Supplementary Information for

Polyelectrolyte Based Hole-transporting Materials for High Performance Solution Processed Planar Perovskite Solar Cells

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Experimental section

- **Materials:** CH₃NH₃I was synthesized through the reaction of 24 mL methylamine (33%wt. in ethanol, Aldrich) 10 and 10 mL hydroiodic acid (57 wt. % in water, Aladdin, China) in 100mL ethanol at ice bath for 2h with stirring under Ar atmosphere. The white powder could be collected with a rotary evaporator at 50 °C to exclude the solvent. Then the product was dissolved in ethanol again and precipitated in diethyl ether. The procedure was repeated three times. At last, the white powder was dried at 60 °C in vacuum oven overnight. And the P3CT-Na was synthesized through the reaction of poly[3-(4-carboxylbutyl)thiophene (Rieke, America) with sodium
- 15 hydroxide. For example, 200mg poly[3-(4-carboxylbutyl)thiophene was reacted with 44 mg NaOH in water with stirring at room temperature for 2 day.

Devices fabrication: ITO glass was cleaned through sequential ultrasonic treatment in detergent, deionized water, acetone, isopropanol for 15 minutes each. Then the substrates were dried using N₂ flow and removed to UV-Ozone chamber for 20 minutes. After that, PEDOT:PSS (Clevios 4083) or P3CT-Na was spincoated on ITO 20 glasses at 4000 rpm for 60 seconds and annealed at 140 °C for 30 minutes in air. Then the substrates were transferred to glovebox (filled with N₂). The precusor solution of perovskite was prepared with CH₃NH₃I and

- $PbCl_2$ (Aldrich) at a mole ratio of 3:1 in anhydrous N, N –dimethylformamide (DMF, Aldrich). For PEDOT:PSS coated ITO, 40% wt solution was spin-coated at 2000 rpm 45 seconds to form 500 nm perovskite layer. While for P3CT-Na coated ITO, 60% wt solution was used to form 500 nm perovskite layer. Then the films were
- 25 annealed on a hotplate at 80 °C for 120 ~ 150 minutes to form CH₃NH₃PbCl_{3-x}l_x films. And PC₆₁BM (American Dye Source) solution in chlorobenzene (20 mg/mL) was spin-coated on CH₃NH₃PbCl_{3-x}l_x layer at 2000 rpm for 60 seconds. Finally, the devices were transferred to vacuum chamber (10⁻⁶ mbar) and 50 nm C60 (American Dye Source) and 100 nm Al were evaporated to form the cathode.

Device characterization: the J-V measurement was conducted using Keithley 2440 sourcemeter controlled by 30 computer. And the J–V curves were measured by masking the active area with a metal mask (area of 9 mm²).

All the solar cells were measured under simulated AM 1.5 spectrum (100 mW/cm²) with an Oriel So13A solar. The EQE measurement was conducted through the Newport quantum efficiency measurement system (ORIEL IQE 200TM) combined with a lock-in amplifier and 150 W xenon lamp. The light intensity at each wavelength was calibrated by one standard Si/Ge solar cell. Notably, the EQE was measured in ambient atmosphere at 5 room temperature.

Ultraviolet photoelectron spectroscopy (UPS): UPS measurement was conducted using Shimadzu Spectrometer (AXIS ULTRA DLD) with a He I (21.2 eV) discharge lamp.

Surface morphology of EDTA derivatives layer: Scanning electron microscopy (SEM, S-4800, Hitachi) and atomic force microscopy (AFM, Dimension 3100V, Veeco, tapping mode) were used to observe the surface 10 morphology of perovskite or P3CT-Na films.

Photoluminescence (PL): time-resolved PL measurement of perovskite films was conducted using Horiba (FL3-111) at ambient atmosphere. The films were photoexcited using a 588 nm monochromatic light and detect the PL at 780 nm.



15 Fig. S1. Ultraviolet photoelectron spectroscopy (UPS) of PEDOT:PSS and P3CT-Na coated ITO glass.



Fig. S2. Transmittance spectrum of bare ITO, PEDOT:PSS and P3CT-Na coated ITO glasses.



Fig. S3. J-V curves of forward (from V_{oc} to J_{sc}) and reverse bias (from J_{sc} to V_{oc}) sweep of p-PSCs with P3CT-Na interlayer; The scan rate was conducted through 50ms sweep delay time between measurement points.



Fig. S4. Statistical analysis of the devices performance with P3CT-Na (20 devices)and PEDOT:PSS (15 devices).



Fig. S5. Time-resolved PL kinetics of $CH_3NH_3PbCl_{3-x}l_x$ on ITO/P3CT-Na and ITO/PEDOT:PSS substrate at 780 nm. The perovskite films were excited using a 588 nm laser head.



Fig. S6. SEM images of P3CT-Na films with different thickness. a) 4 nm; b) 27 nm;c) 52 nm; d) 80 nm; e) bare ITO.

The white dots appeared in S6a-6d may be caused by the aggregation of P3CT-Na on ITO.



Fig. S7. AFM images of PEDT:PSS (a, d) and P3CT-Na films with different thickness: b, e) 4nm; c, f) 10 nm; g, j) 27 nm; h, k) 52 nm; i, l) 80 nm; the scan size was 50*50 μm.



Fig. S8. UV-visible absorbance spectrum of P3CT-Na films with different thickness.

P3CT-Na film more than 20 nm was measured using Stylus Profiler (Dektak150, Veeco). As to the films less than 20 nm, the thickness was estimated through the absorbance-5 thickness curve: the linear dependence of absorbance at 550 nm with films thickness.



Fig. S9. The peak currents of PEDOT:PSS (a) and P3CT-Na (b) surfaces coated on ITO glass measured by the peak force tapping tunneling AFM.



Fig. S10. Photocurrents of perovskite device based on P3CT-Na measured with different delay between measurement points (a) and the stabilized current output at maximum power output (b) inset: the corresponding J-V curves of the devices in (b).