

**Electronic Supporting Information (ESI) for:**

**Improved Photovoltaic Performance of Quinoxaline-Based Polymers by  
Systematic Modulation of Electron-Withdrawing Substituents**

Christyowati Primi Sagita,<sup>a†</sup> Jung Won Yoon,<sup>b†</sup> Minju Kyeong,<sup>c†</sup> Seok Woo Lee,<sup>a</sup> Hyemin  
Bae,<sup>b,c</sup> Dong Ryeol Whang,<sup>d</sup> Hyosung Choi,<sup>b,\*</sup> Seo-Jin Ko,<sup>c,\*</sup> and Dong Wook Chang<sup>a,\*</sup>

*<sup>a</sup>Department of Industrial Chemistry, Pukyong National University, 48513 Busan, Republic of  
Korea*

*E-mail: dwchang@pknu.ac.kr*

*<sup>b</sup>Department of Chemistry, Research Institute for Natural Science and Institute of Nano Science  
and Technology, Hanyang University, 04730 Seoul, Republic of Korea*

*E-mail: hschoi202@hanyang.ac.kr*

*<sup>c</sup>Division of Advanced Materials, Korea Research Institute of Chemical Technology (KRICT),  
Daejeon, 34114, Republic of Korea*

*Email: sjko927@krict.re.kr*

*<sup>d</sup>Department of Advanced Materials, Hannam University, Daejeon, 34054 Republic of Korea.*

<sup>†</sup>C.P. Sagita, J. W. Yoon and M. Kyeong equally contributed to this research

## 1. Experimental Section

### 1.1. Materials and Instruments

4-bromo-1-((2-ethylhexyl)oxy)-2-fluorobenzene (**1**),<sup>S1</sup> 1,4-dimethylpiperazine-2,3-dione (**2**),<sup>S2</sup> 4,7-bis(5-bromothiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (**4**),<sup>S3</sup> 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole-5-carbonitrile (**5**),<sup>S4</sup> 4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)-bis(trimethylstannane (**8**),<sup>S5</sup> and (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo-[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**9**)<sup>S6</sup> were synthesized according to the previous reports. All other chemicals were purchased from Sigma-Aldrich Co. For <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR measurement were carried out on JEOL JNM-ECA-600 spectrometer. UV Visible spectra was recorded on Agilent Technologies Cary 60 UV-Vis spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) measurement was analysed by using Bruker Ultraflex spectrometer. Gel Permeation Chromatography was measured in Agilent 1200 series instrument with THF as the solvent. Cyclic voltammetry was carried out on VersaSTAT3 potentiostat (Princeton Applied Research) with 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile as the electrolyte. The sample of polymers were coated on glassy carbon electrode as working electrode in the CV measurement, whereas the counter electrode and pseudo-reference electrode was used a platinum wire and a silver wire, respectively with a ferrocene/ferrocenium as the external standard.

### 1.2. Fabrication and characterization of photovoltaic device

The ITO-patterned glass substrates were cleaned by deionized water, acetone, and isopropyl alcohol progressively with ultra-sonication for 10 min at each step and dried in the oven at 70 °C. After 15 min treatment of UV-Ozone, Zinc oxide (ZnO) solution was spin-coated onto the

substrates at 3500 rpm for 25 sec, and then were annealed at 140 °C for 15 min. An active layer blends of each quinoxaline-based polymer donor:Y6 ( 1:1.5, weight ratio) were dissolved in chloroform (CF) with 1.0 vol% 1-8-diiodooctane (DIO). All blends were prepared by concentrations of 14 mg/mL and were stirred at 50 °C for 4 hours. The active layer was spin-coated onto ZnO layer, followed by annealing at 100 °C for 10 min. After that, Molybdenum trioxide (MoO<sub>3</sub>) as a hole transfer layer and Ag as an anode were deposited on the active layer under a vacuum of  $2 \times 10^{-6}$  torr and the thickness of each layer were 7nm and 100nm, respectively.

Photovoltaic characteristics were measured under Air Mass 1.5 Global (AM 1.5G) illumination with an irradiation intensity of 100 mW cm<sup>-2</sup>. The current density voltage (*J-V*) curves were recorded by a solar simulator (Keithley 2400). External quantum efficiency (EQE) spectra were obtained using a quantum efficiency measurement system (K3100 IQX, McScience Inc.). Dark current density was measured by a Keithley 2635B source measurement unit. The monochromatic light intensity was calibrated using a Si photodiode and chopped at 20 Hz. The charge mobility was measured by the space-charge limited current (SCLC) method. The structures of hole-only devices and the electron-only and were ITO/PEDOT:PSS/Active layer/Au and ITO/ZnO/Active layer/Al, respectively. The SCLC mobility was calculated by Mott-Gurney square law:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

Where *J* is the current density,  $\varepsilon_0$  is the permittivity of free space ( $8.85419 \times 10^{-12}$  C V<sup>-1</sup> m<sup>-1</sup>),  $\varepsilon_r$  is the relative permittivity of the material,  $\mu$  is the mobility of charge carrier, *V* is the applied voltage, and *L* is the film thickness.<sup>S7</sup> The charge carrier mobility was calculated from the slope of the *J-V* curves. Also, the grazing incidence wide-angle X-ray scattering (GIWAXS) data were carried out using synchrotron radiation at the Pohang Accelerator Laboratory (PAL), Republic of

Korea. The surface morphologies were measured by Park Systems XE-100 as atomic force microscopy (AFM) instrument operated using non-contact scanning mode.

### 1.3. Syntheses

#### 1.3.1. *Synthesis of 1,2-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)ethane-1,2-dione (3)*

Under nitrogen (N<sub>2</sub>) protection, *n*-butyllithium (2.5 M solution in Hexane, 4.4 mL) was added dropwise to a solution of **1** (10.8 mmol) in dry THF (60 mL) at -78°C. After stirring for 1 h, **2** (4.92 mmol) was directly added to the solution. The reaction temperature was gradually increased to room temperature and the mixture was stirred overnight. After the solution of 50 mL of 10% HCl for hydrolysis and mixture was stirred for 1 h. Once the reaction was completed, the mixture was extracted with ethyl acetate (EA). The organic layer was separated and dried over magnesium sulfate. After removal of solvents, the crude product was purified using column chromatography with dichloromethane (MC)/hexane (1/20, v/v) as an eluent. Yield = 36.5% (yellow liquid). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.75 (d, 1H, *J* = 2.4 Hz), 7.72 (d, 1H, *J* = 2.0 Hz), 7.69 (dd, 1H, *J*<sub>1</sub> = 1.6 Hz, *J*<sub>2</sub> = 0.8 Hz), 7.67 (dd, 1H, *J*<sub>1</sub> = 2.4 Hz, *J*<sub>2</sub> = 0.8 Hz), 7.00 (t, 2H, *J* = 8.0 Hz), 3.99 (dd, 4H, *J*<sub>1</sub> = 5.8 Hz, *J*<sub>2</sub> = 1.2 Hz), 1.83-1.77 (m, 2H), 1.54-1.40 (m, 8H), 1.33-1.29 (m, 8H), 0.95-0.90 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 192.0, 153.5 (*J*<sub>C-F</sub> = 10 Hz), 152.5 (*J*<sub>C-F</sub> = 248 Hz), 128.2 (*J*<sub>C-F</sub> = 3 Hz), 125.9 (*J*<sub>C-F</sub> = 6 Hz), 116.8 (*J*<sub>C-F</sub> = 19 Hz), 113.6, 72.1, 39.2, 30.4, 29.1, 23.8, 23.0, 14.1, 11.1. <sup>19</sup>F NMR (564MHz, CDCl<sub>3</sub>): 133.2.

#### 1.3.2. *Synthesis of 2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)-6-fluoro-5,8-di(thiophen-2-yl)quinoxaline (6)*

Firstly, the mixture of **4** (0.63 mmol) and zinc (Zn) powder (12.6 mmol) in acetic acid (15 mL) was stirred for 6 h at 80 °C to generate *ortho*-diamine intermediate. After removal of Zn powder by filtration,  $\alpha$ -diketon (**3**, 0.63 mmol) was added to the filtrate and the mixture was heated to reflux overnight to produce the quinoxaline structure. After cooling down to room temperature, the mixture solution was poured into water and extracted with EA. The organic layer was separated and dried over magnesium sulfate. After removal of solvents, the crude product was purified using column chromatography with MC/hexane (1/10, v/v) as an eluent. Yield = 54.4% (orange solid). <sup>1</sup>H NMR (600 MHz, DMSO):  $\delta$  (ppm) = 7.98 (t, 2H,  $J$  = 6.4 Hz), 7.85 (d, 1H,  $J$  = 3.6 Hz), 7.61-7.56 (m, 4H), 7.43 (t, 2H,  $J$  = 7.2 Hz), 7.24-7.19 (m, 2H), 6.99-6.94 (m, 2H), 3.96 (d, 4H,  $J$  = 5.2 Hz), 1.83-1.78 (m, 2H), 1.58-1.41 (m, 8H), 1.36-1.34 (m, 8H), 0.98-0.92 (m, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): 160.1, 157.6, 153.6, 151.1, 150.4, 149.1, 148.6, 137.2, 134.2, 131.8, 130.8, 130.2, 129.9, 126.7, 118.0, 116.9, 114.1, 71.9, 39.4, 30.4, 29.1, 23.8, 23.0, 14.1, 11.1 (C-F couplings has not been assigned). <sup>19</sup>F NMR (564MHz, CDCl<sub>3</sub>): -105.9, -133.8.

### 1.3.3. Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-((2-ethylhexyl)oxy))-3-fluorophenyl)quinoxaline-6-carbonitrile (**7**)

A procedure similar to that used to prepare **6** was applied to produce **7**. Substance of **5** was used as the reagent instead of **4**. The crude product was purified by using MC/hexane (1/3, v/v) as an eluent. Yield = 70% (orange-red solid). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.24 (s, 1H), 7.86 (d, 1H,  $J$  = 4.0 Hz), 7.58 (d, 1H,  $J$  = 4.4 Hz), 7.54-7.51 (m, 1H), 7.48 (d, 1H,  $J$  = 2.4 Hz), 7.46 (d, 1H,  $J$  = 5.6 Hz), 7.42 (d, 1H,  $J$  = 8.4 Hz), 7.22 (d, 1H,  $J$  = 4.0 Hz), 7.18 (d, 1H,  $J$  = 4.4 Hz), 7.02 (d, 1H,  $J$  = 8.4 Hz), 6.98 (d, 1H,  $J$  = 8.4 Hz), 3.98 (t, 4H,  $J$  = 6.4 Hz), 1.85-1.79 (m, 2H), 1.54-1.45 (m, 8H), 1.37-1.32 (m, 8H), 0.99-0.90 (m, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): 152.4, 150.7,

149.9, 148.3, 136.1, 135.5, 134.0, 132.8, 129.8, 129.4, 128.4, 127.2, 125.8, 125.5, 119.2, 117.9, 116.9, 112.9, 108.1, 70.9, 38.3, 29.4, 28.0, 22.7, 22.0, 13.1, 10.1.  $^{19}\text{F}$  NMR (564MHz,  $\text{CDCl}_3$ ): -133.2. MALDI-TOF MS:  $m/z$  calcd, 921.79; found, 922.403 [ $\text{M}^+$ ].

#### *General polymerization procedure under Stille coupling condition*

In a Schlenk flask, BDT (0.20 mmol), dibrominated quinoxaline monomer (0.20 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (3% mol) were dissolved in 10 mL dry toluene. After bubbling with  $\text{N}_2$  for 15 min, the mixture was stirred at 90 °C for two days under  $\text{N}_2$  protection. The polymerization was finished by adding two end-capping agents (1% mol) of 2-trimethylstannylthiophene and 2-bromothiophene with an interval of 2 h. Once the polymerization was completed, the mixture was cooled down to room temperature and precipitated into methanol. The polymers were further purified via Soxhlet extraction with methanol, acetone, hexane, and chloroform. The final chloroform solution was collected and solvent was evaporated to concentrate the polymer solution. After precipitation of the polymers using methanol, the polymer powders were filtered and dried in vacuum oven at 50 °C.

#### *1.3.4. PB-FQxF*

**8** and **6** were used as monomers. Yield = 86.2% (deep blue solid).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.89-7.64 (br, 2H), 7.64-7.52 (br, 2H), 7.52-7.41 (br, 3H), 7.41-7.31 (br, 4H), 7.23-7.21 (br, 1H), 7.18-7.07 (br, 1H), 7.07-7.01 (br, 1H), 6.99-6.90 (br, 2H), 6.90-6.69 (br, 1H), 4.26-3.84 (br, 4H), 3.20-2.76 (br, 4H), 1.76-1.65 (br, 6H), 1.51-1.49 (br, 4H), 1.49-1.31 (br, 20H), 1.17-0.89 (br, 30H). Molecular weight by GPC: number-average molecular weight ( $M_n$ ) = 48.8 KDa,

polydispersity index (PDI) = 2.85. Elemental analysis: calcd (%) for  $C_{78}H_{85}F_3N_2O_2S_6$ : C 70.23, H 6.57, N 2.10; found: C 70.16, H 6.41, N 2.04.

#### 1.3.5. *PBF-FQ<sub>x</sub>F*

**9** and **6** were used as monomers. Yield = 88.9% (deep blue solid).  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 7.63-7.52 (br, 3H), 7.52-7.41 (br, 5H), 7.41-7.37 (br, 6H), 7.06-6.99 (br, 1H), 4.20-3.90 (br, 4H), 3.04-2.76 (br, 4H), 1.69-1.65 (br, 9H), 1.49-1.33 (br, 21H), 1.15-0.93 (br, 30H). Molecular weight by GPC: number-average molecular weight ( $M_n$ ) = 55.8 KDa, polydispersity index (PDI) = 2.89. Elemental analysis: calcd (%) for  $C_{78}H_{83}F_5N_2O_2S_6$ : C 68.39, H 6.25, N 2.04; found: C 68.40, H 6.15, N 1.97.

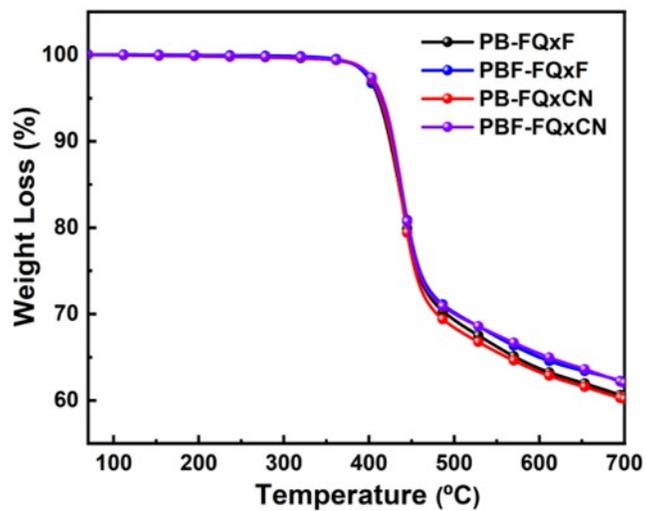
#### 1.3.6. *PB-FQ<sub>x</sub>CN*

**8** and **7** were used as monomers. Yield = 86.7% (deep green solid).  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 7.65-7.54 (br, 4H), 7.50-7.41 (br, 5H), 7.40-7.30 (br, 6H), 7.04-6.90 (br, 2H), 4.18-3.90 (br, 4H), 3.12-2.84 (br, 4H), 1.76-1.73 (br, 2H), 1.69-1.65 (br, 5H), 1.51-1.47 (br, 9H), 1.47-1.34 (br, 14H), 1.12-0.89 (br, 30H). Molecular weight by GPC: number-average molecular weight ( $M_n$ ) = 49.7 KDa, polydispersity index (PDI) = 3.46. Elemental analysis: calcd (%) for  $C_{79}H_{85}F_2N_3O_2S_6$ : C 70.76, H 6.54, N 3.13; found: C 70.34, H 6.34, N 2.98.

#### 1.3.7. *PBF-FQ<sub>x</sub>CN*

**9** and **6** were used as monomers. Yield = 85.2% (deep green solid).  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 7.59-7.52 (br, 2H), 7.49-7.41 (br, 4H), 7.41-7.32 (br, 8H), 7.04-6.99 (br, 1H), 4.16-3.88 (br, 4H), 3.06-2.78 (br, 4H), 1.73-1.69 (br, 4H), 1.69-1.64 (br, 6H), 1.49-1.32 (br, 20H), 1.13-0.90

(br, 30H). Molecular weight by GPC: number-average molecular weight ( $M_n$ ) = 60.8 KDa, polydispersity index (PDI) = 4.26. Elemental analysis: calcd (%) for  $C_{79}H_{83}F_4N_3O_2S_6$ : C 68.91, H 6.22, N 3.05; found: C 69.01, H 6.17, N 2.96.



**Figure S1.** Thermogravimetric analyses of the polymers.

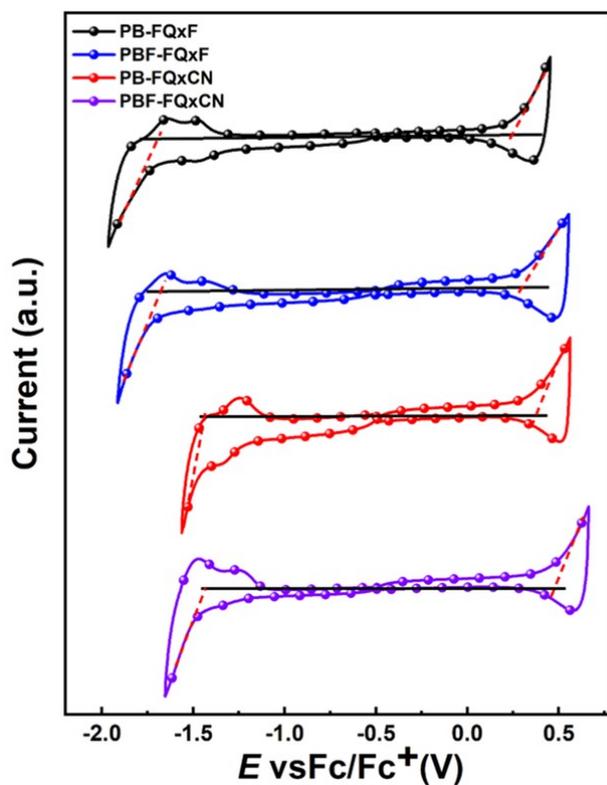


Figure S2. Cyclic voltammograms of the polymers

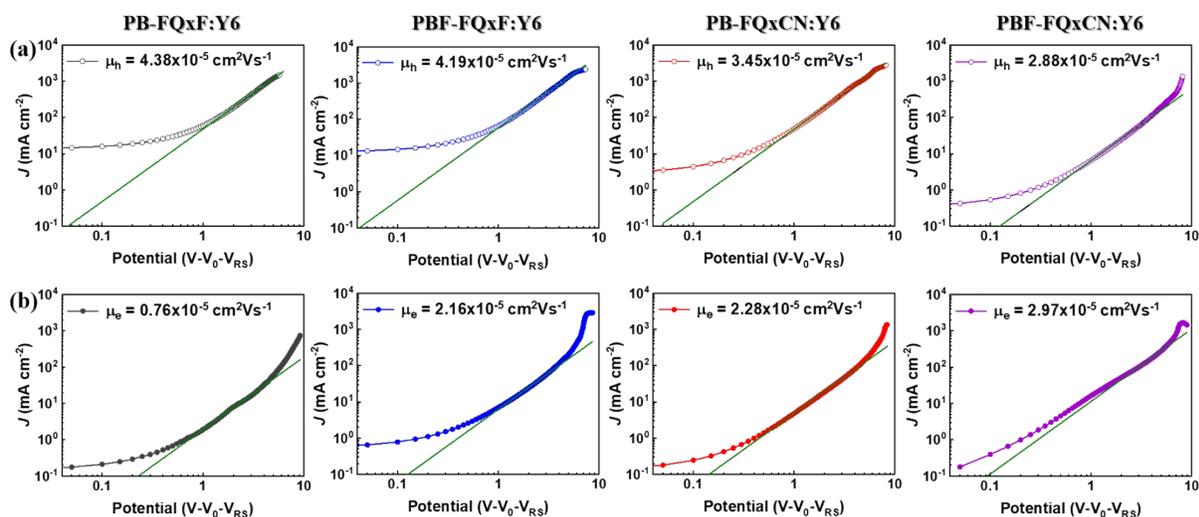


Figure S3. Current density vs. voltage curves of (a) hole- and (b) electron-only devices for the polymers with the calculated mobility values.

**Table S1.** Photovoltaic parameters of OSCs of polymer donor:Y6 with different blend ratios.

All values in parenthesis are the average and standard deviation photovoltaic values from 10 devices.

<b>BHJ</b>	<b>D:A</b>	<b><math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>	<b><math>V_{oc}</math> (V)</b>	<b><math>FF</math> (%)</b>	<b><math>PCE</math> (%)</b>
<b>PB-FQxY6</b>	1:1	13.03 (12.40 ± 0.26)	0.68 (0.68 ± 0.01)	35.31 (35.05 ± 0.22)	3.14 (3.05 ± 0.07)
	1:1.5	14.39 (14.16 ± 0.32)	0.66 (0.66 ± 0.01)	37.62 (37.07 ± 0.46)	3.59 (3.47 ± 0.09)
	1:2	12.74 (12.59 ± 0.20)	0.65 (0.65 ± 0.01)	37.77 (37.79 ± 0.11)	3.14 (3.12 ± 0.03)
<b>PBF-FQxY6</b>	1:1	15.39 (14.81 ± 0.76)	0.74 (0.74 ± 0.01)	38.67 (38.26 ± 0.23)	4.40 (4.20 ± 0.22)
	1:1.5	15.67 (15.33 ± 0.31)	0.72 (0.72 ± 0.01)	40.02 (40.01 ± 0.08)	4.53 (4.44 ± 0.07)
	1:2	15.02 (14.62 ± 0.36)	0.72 (0.72 ± 0.01)	40.60 (40.53 ± 0.18)	4.36 (4.25 ± 0.10)
<b>PB-FQxCN:Y6</b>	1:1	21.39 (21.44 ± 0.06)	0.81 (0.81 ± 0.01)	46.86 (45.78 ± 0.81)	8.14 (7.97 ± 0.15)
	1:1.5	21.82 (21.82 ± 0.09)	0.81 (0.80 ± 0.01)	47.79 (47.79 ± 0.28)	8.45 (8.30 ± 0.18)
	1:2	21.84 (21.82 ± 0.02)	0.78 (0.78 ± 0.01)	48.11 (47.79 ± 0.32)	8.21 (8.17 ± 0.05)
<b>PBF-FQxCN:Y6</b>	1:1	20.29 (20.21 ± 0.09)	0.86 (0.86 ± 0.01)	50.74 (50.13 ± 0.46)	8.82 (8.68 ± 0.12)
	1:1.5	21.08 (20.97 ± 0.12)	0.85 (0.85 ± 0.01)	50.82 (50.15 ± 0.68)	9.05 (8.90 ± 0.15)
	1:2	19.37 (19.20 ± 0.16)	0.84 (0.84 ± 0.01)	49.93 (48.75 ± 0.75)	8.07 (7.83 ± 0.16)

**Table S2.** Photovoltaic parameters of OSCs of PBF-FQxCN:Y6 with different volume ratios of a processing additive, DIO. All values in parenthesis are the average and standard deviation photovoltaic values from 10 devices.

<b>Additive (%)</b>	<b><math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>	<b><math>V_{oc}</math> (V)</b>	<b><math>FF</math> (%)</b>	<b><math>PCE</math> (%)</b>	<b>Cal. <math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>
0.5	19.58 (19.39 ± 0.15)	0.83 (0.82 ± 0.01)	65.15 (64.61 ± 0.51)	10.54 (10.32 ± 0.16)	20.98
1	21.36 (21.52 ± 0.36)	0.81 (0.80 ± 0.01)	62.89 (62.22 ± 0.76)	10.81 (10.77 ± 0.05)	22.16
2	21.04 (21.07 ± 0.04)	0.80 (0.80 ± 0.01)	61.61 (60.94 ± 1.02)	10.43 (10.29 ± 0.16)	20.17

**Table S3.** Crystallographic parameters of neat and BHJ films based on PB-FQxF, PBF-FQxF, PB-FQxCN, and PBF-FQxCN with thin films.

Type	Polymers	Crystallographic parameters							
		Axis	$\pi$ - $\pi$ stack [Å <sup>-1</sup> ]	d-spacing [Å]	Lamellar stack [Å <sup>-1</sup> ]	d-spacing [Å]	FWHM of $\pi$ - $\pi$ peak [Å <sup>-1</sup> ]	CCL [Å]	
neat polymer	PB-FQxF	$q_{xy}$	-	-	0.26	24.48	0.43	13.59	
		$q_z$	1.64	3.82	-	-			
	PBF-FQxF	$q_{xy}$	-	-	0.25	24.69	0.34	17.19	
		$q_z$	1.66	3.79	-	-			
	PB-FQxCN	$q_{xy}$	-	-	0.26	24.48	0.40	14.61	
		$q_z$	1.62	3.89	-	-			
	PBF-FQxCN	$q_{xy}$	-	-	0.25	25.14	0.35	16.70	
		$q_z$	1.65	3.82	-	-			
	BHJ with DIO 1%	PB-FQxF:Y6	$q_{xy}$	-	-	0.24	26.31	0.39	15.03
			$q_z$	1.73	3.62	-	-		
		PBF-FQxF:Y6	$q_{xy}$	-	-	0.24	26.56	0.31	18.85
			$q_z$	1.73	3.63	-	-		
PB-FQxCN:Y6		$q_{xy}$	-	-	0.24	26.56	0.31	18.85	
		$q_z$	1.74	3.62	-	-			
PBF-FQxCN:Y6		$q_{xy}$	-	-	0.24	26.31	0.28	20.82	
		$q_z$	1.73	3.64	-	-			

## References

- S1 D. He, L. Qiu, Z. Zhang, Y. Li, C. Pan and Y. Zou, *RSC Advances*, 2016, **6**, 62923–62933.
- S2 U. T. Mueller-Westerhoff and M. Zhou, *Synthesis of Symmetrically and Unsymmetrically Substituted-Diones from Organometallic Reagents and 1,4-Dialkylpiperazine-2,3-diones*, 1994, vol. 59.
- S3 Y. H. Tseng, W. U. Fang-Iy, P. I. Shih and C. F. Shu, *Journal of Polymer Science, Part A: Polymer Chemistry*, 2005, **43**, 5147–5155.
- S4 S. L. Handoko, M. Jeong, D. R. Whang, J. H. Kim and D. W. Chang, *Journal of Materials Chemistry A*, 2020, **8**, 19513–19521.
- S5 L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li and J. Hou, *Angewandte Chemie - International Edition*, 2011, **50**, 9697–9702.
- S6 M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Advanced Materials*, 2015, **27**, 4655–4660.
- S7 V. D. Mihailetschi, J. Wildeman and P. W. M. Blom, *Physical Review Letters*, 2005, DOI:10.1103/PhysRevLett.94.126602.