## Supporting Information

## Charge Carrier Transport and Contact Selectivity Limit the Operation of PTB7-Based Organic Solar Cells of Varying Active Layer Thickness

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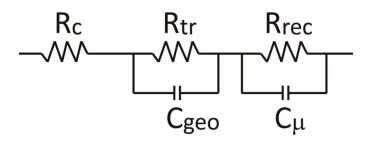
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**Figure SI1:** Equivalent circuit model used in this work. Rc is the series resistance due to contacts and wires. Rtr is a resistance to transport of carriers observed at high frequency for systems limited by transport of carriers. Rrec is the recombination resistance observed at low frequency. Cgeo is the geomentrical capacitance of the device and Cµ a chemical capacitance.

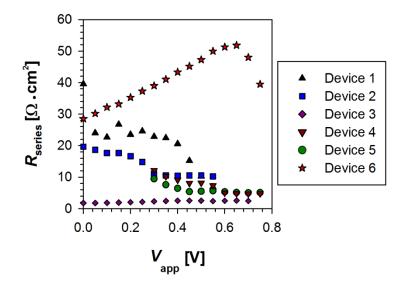
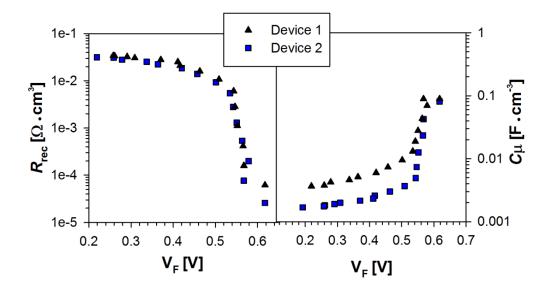


Figure SI2: Calculated total series resistance using Impedance Spectroscopy taking into account the contact resistance and response at high frequencies (  $R_{series} = R_c + R_{tr}$  )



**Figure SI3:** Recombination resistance ( $R_{rec}$ ) and Chemical capacitance ( $C\mu$ ) as a function of the applied voltage corrected to take into account the voltage drop due to the series resistance ( $V_F = V_{app}$ - $j \cdot R_{series}$ ).

## **Capacitance-Voltage analysis**

Active Layer	Donor:Acceptor Ratio	Thickness	V <sub>FB</sub> [V]	Fullerene cathode Fullerene Coverage [%]
P3HT	1:0	100 nm	1.42	0
P3HT:PCBM	1:6	200 nm	0.32	100
Device 1	1:1	100 nm	0.450	90
Device 2	1:1	270 nm	0.377	95
PTB7	1:0	100 nm	1.30	0
PTB7:PCBM	1:6	200 nm	0.52	100
Device 3	1:3	100 nm	0.673	80
Device 4	1:3	100 nm	0.633	85
Device 5	1:1	100 nm	1.022	35
Device 6	1:1	270 nm	0.770	65

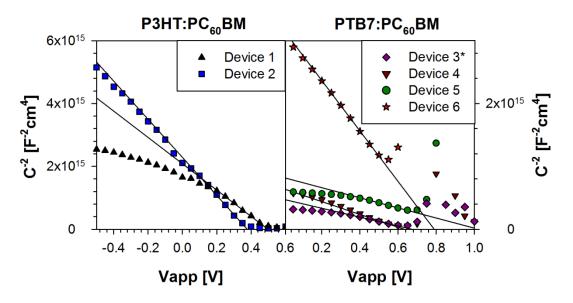


Figure SI4: Mott-Schottky analysis of devices fabricated in this work. Measurements have been carried out at a frequency of 1 kHz and dark conditions. \*PC<sub>70</sub>BM and DIO were used as acceptor molecule and additive, respectively.