

Synthesis and Photovoltaic Properties of Copolymer Containing Fused Donor and Difluoroquinoxaline Moieties

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We report synthesis and photovoltaic properties of two new conjugated copolymers, **PCPDTQxF** and **PDTSQxF**, with 6,7-difluoro-2,3-dihexylquinoxaline unit prepared by Stille coupling reaction. The advantage of 6,7-difluoro-2,3-dihexylquinoxaline based copolymer are high PCEs due to lower HOMO energy level, long wavelength absorption and high hole mobility. The solid films of **PCPDTQxF** and **PDTSQxF** showed absorption bands with maximum peaks at about 623 and 493 nm and the absorption onsets at 711 and 635 nm, corresponding to band gaps of 1.74 and 1.95 eV, respectively. The oxidation onsets of the **PCPDTQxF** and **PDTSQxF** polymers were estimated to be 0.68 and 0.95 V, which correspond to HOMO energy levels of -5.48 and -5.75 eV, respectively. The **PDTSQxF** has lower HOMO energy level as compared to **PCPDTQxF** to lead higher V_{OC} value. The device comprising **PCPDTQxF**:PCBM (1:2) dissolved to a concentration of 1 wt % in ODCB showed V_{OC} value of 0.62 V, J_{SC} value of 1.14 mA/cm², and FF of 0.35, which yielded PCE of 0.25%.

Key Words : Polymer, Photovoltaic, Synthesis, Fluoro atom

Introduction

In the past few decades, solution-processed polymer solar cells (PSCs) have become an active research area caused by their potential, such as flexible, lightweight plastic substrates, and low-cost fabrication,¹ for example ink-jet printing,² brush painting³ and roll-to-roll process.^{4,5} In order to increase the absorption of the solar spectrum, low bandgap polymers that cover the near infrared region have become available in PSCs.⁶ To improve the power conversion efficiency (PCE), the ideal candidate conjugated materials as donor are required in BHJ devices: (1) low band gap in order to improve the absorption of the solar spectrum;⁷ (2) crystalline structure to improve good charge transport characteristics;⁸ (3) a low HOMO energy level to increase the open circuit voltage;⁹ (4) high molecular weight to promote hole mobility, optical property and film morphology.^{1,10,11}

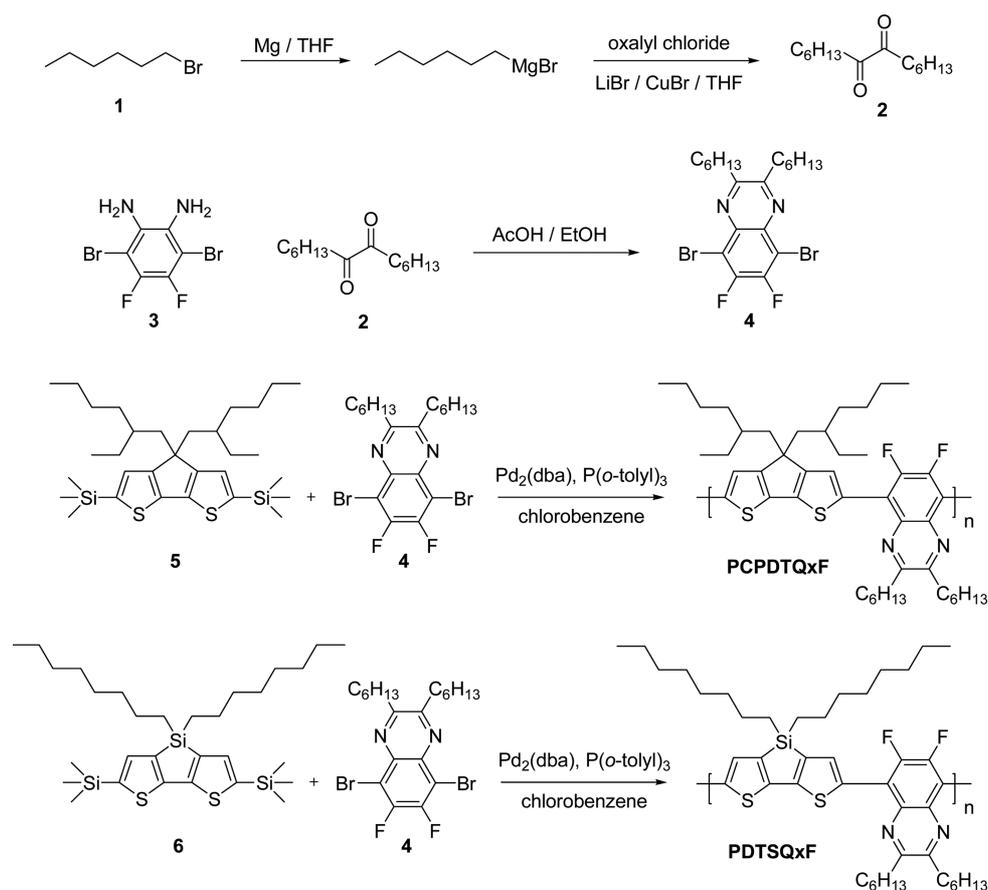
Recently, alternating low-bandgap conjugated polymers containing electron donor and acceptor subunits has been an important strategy in PSC applications caused by intramolecular charge transfer (ICT) from electron rich unit to electron deficient unit.^{1,12,13} Many of the low-bandgap (1.4–1.9 eV) conjugated polymers with excellent efficiencies have electron-deficient heterocycles, such as benzothiadiazole (BT),¹⁴ quinoxaline¹⁵ and benzimidazole,¹⁶ and electron-rich moieties, such as carbazole,¹⁷ cyclopentadithiophene,¹⁸ silolodithiophene¹⁹ and benzodithiophene.²⁰ The cyclopentadithiophene can make the polymer backbone more rigid and coplanar to enhance long conjugation lengths and strong intermolecular π - π interactions.^{21–23} By changing the bridging atom from C of cyclopentadithiophene to Si, the poly-

mers with silolodithiophene unit have been lower HOMO energy levels to enhance the V_{OC} .²⁴ Polymers containing quinoxaline unit with F atoms have been much investigated to give long wavelength absorption caused by minimized electron-withdrawing F atom to lead planarization of the conjugated backbone.^{1,25} The polymers have been much investigated to give high PCEs due to low HOMO, long wavelength absorption and high hole mobility.^{1,25}

In our previous study, new electron deficient unit, 6,7-difluoro-2,3-dihexylquinoxaline,²⁶ has been designed and utilized for the efficient ICT to generate conjugated polymers with low band gaps. Here, we report conjugated donor-acceptor polymers comprising alkyl substituted cyclopentadithiophene or silolodithiophene as the donor and 6,7-difluoro-2,3-dihexylquinoxaline as the acceptor. To the absorption spectrum for the wider coverage of the solar spectrum, these push-pull type conjugated polymers were synthesized by Stille coupling reaction of 4,4-bis-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (or 4,4-dioctyl-2,6-bis(trimethylstannyl)-4*H*-silolo-[3,2-*b*:4,5-*b'*]dithiophene) and 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline. The photovoltaic properties of the polymers were investigated by fabrication of the polymer solar cells with the configuration of ITO/PEDOT:PSS/polymer: zPCBM/TiO_x/Al.

Results and Discussion

Synthesis and Characterization. The general synthetic routes of the monomers and polymers are outlined in Scheme 1. In the first step, 3,6-dibromo-4,5-difluorobenzene-1,2-



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

diamine (3) was cyclized with tetradecane-7,8-dione (2) to obtain 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4). 4,4-Bis-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4H-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (5) (or 4,4-dioctyl-2,6-bis(trimethylstannyl)-4H-silolo[3,2-*b*;4,5-*b'*]dithiophene (6)), as electron-rich moiety, and 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4) as electron-deficient moiety were copolymerized through Stille coupling polymerization with Pd(0)-catalyst to yield PCPDTQxF (or PDTSQxF). The structures and purities of the monomers were confirmed by ¹H-NMR, ¹³C-NMR and HRMS.

Table 1 summarizes the polymerization results including molecular weight, polydispersity index (PDI) and thermal stability of the polymers. The number-average molecular weight (M_n) of 8300 and 12400 and weight-average molecular weight (M_w) of 16100 and 53100 with polydispersity index (PDI, M_w/M_n) of 1.96 and 4.29 of the PCPDTQxF

Table 1. Polymerization Results and Thermal Properties of Polymers

polymer	M_n^a (g/mol)	M_w^a (g/mol)	PDI ^a	TGA (T_d) ^b
PCPDTQxF	8300	16100	1.96	350
PDTSQxF	12400	53100	4.29	313

^aMolecular weight (M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. ^bOnset decomposition temperature (5% weight loss) measured by TGA under N₂.

and PDTSQxF were determined by GPC, respectively. The thermal properties of the PCPDTQxF and PDTSQxF were characterized by thermal gravimetric analysis (TGA) as shown in Figure 1. Thermal gravimetric analysis was performed with TGA 2950 in a nitrogen atmosphere at a heating rate of 10 °C/min to 600 °C. TGA showed that PCPDTQxF and PDTSQxF are thermally stable with only about 5% weight loss in nitrogen at temperatures of 350 and 313 °C, respectively, this high thermal stability of the resulting polymers prevents the deformation of the polymer morphology and is important for organic photovoltaics

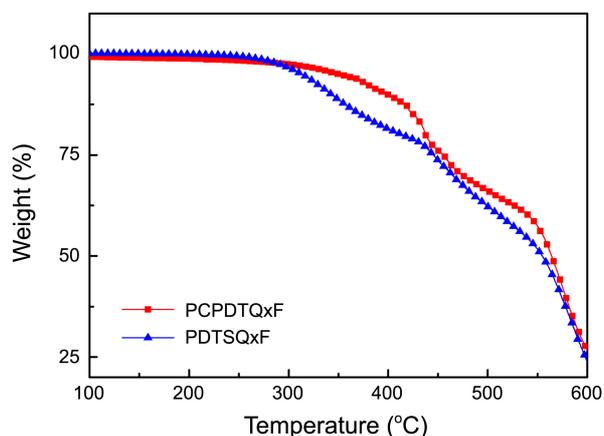
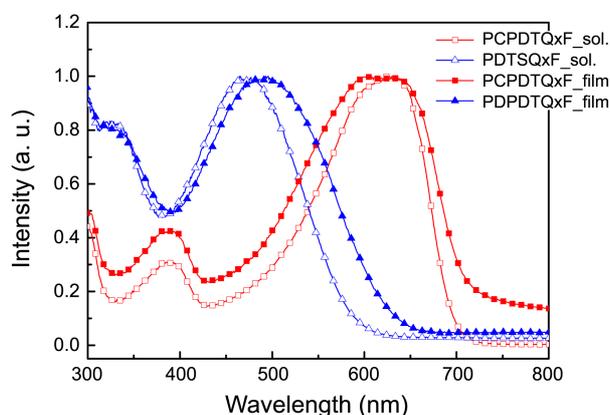


Figure 1. Thermogravimetric analysis of the polymers under N₂.

Table 2. Characteristics of the UV-vis Absorption Spectra

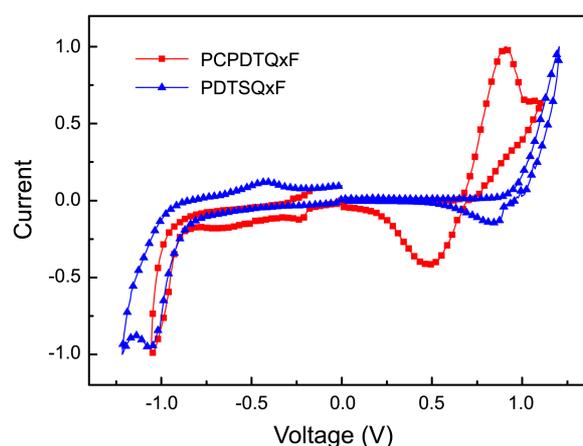
polymer	in solution (nm)	in thin film (nm)
PCPDTQx \mathbf{F}	626	623
PDTSQx \mathbf{F}	464	493

**Figure 2.** UV-visible absorption spectra of polymers in ODCB solution and the solid state.

application.

Optical Properties. The solution was prepared using *o*-dichlorobenzene (ODCB) as a solvent and the thin film by spin-coating on quartz plates from the solution in ODCB at room temperature. The UV-vis absorption spectra of the polymers in solution and as thin films are shown in Figure 2 and summarized in Table 2. The absorption spectra of **PCPDTQx \mathbf{F}** and **PDTSQx \mathbf{F}** in solution exhibited maximum peaks at about 626 and 464 nm, respectively. The solid films of **PCPDTQx \mathbf{F}** and **PDTSQx \mathbf{F}** showed absorption bands with maximum peaks at about 623 and 493 nm and the absorption onsets at 711 and 635 nm, corresponding to band gaps of 1.74 and 1.95 eV, respectively. There is little difference between the absorption spectra of the solutions and the thin films of the polymer, which can be attributed to the π - π^* transitions of the polymer. The **PCPDTQx \mathbf{F}** containing cyclopentadithiophene units has long wavelength absorption caused by rigid structure and strong intermolecular π - π interactions.^{22,23}

Electrochemical Properties. The electrochemical property of the polymer was determined from the bandgap estimated from the absorption onset wavelength, and the HOMO energy level which was estimated from the cyclic voltammetry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in

**Figure 3.** Electrochemical properties of polymers.

acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode ($\sim 0.05 \text{ cm}^2$) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO_3 electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO_3 reference electrode (calibrated by the Fc/Fc^+ redox system) was 4.8 eV below the vacuum level. The CV spectrum is shown in Figure 3, and the oxidation potential derived from the onset of electrochemical p-doping is summarized in Table 3. HOMO and LUMO levels were calculated according to the empirical formula ($E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.8) \text{ eV}$) and ($E_{\text{LUMO}} = -([E_{\text{onset}}]^{\text{red}} + 4.8) \text{ eV}$), respectively. The polymers, **PCPDTQx \mathbf{F}** and **PDTSQx \mathbf{F}** , exhibited the absorption onset wavelengths of 711 and 635 nm in solid thin films, which correspond to band gaps of 1.74 and 1.95 eV, respectively. The polymers exhibited irreversible processes in oxidation scans. The oxidation onsets of the **PCPDTQx \mathbf{F}** and **PDTSQx \mathbf{F}** polymers were estimated to be 0.68 and 0.95 V, which correspond to HOMO energy levels of -5.48 and -5.75 eV, respectively. The reduction onsets of the **PCPDTQx \mathbf{F}** and **PDTSQx \mathbf{F}** polymers were estimated to be -0.89 and -0.86 V, which correspond to LUMO energy levels of -3.91 and -3.94 eV, respectively. The electrochemical band gaps, calculated from cyclic voltammetry data, were determined to be 1.57 and 1.81 eV. The **PDTSQx \mathbf{F}** has lower HOMO energy level as compared to **PCPDTQx \mathbf{F}** to lead higher V_{OC} value.

Polymer Photovoltaic Properties. The OPVs were fabricated by spin-casting a ODCB solution containing PCBM polymers. All polymers were used as electron donors in a conventional BHJ-type OPV device, and PCBM, as is typical, was used as the acceptor. Typical J - V characteristics of

Table 3. Electrochemical Potentials and Energy Levels of the Polymers

polymers	optical band gap ^a (eV)	HOMO ^b (eV)	LUMO ^c (eV)	E_{ox}^d (V)	E_{red}^d (V)	electrochemical band gap ^e (eV)
PCPDTQx\mathbf{F}	1.74	-5.48	-3.91	0.68	-0.89	1.57
PDTSQx\mathbf{F}	1.95	-5.75	-3.94	0.95	-0.86	1.81

^aOptical energy band gap was estimated from the onset wavelength of the optical absorption. ^bCalculated from the oxidation potentials. ^cCalculated from the reduction potentials. ^dOnset oxidation and reduction potential measured by cyclic voltammetry. ^eCalculated from the E_{ox} and E_{red} .

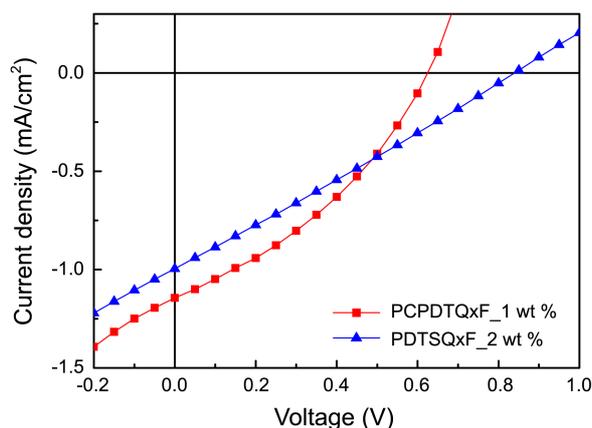


Figure 4. Current density-potential characteristics of the polymers solar cells under the illumination of AM 1.5, 100 mW/cm².

devices with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:PCBM (80 nm)/Al (100 nm) under AM 1.5G irradiation (100 mW/cm²) are depicted in Figure 4. The photovoltaic parameters for all the polymers, such as open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF), and power conversion efficiency (PCE) are summarized in Table 4. The device comprising PCPDTQx F:PCBM (1:2) dissolved to a concentration of 1 wt % in ODCB showed V_{OC} value of 0.62 V, J_{SC} value of 1.14 mA/cm², and FF of 0.35, which yielded PCE of 0.25%. The devices with PCBBTMBIs:PCBM (1:2) dissolved to a concentration of 2 wt % in ODCB demonstrated V_{OC} value of 0.71 V, J_{SC} value of 0.38 mA/cm², and FF of 0.23, leading to the PCE of 0.06%. In case of PCPDTQx F, the device with a 2 wt % polymer solution has lower PCE from lower J_{SC} . The device comprising PDTSQx F dissolved to a concentration of 1 wt % in ODCB showed V_{OC} values of 0.90 and 0.90 V, J_{SC} values of 0.61 and 0.57 mA/cm², and FF of 0.30 and 0.29, which yielded PCEs of 0.17 and 0.15% by blending with PCBM at different weight ratios (1:2 and 1:3), respectively. The device comprising PDTSQx F:PCBM (1:2) dissolved to a concentration of 2 wt % in ODCB showed V_{OC} value of 0.84 V, J_{SC} value of 1.01 mA/cm², and FF of 0.26, with lower PCE of 0.22%, caused by lower solubility in common organic solvent. The devices of synthesized polymers show lower PCE as compared to other reported fluorine substituted quinoxaline-based polymers caused by poor morphology from lower solubility.¹ The PDTSQx F has higher V_{OC} value as compared with PCPDTQx F caused by

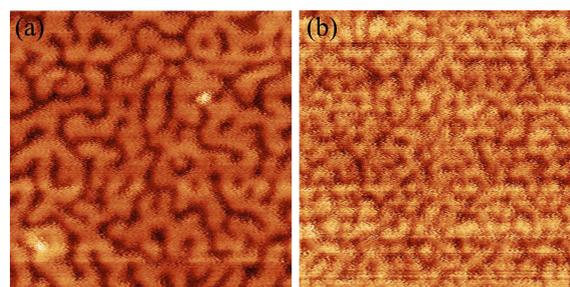


Figure 5. Atomic force microscopy images of PCPDTQx F/PCBM (1:2) (a) and PDTSQx F/PCBM (1:2) (b) dissolved to a concentration of 1 wt % in ODCB.

lower HOMO energy levels.²⁴

The morphologies of the polymer/PCBM films cast from their solutions in ODCB were studied by atomic force microscopy (AFM) as shown in Figure 5, where the images were obtained in a surface area of $2 \times 2 \mu\text{m}^2$ by the tapping mode. The PCPDTQx F:PCBM and PDTSQx F:PCBM pristine films showed surfaces with root-mean-square (rms) value of 0.43 and 0.36 nm, respectively. The devices show higher roughness to lead lower PCE caused by poor solubility.

Conclusions

New copolymers, to broaden the absorption spectrum for the wider coverage of the solar spectrum, were synthesized by Stille coupling reactions of 4,4-bis-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (or 4,4-dioctyl-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene) and 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline to generate PCPDTQx F and PDTSQx F. The absorption spectra of PCPDTQx F and PDTSQx F in solution exhibited maximum peaks at about 626 and 464 nm, and The solid films showed absorption bands with maximum peaks at about 623 and 493 nm, respectively. The HOMO energy levels of the PCPDTQx F and PDTSQx F are -5.48 and -5.75 eV, respectively. The device comprising PCPDTQx F:PCBM (1:2) dissolved to a concentration of 1 wt % in ODCB showed V_{OC} value of 0.62 V, J_{SC} value of 1.14 mA/cm², and FF of 0.35, which yielded PCE of 0.25%. The device comprising PDTSQx F:PCBM (1:2) dissolved to a concentration of 2 wt % in ODCB showed V_{OC} value of 0.84 V, J_{SC} value of 1.01 mA/cm², and FF of 0.26, with

Table 4. Photovoltaic Properties of the Polymer Solar Cells

polymers	wt %	Polymer:PCBM	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
PCPDTQx F	1 wt %	1:2	0.62	1.14	0.35	0.252
		1:3	0.16	0.02	0.24	8.6×10^{-4}
	2 wt %	1:2	0.71	0.38	0.23	0.060
PDTSQx F	1 wt %	1:2	0.90	0.61	0.30	0.165
		1:3	0.90	0.57	0.29	0.150
	2 wt %	1:2	0.84	1.01	0.26	0.219

lower PCE of 0.22%. The PDTSQxF has higher V_{OC} value as compared to PCPDTQxF caused by lower HOMO energy level.

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. ^1H 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(styrenesulfonate) (PEDOT:PSS)/polymer:PCBM/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 40 nm 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:PCBM 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, 100 nm) 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 measured by using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 W m^{-2} . An aperture (12.7 mm^2) was used on top of the cell to eliminate extrinsic effects such as crosstalk, 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 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 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 $\text{C}_{20}\text{H}_{26}\text{Br}_2\text{F}_2\text{N}_2$ 490.0431, found 490.0435.

Polymerization of Poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-*alt*-5,8-(6,7-difluoro-2,3-dihexylquinoxaline)] (PCPDTQxF). Carefully purified 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (5)¹⁸ (500 mg, 1.24 mmol), 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4) (610 mg, 1.24 mmol), $\text{P}(o\text{-tolyl})_3$ (14 mg, 0.062 mmol) and $\text{Pd}_2(\text{dba})_3$ (5 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.

Polymerization of Poly[2,6-(4,4-dioctyl-4H-silolo[3,2-*b*:4,5-*b'*]dithiophene)-*alt*-5,8-(6,7-difluoro-2,3-dihexylquinoxaline)] (PDTSQxF). Carefully purified 4,4-dioctyl-2,6-bis(trimethylstannyl)-4H-silolo[3,2-*b*:4,5-*b'*]dithiophene (6)¹⁹ (681 mg, 0.91 mmol), 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4) (4500 mg, 0.91 mmol), $\text{P}(o\text{-tolyl})_3$ (42 mg, 0.046 mmol) and $\text{Pd}_2(\text{dba})_3$ (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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