

Thiadiazoloquinoxaline-Based Low Band Gap Polymer for Solar Cell Applications

Vellaiappillai Tamilavan, Myungkwan Song,[†] Rajalingam Agneeswari, Sangjun Kim,
Jae-Wook Kang,[†] Sung-Ho Jin,[‡] and Myung Ho Hyun^{*}

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 690-735, Korea

^{*}E-mail: mhhyun@pusan.ac.kr

[†]Department of Material Processing, Korea Institute of Materials Science, Changwon 641-831, Korea

[‡]Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials,
Pusan National University, Busan 609-735, Korea

Received March 21, 2013, Accepted May 16, 2013

Key Words : Bulk heterojunction solar cell, Polymer solar cell, Low band gap polymer, Thiadiazoloquinoxaline

Polymer solar cells (PSCs) consisting of the photoactive layer containing the interpenetrating network of electron donating polymer and electron accepting PCBM derivative has been proved to be quite effective in converting the solar energy into electrical energy.¹⁻⁸ After many efforts, the power conversion efficiency (*PCE*) of the solution-processed PSCs was reached up to 9.2% for single layer PSCs⁷ and that for the tandem structured PSCs was improved up to 10.7%.⁸ The *PCE* of the PSCs was found to be highly influenced by light harvesting ability of the electron donating polymer. In this instance, development of structurally new polymers having broad absorption band is considered as quite interest in the area of PSCs applications. Recently, we reported the opto-electrical and photovoltaic properties of several NIR absorption polymers incorporating electron accepting thiadiazoloquinoxaline (DQ) derivative and electron donating thiophene-pyrrole(*N*-aryl)-thiophene (TPyTDzQ),⁹ fluorene (PFDQ)¹⁰ or indenofluorene (PIFDQ)¹⁰ derivatives as well as two new thiadiazoloquinoxaline-based organic small molecules (TDQ-SM).¹¹

The careful analysis of the absorption spectra of those polymers and small molecules clearly indicated that the absorption band is quite dependent on the bond flexibility of the repeating units.⁹⁻¹¹ Exactly saying, increasing the steric hindrance between the repeating units increases the bond flexibility and, consequently, the absorption band was found to be considerably blue shifted.⁹⁻¹¹ Notably, the second absorption maximum of the reported DQ-based polymers was found to be highly affected by the bond flexibility of the repeating units, but the absorption maximum wavelength was still longer than 800 nm, which is slightly beyond the maximum solar flux region.^{9,10} We expect that the copolymerization of DQ unit with sterically more hindered electron rich monomer or monomer which can increase the dihedral angle between the repeating units would offer new DQ-based polymer showing their second absorption maximum at the maximum solar flux region. In this instance, we copolymerized the DQ unit with benzo[1,2-*b*:4,3-*b'*]dithiophene derivative, which is the structural isomer of most successful electron donating monomers such as benzo[1,2-*b*:4,5-*b'*]dithiophene and benzo[2,1-*b*:3,4-*b'*]dithiophene derivatives.¹²

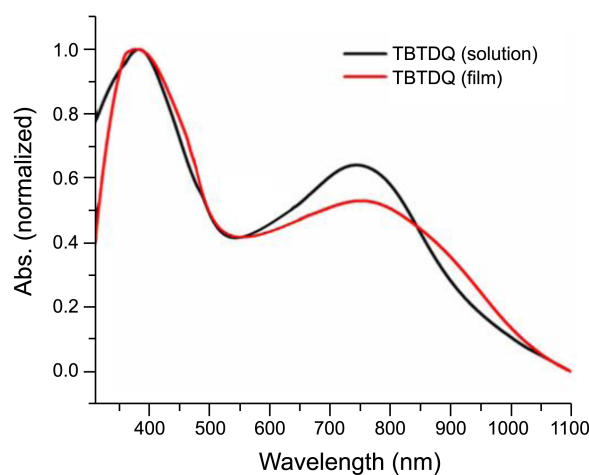
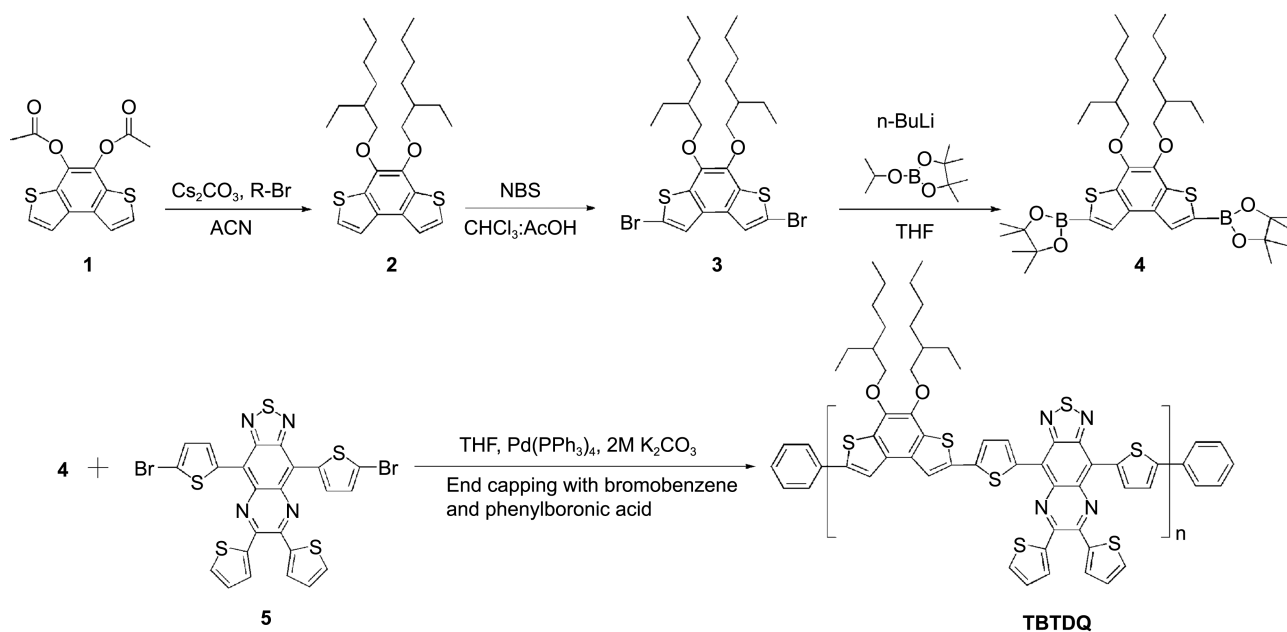


Figure 1. Absorption spectra of TBTDQ.

The synthetic route for the synthesis of a new polymer, TBTDQ, is outlined in Scheme 1. 7,8-Diacetoxybenzo[1,2-*b*:4,3-*b'*]dithiophene (**1**), which was prepared starting from 3,3'-bithiophene by the reported procedure,¹³ was treated with cesium carbonate followed by 2-ethylhexyl bromide to afford compound **2**. The selective bromination of compound **2** with *N*-bromosuccinimide (*NBS*) afforded compound **3**, which was treated with *n*-BuLi followed by 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to yield electron rich monomer **4**. On the other hand, the electron deficient thiadiazoloquinoxaline based monomer **5** was prepared from the known literature procedure reported from our group.⁹ Finally, the Suzuki polycondensation reaction between compounds **4** and **5** followed by end capping with phenylboronic acid and bromobenzene afforded TBTDQ.

The GPC analysis revealed the weight average molecular weight (M_w) and the polydispersity (PDI) of TBTDQ were 8.24×10^3 and 1.34, respectively, and the 5% weight loss temperature of TBTDQ was determined to be 392 °C from the thermogravimetric analysis (TGA), which indicates that the polymer has high thermal stability (Figure S1, see supporting information). TBTDQ showed good solubility in chloroform, tetrahydrofuran, chlorobenzene and dichloro-



Scheme 1. Synthetic route to **TBTDQ**.

benzene.

The absorption spectra of **TBTDQ** were measured in chloroform and as thin films (on glass) at room temperature and shown in Figure 1. **TBTDQ** shows two absorption bands both in solution and as film state. The first absorption band attributed from the π - π^* electronic transition appeared at the region of 300-550 nm and another absorption band originated from the donor-acceptor internal charge transfer (ICT) appeared at the region of 500-1000 nm. The absorption maxima of the **TBTDQ** was found to be at 382 nm, 746 nm and 384 nm, 754 nm, respectively in solution and as film state. As expected, the second absorption maximum of **TBTDQ** was found to be largely (\sim 50-150 nm) blue shifted compared with that of the reported DQ-based polymers^{9,10} and interestingly was found to be located exactly at the maximum solar flux region. Unfortunately, the second absorption band was found to be weaker than the first absorption band. We expect that increased dihedral angle or steric hindrance between the repeating units of **TBTDQ** might diminish the ICT and, consequently, the absorption attributed from the ICT was found to be weaker than the π - π^* electronic transition. The optical band gap ($E_{g,opt}$) of **TBTDQ** was calculated from the onset wavelength of the optical absorption as thin film to be 1.19 eV.

The HOMO and LUMO energy levels of **TBTDQ** were estimated from the cyclic voltammetry (CV) analysis. The onset oxidation ($E_{ox,onset} = 0.65$ V) and reduction ($E_{red,onset} = -0.71$ V) potential of **TBTDQ** were calculated by using the known equations^{9,10} from the CV spectrum presented in Figure 2. The HOMO and LUMO energy levels of **TBTDQ** were calculated to be -5.05 eV and -3.69 eV, respectively, and the electrochemical band gaps ($E_{g,elec}$) of **TBTDQ** were determined from the HOMO and LUMO energy levels to be 1.36 eV. The electrochemical band gap value was found to be slightly higher than that of the optical band gap value.

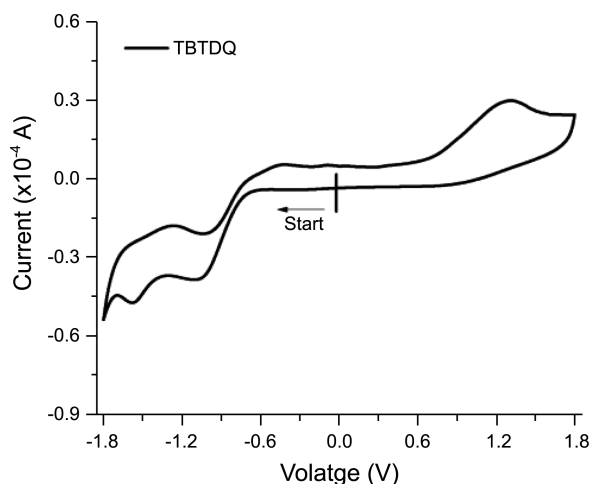


Figure 2. Cyclic voltammogram of **TBTDQ**.

The PSCs were fabricated with the device structure of ITO/PEDOT:PSS/**TBTDQ**:PC₇₁BM (1:1 or 1:3 or 1:5 wt %) /LiF/Al. The current density-voltage (J - V) characteristic curves of the PSC devices measured under the AM 1.5 G irradiation (100 mWcm^{-2}) are shown in Figure 3. The device made from **TBTDQ**:PC₇₁BM (1:1 wt %) as the active layer shows the PCE of 0.07% with a J_{sc} of 0.77 mA/cm^2 , a V_{oc} of 0.34 V, and a FF of 26% while those made from **TBTDQ**:PC₇₁BM (1:3 wt %) and **TBTDQ**:PC₇₁BM (1:5 wt %) as the active layer show the PCE of 0.27% with a J_{sc} of 2.59 mA/cm^2 , a V_{oc} of 0.37 V, a FF of 29% and the PCE of 0.54% with a J_{sc} of 4.59 mA/cm^2 , a V_{oc} of 0.39 V, and an FF of 30%, respectively. The device performance was found to be considerably increased when the content of PC₇₁BM was increased in the photoactive layer of the **TBTDQ**-based PSCs. We expect that the higher PC₇₁BM content might be favorable for the efficient exciton dissociation at donor-

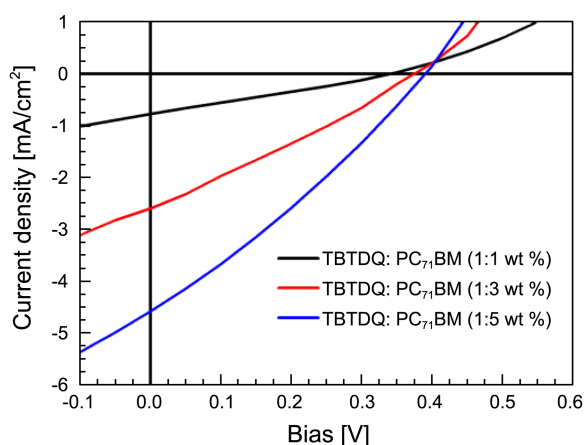


Figure 3. J - V characteristics of ITO/PEDOT:PSS/TBTDQ:PC₇₁BM (1:1 or 1:3 or 1:5 wt %)/LiF/Al devices.

acceptor interface through the better interpenetrating network (low molecular weight of **TBTDQ** might require higher PC₇₁BM content to make efficient heterojunction between the donor and acceptor materials) formation between the polymer and PC₇₁BM. In this instance, the photovoltaic parameters such as J_{sc} , V_{oc} and FF are improved and the improved photovoltaic parameters increase the overall photovoltaic performances. The overall PCE was found to be quite similar with those of the reported DQ-based polymers and small molecules.⁹⁻¹¹

In summary, thiadiazoloquinoxaline-based electron deficient unit was copolymerized with newly synthesized benzo-[1,2-*b*:4,3-*b'*]dithiophene derivative with the aim of preparing new thiadiazoloquinoxaline-based polymer harvesting the sunlight effectively in the range of 300-1000 nm. The absorption maximum of new polymer, **TBTDQ**, was found to show relatively blue shifted compared with those of the reported thiadiazoloquinoxaline-based polymers. Interestingly, the second absorption band of **TBTDQ** was found to be located exactly at the maximum solar flux region. At the same time, the increased dihedral angle between the repeating units of **TBTDQ** highly affects the ICT and, consequently, the absorption was not strong at the longer wavelength region. The photovoltaic studies showed that the overall conversion efficiency was quite similar with the reported thiadiazoloquinoxaline-based polymers. This study is expected to give some helps in designing new polymers for PSC applications in terms of the effect of the steric hindrance or dihedral angle between the repeating units of polymers.

Experimental

Materials and Instruments. All reagents were commercially available from Aldrich or TCI chemicals and used without further purification. ¹H and ¹³C NMR spectra were recorded using a 300-MHz Varian Mercury Plus spectrometer in deuterated chloroform. The weight average molecular weight (M_w) and polydispersity index (PDI) of the polymer was determined by using Agilent 1100 series liquid chromatography

system. Thermogravimetric analysis was performed by using a Mettler Toledo TGA/SDTA 851 analyzer. The absorption spectra were recorded using a JASCO V-570 spectrophotometer. The electrochemical property of the polymer was studied using a CH Instruments Electrochemical Analyzer in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as the supporting electrolyte, Ag/AgCl as reference electrode and platinum as counter and working electrode. The polymer was coated as thin film on platinum working electrode and then used for the electrochemical analysis.

Device Fabrication and Characterization of PSCs. The PSCs was constructed as follows. A 40 nm thick layer of PEDOT:PSS (CLEVIOUS P) was spin-coated onto the pre-cleaned and UV-ozone treated ITO (300 nm thick, 4 Ω/sq sheet resistance) coated glass substrates and baked in air at 150 °C for 10 min. Subsequently, the 80 nm thickness of active layer (TBTDQ:PC₇₁BM (1:1 or 1:3 or 1:5 wt %) in 1,2-dichlorobenzene) was spin coated onto the ITO/PEDOT:PSS substrates, and subjected to solvent annealing for 30 min in a glove box. The film was annealed thermally at 100 °C for 30 min. Finally, LiF (0.7 nm) and Al (100 nm) were evaporated sequentially onto the polymer layer as a cathode to create a device with an area of 0.36 cm² defined by a shadow mask. The PSC device performance was measured using an AM 1.5G solar simulator (Oriel 300 W) at 100 mWcm⁻² light illumination. Current-voltage (J - V) characteristics of the photovoltaic cells were measured using a standard source measurement unit (Keithley 236). The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm.

Synthesis of 7,8-Di-2-ethylhexyloxybenzo[1,2-*b*:4,3-*b'*]dithiophene (2). In a two neck round bottom flask fitted with a reflux condenser and rubber septa was taken 7,8-diacetoxybenzo[1,2-*b*:4,3-*b'*]dithiophene (**1**) (1.70 g, 5.55 mmol) and cesium carbonate (Cs₂CO₃) (9.00 g, 27.75 mmol) under an argon atmosphere. To the mixture was added acetonitrile (60 mL) at room temperature through a syringe and stirred. After 10 min, 2-ethylhexyl bromide (4.95 mL, 27.75 mmol) was added slowly through a syringe and then the reaction mixture was heated to 70 °C. After 3 days, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the remaining solids were partitioned between dichloromethane (CH₂Cl₂) and water. The organic layer was washed with 1 N HCl and with water, dried (anhydrous sodium sulfate, Na₂SO₄), and filtered. The solvent was removed, and the crude product was purified by using column chromatography (silica gel, hexane) to afford compound **2** (2.42 g) as a colorless liquid. Yield: 98%. ¹H NMR (CDCl₃, 400 MHz) δ 7.63 (d, 2H), 7.46 (d, 2H), 4.15 (d, 4H), 1.30-1.88 (m, 18H), 0.86-1.04 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 142.8, 133.6, 131.5, 125.8, 122.4, 76.6, 40.8, 30.6, 29.4, 24.0, 23.4, 14.4, 11.5; HRMS (EI⁺, m/z) [M^+] Calcd for C₂₆H₃₈O₂S₂ 446.2313, found 446.2315.

Synthesis of 2,5-Dibromo-7,8-di-2-ethylhexyloxybenzo[1,2-*b*:4,3-*b'*]dithiophene (3). Compound **2** (1.25 g, 2.80

mmol) was dissolved in a mixture of chloroform (20 mL) and acetic acid (20 mL). NBS (1.00 g, 5.60 mmol) was added to the stirred solution and then the mixture was stirred for 10 h in the dark. The reaction mixture was poured into water (100 mL) and the solution was extracted with chloroform (30 mL \times 3). The combined organic layer was washed with 1N NaOH solution and then brine. The organic layer was then dried over anhydrous Na₂SO₄. The solvent was filtered and removed under reduced pressure, and then the product was purified by column chromatography (silica gel, hexane) to afford compound **3** (1.69 g) as a colorless liquid. Yield: 99%. ¹H NMR (CDCl₃, 400 MHz) δ 7.49 (s, 2H), 4.08 (q, 4H), 1.30-1.80 (m, 18H), 0.86-1.04 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 141.9, 134.8, 130.2, 124.9, 114.6, 40.8, 30.6, 29.4, 24.0, 23.3, 14.3, 11.4; HRMS (EI⁺, *m/z*) [M⁺] Calcd for C₂₆H₃₆Br₂O₂S₂ 602.0523, found 602.0526.

Synthesis of 2,5-Di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-7,8-di-2-ethylhexyloxybenzo[1,2-*b*:4,3-*b'*]dithiophene (4). Under an argon atmosphere, a solution of compound **3** (1.69 g, 2.80 mmol) in dry THF (40 mL) was cooled to -78 °C in a dry-ice bath for 15 min. To the stirred solution, *n*-BuLi (2.50 mL, 6.16 mmol, 2.5 M solution in hexane) was added dropwise and stirred for 1 h at the same bath. Then, the solution was again cooled to -78 °C for 15 min and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.26 mL, 6.16 mmol) was added dropwise. The solution was slowly warm to room temperature and stirred for overnight. The reaction mixture was poured into water (100 mL) and then extracted with diethyl ether (30 mL \times 3). The combined organic layer was washed with brine. The organic layer was dried over anhydrous Na₂SO₄. The solvent was filtered and removed under reduced pressure, and then the product was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford pure product **4** as a light yellow color liquid. Yield: 1.5 g (77%). ¹H NMR (300 MHz, CDCl₃) δ 8.20 (s, 2 H), 4.14 (t, 4H), 1.30-1.86 (m, 42H), 0.86-1.04 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 143.6, 138.4, 132.8, 84.6, 76.6, 40.8, 30.5, 29.4, 25.1, 24.0, 23.4, 14.4, 11.5; HRMS (EI⁺, *m/z*) [M⁺] Calcd for C₃₈H₆₀B₂O₆S₂ 698.4017, found 698.4025.

Synthesis of TBTDQ: A solution of compound **4** (0.14 g, 0.2 mmol) and **5** (0.14 g, 0.2 mmol) in THF (30 mL) was purged well with argon for 45 min. Then, Pd (PPh₃)₄ (0.01 g, 5 mol %) and aq. 2 M K₂CO₃ (5 mL) were added to the stirred solution and the mixture was heated to reflux under

an argon atmosphere. After refluxing for 36 h, 20 mg of phenylboronic acid was added. The whole mixture was refluxed for 6 h and then 0.05 mL of bromobenzene was added and then the mixture was heated to reflux for 6 h. Then, the reaction mixture was cooled to room temperature and then poured into the mixed solvent of methanol and water (100 mL:50 mL) with vigorous stirring. The precipitate was recovered by filtration, and then extracted with methanol for 24 h and acetone for 24 h in a Soxhlet apparatus to afford **TBTDQ** as a greenish-black color solid. Yield: 0.10 g (46%). ¹H NMR (300 MHz, CDCl₃) δ 8.76 (s, 2 H), 7.71 (s, 2 H), 7.63 (s, 2 H), 7.49 (s, 2 H), 7.20 (s, 2 H), 7.09 (s, 2 H), 4.14 (s, 2 H), 1.88-1.05 (m, 18 H), 1.05-0.65 (m, 12 H).

Acknowledgments. This work was supported by a 2-Year Research Grant of Pusan National University.

Supporting Information. The NMR spectra of the synthesized molecules and TGA curve for **TBTDQ** were presented in supplementary.

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