Supplementary Information

Enhanced Performance of Perovskite Solar Cells via Anti-Solvent Nonfullerene Lewis Base IT-4F Induced Trap-Passivation

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Experimental section

Materials synthesis and perovskite film fabrication:

CH_3NH_3I (MAI, 99.999%), PbI_2 (99.999%), DMSO (99.999%) and DMF (99.8%) were purchased from Aladdin. [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was obtained from NANO-C. All the remaining chemical medicine and reagents were purchased from Sigma-Aldrich. The standard precursor solution was prepared in a glovebox by dissolving the MAI (190.8 mg) and PbI_2 (553.2 mg) in DMF/DMSO (0.8 mL: 0.2 mL). The precursor solution was stirred at 60℃ and aged for 12 h before spin coating. The FTO substrates were ultrasonically cleaned with deionized water, ethanol, and acetone successively. The as-cleaned substrates were heated in an oven at 60℃ for 1 h followed by the UV–ozone treatment for 15 min. The Li-NiO_x hole transport layer was deposited on the FTO substrate at 450℃ by a spray pyrolysis method. Then, the perovskite precursor solution was spin coated onto the FTO/NiO_x substrates at 4000 rpm for 30 s, followed by annealing at 100℃ for 10 min to promote the crystal growth and eliminate the by-product. Notably, the antisolvent was added at 24 s during the spin-coating process. The electron transfer layer was spin-coated using chlorobenzene solution containing PCBM (20 mg mL^{-1}) at 2000 rpm for 30 s and then the substrate was baked at 80℃for 10 min. Finally, BCP thin layer (0.5 mg in 1 mL alcohol) was deposited on the top of PCBM layer and an Ag counter electrode was formed by thermal evaporation. The active area was 0.09 cm^2.

Perovskite film characterization and device characterization:

A cold field emission scanning electron microscope (JSM 6700F, Japan) was used to characterize the morphology of the MAPbI3 film. The process of crystal growth and transformation was analyzed by an X-ray diffractometer (D8 Advance, Bruker AXS, Germany) with a monochromatic Cu Ka radiation source (l=1.54056 A) and an ultraviolet-visible (UV-vis) spectrophotometer (CARY5000, Varian, Australia). The chemical composition and kinetic energy spectra of the Li-NiOx films were characterized by an ultraviolet photoelectron spectroscopy (**UPS**) system (Thermo Scientific, Escalate 250Xi). The space charge limited current (**SCLC**) was obtained by a 2400 Source Meter in a dark environment, under bias from 0.008 V to 2 V. The electrochemical impedance spectroscopy (**EIS**) of the devices was performed using an electrochemical workstation (CHI 660D, Shanghai Chenhua Instruments, China). The **J–V curves** and **stabilized Jsc** were recorded using an electrochemical workstation (CHI 660D, Shanghai Chenhua Instruments, China) under 3A grade AM 1.5G simulated sunlight (100 mW cm^{-2}) (ABET Sun 2000 Solar Simulator). The incident light intensity was calibrated with an NREL-calibrated Si solar cell (Newport, Stratford Inc., 91 150 V). The scan rate was 50 mV s^{-1} and delay time was 2 s. The reverse scan was from 1.2 V to -0.2 V, while the forward scan was from -0.2 V to 1.2 V. The incident photon conversion efficiency (**IPCE**) was measured by the direct current (DC) mode using a custom QE/IPCE measurement system (Enli Technology Co. Ltd. China). These characterizations of the PSCs without encapsulation were carried out under ambient air conditions.

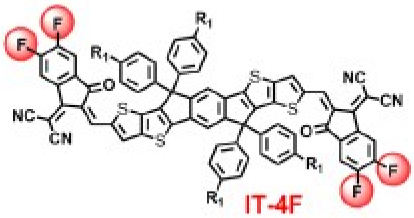

Figure S1. Molecular structure of the IT-4F.

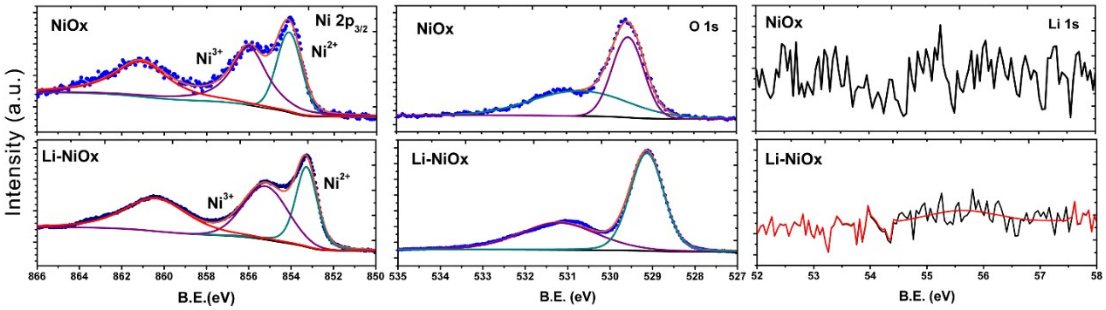

Figure S2. High resolution XPS profiles for the Ni, O and Li elements in the NiO$_x$ and Li:NiO$_x$ films, respectively.

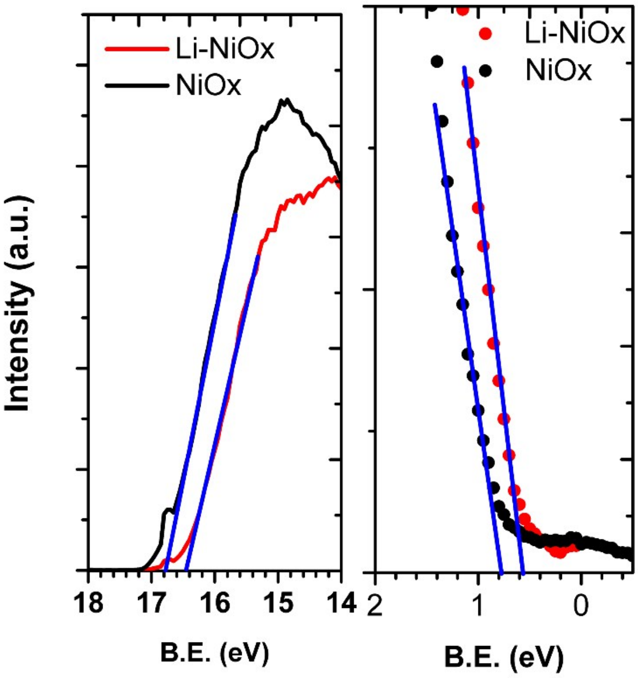

Figure S3. The UPS spectra of the NiO$_x$ and Li:NiO$_x$ film coated on silicon wafer.

The obtained Li content for the films prepared with 310μl Li-TFsi precursor is ≈1.33% indicating that Li is readily incorporated into NiO_x. The peak centered at 861.0 eV corresponds to a shake-up process in the cubic rocksalt structured NiO. The main peak centered at 854.2 eV is ascribed to the standard Ni-O octahedral bonding configuration. The peaks centered around 855–856 eV are ascribed to Ni^{2+} vacancy-induced Ni^{3+} state. These Ni^{2+} vacancies induce positive charge compensation, and result in the p-type conductivity property of NiO_x. Typically, the peak centered at 855.5 eV corresponds to Ni_2O_3 species. Similarly, the peak at 529.5 eV is indicative of Ni-O octahedral bonding in NiO. The peak at 531.1 eV is ascribed to the Ni_2O_3 species or hydroxyl groups absorbed on the surface. Considering the insulating nature of stoichiometric NiO, the nonstoichiometric composition, determined from the XPS studies, endows prepared Li-NiO_x hole transport ability.

Obtained work function (φ) values by UPS measurements demonstrate that φ increased from 4.4 eV for undoped films to 4.8 eV for Li:NiO_x films. Meanwhile, compared to un-doped NiO_x films, Li-doping shift up the valence band, which provided better band alignment and conductivity, facilitating improved hole extraction.

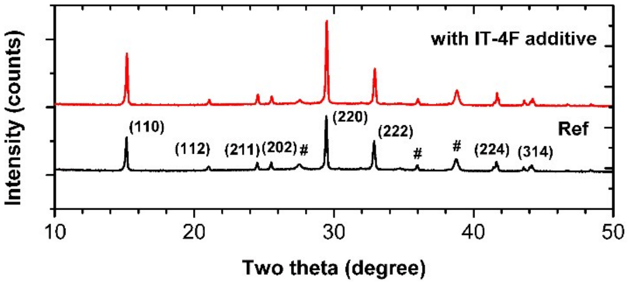

Figure S4. X-ray diffraction patterns of urea (powder) and perovskite film without and with IT-4F additive. Peaks indexed # originate from FTO.

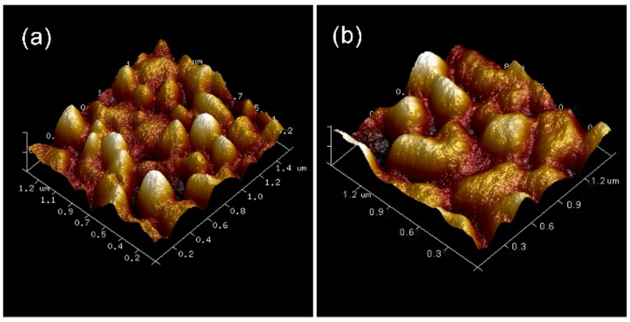

Figure S5. Atomic force microscopy (AFM) images of (a) bare $MAPbI_3$ and (b) $MAPbI_3$ with IT-4F additive on Li-NiO_x coated FTO substrates.

Table S1. Fitting parameters of bi-exponential decay function in time-resolved PL spectra.

Films	A_1	τ_1 (ns)	A_2	τ_2 (ns)	Average decay time τ (ns)[a]
Perovskite	258.2	134.7	319.0	50.1	87.9
Perovskite (IT-4F)	291.1	504.5	267.5	88.9	305.4

[a] Average decay time is calculated according to the equation: $\tau = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.

Table S2. Fitting parameters of bi-exponential decay function in transient photovoltage measurement.

Films	A_1	τ_1 (ms)	A_2	τ_2 (ms)	Average decay time τ (ms)[a]
Perovskite	0.245	0.054	0.422	0.007	0.024
Perovskite (IT-4F)	0.268	0.061	0.625	0.015	0.029

[a] Average decay time is calculated according to the equation: $\tau = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.

Table S3. Fitting parameters of bi-exponential decay function in transient photocurrent measurement.

Films	A_1	τ_1 (μs)	A_2	τ_2 (μs)	Average decay time τ (μs)[a]
Perovskite	0.081	0.310	0.081	0.310	0.310
Perovskite (IT-4F)	0.093	0.317	0.093	0.317	0.317

[a] Average decay time is calculated according to the equation: $\tau = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.

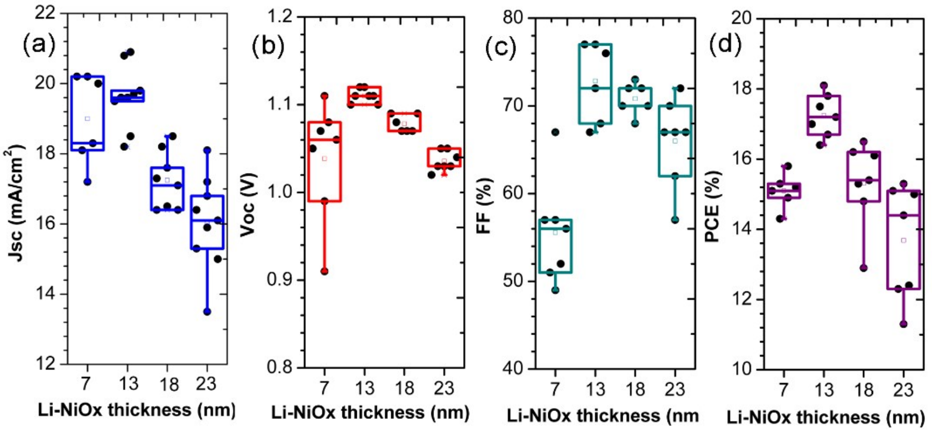

Figure S6. Photovoltaic performance of $MAPbI_3$ PSCs with various thickness of Li-NiO$_x$ as HTMs. (a) J_{SC}, (b) V_{OC}, (c) FF, and (d) PCE measured under reverse voltage scans.

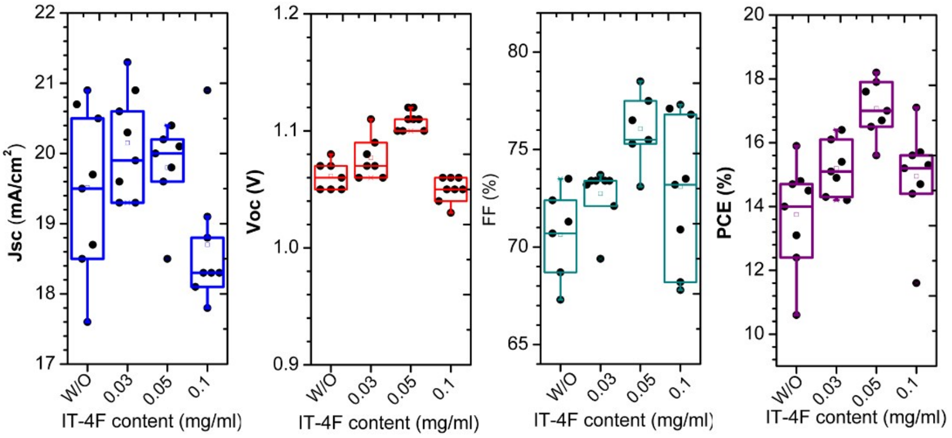

Figure S7. Photovoltaic performance of $MAPbI_3$ PSCs with various concentrations of IT-4F additives in the anti-solvent. (a) J_{SC}, (b) V_{OC}, (c) FF, and (d) PCE measured under reverse voltage scans.

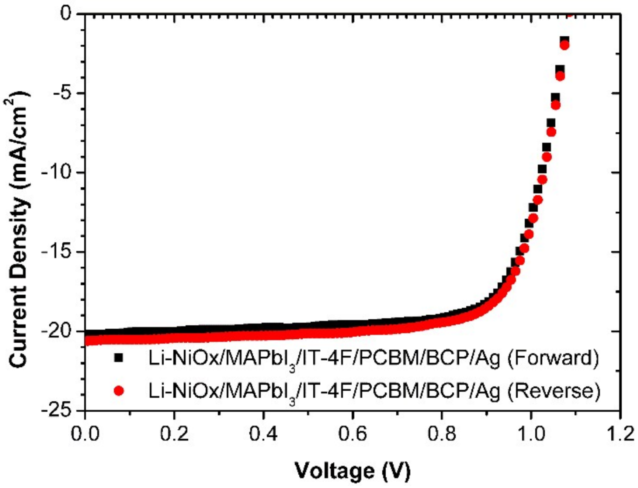

Figure S8. Parameter of devices based on polymer IT-4F as ultrathin interlayer between Perovskite and PCBM.

Table S4. Parameter of devices based on polymer IT-4F as ultrathin interlayer between Perovskite and PCBM.

Devices		J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
IT-4F interlayer	RS	20.16	1.08	75.32	16.40
	FS	20.60	1.08	74.88	16.66

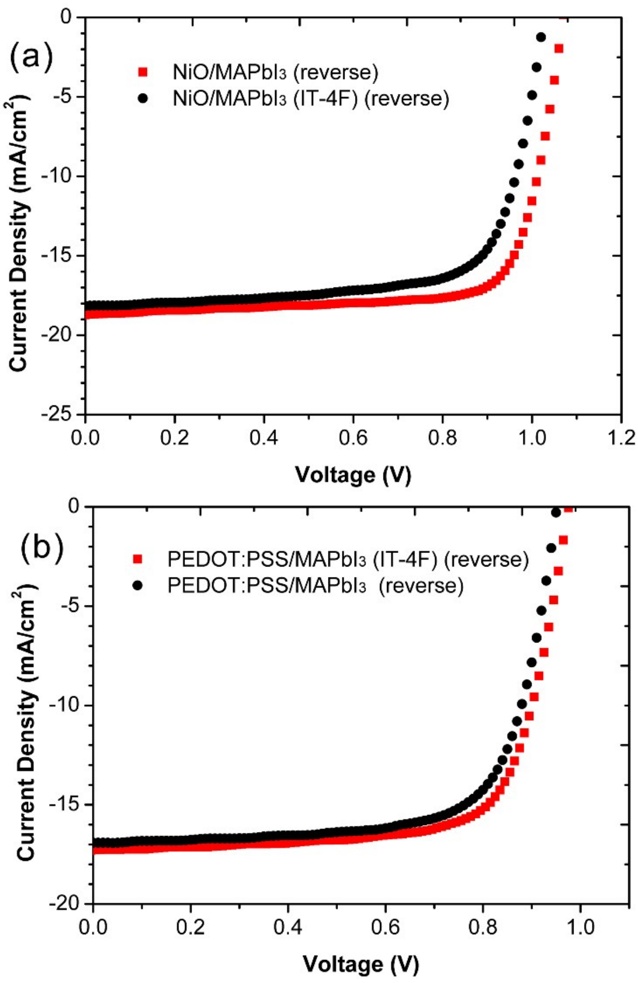

Figure S9. J-V curves of undoped NiO$_x$ and PEDOT:PSS based cells.

Table S4. Parameter of undoped NiO$_x$ and PEDOT:PSS based cells.

HTMs		J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
NiO	FS	18.16	1.025	72.23	13.45
NiO (IT-4F)	RS	18.72	1.065	76.58	15.26
PEDOT:PSS	FS	16.90	0.955	70.91	11.45
PEDOT:PSS (IT-4F)	RS	17.29	0.980	71.79	12.16