Supporting information for

Surface Doping of Non-fullerene Photoactive Layer by Soluble Polyoxometalate for Printable Organic Solar Cells

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Experimental Section:

1.1 Materials

The polymer donor poly([2,6’-4,8-di(5-ethylhexylthienyl)benzo[1,2-b,3,3-b]dithiophene]3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl) (PTB7-Th) and the non-fullerene acceptor 2,2’-((2Z,2’Z)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b:5,6-b’]dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy) thiophene-5,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)) dimalononitrile (IEICO-4F) were purchased from Solarmer Materials Inc. The ingredient zinc acetate dihydrate, monoethanolamine and methoxyethanol for ZnO precursor solutions were purchased from Sigma-Aldrich. Chlorobenzene (99.5%), 1-chloronaphthalene (CN) and phosphomolybdic acid (PMA) was also from Sigma-Aldrich. The highly conducting polymer PH1000 (Clevios PH1000, Heraeus) was purchased from Xi’an Polymer Light Technology Corp. The acetone and isopropanol were obtained from Sinopharm Chemical Reagent Co., Ltd.

1.2 Films characterization

Optical characterization: The polymer donor PTB7-Th and IEICO-4F were first dissolved in chlorobenzene (99.5%) with a concentration of 10 mg/ml, respectively. The solution was stirred vigorously overnight for use. The films were fabricated by spin coating the prepared solution onto a quartz substrate at a speed of 2000 rpm/min for PTB7-Th and 1000 rpm/min for IEICO-4F solutions. Then the films were immersed into a Petri dish with PMA isopropanol solution (0.1 M) for different time and pure isopropanol solution was subsequently used to clean the film surface. Absorption and transmission spectra of the obtained films were performed by UV-vis-NIR spectrophotometer (UV-3600, Shimadzu Scientific Instruments).

UPS and XPS and characterization: The pristine PTB7-Th and PMA-im-PTB7-Th films as well as pure PMA samples were deposited onto a clean ITO substrate for measurements. The UPS measurements were carried out in a Thermo-VG Scientific ESCALAB 250 using an He I (21.22 eV) discharge lamp. A bias of -8.0 V was applied to the samples for separation of the sample and the secondary edge for the analyzer. XPS measurements were performed using a Thermo Scientific K-alpha instrument with an Al Kα source. All recorded peaks were corrected for electrostatic effects by setting the C-C component of the C 1s peak to 285 eV.

Morphology and film thickness: Atomic force morphology (AFM) of the PTB7-Th:IEICO-4F and PMA-im-PTB7-Th:IEICO-4F blend films were measured through tapping mode on Shimadzu SPM9700 in air. All the film thicknesses were recorded by a DEKTAK XT profilometer.

1.3 Solar cells fabrication and characterization

The pre-patterned ITO was sonicated in baths using detergent in deionized water, deionized water, acetone, and isopropanol in sequence. After a treatment of the ITO substrates with air plasma for 3 min, the sol-gel ZnO precursor solutions were spin-coated onto ITO at 4000 rpm for 40 s. Then the substrate was annealed at 200 ^{o}C for 30 min to form a dense metal oxide film. The sol-gel ZnO precursor solutions were prepared by adding 0.5 g zinc acetate dihydrate and 0.14 g monoethanolamine in 5 ml methoxyethanol, and stirring overnight. Subsequently, the non-fullerene active layer PTB7-Th:IEICO-4F (1:1.5 weight ratio) with a concentration of 20 mg/mL in a mixed chlorobenzene (CB) and 1-chloronaphthalene (CN) (96:4 volume ratio) solution was spin-coated at 2500 rpm for 60 s in the N_2-filled glovebox. After that, the substrates containing the active layer blend films were immersed into a Petri dish with PMA isopropanol solution (0.1 M) for different time. To remove any remaining PMA residue at the surface, the doped films were rinsed with pure isopropanol solution several times. The immersion processes are implemented in the atmosphere environment. The samples were then transferred into the vacuum evaporation system. 100 nm Ag was evaporated as the top anode with a metal aperture mask to complete the device fabrication. Device area is 4 mm^2. For the printable OSCs, the highly conducting polymer PH1000 electrode with a formulation (Clevios PH1000, 0.1 wt% surfactant PEG-TmDD and 5wt% ethylene glycol) were deposited on top of the active layer film through transfer-printing or doctor-blading technique. The fabricated devices were measured under a simulated 100 mW cm^{-2} AM 1.5G irradiation in a N_2-filled glovebox. The printable devices were tested through an aperture with an area of 4 mm^2 and an Ag-based total reflective mirror was also used to avoid the illumination loss. A Keithley 2400 was applied to measure the current-voltage characteristics. External quantum efficiency (EQE) test was performed using a 150 W xenon lamp fitted with a monochromator (Cornerstone 74004) as a monochromatic light source.

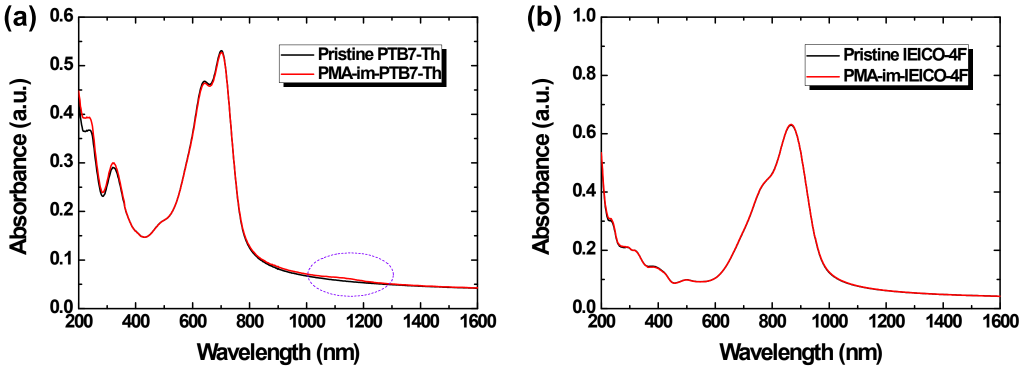

Fig S1. UV-vis-NIR absorption spectra of the donor or acceptor films immersed in 0.1M PMA isopropanol solution. **(a)** 30-nm-thick pristine PTB7-Th and PMA-im-PTB7-Th (after post-process immersion for 30 min in the PMA solution) films; **(b)** 60-nm-thick pristine IEICO-4F and PMA-im-IEICO-4F (after post-process immersion for 30 min in the PMA solution) films.

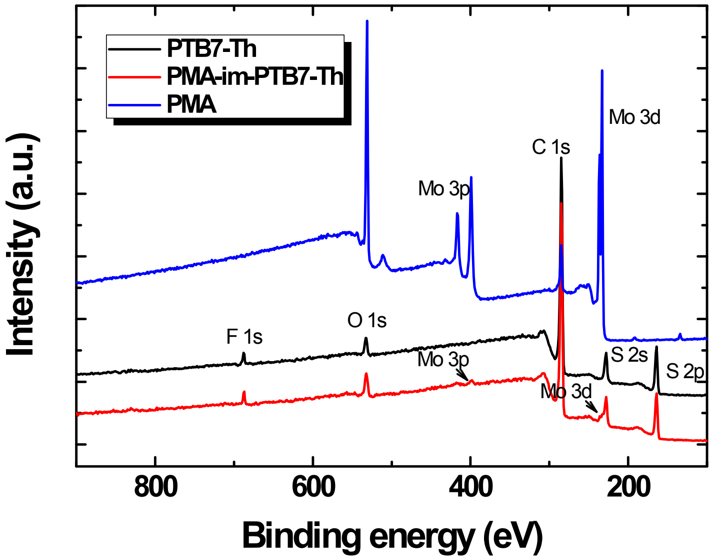

Fig S2. Survey XPS spectra near the surface of 30-nm-thick pristine PTB7-Th and PMA-im-PTB7-Th (after post-process immersion for 30 min in the PMA solution) films as well as pure PMA powder.

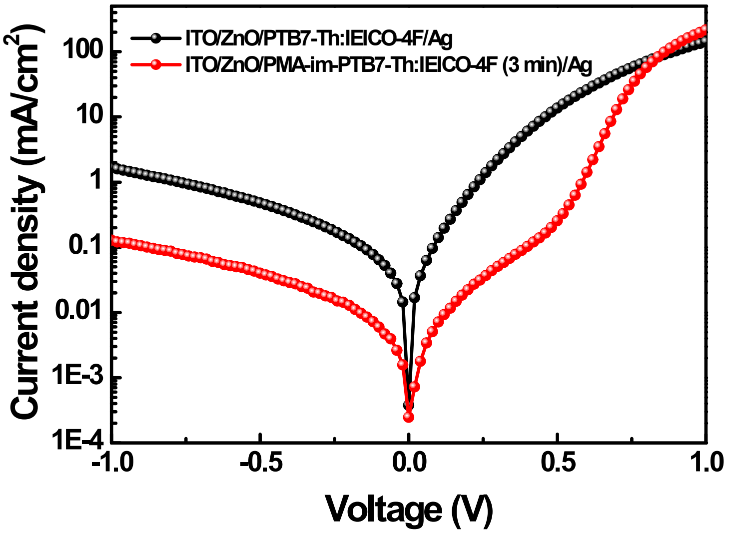

Fig S3. *J*-*V* characteristics in the dark of the reference device without PMA immersion process and the device with PMA immersion for 3 min.

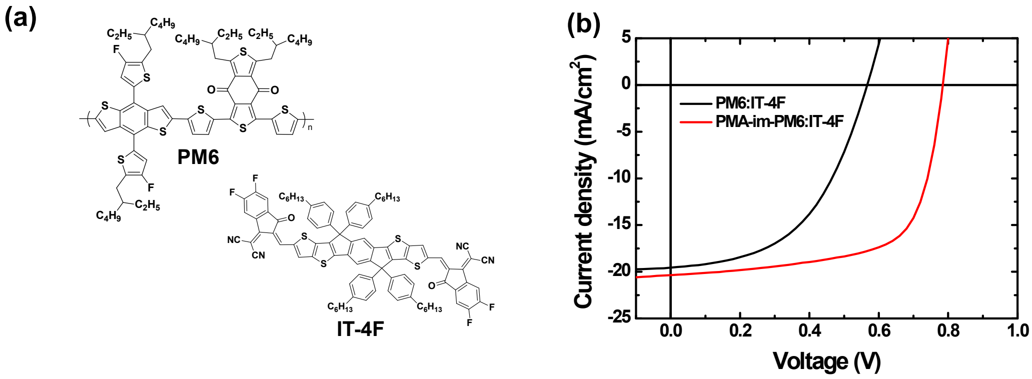

Fig S4. (a) Chemical structures of the PM6 donor and the IT-4F acceptor. (b) *J-V* characteristics of the inverted NF OSCs with a structure: ITO/ZnO/PM6:IT4F/Ag, where the photoactive layer was immersed in PMA solution for 5 min or without immersion process.

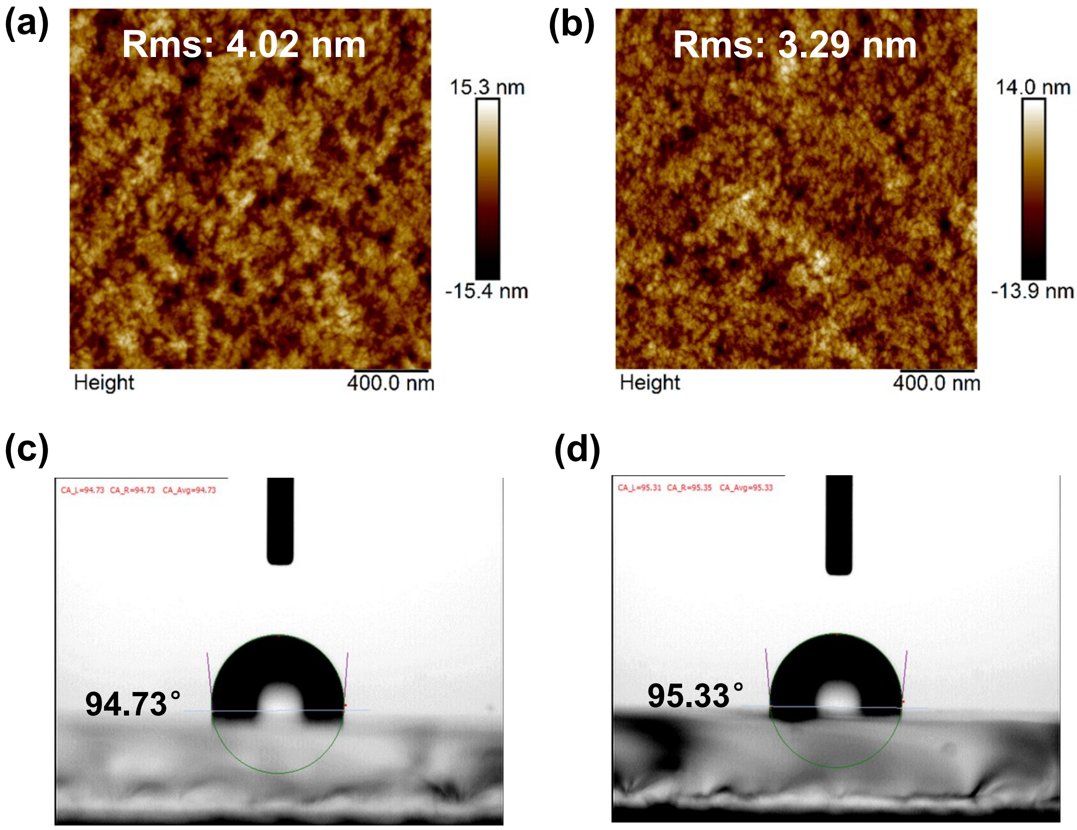

Fig S5. AFM morphology images and the contact angle measurements to deionized water of **(a), (c)** pristine PTB7-Th:IEICO-4F blend and **(b), (d)** PMA-im-PTB7-Th:IEICO-4F (after post-process immersion for 3 min in the PMA solution) films.

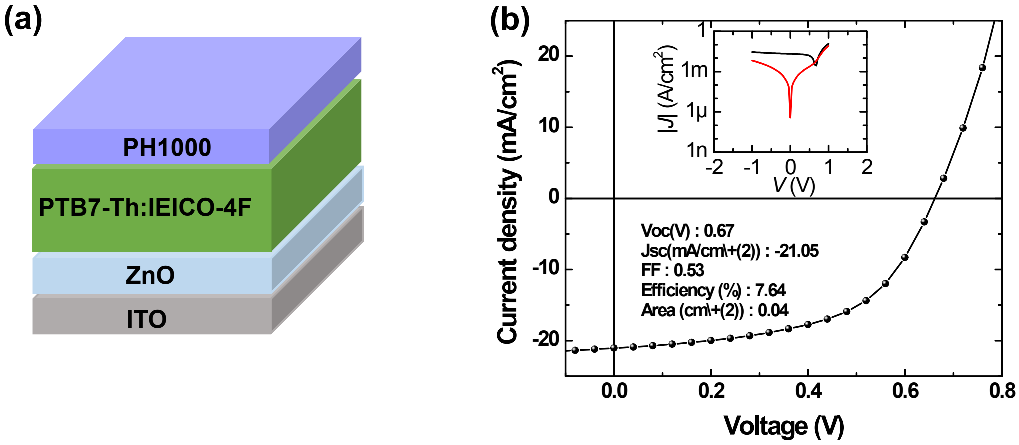

Fig S6. (a) Schematic structure and **(b)** *J*-*V* characteristics of the referenced printable NF OSCs with PH1000 as the top electrode. The cells were tested with an aperture as well as an Ag-based total reflective mirror.

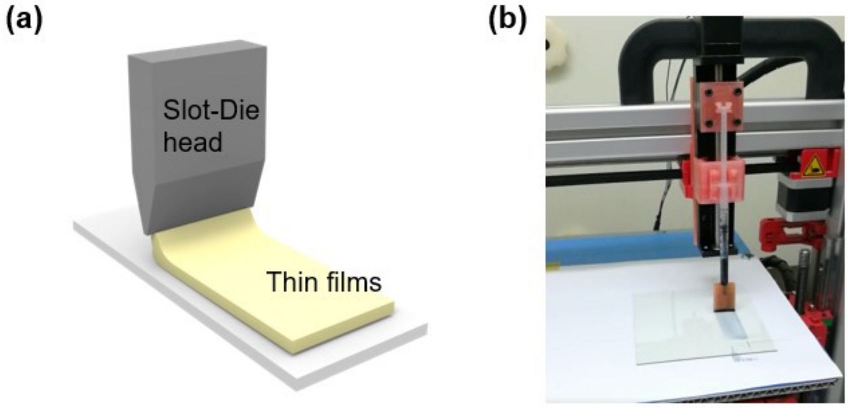

Fig S7. (a) Schematic illustration of the device using slot-die coating for the printable NF OSCs. **(b)** Photo of the computer-controlled slot-die coating setup.

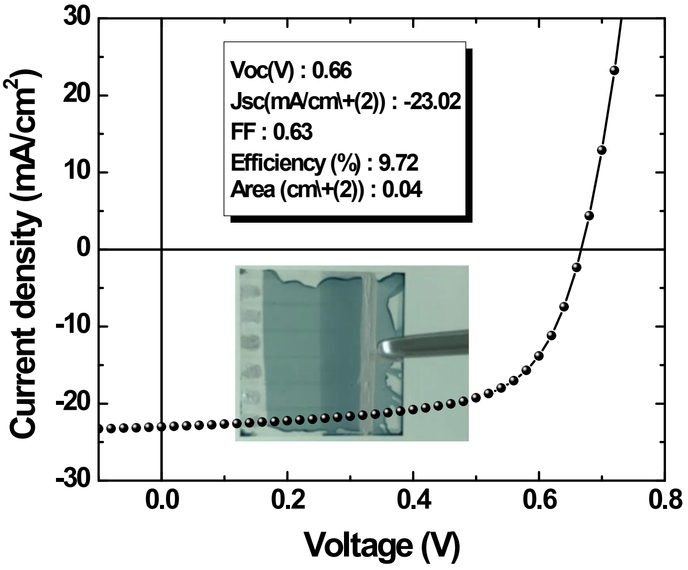

Fig S8. *J-V* characteristic and the corresponding physical display of the printable NF OSCs based PMA-im-PTB7-Th:IEICO-4F with an immersion time for 3 min via doctor-blading PH1000 as the top electrode. The cells were tested with an aperture as well as an Ag-based total reflective mirror.