Electronic supplementary information

Achieving over 21% Efficiency in Inverted Perovskite Solar Cells by Fluorinating a Dopant-Free Hole Transporting Material

Li Wan^{a,b}, Wenxiao Zhang^b, Sheng Fu^b, Lijun Chen^a, Yueming Wang^b, Zhongyuan Xue^c, Youtian Tao^c, Wenjun Zhang^{*,b}, Weijie Song^band Junfeng Fang^{*,a, b}

- a School of Physics and Materials Science, Engineering Research Center of Nanophotonics & Advanced Instrument, Ministry of Education, East China Normal University, Shanghai 200241, China.
- b Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.
- c Key Lab for Flexible Electronics and Institute of Advanced Materials, Nanjing Tech University, Nanjing, 211816, China.

Experimental Section

Synthesis of PFDT-COOH and PFDT-2F-COOH

(1): 2,7-dibromo-9H-fluorene (3.240 g, 10.0 mmol), potassium tert-butoxide (t-BuOK, 11.200 g, 100.0 mmol), tetrabutylammonium bromide (TBAB, 97 mg, 0.3 mmol), and 30.0 mL distilled toluene were mixed and stirred at 60 °C for 1 h under nitrogen atmosphere. Then, tert-butyl acrylate (4.4 mL, 30.0 mmol) was added, and the mixed solution was reacted at 110 °C for 12 h. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane. The combined organic phase was washed with water and dried over Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography with petroleum ether and ethyl acetate (10:1, v:v) as eluent. **1** was obtained as white solid in 72% yield (4.170 g). ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.56-7.54 (d, *J* = 8 Hz, 2H), 7.51-7.49 (d, *J* = 8 Hz, 4H), 2.34-2.30 (m, 4H), 1.50-1.46 (t, 2H), 1.34 (s, 18H). ¹³C-NMR (100 MHz, CDCl₃, ppm): δ 170.20, 149.96, 139.09,

131.05, 126.48, 122.06, 121.43, 80.45, 54.06, 34.40, 29.84, 28.01.

(2) or (3): A mixture of 1 (0.580 g, 1.0 mmol), 5,5'-bis(trimethylstannyl)-2,2'bithiophene (0.492 g, 1.0 mmol) or 3,3'-difluoro-[2,2'-bithiophene]-5,5'-1.0 diyl)bis(trimethylstannane (0.528)mmol), g, tetrakis(triphenylphosphine)palladium (23 mg, 0.02 mmol), and distilled toluene (10.0 mL) were stirred for 24 h at 110 °C under nitrogen atmosphere. After cooling to room temperature, water was added and the mixture was extracted with chloroform. The combined organic phase was washed with water and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was extracted by a Soxhlet Extractor with methanol, petroleum ether, acetone and chloroform sequentially. 2 or 3 was obtained as orange solid in 75% or 72% yield (0.461 g or 0.469 g). ¹H-NMR of 2 (400 MHz, CDCl₃, ppm): δ 7.75-7.73 (br, 2H), 7.68-7.64 (br, 4H), 7.40-7.39 (br, 4H), 2.45 (br, 4H), 1.60 (br, 4H), 1.34 (br, 18H). ¹³C-NMR of **2** (100 MHz, CDCl₃, ppm): δ 172.65, 149.25, 143.30, 140.25, 136.78, 133.56, 125.41, 124.61, 120.56, 119.87, 80.28, 53.75, 34.72, 30.01, 28.08, 27.96. ¹H-NMR of **3** (400 MHz, CDCl₃, ppm): δ 7.76-7.74 (br, 2H), 7.66-7.61 (br, 4H), 7.25 (br, 2H), 2.46 (br, 2H), 1.60 (br, 8H), 1.34 (br, 18H). ¹³C-NMR of **3** (100 MHz, CDCl₃, ppm): δ 172.45, 155.13, 152.50, 149.44, 140.76, 133.02, 129.09, 125.13, 124.93, 120.75, 119.48, 113.36, 113.09, 111.16, 80.37, 53.94, 34.63, 30.02, 28.02. ¹⁹F-NMR of **3** (400 MHz, CDCl₃, ppm): δ -123.08.

PFDT-COOH or PFDT-2F-COOH: 2 (0.310 g) or **3** (0.326 g), trifluoroacetate (2.0 mL) and distilled chloroform (10.0 mL) were mixed and stirred at 60 °C for 24 h under nitrogen atmosphere. Then, the precipitate was obtained by suction filtration and extracted by a Soxhlet Extractor with petroleum ether, acetone and chloroform sequentially. Target product was obtained as brown solid in 50% or 52% yield (0.126 g or 0.139 g). ¹H-NMR of **PFDT-COOH** (400 MHz, DMSO-d6, ppm): δ 11.93 (br, 2H), 7.90 (br, 4H), 7.68 (br, 4H), 7.46 (br, 4H), 1.46-1.35 (br, 4H), 1.22-1.15 (br, 2H). ¹³C-NMR of **PFDT-COOH** (100 MHz, DMSO-d6, ppm): δ 174.35, 149.89, 143.04, 140.23, 136.15, 133.20, 125.68, 120.29, 54.19, 29.41. The number-average molecular weight (M_n) of PFDT-COOH was determined to be 8.7 kDa, with polydispersity indices (PDI) of 2.2. ¹H-NMR of **PFDT-2F-COOH** (400 MHz, DMSO-d6, ppm): δ

11.95 (br, 2H), 7.70 (br, 8H), 3.36 (br, 8H). ¹³C-NMR of **PFDT-2F-COOH** (100 MHz, DMSO-d6, ppm): δ 174.42, 152.25, 140.94, 84.45, 79.63, 65.58, 53.81, 48.74. ¹⁹F-NMR of **PFDT-2F-COOH** (400 MHz, DMSO, ppm): δ -73.70, -122.96. The M_n of PFDT-2F-COOH was determined to be 7.6 kDa, with PDI of 2.7.

Films and devices fabrication

ITO substrates (ITO/glass: $R_S \le 15 \Omega$ per square) were cleaned by ultrasonic cleaner with detergent, deionized water, acetone, isopropanol for 15 min, respectively. PFDT-COOH or PFDT-2F-COOH solutions (0.5 mg in 990 µL methanol and 10 µL methylamine solution) were spin-coated on the ITO glass at 4000 rpm for 30 s to fabricate a thin HTM, next, the films were annealed at 100 °C for 10 min. After that, 1.5 M of PbI₂ in DMF:DMSO (9:1, v:v) solvent was spin-coated on PFDT-COOH at 1500 r.p.m. for 30 s, then annealed at 70 °C for 1 min, and then cooled to room temperature. For FA_{1-x}MA_xPbI₃ perovskite film deposition, a solution of FAI:MAI:MACl (90 mg:6.4 mg:9 mg in 1 mL isopropanol) was spin-coated on PbI₂ at 2000 r.p.m. for 30 s, followed by thermal annealing at 150 °C for 15 min. For the stabilities measurements, a (FAPbI₃)_{1-x} (MAPbBr₃)_x mixed perovskite were also adopted. A solution of FAI:MABr:MACl (90 mg:9.0 mg:9.0 mg in 1 mL isopropanol) was spin-coated on PbI₂ at 2000 r.p.m. for 30 s, followed by thermal annealing at 150 °C for 15 min. The solutions of PCBM in chlorobenzene were prepared with a concentration of 10 mg mL⁻¹. The annealed perovskite films were covered by the PCBM solutions at 2000 rpm for 40 s, followed by the deposition of 20 nm C_{60} , 8 nm BCP, 100 nm patterned Cu top electrodes via thermal evaporation (vacuum degree ≤ 2 x 10⁻⁴ Pa), respectively. The HTL and perovskite precursor solutions were filtered through a 0.45 µm polytetrafluoroethylene filter prior to use. The active area is 0.09 cm^2 .

Measurements and characterization

¹H and ¹³C NMR spectra were recorded using a 400 MHz Bruker at 293 K using TMS as a reference. Gel permeation chromatography (GPC) was carried out on a ShimadzuSIL-20A liquid chromatography instrument using N, N-dimethylformamide as eluent at 160 °C with polystyrenes as standards. Cyclic voltammetry (CV)

measurements were carried out on a CHI 660e electrochemical analyzer with a threeelectrode cell under nitrogen atmosphere in a deoxygenated anhydrous acetonitrile solution of tetra-n-butylammonium-hexa-fluorophosphate (0.1 M) under a nitrogen atmosphere. A platinum disk electrode, platinum-wire, and Ag/AgCl electrode were used as a working electrode, a counter electrode, and a reference electrode, respectively, with the polymer thin film for evaluation coated on the surface of platinum disk electrode. Ferrocene/ferrocenium (Fc/Fc⁺) was used as the external standard (the energy level of Fc/Fc⁺ is -4.8 eV under vacuum). The HOMO energy level was determined from the onset oxidation (E_{onset}^{ox}) as HOMO = -(4.8+ E_{onset}^{ox} - E_{onset}^{Fc}) eV, E_{onset}^{Fc} equals to the onset oxidation of Ferrocene. The LUMO energy level was determined from the onset reduction (E_{onset}^{red}) as LUMO = -(4.8+ E_{onset}^{red} - E_{onset}^{Fc}) eV. UV-vis absorption and reflectance spectras were measured with UV-vis spectrophotometer (Model HP8453).

The density-voltage (J-V) characteristics were recorded with a Keithley 2400 source meter under irradiation of simulated AM 1.5G solar spectrum. The external quantum efficiency measurements were conducted with a Newport quantum efficiency measurement system (ORIEL IQE 200TM) combined with a lock-in amplifier and a 150 W Xe lamp in the ambient atmosphere. Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (UPS) measurements were carried out using a Kratos AXIS ULTRA DALD XPS/UPS system with a He I (21.2 eV) discharge lamp. The cross-sections and top-view SEM of devices were observed by scanning electron microscopy (SEM) (S4800, Hitachi, Japan). The atomic force microscopy (AFM) images were observed by Dimension 3100 V, Veeco, USA, tapping mode. Photoluminescence spectra were analyzed using a fluorescence spectrophotometer (F-4600, Hitachi Ltd., Tokyo, Japan) with a 150 W Xe lamp as the excitation source at room temperature. The transient photocurrent (TPC) decay and transient photovoltage (TPV) decay were recorded by electrochemical workstation (Zahner, Germany) with a white light LED supplied 100 mWcm⁻² light intensity to excite the perovskite solar cells. The stability of humidity and oxygen were recorded by putting the non-encapsulated devices in the air condition. The samples were put on the 60 °C for 30 min before measuring the *J-V* curses. The thermal stability was measurement by storing the non-encapsulated devices on the hot plat. And the *J-V* measurements were performed after the samples cool to room temperature. The light source of long-term stability measurements is the white light LED array with an intensity of 100 mW cm⁻² (white LED) simulating solar intensity. During the MPP tracking, the light intensity can be automatic calibrated with a Si reference diode. The light source of continuous stability measurements is Xenon lamp (Newport Oriel Sol3A solar simulator, 100 mWcm⁻²) without any UV filter and AM 1.5 G illumination is continuously illumination applied on the PSCs.



Scheme 1 The detailed synthetic procedures for PFDT-COOH and PFDT-2F-COOH.



Fig. S1 The CV curve of ferrocene.



Fig. S2 High-resolution XPS at O 1s core levels of the ITO, ITO with HTMs, and the pristine HTM film. A thin film of PFDT-COOH or PFDT-2F-COOH (0.5 mg/mL) was deposited on the ITO to get a XPS data of the interaction of HTM with ITO, while a thick film (5 mg/mL) for the pure HTM film.

The O 1s region of ITO was decomposed into three parts at 530.4 eV, 531.5 eV, 532.7 eV, which correspond to the indium oxides, tin oxides, and hydroxyl groups, respectively. The O 1s region of pure HTM was decomposed into two parts at 532.3 eV and 533.8 eV, which correspond to hydroxyl groups and carbonyl groups, respectively. The O 1s region of ITO/HTM was decomposed into four parts at 530.4 eV, 531.5 eV, 532.4 eV and 533.8 eV. The peaks at 530.4 eV, 531.5 eV and 533.8 eV are attributed to the indium oxides, tin oxides and carbonyl groups respectively. We can see that the binding energy of indium oxides, tin oxides and carbonyl groups are almost unchanged before and after the deposition of HTM on ITO. After the deposition of HTM, the peaks of hydroxyl group at ITO shifted to the higher binding energy, which indicates a strong interaction between the hydroxyl groups on ITO and the carbonyl groups on HTM.



Fig. S3 High-resolution XPS at F 1s core levels of the ITO, ITO with HTMs, and the pristine HTM film.



Fig. S4 High-resolution XPS at Sn 3d and In 3d core levels of the ITO, ITO with HTMs, and the pristine HTM film.



Fig. S5 The cross-sectional SEM image of the whole device.



Fig. S6 (a) Optimization of the PFDT-COOH-based solar cells. (b) Optimization of the PFDT-2F-COOH-based solar cells.



Fig. S7 Top-view SEM images (a, b) and AFM height images (c, d) of PFDT-COOH and PFDT-2F-COOH on ITO, respectively.



Fig. S8 The device efficiency of PFDT-COOH and PFDT-2F-COOH with different scanning directions.

Table S1 Photovoltaic parameters of devices with PFDT-COOH and PFDT-2F-COOH in their optimal thickness from different scanning directions. (Forward: scanning voltage from 1.2 V to - 0.2 V, Reverse: scanning voltage from -0.2 V to 1.2 V)

HTM/Scanning directions	<i>V_{OC}</i> (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
PFDT-COOH Forward	1.079	24.78	77.2	20.64
PFDT-COOH Reverse	1.073	24.76	74.2	19.71
PFDT-2F-COOH Forward	1.111	24.86	78.5	21.68
PFDT-2F-COOH Reverse	1.107	24.79	75.8	20.81



Fig. S9 Diagrams of device PCE, V_{OC}, J_{SC} and FF measured from 30 identical devices.



Fig. S10 (a)-(b) Top-view SEM images of the perovskite on PFDT-COOH and PFDT-2F-COOH, respectively. (c)-(d) The AFM height images of the perovskite on PFDT-COOH and PFDT-2F-COOH, respectively. AFM images is $5 \ \mu m \times 5 \ \mu m$.



Fig. S11 PL quenching spectra of perovskite with various HTLs.

Sample	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	$\tau_{ave} \left(ns \right)$
Perovskite	78.8	47.4	468.4	52.6	283.7
PFDT-COOH/Perovskite	17.2	23.3	182.8	76.7	144.2
PFDT-2F- COOH/Perovskite	10.9	28.7	152.8	71.3	112.1

Table S2 Parameters of the TRPL spectra of perovskite films with different interface (τ_1 and τ_2 represent the time constant of the two decay processes, τ_{ave} is the average carriers lifetime).



Fig. S12 *J-V* curves of the devices based on various HTMs, the active layer is $(FAPbI_3)_{1-x}$ (MAPbBr₃)_x.



Fig. S13 Decay curves of PCE, V_{OC} , J_{SC} and FF for continuous power output at the max power point stabilities measurements.



Fig. S14 Continuous power output at maximum power point under full-sun AM 1.5 G illumination of Xenon lamp without any UV-filter.



Fig. S15 Decay curves of PCE, V_{OC}, J_{SC} and FF for continuous heating stabilities measurements.





Fig. S16 The ¹H NMR spectrum of 1.





Fig. S18 The ¹H NMR spectrum of 2.







Fig. S20 The 1 H NMR spectrum of 3.







Fig. S22 The ¹⁹F NMR spectrum of 3.



Fig. S24 The ¹³C NMR spectrum of PFDT-COOH.



Fig. S25 The ¹H NMR spectrum of PFDT-2F-COOH.



Fig. S26 The ¹³C NMR spectrum of PFDT-2F-COOH.



Fig. S27 The ¹⁹F NMR spectrum of PFDT-2F-COOH.