Supporting Information

Rational Selection of Solvents and Fine Tune of Morphologies toward Highly Efficient Polymer Solar Cells Made by Green Process

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Experimental Section

Materials: The monomer 6,7-difluoro-5,8-dibromo-2,3-bis(3-(2-ethylhexyloxy)phenyl)-quinoxaline (DTQx-2F) were purchased from Solarmer Materials Inc. The monomer 2,6-Bis(trimethyltin)-(4,8-bis(5-(2-ethyllhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-T-2F) were synthesized following procedures reported by our group.[1] All other chemical reagents were used as received.

Measurements: The number-average molecular weight (M_n) and polydispersity index (PDI) was measured on Aligent PL-GPC 50 as eluent at a flow rate of 1.0 mL/min. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 HD spectrometer. MALDI-TOF mass spectra were determined by Bruker BIFLEX III. Elemental analysis was performed on a flash EA1112 analyzer. Atomic Force Microscopy (AFM) was measured by using Bruker Vecoo, Inc., V. Transmission electron microscopy (TEM) was performed using a JEOL 2200FS instrument. GIWAXS, R-SoXS, and reference spectroscopy measurements were performed at beamline 7.3.3[2], beamline 11.0.1.2.[3], and beamline 5.3.2.2[4], respectively at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA.

The current density-voltage (*J-V*) characteristics were measured with a Keithley 2400 measure unit. The power conversion efficiencies were conducted under 1 sun, AM 1.5G (air mass 1.5 global) (100 mW/cm^2) using a XES-70S1 solar simulator (SAN-EI Electric Co.,

Ltd.,AAA grade, 70 mm×70 mm photo-beam size). 20 mm×20 mm monocrystalline silicon reference cell with KG3 filter (Enli Tech Co. Ltd., Taiwan) was selected for accurately measuring the PSCs. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

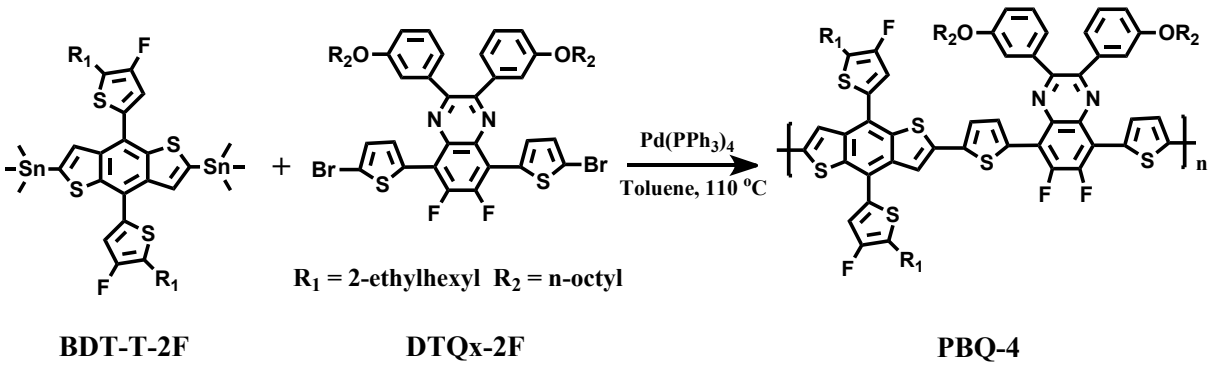
Fabrication of polymer solar cells: Photovoltaic devices were fabricated with the structure of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al. Specific process is as follows: patterned ITO-coated glass was cleaned by oxygen plasma for 20 min and then a ca. 30 nm thick PEDOT:PSS (Bayer baytron 4083) anode buffer layer was spin-cast onto the ITO substrate. Afterwards, the glass was dried at 150 °C for 15 min. The active layer was deposited on top of the PEDOT:PSS layer by spin-coating from *o*-dichlorobenezene, *o*-xylene or anisole solution of polymer and $PC_{71}BM$ using additives or not. The thickness of the active layer was measured on an Bruker Dektak. Finally, 20 nm Ca and 80 nm Al layer were successively deposited by evaporation under a pressure of ca. 3×10^{-4} Pa. Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen drybox containing less than 5 ppm oxygen and moisture.

Synthesis:

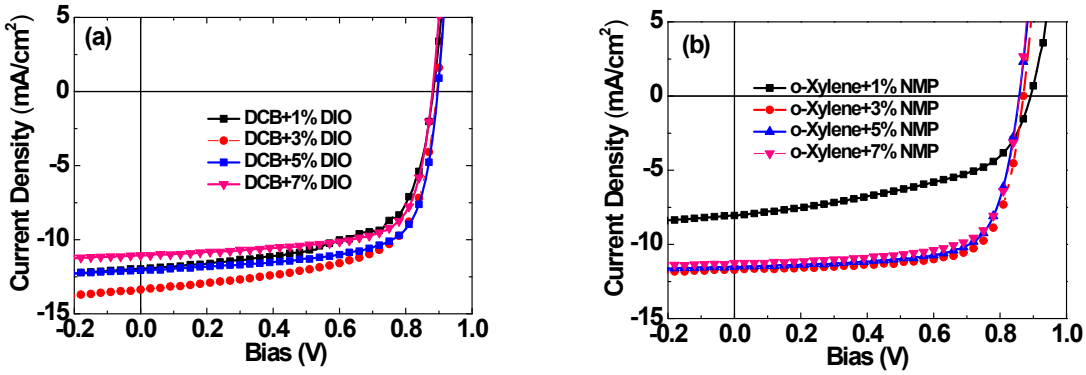
2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-T-2F). MS (MAL DI-TOF): m/z 940.1 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.68 (s, 1H, Ar H), 7.17 (s, 1H, Ar H), 2.80 (d, 2H, CH_2), 1.69 (m, 1H, CH), 1.46 (m, 8H, CH_2), 0.96 (m, 6H, CH_2), 0.47 (t, 9H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 155.5, 153.0, 141.4, 137.2, 135.0, 130.8, 122.0, 117.8, 117.8, 77.3, 77.0, 76.7, 40.9, 32.6, 29.2, 28.9, 25.9, 23.0, 14.2, 10.9, -8.3.

6,7-difluoro-5,8-dibromo-2,3-bis(3-(2-ethylhexyloxy)phenyl)-quinoxaline (DTQX-2F). MS (MAL DI-TOF): m/z 897.1(M^+).^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78 (d, 1H, Ar H), 7.51 (s, 1H, Ar H), 7.23 (t, 1H, Ar H), 7.17 (d, 1H, Ar H), 7.07 (d, 1H, Ar H), 6.99 (dd, 1H, Ar H),

4.04 (t, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 1.34 (m, 8H, CH_2), 0.90 (t, 3H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 159.4, 151.6, 138.8, 129.4, 129.1, 122.9, 118.9, 117.3, 117.1, 115.2, 77.3, 77.0, 76.7, 68.3, 31.9, 29.3, 26.2, 22.7, 14.1 Anal. Calcd for PBQ-1 $(C_{78}H_{88}N_2O_2S_6)_n$: C, 73.31; H, 6.94; N, 2.19; Found: C, 72.55; H, 6.99; N, 2.26. Anal. Calcd for PBQ-2 $(C_{78}H_{86}F_2N_2O_2S_6)_n$: C, 71.30; H, 6.60; N, 2.13; Found: C, 70.44; H, 6.68; N, 2.15. Anal. Calcd for PBQ-3 $(C_{78}H_{86}F_2N_2O_2S_6)_n$: C, 71.30; H, 6.60; N, 2.13; Found: C, 70.22; H, 6.65; N, 2.16. Anal. Calcd for PBQ-4 $(C_{78}H_{84}F_4N_2O_2S_6)_n$: C, 69.4; H, 6.27; N, 2.08; Found: C, 68.15; H, 6.32; N, 2.09. *Mn* (kDa):22.7, *PDI*: 2.40.



Scheme S1. Molecular structures and synthesis method of the polymers.



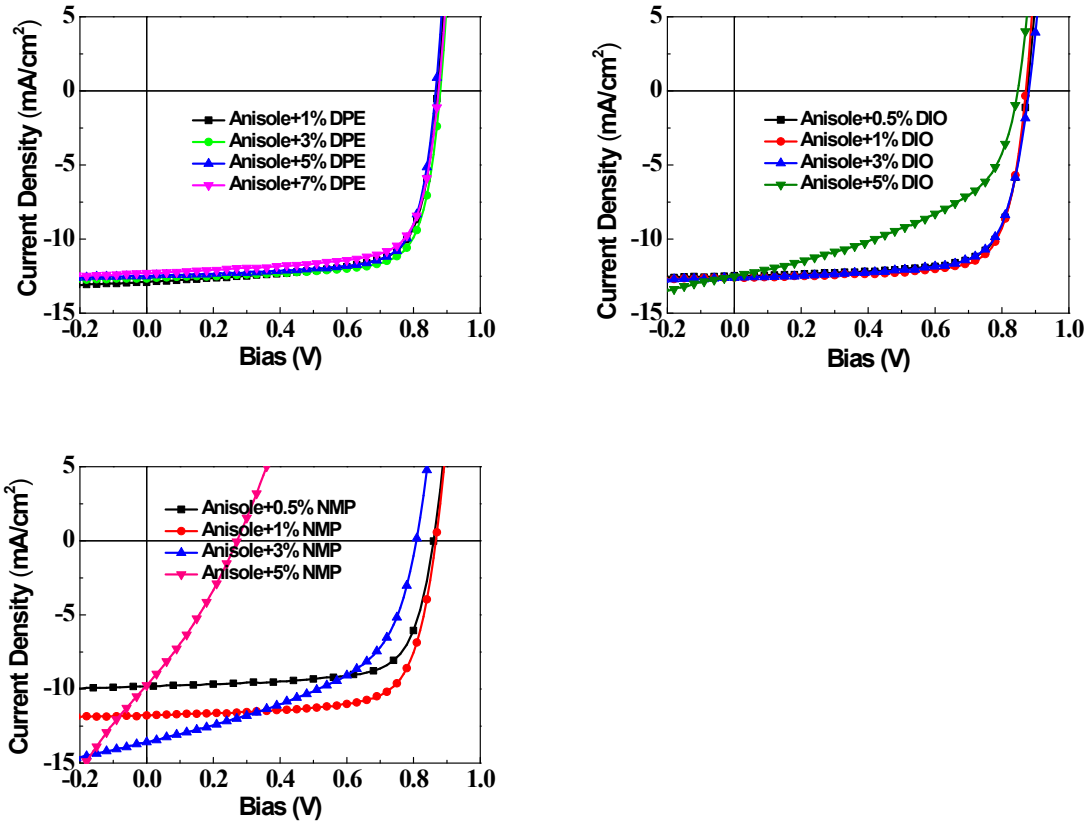


Figure S1. *J-V* curves of PSCs based on PBQ-4/$PC_{71}BM$ processed with different processing solvents.

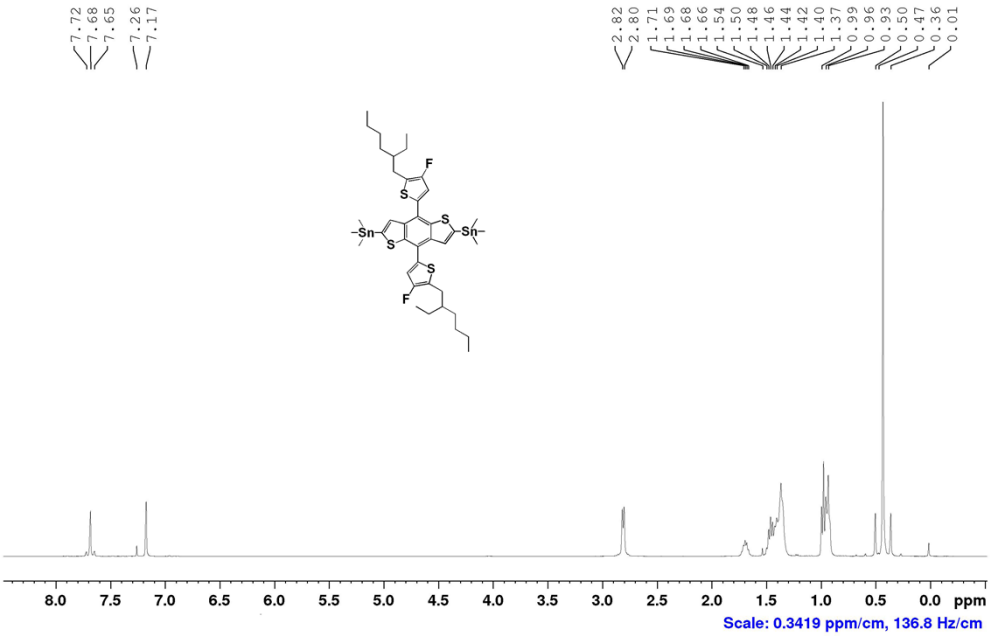


Figure S2. ^1H NMR spectrum of BDT-T-2F.

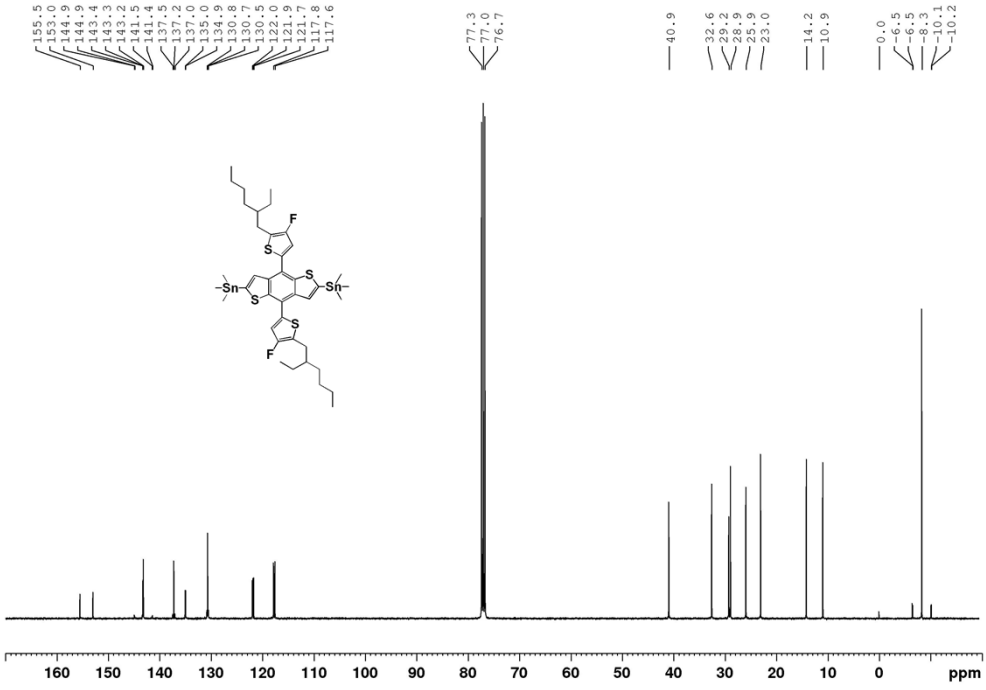


Figure S3. ^{13}C NMR spectrum of BDT-T-2F.

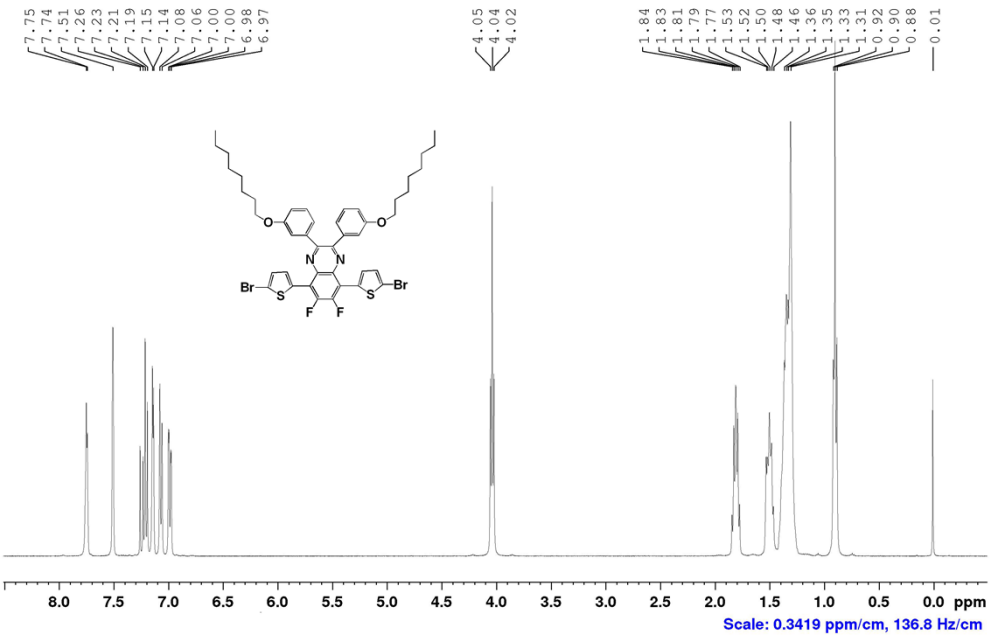


Figure S4. ^{1}H NMR spectrum of DTQx-2F.

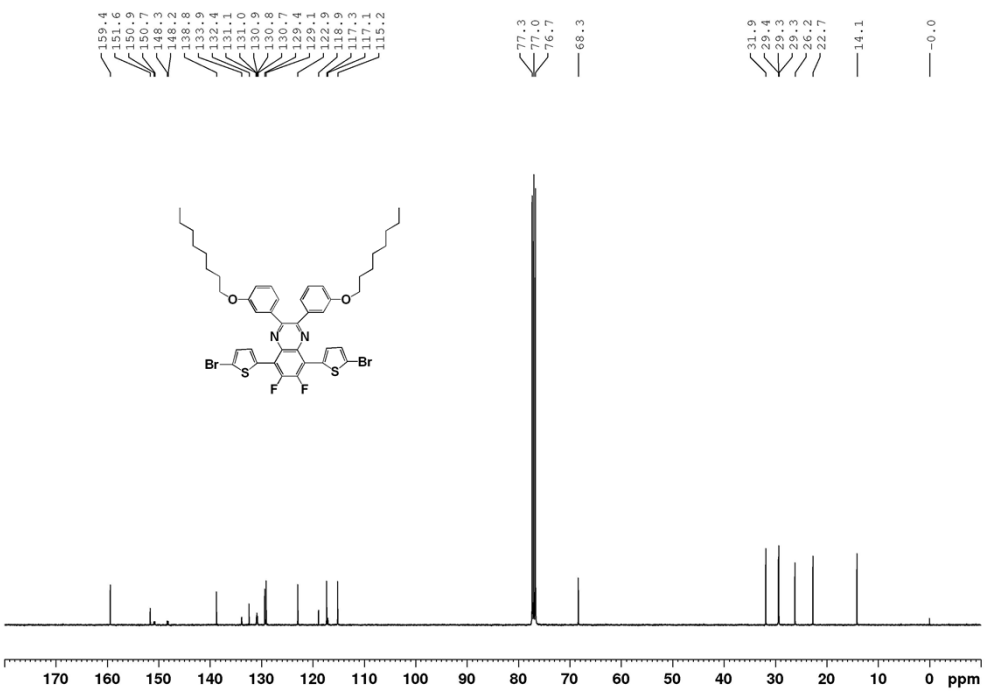


Figure S5. ^{13}C NMR spectrum of DTQx-2F.

Table S1. Device performance of the PSCs based on polymer:$PC_{71}BM$ with different processing solvents.

Processing solvents	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF* (%)	PCE (%)
***o*-DCB/1%DIO**	0.88	11.97	64.22	6.78
***o*-DCB/3%DIO**	0.89	13.36	64.81	7.73
***o*-DCB/5%DIO**	0.89	13.68	69.53	8.47
***o*-DCB/1%DIO**	0.88	11.97	64.22	6.78
***o*-Xylene/1%NMP**	0.89	8.07	50.72	3.65
***o*-Xylene/3%NMP**	0.87	11.82	73.14	7.56
***o*-Xylene/5%NMP**	0.86	11.50	71.77	7.07
***o*-Xylene/7%NMP**	0.86	11.25	71.42	6.90
Anisole/1%DPE	0.87	12.92	72.05	8.11
Anisole/3%DPE	0.88	12.64	75.22	8.37
Anisole/5%DPE	0.87	12.49	74.74	8.08
Anisole/7%DPE	0.88	12.29	72.81	7.83
Anisole/0.5%DIO	0.88	12.47	74	8.08
Anisole/1%DIO	0.87	12.60	75.44	8.28
Anisole/3%DIO	0.88	12.60	72.52	8.05
Anisole/5%DIO	0.85	12.51	47.41	5.02
Anisole/0.5%NMP	0.86	9.84	71.55	6.06
Anisole/1%NMP	0.87	11.79	71.82	7.34
Anisole/3%NMP	0.81	13.59	49.66	5.46
Anisole/5%NMP	0.27	9.73	29.93	0.79

Table S2. The parameters of GIWAXS and calculated coherence length results

Processing solvents	location	FWHM	colength (Å)
***o*-DCB**	1.71	0.61	9.82
***o*-DCB/5%DIO**	1.69	0.55	10.90
***o*-Xylene**	1.71	0.58	10.31
***o*-Xylene/3%NMP**	1.72	0.33	18.31
Anisole	1.74	0.27	23.02
Anisole/3%DPE	1.75	0.16	42.56

Reference

[1] Zhang M. J.; Guo X.; Zhang S. Q.; Hou J. H. *Adv. Mater.* **2014,** *26,* 1118-1123.

[2] A. Hexemer , W. Bras , J. Glossinger , E. Schaible , E. Gann , R. Kirian, A. MacDowell , M. Church , B. Rude , H. Padmore , *J. Phys. Conf. Ser.* **2010** , *247* , 012007.

[3] E. Gann, A. T. Young, B. A. Collins, H. Yan, J. Nasiatka, H. A. Padmore, H. Ade, A. Hexemer, C. Wang, *Rev. Sci. Instrum.* **2012**, *83*, 045110.

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