

Electronic Supplementary Information

**Improving the Efficiency and Stability of Inverted Perovskite Solar
Cells with Dopamine-Copolymerized PEDOT: PSS as Hole
Extraction Layer**

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32 **1 Materials**

33 3-Hydroxytyramine hydrochloride (DA), with a purity of 98%, from Energy Chemical
34 Co. Ltd. (Shanghai, China), was kept in temperature of 0 °C. Polystyrene sulfonic acid
35 (PSS, Mw=75000 Da, 30 wt.%) was brought from Alfa. 3, 4-ethylenedioxy thiophene
36 (EDOT), preserved with low temperature of 0 °C, was purchased from Bayer AG.
37 Ammonium persulphate ((NH₄)₂S₂O₈, APS) was obtained from Sigma and used as
38 oxidant in this experiment. The concentration of 1.0% by weight of PEDOT: PSS
39 (Baytron PVPAl 4083) was used for contrast. All other chemicals were of analytical
40 grade. The water used in laboratory was deionized water.

41 **2. Experiment sections**

42 **2.1 Preparation of DA-PEDOT: PSS**

43 The mixed solution containing PSS (20 g, with a mass fraction of 30%) and EDOT
44 monomer (1 g) was adjusted to pH=2. After stirring for 30min, oxidizing agent APS
45 (2.17 g) and DA monomer (0.2 g) were simultaneously added. Subsequently, the color
46 changed from light yellow to dark blue after 24h stirring at room temperature. Thus,
47 the rough product **DA-PEDOT: PSS** was obtained. The rough product was
48 dialyzed by a dialysis membrane (Special products laboratory, USA, MWCO of
49 1000 Da) to remove inorganic salt and the pure product (PEDOT+PDA): PSS
50 was available.

51 2.2 Characterization of Techniques

52 FTIR spectra were performed using the KBr pellets in the 4000-400 cm^{-1} region by
53 Auto system XL/I-series/Spectrum 2000 spectrometry (Thermo Nicolet Co., Madison,
54 WI, USA). Element contents of C, H and S were rationed by Vario EL cube
55 (Elementar, Germany) with about 5.0 mg packed in aluminized paper. UV-vis
56 absorption and transmittance spectra were measured by Shimadzu UV-3600
57 spectrophotometer (Japan) and ShimadzuUV-2600 spectrophotometer (Japan),
58 respectively. The films thicknesses were tested by a step profiler (Dektak150, Veeco,
59 USA). Dynamic light scattering (DLS) experiments were performed on a Zeta PALS
60 instrument (Brookhaver, America). Cyclic voltammetry (CV) test was conducted with
61 a film on glassy carbon electrode against Ag/AgCl (3M KCl solution) reference
62 electrode at scanning rate 100mV/s. The conductivity and sheet resistance of PEDOT:
63 PSS and **(PEDOT+PDA): PSS** films were measured with a KDY-1four point
64 probesresistivity/resistance measurement system. The films were prepared by
65 dropping the sample on glass and air drying at room temperature. UPS and XPS
66 measurements were conducted on a Thermo Scientific ESCALAB 250Xi with a He (I)
67 UV source (21.22 eV) in ultrahigh vacuum. For testing UPS and XPS, the samples
68 were spin-coated onto ITO glass and kept in an oven at 110 °C for 15 min before the
69 measurement, and all of the experimental processes were conducted in ultrahigh
70 vacuum environment. Atomic force microscopy (AFM) images were observed by a
71 Park XE-100in tapping mode. Surface wettability was measured using a static contact
72 angle instrument (Powereach JC2000 C1, Shanghai, China).

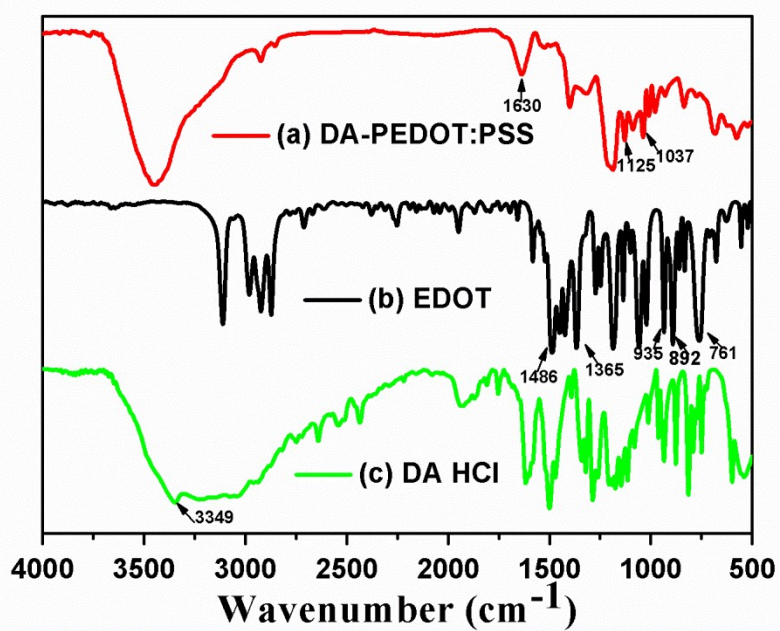
73 2.3 Fabrication and Characterization of PSCs

74 The configurations of PSCs were ITO/HTLs/ $\text{MAPbI}_{3-x}\text{Cl}_x$ /PC₆₁BM/BCP/Ag. ITO-
75 coated glass substrates were cleaned via a series of ultrasonication in detergent,
76 acetone, DI water, isopropyl alcohol and followed by UV-ozone plasma treatment.
77 **(PEDOT+PDA): PSS** layer was spin-coated onto the pre-patterned ITO glass

78 substrate and annealed using a hot plate at 140°C for 15 min to remove residual
79 solvents. PEDOT: PSS (Baytron PVPAl 4083) based device was also fabricated as
80 comparison with the same method. The substrates with (PEDOT+PDA): PSS or
81 PEDOT:PSS were then transferred into a glove box filled with highly pure N₂. Then
82 MAPbI_{3-x}Cl_x precursor solution (1.26 M PbI₂, 0.14M PbCl₂ and 1.35 M MAI in
83 cosolvent of DMSO: GBL at Vol ratio of 3:7) was spin-coated to form a perovskite
84 layer of about 280 nm on the modified ITO substrate. After annealing at 100°C for 20
85 min, the PCBM layer (~55 nm) was deposited by spin coating onto the surface of
86 perovskite layer. After that, 0.5 mg/mL BCP solution was spin coated onto
87 PCBM layer. The devices were completed by thermal deposition a layer of 100 nm
88 A gas cathode in a vacuum of <1×10⁻⁶ Torr. The devices area was 0.07cm² defined
89 by shadow mask.

90 The photovoltaic performance of the PSCs was tested in air with a computer-
91 programmed Keithley 2400 source/meter and a Newport's Oriel class solar simulator,
92 which simulated the AM1.5 sunlight with energy density of 100 mW/cm² and was
93 certified to the JIS C 8912 standard. IPCEs of PSCs were measured with a 300W
94 Xenon Lamp (Oriel 6258) and a Cornerstone 260 Oriel 74125 monochromator. The
95 photovoltaic stability of PSCs was investigated by storing the unencapsulated devices
96 in N₂inert atmosphere for 28 days. The UV-visible absorption spectra were
97 measured on a Perkin-Elmer Lambda 950 spectrophotometer.
98 Photoluminescence spectra were collected on an Edinburgh Instruments
99 FLS920 spectrofluorometer, the excitation wavelength was 630 nm. Scanning
100 electron microscopy (SEM) images were obtained on a JSM-7800F SEM. Thin
101 film X-ray diffraction (XRD) measurements were conducted on a Bruker D8
102 Advance XRD instrument.

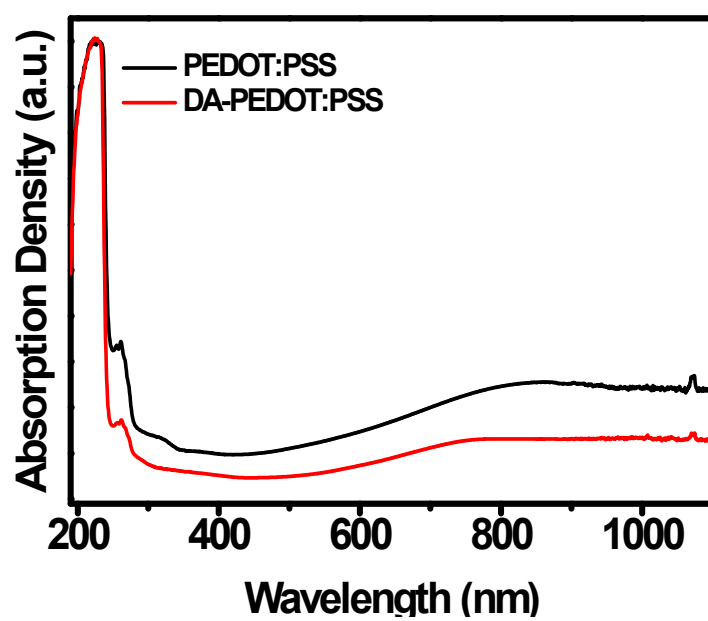
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105 **Figure S1.** The IR spectra of (a) PEDOT: PSS: PDA, (b) EDOT and (c) DA·HCl

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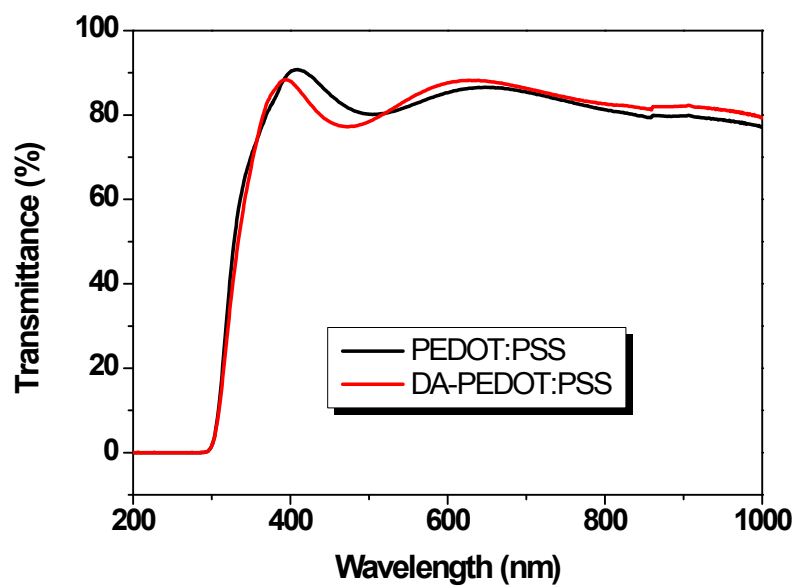
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Figure S2. UV-vis absorption spectra of PEDOT: PSS and DA-PEDOT: PSS aqueous solutions

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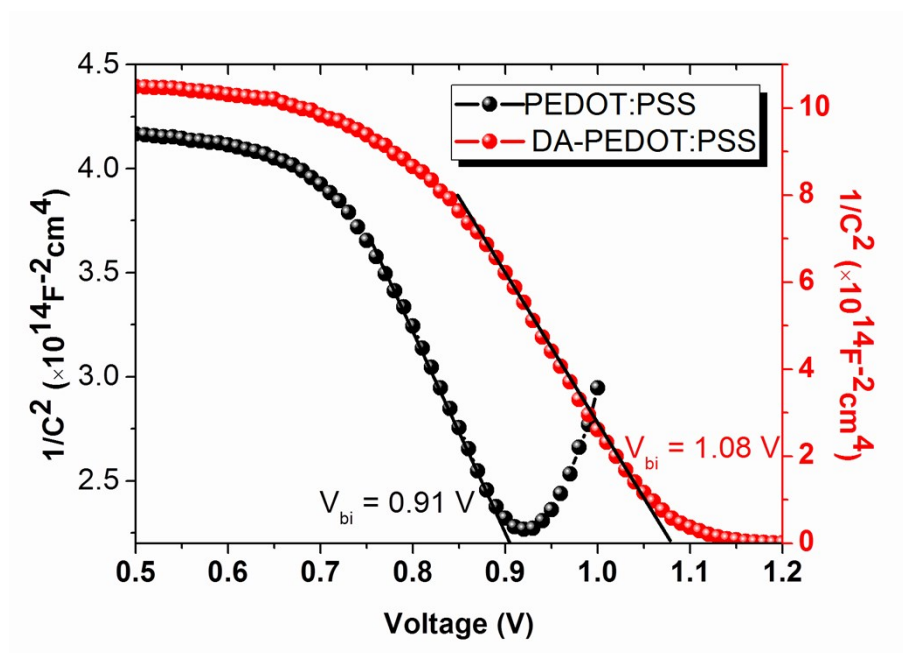
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113 **Figure S3.** Transmittance spectra of PEDOT: PSS and DA-PEDOT: PSS on ITO substrates.

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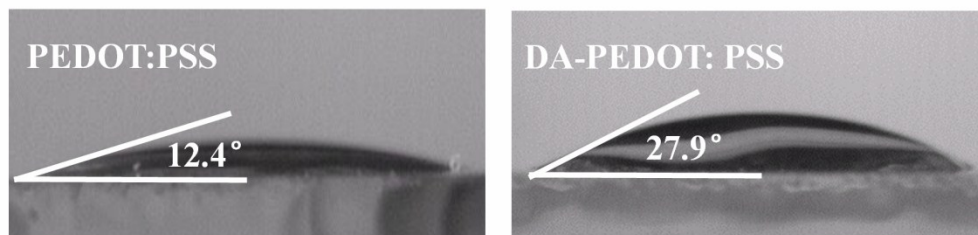


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Figure S4. $1/C^2$ -V curves of devices with PEDOT:PSS and DA-PEDOT:PSS as the HTLs.

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119 **Figure S5.** Contact angel of solutions of PEDOT:PSS and DA-PEDOT:PSS droplets on glass.
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Table S1. Photovoltaic parameters of PSCs by applying PEDOT: PSS and DA-PEDOT: PSS solutions with different concentration as HELs.

	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)
PEDOT:PSS	18.74 (20.63)	1.00 (0.97)	0.71 (0.98)	13.31 (15.21)
DA-PEDOT: PSS (1.2 wt%)	14.11	0.96	0.38	5.15
DA-PEDOT: PSS (0.6 wt%)	19.47	0.95	0.62	11.47
DA-PEDOT: PSS (0.3 wt%)	19.79 (20.10)	1.04 (1.09)	0.66 (0.70)	13.58 (14.77)
DA-PEDOT: PSS (0.15 wt%)	20.53 (20.10)	1.06 (1.05)	0.70 (0.76)	15.23 (16.65)

The performance in bracket were obtained from samples filtered with 0.22 um filter film before spin- coating.