A polymer gel electrolyte to achieve $\geq 6\%$ power conversion efficiency with a novel organic dye incorporating a low-band-gap chromophore

Jeum-Jong Kim,^a Hyunbong Choi,^a Ji-Won Lee,^b Moon-Sung Kang,^b Kihyung Song,^c Sang Ook Kang^{*a} and Jaejung Ko^{*a}

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A quasi-solid-state dye-sensitized solar cell with novel organic sensitizers incorporating a benzothiadiazole chromophore showed excellent long-term stability, which exhibited 10% decrease during the 1000 h light soaking; the optimized cell gave a short circuit photocurrent density of 12.03 mA cm^{-2} , an open circuit voltage of 0.720 V and a fill factor of 0.76, corresponding to an overall conversion efficiency of 6.61% under standard global AM 1.5 solar conditions.

Introduction

Increasing energy demands and depletion of fossil fuels have led to the search for renewable energy sources in recent years.¹ Dye-sensitized solar cells (DSSCs) have attracted significant attention as an alternative to the conventional solar cells due to their low-cost of production and high performance.² Some polypyridyl ruthenium complexes have achieved power conversion efficiencies over 10%.³ Although the ruthenium complexed dyes exhibited high efficiency and long-term stability, they are quite expensive and hard to purify. Recently, the solar cell performance of DSSCs based on organic dye photosensitizers has been remarkably improved and obtained efficiencies in the range of 7–9%.⁴ One of the main drawbacks of organic sensitizers is the sharp and narrow absorption bands in the blue region of the visible region, impairing their light-harvesting capabilities. Another disadvantage of organic dyes in DSSCs is the low stability under thermal stress and light-soaking stress. Therefore, molecular engineering of organic sensitizers with a high photovoltaic performance and an enhanced stability is paramount. Recently, a successful approach was introduced by incorporating a nonplanar bis-dimethylfluorenylamino moiety and a bi- or terthiophene unit into the organic framework,⁵ which not only achieves high efficiency but also stabilizes device performance under long-term light soaking. Using solvent-free ionic liquid electrolytes, the JK-46 sensitizer thus formed yielded a strikingly high conversion efficiency of 7%.6 To further improve the photovoltaic performance of this system, an enhanced spectral response of the sensitizer in the red region is required. The introduction of low-band gap chromophores such as the benzothiadiazole unit in the bridging framework is presumed to be increased for the spectral response in the red portion of the solar spectrum.7

While high conversion efficiency of 7% has been reached with **JK-46** using an ionic liquid under solvent-free conditions, the long-term stability still remains a major challenge due to the leakage. Extensive studies have been conducted to substitute liquid electrolytes with solid-state or quasi-solid-state electrolytes.⁸ In this article, we report meticulously designed organic sensitizers containing a low-band-gap chromophore (Fig. 1). We also investigated the effect of bridged structural modifications on the power conversion efficiency and long-term-stability with quasi-solid-state electrolytes.

Results and discussion

The organic sensitizers **JK-68** and **JK-69** were readily prepared by the stepwise synthetic protocol illustrated in Scheme 1. The 4,7-dithiophen-2-yl-benzo[1,2,5]thiadiazoles 3 were synthesized



Fig. 1 Molecular structure of JK-68 and JK-69.

^aDepartment of New Material Chemistry, Korea University, Jochiwon, Chungnam, 339-700, Korea. E-mail: jko@korea.ac.kr; Fax: +82 41 867 5396; Tel: +82 41 860 1337

^bEnergy & Environment Lab., Samsung Advanced Institute of Technology (SAIT), Yongin, 446-712, Korea

^cDepartment of Chemistry, Korea National University of Education, ChongwonChungbuk, 363-791, Korea



Scheme 1 Synthesis of JK-68 and JK-69. Reactants: (a) $PdCl_2(PPh_3)_2$, tributyl(2-thienyl)stannane 2a or 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane 2b, dry THF; (b) NBS, (CH₂Cl₂ : AcOH = 50 : 50, V/V); (c) 4, Pd(Ph_3)_4, Na₂CO₃, toluene–EtOH–H₂O; (d) POCl₃, DMF; (e) cyanoacetic acid, piperidine, CHCl₃.

by Stille⁹ or Suzuki¹⁰ coupling reactions of 4,7-dibromo-2,1,3benzothiadiazole 1^{7a} with stannylthiophene **2a** or 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane **2b**. The bromothiophenyl derivatives **4** were synthesized by bromination of **3** with NBS (*N*-bromosuccinimide) in CH₃COOH and CH₂Cl₂. The Suzuki coupling reaction of **4** with bis(9,9dimethyl-9*H*-fluoren-2-yl)-[4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-phenyl]amine **5** yielded **6a–6b**. The thiophene derivatives were converted to their corresponding carbaldehydes **7a–7b** according to the Vilsmeier–Haack reaction.¹¹ The aldehydes **7a** and **7b**, upon reaction with cyanoacetic acid in the presence of piperidine in chloroform, produced the sensitizers **JK-68** and **JK-69**.

Fig. 2 shows the absorption and emission spectra of sensitizers JK-68 and JK-69 measured in THF and the data are listed in Table 1. The absorption spectrum of JK-68 displays two absorption maxima at 534 nm ($\varepsilon = 19\ 700\ dm^3\ mol^{-1}\ cm^{-1}$) and 374 nm ($\varepsilon = 36~690~\text{dm}^3~\text{mol}^{-1}~\text{cm}^{-1}$), which are assigned as the π - π * transitions of the conjugated system. Under the same conditions the JK-69 that contains the hexyl group on thiophene units exhibits absorption maxima at 468 nm ($\varepsilon = 19290 \text{ dm}^3$ $mol^{-1} cm^{-1}$) and 370 nm ($\varepsilon = 72\ 000\ dm^3\ mol^{-1}\ cm^{-1}$). The introduction of a low-band-gap chromophore instead of the middle thiophene unit in JK-45 caused a red shift to 38-104 nm. On the other hand, a significant blue shift of JK-69 compared to JK-68 can be readily interpreted by the molecular modeling study of the two sensitizers. The ground state structure of JK-68 possesses a 20.6° twist between N,N-bis(9,9-dimethylfluoren-2-yl)aniline and thienyl unit. The dihedral angle of the thienyl and benzothiadiazole units in JK-68 is 5.8° (Fig. 3). For JK-69, the dihedral angles of the corresponding units are 21.2° and 44.4°, respectively. Accordingly, a significant red shift of JK-68 relative to JK-69 derives from more delocalization over an entire



Fig. 2 Absorption and emission spectra of JK-68 (solid line) and JK-69 (dotted line) in THF, and absorption spectra of JK-68 (dashed line) and JK-69 (dash-dotted line) absorbed on TiO_2 film.

conjugated system. Similar phenomena were observed in julolidine dyes or conjugated organic dyes.¹² When the **JK-69** sensitizer was absorbed on a TiO₂ electrode, a slight red shift from 468 to 488 nm was found due to the *J*-aggregation on TiO₂ electrode. The absorption spectra of the two dyes on TiO₂ electrode are broad. Such a broadening of the absorption spectra is due to an interaction between the dyes and TiO₂.¹³

Electrochemical properties of the two sensitizers **JK-68** and **JK-69** were evaluated by cyclovoltammetry in CH₃CN with 0.1 M tetrabutylammonium hexafluorophosphate. TiO₂ films stained with the sensitizers were used as working electrodes. The oxidation potential of the two sensitizers absorbed on TiO₂ film show a quasi-reversible couple at 0.98 V and 1.08 V *versus* NHE (normal hydrogen electrode). The reduction potential of the two dyes calculated from the oxidation potential and the E_{0-0} determined from the intersection of absorption and emission spectra is summarized in Table 1. The excited state oxidation potentials (E_{cox}) of the dyes (**JK-68**: -0.95 V *vs*. NHE; **JK-69**: -0.99 V *vs*. NHE) are much more negative than the conduction band of TiO₂ at approximately -0.5 V *vs*. NHE.

We performed the molecular orbital calculation of **JK-68** and **JK-69** to gain insight into the geometrical configuration and photophysical properties using the B3LYP/3-21G* (Fig. 4). The calculation illustrates that the HOMO of **JK-68** and **JK-69** is delocalized over the π -conjugated system through the phenyl amino unit and the LUMO is delocalized over the cyanoacrylic unit. Examination of the HOMO and LUMO of both dyes indicates that HOMO–LUMO excitation moves the electron distribution from the phenyl amino unit to the cyanoacrylic acid moiety, and the photo-induced electron transfer from the dyes to TiO₂ electrode can occur efficiently at the HOMO–LUMO transition.

The photovoltaic performance of the DSSCs was obtained using a polymer gel electrolyte comprising 0.6 M 1,2-dimethyl*n*-propylimidazolium iodide, 0.1 M I₂, poly(vinylidenefluoride*co*-hexafluoro)propylene (5% PVDF–HFP) and 0.5 M NMBI in 3-methoxypropionitrile (MPN). Fig. 5 shows a photocurrent density–voltage curve for the DSSCs based on the **JK-68** and **JK-69** dyes and the polymer gel electrolyte under standard global

Table 1 Optical, oxidation and DSSC performance parameters of dyes

Dye	$\lambda_{abs}^{a}/nm \ (\epsilon/M^{-1} \ cm^{-1})$	$E_{\rm ox}{}^b/{\rm V}$	$E_{0-0}{}^{c}/V$	$E_{\text{LUMO}}^{d}/\text{V}$	$J_{ m sc}/ m mA~ m cm^{-2}$	$V_{\rm oc}/{ m V}$	FF	η^{e} (%)
JK-68	534 (19 740); 374 (36 690)	0.98	1.93	$-0.95 \\ -0.99$	9.58	0.643	75.54	4.66
JK-69	468 (19 290); 370 (72 000)	1.08	2.07		12.03	0.720	76.19	6.61

^{*a*} Absorption spectra were measured in ethanol solution. ^{*b*} Oxidation potentials of dyes on TiO₂ were measured in CH₃CN with 0.1M (*n*-C₄H₉)₄NPF₆ with a scan rate of 50 mV s⁻¹ (*vs.* NHE). ^{*c*} E_{0-0} was determined from intersection of absorption and emission spectra in ethanol. ^{*d*} E_{LUMO} was calculated by $E_{ox} - E_{0-0}$. ^{*e*} Performances of DSSCs were measured with 0.18 cm² working area. Electrolyte: DMPImI (0.6 M), I₂ (0.1 M), NMBI (0.5 M), PVDF–HFP (5 wt%) in MPN.



Fig. 3 The optimized structure calculated with TD-DFT on B3LYP/3-21G* of a) **JK-69** and b) **JK-68**.



Fig. 4 Isodensity surface plots of the HOMO and LUMO of a) JK-68 and b) JK-69.

AM 1.5 solar conditions. The **JK-68** and **JK-69** sensitized cells gave the short circuit photocurrent density (J_{sc}) of 9.58 and 12.03 mA cm⁻², open circuit voltage (V_{oc}) of 0.643 and 0.720 V and a fill factor of 0.75 and 0.76, corresponding to an overall conversion efficiency of 4.66 and 6.61%, respectively. To the best of our knowledge, the efficiency of 6.61% is the highest ever reported for DSSCs based on organic sensitizer, even higher than 6.1% efficiency obtained by combining an amphiphilic polypyridyl ruthenium sensitizer (**Z-907**) with a polymer gel electrolyte.^{14a} It is noteworthy that the open circuit voltage (V_{oc}) for DSSCs based on **JK-69** is significantly higher than that for **JK-68**



Fig. 5 Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) & J-V curve for DSSC based on spectra of **JK-68** (solid line) and **JK-69** (dashed line), Electrolyte: DMPImI (0.6 M), I₂ (0.1 M), NMBI (0.5 M), PVDF–HFP (5 wt%) in MPN.

under the same conditions. A significant increase of $V_{\rm oc}$ in **JK-69** is related to the introduction of hexyl groups substituted at the thiophene units. The alkyl chains are quite effective in increasing the electron lifetime by preventing the dark current, improving $V_{\rm oc}$ of the cell (Fig. 7) and reducing the reorganization energy of the dye, improving J_{sc} of the cell.^{14b} The J-V curve of both sensitizers is shown in the inset of Fig. 5. The incident photon to current conversion efficiency (IPCE) of JK-69 exceeds 65% in a spectral range from 430 to 610 nm, reaching its maximum of 73% at 520 nm. For comparison, we measured the photovoltaic performance by using a volatile electrolyte. The power conversion efficiency of the JK-68, JK-69 and JK-2 based DSSCs can be increased to 7.51, 8.19 and 8.01% (for JK-68: $J_{sc} = 17.10$ mA cm⁻²; $V_{oc} = 0.61$ V; ff = 0.72. for **JK-69**: $J_{sc} = 14.98$ mA cm⁻²; $V_{\rm oc} = 0.77$ V; ff = 0.77. for **JK-2**: $J_{\rm sc} = 14.80$ mA cm⁻²; $V_{\rm oc} =$ 0.74 V; ff = 0.74), respectively, by using an acetonitrile electrolyte comprising 0.6 M DMPImI, 0.05 M I₂, 0.1 M LiI, and 0.5 M tert-butylpyridine.

Fig. 6 shows the photovoltaic performance during long-term accelerated aging of **JK-68** and **JK-69** sensitized solar cells using a quasi-solid electrolyte. In particular, the device employing **JK-69** showed an excellent long-term stability, the initial efficiency of 6.61% slightly decreased to 6.0% during the 1000 h light-soaking test. After 1000 h of light soaking, the V_{oc} of **JK-69** decreased by 73 mV, but the loss was compensated by an increase in the short-circuit current density. The long-term stability of the



Fig. 6 Evolution of solar cell parameters with **JK-68** (blue line, ▲) and **JK-69** (red line, ■) during visible-light soaking (AM 1.5G, 100 mW cm⁻²) at 60 °C. A 420 nm cut-off filter was put on the cell surface during illumination. Electrolyte: DMPImI (0.6 M), I₂ (0.1 M), NMBI (0.5 M), PVDF–HFP (5 wt%) in MPN.

device is remarkable because only a few ruthenium polypyridyl sensitizers passed the light-soaking stress for 1000 h while retaining an efficiency over 6% using a quasi-solid electrolyte. The enhanced stability of **JK-69** compared to **JK-68** can be attributed to the substituted hexyl chains by preventing the approach of acceptors to the TiO₂ surface, resulting in preventing the dark current.

To understand the electron-injection property and the change in $V_{\rm oc}$ of **JK-68** and **JK-69** more clearly, we measured the electrondiffusion coefficient and lifetimes of the photoelectrode. Fig. 7 shows the electron-diffusion coefficient ($D_{\rm e}$) and lifetime ($\tau_{\rm e}$) of the DSSCs employing different dyes (i.e. JK-68, JK-69, and JK-2) as a function of the J_{sc} . Note that we considered the similar structured organic dye (*i.e.* **JK-2**) for the comparison. The J_{sc} values in the x-axis increased with an increase in the initial laser intensity controlled by ND filters with different optical densities. The $D_{\rm e}$ and $\tau_{\rm e}$ values were determined by the photocurrent and photovoltage transients induced by a stepwise change in the laser light intensity controlled with a function generator.^{15–18} 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 TiO₂ film thickness (ω) using the equation, $D_{\rm e} = \omega^2 / (2.77 \tau_{\rm c})$.¹⁵ The $\tau_{\rm e}$ value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau)$.¹⁵ The D_e values of the photoanodes adsorbing the organic dyes are shown to be very similar to each other at the identical short-circuit current conditions. This result indicates that the $D_{\rm e}$ values are hardly affected by the kind of dye molecules, showing the similar trend to those of coumarin dyes. However, the τ_e values of JK-69 were drastically enhanced, compared with those of JK-68, with the help of the hydrophobic aliphatic chains retarding the electron recombination originated from the direct contact between the electrons on TiO2 surface and I_3^- ions in the electrolyte. The results of the electron lifetime are also consistent with those of the $V_{\rm oc}$ shown in Table 1.

The ac impedances of the cells were measured under dark and illumination conditions. Fig. 8 shows the ac impedance spectra



Fig. 7 Electron diffusion coefficients (a) and lifetimes (b) in the photoelectrodes adsorbing different dyes (*i.e.* JK-68, JK-69, and JK-2).

measured under (a) illumination and (b) dark conditions. Under the illumination (100 mW cm⁻², open-circuit voltage (OCV) conditions), the radius of the intermediate frequency semicircle in the Nyquist plot decreased in the order of JK-69 (75.8 Ω) > JK-2 $(64.9 \ \Omega) > JK-68 \ (46.1 \ \Omega)$, indicating the improved electron generation and transport. This result also corresponds well to that of the short-circuit current shown in Table 1. 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 TiO₂ to I₃⁻ ions in electrolyte.19 The increased radius of the semicircle in the intermediate frequency regime means the reduced electron recombination rate at the dyed TiO2-electrolyte interface. In the dark, the radius of the intermediate-frequency semicircle showed the increasing order of **JK-68** (33.4 Ω) < **JK-69** (121.3 Ω) < **JK-2** (124.8 Ω), in accord with the trends of the V_{oc} and τ_e values.

In conclusion, we designed and synthesized two highly efficient organic sensitizers containing a low-band-gap chromophore (**JK-68** and **JK-69**). The device based on the sensitizer **JK-69** and a polymer gel electrolyte gave an overall conversion efficiency of 6.61%. The efficiency is the highest one reported for DSSCs based on organic sensitizer. Moreover, the **JK-69** sensitized solar cell with a polymer gel electrolyte showed an excellent stability under light soaking at 60 °C for 1000 h. We believe that the development of highly efficient organic sensitizers with excellent



Fig. 8 Electrochemical impedance spectra measured under the illumination (100 mW cm⁻²) and at the dark for the cells employing different dyes (*i.e.* JK-68, JK-69, and JK-2).

stability is possible through sophisticated structural modifications, and work on these is now in progress.

Experimental

Electron diffusion coefficients and lifetimes were measured by the stepped light-induced transient measurements of photocurrent and voltages (SLIM-PCV).¹⁵⁻¹⁷ The transients were induced by a stepwise change in the laser intensity. A diode laser ($\lambda = 635$ nm) as a continuous 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 cm²). The laser was operated at a 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 TiO₂ thickness of the photoelectrode was controlled at approximately 3.3 µm. The measurements were carried out at ambient temperature and atmosphere and low relative humidity (<10%) conditions. We have checked the cell temperature using a thermocouple and were not aware of significant changes in the temperature during the measurements.

Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to give 1000 W m^{-2} , the equivalent of one sun at Air Mass(AM) 1.5, at the surface of the test cell. The light intensity was adjusted with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current–voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software.

Fluorine-doped tin oxide (FTO) glass plates (Pilkington TEC Glass-TEC 8, solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. Then, the plates were immersed in 40 mM TiCl₄ (aqueous) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer was prepared on the FTO glass plates by using a doctor blade printing TiO₂ paste (Solaronix, Ti-Nanoxide T/SP), which was then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA). A paste containing 400 nm sized anatase particles (CCIC. PST-400C) was deposited by means of doctor blade printing to obtain the scattering layer, and then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The resulting film was composed of a 10 µm thick transparent layer and a 4 µm thick scattering layer. The TiO₂ electrodes were treated again with TiCl₄ at 70 °C for 30 min and sintered at 500 °C for 30 min. Then, they were immersed in JK-68 (0.3 mM in tetrahydrofuran and 10 mM CDCA) and JK-69 (0.3 mM in tetrahydrofuran) solutions and kept at room temperature for 24 h. FTO plates for the counter electrodes were cleaned in an ultrasonic bath in H₂O, acetone, and 0.1M aqueous HCl, subsequently. The counter electrodes were prepared by placing a drop of an H₂PtCl₆ solution (2 mg Pt in 1 mL ethanol) on an FTO plate and heating (at 400 °C) for 15 min. The dye adsorbed TiO₂ electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating at 80 °C using a hot-melt ionomer film (Surlyn) as a spacer between the electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness).

4,7-Di-thiophen-2-yl-benzo[1,2,5]thiadiazole (3a)

To a stirred solution of 4,7-dibromo-2,1,3-benzothiadiazole **1** (2 g, 6.8 mmol) and tributyl(2-thienyl)stannane **2a** (5.2 mL, 16.4 mmol) in dry THF (50 mL) was added PdCl₂(PPh₃)₂ (97 mg, 2 mol%). The mixture was refluxed under a nitrogen atmosphere for 3 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (CH₂Cl₂ : hexane = 1 : 2, $R_{\rm f}$ = 0.32). Recrystallization from ethanol gave the title compound **3a** (1.8 g) as red–orange needles. Yield: 88%. mp 124–125 °C. ¹H NMR (CDCl₃): δ 8.10 (d, 2H, J

= 2.4 Hz), 7.84 (s, 2H), 7.45 (d, 2H, J = 4.5 Hz), 7.21 (dd, 2H, J = 3.9 and 5.1 Hz). ¹³C NMR (CDCl₃): δ 153.0, 139.8, 128.4, 127.9, 127.2, 126.4, 126.2. Anal. calcd for C₁₄H₈N₂S₃: C, 55.97; H, 2.68. Found: C, 55.78; H, 2.71.

4,7-Bis-(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (3b)

4,7-Dibromo-2,1,3-benzothiadiazole 1 (673 mg, 2.3 mmol) and 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane **2b** (1.35 g, 4.59 mmol), Pd(PPh₃)₄ (266 mg, 5 mol%), and Na₂CO₃ (488 mg, 4.6 mmol) were dissolved in toluene (30 ml)-EtOH (20 ml)-H₂O (20 ml) and the mixture was refluxed for 20 h. After evaporating the solvent under reduced pressure, H₂O (50 ml) and methylene chloride (50 ml) were added. The organic layer was separated and dried in MgSO₄. The solvent was removed under reduced pressure. The pure product 3b was obtained by column chromatography on silica gel (CH₂Cl₂ : hexane = 1 : 2, $R_f = 0.41$). Yield: 70%. ¹H NMR (CDCl₃): 7.64 (s, 2H), 7.44 (d, 2H, J = 5.7 Hz), 7.10 (d, 2H, J = 5.1 Hz), 2.66 (t, 4H, J = 7.8 Hz), 1.62 (m, 2H), 1.20 (m, 12H), 0.80 (t, 6H, J = 6.9 Hz). ¹³C NMR (CDCl₃): 154.4, 141.8, 132.3, 130.0, 129.4, 127.6, 126.0, 31.7, 30.8, 29.5, 29.2, 22.7, 14.2. Anal. calcd for C₂₆H₃₂N₂S₃: C, 66.62; H, 6.88. Found: C, 66.76; H, 6.43.

4-(5-Bromothiophen-2-yl)-7-(thiophen-2yl)benzo[1,2,5]thiadiazole (4a)

A solution of 4,7-di-2-thienyl-2,1,3-benzothiadiazole **3a** (350 mg, 1.17 mmol) in acetic acid (50 ml) and CH₂Cl₂ (50 ml) was stirred at room temperature. Then NBS (229 mg, 1.28 mmol) was added in small portions over 30 min. The solution was stirred overnight, The mixture was poured into water (100 ml) and the separated organic layer was dried over magnesium sulfate, and the solvent was evaporated. The crude product was separated by flash column chromatography on silica gel (CH₂Cl₂ : hexane = 1 : 4, R_f = 0.46). Compound **4a** was obtained as a orange powder. Yield: 70%. mp 126 °C. ¹H NMR (CDCl₃): 8.12 (d, 1H, J = 3.3 Hz), 7.82 (m, 3H), 7.47 (d, 1H, J = 5.1 Hz), 7.21 (dd, 1H, J = 3.9 and 4.5 Hz), 7.15 (d, 1H, J = 3.9 Hz). ¹³C NMR (CDCl₃): 152.6, 152.3, 140.8, 139.3, 130.8, 128.2, 127.8, 127.2, 127.1, 126.4, 125.7, 125.2, 125.0, 114.6. Anal. calcd for C₁₄H₇BrN₂S₃: C, 44.33; H, 1.86. Found: C, 44.46; H, 2.00.

4-(5-Bromo-3-hexylthiophen-2-yl)-7-(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole(4b)

The product **4b** was prepared using the same procedure for **4a** except that **3b** was used instead of **3a**. Yield: 56%. ¹H NMR (CDCl₃): 7.63 (m, 2H), 7.44 (d, 1H, J = 5.1 Hz), 7.11 (d, 1H, J = 4.5 Hz), 7.07 (d, 1H, J = 1.2 Hz), 2.65 (m, 4H), 1.61 (m, 4H), 1.21 (m, 12H), 0.81 (m, 6H). ¹³C NMR (CDCl₃): 154.2, 153.9, 142.3, 141.8, 133.8, 132.0, 131.9, 129.8, 129.2, 127.9, 126.1, 126.0, 113.0, 31.6, 31.5, 30.7, 30.5, 29.4, 29.1, 29.0, 22.5, 14.1. Anal. calcd for $C_{26}H_{31}BrN_2S_3$: C, 57.02; H, 5.71. Found: C, 56.90; H, 5.53.

Bis(9,9-dimethyl-9*H*-fluoren-2-yl)-{4-[5-(7-thiophen-2-ylbenzo[1,2,5]thiadiazol-4-yl)-thiophen-2-yl]-phenyl}amine (6a)

A mixture of 4a (170 mg, 0.45 mmol), bis(9,9-dimethyl-9*H*-fluoren-2-yl)-[4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-

phenyl]amine **5** (272 mg, 0.45 mmol), Pd(PPh₃)₄ (56 mg), Na₂CO₃ (50 mg) was dissolved in toluene (20 ml)–EtOH (20 ml)–H₂O (20 ml) and the mixture was refluxed for 12 h. After evaporating the solvent under reduced pressure, H₂O (50 ml) and methylene chloride (50 ml) were added. The organic layer was separated and dried in MgSO₄. The solvent was removed under reduced pressure. The pure product **6a** was obtained by column chromatography on silica gel using CH₂Cl₂ as an eluent (R_f = 0.63). Yield: 68%. mp 137 °C. ¹H NMR (CDCl₃): 8.13 (d, 2H, *J* = 3.3 Hz), 7.88 (s, 2H), 7.68–7.13 (m, 6H), 7.46–7.13 (m, 15H), 1.44 (s, 12H). ¹³C NMR (CDCl₃): 155.3, 153.7, 152.8, 152.6, 147.9, 147.1, 145.7, 139.6, 139.1, 139.0, 137.8, 134.6, 134.2, 128.9, 128.2, 127.5, 127.2, 126.9, 126.7, 126.1, 126.0, 125.7, 125.2, 123.8, 123.5, 123.3, 122.7, 120.8, 119.6, 119.0, 47.0, 29.8. Anal. calcd for C₅₀H₃₇N₃S₃: C, 77.38; H, 4.81. Found: C, 77.98; H, 4.84.

Bis(9,9-dimethyl-9*H*-fluoren-2-yl)-(4-{4-hexyl-5-[7-(3-hexylthiophen-2-yl)benzo[1,2,5-]thiadiazol-4-yl]-thiophen-2-yl}phenyl)amine (6b)

The product **6b** was prepared using the same procedure for **6a** except that **4b** was used instead of **4a**. Yield: 71%. mp 100 °C. ¹H NMR (CDCl₃): 7.74–7.64 (m, 8H), 7.50–7.16 (m, 15H), 2.76 (m, 4H), 1.74 (m, 4H), 1.51 (s, 12H), 1.29 (m, 12H), 0.90 (m, 6H). ¹³C NMR (CDCl₃): 155.2, 154.4, 154.2, 153.6, 147.6, 147.1, 144.5, 142.9, 141.7, 139.0, 134.4, 132.3, 131.1, 130.0, 129.6, 129.3, 128.5, 127.5, 127.3, 127.1, 126.6, 126.0, 124.7, 123.9, 123.4, 122.6, 120.8, 119.5, 118.8, 46.9, 31.7, 30.8, 29.8, 29.5, 29.2, 29.1, 27.1, 22.7, 22.6, 14.2, 14.1. Anal. calcd for $C_{62}H_{61}N_3S_3$: C, 78.85; H, 6.51. Found: C, 78.69; H, 6.88.

5-[7-(5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]phenyl}thiophen-2-yl)benzo[1,2,-5]thiadiazol-4yl]thiophene-2-carbaldehyde (7a)

Phosphorus oxychloride was added to **6a** in *N*,*N*-dimethylformamide (DMF, 5 ml) at 0 °C. The solution was stirred for 24 h at 80 °C. After removal of DMF *in vacuo*, the reaction mixture was neutralized with sodium acetate and extracted with methylene chloride. The crude product was purified by column chromatography using methylene chloride as an eluent ($R_f = 0.34$). Yield: 65%. mp 145 °C. ¹H NMR (CDCl₃): 9.97 (s, 1H), 8.20 (m, 2H), 8.01 (d, 1H, J = 7.9 Hz), 7.91 (d, 1H, J = 8.1 Hz), 7.84 (d, 1H, J = 3.9 Hz), 7.68–7.59 (m, 6H), 7.42–7.12 (m, 13H), 1.43 (s, 12H). ¹³C NMR (CDCl₃): 182.4, 155.7, 155.1, 155.8, 153.8, 147.4, 146.9, 145.1, 143.5, 143.1, 143.3, 142.7, 139.8, 138.2, 134.4, 130.2, 130.0, 129.1, 129.0, 128.2, 127.0, 126.7, 126.4, 125.7, 124.8, 123.6, 123.4, 122.4, 120.8, 119.5, 118.3, 46.7, 29.6. Anal. calcd for C₅₁H₃₇N₃OS₃: C, 76.18; H, 4.64. Found: C, 76.02; H, 4.50.

5-[7-(5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)-amino]phenyl}-3hexylthiophen-2-yl)b-enzo[1,2,5]thiadiazol-4-yl]-4hexylthiophene-2-carbaldehyde (7b)

The product **7b** was prepared using the same procedure for **7a** except that **6b** was used instead of **6a** and excess phosphorus oxychloride (10 equiv.). Yield: 60%. mp 93 °C. ¹H NMR (CDCl₃): 9.96 (s, 1H), 7.79–7.13 (m, 22H), 2.70 (m, 4H), 1.66 (m, 4H), 1.44 (s, 12H), 1.25 (m, 12H), 0.87 (m, 6H). ¹³C NMR (CDCl₃): 183.1, 155.2, 154.1, 153.8, 153.7, 147.8, 147.1, 145.1,

143.4, 143.2, 143.0, 142.7, 139.0, 138.0, 134.5, 130.6, 130.5, 129.2, 129.1, 128.3, 127.2, 126.7, 126.6, 125.7, 124.9, 123.8, 123.5, 122.6, 120.8, 119.6, 118.9, 47.0, 31.7, 31.6, 30.8, 30.5, 29.9, 29.5, 29.3, 29.1, 27.2, 22.7, 22.6, 14.2, 14.1. Anal. calcd for $C_{63}H_{61}N_3OS_3$: C, 77.82; H, 6.32. Found: C, 77.87; H, 6.43.

3-{5-[7-(5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino]phenyl}thiophen-2-yl)benzo-[1,2,5]thiadiazol-4yl]thiophen-2-yl}-2-cyanoacrylic acid (8a)

A mixture of **7a** (48 mg, 0.06 mmol) and cyanoacetic acid (10 mg, 0.12 mmol) was vacuum-dried and CHCl₃ and piperidine were added. The solution was refluxed for 15 h. Then H₂O (50 ml) was added. The organic layer was separated and dried over MgSO₄. The solvent was removed under reduced pressure. The pure product **8a** was obtained by column chromatography on silica gel (CH₂Cl₂ : MeOH = 6 : 1, R_f = 0.27). Yield: 58%. mp 290 °C. ¹H NMR (DMSO-d₆): 8.49 (s, 1H), 8.24–8.04 (m, 5H), 7.74–7.49 (m, 9H), 7.31 (m, 6H), 7.10 (m, 4H), 1.37(s, 12H). ¹³C NMR (DMSO-d₆): 169.9, 163.1, 154.9, 153.2, 151.7, 151.5, 147.3, 146.4, 145.7, 143.5, 140.9, 138.4, 138.2, 136.6, 135.6, 134.2, 129.6, 129.4, 127.8, 127.1, 127.0, 126.8, 126.5, 126.0, 125.0, 124.1, 123.7, 123.3, 123.2, 122.7, 121.3, 119.7, 119.1, 118.7, 46.5, 26.7. Anal. calcd for C₅₄H₃₈N₄O₂S₃: C, 74.46; H, 4.40. Found: C, 74.11; H, 4.30.

3-{5-[7-(5-{4-[Bis(9,9-dimethyl-9*H*-fluoren-2-yl)-amino]phenyl}-(3-hexylthiophen-2-yl)benzo[1,2-,5]thiadiazol-4-yl]-4hexylthiophen-2-yl}-2-cyanoacrylic acid (8b)

The product **8b** was prepared using the same procedure for **8a** except that **7b** was used instead of **7a**. Yield: 64%. mp 224 °C. ¹H NMR (DMSO-d₆): 8.32 (s, 1H), 7.75–7.11 (m, 22H), 3.42 (m, 4H), 2.45 (m, 4H), 1.36 (s, 12h), 1.10 (m, 12H), 0.71 (m, 6H). ¹³C NMR (DMSO-d₆): 168.5, 162.7, 155.1, 153.5, 151.6, 151.3, 147.7, 146.4, 145.5, 143.3, 140.6, 138.0, 137.7, 136.5, 135.8, 134.1, 129.6, 129.3, 127.3, 127.1, 126.9, 126.8, 126.3, 126.0, 124.9, 124.0, 123.6, 123.1, 123.0, 122.7, 121.8, 120.0, 118.9, 117.7, 47.5, 33.7, 32.6, 30.7, 30.5, 30.0, 29.6, 29.2, 29.1, 27.0, 22.0, 21.6, 13.9, 13.8. Anal. calcd for $C_{66}H_{62}N_4O_2S_3$: C, 76.26; H, 6.01. Found: C, 76.61; H, 6.31.

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