# **Supporting information**

# Ladder-LikeType Conjugated Polymers Used as Hole Transporting Materials for High Efficiency Perovskite Solar Cells

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# **Experimental Section**

Materials: N,N-dimethylformamide (DMF, anhydrous, 99.8%, J&K), dimethylsulfoxide (DMSO, anhydrous, 99.8%, J&K), lead (II) bromide (PbBr2, 99.9985%, Sigma-Aldrich), lead (II)iodide (PbI2, 99.9985%, Alfa Aesar), methylammonium bromide (MABr, TCI), formamidinium iodide (FAI, TCI), titanium(**IV**) isopropoxide (TTIP, 97%, Sigma-Aldrich), 1-butanol (99.9%,Sigma-Aldrich), hydrochloric acid (36-38 wt% in water), 2,2',7,7'-tetrakis(N,N-di(p-methoxyphenyl)amine)-9,9-spirobifluorene(Spiro-OMeTAD, Chemlin Chemical Industry Co.,Ltd), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 99%, J&K), 4-tert-butylpyridine (TBP,TCI) were used as received without further purification. (4,8-bis(5-(nonan-3-yl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane), (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (132 mg) and (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) were bought from Derthon Optoelectronic Materials Science Technology Co LTD

Device fabrication: Initially the laser-patterned FTO glass substrates ( $15\Omega$ /sq resistance) were cleaned sequentially by ultrasonication in detergent, deionized water, acetone, and isopropanol. Afterwards, these FTO glasses were treated with UV-ozone for 15 min. The precursor solution for perovskite flms was prepared by dissolving PbI2 (608.5mg), PbBr2 (44mg), FAI (185.7mg), MABr (13.44mg), MAI (38.16mg) in 1000µL DMF /DMSO mixed solvent (v: v = 4: 1). The compact TiO2 layer was deposited on the FTO glass by spin coating titanium isopropoxide solgel precursor solution (0.125 m) at 3000 rpm, then sintered at 500 °C for 1 h. As-prepared TiO2

flms were treated with TiCl4 aqueous solution (0.025 m) for 30 min, then sintered at 500 °C for 1 h. [6,6]-phenyl-C61-butyric acid (PCBA, 0.1 mg/mL) in CB was spin-coated on the top of TiO2 compact flm. Perovskite flms were fabricated by one-step antisolvent spin-coating method. In details, perovskite precursor solution was spin-coated at 1000 rpm for 10 s and subsequently at 5000 rpm for 30 s, CB (120  $\mu$ L) was poured onto the spinning substrate at 10 s in the second spinning step. The perovskite flm was heated at 150 °C for 10 min, then at 100 °C in vacuum for 40 min. For a deposition of the hole transport layer, P1, P2, P3 and spiro-OMeTAD (80 mg/mL) were prepared by adding 28.8  $\mu$ L of 4-tert-butylpyridine (TBP) and 17.5  $\mu$ L of lithium bis(trifluoromethylsulfonyl)imide salt (Li-TFSI) (520 mg/mL in acetonitrile) in 1 mL chlorobenzene, and Polymer-HTM (~10 mg/mL) without any addition. The HTMs were spin-coated at 4000 rpm for 30 s in ambient atmosphere. Finally, 80 nm of Au was deposited by thermal evaporation on the top of the HTM as the back contact.

Measurements and instruments: UV-vis (ultraviolet-visible) absorption spectra were recorded on a PerkinElmer UV-vis spectrometer model Lambda 750. PL (photoluminescence) spectra and time resolved PL spectra were obtained on PL spectrometer FLS 900 (Edinburgh Instruments). SEM (scanning electron microscope) imageswere obtained by S-4800 (Hitachi) field-emission scanning electron microscope (FESEM). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10° C min-1 to record TGA and DSC curves. The photovoltaic performance of the devices was measured using the Agilent B2902A Source Meter under the illumination of AM 1.5G (100 mW cm-2) AAA class solar simulator (model XES-301S, SAN-EI) in nitrogen and the solar cells were masked with a black aperture to define the active area of 0.04 cm2. And the white light intensity was calibrated with a standard single-crystal Si solar cell. External quantum efficiency (EQE) of the cells was measured with a lab-made setup under 0.3-0.9 mW cm-2 monochromic light illumination without bias illumination.

## Materials synthesis:

The target molecule P1, P2 and P3 was synthesized according to a published procedure

with some modification.







(b) Synthetic route to P2 Reagents and conditions



(c) Synthetic route to P3 Reagents and conditions

# Polymer P1 (S1)

Into a pre-dried 100 mL flask were charged with (4,8-bis(5-(nonan-3-yl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (137 mg) and 1,4-dibromo-2,5-bis(octyloxy)benzene (74.8 mg). The flask was successively evacuated and refilled with

nitrogen for 3 cycles. Then toluene (10 mL) and DMF (2 mL) were added, and the mixture was purged with nitrogen for 10 min. After the addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (11 mg) purging for another 30 min was conducted. The reaction mixture was stirred at 100 °C for 48 hours. After cooling to room temperature, the crude product was collected by precipitating from methanol. The solid was rinsed in a Soxhlet extractor with acetone, hexane, dichloromethane and chloroform successively. The solution in chloroform was concentrated, and then precipitated in methanol. The polymer was obtained after drying at a reduced pressure. 103.7 mg, yield: 72.8%.  $M_{\rm B}$ : 48,114; PDI: 1.6

## Polymer P2 (S1)

Into a pre-dried 100 mL flask were charged with (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (132 mg) and 1,4-dibromo-2,5-bis(octyloxy)benzene (84.3 mg). The flask was successively evacuated and refilled with nitrogen for 3 cycles. Then toluene (10 mL) and DMF (2 mL) were added, and the mixture was purged with nitrogen for 10 min. After the addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg) purging for another 30 min was conducted. The reaction mixture was stirred at 100 °C for 48 hours. After cooling to room temperature, the crude product was collected by precipitating from methanol. The solid was rinsed in a Soxhlet extractor with acetone, hexane, dichloromethane and chloroform successively. The solution in chloroform was concentrated, and then precipitated in methanol. The polymer was obtained after drying at a reduced pressure. 91.8 mg, yield: 69.1%. *M*<sub>n</sub>: 48,114; PDI: 1.6

## Polymer P3 (S1)

Into a pre-dried 100 mL flask were charged with (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (165 mg) and 2,5-dibromothiophene (51.8 mg). The flask was successively evacuated and refilled with nitrogen for 3 cycles. Then toluene (10 mL) and DMF (2 mL) were added, and the mixture was purged with nitrogen for 10 min. After the addition of Pd(PPh\_3)4 (12.3 mg) purging for another 30 min was conducted. The reaction mixture was stirred at 100 °C for 48 hours. After cooling to room temperature, the crude product was collected by precipitating from methanol. The solid was rinsed in a Soxhlet extractor with acetone, hexane, dichloromethane and chloroform successively. The solution in chloroform was concentrated, and then precipitated in methanol. The polymer was obtained after drying at a reduced pressure. 85.3 mg, yield: 75.8%.  $M_{\rm n}$ : 48,114; PDI: 1.6



Figure S1. (a) DSC and (b) TGA curves of P1, P2 and P3 under N2 atmosphere.



Figure S2. CV oxidation peak of (b)P1, (c)P2 and (d)P3, which ferrocene as a reference.



Figure S3. CV redox peak of (b)P1, (c)P2 and (d)P3, which ferrocene as a reference.

HTM	E <sub>HOMO</sub> [eV]	E <sub>LUMO</sub> [eV] <sup>a</sup>	E <sub>g</sub> [eV] <sup>a</sup>	E <sub>LUMO</sub> [eV] <sup>b</sup>	E <sub>g</sub> [eV] <sup>b</sup>
P1	-5.43	-3.35	2.09	-3.60	1.83
P2	-5.76	-3.56	2.20	-3.71	2.05
P3	-5.30	-3.17	2.13	-3.63	1.67

<sup>*a*</sup> Data based on absorption spectrum; <sup>*b*</sup> Data based on CV method;

**Table S1.** HOMO, LUMO and  $E_g$  data of polymers obtained by absorption spectra (a) and CV curve (b)

#### **Device Fabrication**

The precursor solution for perovskite flms was prepared by dissolving PbI2 (1.15 m), PbBr2 (0.20 m), FAI (1.10 m), MABr (0.20 m), MAI (0.20 m) in DMF /DMSO mixed solvent (v: v = 4: 1). The compact TiO2 layer was deposited on the FTO glass by spin coating titanium isopropoxide sol–gel precursor solution (0.125 m) at 3000 rpm, then sintered at 500 °C for 1 h.

As-prepared TiO2 flms were treated with TiCl4 aqueous solution (0.025 m) for 30 min, then sintered at 500 °C for 1 h. [6,6]-phenyl-C61- butyric acid (PCBA, 0.1 mg/mL) in CB was spin-coated on the top of TiO2 compact flm.[2,32] Perovskite flms were fabricated by one-step antisolvent spin-coating method. In details, perovskite precursor solution was spin-coated at 1000 rpm for 10 s and subsequently at 5000 rpm for 30 s, CB (120  $\mu$ L) was poured onto the spinning substrate at 15 s in the second spinning step. The perovskite flm was heated at 150 °C for 10 min, then at 100 °C in vacuum for 40 min. Average 200 nm thickness spiro-OMeTAD layer with Li and Co-doped was deposited onto the perovskite flm at a speed of 3500 rpm and then heated for 5 min at 60 °C on a hot plate. The precursor preparation, perovskite, and spiro-OMeTAD spin-coating processes were carried out in the glove box. At last, 80 nm thickness Au electrode was deposited via thermal evaporation under the vacuum of 10<sup>-7</sup> Torr.



**Figure S4.** Cross-sectional image of the device based on FTO/c-TiO2/PCBA/(FAPbI3)0.85(MAPbBr3)0.15/Polymer-HTM/Au.



**Figure S5.** Cross-sectional image of the device based on FTO/c-TiO2/PCBA/(FAPbI3)0.85(MAPbBr3)0.15/Spiro-OMeTAD/Au.



Figure S6. The water contact angles of (a)\_P1, (b)\_P2 and (c)\_P3 on glass substrates.



**Figure S7.** UV-Vis transmittance curve of (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> film and (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub>/P-1 film

	τ <sub>1</sub> [ns]	A <sub>1</sub>	τ <sub>2</sub> [ns]	A <sub>2</sub>
PVSK	29.99	0.23	123.21	0.42
Spiro-OMeTAD	2.83	39.57	10.18	1.09
P1	3.29	24.21	17.05	0.58
P2	4.87	7.27	25.37	0.48
Р3	4.78	8.45	42.48	0.23

Table S2. The parameters of fitting TRPL curve

The time-resolved photoluminescence (TRPL) spectra were fitted with a two-component exponential decay model

$$I(t) = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)}$$