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Improving the hole transport performance of perovskite solar cells through adjusting the mobility of the as-synthetic conjugated polymer

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General materials and methods

All purchased reagents were used as received. All reactions were carried out under argon atmosphere and all used solvents were dehydrated following standard methods. ^{1}H NMR (400 MHz) was recorded on a Varian Mercury spectrometer with tetramethylsilane (TMS) as an internal reference. Elemental analysis on carbon, hydrogen and nitrogen contents of samples was carried out on an Elementar vario EL III elemental analyzer. UV-Vis absorption spectroscopy was performed on the Hitachi U-3310 spectrophotometer. Cyclic voltammetry (CV) measurements were conducted on a CHI 660C instrument with a three-electrode cell using glass carbon as working electrode, platinum wire as counter electrode, and $Ag/AgNO_3$ as reference electrode in acetonitrile containing 0.1 M Bu_4NPF_6 electrolyte at a scan rate of 50 mV s^{-1}. All samples were prepared by casting their chlorobenzene solutions onto glass carbon electrodes. The XRD measurements of perovskite layers and HTLs with perovskite substrate were realized by D8 advanced with CuKα radiation (λ = 0.15418 nm operated at 40 kV and 30 mA). The surface morphology of perovskite film was investigated by AFM (AFM Asylum Research Cypher S). The absorption spectra of the perovskite layer were characterized on UV–vis spectroscopy (UV–vis–NIR, Lambda 900, Perkin Elmer). The PL characteristics were measured on Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). The perovskite films were stored in the glovebox before measurements. The measurement of PL spectra was performed in ambient condition. The excited wavelength was 532 nm, the scan scope was 700 nm-850 nm, the scan rate was 600 nm/min, the averaging time was 0.1 s, and scan step was 1 nm.

The polymer **P5NH** was synthesized following the same method as reported for the preparation of **P25NH** [1]. As shown in Scheme 1, the precursor polymer **P5PTI** was firstly prepared by the polymerization among DPP monomer **M1**, distannylated thiophene monomer **M2**, and phthalimide(PTI)-tethered dibromothiophene monomer **M3** in a molar feeding ratio of 95:100:5. Then, **P5PTI** was treated with NH_2NH_2 under the refluxing condition in toluene/methanol and successfully converted into the target primary amine-tethered polymer **P5NH**.

Synthesis

P5PTI: To an argon bubbled solution of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M1**, 344.7 mg, 380 μmol), 2,5-bis(trimethylstannyl)thiophene (**M2**, 163.9 mg, 400 μmol), **M3** (9.4 mg, 20 mmol) in toluene (5 ml), a mixture of tris(dibenzylideneacetone)dipalladium (1.83 mg, 2 μmol) and tri-o-tolylphosphine (2.43 mg, 8 mmol) was added. This mixture was stirred for 3 days at 80 °C, then successively added 2-bromothiophene (2 μl) and tributyl(thiophen-2-yl)stannane (6.35 μl) as end-capping reagent. After precipitation with MeOH, the crude polymer was further purified by Soxhlet extraction using methanol, hexane and $CHCl_3$, respectively, affording 358 mg pure product as a green solid in a yield of 73 %. ^{1}H NMR (ppm, 1,1,2,2-tetrachloroethane-d4, 80 ^{o}C): 8.90 (br, 2H), 7.77 (d, 0.21H), 7.3 - 7.0 (m, 4.16H), 4.02 (br, 4H), 1.96 (br, 2H), 1.64-1.00 (m, 48.95H), 0.98-0.61 (m, 12H).

P5NH. A solution of **P5PTI** (116 mg, 94.9 μmol), $N_2H4 \cdot H_2O$ (2ml,), MeOH (2 ml), toluene (30 ml) was stirred overnight at 80 ºC. Then, the polymer was precipitated in methanol, and fractionated by Soxhlet extraction using methanol, hexane and $CHCl_3$, respectively. The polymer was obtained in 90 mg as a green solid (82 % yield). ^{1}H NMR (ppm, 1,1,2,2-tetrachloroethane-d_4, 80 ^{o}C): 8.87 (br, 2H), 7.3 -7.0 (m, 4.16H), 4.04 (br, 4H), 1.98 (br, 2H), 1.7 - 1.2 (m, 48.95H), 1.05 - 0.8 (m, 12H). GPC (o-DCB, 80 ºC): *M*n = 26.2 kDa, PDI = 2.51.

Perovskite solar cell fabrication. The ITO-coated glass substrates were cleaned successively with Decon 90 (detergent) diluted solution, deionized water, acetone, isopropanol and ethanol in an ultrasonic bath for 20 min, respectively, and dried with nitrogen gas. An electron transport layer (ETL) of SnO_2/H_2O (1:5, v/v) was spin-coated onto cleaned ITO transparent glass substrates at 6000 rpm for 60 s in ambient condition and annealed at 150 °C for 30 min. The perovskite films were deposited using a single-step deposition method from the precursor solution containing FAI (0.26 M), PbI_2 (1.26 M), MAI (1.08 M) and $PbCl_2$ (0.14 M) in DMSO/GBL (3:7, v/v). The precursor solution was spin-coated onto the surface of SnO_2 layers in a two-step method at 1200 and 4300 rpm for 18 and 60 s, respectively. During the second step, 600 μl of toluene was dropped on the spinning substrate 30 s prior to the end of the spin coating. After spin-coating of precursor solution, the substrates were transferred to the hot plate and heated at 105 °C for 30 min. Hole transport materials (HTM) in DCB solution with different concentration were spun at 2000 rpm for the 60s, and immediately heat-treated at 100 °C for 10 min. Finally, about 100nm silver was deposited on the surface of the hole transport layer (HTL) through high-temperature vacuum evaporation.

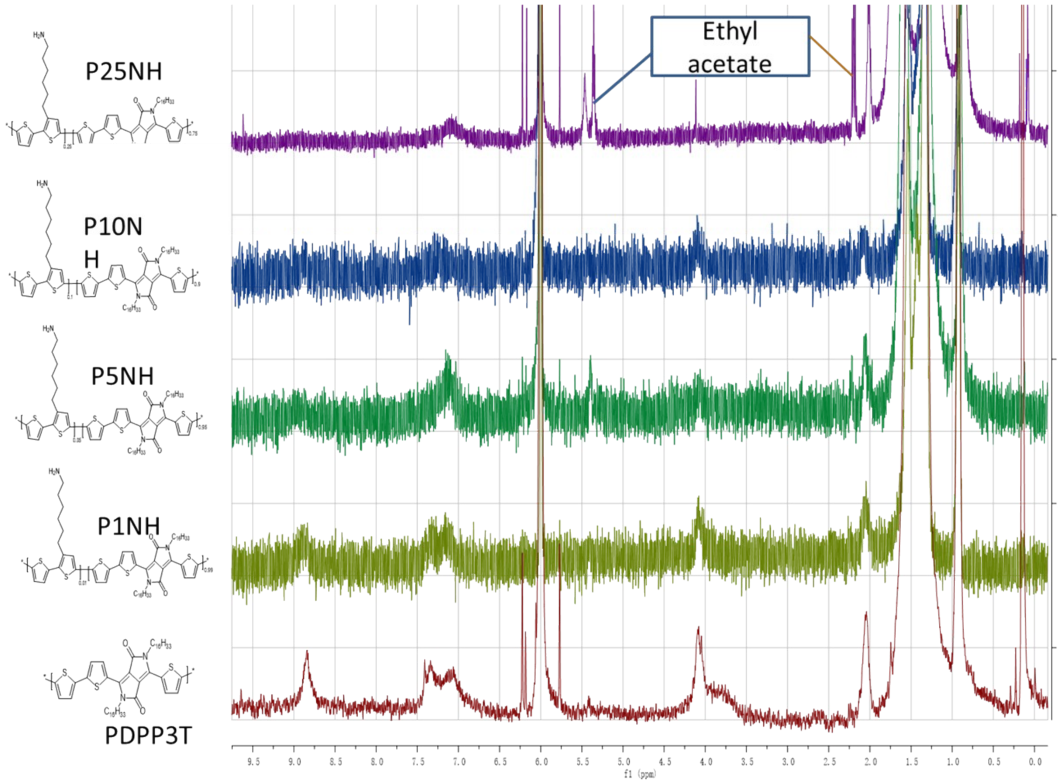

Figure S1. ^{1}H NMR of a series of the as-synthesized compounds.

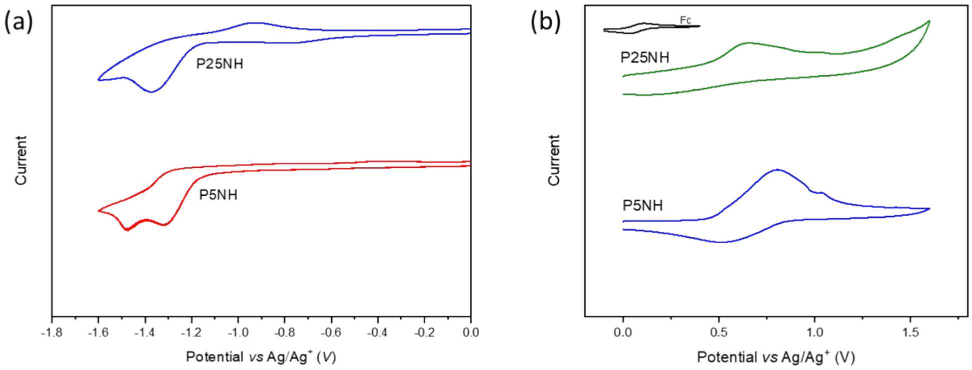

Figure S2. CV profile of P25NH and P5NH. Cyclic voltammetry (CV) measurements were performed on a CHI 660C instrument with a three-electrode cell using a glass carbon working electrode, a platinum wire counter electrode, and an Ag/AgNO$_3$ reference electrode in acetonitrile containing 0.1 M Bu$_4$NPF$_6$ electrolyte at a scan rate of 50 mV s^{-1}.

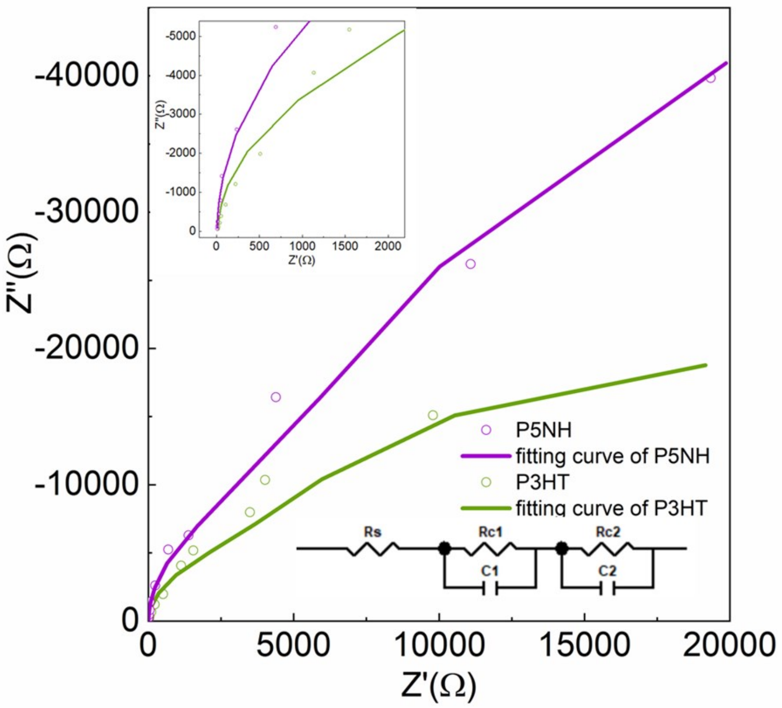

Figure S3. Nyquist plots of PSCs with fitting curve based on P5NH and P3HT as HTL at forwarding bias Vappl (0.4V) under dark conditions. The inserted graph is the Nyquist plots of PSCs based on P5NH and P3HT under high frequency. The insert circuit is the equivalent circuit to fit the Nyquist plots.

Table S1 Molecular Weight and Elemental Analysis

Polymer		P5NH	P25NH
M_n (kDa)		18.1	17.9
M_w (kDa)		45.9	48.9
PDI		2.54	2.73
Elemental analysis	C	70.62%	70.74%
	H	8.89%	8.54%
	N	3.67%	3.95%

Table S2. Stimulated data of EIS of solar cells based on P5NH and P3HT as HTLs.

	Rs(Ω)	Rc1(Ω)	Rc2(Ω)	C1(nF)	C2(nF)
P5NH	19.48	3904	37320	6.38	7.49
P3HT	27.9	659	22970	2.6	5.4

Table S3. **The results of simulated TRPL curve. The fitted equation is** $y = y_0 + A_1 \cdot e^{-x/\tau_1} + A_2 \cdot e^{-x/\tau_2}$

	y_0	A_1	τ_1	A_2	τ_2
Perovskite	0.06225 ± 0.00476	135657.83435 ± 49128.3307	18.04097 ± 0.49319	2.29014 ± 0.04906	185.84071 ± 3.4271
Perovskite/P5NH	0.05096 ± 9.2289E-4	3.98099E16 ± 1.3212E16	6.21339 ± 0.05286	6477.58059 ± 222.12988	22.52195 ± 0.06151
Perovskite/P3HT	0.0118 ± 3.81468E-4	9.42753E16 ± 1.4514E16	6.08747 ± 0.02345	1.47543E11 ± 5.75048E10	8.98173 ± 0.11308