Conjugated polyelectrolyte with potassium cations enables inverted perovskite solar cells with an efficiency over 20%

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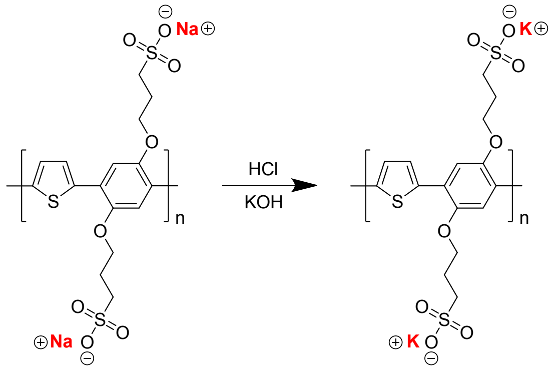
Synthesis of the polymer

All the reagents were purchased from Aladdin, J&K Scientific Ltd., or Sigma-Aldrich. The synthetic procedure to polymers TB(Na) and TB(K) is very similar to the reported one.[1]



Scheme S1. Synthetic route to the TB(K) CPE.

TB(K): Yield: 73.2%.

General characterization

UPS analysis was conducted to measure the energy level of HTLs with an unfiltered He I (21.22 eV) gas discharge lamp and a hemispherical analyzer (PHI 5000 VersaProbe II). The absorption/transmittance spectrum was measured with a PerkinElmer Lambda 650 S UV/VIS spectrometer. The contact angle was determined by a contact angle tester (AST VCA Optima XE). XRD patterns were recorded on a BRUKER ECO D8 (1KW) instrument. Atomic force microscopy (AFM) and field emission scanning electronic microscopy (FESEM) were conducted on a Bruker Dimension Edge system in a tapping mode and ZEISS Merlin system, respectively. Photoluminescence spectra were checked on ISS PC1 photon counting spectrofluorimeter with a pulsed laser and an excitation wavelength of 405 nm. Based on the same device configuration as PSC, TAS measurement was carried out on CHI660e at 0 V bias in the dark with a tuned frequency from 1 MHz to 100 Hz and an AC amplitude of 10 mV.

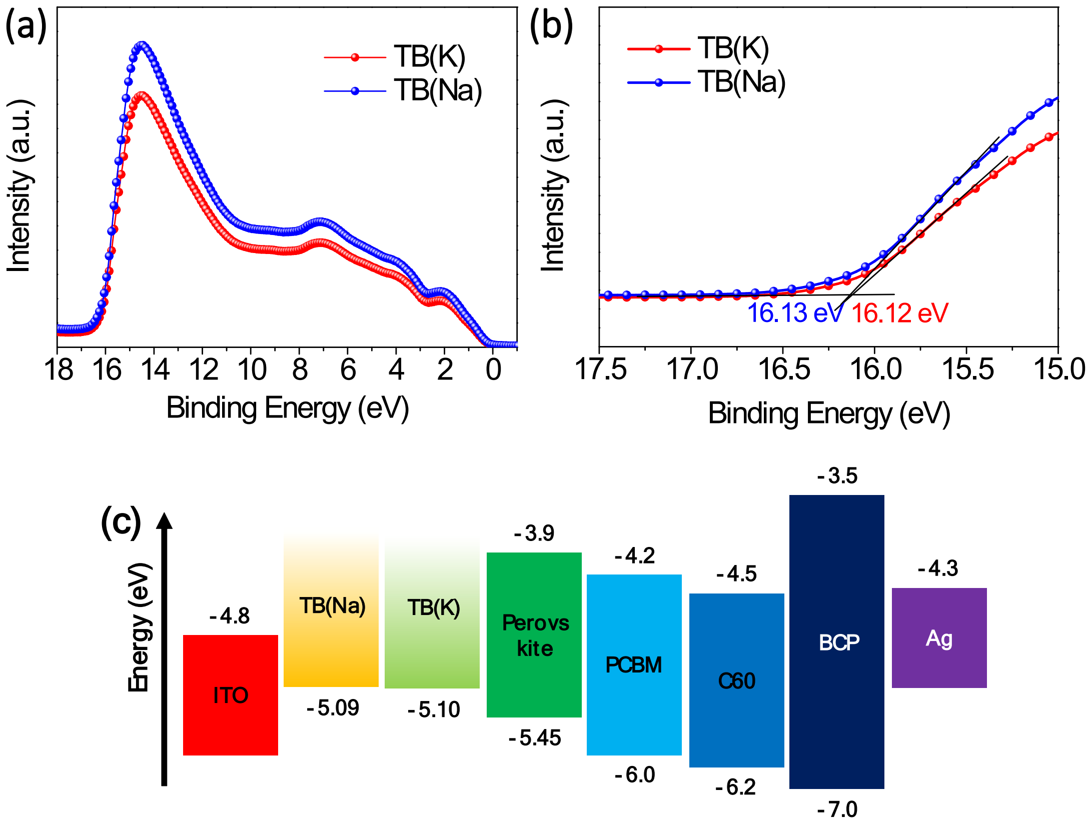


Figure S1. (a) (b) UPS charts of CPEs on ITO substrate and (c) the energy diagram of PSC device.

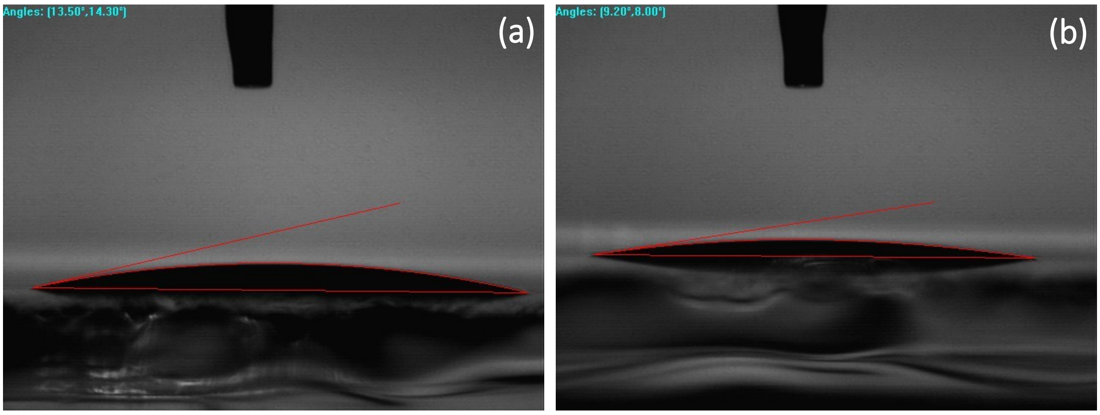


Figure S2. Wettability test of ITO/CPE film to DMF drop: (a) TB(Na) and (b) TB(K).

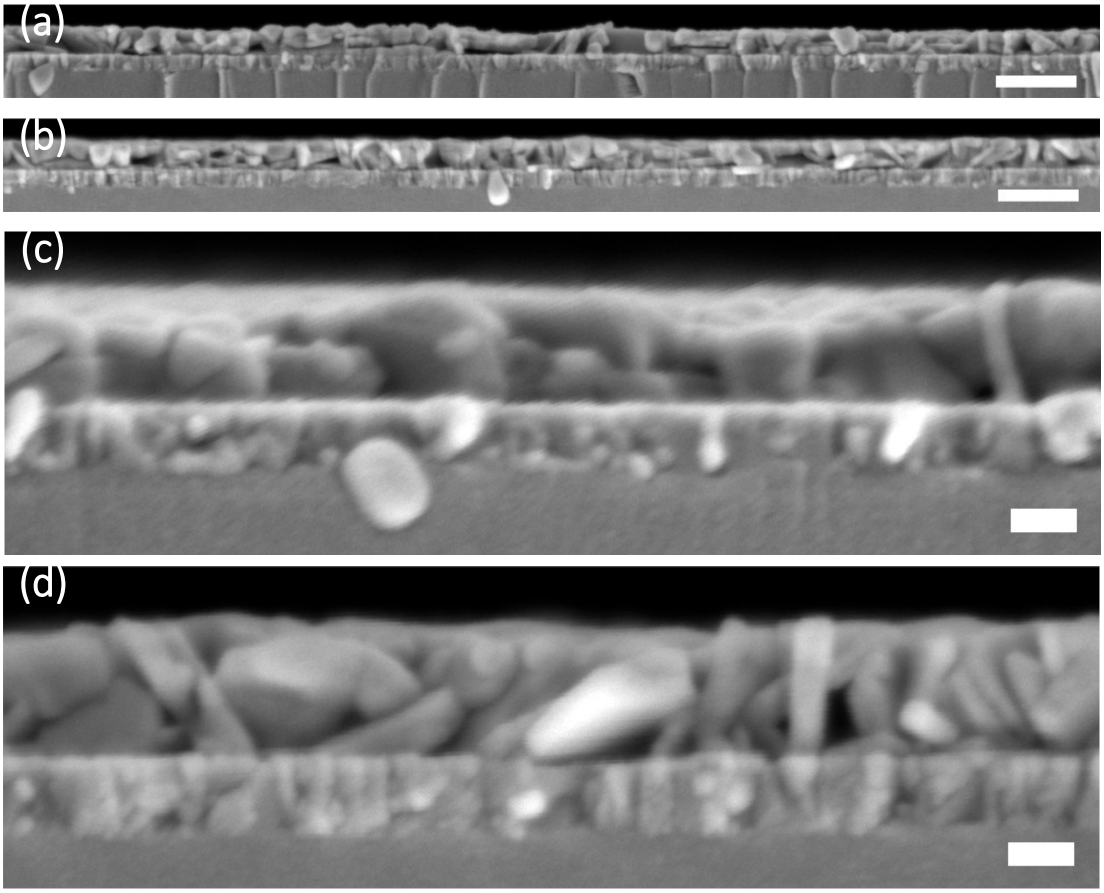


Figure S3. Cross-sectional SEM images of ITO/CPE/perovskite. (a) TB(Na) and (b) TB(K) with a scale bar of 1 micron; (c) TB(Na) and (d) TB(K) with a scale bar of 200 nm.

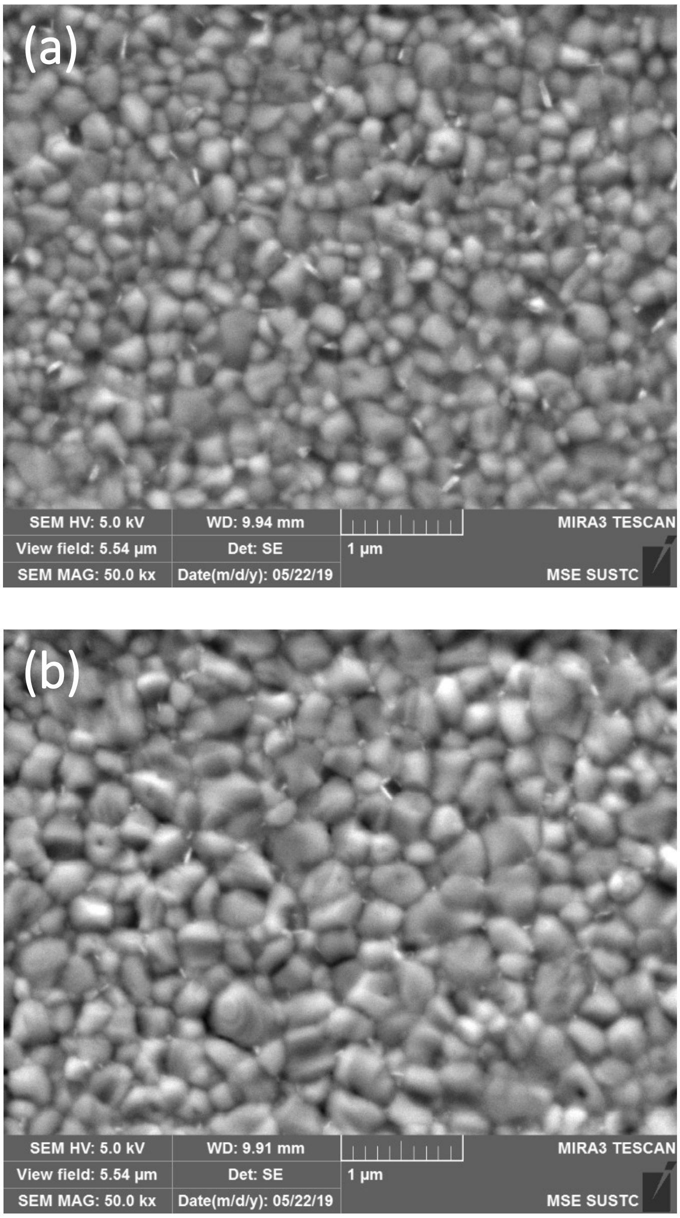


Figure S4. SEM images of $MAPbI_xCl_{3-x}$ films on different CPEs: (a) TB(Na) and (b) TB(K).

Perovskite films with a component of $MAPbI_xCl_{3-x}$ ($x \approx 0.02$) were also presented to demonstrate the effect of K replacement. The $MAPbI_xCl_{3-x}$ solution was prepared by mixing MAI (1.033 g), $PbCl_2$ (0.181 g), PbI_2 (2.697 g) powder in 4.5 ml DMF and 0.5 ml DMSO, and then spin-coated to form a film with the same procedure as that used for $FA_{0.85}MA_{0.15}Pb(Br_{0.15}I_{0.85})_3$.

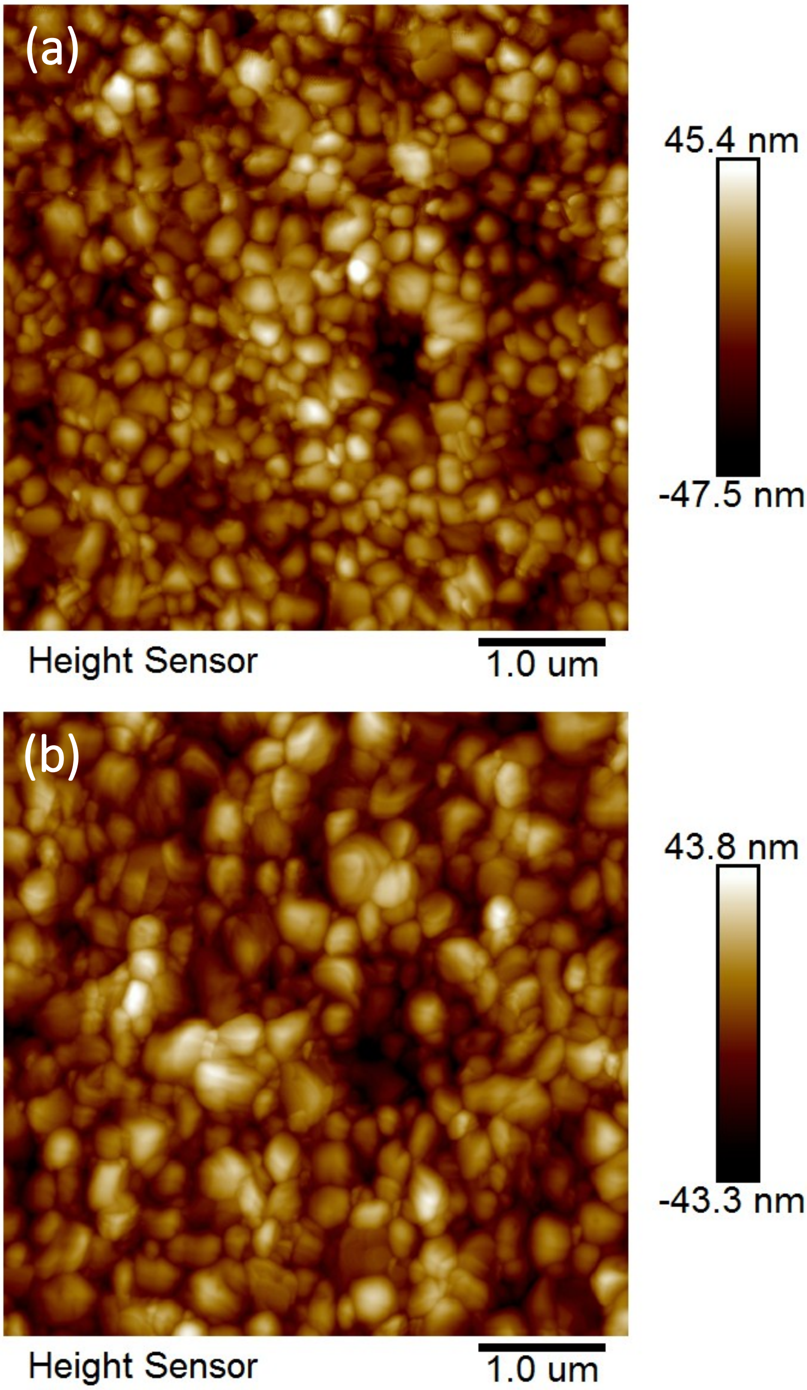


Figure S5. AFM images of $MAPbI_xCl_{3-x}$ films on different CPEs: (a) TB(Na) with RMS of 13.3 nm; (b) TB(K) with RMS of 12.7 nm.

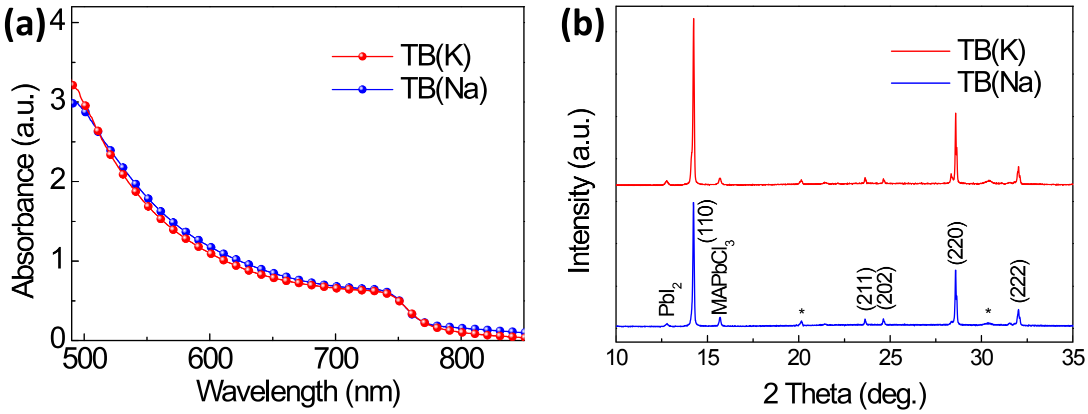


Figure S6. (a) Absorbance spectra and (b) XRD patterns of $MAPbI_xCl_{3-x}$ on different CPEs.

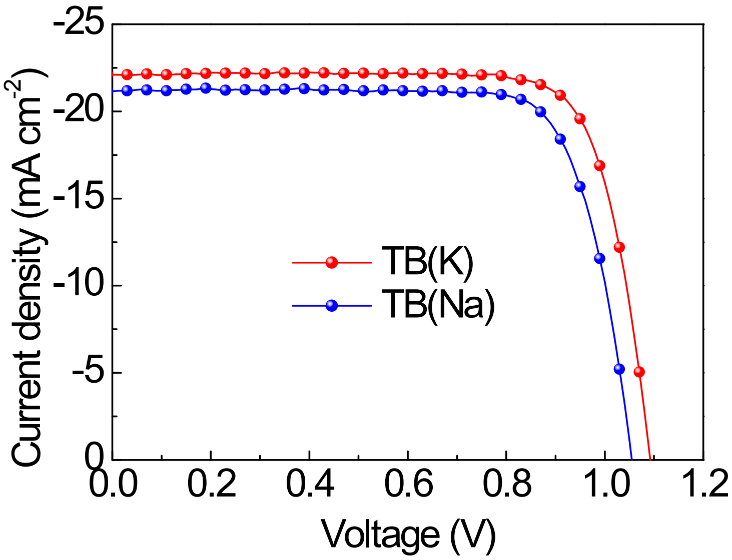


Figure S7. *J-V* curves of PSC devices based on $MAPbI_xCl_{3-x}$ on different CPEs.

Table S1. Summary of the photovoltaic properties of the champion devices based on $MAPbI_xCl_{3-x}$.

HTM	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
TB(Na)	1.05	21.25	0.77	17.18
TB(K)	1.09	22.09	0.79	19.02

Time-resolved photoluminescence results

The time-resolved photoluminescence (TRPL) spectra were fitted with a two-component exponential decay model based on the following equation according to the literature,[2]

$$I(t) = A_1 exp\left(- {}^{t}\!/_{\tau_1} \right) + A_2 exp\left(- {}^{t}\!/_{\tau_2} \right)$$

and the average time constant is calculated with the following equation,

$$\tau_a = A_1\tau_1 + A_2\tau_2$$

Table S2. Lifetimes extracted from the TRPL spectra.

HTM	τ_1 [ns]	A1 [%]	τ_2 [ns]	A1 [%]	τ_a [ns]
TB(Na)	8.67	2.75	49.30	97.25	48.16
TB(K)	5.20	30.80	22.00	69.20	16.82

Thermal admittance spectroscopy (TAS)

TAS was carried out on a CHI660e electrochemical workstation at 0 V bias in dark with a similar procedure to the reported literature,[3, 4] and a tuned frequency from 100 Hz to 1 MHz and an AC amplitude of 10 mV were employed. The static permittivity and the attempt-to-escape frequency were chosen to be 25 and 5.0×10^{10} rad/s due to the limited experimental conditions. The final density of state (DOS) value was calculated based on the data extracted from the Mott-Schottky curve and Capacitance-Frequency spectrum with the following equation,

$$DOS\ (E_{\omega}) = -\frac{V_{bi}\, dC\ \omega}{qWd\omega kT}$$

Where V_{bi}, W, C, ω, k and T are built-in potential, depletion width, capacitance, angle frequency, Boltzmann constant, and temperature respectively. The values of V_{bi} and W can be obtained from the Capacitance-Frequency spectrum.

E_{ω} can be calculated by the following equation,

$$E_{\omega} = kTln\frac{\omega_0}{\omega}$$

where ω_0 is the attempt-to-escape frequency.

Table S3. Trap densities extracted from the TAS analysis.

HTM	Shallow trap [cm^{-3}]	Deep trap [cm^{-3}]	Total [cm^{-3}]
TB(Na)	1.75E15	9.19E15	1.09E16
TB(K)	2.09E15	6.97E15	9.06E15

Reference

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