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Supporting Information

Dopant-Free F-substituted Benzodithiophene Copolymer Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells

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Supporting Information

Experimental Sections

Material: 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene(Spiro-OMeTAD), polytriarylamine (PTAA), methylammonium iodide(MAI), lead iodide (PbI_2 99%) (Yingkou You Xuan Trade Co. Ltd), bis(trifluoromethanesulfonyl)imide (Li-TFSI), tert-butylpyridine (t-BP), (Sigma–Aldrich), $SnCl_2 \cdot 2H_2O$ (Alfa Aesar) were used as received. Solvent: dimethyl formamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (CB, 99.8%), acetonitrile, ethanol and isopropanol were purchased from Sigma–Aldrich without further purification. FTO glasses (FTO, 7 Ω/sq) were purchased from Yingkou You Xuan Trade Co. Ltd.

***Preparation of Colloidal SnO_2 NCs Solution*:** SnO_2 NCs Solution was prepared by our previous method[1-2], Typically, $SnCl_2 \cdot 2H_2O$ solution (0.1 M) was prepared by dissolving $SnCl_2 \cdot 2H_2O$ separately in ethanol, isopropanol, butanol, butanol containing certain content of water in a flask. Then the solution was separately stirred at room temperature for 10 min. To synthesize colloidal SnO_2 NCs, the $SnCl_2 \cdot 2H_2O$ solution was refluxed at 110℃ for 2~4 hours with open refluxing apparatus.

Perovskite Solar Cells Fabrication:

***Substrate preparation**:* FTO-coated glasses were sequentially ultrasonically cleaned with detergent, deionized water, acetone, and isopropanol for 30 min. All substrates were further cleaned by UV-Ozone for 10 min before deposing SnO_2 ESLs. The SnO_2 ETLs were prepared by spin-coating SnO_2 NCs solution on FTO substrates at 3000 rpm for 30 s, followed by thermal annealing at 150℃ for 30min. After cooling down, the substrates were immediately transferred in a nitrogen atmosphere glove box for the deposition of the perovskite films.

***Perovskite precursor solution and film preparation**:* Perovskite precursor was prepared as reported. Typically, 922 mg of PbI_2 and 320 mg of MAI were dissolved in 1.6 ml mixed solvent of DMF and DMSO (7:3 V/V), stirring at 60℃ for 48h before use. The $MAPbI_3$ precursor solution was spin-coated on FTO/SnO_2 substrates at 500 rpm for 3 s and 4000 rpm for 30 s, with quickly dripping of 400 μL chlorobenzene onto the rotating perovskite film at the beginning of 8-10 s of the second spin-coating step. Then the films were annealed at 100 ^{o}C for 10 min.

***Hole transporting layer and the top electrode**:* After the perovskite annealing, the substrates were cooled down for few minutes and the HTM solution was spun at 3000 rpm for 30 s. The solutions were prepared as follows: 72.3 mg spiro-OMeTAD, 18 μL Li-TFSI solution (520 mg in 1 ml acetonitrile), 30 μL t-BP was dissolved in 1 ml chlorobenzene at a concentration of 10 mg ml^{-1}. A polytriarylamine (PTAA) solution was prepared by dissolving PTAA (36mg), a Li-TFSI (18 μL), and t-BP (36ul) in 1ml of CB solution, while the novel polymers were dissolved in chlorobenzene.

The schematic illustration of the spin-coating process for fabricating HTLs film is shown in Figure S2a. Specifically, the as synthesis polymers were dissolved in chlorobenzene at a concentration of 8 mg ml^{-1}. The solubility of polymers is not very good, there are some undissolved particles are attached to the inner wall of the bottles (Figure 1b). The preheated solution (about 110 ℃) is drop casted onto the substrate using a pipette and the spin coating process is started immediately. The spin coater is programed to reach a speed of 5000 rpm in 1-2 seconds in order to avoid the temperature from quenching. During this process, the film dries within the 3-5 seconds and temperature quenches rapidly. It's important to note that the solvent volatilization will cause a change in the concentration of the solution, so this step needs to be completed quickly. Finally, 100 nm of Ag electrode was thermally evaporated on top of the device at a speed of 0.8 Å.

Characterization.

Morphology: The morphology and microstructures were investigated by FE-SEM (ZEISS Ultra-55). The absorption spectra of ESLs deposited on quartz were measured by UV–vis spectrometer (SHIMADZU UV-2550) in a wavelength range at 250-800 nm.

PL and TRPL: Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were measured by fluorescence spectrometer (HITACHI F-5000) exited at 530 nm and FLS980 with excitation wavelength of 450 nm.

Thermogravimetric analyses: The thermogravimetric analyses were performed on a TA Q500 using a 10°C/min heating rate under a nitrogen flow. Differential scanning calorimetry (DSC) was performed on a DSC^{3+} Mettler Toledo at a scan rate of 20 °C/min in the nitrogen atmosphere.

J-V characterizations: The current–voltage (J-V) curves of the non-encapsulated solar cells were measured by Keithley 2400 in a glovebox under AM1.5G illuminations (1000 W·m^{-2}) from a solar simulator (Newport, 91160), which was calibrated using a standard silicon solar cell device by the NREL.

EQE measurement: The EQE measurements of photovoltaic devices were carried out using EQE system (Newport 66902), consist of a xenon light source, a monochromator, and a potentiostat.

EIS characterization: The electrochemical impedance spectroscopy (EIS) measurements were performed on the Zahner Zennium electrochemical workstation with an illumination of 300 W m^{-2} light source.

SCLC measurement: Space charge limited current (SCLC) characteristics of the devices was measured using a Keithley 2400 in the dark. The devices configuration follows: ITO/PEDOT:PSS/Perovskite/HTM/Au for hole-only devices. The perovskite films and Spiro-OMeTAD films were made by the same protocols used in solar cell fabrication. PEDOT:PSS films were prepared by spin-coated PEDOT:PSS aqueous solution on ITO at 3000 r.p.m. for 30 s, and then baked at 120 °C for 10 min. According to SCLC theory, the defect (trap) density (ntraps) can be estimated as follows: $n_{trap} = \frac{2\varepsilon\varepsilon_0 V_{TFL}}{eL^2}$, where L, ε, ε_0, and e are the thickness of the perovskite film, dielectric constant of the material, permittivity of vacuum, and electronic charge, respectively.

GIWAXS characterization: The samples used for GIWAXS （Xeuss 2.0） measurements were prepared by spin-coating the solutions onto Si wafers.

AFM measurement: The surface potentials and conductivity of films were obtained from the atomic force microscope (AFM) (Asylum Research, Cypher).[3-4]

Supporting Figures and Tables

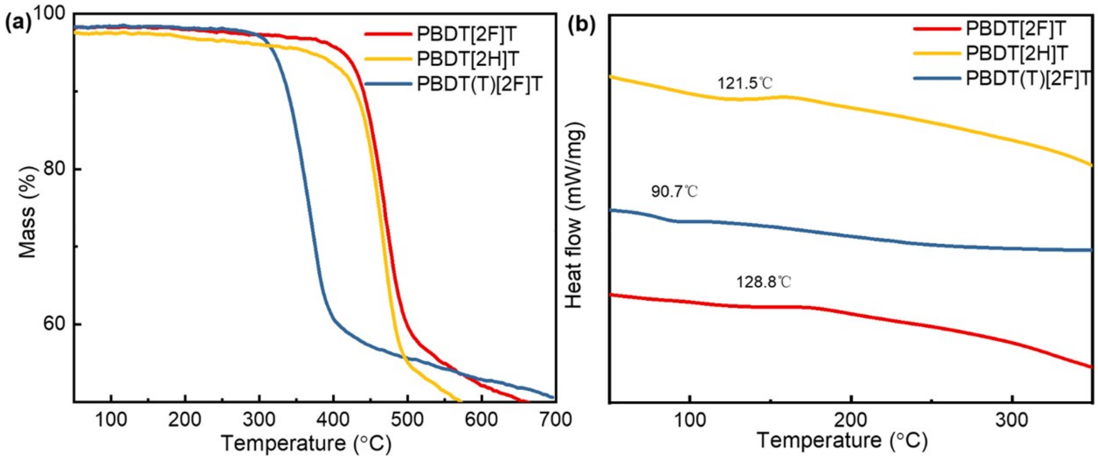
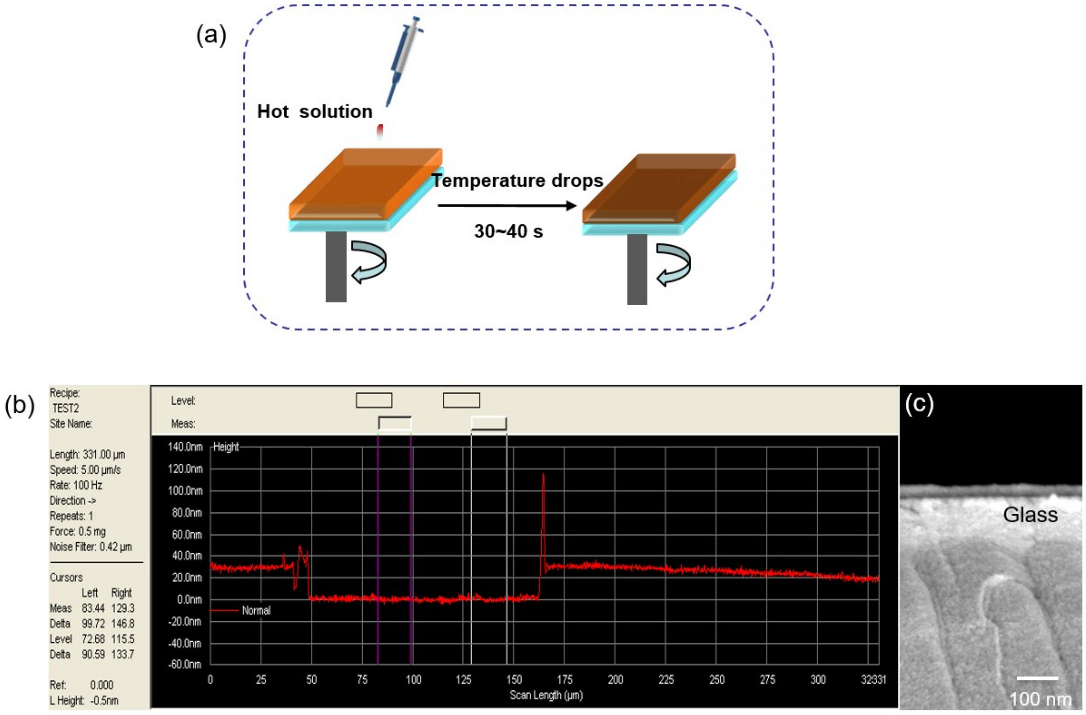


Fig. S1 a) Thermogravimetric heating curves of polymers (heating rate 10 °C/min). b) Differential scanning calorimetry second heating curves for polymers (heating rate 20 °C/min)



Recipe:
TEST2
Site Name:

Length: 331.00 µm
Speed: 5.00 µm/s
Rate: 100 Hz
Direction ->
Repeats: 1
Force: 0.5 mg
Noise Filter: 0.42 µm

Cursors

	Left	Right
Meas	83.44	129.3
Delta	99.72	146.8
Level	72.68	115.5
Delta	90.59	133.7

Ref: 0.000
L Height: -0.5nm

Fig. S2. a) Schematic illustration of the spin-coating process for fabricating HTM films. b) Step profiler test result. c) Cross-sectional scanning electron microscope (SEM) images of PBDT[2F]T on glass.

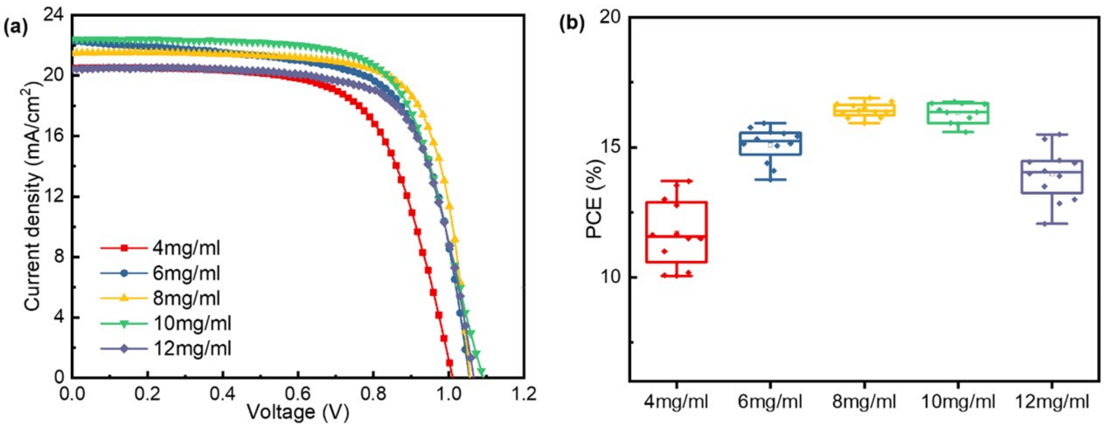


Fig. S3. (a) Current-voltage curves and (b) *PCE* statistics of 12 devices based on HTMs with different concentrations, (c) Current-voltage curves based on spiro-OMeTAD, PTAA, PBDT[2F]T.

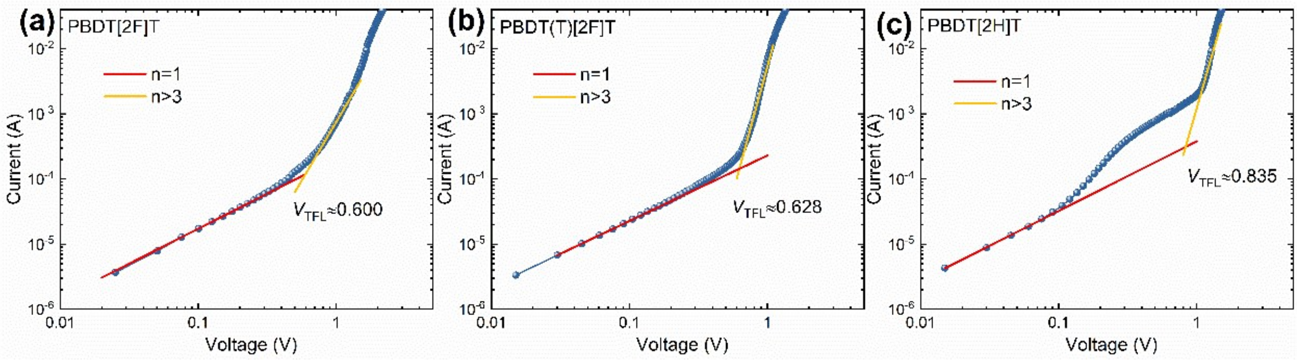


Fig. S4 SCLC measurements with the device configuration of ITO/PEDOT:PSS/perovskite/HTM/Au.

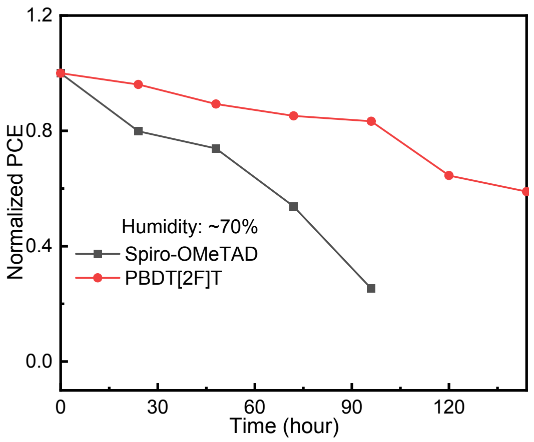


Fig. S5 Normalized *PCE* versus time, stored at ambient condition with relative humidity around 70% without encapsulation.

Table S1. SEC analyses, optical bandgap and HOMO LUMO energy level of the PBDT[2H]T, PBDT[2F]T and PBDT(T)[2F]T polymers.[5]

Polymer	Mn [kDa]	Mw [kDa]	PDI	Eopt [eV]	E_{HOMO} (IP) [eV]	E_{LUMO} [eV]
PBDT[2H]T	28	48	1.7	2.1	5.03	2.93
PBDT[2F]T	13	28	2.1	2.1	5.29	3.19
PBDT(T)[2F]T	32	49	1.5	2.0	5.22	3.22

Table S2. Photovoltaic parameters for the PSCs devices based on PBDT[2F]T with different concentrations.

HTL	*Voc* (V)	*Jsc* (mA/cm^2)	*FF* (%)	*PCE* (%)
4mg/ml	1.01	20.47	66.31	13.72
6mg/ml	1.05	22.25	67.96	15.94
8mg/ml	1.11	22.15	68.80	16.98
10mg/ml	1.09	22.38	68.58	16.74
12mg/ml	1.06	20.40	71.34	15.51

Table S3. The time constant and amplitude extracted from fitting the TRPL data with biexponential decay equation for different HTMs.

Polymer	τ_1 (ns)	A1	τ_2 (ns)	A2	Kct
Spiro-OMeTAD	2.29	1749	82.84	0.22	-
PBDT[2H]T	2.97	237	111.37	0.34	2.93
PBDT[2F]T	2.38	1229	97.54	0.25	3.19
PBDT(T)[2F]T	3.18	124	128.85	0.28	3.22

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