## The temporal and spatial pinhole constraint in small molecule hole transport layers for stable and efficient perovskite photovoltaics

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Figure S1 The chemical structure of poly(4-vinylpyridine) (P4VP).



Figure S2 The RMS roughness data for Spiro and Spiro:P4VP based sample



Figure S3. a) The open circuit voltage. b) The short-circuit current. c) The fill factor. d) The power conversion efficiency of multi-devices based on Spiro and Spiro:P4VP as HTLs.



Figure S4. Certificated results by National Institute of Metrology, China (NIM, China). The forward scan is performed from -0.1 V to 1.2 V at 33 mV/s, with a PCE of 19.8% (Voc=1.09 V, Isc=2.23 mA, FF=77.0%). The reverse scan is performed from 1.2 V to -0.1 V at 33 mV/s, with a PCE of 20.6% (Voc=1.13 V, Isc=2.23 mA, FF=77.0%). The device has an active area of 0.09408 cm<sup>2</sup>.



Figure S5. The steady-state photoluminescence (PL) spectroscopy based on Spiro and Spiro:P4VP as HTLs.



Figure S6.The normalized time-resolved photoluminescence (TRPL) spectroscopy based on Spiro and Spiro:P4VP as HTLs.

Table S1. The obtained carrier lifetimes of perovskite films based on Spiro and Spiro:P4VP as HTLs.

Sample	Spiro	Spiro:P4VP
Lifetime $\tau_1/ns$	12.03	23.60
Lifetime $\tau_2/ns$	112.1	100.0

Sample	$\tau_{recombination}$	$\tau_{transport}$
Spiro	0.51µs	310ns
Spiro:P4VP	0.70µs	220ns

Table S2. The obtained photovoltage decay time ( $\tau_{recombination}$ ) and photocurrent decay time ( $\tau_{transport}$ ) of perovskite solar cells based on Spiro and Spiro:P4VP as HTLs.



Figure S7 . XPS survey spectra of Pb atom in perovskite films without and with P4VP  $(0.1 \text{ mg mL}^{-1})$ 



Figure S8. The stability of this work stored in air was compared with other works.

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