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Supporting Information

Achieving over 10% efficiency by new acceptor ITTC and its blends with hexafluoroquinoxaline based polymer

Zhenzhen Zhang[a], Liuliu Feng[a], Shutao Xu[a], Jun Yuan[a], Zhi-Guo Zhang[b], Hongjian Peng[a], Yongfang Li[b], Yingping Zou[a,c,*]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China.
[b] Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
[c] State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China.
*email - yingpingzou@csu.edu.cn

1. Characterization

^{1}H NMR and ^{13}C NMR were recorded using a Bruker DMX-400 and DMX-500 spectrometers with deuterated chloroform as solvent at 298 K. Chemical shifts were reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. Ultraviolet-visible (UV-Vis) absorption spectra were measured with a SHIMADZU UV-2600 spectrophotometer. Cyclic voltammetry (CV) was recorded with a computer controlled CHI660E electrochemical workstation using ITTC film on platinum electrode (1.0 cm^2) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) was used for the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scanning rate of 50 mV·s^{-1}. PL spectra were measured with a Hitachi F-4600 fluorescence spectrophotometer. The morphologies of the HFQx-T: ITTC blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 5 μm scanner. Transmission electron microscope (TEM) measurements were performed in a JEM-2100F.

2. Fabrication and characterization of polymer solar cells

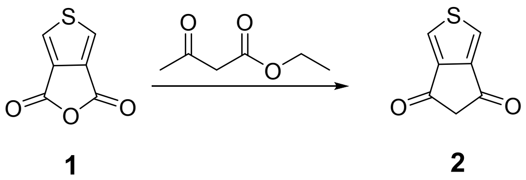
The non-fullerene PSCs were fabricated with a configuration of ITO/PEDOT:PSS/active layer/PDINO/Al. A thin layer of PEDOT:PSS was deposited through spin-coating on precleaned ITO-coated glass from a PEDOT:PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 4000 rpm and dried subsequently at 150 °C for 15 min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer was spin-coated from chloroform solution containing a blend of HFQx-T and ITTC onto the PEDOT:PSS layer. The optimized conditions are with a spin rate of 2800 rpm and with a blend chloroform solution containing 9 mg/mL HFQx-T and 9 mg/mL ITTC. All blend films were thermally annealed at 130^{o}C for 10 min, the thickness of active layer was typically 100 nm. After cooling to room temperature, methanol solution of PDINO at a concentration of 1.0 mg/mL was deposited atop the active layer at 3000 rpm for 30 s to afford a thickness of 10 nm. Finally, top Al electrode was deposited in vacuum onto the cathode buffer layer at a pressure of ca. 8.0×10^{-5} Pa. The active area of the device was 4.5 mm^2. The current density-voltage (J-V) characteristics of the PSCs were measured in glovebox on a computer-controlled Keithley 2450 Source-Measure Unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450 W xenon lamp and an air mass (AM) 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm^{-2} by a Newport Oriel 91150V reference cell. The EQE measurements of PSCs were performed by Stanford Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

3. Materials

All starting materials and reagents were obtained from J&K and Alfa Asia Chemical Co. and used without further purification. Compound 1 was synthesized according to literature procedures.[1]

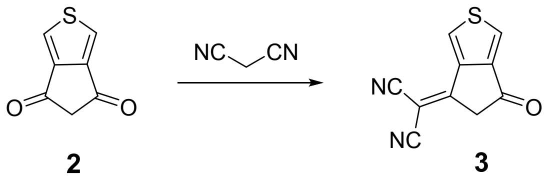
4. Synthesis

4H-cyclopenta[c]thiophene-4,6(5H)-dione (2)



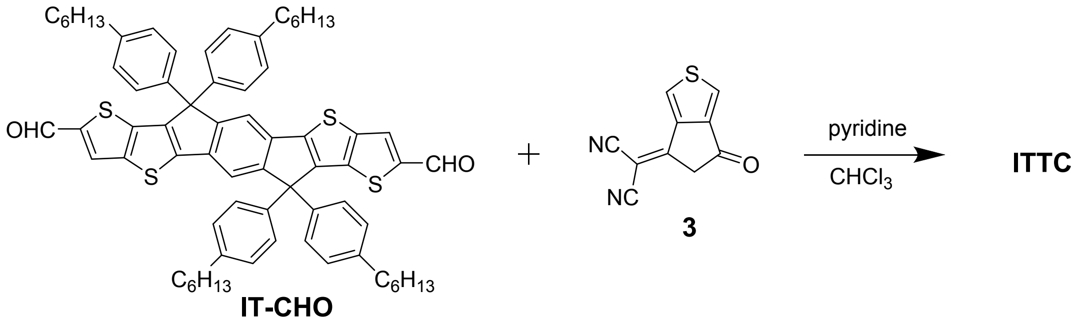
Triethylamine (2.63 g, 26 mmol) and ethylacetoacetate (1.83 g, 14.09 mmol) were added to the solution of compound 1 (2 g, 13 mmol) in acetic anhydride (13.27 g, 130 mmol) under nitrogen. The mixture was stirred overnight at 65 °C. The mixture was poured into ice-water with HCl and then extracted with dichloromethane. The organic phase was evaporated and refluxed in conc.HCl for 1 h. After cooling to room temperature, the crude product was extracted with dichloromethane and then purified by column chromatography using dichloromethane as eluent, yellowish solid was obtained (0.67 g, 34%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 2H), 3.57 (s, 2H).

2-(6-oxo-5,6-dihydro-4H-cyclopenta[c]thiophen-4-ylidene)malononitrile (3)



Compound 2 (0.66 g, 4.34 mmol) and malononitrile (0.79 g, 12.05 mmol) were dissolved in 10 mL ethanol. The mixture was stirred for 30 min, and then anhydrous sodium (0.46 g, 5.64mmol) acetate was added. After 1 h, the mixture was poured into water, and acidified to pH 1–2 by addition of the hydrochloric acid. The precipitate was filtered and washed with water. The crude product was purified by column chromatography using dichloromethane as eluent, light yellow solid was obtained (0.37 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, 1H), 8.09 (d, 1H), 4.02 (s, 2H).

Synthesis of ITTC



To a solution of IT-CHO (0.16 g, 0.15 mmol) and compound 3 (0.30 g, 1.50 mmol) in $CHCl_3$ (50 mL) was added pyridine (1 mL) under argon, and then the mixture was refluxed for 20 h . After cooling to room temperature, the mixture was poured into methanol and filtered. The residue was purified by column chromatography using hexane/ dichloromethane (1:1, *v/v*) as eluent, yielding a dark blue solid (120 mg, 52%).^1H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 2H), 8.40 (d, 2H), 8.20 (s, 2H), 7.95 (d, 2H), 7.66 (s, 2H), 7.23 (d, 8H), 7.16 (d, 8H), 2.58 (t, 8H), 1.60 (m, 8H), 1.34 (m, 24H), 0.88 (m, 12H). ^{13}C NMR (125 MHz, CDCl3) δ 181.35, 156.05, 155.67, 153.33, 147.68, 147.42, 143.66, 142.47, 142.04, 139.60, 139.38, 138.78, 137.01, 128.80, 128.68, 128.07, 127.59, 125.35, 118.73, 114.67, 114.36, 67.81, 63.02, 35.13, 31.70, 31.25, 29.03, 22.42, 14.15. Anal.: Calc. for $C_{90}H_{78}N_4O_2S_6$: C, 75.07; H, 5.46; N, 3.89. Found: C, 74.89; H, 5.28; N, 3.81%.

5. ^1H NMR and ^{13}C NMR

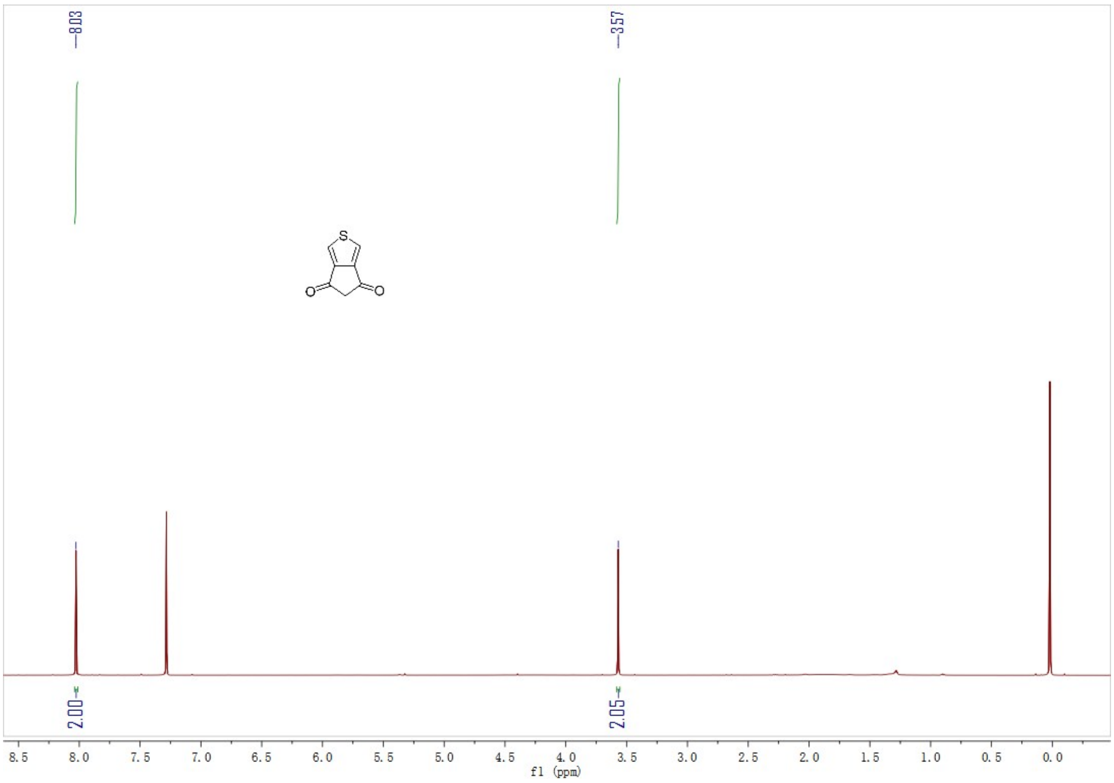


Figure S1. ^{1}H NMR spectrum of 4H-cyclopenta[c]thiophene-4,6(5H)-dione (2).

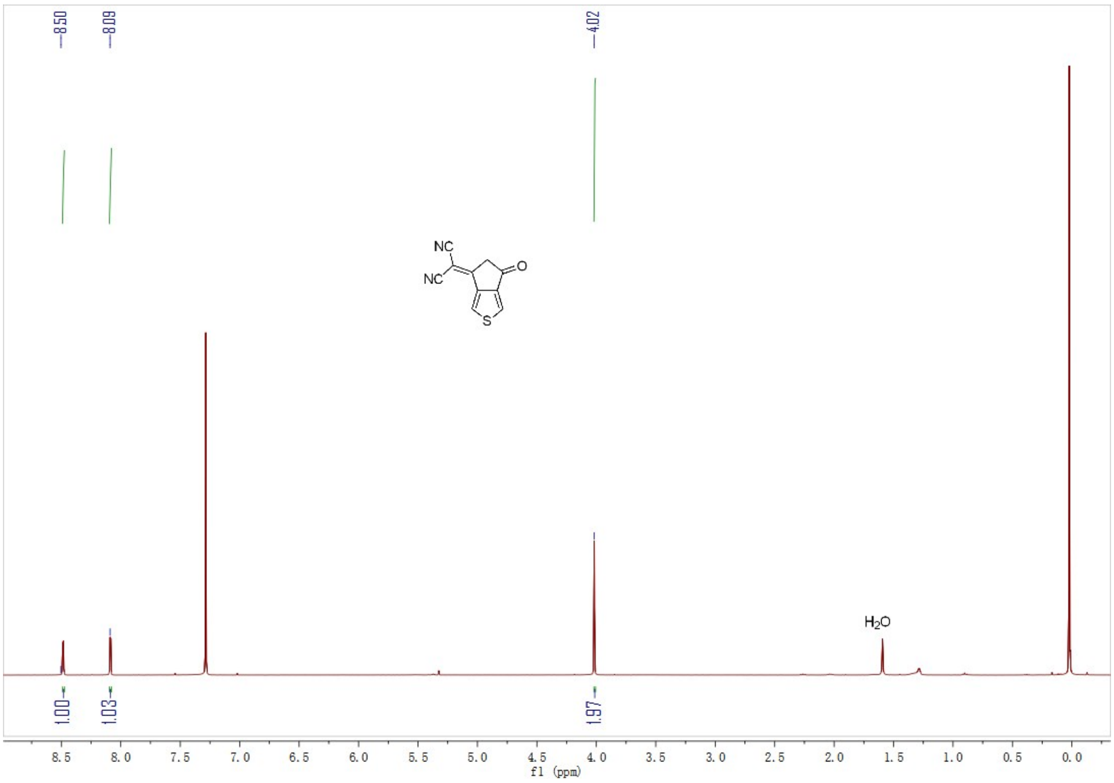


Figure S2. ^{1}H NMR spectrum of 2-(6-oxo-5,6-dihydro-4H-cyclopenta[c]thiophen-4-ylidene)malononitrile (3).

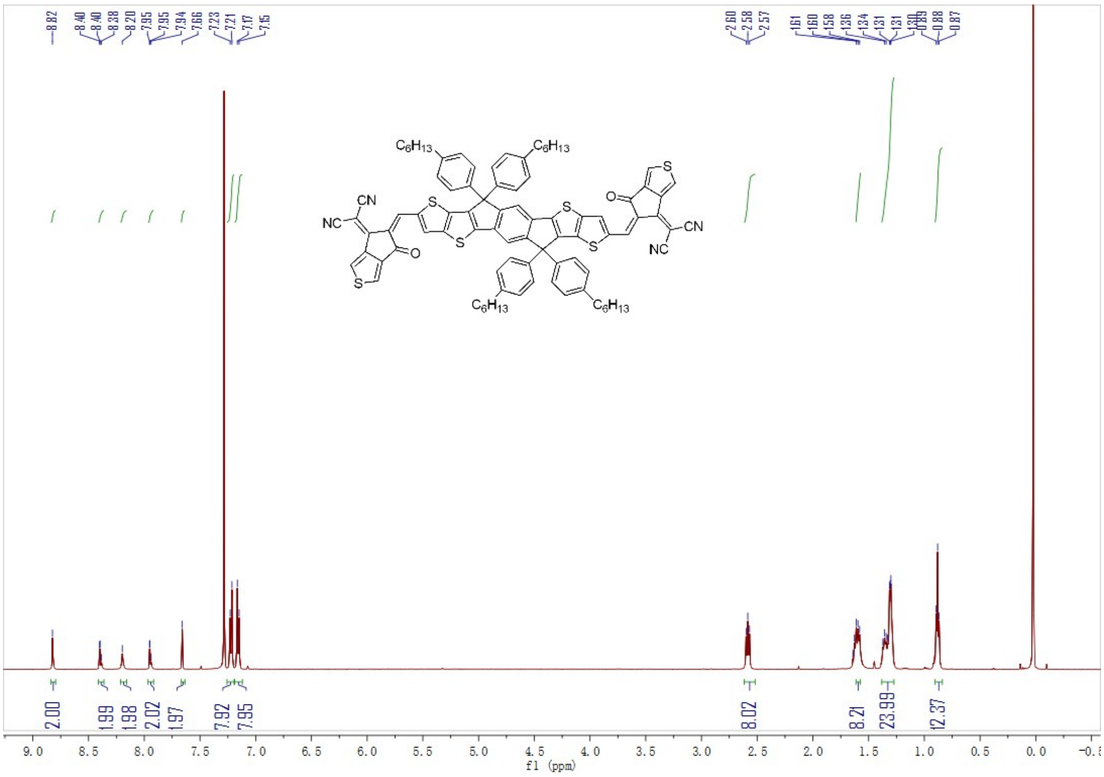


Figure S3. ^{1}H NMR spectrum of ITTC.

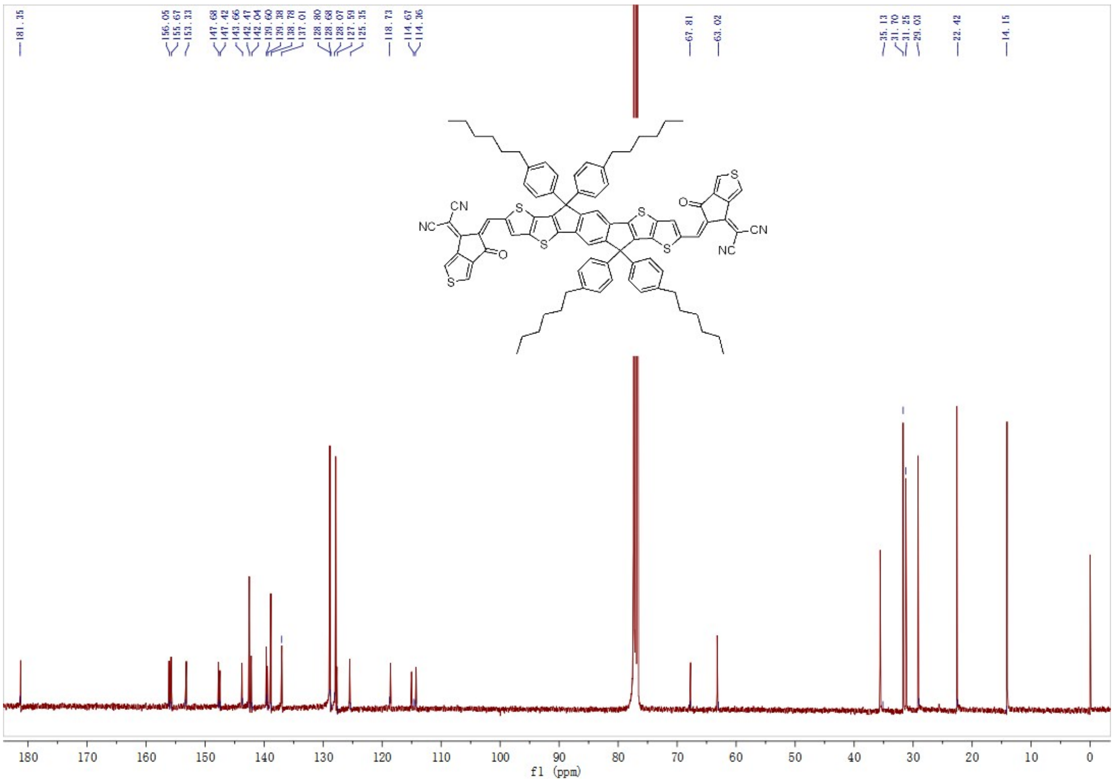


Figure S4. ^{13}C NMR spectrum of ITTC.

6. CV

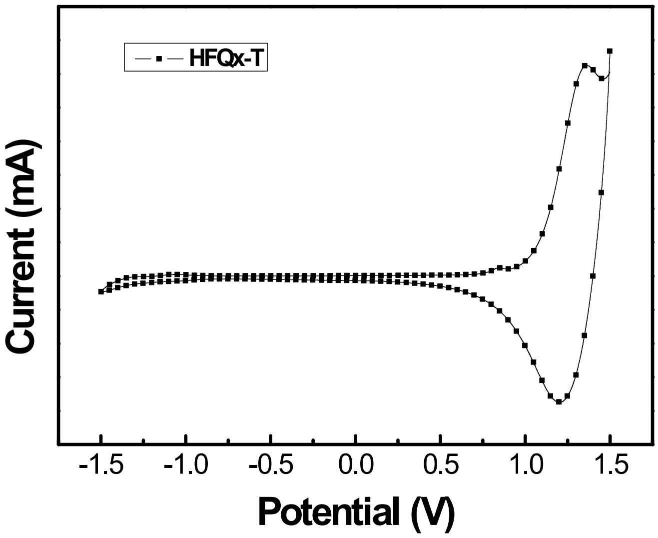


Figure S5. Cyclic voltammogram of HFQx-T in CH_3CN/0.1M Bu_4NPF_6.

7. AFM

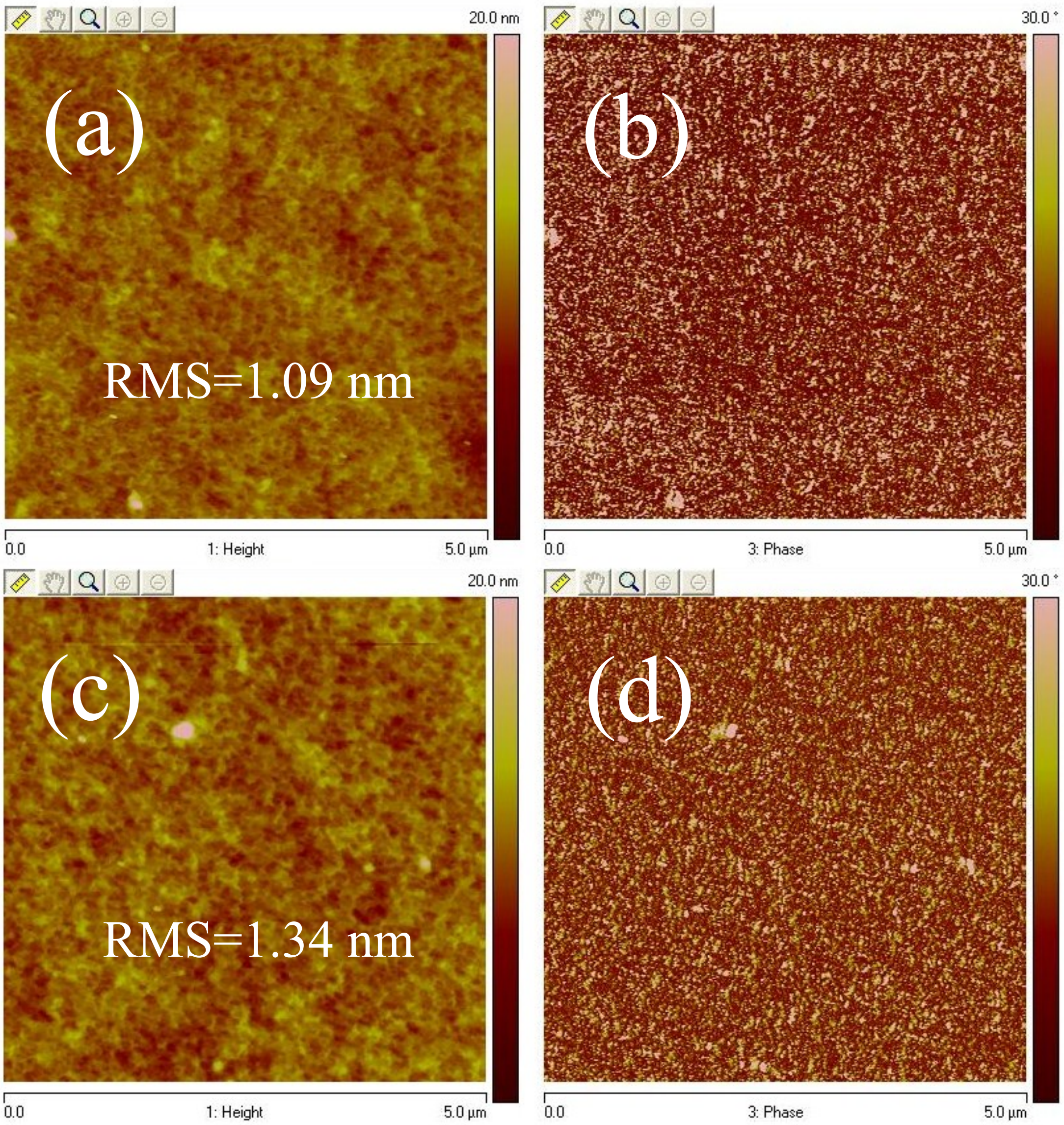


Figure S6. Tapping-mode AFM height images of HFQx-T: ITTC blend films without TA (a) and with TA (c), AFM phase images of HFQx-T: ITTC blend films without TA (b) and with TA (d).

8. Photovoltaic data

Table S1. The photovoltaic characteristics of the HFQx-T : ITTC blend films

	Ratio	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	PCE$_{avg}$ (%)[e]
HFQx-T:ITTC	1:1[a]	0.88	15.05	61	8.19	8.10
	1:1[b]	0.87	14.94	65	8.44	8.37
	1:1[c]	0.88	16.49	71	10.40	10.11
	1:1[d]	0.86	15.53	65	8.70	8.47
	1:1.5[a]	0.89	15.00	66	8.94	8.80
	1:1.5[c]	0.88	16.16	71	10.12	9.98
	1.5:1[a]	0.87	15.58	69	9.31	9.21
	1.5:1[c]	0.89	15.45	70	9.74	9.68

[a] As-cast film.
[b] with thermal annealing at 120 °C for 10 min.
[c] with thermal annealing at 130 °C for 10 min.
[d] with thermal annealing at 150 °C for 10 min.
[e] the reported values are average PCEs from 10 devices

Reference

1. Y. Zou, A. Najari, P. Berrouard, S. Beaupre, B. Aı¨ch, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.*, 2010, **132**, 5330－5331.