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Graphical Abstract

A series of trifluoromethylated quinoxaline-based polymers were systematically synthesized by Stille coupling reaction. The results obtained in this study clearly reveal the significant contribution of the electron-withdrawing trifluoromethyl groups in enhancing the open-circuit voltages, as well as producing a sharp improvement in the power conversion efficiencies of polymer solar cells with bulk-heterojunction structure.



Enhanced Open-Circuit Voltages of Trifluoromethylated Quinoxaline-Based Polymer Solar

Cells

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Abstract

Three quinoxaline-based conjugated polymers with donor- π -acceptor configurations have been synthesized by Stille coupling reaction. The electron-donating 2,3-dioctylthienylsubstituted benzodithiophene (BDT) unit was linked to the electron-accepting 2,3diphenylquinoxaline (DPQ) group through a thiophene bridge, to produce a reference polymer **PTBDT-Qx**. Furthermore, the strong electron-withdrawing trifluoromethyl moieties were introduced at the *para*-position of the phenyl groups in the 2,3-positions of DPQ and 6,7-difluorinated DPQ, to afford **PTBDT-QxCF3** and **PTBDT-FQxCF3**, respectively. Owing to the continuous reduction in their HOMO energy levels with increasing number of electron-withdrawing groups, the open-circuit voltage (V_{oc}) in polymer solar cells (PSCs) shows a gradual improvement in the order of **PTBDT-QxCF3** with a configuration of ITO/ZnO/polymer:PC₇₁BM/MoO₃/Al provides the best power conversion efficiency of 6.47%, together with a V_{oc} of 0.99 V, a short-circuit current of 10.03 mA/cm², and a fill factor of 65.1%.

Keywords. Quinoxaline; electron-withdrawing; 2,3-diphenylquinoxaline; trifluoromethyl; polymer solar cells

1. Introduction

Polymer solar cells (PSCs) based on bulk heterojunction (BHJ) structures between polymeric semiconductors and fullerene derivatives have attracted significant attention in the last decades, due to their unique advantages such as low cost, light weight, easy preparation, and outstanding flexibility [1, 2]. As a result of continuous efforts to optimize the material design as well as the device fabrication process, the power conversion efficiencies (PCEs) of state-of-the-art PSCs can exceed 10% [3-6]. In order to prepare conjugated polymers appropriate for high-performance PSCs, various studies have attempted to incorporate alternating electron-donating (D) and electron-accepting (A) units along the polymer backbones [7]. In this D-A configuration, the band gap of the polymers can be significantly reduced by the facile formation of an intramolecular charge transfer (ICT) state. Furthermore, important parameters of the D-A polymers including energy levels, band gap and carrier mobility can be easily tuned by the selection and combination of the suitable D and A components [8]. Among various building blocks for constructing the D-A polymers, the quinoxaline (Qx) unit has attracted attention as a promising moiety for the A component, due not only to its strong electron-withdrawing capability but also to other beneficial features such as simple synthesis and a rigid/flat conjugated structure [9-11].

Increasing the open-circuit voltage (V_{oc}) by controlling the energy levels of the conjugated polymers in the active layer of PSCs is currently considered one of the critical tasks for improving the photovoltaic properties of these systems [12]. The V_{oc} of BHJ PSCs is usually determined as the difference between the lowest unoccupied molecular orbital (LUMO) of the electron acceptor and the highest occupied molecular orbital (HOMO) of the electron donor [13]. Therefore, the development of polymeric donors with a low-lying HOMO energy level has become a task of great importance. In this regard, the simple strategy involving the incorporation of electron-withdrawing

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substituents such as fluorine into the polymer backbone has been intensively investigated [14-18]. Compared to their non-fluorinated counterparts, fluorinated polymers exhibit a substantial reduction in both LUMO and HOMO without significant alteration of their band gaps, which implies an enhanced V_{oc} value when applied in PSCs. Furthermore, the energy levels and photovoltaic properties of D-A type polymers are strongly influenced by the location and concentration of F atoms in their structures [19-21].

Besides fluorine atoms, the introduction of strong electron-withdrawing trifluoromethyl (CF₃) groups in the polymer chains can also lead to a sharp improvement in the V_{oc} of PSCs, through the efficient lowering of the HOMO energy level of the polymers [22, 23]. In particular, the CF₃ groups not only possess a higher electron-withdrawing capability than fluorine atoms but also impart unique advantages to the resultant polymers such as high thermal and chemical stability, along with good solubility [24]. The Hammett constants (σ , which are important parameters to determine the electronic characteristics of the substituents) of CF₃ and F at the *para*-position (σ_p) of benzene rings were determined to be 0.54 and 0.06, respectively [25]. For example, the presence of the CF₃ unit either on the electron-withdrawing or electron-donating moiety in D-A polymers can induce the sharp increase in the V_{oc} value of the related PSCs [22, 23, 26, 27].

Herein, we synthesized a series of D-A polymers, in which the electron-donating 2,3dioctylthienyl substituted-benzodithiophene (BDT) unit was connected to the electron-withdrawing 2,3-diphenylquinoxaline (DPQ) derivatives through a thiophene bridge. Owing to advantageous features including high electron affinity, simple preparation, and facile modification, the DPQ unit was selected as one of basic building blocks for the preparation of reference **PTBDT-Qx** polymer (Figure 1). It has also been reported that the incorporation of the electron-withdrawing F atoms at the *para*-position of the phenyl rings located in the 2,3-positions of DPQ can efficiently enhance the V_{oc} of the corresponding BHJ PSCs [19, 28]. Inspired by these results, strong electron-withdrawing CF₃ moieties (in alternative to fluorine atom) were incorporated at the same positions of DPQ and 6,7-difluorinated DPQ, to afford the target polymers **PTBDT-QxCF3** and **PTBDT-FQxCF3**, respectively (Figure 1). Owing to the presence of the strong electron-withdrawing moieties, **PTBDT-QxCF3** and **PTBDT-FQxCF3** provide markedly different optical and electrochemical properties compared to the reference **PTBDT-Qx** polymer. In particular, the V_{oc} of inverted-type PSCs based on the three polymers shows a gradual increase in the order of **PTBDT-Qx < PTBDT-QxCF3** with corresponding values of 0.71, 0.91, and 0.99 V, respectively. The increasing trend of V_{oc} is also in good agreement with the progressive increase in the PCEs of PSCs prepared using **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3** (2.61, 4.61, and 6.47%, respectively).



Figure 1. Chemical structures of PTBDT-Qx, PTBDT-QxCF3, and PTBDT-FQxCF3.

2. Results and Discussion

2.1. Synthesis and characterization

The synthetic approaches used to prepare monomers and polymers are illustrated in Scheme 1. First, the dithiophene-attached benzothiadiazole derivatives of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (1) and 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2)

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were converted to the associated DPQ units through zinc-mediated reduction followed by a condensation process between the intermediate *o*-diamine and α -diketone (Scheme 1). The reaction of **1** with benzyl and 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione afforded 2,3-diphenyl-5,8-di(thiophen-2-yl)quinoxaline (**3**) and 5,8-di(thiophen-2-yl)-2,3-bis(4-(trifluoromethyl)phenyl)quinoxaline (**4**), respectively. Moreover, the DPQ possessing two CF₃ groups and two F atoms on its 2,3- and 6,7-positions, respectively, (**5**) was successfully produced by the reaction between **2** and 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione. Finally, bromination of **3**, **4**, and **5** using *N*-bromosuccinimide (NBS) yielded the dibrominated DPQ-based monomers **6**, **7**, and **8**, respectively.



Scheme 1. Synthesis of monomers and polymers: (i) Zn/acetic acid, at 100 °C for 12 h; (ii) α -diketone/acetic acid, reflux for 12 h; (iii) NBS, room temperature (RT) overnight; (iv) tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), at 90 °C for 48 h.

In order to prepare conjugated polymers with a typical D-A configuration, the electron-donating 2,3-dioctylthienyl-substituted BDT monomer (9) was polymerized with the electron-withdrawing DPQ-based monomers 6, 7, and 8 under Stille coupling conditions affording the PTBDT-Qx, PTBDT-QxCF3, and PTBDT-FQxCF3 target polymers, respectively. The number average molecular weights (M_n) of PTBDT-Qx, PTBDT-QxCF3, and PTBDT-FQxCF3, recorded by gel permeation chromatography (GPC), were 23.05, 20.21, and 14.61 KDa, respectively, with polydispersity indexes of 2.74, 2.86, and 2.83, respectively. In addition, the three polymers exhibited not only good solubility in common organic solvents such as chloroform, tetrahydrofuran (THF), and toluene, but also high thermal stability. The onset decomposition temperature at 5% weight loss ($T_{d5\%}$) for all polymers could reach up to 415°C (Figure 2).



Figure 2. Thermogravimetric analysis (TGA) thermograms of **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3** at a heating rate of 10 °C/min under N₂.

2.2. Optical and electrochemical properties

The UV-Vis absorption spectra of **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3** measured for films grown on a glass substrate are shown in Figure 2a, and the corresponding data are summarized in Table 1. Two distinct UV-Vis absorption bands at 400–490 and 500–750 nm

were observed for all polymers. The peak at shorter wavelengths (400–490 nm) corresponds to the localized π - π * transition of polymer chains, while the peak in the longer wavelength region (500–750 nm) is related to the ICT between the D and A components in the polymer backbone. Interestin gly, the absorption maxima of **PTBDT-QxCF3** and **PTBDT-FQxCF3** at longer wavelengths were s hifted to the higher-energies compared to the corresponding peak of **PTBDT-Qx**. These results wer e attributed to the increased band gap caused by the significant reduction in the HOMO levels of **PT BDT-QxCF3** and **PTBDT-FQxCF3** (*vide infra*). The similar blue-shift in absorption spectra have b een also reported for other conjugated polymers possessing electron-withdrawing groups [22, 29]. In addition, weak shoulders at ca. 650 nm were observed in the absorption spectra of **PTBDT-QxCF3** and **PTBDT-FQxCF3**, respectively, due to the forced intermolecular aggregation through existing F-F and F-H interactions [30, 31]. The optical band gaps of **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3** determined from the absorption edges were 1.68, 1.69, and 1.71 eV, respectively (Table 1).

Cyclic voltammetry (CV) measurements were carried out to investigate the energy levels of the polymers, and the results are shown in Figure 2b. The HOMO energy level of the polymers was calculated from the onset potential of oxidation by assuming the absolute energy level of ferrocene is 4.8 eV below the vacuum level. The HOMO energy levels of **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3**, calculated from the oxidation onset potential of the cyclic voltammograms with a ferrocene(Fc)/ferrocenium(Fc⁺) external standard were -5.19, -5.47, and -5.57 eV, respectively. Upon incorporation of the strong electron-withdrawing CF₃ moieties into the polymer structure, the HOMO energy of **PTBDT-QxCF3** (-5.47 eV) was significantly reduced compared to that of **PTBDT-Qx** (-5.19 eV). A further slight decrease of the HOMO energy (from -5.47 to -5.57 eV) was observed for **PTBDT-FQxCF3**, due to the additional introduction of two F atoms. In addition, the

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LUMO energy levels of **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3**, calculated from the difference between HOMO level and the optical band gap, were -3.55, -3.78, and -3.86 eV, respectively. The electrochemical parameters of all polymers are also listed in Table 1. Again, the overall results of the UV-Vis and CV measurements highlight the marked effect of the electron-withdrawing CF_3 unit on the optical and electrochemical properties of DPQ-based polymers.



Figure 3. (a) UV-visible spectra of polymer films on a glass substrate (spectra are offset for clarity) and (b) cyclic voltammograms of polymers.

	$\lambda_{edge}(nm)^{a}, E_{gap}^{opt}(eV)^{b}$	λ_{max}^{film} (nm) ^c	HOMO (eV) ^c	LUMO (eV) ^d
PTBDT-Qx	738, 1.68	441, 622	-5.19	<mark>-3.55</mark>
PTBDT-QxCF3	733, 1.69	443, 597	<mark>-5.47</mark>	<mark>-3.78</mark>
PTBDT- FOxCF3	725, 1.71	441, 601	<mark>-5.57</mark>	<mark>-3.86</mark>

Table 1. Summary of optical and electrochemical properties.

^a absorption edge of polymer film; ^b estimated from the absorption edge; ^c maximum absorption wavelength of the film; ^c estimated from the oxidation onset potential; ^d estimated from the HOMO and the optical band gap.

2.3. Theoretical calculations

To investigate the electronic structures and frontier molecular orbitals of **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3**, density functional theory (DFT) calculations were performed at the B3LYP/6-31G** level using the Gaussian 09 program [32]. For simplicity, the octyl side chains of the polymers were replaced by short methyl groups, and a two-repeating unit model was adopted in calculations. As shown in Figure 4, the electron density of the HOMO is almost completely delocalized along the polymer backbone, while that of the LUMO is localized on the electron-withdrawing DPQ units. The calculations also show that the introduction of the strong electron-withdrawing CF₃ substituents significantly lowers both the HOMO and LUMO energy levels of the polymers (from -4.73 and -2.43 eV for **PTBDT-Qx**, respectively, to -4.93 and -2.71 eV for **PTBDT-QxCF3**, respectively). Moreover, the incorporation of two additional fluorine atoms in the DPQ unit to afford **PTBDT-QxCF3** causes further reduction in the HOMO and LUMO energy levels of the polymers (-4.95 and -2.80 eV). The trends in the theoretical HOMO and LUMO levels of the polymers agree well with determined from the experimental results (Table 1).



Figure 4. Frontier molecular orbitals of two-repeating unit models with HOMO and LUMO energy levels calculated at the B3LYP/6-31G** level for (a) **PTBDT-Qx**, (b) **PTBDT-QxCF3**, and (c) **PTBDT-FQxCF3**.

2.4. Photovoltaic properties

The photovoltaic properties of the polymers were investigated by fabricating inverted-type PSCs with indium tin oxide(ITO)/ZnO(25 nm)/active layer(polymer: [6,6]-Phenyl C₇₁ butyric acid methyl ester (PC₇₁BM))(80 nm)/MoO₃(10 nm)/Ag(100 nm) structure. The energy levels of all materials used for the device fabrication, shown in Figure 5, demonstrate the efficient charge separation and charge transport process in the PSCs. We tested different polymer:PC₇₁BM weight rations (from 3:2 to 3:7), in the active layer of BHJ PSC, and the optimum blend ratios of **PTBDT-Qx**, **PTBDT-**

QxCF3, and **PTBDT-FQxCF3** to PC₇₁BM were determined to be 3:3, 3:5, and 3:5, respectively (Table S1).



Figure 5. Energy level diagram of all materials used for the fabrication of inverted-type PSCs.

Figure 6a shows the optimized current density-voltage (*J-V*) curves of the polymers with the highest PCEs under 1.0 sun condition (the inset shows the curves obtained under dark conditions), and the corresponding device parameters are summarized in Table 2. Interestingly, the PCEs of the polymers gradually increased in the order of **PTBDT-Qx** (2.61%) < **PTBDT-QxCF3** (4.61%) < **PTBDT-FQxCF3** (6.47%). Moreover, the trend in the PCE values is strongly correlated with the similar gradual increase in the V_{oc} of the PSCs. The V_{oc} values measured for the devices fabricated with **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3** were 0.71, 0.91, and 0.99 V, respectively. Therefore, the introduction of CF₃ groups at the *para*-position of the phenyl rings located in the 2,3-positions of DPQ moieties in the polymer structure can induce a sharp increase in V_{oc} , of about 28% relative to the original value (from 0.71 V for **PTBDT-Qx** to 0.91 V for **PTBDT-QxCF3**). A similar improvement in the V_{oc} of the corresponding PSCs was obtained upon the incorporation of fluorine atoms at the same positions of DPQ moieties of D-A type polymers [19]. The attachment of fluorine atoms (in addition to the CF₃ groups) on the 6,7-positions of DPQ,

affording **PTBDT-FQxCF3** resulted in a further enhancement in V_{oc} up to 0.99 V. The observed changes in the Voc values of PSCs in good agreement with the HOMO levels of the applied polymers (vide supra). In addition to the V_{oc} values, the incorporation of the electron-withdrawing groups in the polymer skeleton also improve fill factors (FFs) of the devices, and the highest value of 65.1% was achieved for the PSC fabricated with PTBDT-FQxCF3. The device based on **PTBDT-FQxCF3** also displayed the highest short-circuit current (J_{sc}) value of 10.03 mA/cm², relative to those of the devices based on PTBDT-Qx (9.13 mA/cm²) and PTBDT-QxCF3 (8.38 mA/cm²). Overall, these results show that the incorporation of the strong electron-withdrawing CF₃ groups in the polymer backbone is highly beneficial for the photovoltaic properties of PSCs, mainly, through a significant enhancement in the V_{oc} and FF values. As shown in Figure 6b, the incident photon-to-current efficiency (IPCE) curves of all PSCs are well consistent with the absorption behavior of the polymers in the range of 300-800 nm, and provide an adequate explanation for the trend of the J_{sc} values. The calculated J_{sc} values based on incident photon-to-current efficiency (IPCE) spectra showed very good agreement with the J_{sc} data of the devices under 1.0 sun. Furthermore, the series resistance (R_s) of the devices was calculated from the J-V curves under dark conditions (inset of Figure 6a). was calculated. The R_s of the device based on **PTBDT-Qx** (9.61 Ω cm²) was much larger than the values measured for the devices based on **PTBDT-QxCF3** (3.36 Ω cm²) and **PTBDT-FQxCF3** (2.54 Ω cm²) (Table 2). Therefore, the R_s values are gradually decreased with increasing number of electron-withdrawing groups on the DPQ unit, in good agreement with the photovoltaic properties of the devices.



Figure 6. (a) Current density vs. voltage curves of PSCs with optimum blend ratio of polymeric donors to PC₇₁BM, showing the best performances under 1.0 sun condition (inset: under dark conditions); (b) IPCE spectra of PSCs based on **PTBDT-Qx** (squares), **PTBDT-QxCF3** (circles), and **PTBDT-FQxCF3** (triangles).

Table 2. Best photovoltaic parameters of the PSCs. The average photovoltaic parameters of each device are shown in parentheses.

	$\mathbf{I}_{\rm c}$ (m A (orm ²)	Calculated J _{sc}		EE (0/)	DCE(0/)	$\mathbf{B} (\mathbf{O} \mathrm{am}^2)^{\mathrm{b}}$
	J_{sc} (mA/cm)	(mA/cm ²) ^a	V _{oc} (V)	FF (%)	FCE (%)	\mathbf{K}_{s} (S2 CIII)
	9.13		0.71	40.3	2.61	0.44
PTBDT-Qx	(9.05)	9.07	(0.71)	(39.7)	(2.55)	9.61

PTRDT-OxCF3	8.38	8 43	0.91	60.5	4.61	3 36
	(8.07)	0.45	(0.91)	(60.9)	(4.47)	5.50
DTDDT FOrCE2	10.03	10.11	0.99	65.1	6.47	2.54
PIBDI-FQXCF3	(10.04)	10.11	(0.99)	(<mark>64.0</mark>)	(6.46)	2.54

^acalculated from the IPCE curves, ^bSeries resistance estimated for the corresponding best device.

To investigate the charge carrier transport properties of the polymers, we fabricated and tested hole- and electron-only devices with ITO/PEDOT:PSS (35 nm)/ polymer:PC₇₁BM (~ 90 nm)/Au (50 nm) and ITO/Al (50 nm)/polymer:PC₇₁BM (~ 90 nm)/Al (100 nm) structures, respectively. As shown in figure 7a and 7b, the *J-V* curves of all polymers exhibited space charge-limited current (SCLC) behavior, and could be fitted by the well-known Mott-Gurney law [33]. We calculated the charge mobility using the permittivity of 3.9 for the active layer. The hole mobilities of the devices based on **PTBDT-Qx**, **PTBDT-QxCF3**, and **PBDT-FQxCF3** were 6.03×10^{-4} , 5.61×10^{-4} , and 6.29×10^{-4} cm²V⁻¹s⁻¹, respectively. In addition, the electron mobilities of the devices fabricated with **PTBDT-Qx**, **PTBDT-QxCF3**, and **PBDT-FQxCF3** were 6.00×10^{-4} , 4.98×10^{-4} , and 7.25×10^{-4} cm²V⁻¹s⁻¹, respectively. The hole and electron mobilities of **PBDT-FQxCF3** were higher than those of **PTBDT-Qx** and **PTBDT-QxCF3**. This result is also consistent with the better performances of the **PTBDT-FQxCF3**-based device compared with those of based on **PTBDT-Qx** and **PBDT-FQx**.



Figure 7. Current density vs. voltage curves of (a) hole-only (ITO/PEDOT:PSS (35 nm)/ polymer:PC₇₁BM (~ 90 nm)/Au (50 nm)) and (b) electron-only (ITO/Al (20 nm)/polymer:PC₇₁BM (~ 90 nm)/Al (100 nm)) devices based on **PTBDT-Qx** (squares), **PTBDT-QxCF3** (circles), and **PTBDT-FQxCF3** (triangles) The insets show square root of current density vs. voltage (V)-built-in voltage (V_{bi}), together with fitted lines.

The morphologies of the active layers in PSCs were investigated by the transmission electron microscopy (TEM) and the results were shown in figure 8. In comparison with the active layer based on **PTBDT-QxCF3** and **PTBDT-FQxCF3**, the active layer based on **PTBDT-Qx** showed relatively larger phase separation and aggregation. In addition, the active layer based on **PTBDT-QxCF3** and **PTBDT-FQxCF3** showed the better bicontinuous interpenetrating networks than that of the active layer based on **PTBDT-Qx**. The best FF of the device based on **PTBDT-QxCF3** and **PTBDT-FQxCF3** were 60.5 and 65.1%, respectively, which are a 50 and 61% increase compared to that of the device based on **PTBDT-Qx**. The morphologies of the active layer support that the FFs of the devices based on **PTBDT-QxCF3** and **PTBDT-QxCF3** and **PTBDT-QxCF3** and **PTBDT-QxCF3** and **PTBDT-QxCF3**, and **PTBDT-QxCF3**, inspected by tapping-mode atomic force microscopy (AFM) measurements as well, are shown in **Figure S1**. The root-mean-square (RMS) of the surfaces of the active layers based on **PTBDT-QxCF3** were 1.56, 1.70, and 1.60 nm, respectively, indicating that the performances of PSCs are almost independent of the surface morphology and roughness.



Figure 8. TEM images of the active layer based on (a) **PTBDT-Qx**, (b) **PTBDT-QxCF3**, and (c) **PTBDT-FQxCF3**.

3. Conclusions

Three conjugated polymers, in which the electron-donating 2,3-dioctylthienyl-substituted BDT unit was connected to the electron-accepting DPQ derivatives through a thiophene bridge, have been prepared by Stille coupling reaction. To investigate the effects of the strong electron-withdrawing CF₃ substituent on the intrinsic properties of the polymers, CF₃ was systematically incorporated at the para-position of the phenyl groups located in the 2,3-positions of both DPQ, 6,7-difluorinated DPQ, to afford **PTBDT-QxCF3** and **PTBDT-FQxCF3**, respectively. Owing to the strong influences of the CF₃ unit, **PTBDT-QxCF3** and **PTBDT-FQxCF3** exhibit the significant lowering of the HOMO energy levels, which can induce the great enhancement in V_{oc} values of photovoltaic cells. In addition, the incorporation of additional F atom in the presence of CF3 can trigger other positive effects such as enhancement of charge carrier mobility, and formation of better bicontinuous interpenetrating networks in an active layer of device. So, J_{sc} and *FF* of the photovoltaic cells with CF3/F groups can increase sharply. As a result, the PCEs of inverted-type PSCs based on these polymers show a gradual increase in the order of **PTBDT-Qx < PTBDT-QxCF3**, with corresponding values of 2.61, 4.61, and 6.47%, respectively. The

PCE enhancement can be attributed to the beneficial effect of the CF₃ and CF₃/F substituents incorporated in the polymer backbone, such as the increase in V_{oc} through the lowering HOMO energy levels and the concomitant enhancement in *FF*. Therefore, this study provides meaningful insight into the synthesis and structure-property relationships of conjugated polymers with strong electron-withdrawing CF₃ substituents, which will support their use in various applications such as photovoltaic cells and field-effect transistors.

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Supplementary information (experimental details including materials, methods, and the synthesis of monomer and polymers. In addition, summary of the photovoltaic parameters of the PSCs based on **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3** at different weight ratios between donor and PC₇₁BM, AFM images of the active layers based on **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3**, and

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Electronic Supporting Information (ESI) for:

Enhanced Open-Circuit Voltages of Trifluoromethylated Quinoxaline-Based Polymer Solar Cells

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Table S1. The photovoltaic parameters of the PSCs based on **PTBDT-Qx**, **PTBDT-QxCF3**, and **PTBDT-FQxCF3**. The average and deviation (10 devices are averaged) for the photovoltaic parameters of each device are given in parentheses.

Donor	Blend	$J_{ m sc}$	$V_{ m oc}$	FF	PCE	R_s
	ratio ^a	(mA/cm ²)	(V)	(%)	(%)	$(\Omega \text{ cm}^2)$

	3.3	9.13	0.71	40.3	2.61	0.61
PTBDT-Qx	5.5	(9.05±0.08)	(0.71±0.00)	(39.7±0.58)	(2.55±0.04)	9.01
	2.4	8.92	0.68	40.9	2.48	
	5.4	(8.84±0.06)	(0.68±0.00)	(40.4±0.36)	(2.43±0.03)	
	3.5	8.42	0.68	40.6	2.32	
	5.5	(8.37±0.09)	(0.68±0.00)	(40.5±0.23)	(2.31±0.02)	
	3.3	8.06	0.93	52.6	3.94	<u> </u>
	5.5	(7.98±0.06)	(0.93±0.00)	(52.7±0.15)	(3.91±0.04)	
	3.1	8.03	0.92	60.4	4.46	
PTBDT-OxCF3	5.4	(8.03±0.13)	(0.92±0.00)	(59.6±0.92)	(4.40±0.05)	-
	3.5	8.38	0.91	60.5	4.61	3 36
	5.5	(8.07±0.21)	(0.91±0.00)	(60.9±0.52)	(4.47±0.09)	5.50
	3.6	7.63	0.89	58.5	3.97	
	5.0	(7.70±0.14)	(0.87±0.02)	(55.3±2.16)	(3.70±0.17)	-
	3.2	8.44	1.00	55.5	4.69	
	5.2	(8.46±0.15)	(1.00±0.00)	(54.1±1.23)	(4.57±0.08)	-
_	3.3	9.56	1.00	61.0	5.83	
	5.5	(9.34±0.22)	(1.00±0.00)	(60.7±0.08)	(5.67±0.16)	-
	3.4	10.00	0.99	63.6	6.30	_
PTBDT-FQxCF3	5.1	(9.90±0.06)	(0.99±0.00)	(63.8±0.54)	(6.25±0.04)	
	3.5	10.03	0.99	65.1	6.47	2.54
	5.5	(10.04±0.01)	(0.99±0.00)	(64.9±0.20)	(6.46±0.01)	
	3.6	8.78	0.98	66.4	5.71	_
	5.0	(8.67±0.07)	(0.98±0.00)	(66.7±0.62)	(5.68±0.03)	-
	3.7	8.35	0.98	67.0	5.49	
	5.1	(8.21±0.13)	(0.98±0.00)	(67.2±0.24)	(5.41±0.08)	-

^a mass ratio of polymeric donor to PC₇₁BM, ^b series resistance estimated from the corresponding best device.

Experimental section

Materials and methods. 1 [1], **2** [2], **3** [3], 5,8-di(5-bromothiophen-2-yl)-2,3diphenylquinoxaline (**6**) [3], and 2,6-bis(trimethyltin)-4,8-di(2,3-dioctylthiophen-5-yl)-benzo[1,2b:4,5-b']dithiophene (**9**) [4], and 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione [5] were prepared following previously reported methods. All other chemicals and solvents were purchased from Aldrich. ¹H, ¹³C, and ¹⁹F NMR spectra were obtained with a JEOL JNM ECP-400 spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analyses were carried out using an Ultraflex spectrometer (Bruker). UV-Vis spectra were recorded using a JASCO V-530 spectrometer. GPC measurements were conducted on an Agilent 1200 series instrument in the presence of THF eluent. CV analyses were carried out using a VersaSTAT3 potentiostat (Princeton Applied Research), with tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) electrolyte in acetonitrile. A glassy carbon electrode coated with polymers and a platinum wire were used as a working and counter electrode, respectively. A silver wire was used as pseudo-reference electrode with a Fc/Fc⁺ external standard. AFM imaging measurement were carried out using a NanoScope V (Bruker) microscope operated in tapping mode.

Fabrication and analysis of PSCs. PC₇₁BM,(catalog no. nano-cPCBM-SF) was purchased from Nano-C, Inc. Inverted-type of PSCs with ITO/ZnO/active layer (polymer:PC₇₁BM)/MoO₃/Ag structure were fabricated to investigate the photovoltaic properties of the polymers. First, a ZnO film was deposited on a cleaned ITO surface by a sol-gel process followed by thermal curing at 200 $^{\circ}$ C for 10 min. Then, the active layer composed of polymer and PC₇₁BM was spin-coated using chlorobenzene solution at 600 rpm for 60 s. 1.8-diiodooctane (DIO, 3% v/v) was added to as a processing additive during the formation of the active layer. Finally, MoO₃ and Ag layers were sequentially deposited by thermal evaporation at 2 × 10⁻⁶ Torr through a shadow mask with an active area of 0.13 cm². The *J-V* characteristics of the PSCs were examined using a Keithley 2400

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source- measure unit under AM 1.5G illumination at 100 mW/cm² from a 150 W Xe lamp. The calibration of the solar simulation was conducted using a Si reference cell with a KG5 filter certified by the National Institute of Advanced Industrial Science and Technology.

Synthesis of 5,6-di(thiophen-2-yl)-2,3-bis(4-(trifluoromethyl)phenyl)quinoxaline (4). A mixture of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (1) (0.70 g, 2.33 mmol) and zinc powder (3.05 g, 46.66 mmol) in acetic acid (60 mL) was stirred at 80 °C for 12 h. Once the reaction was completed, zinc powder was removed by filtration and the filtrate was carefully collected. After adding 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione (0.81 g, 2.34 mmol) to the filtrate, the mixture was refluxed overnight. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The ethyl acetate fractions were the separated and dried over magnesium sulfate. Solvents were removed using a rotary evaporator, and the crude residue was purified by recrystallization (ethanol/chloroform 1:4, v/v) to give **3** as a light brown solid (0.61 g, yield = 45%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.20 (s, 2H), 7.85-7.83 (m, 6H), 7.66 (d, 4H, J = 8.32 Hz), 7.53 (d, 2H, J = 5.12 Hz), 7.19 (dd, 2H, J = 5.12, 3.76 Hz). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 149.8, 141.5, 138.1, 137.3, 131.3, 130.7, 129.2, 127.7, 126.7, 126.6, 125.4, 124.9, 123.1. ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -62.5. MALDI-TOF, m/z: Calcd, 582.066; found, 582.202 [M⁺].

Synthesis of 6,7-difluoro-5,8-di(thiophen-2-yl)-2,3-bis(4-(trifluoromethyl)phenyl)quinoxaline (5). A mixture of 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2) (0.3 g, 0.9 mmol), zinc powder (1.17 g, 18 mmol), and acetic acid (24 mL) was stirred at 80 °C for 12 h. After filtering, 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione (0.31 g, 0.9 mmol) was added to the filtrate, followed by heating under reflux overnight. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The ethyl acetate fractions were separated

and dried over magnesium sulfate. Solvents were removed using a rotary evaporator, and the crude residue was purified by recrystallization (ethanol/chloroform 1:3, v/v) to give **5** as a yellow solid (0.14 g, yield = 32%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.04 (d, 2H, *J* = 3.76 Hz), 7.83 (s, 4H, *J* = 8.32 Hz), 7.68 (m, 6H), 7.28 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 149.8, 141.0, 135.2, 131.5, 131.3, 131.1, 130.7, 130.5, 130.3, 126.8, 125.6, 124.8, 123.0. ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -62.6, -126.8. MALDI-TOF, *m/z*: Calcd, 618.563; found, 619.046 [M⁺].

Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(trifluoromethyl)phenyl)quinoxaline (7). 5,6-di(thiophen-2-yl)-2,3-bis(4-(trifluoromethyl)phenyl)quinoxaline (4) (0.35 g, 0.60 mmol) and NBS (0.24 g, 1.32 mmol) were dissolved in dry THF (20 mL). The mixture was stirred at room temperature for 12 h in the dark. Once the reaction was completed, the mixture was poured into water and extracted with ethyl acetate. The ethyl acetate fractions were separated and dried over magnesium sulfate. Solvents were removed using a rotary evaporator, and the crude residue was purified by recrystallization (methanol/ethyl acetate 1:4, v/v) to give **7** as a red solid (0.32 g, yield = 72%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8,17 (s, 2H), 7.81 (d, 4H, *J* = 5.36 Hz), 7.72 (d, 4H, *J* = 5.36 Hz), 7.59 (d, 2H, *J* = 2.68 Hz), 7.16 (d, 2H, *J* = 2.68 Hz). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 150.8, 141.2, 139.0, 136.9, 130.8, 130.7, 129.4, 126.6, 126.0, 125.6, 124.8, 123.0, 117.5. ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -62.5. MALDI-TOF, m/z: Calcd, 739.885; found, 739.888 [M⁺].

Synthesisof5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-bis(4-(trifluoromethyl)phenyl)quinoxaline(8).6,7-difluoro-5,8-di(thiophene-2-yl)-2,3-bis(4-(trifluoromethyl)phenyl)quinoxaline(5)(0.14 g, 0.23 mmol) and NBS (0.09 g, 0.51 mmol) weredissolved in THF (15 mL). The reaction mixture was stirred at room temperature for 12 h in a darkroom. After that, the mixture was poured into water and extracted with chloroform. The chloroform

fractions were separated and dried over magnesium sulfate. Solvents were removed using a rotary evaporator, and the crude residue was purified by recrystallization (methanol/chloroform 1:4, v/v) to give **8** as an orange solid (0.14 g, yield = 81%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83-7.78 (m, 6H), 7.72 (d, 4H, *J* = 8.32 Hz), 7.22 d, 2H, *J* = 4.32 Hz). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 150.2, 140.5, 134.7, 131.9, 131.7, 131.6, 131.5, 131.4, 129.7, 127.1, 125.7, 119.7, 117.6. ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -62.6, -126.5. MALDI-TOF, *m/z*: Calcd, 776.355; found, 775.893 [M⁺].

Synthesis of polyquinoxalines via Pd-catalyzed Stille reaction

BDT monomer (0.20 mmol), dibrominated quinoxaline monomer (0.20 mmol), and Pd(PPh₃)₄ (3 mol%) were dissolved in dry toluene (10 mL) in a Schlenk flask. After flushing with N₂ for 15 min, the reaction mixture was stirred at 90 °C for 48 h under N₂ atmosphere. At the end of the polymerization, 2-trimethylstannylthiophene and 2-bromothiophene were successively added as end-capping agents with an interval of 3 h. After cooling to room temperature, the mixture was poured into methanol, and the precipitated dark solids were collected by filtration. The solids were further purified by sequential Soxhlet extractions with methanol, acetone, hexane, and chloroform. The polymers in the chloroform fraction were recovered by precipitation into methanol, and finally dried in a vacuum oven at 50 °C.

PTBDT-Qx: **9** and **6** were used as monomers. Yield: 87% (deep purple solid). GPC (THF): $M_n = 23.04 \text{ KDa}$, $M_w = 63.24 \text{ KDa}$, PDI = 2.74. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.93-7.72 (br, 4H), δ 7.65-7.10 (br, 14H), δ 3.15-2.62 (br, 8H), δ 1.88-1.66 (br, 8H), δ 1.52-1.21 (br, 40H), δ 0.97-0.81 (br, 12H). Elemental analysis calcd (%) for C₇₈H₉₀N₂S₆: C 75.07, H 7.27, N 2.24; found: C 74.65, H 7.01, N 2.22.

PTBDT-QxCF3: **9** and **7** were used as monomers. Yield: 85% (deep purple solid). GPC (THF): $M_n = 20.31 \text{ KDa}, M_w = 58.16 \text{ KDa}, \text{PDI} = 2.86.$ ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.99-7.81 (br, 4H), δ 7.78-7.59 (br, 4H), δ 7.37-7.08 (br, 8H), δ 3.12-2.58 (br, 8H), δ 1.90-1.64 (br, 8H), δ 1.53-1.19 (br, 40H), δ 0.96-0.79 (br, 12H). Elemental analysis calcd (%) for C₈₀H₈₈F₆N₂S₆: C 69.43, H 6.41, N 2.02; found: C 69.05, H 6.19, N 1.96.

PTBDT-FQxCF3: **9** and **8** were used as monomers. Yield: 83% (deep purple solid). $M_n = 14.61$ KDa, $M_w = 41.40$ KDa, PDI = 2.83. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.05-7.82 (br, 4H), δ 7.77-7.52 (br, 4H), δ 7.41-7.11 (br, 6H), δ 3.09-2.54 (br, 8H), δ 1.91-1.63 (br, 8H), δ 1.54-1.18 (br, 40H), δ 0.98-0.77 (br, 12H). Elemental analysis calcd (%) for C₈₀H₈₆F₈N₂S₆: C 67.67, H 6.10, N 1.97; found: C 67.34, H 6.09, N 1.89.



Figure S1. AFM topography of the active layer based on (a) PTBDT-Qx, (b) PTBDT-QxCF3, and (c) PTBDT-FQxCF3.

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- \cdot A series of conjugated polymers based on quinoxaline have been synthesized
- \cdot Incorporation of trifluoromethyl group on the quinoxaline acceptors
- \cdot Optical, electrochemical and photovoltaic properties have been investigated

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