Supporting Information

Non-conjugated electrolytes as thickness-insensitive interfacial layers for high-performance organic solar cells

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S1 Experimental Section

1. Materials

PTB7-Th (**1-Materials Inc.), $PC_{71}BM$ (Solarmer Materials Inc), PM6 (Solarmer Materials Inc) and Y6 (Derthon Optoelectronic Materials Science & Technology Co., Ltd.) were used as received. PMDETA and 1,8-diiodooctane were purchased from Sigma Aldrich LLC.** 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA) and 2,2'-diaminodiethylamine (DETA) were purchased form Tokyo Chemical Industry Co., Ltd.

2. Synthesis of PEDETA

1,2-Epoxyethane (200 mmol) was added to 50 mL methanol under 0 ℃, then 2,2'-diaminodiethylamine (10 mmol) was added dropwise. The mixture was stirred for 4h, then the residual 1,2-epoxyethane was removed by distillation under reduced pressure and ice bath conditions. Finally, methanol was also removed by rotary evaporation, and a yellow viscous liquid was obtained, which was used without further purification. ^1H NMR (400 MHz, D_2O) δ 3.63(t, 10H), 2.66 (t, 18H).

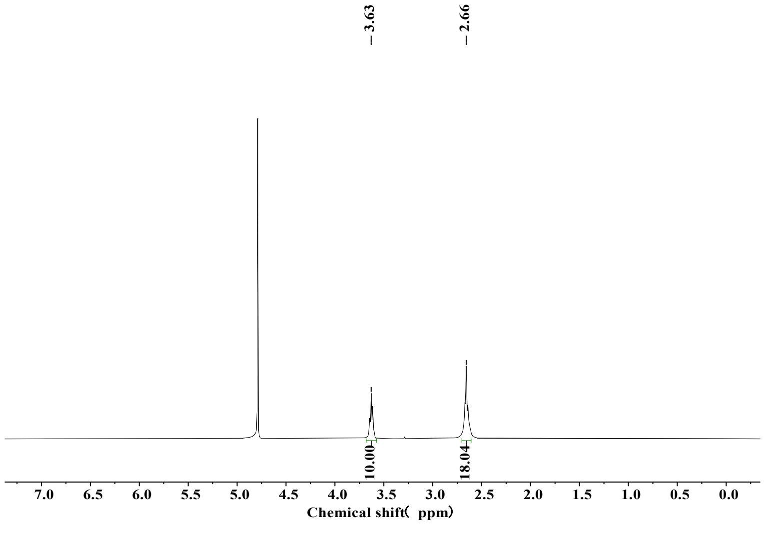

Fig. S1 ^1H NMR spectrum of PEDETA

3. Preparation of PMDETA-DBO and PEDETA-DBO

PMDETA and 1,8-dibromooctane (DBO) with the molar ratio (PMDETA: DBO=1:1.5) were added to 2-methoxyethanol, then the solution was stirred at 70 °C for 24 h to obtain the PMDETA-DBO solution. PEDETA-DBO solution was prepared with the same reaction conditions with PEDETA and DBO. The ETL layers were prepared by spin-coating the corresponding solutions on ITO with a speed of 5000 rpm for 60 s and subsequently annealing at 70 °C for 20 minutes, and the thickness of ETLs is controlled by the concentration of PMDETA or PEDETA (0.12 for 10 nm, 0.6 wt% for 30 nm, 1.0 wt% for 50 nm).

4. Fabrication of PSCs

The inverted PSC device configuration is ITO/ETLs/ photoactive layer/MoO_3/Al. The indium tin oxide (ITO) glass was cleaned by sequential ultrasonication in acetone, detergent, deionized water, acetone and isopropyl alcohol and then dried with a flowing nitrogen stream. ETLs were prepared by spin coating at a speed of 5000 rpm for 60 s and subsequently annealing at 70 °C for 20 minutes. The PTB7-Th: $PC_{71}BM$ photoactive layer was deposited by spin-coating from a blended solution of PTB7-Th (10 mg) and $PC_{71}BM$ (15 mg) in chlorobenzene (1 mL) with 1,8-diiodooctane (DIO, 1.5 vol%) and *N*-methylpyrrolidone (NMP, 1.5 vol%) under 1300 rpm for 60 s. The PTB7-Th: $PC_{71}BM$ photoactive layer was not annealed, and its thickness is about 100 nm. The PBDB-T-SF: IT-4F photoactive layer was deposited by spin-coating from a blended solution of PBDB-T-SF (10 mg) and IT-4F (10 mg) in chlorobenzene (1 mL) with 0.5 vol% of 1,8-diiodooctane (DIO) under 2300 rpm for 60 s, and it was annealed at 100 °C for 10 min. The PM6: Y6 photoactive layer was deposited by spin-coating from a blended solution of PM6 (6 mg) and Y6 (7.2 mg) in chloroform (1 mL) with 0.5 vol% of 1-chloronaphthalene (CN) under 1800 rpm for 40 s, and it was annealed at 110 °C for 10 min. Finally, the MoO_3 (5nm) and Al (100 nm) layers were thermally evaporated through a shadow mask onto the active layer under 2.0×10^{-4} Pa.

5. Fabrication of electron-only devices

Electron-only devices with structure of ITO/Al/ETLs (10nm)/PTB7-Th: $PC_{71}BM$ /Al were fabricated to characterize the electron mobilities using a space charge limited current (SCLC) method. The mobilities were determined by fitting the dark current to the model at low voltage, which is described as $J=(9/8)\varepsilon_0\varepsilon_r\mu((V^2)/(L^3))$, where J is the current, μ is the electron mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, L is the thickness of the ETLs layers and blend films, and V is the effective voltage which can be obtained according the equation $V= V_{appl} -V_{bi} - V_s$, where V_{bi} is the built-in voltage, V_s is the voltage drop from the substrate's series resistance, V_{appl} is the applied voltag.

6. Instruments and measurements

The chemical structures of compounds were identified by Bruker AV-400. The current density voltage (J–V) characteristics for the devices were measured in a glove box using a Keithley 2400 source meter and an AM 1.5 Global solar simulator (Enlitech model-SS-F5-3A). A standard Si photodiode detector was used to calibrate the intensity of the simulated solar light. The EQE spectra were measured on a quantum efficiency test system (Zolix Solar Cell Scan100). Absorption and transmittance spectra were measured using a UV–Vis spectrophotometer (Agilent Cary 60). The thickness of the ETLs was obtained by measuring the difference between the thickness of ETL/Ag bilayer and the thickness of the corresponding Ag layer on ITO substrate with a surface profilomer (Ambios XP-100). The surface morphologies were acquired by an atomic force microscope (Veeco Dimension 3100V). X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Thermo Scientific K-Alpha+ system. Ultraviolet photoelectron spectrometer (UPS) measurements of the onset of photoemission for determining the WF were performed using standard procedures with a bias of −5 V (Thermo Fisher ESCALAB 250Xi). Impedance measurements were obtained on an electrochemical workstation (ZAHNER, Germany) under a bias of - 0.8 V with the amplitude of 500 mV (1 M to 100 Hz).

S2 XPS spectra

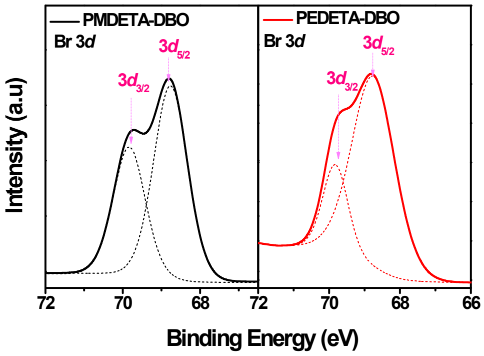

Fig. S2 High-resolution XPS spectra of Br (3*d*) for PMDETA-DBO and PEDETA-DBO

S3 UV–Vis absorption spectra

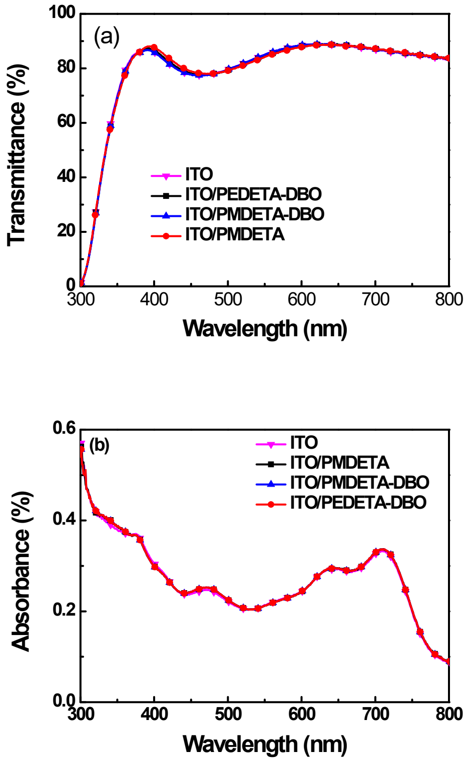

Fig. S3 (a) Transmission spectra of the ETLs-covered ITO and bare ITO glass; (b) UV-Vis absorption spectra of PTB7-Th: $PC_{71}BM$ blend films on various ETLs.

S4 AFM images

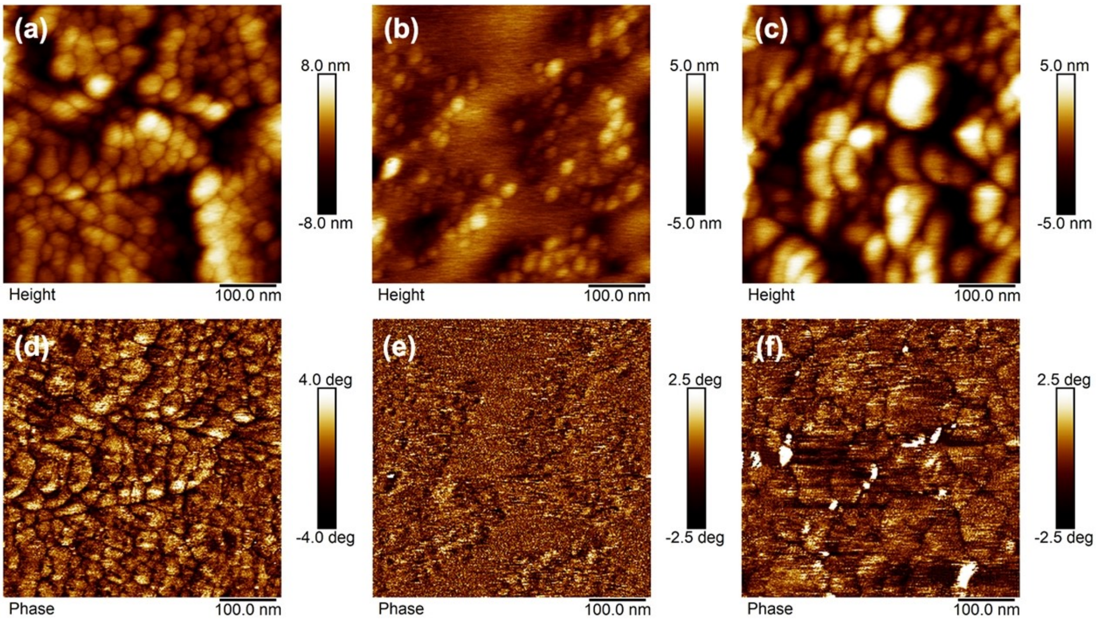

Fig. S4 AFM height and phase images of (a, d) PMDETA, (b, e) PMDETA-DBO, (c, f) PEDETA-DBO on ITO

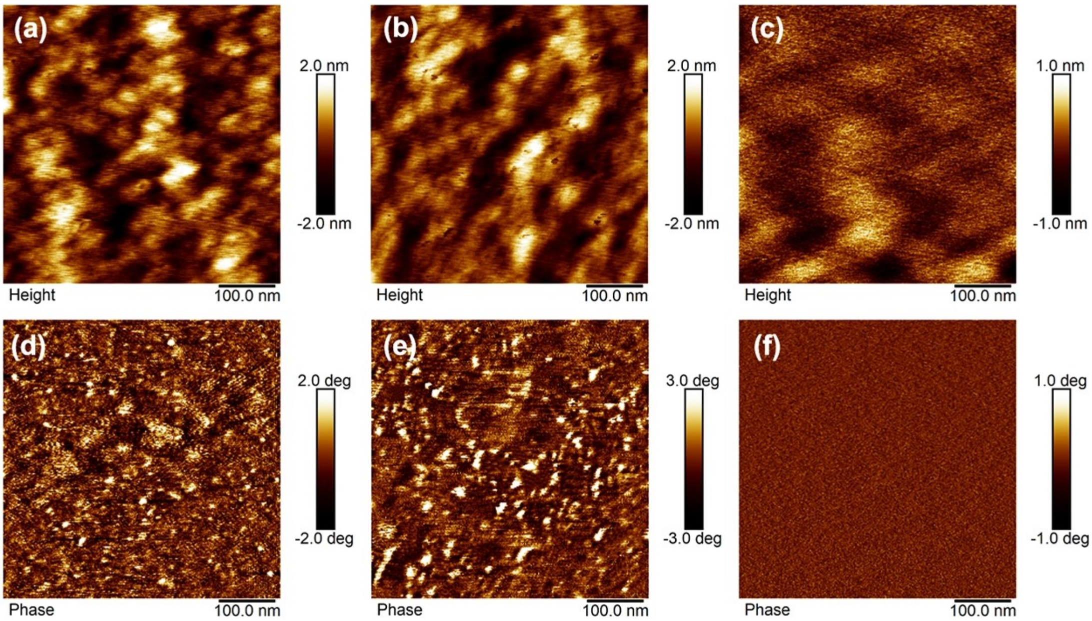

Fig. S5 AFM height and phase images of PTB7-Th: $PC_{71}BM$ blend films on (a, d) PMDETA, (b, e) PMDETA-DBO, (c, f) PEDETA-DBO.

S5 *J-V* curves of the i-OSCs

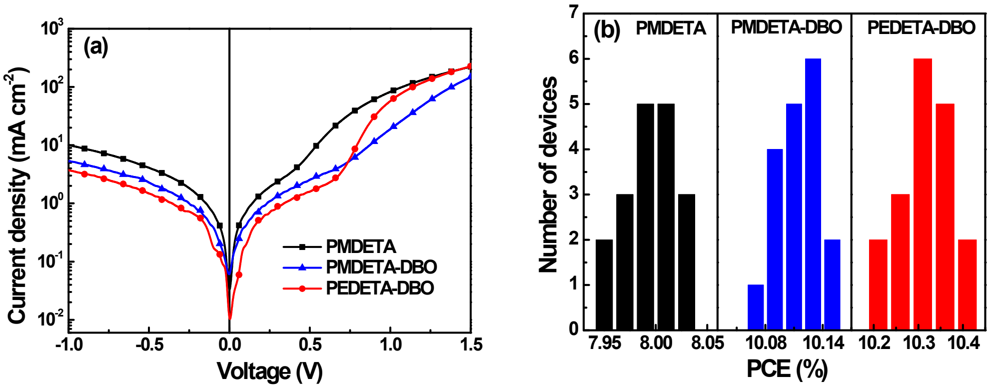

Fig. S6 (a) *J-V* curves of the i-OSCs (PTB7-Th: $PC_{71}BM$) in dark condition and (b) PCE distribution of the i-OSCs (PTB7-Th: $PC_{71}BM$) under illumination with PMDETA, PMDETA-DBO and PEDETA-DBO as the ETLs.

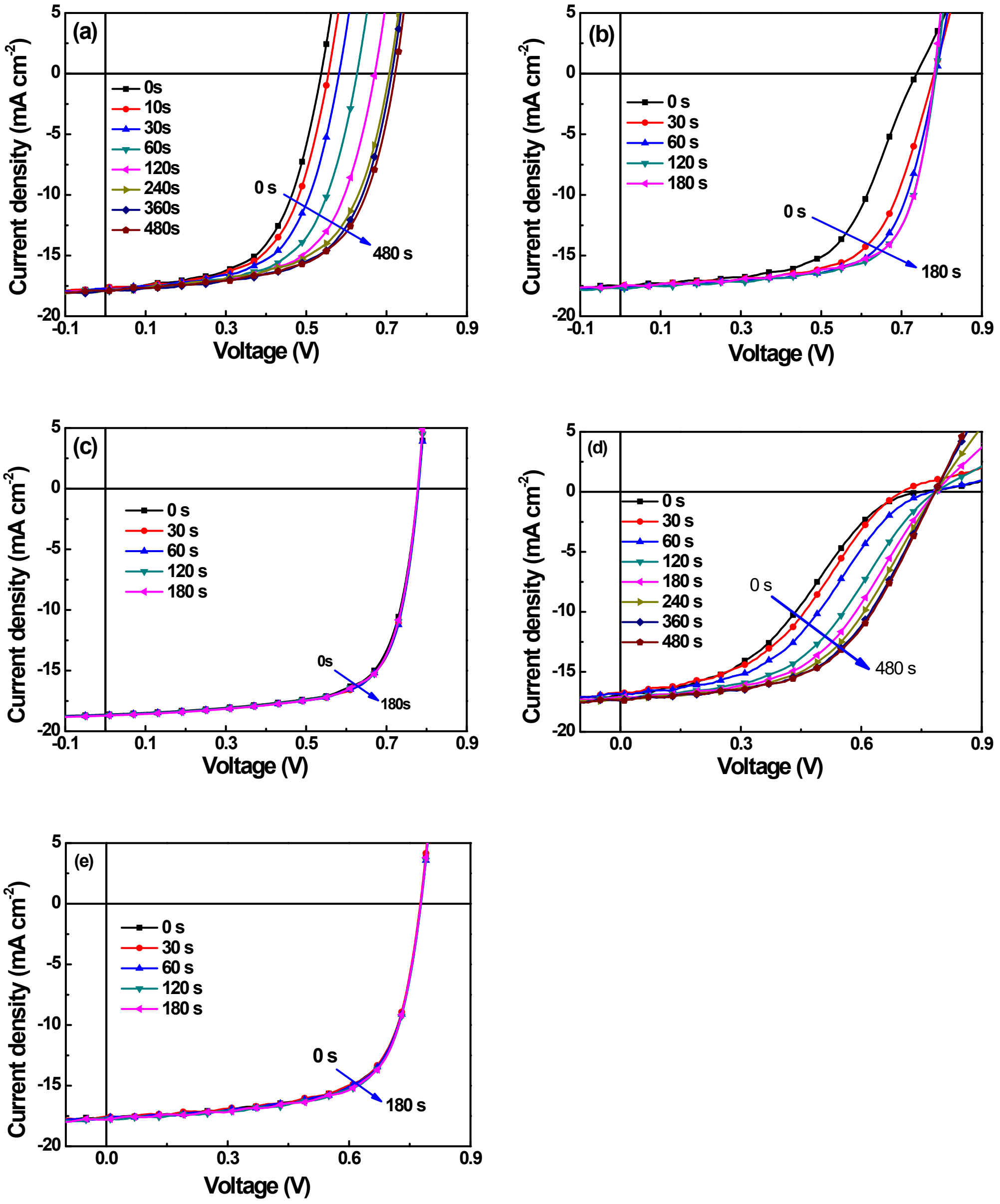

Fig. S7 Time-dependent *J-V* curves of the OSCs (PTB7-Th: $PC_{71}BM$) based on (a) PMDETA (7 nm), (b) PMDETA-DBO (10 nm), (c) PEDETA-DBO (10 nm), (d) PMDETA-DBO (30 nm), and (e) PEDETA-DBO (50 nm).

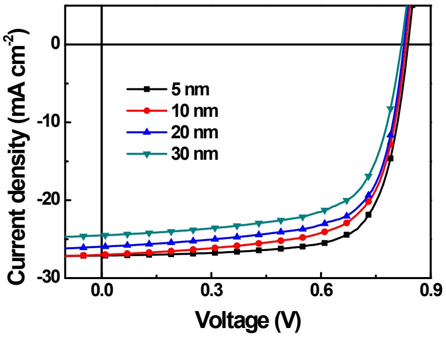

Fig. S8 *J*-*V* curves of the i-OSCs (PM6: Y6) based on PEDETA-DBO with various thickness.

S6 Characterization of the reaction between ITIC and tertiary amine

Fig. S9 The ITIC solution mixed with tetraethylammonium bromide (TEAB) and triethylamine (TEA) for 10 days under room temperature.

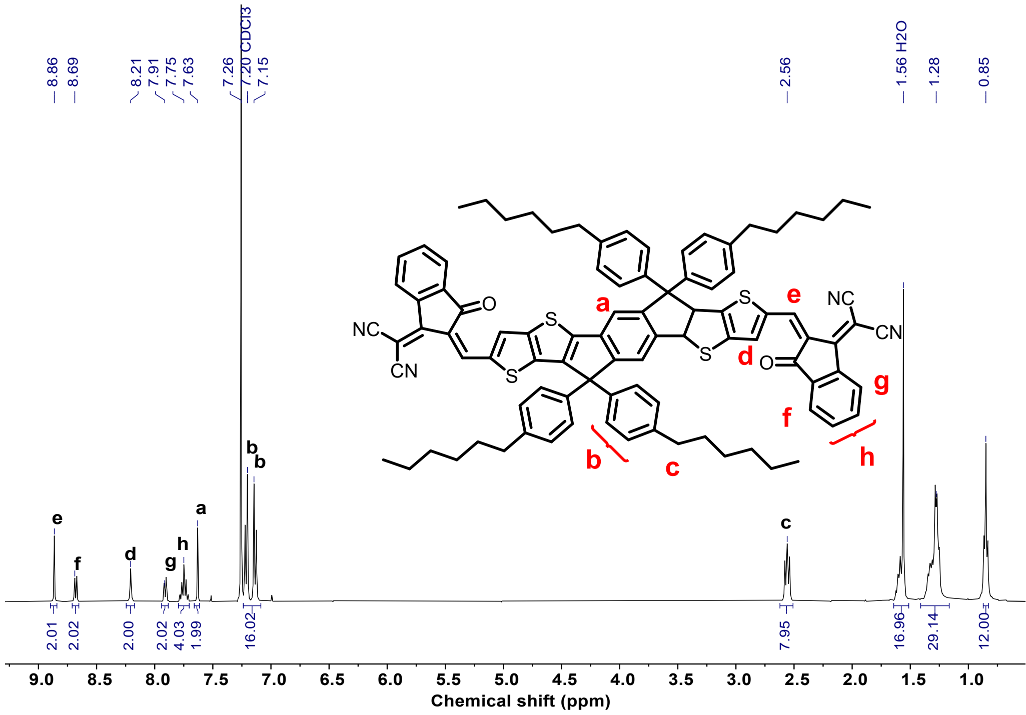

Fig. S10 ^{1}H-NMR spectrum of ITIC in CDCl$_3$ (400 MHz).

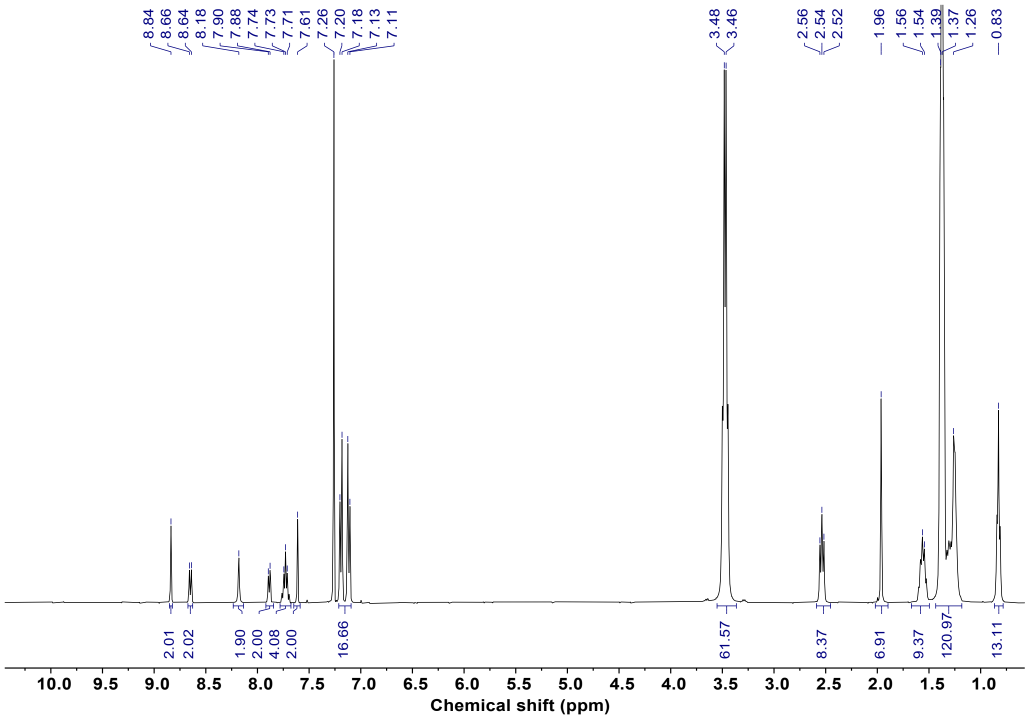

Fig. S11 ^{1}H-NMR spectrum of the mixture which ITIC was mixed with tetraethylammonium bromide for 10 days under room temperature (CDCl$_3$, 400 MHz).

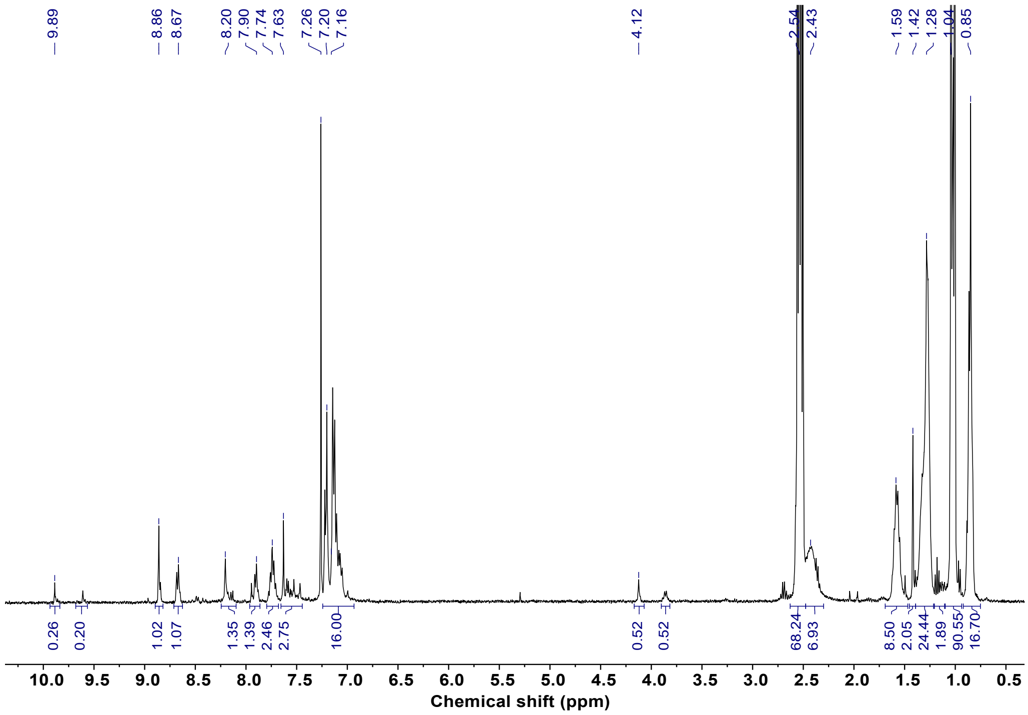

Fig. S12 ^{1}H-NMR spectrum of the mixture which ITIC was mixed with triethylamine for 10 days under room temperature ($CDCl_3$, 400 MHz).

S7 Photovoltaic parameters of the i-OSCs

Table S1 Device parameters of the PSCs based on different ETLs with various thicknesses under the illumination of AM 1.5G, 100 mW cm^{-2}.

ETLs	Thickness (nm)	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE$_{max}$ (PCE$_{avg}$) [%]
PMDETA-DBO	10 nm	0.783±0.002	18.31±0.11	70.51±0.55	10.15 (10.12)
	20nm	0.778±0.003	17.50±0.15	64.56±0.83	9.01 (8.94)
	30 nm	0.771±0.007	17.12±0.21	55.02±1.21	7.43 (7.33)
PEDETA-DBO	10 nm	0.783±0.005	18.62±0.17	70.60±0.34	10.41 (10.31)
	20nm	0.782±0.004	18.60±0.13	69.20±0.91	10.12 (10.07)
	30 nm	0.783±0.005	18.08±0.15	68.14±0.90	9.72 (9.65)
	50 nm	0.780±0.006	17.95±0.19	67.42±1.11	9.63 (9.48)