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PII: S1566-1199(17)30329-4

DOI: 10.1016/j.orgel.2017.07.005

Reference: ORGELE 4197

To appear in: Organic Electronics

Received Date: 10 June 2017

Revised Date: 4 July 2017

Accepted Date: 5 July 2017

Please cite this article as: S. Xu, L. Feng, J. Yuan, Vě. Cimrová, G. Chen, Z.-G. Zhang, Y. Li, H. Peng, Y. Zou, New *m*-alkoxy-*p*-Fluorophenyl difluoroquinoxaline based polymers in efficient fullerene solar cells with high fill factor, *Organic Electronics* (2017), doi: 10.1016/j.orgel.2017.07.005.

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Two *m*-alkoxyl-*p*-fluorophenyl difluoroquinoxaline based polymers in fullerene based solar cells delivered efficient PCEs of 7.60% and 8.44% with high fill factor.

New *m*-Alkoxy-*p*-Fluorophenyl Difluoroquinoxaline Based Polymers in Efficient Fullerene Solar Cells with High Fill Factor

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Abstract

Two new donor (D) - acceptor (A) copolymers, named *m*-O-*p*-F-DFQx-BDT (OFQx-T) and *m*-EH-*p*-F-DFQx-BDT (EHFQx-T), which were based on *meta*-octyloxy-*para*-fluorophenyl and *meta*-ethylhexyloxy-*para*-fluorophenyl difluoroquinoxaline as acceptor units (O-DFQx/EH-DFQx) and alkylthienyl substituted benzodithiophene (BDT) as a donor unit, were designed and synthesized. EHFQx-T had higher absorption coefficient than OFQx-T which contributed to larger short-circuit current density (J_{sc}). EHFQx-T showed a lower the highest occupied molecular orbital (HOMO) which is beneficial for the voltage open-circuit (V_{oc}). The polymer solar cells (PSCs) based OFQx-T:PC₇₁BM and EHFQx-T:PC₇₁BM blended

film as active layer showed high power conversion efficiency (PCE) of 7.60% and 8.44%, respectively, with 1,8-diiodooctane (DIO) solvent additive treatment. More importantly, OFQx-T:PC₇₁BM and EHFQx-T:PC₇₁BM had good fill factor (FF), especially the FF of OFQx-T:PC₇₁BM was over 70%. The high FF contributed to obtain high PCEs for OFQx-T and EHFQx-T. The more balanced and higher charge mobility, smaller geminate recombination and suitable nanoscale phase separation size of EHFQx-T demonstrate that changing octyl chain to ethylhexyl chain in DFQx acceptor unit is efficient to improve photovoltaic properties in fullerene solar cells.

Keywords: Quinoxaline; D-A copolymer; Fullerene solar cells; Solvent additive; High fill factor

1. Introduction

With the increasing depletion of fossil energy, the renewable and clean energy resource such as solar energy attracted much attention.[1, 2] In recently decade, bulk heterojunction (BHJ) polymer solar cells (PSCs) have become one of the most popular research subject due to the advantages of low-cost, lightweight, easy modification and. flexibility[3-6] The PSCs, using fullerene derivatives such as [6,6]-phenyl-C₆₁/C₇₁-butyric acid methyl ester (PC₆₁BM/ PC₇₁BM) as an acceptor materials, have made great progress and the power conversion efficiency (PCE) was over 10% in single junction device.[7-10] The donor (D)-acceptor (A) structure in conjugated polymer is the most efficient structure for photovoltaic properties due to their unique features of easy modifications of the chemical structure to adjust the

absorption range, enhance the charge mobility and tune the HOMO energy level and band gap.[11-17]

Quinoxaline (Qx) is a typical strong electron-withdrawing unit and is widely used to fabricate D-A copolymer in PSCs owing to easy modification through flexible side chains and conjugated backbones.[18-21] The simple copolymer structure based on one-dimensional benzodithiophene (BDT) and alkyl substituted Qx was synthesized by Yang group with low PCE of 1.37%.[22] Two-dimensional BDT and side chains in Qx can obviously improve the PCE, many research groups introduce aryl side chains onto Qx unit to get big improvement with the PCE over 7%.[23-27] Moreover, introducing alkyl and alkoxyl onto aryl side chains can increase dissolution and tune the planarity of copolymers to change photovoltaic properties.[28] Because the van der Waals interactions between side-chains and solvent could enhance total interaction energy between copolymers and solvents; in the solid state, vibrational motions of flexible chains maybe change the twist degree and molecular arrangements.[18]

Then, fluorination of Qx conjugated backbone and side chains also make great promotion in PCE.[29-36] Fluorination in polymer can modulate optical and electrochemical properties in several aspects to affect the photovoltaic performance: (1) Fluorination can efficiently lower the highest occupied molecular orbital (HOMO) energy level due to its strong electronegativity which will help to get higher V_{oc} and the lowest occupied molecular orbital (LUMO) energy level to tune the band gap $(E_g).[37, 38]$ (2) Fluorine has strong interactions with hydrogen, carbon and sulfur

which can enhance molecular arrangement and aggregation to modify the film morphology and change the solubility.[39-41] (3) Fluorine can change the hydrophobicity and adjust the polarity of molecular to improve the charge mobility and stability.[42-45] For instance, a copolymer named PBQ-1 with alkylthienyl substituted BDT as donor unit and Qx without any fluorine as acceptor unit, obtained PCE of 5.63% (V_{oc} of 0.63 V, J_{sc} of 12.39 mA/cm⁻² and FF of 69.81%) while two fluorine onto Qx conjugated backbone based copolymer, named PBQ-3, with the PCE up to 7.39% (V_{oc} of 0.79 V, J_{sc} of 13.46 mA/cm⁻² and FF of 67.58%)[46]. The introduction of two fluorine atoms in Qx unit can efficiently improve the V_{oc} from 0.63 V to 0.79 V to enhance the PCE of devices which is attributed to the lower HOMO level of PBQ-3 (-5.19 eV) than PBQ-1 (-5.05 eV). Therefore, we want to introduce four fluorine onto Qx unit to further decrease the HOMO level of polymer to obtain higher V_{oc} .

According to above strategies, we introduce two fluorine onto Qx side chains to synthesize two new acceptor unit: *meta*-octyloxy-*para*-fluoropheyl and *meta*-ethylhexyloxy- *para*-fluoropheyl difluoroquinoxaline (O-DFQx/EH-DFQx). Two new copolymer *m*-O-*p*-F-DFQx-BDT (OFQx-T) and *m*-EH-*p*-F-DFQx-BDT (EHFQx-T) was obtained with O-DFQx/EH-DFQx as acceptor unit and alkylthienyl substituted BDT as donor unit. Further introducing fluorine indeed decrease the HOMO level of polymers to obtain higher V_{oc} of 0.86 V and 0.91 V and enhance the PCE of 7.59% and 8.44% for the OFQx-T and EHFQx-T based devices, respectively. We carefully investigated the optical, electrochemical and photovoltaic properties and discussed the effects of replacing octyloxy side chains with ethylhexyloxy side chains in PSCs.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic routes of the monomers, OFQx-T and EHFQx-T are displayed in Scheme 1 and experimental details are shown in the supporting information. Through reduction reaction using NaBH₄, compound 2 was obtained. Compound 4 was obtained at 150 °C under argon by Williamson reaction. White solid compound 5 was obtained via Grignard reaction. Compound 2 and Compound 5 were dissolved in glacial acetic acid in 90 °C at overnight to obtain compound 6. Compound 7 was synthesized by the Stille coupling reaction using $PdCl_2(PPh_3)_2$ as catalyst at 110 °C. Using NBS as bromination reagent, the monomer (M1 and M2) was prepared. The polymers OFQx-T and EHFQx-T were obtained with Pd(PPh₃)₄ as catalyst in toluene at 110 °C. All crude product were purified by silica gel column chromatography and characterized by NMR spectroscopy. The polymer was purified via continuous Soxhlet extractions with methanol, hexane, acetone and chloroform (CF) successively. Both OFQx-T and EHFQx-T have good solubility in general organic solvents such as CF, dichloromethane (DCM) and toluene etc. The molecular weights of OFQx-T and EHFQx-T are determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as eluent and polystyrene as the standard.[47] OFQx-T and EHFQx-T have a number average molecular weight (M_n) of 31.11 kDa and 51.67 kDa, respectively. The polydispersity indices (PDI: M_w/M_n) of OFQx-T and EHFQx-T are

1.59 and 1.86, respectively. The thermal properties of the OFQx-T and EHFQx-T are investigated by thermogravimetric analysis (TGA). The TGA graph is shown in Figure S15. The onset temperature at 5% weight loss are 431 °C and 405 °C for OFQx-T and EHFQx-T under nitrogen, which demonstrated that the thermal stability of the OFQx-T and EHFQx-T is high enough for device applications.[48] The related data including the molecular weights and TGA of OFQx-T and EHFQx-T are summarized in Table 1.



Figure 1. (a) Chemical structures of OFQx-T and EHFQx-T; (b) Molecular energy-level alignment of the materials involved in the PSCs; (c) Device structure used for PSCs fabrication, ETL used is ZrAcac with OFQx-T:PC₇₁BM BHJ or EHFQx-T: PC₇₁BM BHJ layer.



Table 1. Molecular weights and thermal properties of the OFQx-T and EHFQx-T. T_d

Scheme 1. Synthetic routes of monomers, OFQx-T and EHFQx-T.

polymer	M_n (kDa)	M_w (kDa)	PDI	T_d (°C)
OFQx-T	31.11	49.39	1.59	431
EHFQx-T	51.67	96.22	1.86	405

temperature at 5% weight loss)

2.2. Optical and electrochemical properties

Ultraviolet-visible (UV-Vis) normalized absorption spectra of OFQx-T and EHFQx-T in dilute chloroform solution and OFQx-T and EHFQx-T films are showed in Figure 2a. The absorption coefficient of OFQx-T and EHFQx-T films is shown in Figure 2b. The detailed optical data are summarized in Table 2. Both OFQx-T and EHFQx-T show three absorption peaks at the range of 300-800 nm. In the wavelength range of 300-500 nm, the absorption is attributed to π - π * transition.[49] A broad and intense absorption in the range of 500-700 nm is attributed to the intramolecular charge transfer (ICT) between the D-A unit.[50] The OFQx-T and EHFQx-T film absorptions show a slightly blue shift than CF solution which could be attributed to the H-aggregation of polymer and interchain packing in solid state.[51, 52] The absorption maxima of OFQx-T and EHFQx-T thin film spectra are 614 nm and 612 nm, and corresponding optical bandgap ($E_g^{opt} = 1240/\lambda_{edge}$) of 1.70 eV and 1.71 eV, respectively. Increasing temperature from 20 to 90 °C, both OFQx-T and EHFQx-T show the long-wavelength maxima in chlorobenzene (CB) solution slightly blue shift

in the absorption spectra (Figure S16), which could be associated with changes in chain conformation.[53] Significantly, the OFQx-T and EHFQx-T absorption coefficient are 4.57×10^4 cm⁻¹ and 4.65×10^4 cm⁻¹ (in Figure 2b), respectively. EHFQx-T has better light harvesting capacity which is beneficial for high J_{sc} .

The electrochemical properties of OFQx-T and EHFQx-T have well been investigated by cyclic voltammetry (CV). We use the ferrocene/ferrocenium (Fc/Fc^+) redox couple as the standard with tetra-n-butylammoniumhexafluorophosphate (n-Bu₄NPF₆, 0.1 M in acetonitrile) as the supporting electrolyte and the CV curves, related data are shown in Figure 2c and Table 2. The HOMO and LUMO energy levels can be calculated of E_{HOMO} = -5.36 eV, E_{LUMO} = -3.63 eV for OFQx-T and E_{HOMO} = -5.45 eV, E_{LUMO} = -3.70 eV for EHFQx-T, and corresponding electrochemical band gap of 1.73 eV and 1.75 eV for OFQx-T and EHFQx-T, respectively. The band offset between LUMO energy level of OFQx-T or EHFQx-T and LUMO energy level of PC71BM are all over 0.3 eV, which have enough driving force to conquer the exciton binding energy.[48, 54] As well known, the band offset between LUMO energy level of $PC_{71}BM$ and HOMO energy level of polymer is proportional to the V_{oc} [55] The HOMO energy level of EHFQx-T is lower than OFQx-T which suggested EHFQx-T energy level is more suitable to match with PC₇₁BM to get high V_{oc} .

To further investigate the exciton dissociation and charge transport from polymer to $PC_{71}BM$ in the BHJ layer, we adopt the photoluminescence (PL) quenching tests and the PL spectra are shown in Figure 3. When the excited wavelength at 650 nm, the pure OFQx-T and EHFQx-T all show a broad PL emission range from 670-870 nm, while the OFQx-T:PC₇₁BM or EHFQx-T:PC₇₁BM blend film show the PL emission quenched by 88% and 96.5%. When using DIO as additive, the PL emission of OFQx-T and EHFQx-T quenched by 94% and 97.5%. The DIO can obviously accelerate the exciton dissociation and transport to obtain high J_{sc} . From the PL spectra, we also find that the EHFQx-T have higher quenching efficiency for more efficient exciton dissociation and charge transport.

Polymer	Absorption spectra				Cyclic voltammetry		
	Sol ^a	Film ^b			<i>p</i> -doping	<i>n</i> -doping	
	λ _{max}	λ_{max}	λ_{onset}	$E_g^{opt_c}$	$E_{on}^{ox}/E_{\rm HOMO}^{\rm d}$	$E_{on}^{red}/E_{\rm LUMO}^{\rm d}$	E_g
	(nm)	(nm)	(nm)	(eV)	(V)/(eV)	(V)/(eV)	(eV)
OFQx-T	630	614	731	1.70	1.03/-5.36	-0.70/-3.63	1.73
EHFQx-T	630	612	725	1.71	1.12/-5.45	-0.63/-3.70	1.75
^a Measured in chloroform solution. ^b Cast from chloroform solution. ^c Bandgap							
estimated from the onset wavelength of the optical absorption. ${}^{d}E_{\text{HOMO}}$ =							
-(4.80- $E_{1/2,Fc/Fc}^++E_{ox}$) (eV); E_{LUMO} = -(4.80- $E_{1/2,Fc/Fc}^++E_{red}$) (eV) using Ag/AgCl as the							
reference electrode.							

Table 2. Optical and electrochemical data of OFQx-T and EHFQx-T.





Figure 2. (a) Normalized absorption spectra of OFQx-T and EHFQx-T in dilute CF solution and in film states; (b) Absorption coefficients of OFQx-T and EHFQx-T film;
(c) CV curves of OFQx-T, EHFQx-T in 0.1M Bu₄NPF₆ acetonitrile solution.





Figure 3. (a) PL spectra of pure OFQx-T, OFQx-T:PC₇₁BM blend (1:1.5, *w:w*) and with 1.0 vol% DIO (excited at 650 nm); (b) PL spectra of pure EHFQx-T, EHFQx-T:PC₇₁BM blend (1:1.5, *w:w*) and with 0.8 vol% DIO (excited at 650 nm). The inset figure is the amplifying PL spectra of Figure 3.

2.3. Photovoltaic properties

To further explore the OFQx-T and EHFQx-T photovoltaic properties, conventional photovoltaic devices with configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/polyme r:PC₇₁BM/Zirconium (IV) Acetylacetonate (ZrAcac)/Al were fabricated. We carefully investigated the D/A weight ratio, solvent additives, thermal annealing (TA) and solvent vapor annealing (SVA) to obtain the optimal photovoltaic properties. The photovoltaic data are shown in Table 3 and more related data have been listed in Table S1. When OFQx-T:PC₇₁BM weight ratio is 1:1.5, the device shows a low PCE of 2.91% with V_{oc} of 0.90 V, J_{sc} of 6.07 mA/cm² and FF of 53.24%. After 1.0 vol% DIO treatment, the PCE increases to 7.59%. Surprisingly, the J_{sc} is enhanced by 2 times and FF is heightened by 1.18 times so that the PCE gets enhanced by 261%. Similarly, the PCE of EHFQx-T is improved from 3.23% to 8.44%, the J_{sc} of 8.50 mA/cm² and FF of 42.04% are increased to 13.31 mA/cm² and 69.70% after the 0.8 vol% DIO treatment. The J_{sc} and FF are improved by 1.57 times and 1.66 times, respectively, which lead to the PCE intensively enlarge by 2.61 times. The TA and SVA treatment don't show obvious improvement for the PCEs of OFQx-T and EHFQx-T (shown in Table S1). The corresponding *J-V* curves are shown in Figure 4a and 4b.

The external quantum efficiency (EQE) spectra are shown in Figure 4c. The maximum EQE of OFQx-T is 64.72% at 479 nm and the maximum EQE of EHFQx-T is 65.81% at 559 nm in the wavelength range of 300 nm to 800 nm. The higher EQE of EHFQx-T may be attributed to higher absorption coefficient than OFQx-T.[38] The J_{sc} of OFQx-T and EHFQx-T based device integrating from EQE is 11.38 mA/cm² and 12.28 mA/cm², respectively. The J_{sc} of OFQx-T and EHFQx-T based device with J_{sc} obtained from the J-V is 12.43 mA/cm² and 13.31 mA/cm². In addition, the deviation between the J_{sc} from the J-V and the integral of the EQE are less than 8% so that the J_{sc} is valid.[56]

The hole and electron mobility (μ_h and μ_e) are measured by the space-charge limited current (SCLC) method through the hole-only device of ITO/PEDOT:PSS/active layer/Au and electron-only device of ITO/ZnO/active layer/ZrAcac/Al, respectively. As shown in Figure 5. The hole mobility and electron mobility of OFQx-T is 1.09×10^{-4} cm²·V⁻¹·s⁻¹ and 0.704×10^{-4} cm²·V⁻¹·s⁻¹, respectively without DIO while 1.68×10^{-4} cm²·V⁻¹·s⁻¹ and 1.38×10^{-4} cm²·V⁻¹·s⁻¹ with 1.0 vol% DIO treatment. The hole mobility and electron mobility get improved by 1.5 and 2 times, respectively, after DIO treatment which suggests that DIO can efficiently improve the charge mobility to obtain high J_{sc} and FF.[57] Optimal hole mobility and electron mobility of EHFQx-T reached 1.79×10^{-4} cm²·V⁻¹·s⁻¹ and 1.89×10^{-4} cm²·V⁻¹·s⁻¹ with 0.8 vol% DIO treatment. The hole mobility and electron mobility are intensively larger by 1.4 and 3.34 times, respectively. Moreover, the μ_h/μ_e are used to understanding the exiton recombination and formation of space charge density. The μ_h/μ_e of OFQx-T and EHFQx-T are 1.22 and 0.95, respectively. The more balanced μ_h/μ_e of EHFQx-T is one of the reasons why EHFQx-T have higher J_{sc} . The details and related data are shown in Table S2.

Generally, geminate recombination is relevant to charge carrier density and light intensity, to further understand charge recombination, we investigated the relationship between J_{sc} and light intensities[58]. We use empirical formula of $J_{sc} \propto P_{light}^{\alpha}$ to explain the relationship between J_{sc} and light intensity (P_{light}). When the α is equal to 1, the geminate recombination in PSC can be ignored.[59] In the OFQx-T:PC₇₁BM device without DIO treatment, the α is 0.89 while the α is up to 0.93 with DIO treatment. In the EHFQx-T:PC₇₁BM device, the α has improved from 0.90 to 0.96 after DIO treatment. The DIO additive can decrease the geminate recombination and EHFQx-T has higher α =0.96 than OFQx-T (α =0.93) which is in accordance with the result of higher J_{sc} in EHFQx-T: PC₇₁BM device.





Figure 4. (a) The *J-V* curves of PSCs based on OFQx-T:PC₇₁BM under the illumination of AM 1.5G, 100 mW/cm²; (b) The *J-V* curves of PSCs based on EHFQx-T:PC₇₁BM under the illumination of AM 1.5G, 100 mW/cm²; (c) EQE curves of the corresponding devices.







Figure 5. The dependence of square root of current density $(J^{1/2})$ on voltage for hole-only devices of ITO/PEDOT:PSS/active layer/Au (a,c) and electron-only devices of ITO/ZnO/active layer/ZrAcac/Al (b,d) with active layers (**a**) and (**b**) OFQx-T:PC₇₁BM blends; (**c**) and (**d**) EHFQx-T:PC₇₁BM blends.





Figure 6. Light intensity dependence of the J_{sc} density based on (a) OFQx-T:PC₇₁BM and (b) EHFQx-T: PC₇₁BM

Table 3. Summary of the photovoltaic characteristics of the OFQx-T:PC₇₁BM and EHFQx-T:PC₇₁BM blend films.

BHJ Layer	Additive ^a	V _{oc}	J _{sc}	FF	Р	CE (%)
(Ratio)	(%)	(V)	(mA/cm ²)	(%)	Max ^b	Ave ^c
		0.90	6.07	53.24	2.91	2.85±0.08
OFQx-T:PC71BM	INOne	(0.893±0.007)	(6.13±0.08)	(52.06±0.86)		
(1:1.5)		0.86	12.43	70.70	7.50	7.241.0.10
			(12.26±0.55)	(69.71±1.98)	1.39	7.34 <u>±</u> 0.19
Y.	Nama	0.94	8.07	47.88	2.64	2 47 1 0 11
EHFQx-T:PC71BM	none	(0.932±0.01)	(8.13±0.3)	(45.87±2.54)	3.04	3.47±0.11
(1:1.5)	0.8	0.91	13.31	69.70	8.44	8.27±0.11
	0.8	(0.908±0.005)	(13.04±0.22)	(69.83±0.99)		

^aThe additive is 1,8-diiodooctane. ^bThe maximum PCE value of device. ^cThe average PCE values of 10 devices.

Morphological characterization

To further understand the influence of replacing the octyloxy chain with ethylhexyloxy chain and DIO treatment in photovoltaic properties, the tapping-mode atomic force microscopy (AFM) and transmission electron microscopy (TEM) are measured to analyze the film morphology of the active layer. The AFM, TEM images of OFQx-T and EHFQx-T with or without DIO are shown in Figure 7 and 8. In the OFQx-T:PC₇₁BM device, the AFM images shows the root-mean-square (RMS) roughness of 3.44 nm without DIO, while a rougher surface is obtained with the RMS roughness of 3.61 nm with 1.0 vol% DIO process. The rougher surface morphology suggested that clearer and stronger phase separation features is in favor of exciton dissociation and charge transport in the donor and acceptor to gain higher J_{sc} and FF.[60] In the EHFQx-T:PC₇₁BM device, the RMS roughness improved from 2.35 nm to 2.53 nm after 0.8 vol% DIO process. Because the branched chains (ethylhexyl chain) have larger steric hindrance than linear chains (octyl chain), compared to the AFM images of OFQx-T (with 1.0 vol% DIO) and EHFQx-T (with 0.8 vol% DIO), we can find that the EHFQx-T has more smooth and suitable morphology. The suitable aggregation of polymer and $PC_{71}BM$ in blend film is better for the exiton separation and charge transport which is the same with the performance in photovoltaics. From TEM images, both OFQx-T and EHFQx-T showed more uniform and suitable morphology after DIO treatment which means that using the DIO

additive can obviously change the aggregation of polymer and PC₇₁BM and form a bicontinuous D/A interpenetrating network morphology.[61] The TEM images of EHFQx-T with 0.8 vol% DIO shows better nano-scale phase separation size and more uniform morphology than OFQx-T with 1.0 vol% DIO which agrees with the results of AFM so that EHFQx-T have better photovoltaic properties than OFQx-T.



Figure 7. Topographic AFM images (height and phase): (a)(e) OFQx-T:PC₇₁BM blend films (1:1.5, w:w); (b)(f) with 1.0 vol% DIO (1:1.5, w:w); (c)(g) EHFQx-T:PC₇₁BM blend films (1:1.5, w:w); (d)(h) with 0.8 vol% DIO (1:1.5, w:w). Dimension of images: $3x3 \mu m^2$.



Figure 8. Topographic TEM images $(1*1 \ \mu m^2)$: (a) OFQx-T:PC₇₁BM blend films (1:1.5, w:w); (b) with 1.0 vol% DIO (1:1.5, w:w); (c) EHFQx-T:PC₇₁BM blend films $(1:1,5 \ w:w)$; (d) with 0.8 vol% DIO (1:1.5, w:w).

3 Conclusion

In conclusion, we designed and synthesized two new D-A copolymers, *meta*-octyloxy-*para*-fluoropheyl meta-ethylhexyloxypara-fluoropheyl and (O-DFQx/EH-DFQx) difluoro-quinoxaline acceptor as units and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b']dithio phene as a donor unit, named OFQx-T and EHFQx-T, respectively. We carefully investigated the optical, electrochemical and photovoltaic properties of OFQx-T and EHFQx-T. From the above results, we find that replacing octyloxy chain with ethylhexyloxy chain in DFQx system can improve the absorption coefficient, reduce the geminate recombination and affect film morphology to benefit the charge mobility and more balanced μ_h/μ_e then higher J_{sc} and FF were obtained; lower HOMO energy level is beneficial to enhancing the V_{oc} . Moreover, the DIO additive can efficiently optimize the photovoltaic properties. Hence, a higher PCE of 8.44% (J_{sc} of 13.31 mA/cm², V_{oc} of 0.91 V and FF of 69.70%) was obtained in EHFQx-T:PC₇₁BM device (1:1.5, w:w) with 0.8 vol% DIO treatment compared to PCE of 7.60% in OFQx-T:PC₇₁BM based device (1:1.5, w:w) with 1.0 vol% DIO treatment (J_{sc} of 12.43 mA/cm², V_{oc} of 0.86 V and FF of 70.70%). The EH-DFQx based polymer -EHFQx-T is a promising candidate for PSCs. This work can provide some insights that some minor changes of side chains also make the big differences in performances.

4 Acknowledgements

This work has been financially supported by National Key Research & Development Projects of China (2017YFA0206600), the National Natural Science Foundation of China (51673205), Science Fund for Distinguished Young Scholars of Hunan Province (2017JJ1029), Project of Innovation-driven Plan in Central South University, China (2016CX035), State Key Laboratory of Powder Metallurgy, Central South University, China, the Fundamental Research Funds for the Central Universities of Central South University (2016zzts023), and the Czech Science Foundation (grant 13-26542S).

Supporting information

Supporting information (SI) available: experimental details including general measurement, fabrication and characterization of PSC, materials, synthesis, ¹H NMR, ¹³C NMR, thermal, optical and photovoltaic data, related figures and tables.

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Highlights

•Two D-A copolymers, *meta*-octyloxy-*para*-fluoropheyl and *meta*-ethylhexyloxy*para*-fluoropheyl difluoroquinoxaline (O-DFQx/EH-DFQx) as acceptor units and 4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene as donor unit, named *m*-O-*p*-F-DFQx-BDT (OFQx-T) and *m*-EH-*p*-F-DFQx-BDT (EHFQx-T), are designed and synthesized.

• Replacing octyloxy chain with ethylhexyloxy group in DFQx based system can improve the absorption coefficient, reduce the geminate recombination and achieve higher charge mobility and more balanced μ_h/μ_e .

• A higher PCE of 8.44% was obtained in EHFQx-T:PC₇₁BM device (1:1.5, *w:w*) compared to a PCE of 7.60% in OFQx-T:PC₇₁BM based device (1:1.5, *w:w*) after DIO treatment.