Supporting Information

Dopant-Free Tetrakis-Triphenylamine Hole Transporting Material for Efficient Tin-Based Perovskite Solar Cells

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Synthesis of compound 2

Under anhydrous conditions, $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol) was added to a solution of dibromobenzophenone (1.0 g, 2.94 mmol) and stannylated triphenylamine (4.0 g, 6.76 mmol) in dry toluene. The resulting mixture was refluxed overnight under nitrogen. After removal of the solvent, the desired product was purified by column chromatography (DCM/Hexanes). The title compound was obtained as a pale yellow solid (1.2 g, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.5 Hz, 4 H), 7.66 (d, *J* = 8.0 Hz, 4 H), 7.48 (d, *J* = 9.0 Hz, 4 H), 7.11 (d, *J* = 9.0 Hz, 8 H), 6.99 (d, *J* = 9.0 Hz, 4 H), 6.86 (d, *J* = 9.0 Hz, 8 H), 3.81 (s, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.96, 156.31, 149.14, 144.84, 140.67, 135.78, 131.38, 130.85, 127.85, 127.05, 126.11, 120.31, 114.94, 55.63. HRMS (*m/z*, FAB+) calcd for $C_{53}H_{44}N_2O_5$: 788.3250, found 788.3245.

Materials, Films, and Devices Characterization

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance III 600 MHz system with BBI probe. XRD patterns of the perovskite film were characterized by a Rigaku Miniflex600 pXRD (Cu Kα graphite, λ = 1.5406 Å) operating at 40 kV/15 mA with a Kβ foil filter. UV-vis absorption spectrum of the perovskite film was recorded on a Shimadzu UV-3600 UV-vis NIR spectrometer operating in the 200- 2000 nm region at room temperature. The morphology of the films was measured by a high-resolution field emission SEM (Hitachi SU8030). EQE plots were characterized by an Oriel model QE-PV-SI instrument equipped with a National Institute of Standards and Technology-certified Si diode. *J-V* plots were measured by a Keithley model 2400 instrument under AM1.5G simulated irradiation with a standard solar simulator (Abet Technologies). The light intensity of the solar simulator was calibrated by a National Renewable Energy Laboratory-certified monocrystalline silicon solar cell. TGA and DSC measurements were performed on a Netzsch's Simultaneous Thermal Analysis system with a scan rate of 10 °C/min in helium atmosphere. UV-vis absorption of TPE was done in the indicated solvents at room temperature with JASCO V-530 spectrometer. Differential pulse voltammetry (DPV) experiments were performed with a conventional three-electrode configuration (a platinum disk working electrode, an auxiliary platinum wire electrode, and a non- aqueous Ag reference electrode, with a supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in the specified dry solvent) using a CHI621C Electrochemical Analyzer (CH Instruments). All electrochemical potentials were referenced to an Fc^+/Fc internal standard (at 0.6 V).

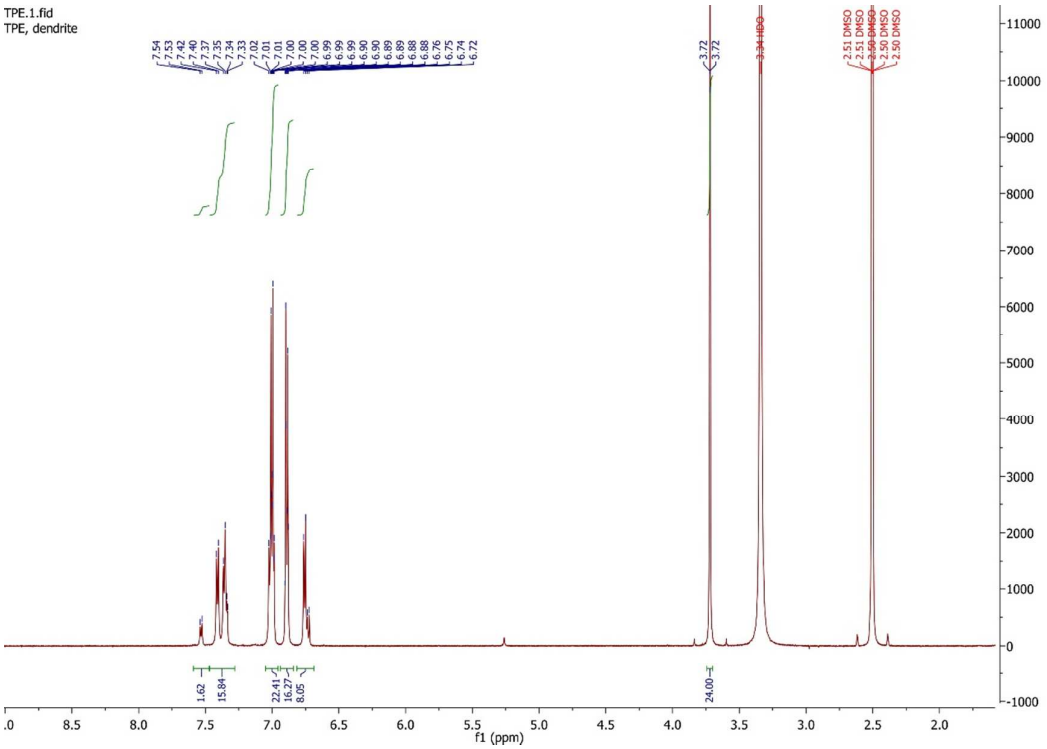

Figure S1. ^{1}H NMR spectrum of TPE (1) in DMSO-d_6.

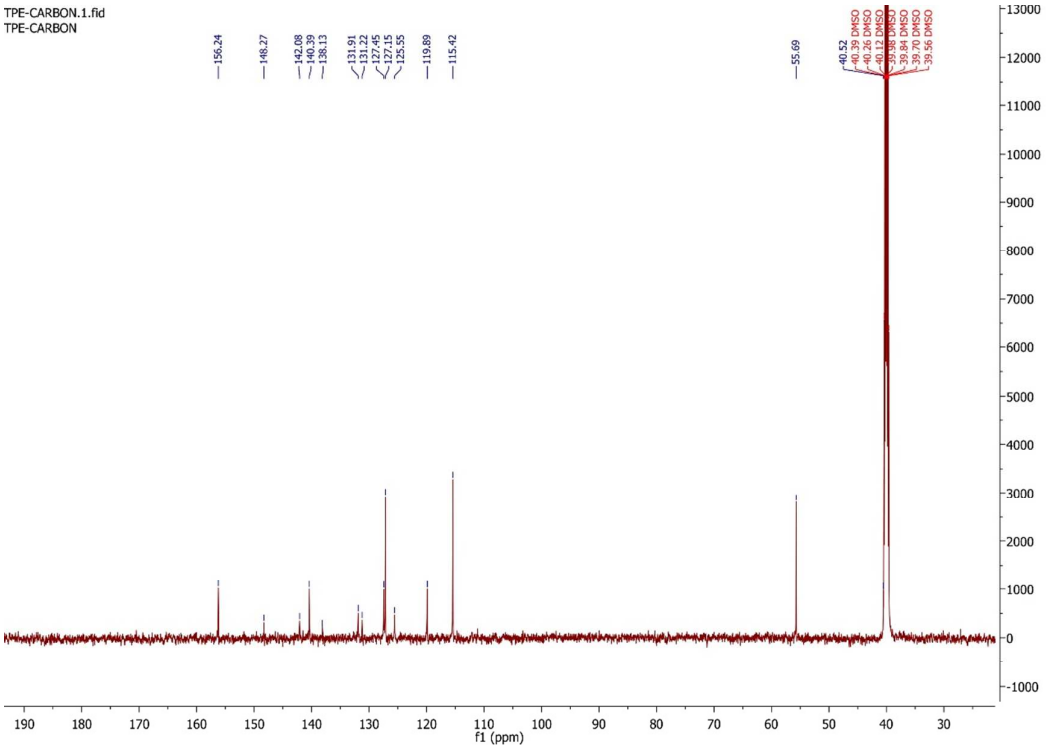

Figure S2. ^{13}C NMR spectrum of TPE (1) in DMSO-d_6.

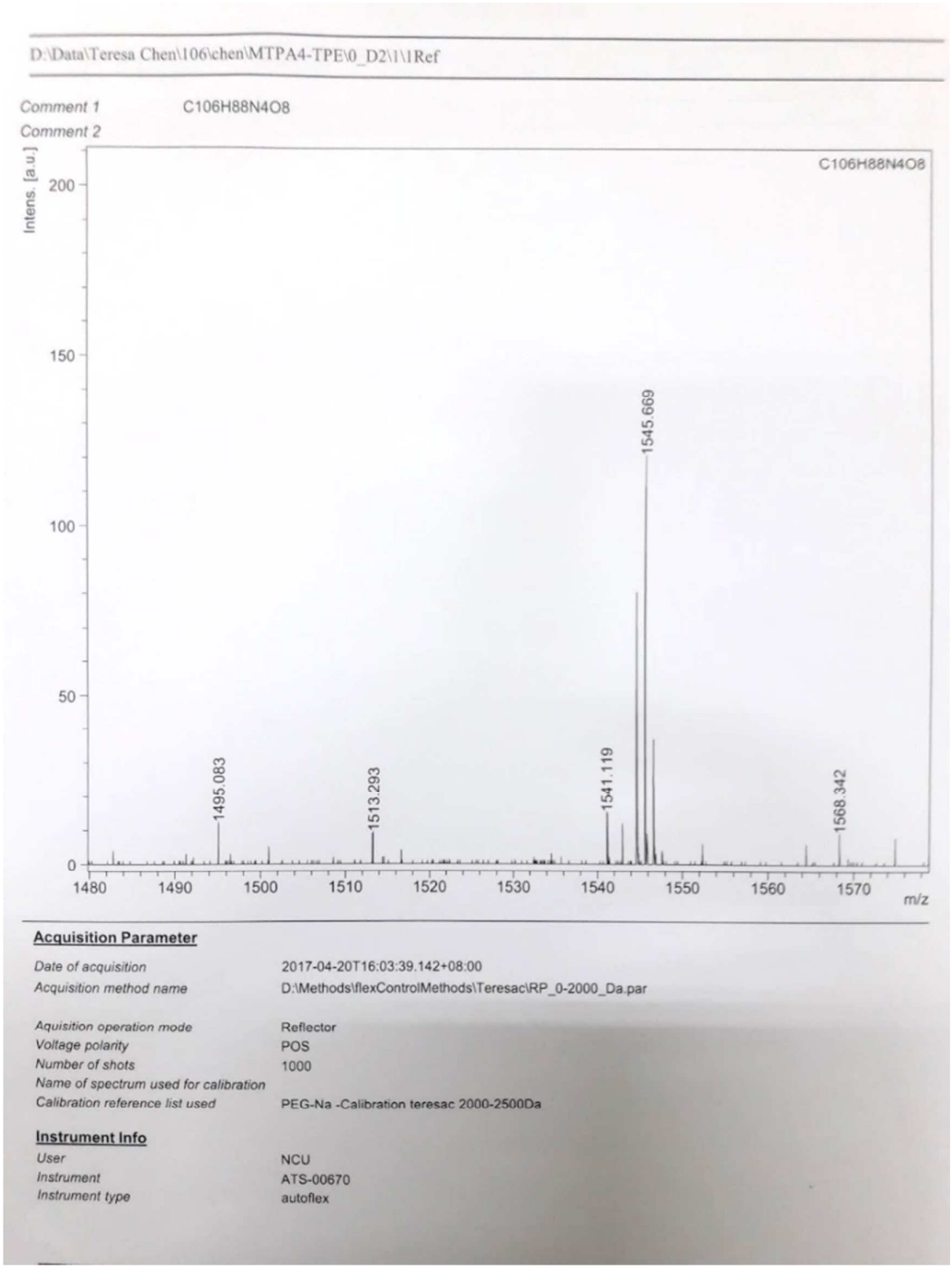

Figure S3. HRMS spectrum of TPE (**1**).

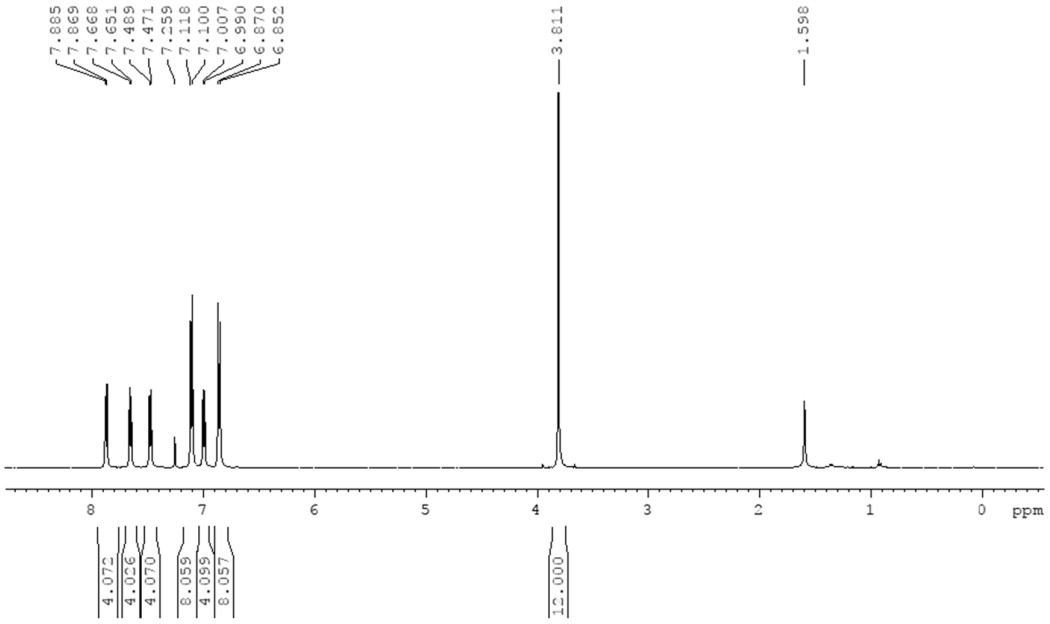

Figure S4. ^{1}H NMR spectrum of compound **2**.

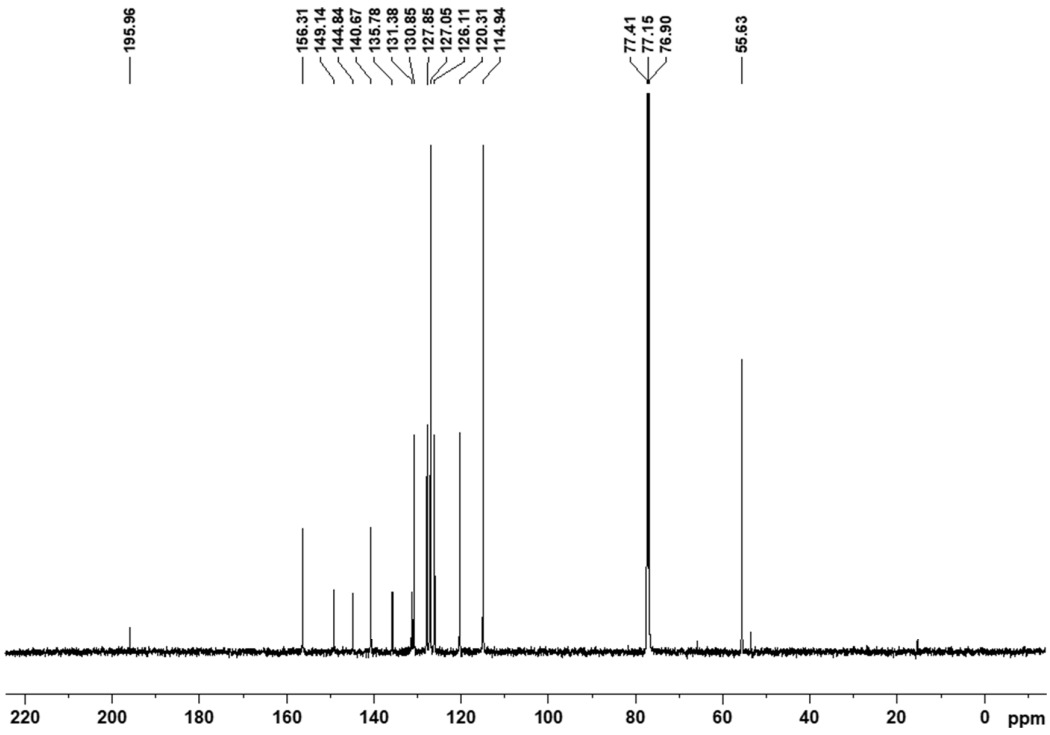

Figure S5. ^{13}C NMR spectrum of compound **2**.

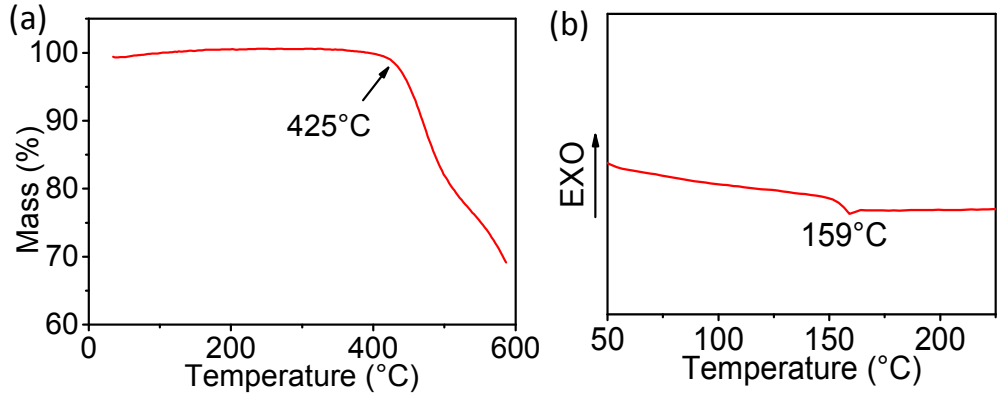

Figure S6. (a) TGA, and (c) DSC plots of TPE.

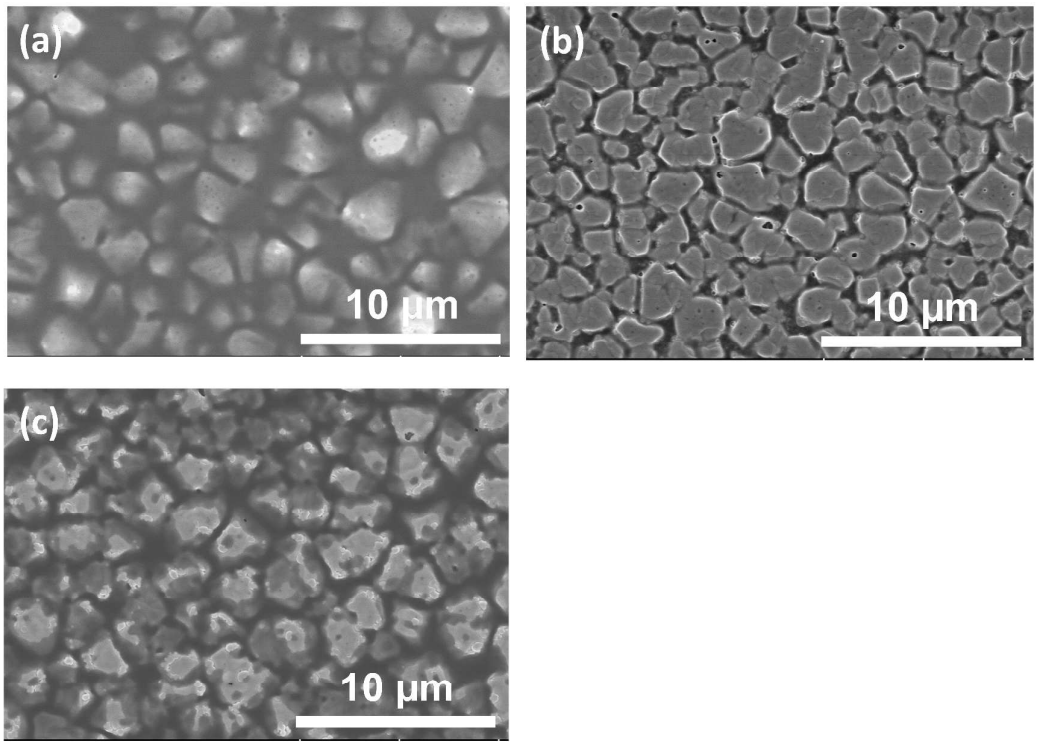

Figure S7. Top view SEM images of the perovskite films coated with (a) spiro-OMeTAD, (b) PTAA, (c) and TPE films.

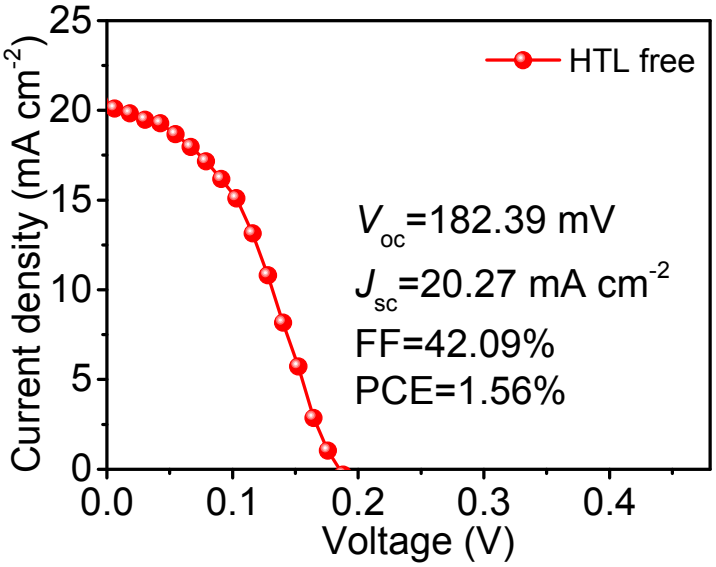

Figure S8. *J-V* plot of an {en}$FASnI_3$ solar cell without HTL measured under reverse voltage scan.

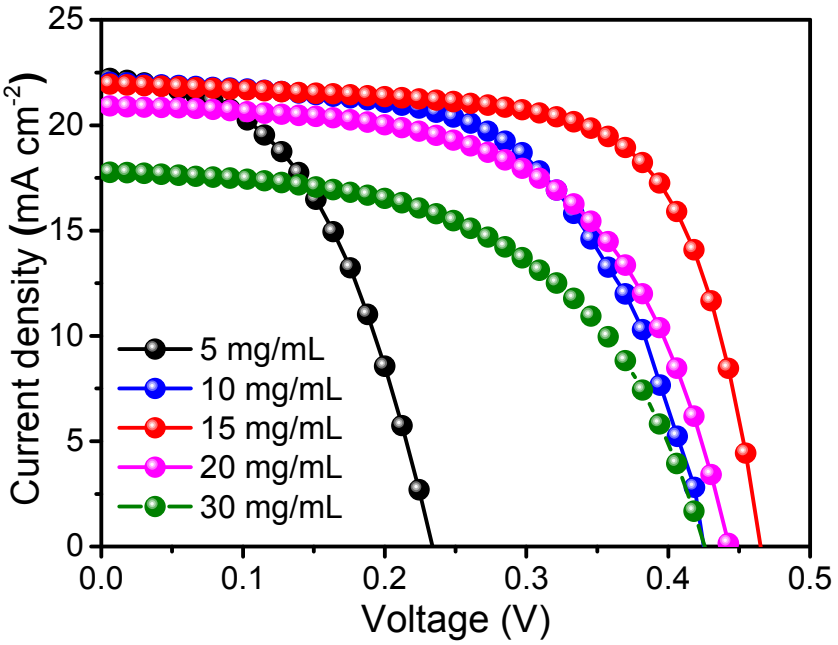

Figure S9. *J-V* plots of the {en}$FASnI_3$ solar cells using various concentrations of TPE HTLs in a mixed solvent of CF and CB (1:1 in volume ratio) measured under reverse voltage scan.

Table S1. Summary of the photovoltaic parameters of the {en}$FASnI_3$ solar cells using various concentrations of TPE HTLs.

	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
5 mg/mL	233.60	22.25	48.05	2.50
10 mg/mL	424.81	22.04	59.29	5.55
15 mg/mL	465.47	21.96	68.52	7.00
20 mg/mL	442.94	20.92	58.70	5.44
30 mg/mL	425.42	17.77	53.87	4.07

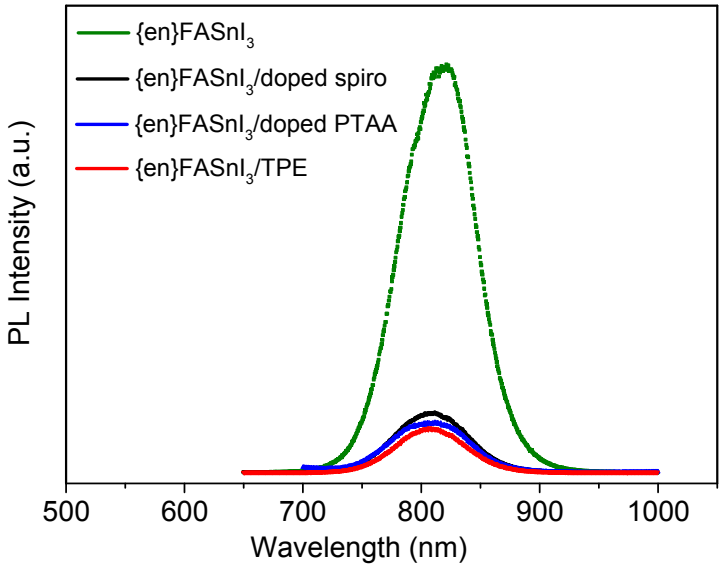

Figure S10. PL spectra of the perovskite films coated with and without various HTLs.

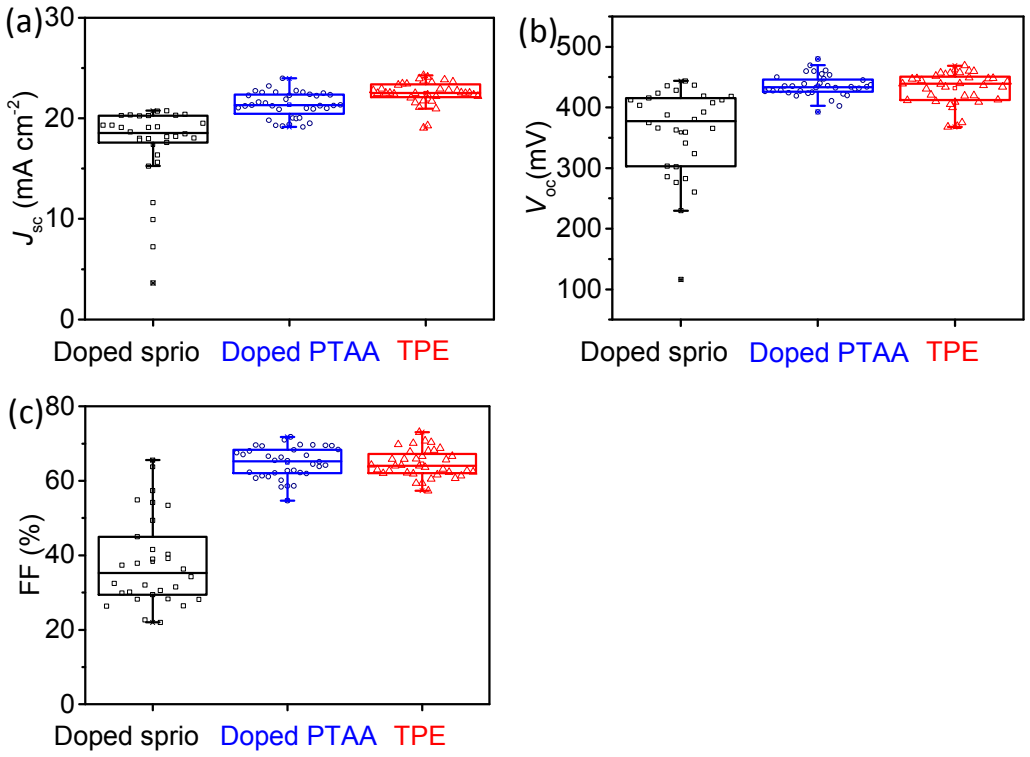

Figure S11. Statistics of (a) the J_{sc}, (b) V_{oc}, and (c) FF for the {en}$FASnI_3$ solar cells using various HTLs.

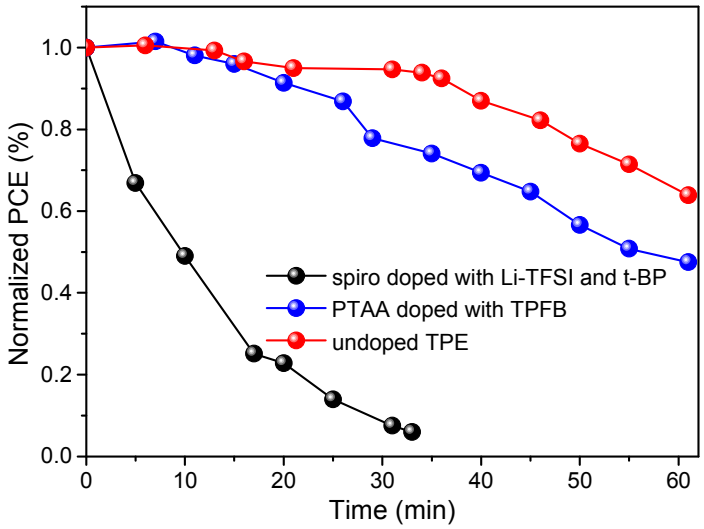

Figure S12. Aging test on the unencapsulated solar cells using various HTLs in ambient air with a moisture of 15% and a temperature of 20 °C.

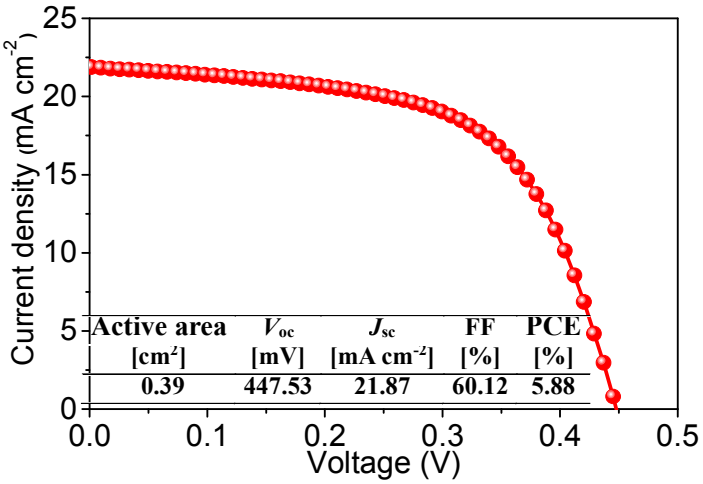

Figure S13. *J-V* plot of a {en}$FASnI_3$ solar cell with an active area of 0.39 cm^2 using a TPE HTL measured under reverse voltage scan.