

Supplementary information

Molecular Tailoring of a Trifluoromethyl-substituted Conjugated Polymer for Efficient Organic Solar Cells

Xueqiao Zhang,^{a,†} Chao Yao,^{a,†} Jiajun Zhao,^a Muhammad Umair Ali,^b Aiyuan Li,^a Clifton Kwang-Fu Shen,^c Chaoyi Yan,^{*a} Yaowu He,^{*a} Jingsheng Miao,^{*a} and Hong Meng^a

^aSchool of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen, 518055, China.

^bTsinghua-Berkeley Shenzhen Institute (TBSI), Tsinghua University, Shenzhen 518055, China.

^cGuangdong LEPUTAI New Materials Technology Co., Ltd, Dongguan, 523808, China.

[†]These authors contributed equally to this work.

*Corresponding Author. E-mail address: yancy@pkusz.edu.cn (C. Yan), heyw@pkusz.edu.cn (Y. He), jingshengmiao@163.com (J. Miao).

1. Materials and Methods

All chemicals and solvents were reagent grade and purchased from Aldrich, Alfa Aesar and TCI (Shanghai) Development Co., Ltd. (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (monomer 1) and 1,3-Bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (monomer 2) was purchased from SunaTech Inc. 2,5-Dibromothiophene-3-carboxylic acid (monomer 3) was synthesized according to a previously-reported procedure.¹

All the polymers were synthesized through similar procedure. In a typical procedure, monomer 1 (0.090 g, 0.1 mmol), monomer 2 ((1-x) mmol) and monomer 3 (x mmol) were dissolved in 6 mL of toluene/DMF (volume ratio 5/1) in a two-neck round-bottom flask. The value for x is 0, 0.02, 0.05, 0.08 and 0.1 for FF0, FF0.2, FF0.5, FF0.8 and FF1, respectively. The solution was flushed with argon for 5 min, and 5 mg of Pd (PPh₃)₄ was added into the flask subsequently. The mixture was flushed with argon for another 15 min and then allowed to stir at 110 °C for 24 h in argon atmosphere. Then, the reactant was cooled down to room temperature, and the polymer was precipitated into 100 mL of methanol. The polymer was collected

by filtration and further purified by Soxhlet extraction (acetone, hexane and chloroform). The polymer was precipitated again in 100 mL of methanol, then filtrated and dried.

2. Device Fabrication and Characterization

OSCs were fabricated with a conventional structure that comprises of indium tin oxide (ITO)/PEDOT:PSS/photoactive layer/PFN-Br/Al. The ITO glasses were ultrasonically cleaned using deionized water, acetone and highly purified isopropanol for 30 min, respectively, and dried by nitrogen. Subsequently, the pre-cleaned ITO glasses were treated with UV-ozone for 15 min. PEDOT:PSS was spin-coated on the ITO at 3000 rpm, and immediately annealed in air at 200 °C for 20 min. The donor/acceptor solution (20 mg/mL in chlorobenzene) was stirred at room temperature for 12 hours before the spin-coating. The solution was spin-coated on the substrate followed by annealing to obtain the photoactive layer. Afterwards, PFN-Br solution (0.5 mg/ml in methanol) was spin-coated on top of the active layer at 3000 rpm. Finally, the devices were completed by thermal evaporating Al (80 nm) under high vacuum.

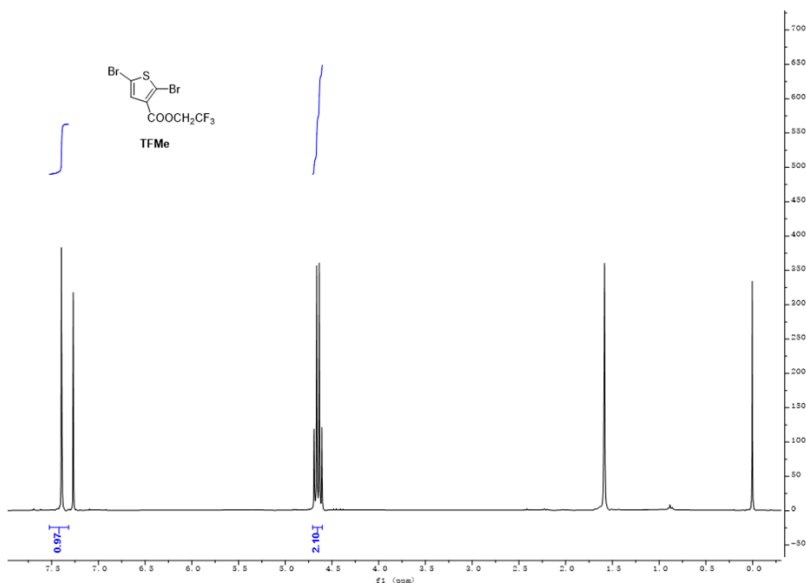
The current density–voltage (J–V) curves of the OSCs were obtained with a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated AM 1.5G (100 mW cm⁻²) irradiation using a SAN-EI XES-70S1 solar simulator, which was calibrated with a standard Si solar cell. EQEs were measured by Stanford Research Systems SR810 lock-in amplifier. The active area of the devices was ca. 0.045 cm².

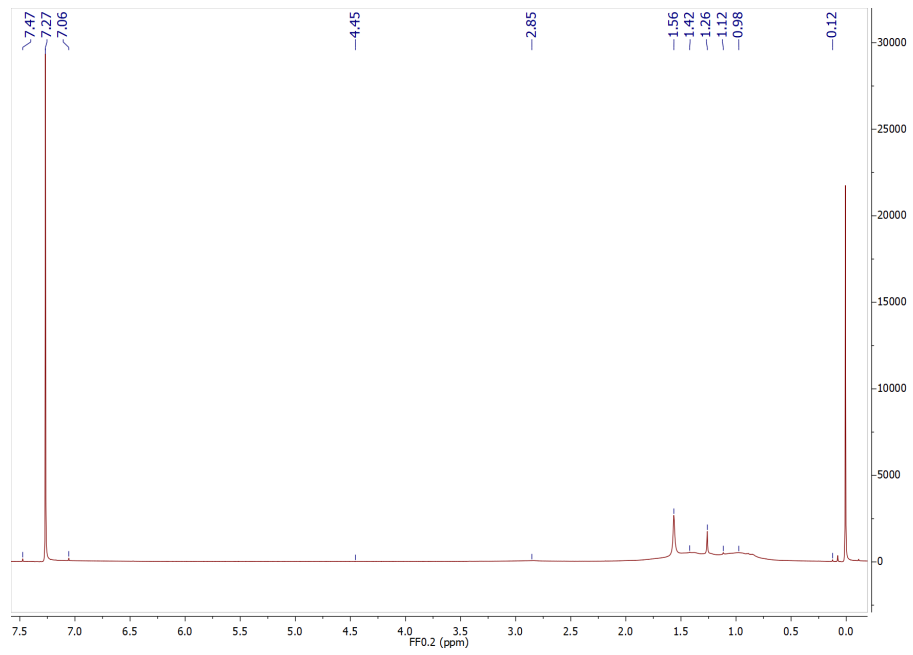
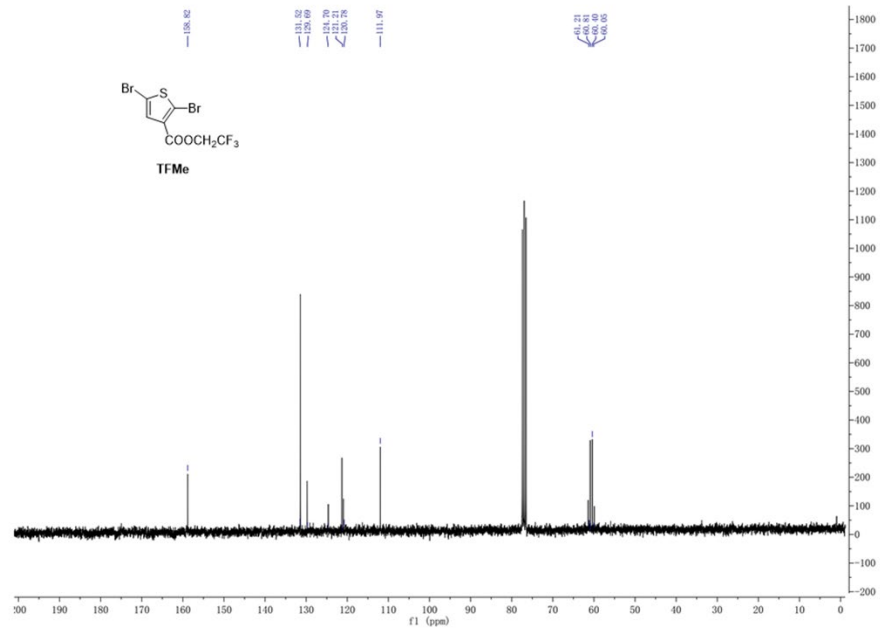
3. Measurements and Instruments

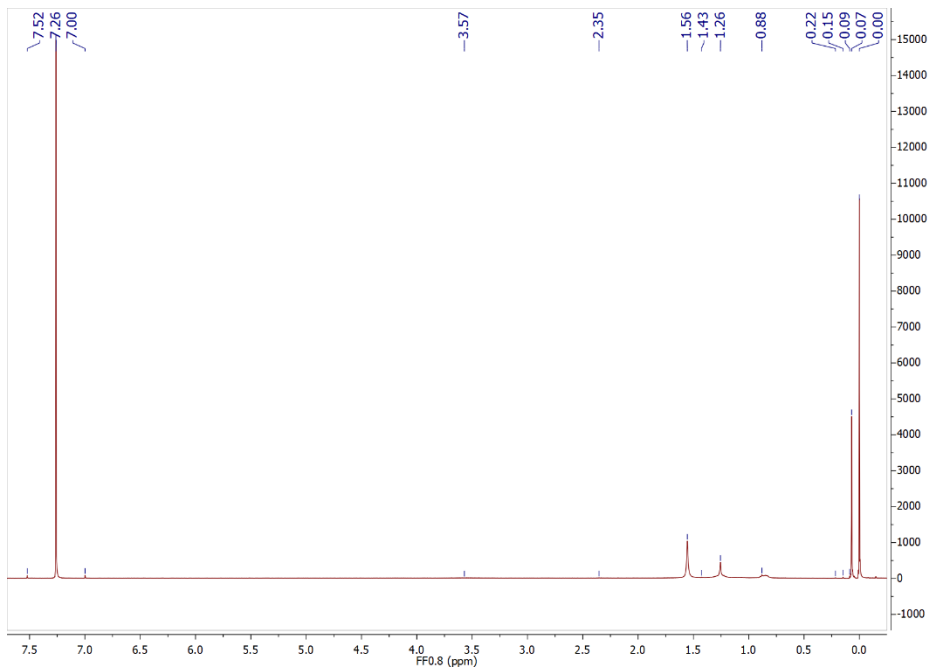
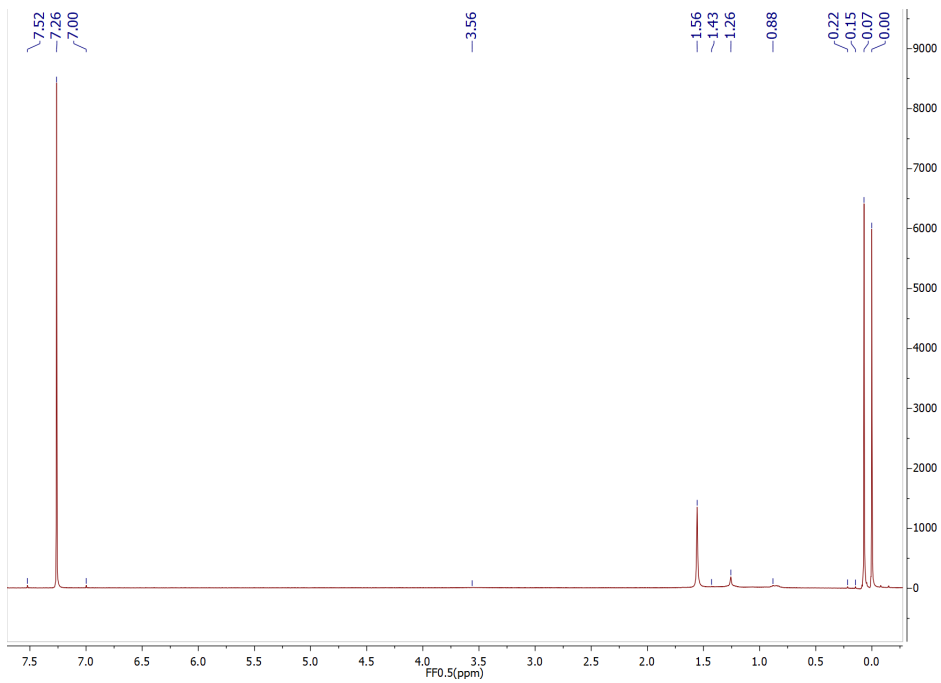
The NMR spectra were measured using Bruker AVANCE 300 or 400 or 500 MHz spectrometer. The average molecular weights and polymer dispersity index (PDI) were measured by gel permeation chromatography (GPC; Waters 1515-2414). The thermogravimetry analysis (TGA) measurements were performed on a Mettler-Toledo TGA thermal analyzer at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. UV-vis absorption spectra were recorded using a JASCO V-570 spectrophotometer. The photochemical stability

was measured by recording the UV-vis spectra of the neat polymer films in air under different irradiation time of illumination simulated AM 1.5G (100 mW cm^{-2}) irradiation using a SAN-EI XES-70S1 solar simulator. Photoluminescence (PL) spectra were measured using a PerkinElmer LS55 fluorescence spectrometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetrabutylammonium phosphorus hexafluoride ($n\text{-Bu}_4\text{NPF}_6$, 0.1 M) in dry acetonitrile employing a computer-controlled CHI660C electrochemical workstation, glassy carbon working electrode coated with donor polymer films, an Ag/Ag^+ reference electrode, and a platinum-wire auxiliary electrode. The potentials were referenced to a ferrocenium/ferrocene (Fc^+/Fc) couple using ferrocene as an internal standard. Atomic force microscopy (AFM) was performed using Multimode 8 atomic force microscope in tapping mode. X-ray diffraction (XRD) was performed on a Bruker D8-Advantage powder diffractometer ($\text{Cu-K}\alpha$ radiation) $2\theta = 0^\circ\text{--}60^\circ$ at 1s per step of 5° . The XRD samples were spin-coated from a 10 mg/mL chlorobenzene solution on the quartz substrate.

4. Supporting Figures and Tables







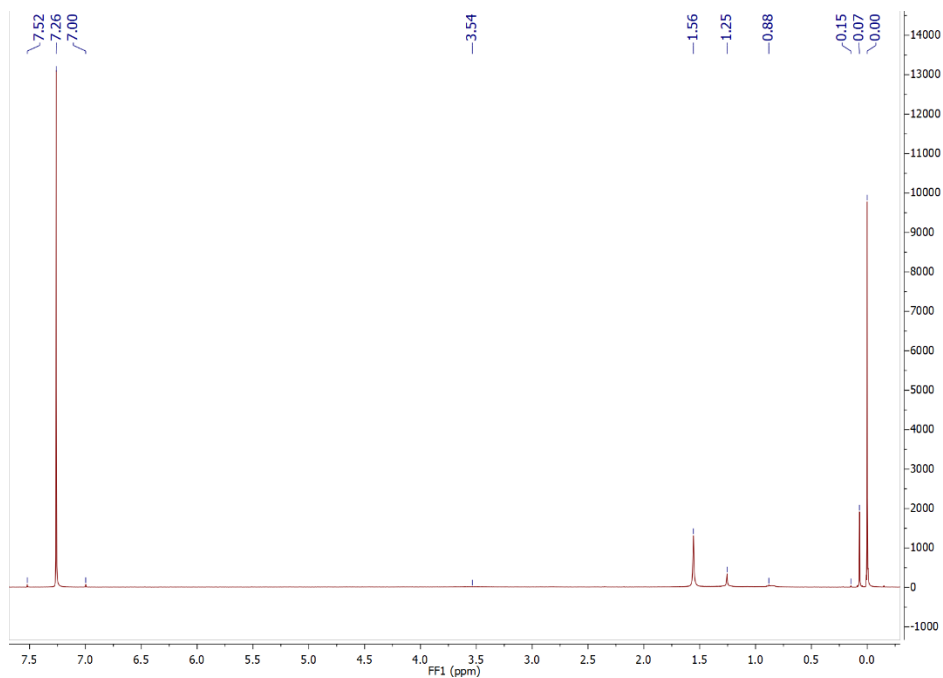


Figure S1. H-NMR spectrum and C-NMR spectra of monomer 3; H-NMR spectrum FF0.2, FF0.5, FF0.8 and FF1.

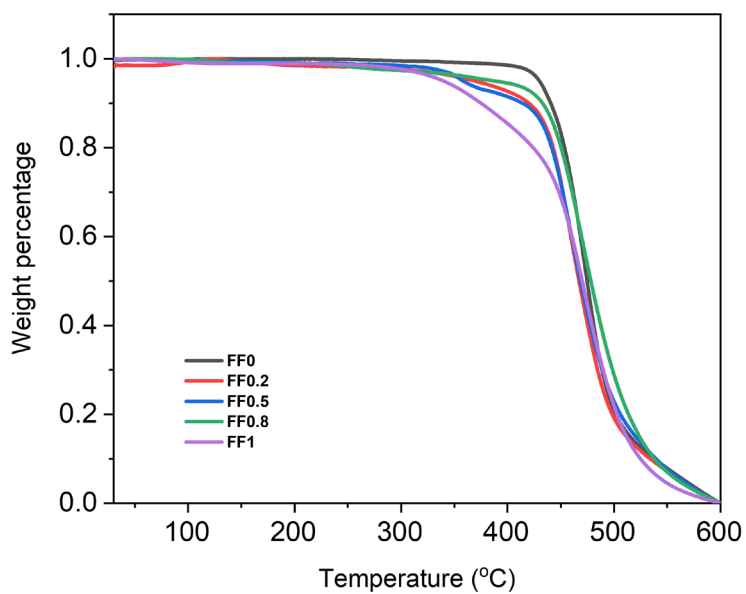


Figure S2. TGA plots of polymers under the protection of nitrogen with a heating rate of $10^{\circ}\text{C min}^{-1}$.

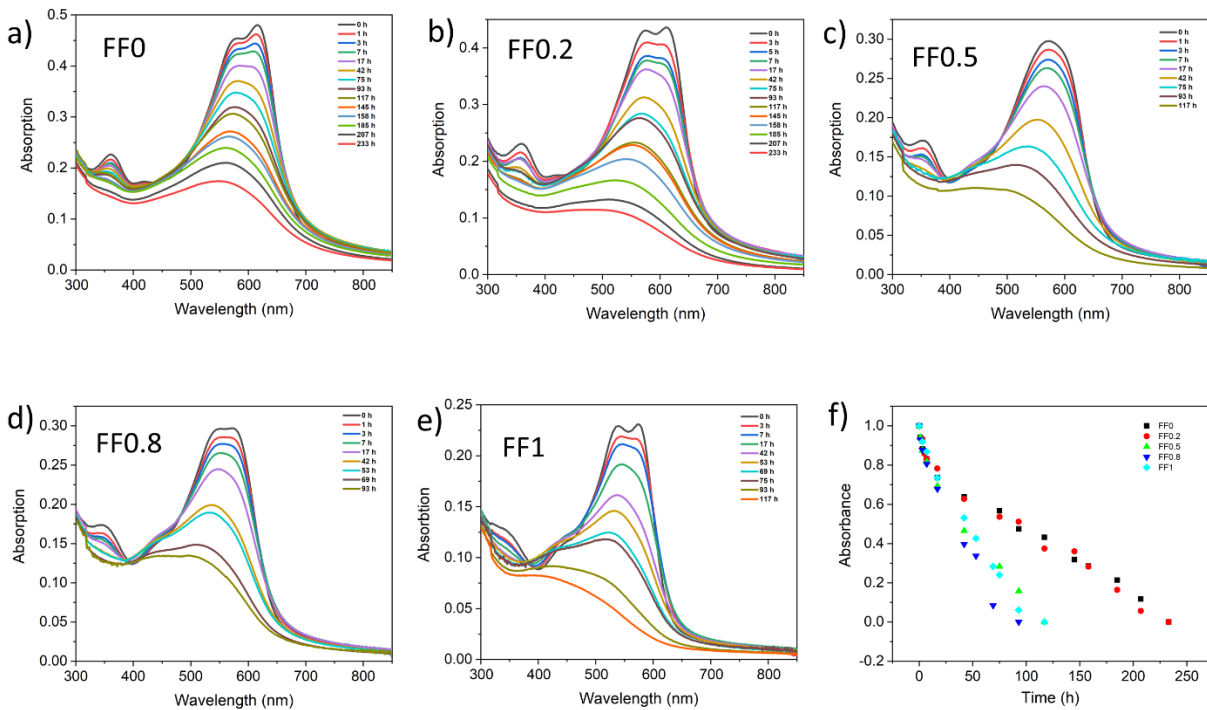


Figure S3. a)- e) Absorption profiles of FF0, FF0.2, FF0.5, FF0.8 and FF1 in the UV-visible region. (f) The maximum absorbance as a function of irradiation time for polymer films. The absorbance has been normalized to allow for comparison of the degradation rate.

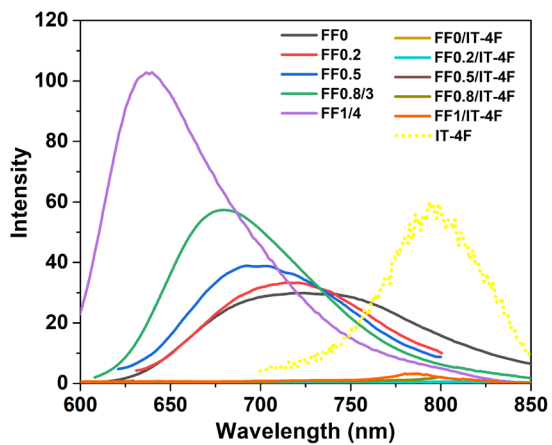


Figure S4. PL spectra of polymers, IT-4F and polymers/IT-4F in films.

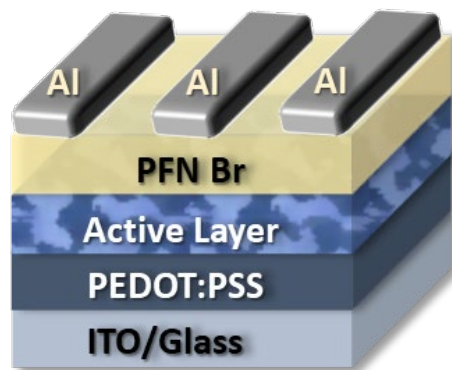


Figure S5. Device architecture of conventional structured OSCs.

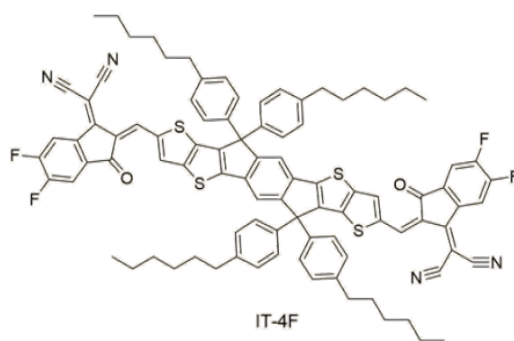


Figure S6. Chemical structure of IT-4F.

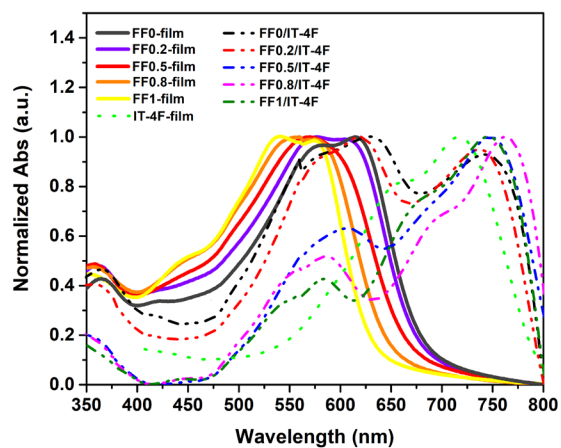


Figure S7. UV-vis absorption spectra of neat polymers and polymers/IT-4F in films.

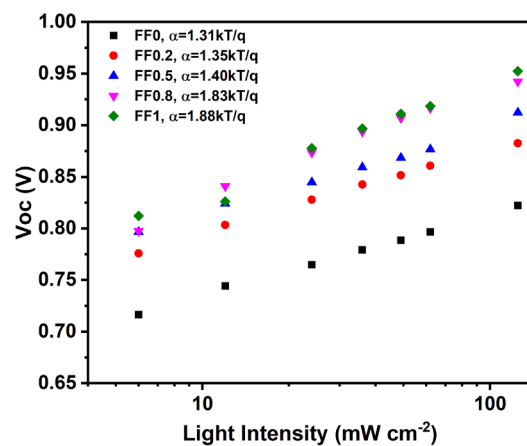


Figure S8. Light intensity dependence of V_{oc} of all the fabricated OSCs.

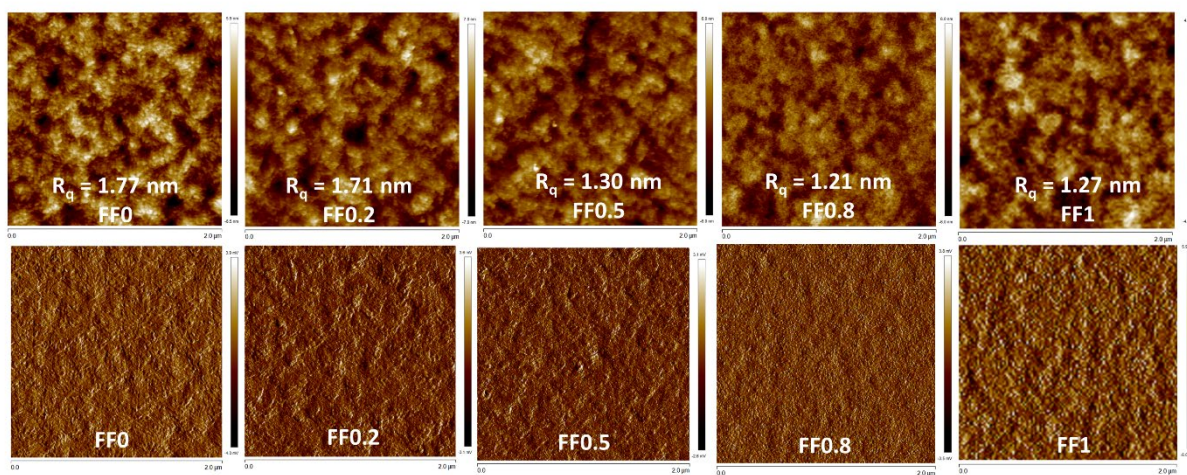


Figure S9. Tapping-mode AFM height and phase images of neat polymer films.

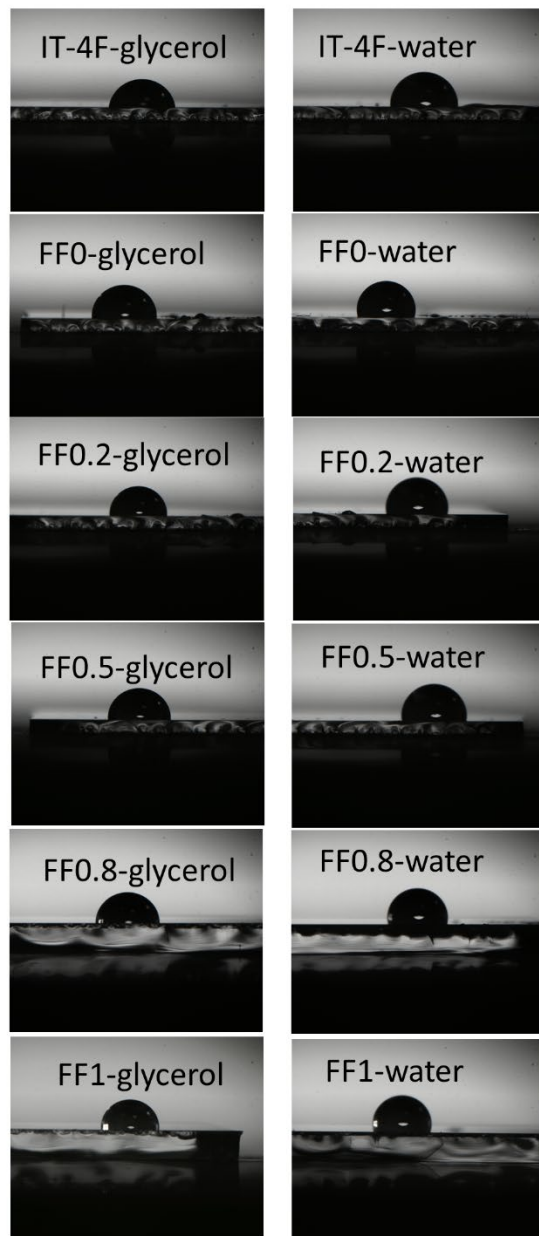


Figure S10. Contact angle of water and glycerol on IT-4F, FF0, FF0.2, FF0.5 FF0.8, and FF1 films.

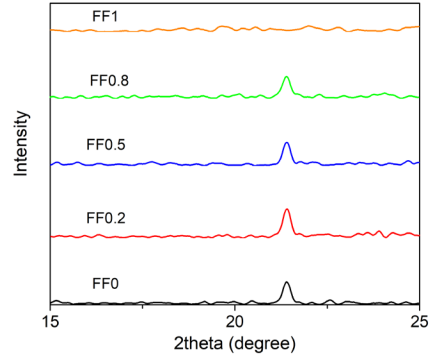


Figure S11. X-ray diffraction patterns of FF0, FF0.2, FF0.5, FF0.8, FF1 films on glass substrates.

Table S1. Photovoltaic parameters of FF0.2 based devices with different D/A ratios (the average values of PCE for five devices in the brackets)

D/A	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
1/1	0.88	18.85	72.70	12.02 (11.69±0.28)
1.25/1	0.90	19.95	65.29	11.72 (11.30±0.21)
1/1.25	0.88	20.25	64.30	11.48 (11.07±0.46)

Table S2. Photovoltaic parameters of FF0.2 based devices with different DIO ratios (the average values of PCE for five devices in the brackets)

DIO	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
0%	0.92	19.11	57.36	10.19 (9.85±0.54)
0.25%	0.88	19.51	68.37	11.73 (11.52±0.15)
0.5%	0.88	18.85	72.70	12.02 (11.69±0.28)
1%	0.88	18.77	65.70	10.84 (10.47±0.46)

Table S3. Photovoltaic parameters of FF0.2 based devices under different annealing temperature (the average values of PCE for five devices in the brackets)

Annealing T (°C)	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
25	0.89	19.60	56.69	9.93 (9.85±0.08)
70	0.89	20.00	62.88	11.21 (11.05±0.14)
100	0.88	18.85	72.70	12.02 (11.69±0.28)
130	0.88	20.34	67.03	11.92 (11.52±0.45)

Table S4. Photovoltaic parameters of FF0.5 based devices under different D/A ratios (the average values of PCE for five devices in the brackets)

D/A	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
1.25/1	0.92	17.57	57.42	9.33 (9.09±0.20)
1/1	0.92	16.52	65.09	9.93 (9.75±0.22)
1/1.25	0.91	17.24	63.28	9.93 (9.25±0.32)

Table S5. Photovoltaic parameters of FF0.5 based devices with different DIO ratios (the average values of PCE for five devices in the brackets)

DIO	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
0%	0.97653	16.65955	55.3831	9.01 (8.76±0.17)
0.25%	0.916686	16.72865	63.2683	9.70 (9.39±0.49)
0.5%	0.923405	16.5228	65.09	9.93 (9.75±0.22)
1%	0.918884	16.29324	63.943	9.57 (9.54±0.08)

Table S6. Photovoltaic parameters of FF0.5 based devices under different annealing temperature (the average values of PCE for five devices in the brackets)

Annealing T (°C)	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
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25	0.93	13.27	43.33	5.35 (5.31±0.05)
70	0.94	17.63	59.77	9.87 (9.16±0.50)
100	0.92	16.53	65.09	9.90 (9.75±0.22)
130	0.90	17.8	60.97	9.77 (9.34±0.67)

Table S7. Photovoltaic parameters of FF0.8 based devices under different D/A ratios (the average values of PCE for five devices in the brackets)

D/A	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
1/1	0.95	16.02	48.13	7.31 (6.99±0.31)
1.25/1	0.91	13.09	52.81	6.58 (6.19±0.47)
1/1.25	0.88	11.82	51.79	5.63 (5.32±0.39)

Table S8. Photovoltaic parameters of FF0.8 based devices with different DIO ratios (the average values of PCE for five devices in the brackets)

DIO	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
0%	0.95	12.46	38.51	4.77 (4.55±0.46)
0.25%	0.90	15.49	49.20	7.22 (6.59±0.45)
0.5%	0.95	16.02	48.13	7.31 (6.99±0.31)
1%	0.88	15.89	48.38	7.12 (6.91±0.19)

Table S9. Photovoltaic parameters of FF0.8 based devices under different annealing temperature (the average values of PCE for five devices in the brackets)

Annealing T (°C)	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
70	0.95	15.01	42.10	6.25 (5.71±0.47)

100	0.95	16.02	48.13	7.31 (6.99±0.31)
130	0.90	14.63	50.38	6.97 (6.84±0.11)

Table S10. Photovoltaic parameters of FF1 based devices under different D/A ratios (the average values of PCE for five devices in the brackets)

D/A	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
1/1	0.96	9.12	50.42	4.42 (4.31±0.23)
1.25/1	0.96	7.06	49.92	3.60 (3.29±0.35)
1/1.25	0.94	6.07	48.26	2.95 (1.82±0.18)

Table S11. Photovoltaic parameters of FF1 based devices with different DIO ratios (the average values of PCE for five devices in the brackets)

DIO	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
0%	0.95	9.78	40.75	4.04 (3.83±0.16)
0.25%	0.93	9.39	47.28	4.39 (4.17±0.32)
0.5%	0.96	9.12	50.42	4.42 (4.31±0.23)
1%	0.90	7.05	50.35	3.39 (2.88±0.39)

Table 12. Photovoltaic parameters of FF1 based devices under different annealing temperature (the average values of PCE for five devices in the brackets)

Annealing T (°C)	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
70	0.92	9.86	43.53	4.21 (3.56±0.66)
100	0.96	9.12	50.42	4.42 (4.31±0.23)
130	0.92	8.56	49.77	4.21 (3.83±0.41)

Reference

1. Pomerantz, M.; Yang, H.; Cheng, Y., Poly(alkyl thiophene-3-carboxylates). Synthesis and Characterization of Polythiophenes with a Carbonyl Group Directly Attached to the Ring. *Macromolecules* **1995**, *28* (17), 5706-5708.