Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information (ESI) for

Efficient and Moisture-resistant Hole Transport Layer for Inverted Perovskite Solar Cells Using Solution-processed Polyaniline

Kisu Lee[a], Haejun Yu[a], Jong Woo Lee[b], Jungkyun Oh[a], Sohyeon Bae[b], Seong Keun Kim[b], and Jyongsik Jang[a,*]

[a]School of Chemical and Biological Engineering, College of Engineering, Seoul National University (SNU), 599 Gwanangno, Gwanak-gu, Seoul, 151-742 (Korea).

Fax: +82-2-888-1604; Tel: 82-2-880-7069; E-mail: jsjang@plaza.snu.ac.kr

[b]Department of Biophysics and Chemical Biology and Department of Chemistry, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

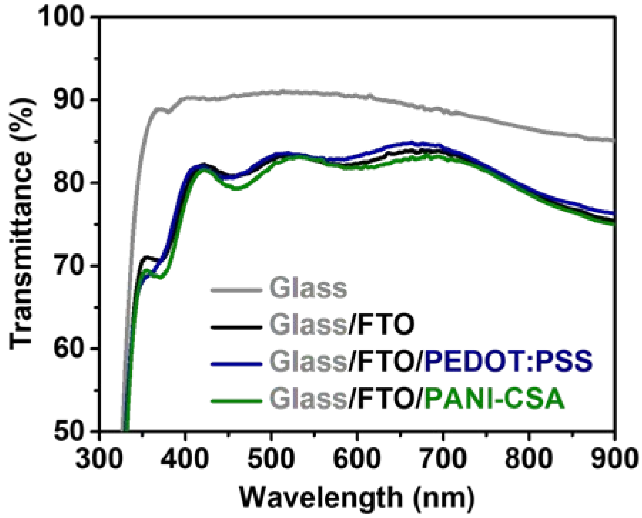

Figure S1. Transmittance spectra of glass, glasss/FTO, and glass/FTO/PEDOT:PSS or PANI-CSA.

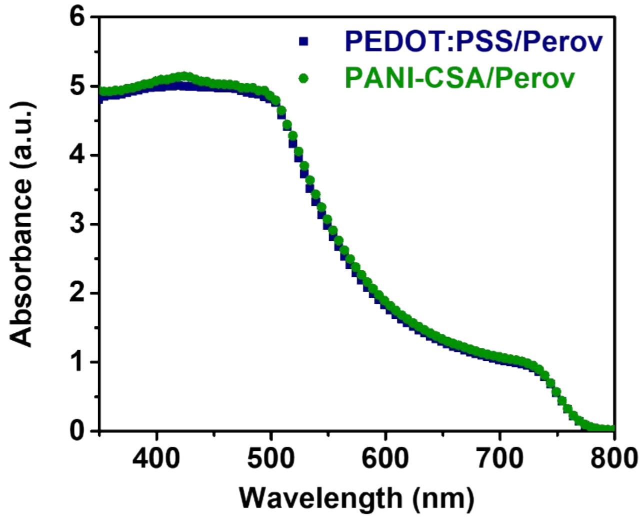

Figure S2. Ultraviolet-visible (UV-Vis) absorption spectra of perovskite films deposited on PEDOT:PSS and PANI-CSA film.

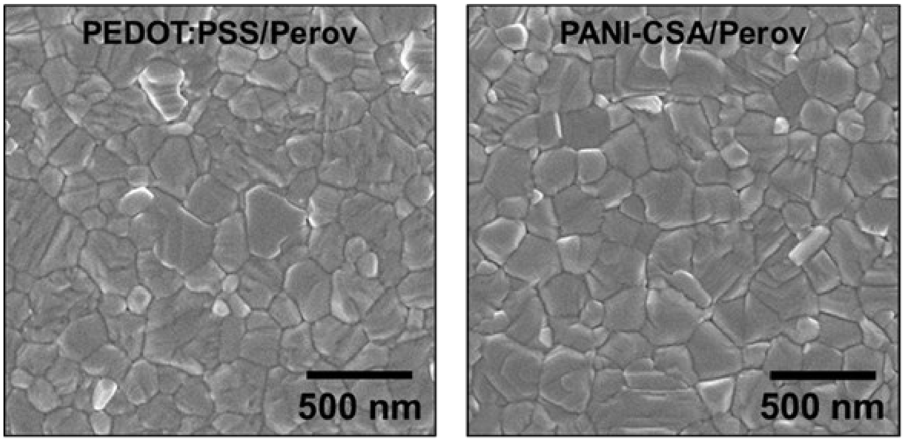

Figure S3. Top-view FE-SEM images of perovskite films deposited on PEDOT:PSS and PANI-CSA film.

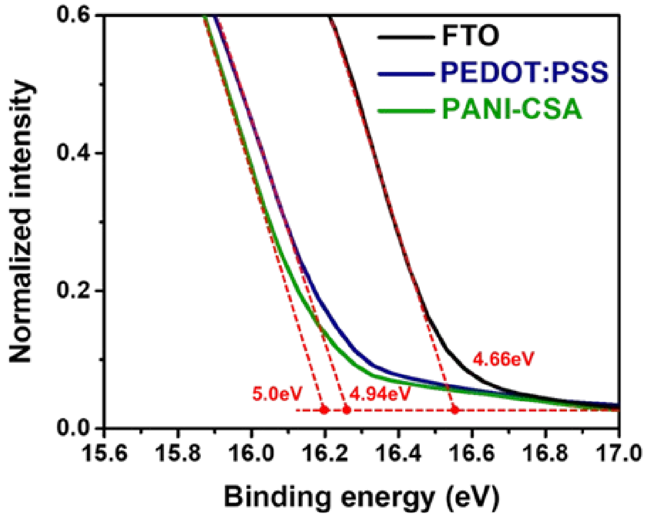

Figure S4. Ultraviolet photoelectron spectra (UPS) of FTO, PEDOT:PSS, and PANI-CSA. The spectra show the secondary cut-off region and circles indicate the cut-off position. Work function of the samples was determined by following equation,

$$\Phi = h\omega - | E_{sec} - E_{FE} |$$

where $h\omega$= 21.2 eV (He(I) source), E_{sec} is the onset of the secondary emission, and E_{FE} is the Fermi edge. The Fermi edge was set to 0 eV.

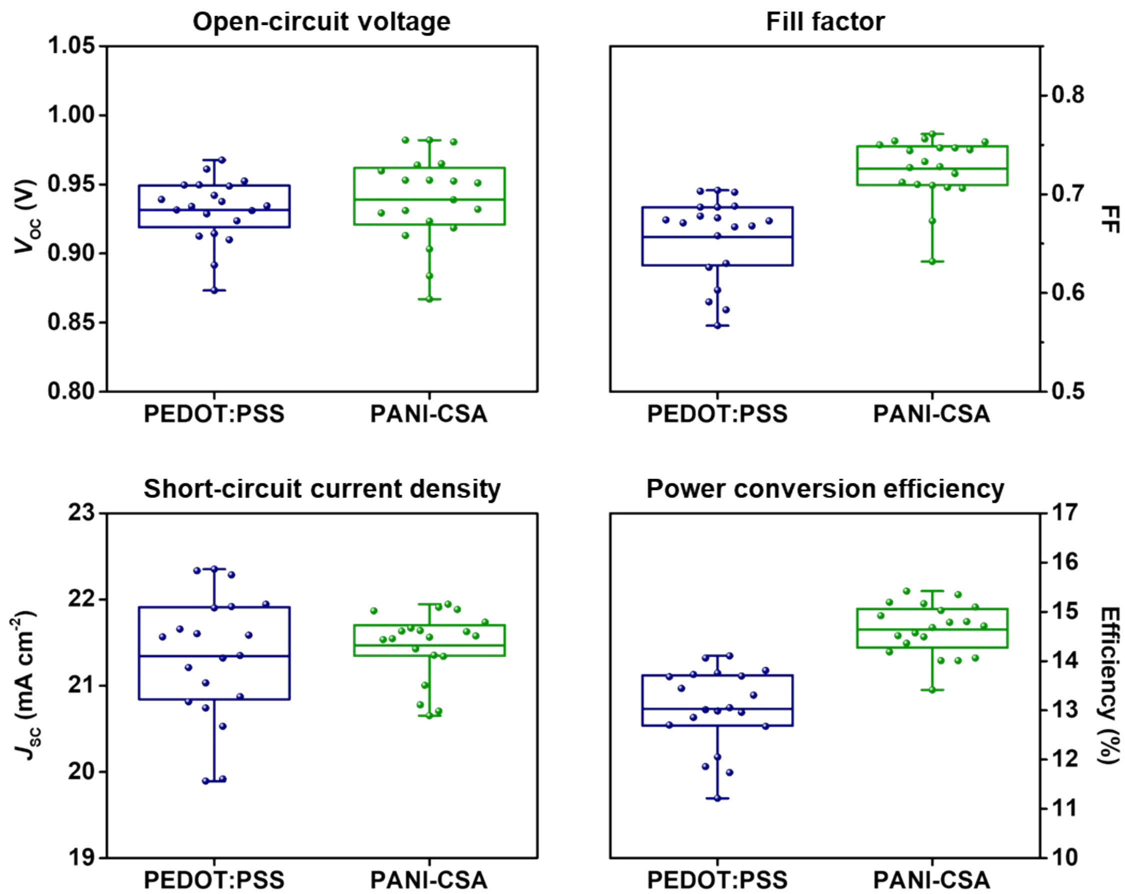

Figure S5. Distribution of photovoltaic parameters (V_{OC}, FF, J_{SC}, and PCE) of PSCs with PEDOT:PSS and PANI-CSA. The mean values are expressed as solid line inside of the boxes.

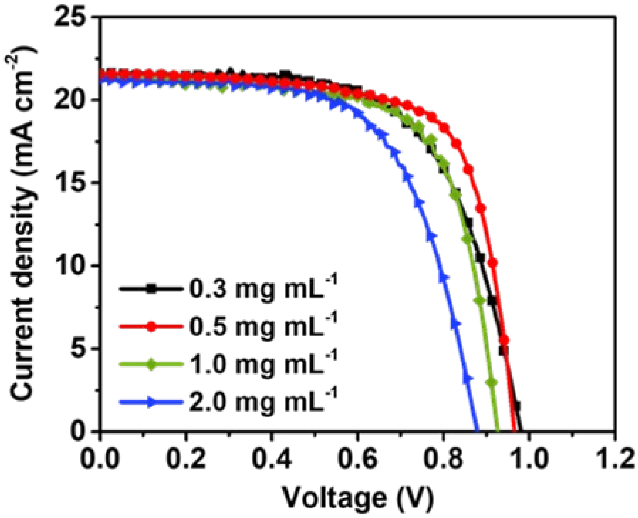

Figure S6. Comparison of *J–V* characteristic for PSCs using PANI-CSA HTL depending on concentration of PANI-CSA dispersion.

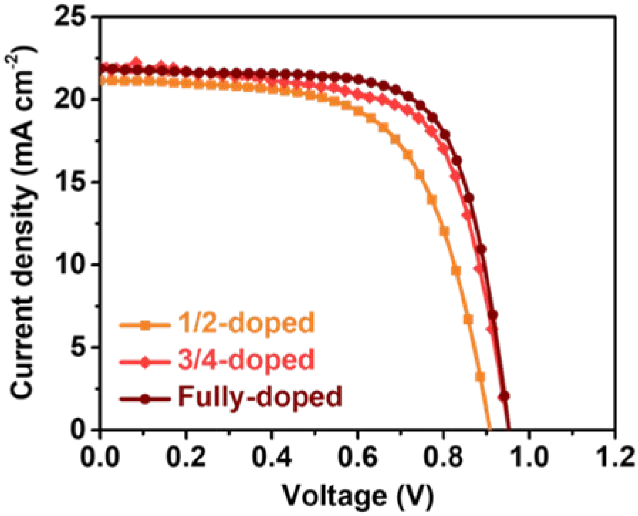

Figure S7. Comparison for *J–V* characteristic of PSCs using PANI-CSA HTL depending on protonation level of PANI.

To obtain highly conductive polyaniline (PANI) film, synthesized PANI (hydrochloric acid-doped) is dedoped with ammonia and re-doped with camphorsulfonic acid (CSA). Dedoped (un-protonated) PANI, which is emeraldine base form, has an insulating nature, and protonation by CSA molecules induces charge carrier delocalization along the polymer backbone and achieves conductive emeraldine salt form. In this step, the degree of protonation level in PANI can be controlled by molar ratio of CSA to repeat unit. “1/2-doped” stands for the protonation of one nitrogen atom in repeat unit and “fully-doped” stands for the protonation of two nitrogen atom in repeat unit. It is reported that this protonation level (doping level) of PANI is directly related to the conductivity, optical transparency, and work function.[1,2] Thus, we prepared three kinds of PANI-CSA with the varied protonation level (1/2, 3/4, and full) and fabricated PSCs to test their hole transport ability. The *J–V* characteristics and photovoltaic parameters are presented in **Figure S7** and **Table S2**. Fully-doped PANI-CSA shows the best performance as HTL for PSCs. Fully-doped PANI-CSA has the highest conductivity since bipolaronic form of PANI is favorable for expanded coil conformation and longer charge carrier delocalization,[1,3] and it might positively affect the device performance.

[1] O. Abdulrazzaq, S. E. Bourdo, V. Saini, V. G. Bairi, E. Dervishi , T. Viswanathan, Z. A. Nima, A. S. Biris, *Energy Technol.* 2013, **1**, 463-470.

[2] O. Abdulrazzaq, S. E. Bourdo, M. Woo, V. Saini, B. C. Berry, A. Ghosh, A. S. Biris, *ACS Appl. Mater. Interfaces* 2015, **7**, 27667-27675.

[3] O. Abdulrazzaq, S. E. Bourdo, V. Saini, F. Watanabe, B. Barnes, A. Ghosh, A. S. Biris, *RSC Adv.* 2015, **5**, 33-40.

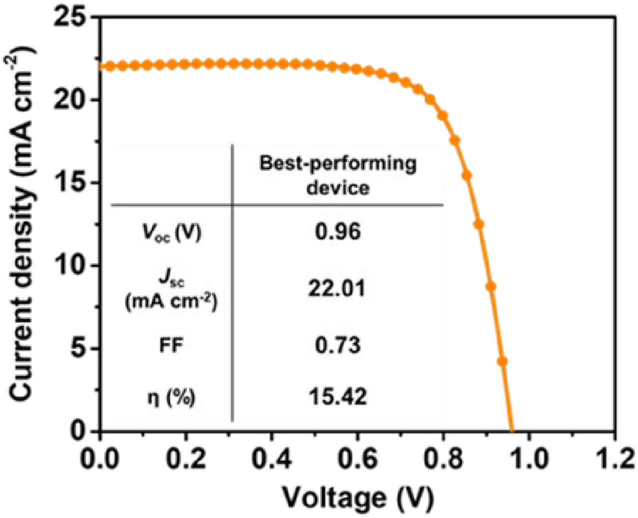

Figure S8. *J*–*V* characteristic for the best-performing device with PANI-CSA HTL.

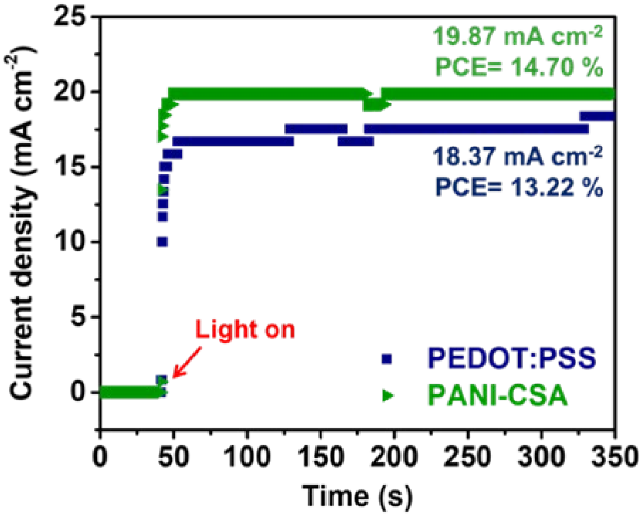

Figure S9. Steady-state photocurrent density of PSCs measured at each maximum power voltage (0.72 and 0.74 V) under continuous illumination.

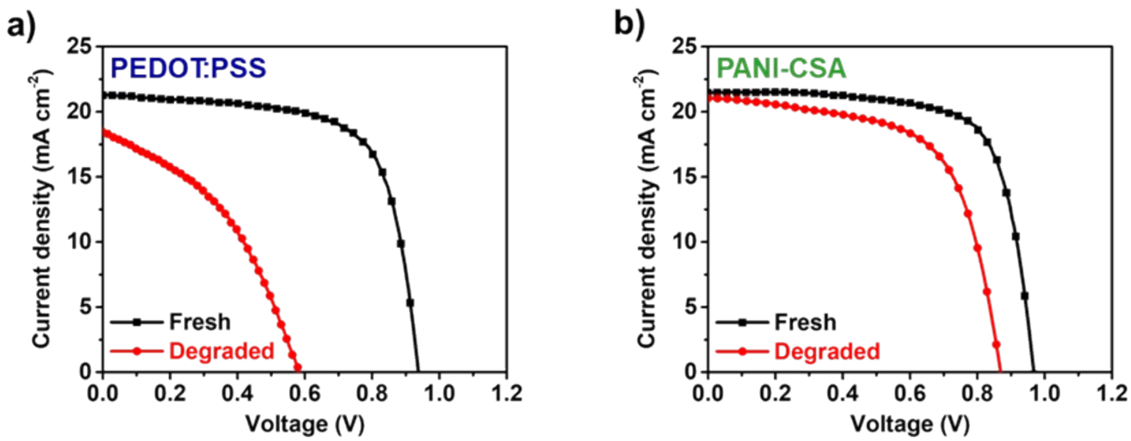

Figure S10. Comparison of *J–V* characteristics for PSCs with (a) PEDOT:PSS and (b) PANI-CSA before and after the stability test.

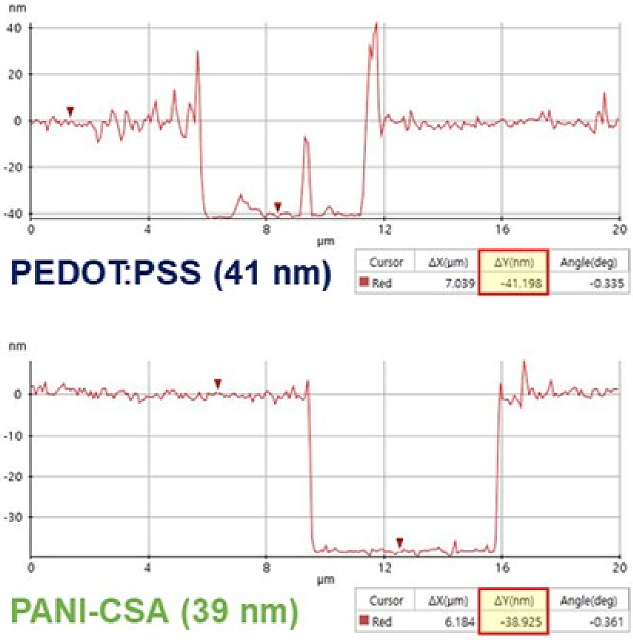

Figure S11. Line profiles of PEDOT:PSS and PANI-CSA films obtained from AFM system.

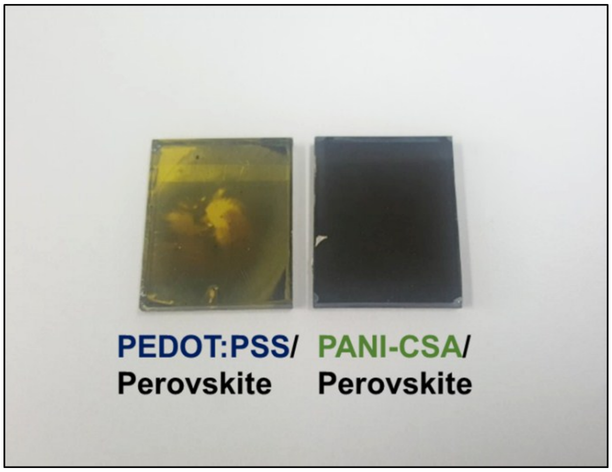

Figure S12. Digital photograph of perovskite films deposited on PEDOT:PSS and PANI-CSA which are stored for 7 days in in ambient air (temperature = 25 ˚C, relative humidity = 50%). Photograph was taken from the glass side of the sample (glass/FTO/PEDOT:PSS or PANI-CSA/perovskite).

Table S1. Photovoltaic parameters of PSCs using PANI-CSA HTL depending on concentration of PANI-CSA dispersion.

Concentration (mg mL^{-1})	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
0.3	0.98	21.63	0.63	13.41
0.5	0.97	21.55	0.71	14.80
1.0	0.92	21.30	0.69	13.66
2.0	0.84	21.19	0.66	11.69

Table S2. Photovoltaic parameters of PSCs using PANI-CSA HTL depending on protonation level of PANI.

Protonation level	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
1/2-doped	0.91	21.14	0.63	12.11
3/4-doped	0.95	21.94	0.67	14.06
Fully-doped	0.95	21.86	0.71	14.71

Table S3. Photovoltaic parameters of the PSCs with PEDOT:PSS and PANI-CSA HTLs as a function of storage time in ambient air (temperature = 25°C, relative humidity = 40 ± 5%).

HTL	Storage time (day)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
PEDOT:PSS	0	0.93	21.24	0.69	13.70
	10	0.58	18.41	0.41	4.43
PANI-CSA	0	0.96	21.41	0.73	15.09
	30	0.87	21.04	0.63	11.43

Table S4. Time-resolved photoluminescence (TrPL) decay parameters for glass/none or PEDOT:PSS or PANI-CSA/perovskite samples. The bi-exponential decay equation was used for fitting the curves.

Sample	τ_1 (ns)	τ_2 (ns)	[a]τ_{avg} (ns)	A_1	A_2
Glass/perovskite	5.1	90.6	89.7	0.12	0.55
Glass/PEDOT:PSS/perovskite	2.3	18.0	16.0	0.56	0.49
Glass/PANI-CSA/perovskite	1.7	10.1	8.9	0.52	0.54

[a] $\tau_{avg} = \Sigma_i A_i \tau_i^2 / \Sigma_i A_i \tau_i$

Table S5. Electrochemical impedance spectroscopy (EIS) parameters of PSCs with PEDOT:PSS and PANI-CSA obtained by fitting the Nyquist plots in **Figure 4d**.

HTL	R_S (Ω)	R_{CT} (Ω)
PEDOT:PSS	176	5.55×10^3
PANI-CSA	56	3.24×10^3