## Supporting Information for

Inverse-Architecture Perovskite Solar Cells with 5,6,11,12tetraphenylnaphthacene as a Hole Conductor

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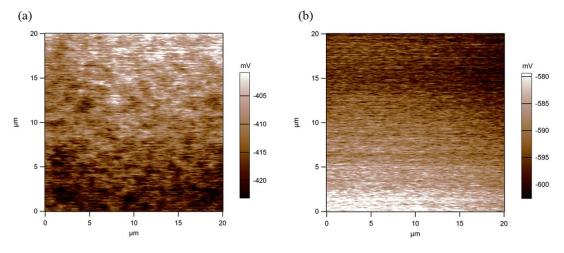
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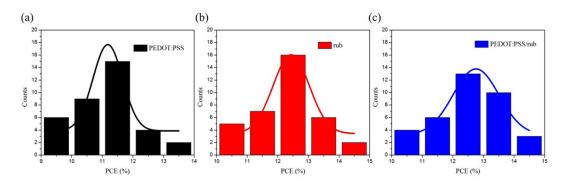
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**Fig. S1** Two-dimensional surface potential distributions of (a) PEDOT:PSS and (b) rub films. The average values of the contact potential difference between sample and the probe are -412 and -594 mV for PEDOT:PSS and rub, respectively.



**Fig. S2** Photographs of the contact angle for the PEDOT:PSS, rub and PEDOT:PSS/rub substrate. The water contact angle for PEDOT:PSS, rub and PEDOT:PSS/rub are 9.5°, 80.3° and 77.2°, respectively.



**Fig. S3** Histogram of solar cell efficiencies for 36 devices with (a) PEDOT:PSS, (b) rub, (c) PEDOT:PSS/rub as HTL, respectively. Black, red and blue solid lines represent the Gaussian distribution fitting for the statistics on efficiencies. The PCE mean values of Gauss distribution are 11.5%, 12.4%, 12.8% for PEDOT:PSS, rub and PEDOT:PSS/rub hole transport layer, respectively.

**Table S1** The calculated surface potential of PEDOT:PSS and rub with scanning Kelvin probe microscope. The formula is  $\varphi_s = \varphi_{Tip} + e \cdot V_{CPD}$ , of which  $\varphi_s$  is surface potential of sample,  $\varphi_{Tip}$  is the tip potential of yttrium probe, and  $V_{CPD}$  is the contact potential difference between sample and the probe.

sample	$\phi_{Tip}(eV)$	$V_{\mathrm{CPD}}\left(\mathbf{V}\right)$	φ <sub>s</sub> (eV)
PEDOT:PSS	-4.47	-0.412	-4.88
rub	-4.47	-0.594	-5.06

**Table S2** Summarized PL lifetimes of perovskite layer on the hole transport layer of PEDOT:PSS, rub or PEDOT:PSS/rub. The PL lifetimes were fitted with a bi-exponential decay function including a fast decay ( $t_1$ ) and a slow decay ( $t_2$ ) process.

HTL	$\mathbf{A}_1$	$t_1$ (ns)	$A_2$	<i>t</i> <sub>2</sub> (ns)
PEDOT:PSS	$1.7 \times 10^{13}$	0.68	1.6×10 <sup>4</sup>	7.6
rub	$8.6 \times 10^{13}$	0.63	$1.4 \times 10^{4}$	6.9
PEDOT:PSS/rub	$1.7 \times 10^{13}$	0.68	$1.7 \times 10^{4}$	7.2