eluent MC/MeOH=2:1, R_f=0.6) to afford **JK-16** in 51% yield. Mp: 231 °C. ^{1}H NMR (DMSO-d_6): δ 8.14 (s, 1H), 7.73 (d, J=9.0 Hz, 1H), 7.72 (t, J=7.2 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H), 7.64 (s, 1H), 7.48 (d, J=3.8 Hz, 1H), 7.47 (s, 1H), 7.33–7.23 (m, 7H), 7.23 (d, J=3.8 Hz, 1H), 7.22 (s, 2H), 7.02 (d, J=8.1 Hz, 2H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 164.0, 157.8, 154.8, 153.2, 148.6, 146.8, 145.4, 141.6, 140.4, 138.3, 137.0, 136.3, 135.7, 133.9, 128.1, 127.1, 126.7, 125.4, 122.9, 122.7, 121.7, 121.2, 119.6, 119.0, 118.3, 116.7, 109.0, 46.5, 26.7. MS: *m/z* 710 [M$^+$]. Anal. Calcd for $C_{46}H_{34}N_2O_2S_2$: C, 77.72; H, 4.82; N, 3.94. Found: C, 77.48; H, 4.81; N, 3.93.

3.1.10. (*Z*)-3-(5-((*E*)-2-(6-(Bis(9,9-dimethylfluoren-2-yl)amino)benzothiophen-2-yl)vinyl)thiophen-2-yl)-2-cyanoacrylic acid (JK-17). A mixture of **7** (0.28 g, 0.41 mmol) and cyanoacetic acid (0.07 g, 0.83 mmol) was vacuum-dried and MeCN (60 ml) and piperidine (0.041 ml, 0.41 mmol) were added. The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed in vacuo. The pure product **JK-17** was obtained by silica gel chromatography (eluent MC/MeOH=2:1, R_f=0.5) to afford **JK-17** in 51% yield. Mp: 243 °C. ^{1}H NMR (DMSO-d_6): δ 8.07 (s, 1H), 7.73 (d, J=7.1 Hz, 1H), 7.72 (t, J=7.3 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H), 7.61 (d, J=3.9 Hz, 1H), 7.58 (s, 1H), 7.51 (d, J=8.1 Hz, 2H), 7.48 (d, J=7.1 Hz, 1H), 7.41 (d, J=15.6 Hz, 1H), 7.34 (d, J=3.9 Hz, 1H), 7.29 (d, J=7.3 Hz, 2H), 7.27 (t, J=9.0 Hz, 2H), 7.25 (s, 2H), 7.14 (d, J=15.6 Hz, 1H), 7.09 (s, 1H), 7.01 (d, J=9.0 Hz, 2H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 163.6, 154.8, 153.2, 151.7, 148.8, 146.8, 146.7, 145.3, 140.4, 140.1, 138.3, 136.1, 135.6, 133.9, 127.8, 127.1, 126.7, 125.2, 124.6, 124.4, 122.9, 122.8, 122.7, 122.2, 121.2, 119.6, 118.2, 116.7, 109.1, 46.4, 26.2. MS: *m/z* 732 [M$^+$]. Anal. Calcd for $C_{48}H_{36}N_2O_2S_2$: C, 78.23; H, 4.92; N, 2.09. Found: C, 77.99; H, 4.90; N, 2.08.

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References and notes

1. (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737; (b) Grätzel, M. *Nature* **2001**, *414*, 338; (c) Yanagida, M.; Yamaguchi, T.; Kurashige, M.; Hara, K.; Katoh, R.; Sugihara, H.; Arakawa, H. *Inorg. Chem.* **2003**, *42*, 7921; (d) 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) Nazeeruddin, 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; (c) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. *Jpn. J. Appl. Phys.* **2006**, *45*, L638.
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.; Dan-oh, 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, Z.-S.; Li, F.-Y.; Huang, C.-H. *Chem. Commun.* **2000**, 2063.
8. Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J.-H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, Md. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701.
9. (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.
10. Bushby, R. J.; McGill, D. R.; Ng, K. M.; Taylor, N. *J. Mater. Chem.* **1997**, *7*, 2343.
11. Raposo, M. M. M.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2004**, *60*, 4071.
12. Zhang, C.; Harper, A. W.; Dalton, L. R. *Synth. Commun.* **2001**, *31*, 1361.
13. 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.
14. Kay, A.; Grätzel, M. *J. Phys. Chem.* **1993**, *97*, 6272.
15. (a) Nüesch, F.; Maser, 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.
16. Justin Thomas, K. R.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. *Chem. Commun.* **2005**, 4098.
17. (a) Beck, J. R. *J. Org. Chem.* **1972**, *37*, 3224; (b) Iddon, B.; Pickering, M. W.; Suschitzky, H. D.; Taylor, S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1686.