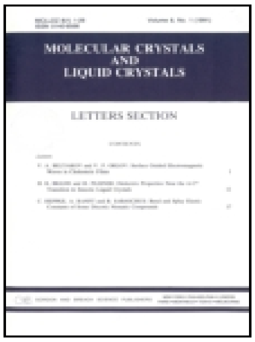

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Synthesis and Properties of Copolymer with Carbazole and F-Quinoxaline Units for OPVs

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*A new accepter unit, 6,7-difluoro-2,3-dihexylquinoxaline, was prepared and utilized for organic photovoltaics. The solid film of the synthesized conjugated polymer, poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,8-(6,7-difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline)] (**PCDTQxF**), shows absorption band with maximum peak at about 502 nm and the absorption onset at 580 nm, corresponding to band gap of 2.14 eV. The oxidation onset of the **PCDTQxF** was estimated to be 0.67 V, which correspond to HOMO energy level of −5.47 eV. The deep HOMO energy level of **PCDTQxF** leads to higher V_{OC}. The device of **PCDTQxF**:$PC_{71}BM$ (1:1) showed V_{OC} of 0.80 V, J_{SC} of 2.41 mA/cm^2, and FF of 0.37, giving PCE of 0.7%.*

Keywords Polymer; Solar Cells; Synthesis; Fluoro atom

1. Introduction

Organic photovoltaics (OPVs) have carried out extensive research into renewable energy due to their potential for low cost and large-area processability[1–3]. To accomplish high efficiency, low band gap conjugated polymers have been developed to enhance light absorption. The development of novel materials is necessary to enhance the coverage of the solar spectrum and the high V_{OC} and J_{SC}. To obtain high V_{OC}, the low band gap conjugated polymers have been researched with lower highest occupied molecular orbital (HOMO) energy levels that can potentially increase V_{OC}[4].

Recently, research into low-bandgap conjugated polymers containing electron rich-electron deficient pairs for OPVs has become quite vigorous. Semiconducting copolymers with quinoxaline units are emerging as interesting materials for OPVs[5]. Almost quinoxaline based polymers used in OPVs contain synthetically elaborate comonomers, such as carbazole,[6, 7] thiophene, [8] and benzodithiophene[9]. The quinoxaline moieties with F atoms have been reported to lead high efficiency caused by deeper HOMO, long wavelength absorption and high hole mobility[5, 10].

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In this study, we report new conjugated copolymer, **PCDTQxF** for OPVs utilizing a new type of acceptor, 6,7-difluoro-2,3-dihexylquinoxaline. The push-pull conjugated polymer was synthesized by Suzuki polymerization of 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-*N*-9"-heptadecanylcarbazole and 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline. The photovoltaic properties of the polymer were investigated by fabrication of the polymer solar cell with the configuration of ITO/PEDOT:PSS/polymer:PCBM/Al.

2. Results and Discussion

2.1. Synthesis and Characterization

The general synthetic routes of the monomer and polymer are outlined in Scheme 1. 2,7-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-*N*-9"-heptadecanylcarbazole (**7**), as electron-rich moiety, and 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (**6**), as electron-deficient moiety, were copolymerized through Suzuki polymerization with $Pd_2(dba)_3$ catalyst to yield **PCDTQxF**. The structures and purities of the monomers were confirmed by ^{1}H-NMR, ^{13}C-NMR and HRMS.

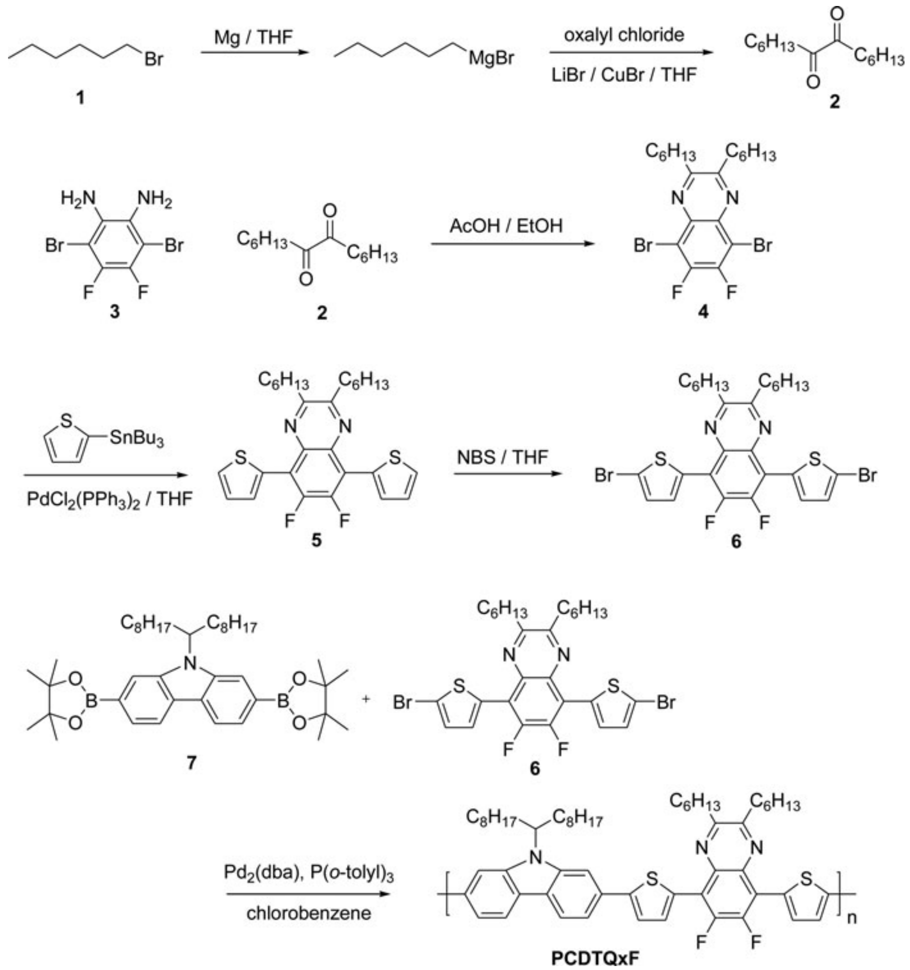
PCDTQxF was determined by GPC to have number-average molecular weight (M_n) of 3000 and weight-average molecular weight (M_w) of 3500 with polydispersity index (PDI, M_w/M_n) of 1.17. The **PCDTQxF** with thiophene units has lower molecular weight caused by lower solubility of chlorobenzene during synthesis process. Thermal gravimetric analysis was performed with TGA 2950 in a nitrogen atmosphere at a heating rate of 10°C/min to 600°C. The decomposition temperature (T_d) for **PCDTQxF** under N_2 was determined to be 410°C, which shows higher than other polymers with 6,7-difluoro-2,3-dihexylquinoxaline caused by introducing thiophene units.[11–12] The high thermal stability of the synthesized polymer prevents the deformation of the morphology and is important for OPV device applications.

2.2. Optical Properties

The optical properties of chloroform solution and film of the synthesized polymer were investigated by UV-vis absorption spectroscopy as shown Figure 1. Uniform film was prepared on quartz plate by spin-casting from ODCB solution at room temperature. The absorption spectra of **PCDTQxF** exhibited maximum peak at about 491 nm in solution. The solid film of **PCDTQxF** shows absorption band with maximum peak at about 502 nm and the absorption onset at 580 nm, corresponding to band gap of 2.14 eV. The absorption spectrum of the film is red shifted as compared to that of solution state caused by the increased intermolecular interactions of thiophene units.

2.3. Electrochemical Properties

The electrochemical properties of the polymer were determined from the band gap, which was estimated from the absorption onset wavelength, and the HOMO energy level which was estimated from cyclic voltammetry (CV).[13] The CV spectrum is shown in Figure 2. The optical band gap of the **PCDTQxF** in thin film was determined to be 2.14 eV, which was calculated from the absorption onset wavelength of 580 nm. The oxidation onset of the **PCDTQxF** was estimated to be 0.67 V, which correspond to HOMO energy level



Scheme 1. Synthetic route for the synthesis of the monomer and polymer.

of −5.47 eV. The HOMO energy level of **PCDTQxF** shows lower than other polymer with 6,7-difluoro-2,3-dihexylquinoxaline.[11–12] The reduction onset of the **PCDTQxF** was estimated to be −0.87 V, which correspond to LUMO energy level of −3.93 eV. The electrochemical band gap, calculated from cyclic voltammetry data, was determined to be 1.54 eV, which is lower than the optical band gap estimated from the absorption spectra.

2.4. Polymer Photovoltaic Properties

The photovoltaic properties of polymers were investigated by fabricating the OPVs with ITO as positive electrode, the blend with small molecules and PCBM as active layer, and Al as negative electrode. Figure 3 showed the current-voltage (*I-V*) curves of the OPVs with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:$PC_{71}BM$ (100 nm)/Al (100 nm) under AM 1.5G irradiation (100 mW/cm^2). BHJ device was fabricated by spin-coating of 1% (w/v) ODCB solution comprising blend of polymer and $PC_{71}BM$. The device comprising

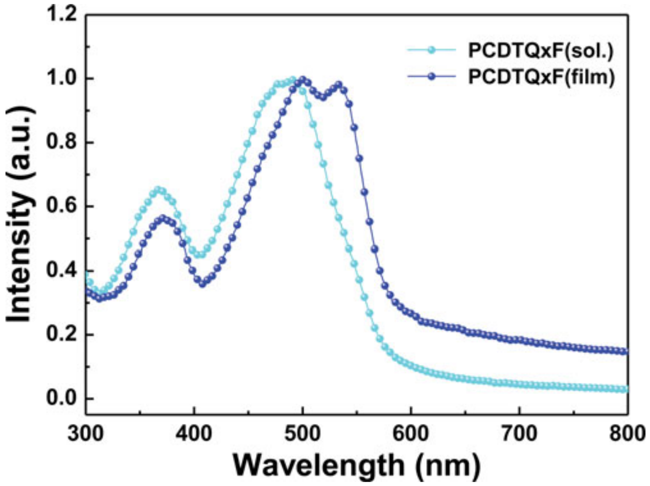


Figure 1. UV-visible absorption spectra of polymer in chlorofrom solution and the solid state.

PCDTQxF with $PC_{71}BM$ (1:1) showed open-circuit voltage (V_{OC}) of 0.80 V, short-circuit current density (J_{SC}) of 2.41 mA/cm^2, and fill factor (FF) of 0.37, giving a power conversion efficiency (PCE) of 0.70%. The deep HOMO level of **PCDTQxF** leads to higher V_{oc}- as compared with other polymer with 6,7-difluoro-2,3-dihexylquinoxaline.[11–12] The device performance of **PCDTQxF** does not have a good efficiency caused by lower molecular weight and poor solubility.

3. Conclusions

The Synthesized polymer, **PCDTQxF** utilizing 6,7-difluoro-2,3-dihexylquinoxaline, was synthesized at room temperature in organic solvents. The solid film of **PCDTQxF** shows absorption band with maximum peak at about 502 nm. The oxidation onset of the **PCDTQxF**

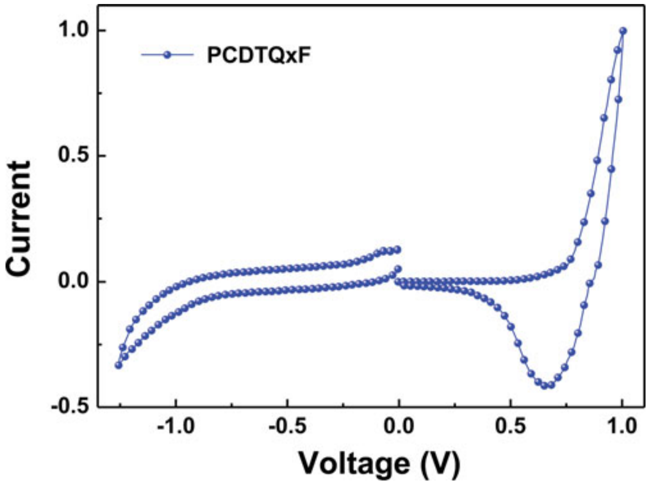


Figure 2. Electrochemical properties of polymer.

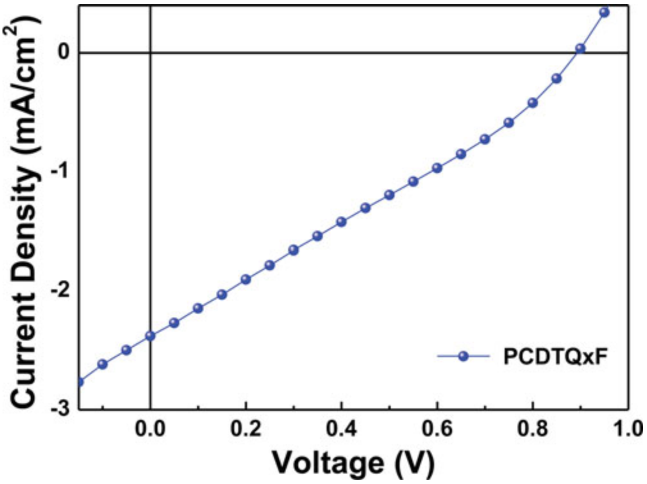


Figure 3. Current density-potential characteristics of the polymer solar cells under the illumination of AM 1.5, 100 mW/cm^2.

was estimated to be 0.67 V, which correspond to HOMO energy level of −5.47 eV. The device of **PCDTQxF**:$PC_{71}BM$ (1:1) showed V_{OC} of 0.80 V, J_{SC} of 2.41 mA/cm^2, and *FF* of 0.37, giving PCE of 0.7%. The deep HOMO level of **PCDTQxF** leads to higher V_{oc}- as compared with other polymer with 6,7-difluoro-2,3-dihexylquinoxaline. The device performance of **PCDTQxF** does not have a good efficiency caused by lower molecular weight and poor solubility.

Experimental Section

General. All reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. ^{1}H and ^{13}C NMR spectra were recorded with a JNM ECP-400 (400 MHz, JEOL) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) conditions in the Korea Basic Science Institute (Daegu). Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer, while the Oriel InstaSpec IV CCD detection system with xenon lamp was used for the photoluminescence and electroluminescence spectra measurements.

Solar cells were fabricated on an indium tin oxide (ITO)-coated glass substrate with the following structure; ITO-coated glass substrate/ poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) (PEDOT:PSS)/polymer: $PC_{71}BM$/Al. The ITO-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT:PSS (Baytron PH) was spin-casted from aqueous solution to form a film of 40nm thickness. The substrate was dried for 10 min at 140°C in air and then transferred into a glove box to spin-cast the charge separation layer. A solution containing a mixture of polymer:$PC_{71}BM$ in ODCB solvent with concentration of 7 wt/ml% was then spin-casted on top of the PEDOT/PSS layer. The film was dried for 60 min at 70°C in the glove box. The sample was heated at 80°C for 10 min in air. Then, an aluminum (Al, 100nm) electrode was deposited by thermal evaporation in a vacuum of about 5×10^{-7} Torr. Current density-voltage (*J-V*) characteristics of the devices were measured using a Keithley 236 Source Measure Unit. Solar cell performance was measure by using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 Wm^{-2}. An aperture (12.7 mm^2) was used on top of the cell to eliminate extrinsic effects such as cross-talk, waveguiding, shadow effects etc. The spectral mismatch factor was calculated by comparison of solar simulator spectrum with AM 1.5 spectrum at room temperature.

*Synthesis of 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (**4**).* A solution of tetradecane-7,8-dione (**2**) (1.8 ml, 7.95 mmol), 3,6-dibromo-4,5-difluorobenzene-1,2-diamine (**3**) (2.03 g, 6.62 mmol), and ethanol (150 ml) was heated at 70°C overnight. After cooling to room temperature, the reaction mixture was treated with water and ethyl acetate. The aqueous phase was extracted with ethyl acetate and combined organic layer was dried with $MgSO_4$. After concentration of the organic phase under reduced pressure, the residue was purified by column chromatography to give compound **4** as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.89 (t, 6H, $J = 7.0$ Hz), 1.33-1.40 (m, 12H), 1.88 (quin, 4H, $J = 7.8$ Hz), 3.04 (t, 4H, $J = 7.5$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 14.06, 22.60, 27.43, 29.12, 31.73, 34.57, 109.15, 135.61, 149.5 (d, $J = 254$ Hz, C−F), 158.03. HRMS(*m/z*, EI^+) calcd for $C_{20}H_{26}Br_2F_2N_2$ 490.0431, found 490.0435

*Synthesis of 6,7-difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline (**5**).* A solution of 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (**4**) (5.63 g, 11.44 mmol) and tributyl(2-thienyl)stannane (17.08 g, 6.42 mmol) in 250 ml of THF at room temperature was treated with dichlorobis(triphenylphosphine)palladium(II) (2 mol%). The reaction mixture was stirred for 12 hr at 110°C, concentrated under reduced pressure, and the residue was purified by flash column chromatography to give compound **5** as a red solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.89 (t, 6H, $J = 7.0$ Hz), 1.35-1.48 (m, 12H), 1.97 (quin, 4H, $J = 7.7$ Hz), 3.07 (t, 4H, $J = 7.5$ Hz), 7.21 (d of d, 2H, $J = 5.4$ and 4.0 Hz), 7.59 (d, 2H, $J = 5.4$ Hz), 7.99 (d, 2H, $J = 3.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 14.10, 22.63, 27.88, 29.29, 31.78, 34.63, 117.24, 126.12, 129.37, 130.22, 130.99, 134.31, 148.68 (d, $J = 255$ Hz, C−F), 154.87.

*Synthesis of 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (**6**).* 6,7-Difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline (**5**) (0.7 g, 1.4 mmol) was brominated with *N*-bromosuccinimide (NBS) (0.5 g, 2.8 mmol) in THF (10 mL) at room temperature. After stirring for 24 h, water (100 mL) and ethyl acetate (200 mL) were added. The organic phase was washed with 3 × 200 mL of water. The organic phase was concentrated under reduced pressure and the residue was purified by flash column chromatography to give compound **6** as a red solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.91 (t, 6H, $J = 7.0$ Hz), 1.38-1.48 (m, 12H), 1.98 (quin, 4H, $J = 7.5$ Hz), 3.09 (t, 4H, $J = 7.5$ Hz), 7.15 (d, 2H, $J = 4.3$ Hz), 7.75 (d, 2H, $J = 4.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 14.21, 22.59, 27.52, 29.42, 31.91, 34.88, 115.58, 118.52, 128.49, 129.68, 132.13, 132.45, 147.91(d, $J = 256$ Hz, C−F), 154.50.

*Polymerization of poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,8-(6,7-difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline)] (**PCDTQxF**).* Carefully purified 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-*N*-9"-heptadecanylcarbazole (**7**) (552 mg, 0.84 mmol), 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (**6**) (550 mg, 0.84 mmol), P(*o*-tolyl)$_3$ (40 mol%) and Pd$_2$(dba)$_3$ (3 mol%) were dissolved in 5 mL of chlorobenzene. The mixture was refluxed with vigorous stirring for 2 days under argon atmosphere. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was recovered by filtration. The resulting solid material was reprecipitated using 100 mL of THF/1.0 L of methanol several times to remove residual amount of catalyst. The resulting polymer was soluble in THF, CHCl$_3$, ODCB and toluene.

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