Electronic Supplementary Information For:

**High Efficiency Inverted Polymer Solar Cells with Room-Temperature Titanium Oxide/Polyethylenimine Films as Electron Transport Layers**

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Experimental Section

Materials

PTB7 and PC\textsubscript{71}BM were purchased from 1-material Chemscitech and Solenne BV, respectively. Branched PEI (25,000 g/mol), 2-methoxyethanol (99.8%), o-dichlorobenzene (99%) and 1,8-diiodoctane (98%) were purchased from Sigma-Aldrich Inc. All materials were used as received.

Preparation and characterization of the TiO\textsubscript{x}, PEI and TiO\textsubscript{x}/PEI films

TiO\textsubscript{x} thin films were fabricated on top of ITO substrates with sheet resistance of 10 Ω sq\textsuperscript{-1} by magnetron sputtering. ITO was purchased from AimCore Technology Co., Ltd, and cleaned with acetone, isopropyl alcohol and deionized water successively in ultrasonic baths for 30 min. All of the substrates were dried by nitrogen gas and treated by UV–ozone chamber (Ultraviolet Ozone Cleaned, Jelight Company USA) for 15 min. TiO\textsubscript{x} thin films were sputtered on ITO substrates by the PVD-75 vacuum system (Kurt J. Lesker, U.S.A). DC magnetron sputtering power was 400 W and performed from a 3-inch-diameter metallic plate of Ti (99.995%) in an atmosphere of Ar (99.998%) and O\textsubscript{2} (99.998%). The O\textsubscript{2}/Ar gas flow ratio was kept at a constant value during each deposition by mass-flow-controlled gas inlets. The base pressure of the system was less than $1.5 \times 10^{-7}$ Torr. The sputtering pressure was kept at $7.5 \times 10^{-3}$ Torr with a mixture gas of Ar and O\textsubscript{2} (85:15) during the sputtering processes. Before deposition, the target was pre-sputtered for 15 min in order to remove the oxide layer on the target surface. The thickness of 82 nm TiO\textsubscript{x} thin films was tuned by sputtering time and determined by a Bruker 150 surface profiler. Branched PEI was dissolved in 2-methoxyethanol with a weight concentration of 0.5%. The solution was spin coated onto the ITO or ITO/TiO\textsubscript{x} substrates at speed of 5000 rpm for 1 min and an acceleration of 800 rpm/s. The thickness of the PEI film was below 10 nm both on the ITO and ITO/TiO\textsubscript{x} substrates. AFM height images of the different thickness of TiO\textsubscript{x} and TiO\textsubscript{x}/PEI films were obtained using a Bruker Metrology Nanoscope III-D atomic force microscope in tapping mode under atmospheric conditions. The
work function of TiO\textsubscript{x} and TiO\textsubscript{x}/PEI films were measured in air by SKPM with a Bruker Metrology Nanoscope VIII atomic force microscope in ambient atmosphere. Conducting AFM tips (SCM-PIT/PtIr, Bruker, USA) used for this study had a typical spring constant of 2.8 N m\textsuperscript{-1} and a resonance frequency of 75 kHz. Typical scan line frequency was 0.3 Hz and each image contained 512 \( \times \) 512 pixels. The surface potential images were unprocessed original data. XPS measurements were performed using a VG ESCALAB MK2 system with a monochromatized Al K\textalpha under a pressure of \( 3.75 \times 10^{-9} \) Torr. Optical transmission spectra was acquired using a Varian UV–Vis spectrometer, Cary 5000. Raman scattering spectra were recorded on an Acton Raman spectrometer by 532 nm semiconductor laser as excitation source with the power of 10 mW.

**Fabrication and characterization of IPSCs and electron only devices**

TiO\textsubscript{x} thin films were fabricated on ITO substrates by magnetron sputtering at room-temperature. The PTB7:PC\textsubscript{71}BM solution was prepared with ratio of 1:1.5 by weight in chlorobenzene/1,8-diiodoctane (97:3 vol\%). The solution with an overall concentration of 25mg/ml was stirred on a hotplate at 40\textdegree C for one night before film casting. Subsequently, the solution was spin coated at 4000 rpm for 1 min onto the ITO, ITO/TiO\textsubscript{x} and ITO/TiO\textsubscript{x}/PEI substrates in a N\textsubscript{2} filled glove box. The thickness of the PTB7:PC\textsubscript{71}BM films were \~ 83 nm. The samples were transferred to a vacuum thermal evaporation system and 10 nm of MoO\textsubscript{3} and 100 nm of Ag were deposited at \( 3.8 \times 10^{-6} \) Torr with a shadow mask. The effective area of metal electrodes was 6.2 mm\textsuperscript{2}. All devices were characterized with a computer-controlled Keithley 2400 source measure unit under ambient conditions, and the illumination intensity was 100 mW/cm\textsuperscript{2} (AM 1.5G Oriel solar simulator). EQE was characterized on the QTest Station 2000ADI system (Crowntech. Inc., USA). Electron only devices were fabricated to calculate electron mobility of the TiO\textsubscript{x} and TiO\textsubscript{x}/PEI films by the SCLC. The 10 nm of Ca and 100 nm of Al were deposited on to TiO\textsubscript{x} or TiO\textsubscript{x}/PEI films at \( 3.8 \times 10^{-6} \) Torr with a shadow mask. The dark \( J-V \) was measured by a Keithley 2400 source measurement unit.
To optimize the thickness of the TiOx film, PTB7:PC$_71$BM IPSCs with TiO$_x$ thickness ranging from 32 nm to 166nm were fabricated. The $J-V$ curves are shown Fig. S1 and the parameters of the IPSCs are listed in Table S1. When the thickness of TiOx is increased from 32 nm to 82 nm, the PCE of devices is increased from 5.38% to 7.38%, while the PCE drops down to 5.79% when the thickness of TiO$_x$ is further increased up to 166nm. Fig. S2 shown the AFM images of the morphology of TiOx films with different thickness. The 32nm-thick TiOx cannot fully cover ITO substrate, which leads to the direct contact of acceptors and ITO in IPSCs, and then brings serious carrier recombination at the ITO interface. The 166 nm of TiO$_x$ film can fully cover the ITO surface, but the $R_s$ is increased up to 8.35 $\Omega$ cm$^2$.

**Electron extraction enhancement in TiO$_x$/PEI film**

IS measurement is conducted to analysis the conjugated polymer and interface properties of the PTB7:PC$_71$BM IPSCs with TiO$_x$ or TiO$_x$/PEI ETLs. Nyquist plots of devices were measured at open-circuit voltage based on TiO$_x$ and TiO$_x$/PEI. Fig. S7 displays the equivalent circuit model for two IPSCs in impedance spectra (Fig. 4a). The fitted equivalent circuit model composed of series resistance ($R_s$) and three components $R_1$, $R_2$, and $R_3$ forming a parallel circuit with capacitors ($C_1$, $C_2$, and $C_3$, respectively). The parameters of the IPSCs equivalent circuit with TiO$_x$ or TiO$_x$/PEI ETLs are summarized in Table S2. The ($R_1$, $C_1$) components are primarily affect by the ETLs and the ($R_2$, $C_2$) component is root in the active layer. The Nyquist plots that follow shows the $R_1$, $R_2$ and $R_3$ of the devices with TiO$_x$ ETLs are 1279 $\Omega$, 42.9 $\Omega$ and 10.6 $\Omega$, respectively, while the devices based on TiO$_x$/PEI, the $R_1$, $R_2$ and $R_3$ suddenly decreases to 357.1 $\Omega$, 14.1 $\Omega$ and 3.3 $\Omega$, respectively. The extracted contact resistance is notable reduced when the devices with TiO$_x$/PEI ETLs. Meanwhile, the $C_2$ is distinct decreases from $5.21\times10^{-9}$ F to $9.30\times10^{-10}$ F for devices with TiO$_x$/PEI ETLs. This indicates the few carriers exist in active layer based on TiO$_x$/PEI and the result is in good agreement with the previously observed that the TiO$_x$/PEI has high
electron mobility which insure that the carriers can timely extract from active layer to ETLs. The increase of $C_1$ (from $3.21 \times 10^{-8}$ F to $6.34 \times 10^{-8}$ F) is demonstrated that the process occurs in device.
Fig. S1. $J-V$ characteristics of the inverted PSCs with different thickness of TiO$_x$ films as ETLs under AM 1.5G irradiation at 100 mW cm$^2$. 
Fig. S2. AFM images of TiO$_x$ films in different thicknesses.
Fig. S3 Surface potential images of the TiOₓ and TiOₓ/PEI. Scale size is 1 µm for all images.
Fig. S4 (a) XPS for ITO/PEI, ITO/TiO\textsubscript{x} and ITO/TiO\textsubscript{x}/PEI. XPS focus on the Ti2p (b) and O1s (c) peaks for ITO/TiO\textsubscript{x} and ITO/TiO\textsubscript{x}/PEI samples.
Fig. S5 The schematic diagram of the decreased the work function of TiO$_x$ due to the presence of interfacial dipole.
Fig. S6 The $J-V$ curve of the best IPSC with TiO$_x$/PEI ETL.
Fig. S7 The equivalent circuit model for IPSCs in electrochemical impedance spectra.

Fig. S8 Photoluminescence spectra of pristine PTB7, TiO$_x$/PTB7 and TiO$_x$/PEI/PTB7 films.
Table S1. The parameters of the IPSCs with different thickness of TiO\textsubscript{x} as ETLs.

<table>
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<tr>
<th>Thickness of TiO\textsubscript{x}</th>
<th>( J_{sc} ) (mA cm(^{-2} ))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>( R_s ) (( \Omega ) cm(^2))</th>
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<tr>
<td>32 nm</td>
<td>14.70</td>
<td>0.64</td>
<td>0.62</td>
<td>5.83</td>
<td>4.13</td>
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<tr>
<td>82 nm</td>
<td>16.69</td>
<td>0.68</td>
<td>0.65</td>
<td>7.38</td>
<td>4.96</td>
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<tr>
<td>166 nm</td>
<td>13.74</td>
<td>0.68</td>
<td>0.62</td>
<td>5.79</td>
<td>8.35</td>
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Table S2. Summarized parameters of the IPSCs equivalent circuit with TiO$_x$ or TiO$_x$/PEI ETLs measured at open voltage.

<table>
<thead>
<tr>
<th></th>
<th>TiO$_x$</th>
<th>TiO$_x$/PEI</th>
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<tbody>
<tr>
<td>$R_s$ (Ω)</td>
<td>24.4</td>
<td>21.6</td>
</tr>
<tr>
<td>$R_1$ (Ω)</td>
<td>1279</td>
<td>357.1</td>
</tr>
<tr>
<td>$R_2$ (Ω)</td>
<td>42.9</td>
<td>14.1</td>
</tr>
<tr>
<td>$R_3$ (Ω)</td>
<td>10.6</td>
<td>3.3</td>
</tr>
<tr>
<td>$C_1$ (F)</td>
<td>$3.21 \times 10^{-8}$</td>
<td>$6.34 \times 10^{-8}$</td>
</tr>
<tr>
<td>$C_2$ (F)</td>
<td>$5.21 \times 10^{-9}$</td>
<td>$9.30 \times 10^{-10}$</td>
</tr>
<tr>
<td>$C_3$ (F)</td>
<td>$3.65 \times 10^{-10}$</td>
<td>$3.21 \times 10^{-11}$</td>
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References: