

## **Hole transporting electrodeposited PEDOT–polyelectrolyte layers for perovskite solar cells**

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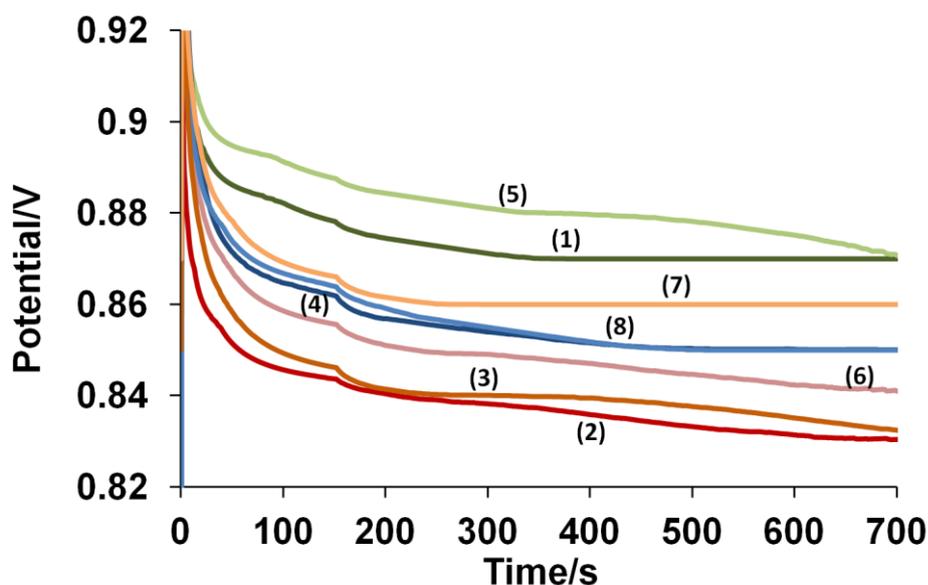
### **S1. Experimental**

EDOT was electrochemically polymerized in aqueous solutions consisting of 10 mM EDOT and 20 mM of the following polyelectrolytes<sup>1</sup>: flexible-chain poly(styrenesulfonic acid) (PSSA (Aldrich,  $M_w$  1 000 000, 25 % aqueous solution)) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA (Aldrich,  $M_w$  2 000 000, 15 % aqueous solution)), semi-rigid-chain poly(4,4'-(2,2'-disulfonic acid)-diphenylene-iso-phthalamide) (i-PASA), rigid-chain poly(4,4'-(2,2'-disulfonic acid)-diphenylene-tere-phthalamide) (t-PASA) and their sodium salts.  $\text{Na}^+$ -salts of i-PASA and t-PASA ( $M_n = 40\,000$ ) were synthesized as described in<sup>2</sup>. The synthesis solutions were prepared as described in<sup>1,3</sup>. The EDOT electropolymerization was performed in a galvanostatic ( $0.05\text{ mA cm}^{-2}$ ) regime on ITO-glass substrates from Kavio, and the electrodeposition charge was controlled to be  $10\text{ mC cm}^{-2}$ . A platinum foil and a saturated silver–silver chloride electrode were used as counter and reference electrodes, respectively. All the layers with the surface area of  $2.75\text{ cm}^2$  were thoroughly rinsed with deionized water after the synthesis. UV-Vis-NIR spectra of PEDOT layers in the range up to 1300 nm were performed using a UV3101PC spectrophotometer (Shimadzu). The surface morphology and roughness of PEDOT layers was recorded using Enviroscope AFM with a Nanoscope V controller (all by Bruker) in tapping mode.

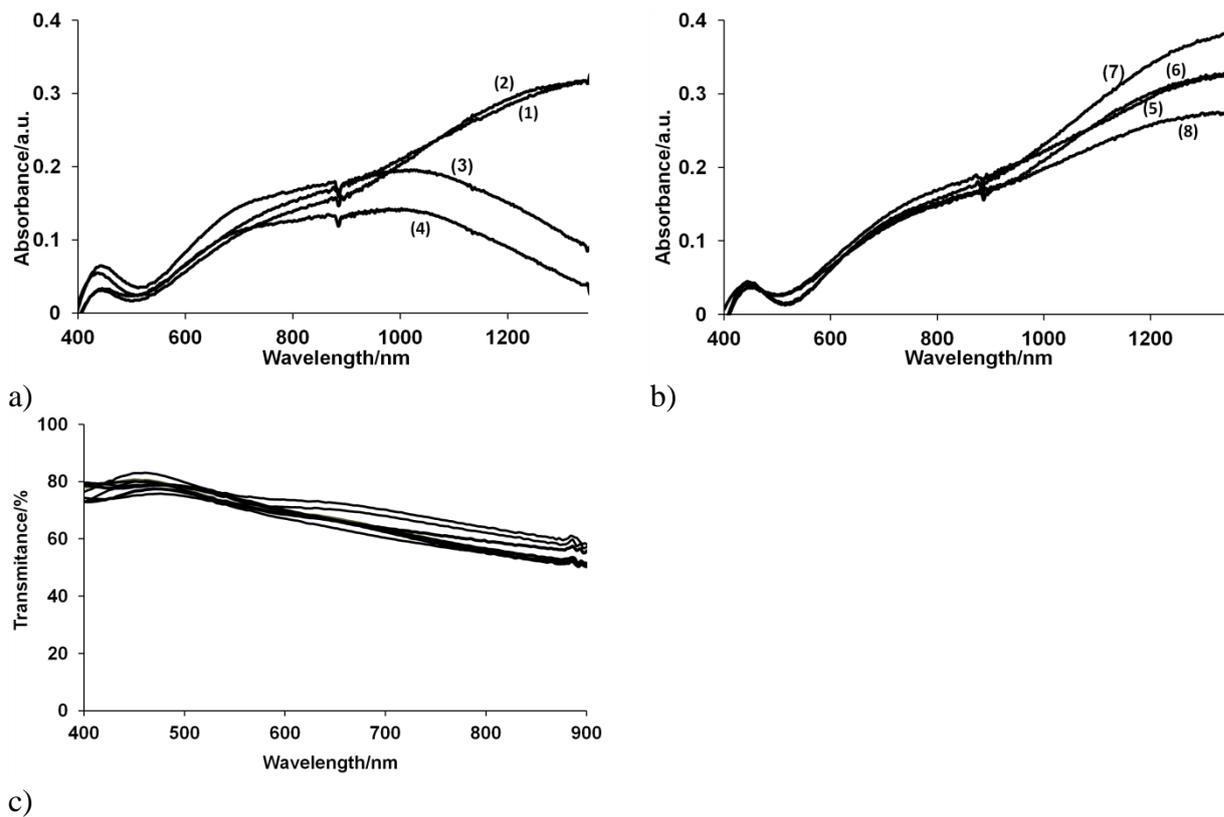
A solution of PEDOT:PSS (1:6 wt. %) Al 4083 from Ossila referred as PEDOT:PSS(SC) was used to prepare a reference HTL, which was spin-coated at 2000 RPM.

A configuration of the studied PSCs was the following: glass/ITO/PEDOT/Perovskite/ $\text{C}_{60}$ /BCP/Al. PEDOT-polyelectrolyte layer of 30-40 nm thick on ITO/glass substrate was annealed at  $70\text{ }^\circ\text{C}$  for 10 min to eliminate water residues. Perovskite was prepared in 1.5 M concentration in anhydrous dimethylformamide (DMF from Sigma-Aldrich) with  $\text{CH}_3\text{NH}_3\text{I}$  (MAI, 99.99 % purity from GreatCellSolar) and  $\text{PbI}_2$  (ultrapure 99.999 % from Alfa-Aesar)<sup>4</sup>. A 400-nm-thick layer of perovskite was deposited onto the PEDOT layers by centrifugation (5000 rpm, 30 s). 400  $\mu\text{L}$  of toluene (Sigma-Aldrich) were quickly added 5 s after the start of centrifugation. Then, the layers were annealed at  $100\text{ }^\circ\text{C}$  for 10 min. Thereafter,

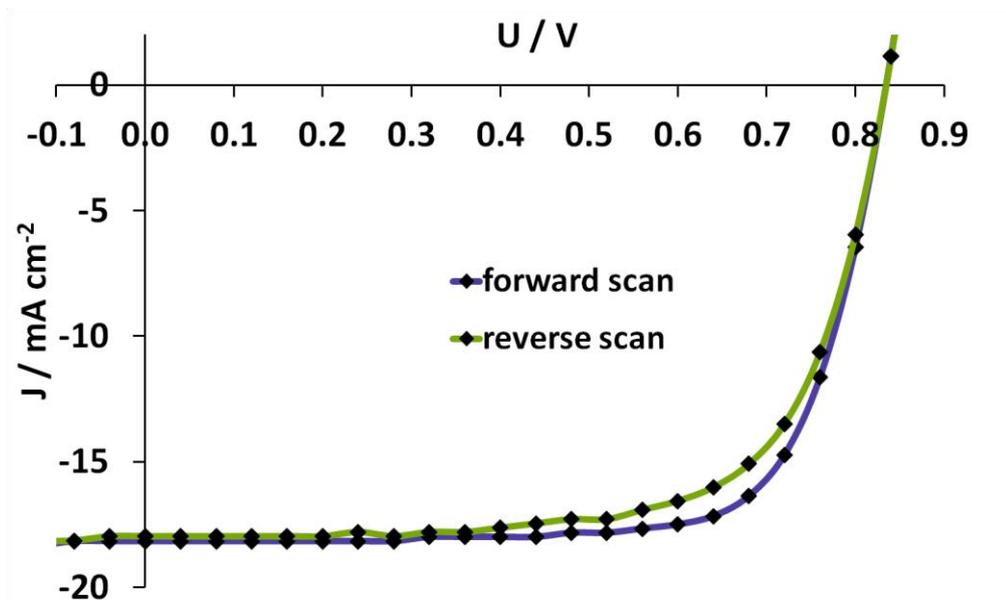
thermal vacuum evaporation was used to successively deposit the electron-transport layer of fullerene C<sub>60</sub> (Ossila Ltd.), blocking layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Sigma-Aldrich), and Al cathode with the thicknesses of 40, 7, and 80 nm, respectively. The thicknesses were determined with a KLA-Tencor D-100 Profiler stylus profile meter. The current–voltage characteristics of the PSC samples were measured with a Keithley 2400 and Oriel 96000 solar simulator (Newport Corp.) at intensity P = 100 mW cm<sup>2</sup> (AM1.5 conditions) in a glovebox with dry atmosphere of argon.



**Figure S1** Time dependences of the potential during PEDOT synthesis in galvanostatic mode (0.05 mA/cm<sup>2</sup>) in aqueous solutions containing: PAMPSA (1), PSSA (2), i-PASA (3), t-PASA (4), PAMPSNa (5), PSSNa (6), i-PASNa (7), t-PASNa (8).



**Figure S2** Absorption spectra of the layers of PEDOT complexes with acid form of PE (a): PAMPSA (1), PSSA (2), i-PASA (3), t-PASA (4) and salt form of PE (b): PAMPSNa (5), PSSNa (6), i-PASNa (7), t-PASNa (8). Transmission spectra of PEDOT layers (c).



**Figure S3** Current density versus voltage characteristics for the best device based on electrodeposited PEDOT-t-PASA.

## References

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