## Supplementary Information

## Perfluorinated Ionomer and Poly(3,4-ethylenedioxythiophene) Colloid as a Hole Transporting Layer for Optoelectronic Devices

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**Fig. S1.** FTIR spectrum of the PEDOT:PFI colloid. The spectrum was acquired from a compressed tablet made of CsI power and the PEDOT:PFI colloid solution. A spectrum of pure CsI tablet was measured first for the backgroung signal substraction.



**Fig. S2.** UV-visible transmittance spectra obtained from PEDOT:PFI and PEDOT:PSS films. The films were prepared onto quartz substrates and deducted the reference signal during the measurement.



**Fig. S3.** XPS analysis results of the PEDOT:PFI (1:15) fim deposited on a ITO substrate. (a) The survay XPS spectrum, (b) the surface element concentration of the PEDOT:PFI film, and the fine-scan (c) C 1s, (d) F 1s, (e) O 1s, (f) S 2p spectrum.



**Fig. S4.** ToF-SIMS depth profiles of the PEDOT:PFI film deposited on (a) ITO and (b) organic BHJ layer. A concentrated PEDOT component near the bottom interface could be identified in each profile.



**Fig. S5.** ToF-SIMS 3D images of the PEDOT:PFI film deposited on (a) ITO and (b) organic BHJ layer. The analysis area was<sup>50</sup>  $\mu m \times 50 \mu m$ . An interpenetrating PEDOT:PFI morphology was confirmed by the solely presented PEDOT and PFI 3D images, regardless of the substrate material.



Fig. S6. Water contact angle images of (a) ITO, (b) PEDOT:PSS-coated ITO and (c) PEDOT:PFI (1:15)-coated ITO.



**Fig. S7**. The AFM images of (a) ITO, (b) PEDOT:PSS-coated ITO, and (c) PEDOT:PFI (1:15)-coated ITO.



**Fig. S8** J-V characteristics of the PSCs utilizing the PEDOT:PSS (blue circles) and the PEDOT:PFI (1:15) (red triangles) as the HTL.

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	On-Set (eV) <sup>†</sup>	Cut-Off (eV)	HOMO (eV)	Work function (eV)
Ag	0	16.9	-	4.3
PEDOT:PSS	0.08	15.64	-5.64	5.56
PEDOT:PFI (1:15)	0.74	15.99	-5.95	5.21
PEDOT:PFI (1:30)	1.08	16.29	-5.99	4.91
PV2001	0.46	17.29	-4.37	3.91
PV-D4610	0.25	17.15	-4.3	4.05
PV2300	0.74	17.31	-4.64	3.9
PD2001	0.49	17.43	-4.25	3.76
Au	0	16.01	-	5.19
AZO	0.89	17.06	-5.03	4.14
ND1000	1.18	16.01	-6.37	5.19
PD-A2	0.56	17.08	-4.68	4.12

**Table S1.** Summary of the on-set and cut-off positions determined by the UPS spectra and the corresponding HOMO and work function values of the investigated materials.

<sup>†</sup>By definition, the magnitude of HOMO off set is equal to the on-set value.