Electronic Supplementary Information

Electrolyte-gated transistors based on phenyl-C61-butyric acid methyl ester (PCBM) films: bridging redox properties, charge carrier transport and device performance

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Experimental

SiO_2/Si substrates were photolithographically patterned with source and drain electrodes (Au 40 nm- thick on Ti adhesion film, 4 nm-thick) with interelectrode distance, *L*, of 10 µm and width, *W*, of 4 mm. A layer 1.6 µm-thick of Parylene C (Cookson Electronics, MW 500 kDa) was deposited on the patterned substrate and a rectangle of 1 mm × 5 mm, centered on the transistor channel, was etched away through photolithography and reactive ion etching. Prior to deposition of the PCBM semiconducting films, the substrates were cleaned with sequential steps of 5 min in isopropyl alcohol, 10 min in acetone and 5 min in isopropyl alcohol in ultrasonic baths. PCBM solutions consisting of 5 mg PCBM (Solaris Chem Inc) in 1 ml chlorobenzene stirred overnight in a N_2 glove box at room temperature were prepared. PCBM thin film were deposited by drop-cast on the substrates and set on a hot plate at 50 °C for 2 h in N_2 glove box (< 5 ppm O_2, H_2O). The typical thickness of the films measured with profilometer was 380 nm. [EMIM][TFSI] or [PYR_{14}][TFSI]

(IoLiTec, >99%) ionic liquids were purified at 100 °C, 10^{-5} Torr overnight. The ionic liquids were contained in a Durapore® membrane, 4 mm × 9 mm-sized, 125 µm-thick, laminated on top of the PCBM channel. The gate electrodes consisted of high surface area carbon paper (Spectracarb 2050), 6 mm × 3 mm, 170 µm thick, coated with an ink of activated carbon (PICACTIF SUPERCAP BP10, Pica, 28 mg ml^{-1}) and polyvinylidene fluoride (PVDF, KYNAR HSV900, 1.4 mg ml^{-1}) binder, in N-methyl pyrrolidone (NMP, Fluka). The microfabrication process flow is shown in S1. Transistor electric characteristics were acquired employing an Agilent B1500A semiconductor parameter analyzer connected to a house-made micromanipulated electrical probe station. Electrochemical characterizations were measured in situ with a VersaSTAT 4 potentiostat. X-ray diffraction (XRD) spectra of the PCBM thin films was taken using Bruker D8 diffractometer equipped with a copper source for X-rays with a wavelength (Cu K_a) of 1.54 Å. Scanning Electron Microscopy (SEM) images were taken in air, at room temperature on a Digital Instruments Dimension 3100 in tapping mode with Al-coated silicon cantilevers. 4M [Li][TFSI] (Sigma Aldrich, 99.95%) in tetraethylene glycol dimethyl ether (TEGDME) (Sigma Aldrich, ≥99%) was prepared stirring overnight in a N_2 glove box at room temperature.

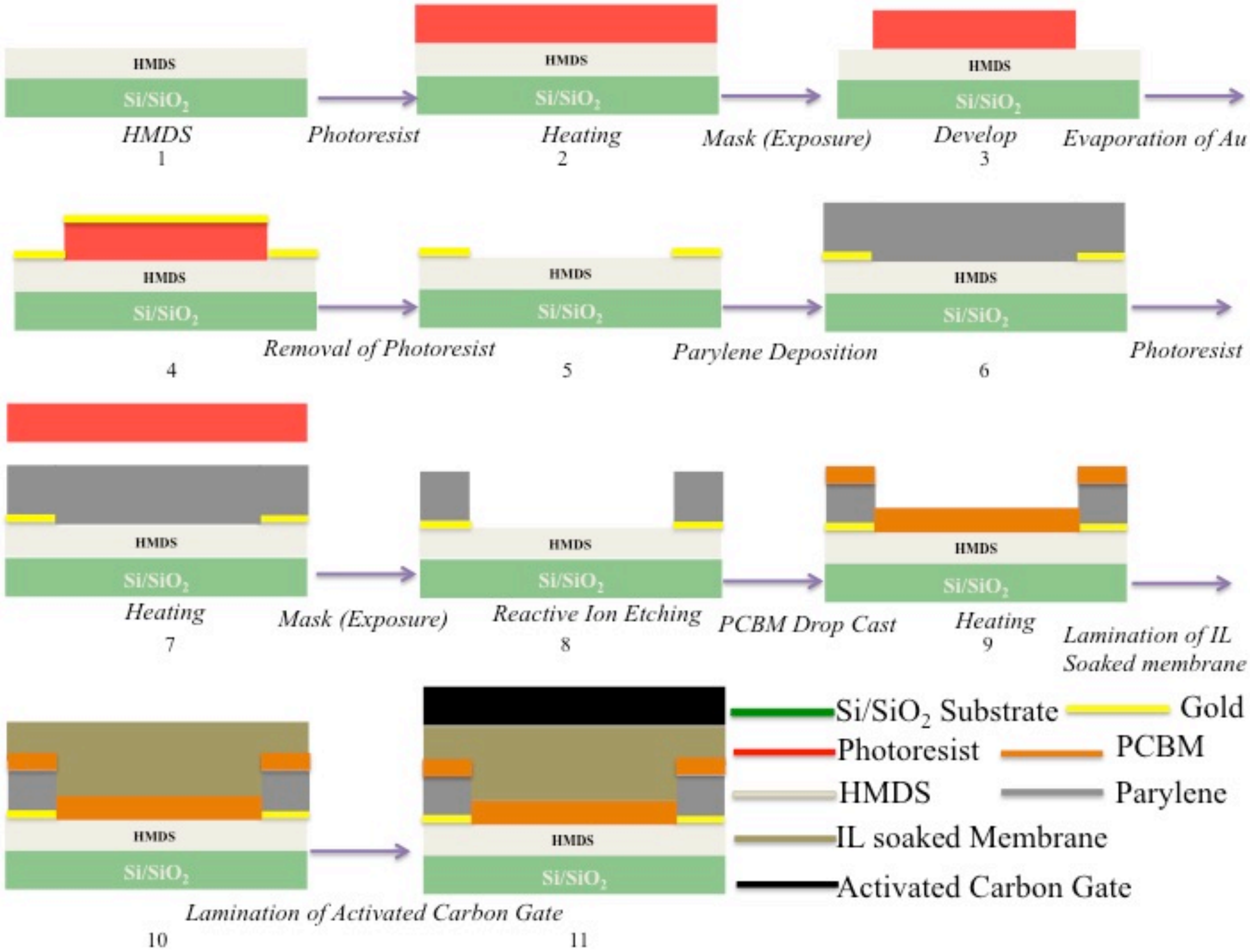

Fig. S1. Microfabrication process flow.

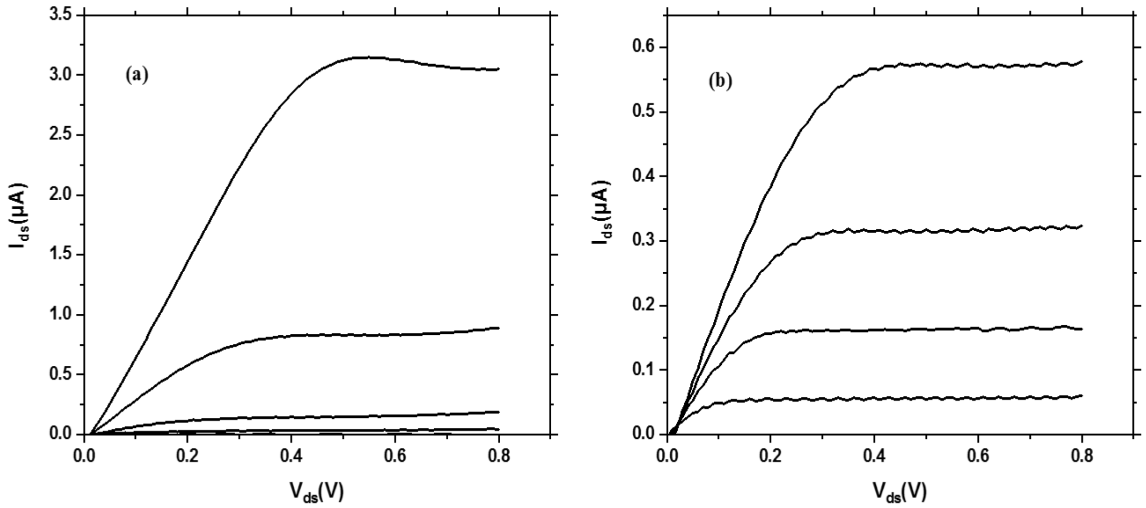

Fig. S2. Output characteristics for V_{gs} = 0, 0.8, 0.9, 1, 1.1 V, at 10 mVs^{-1}, for (a) [EMIM][TFSI]- and (b) [PYR_{14}][TFSI]- gated PCBM transistors.

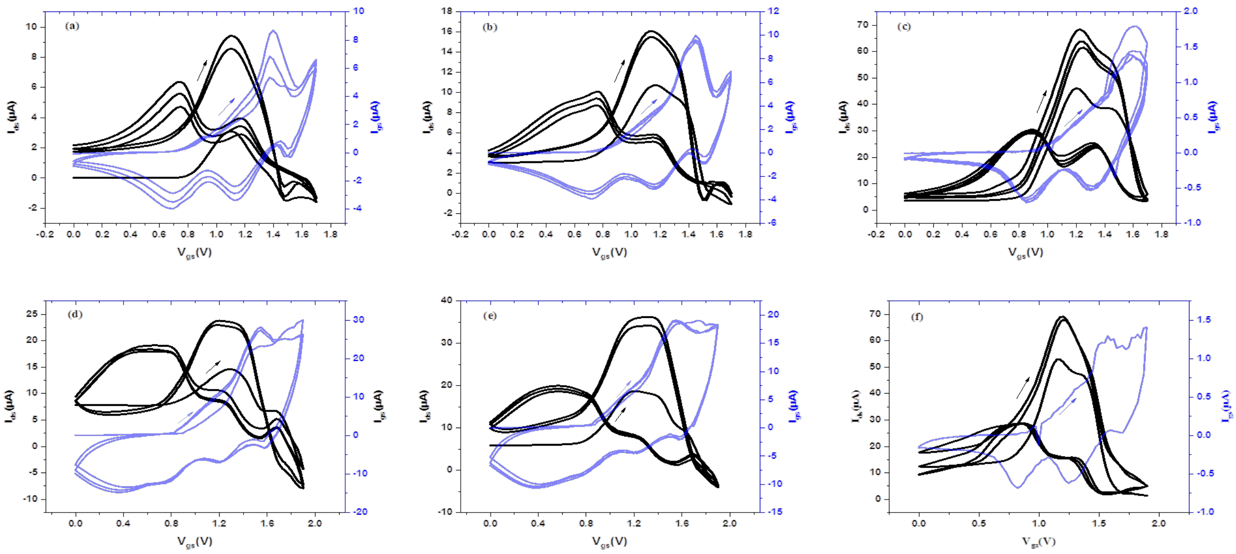

Fig. S3. Transfer characteristics obtained for increased values of V_{gs} for [EMIM][TFSI]-gated PCBM transistors. For (a) (b) (c) the interval is 0 V / 1.7 V. For (d) (e) (f) the interval is 0 V /1.9 V. V_{gs} sweeping rates: (a) and (d) 100 mVs^{-1}, (b) and (e) 50 mVs^{-1}, (c) and (f) 1 mVs^{-1}. In Fig. S4 f only the 3^{rd} cycle of the I_{gs} vs V_{gs} is reported due to the weak (and as such relatively noisy) values of I_{gs} measured for the 1^{st} and 2^{nd} cycles.

In [EMIM][TFSI], for V_{gs} up to 1.7 V, at 100 mVs^{-1}, during the 1^{st} forward scan of the I_{ds} vs V_{gs} plots (three cycles are shown in Fig. S3a) one peak is observable, located at ca 1.1 V. A peak shoulder is observable at 1.45 V (a second peak, of weak intensity, is located at ca.1.6 V). The peak at ca 1.1 V is more intense during the 2^{nd} and 3^{rd} cycle, with respect to the 1^{st} one. In the backward scan, two peaks are observable; the peak position shift towards lower potentials from the 1^{st} to the 3^{rd} cycle. The decrease of the rate from 100 mVs^{-1} to 50 mVs^{-1} and 1 mVs^{-1} leads to a clear increase of the transistor current, as expected. The position of the peak current slightly shifts to higher potentials with the decrease of scan rate. I_{gs} vs V_{gs} plots recorded at 100 mVs^{-1} and 50 mVs^{-1} (Fig. S3a and S3b) show, on the forward scan, one shoulder at ca 1 V and a peak at ca 1.375(1.475) V for 100(50) mVs^{-1}. There are three peaks in the I_{gs} vs V_{gs} backward scans at high sweeping rates whereas only two peaks are observable at 1 mVs^{-1}. I_{ds} vs V_{gs} and I_{gs} vs V_{gs} plots show comparable values of the current for 100 mVs^{-1} and 50 mVs^{-1} whereas I_{ds} has clearly higher values than I_{gs} at 1 mVs^{-1}.

In [EMIM][TFSI], for V_{gs} up to 1.9 V, during the first forward scan of the I_{ds} vs V_{gs} plots (three cycles are shown in Fig. S3d) one peak is observable, located at ca 1.275 V, 1.225 V and 1.175 V from the highest to the lowest scan rate. One shoulder is found at ca. 1.425 V. The peaks are more intense during the 2nd and 3rd cycle, with respect to the 1st one. In the backward scan, three peaks are observable at 100 mV s^{-1} and 50 mV s^{-1}, whereas only two peaks are observable at 1 mVs^{-1}. I_{gs} vs V_{gs} plots show, on the forward scan of the 1st cycle, one shoulder at ca 1.2 V, together with a peak at ca 1.55 V for 100 mVs^{-1} and 50 mVs^{-1}; on the other hand, three peaks are observable in the backward scans. I_{ds} vs V_{gs} and I_{gs} vs V_{gs} plots also show comparable values of the current for I_{ds} and I_{gs} for 100 mVs^{-1} and 50 mVs^{-1} whereas I_{ds} is clearly more intense than I_{gs} at 1 mVs^{-1}. With respect to [PYR14][TFSI] (see main file), I_{ds} vs V_{gs} plots observed with PCBM films in [EMIM][TFSI] seems mainly governed by the ionic component of the transport, in agreement with the results observed for excursions of V_{gs} carried out up to V_{gs}=1.25 V; in [EMIM][TFSI], it is more challenging to extract information on the electronic contribution of the transport.

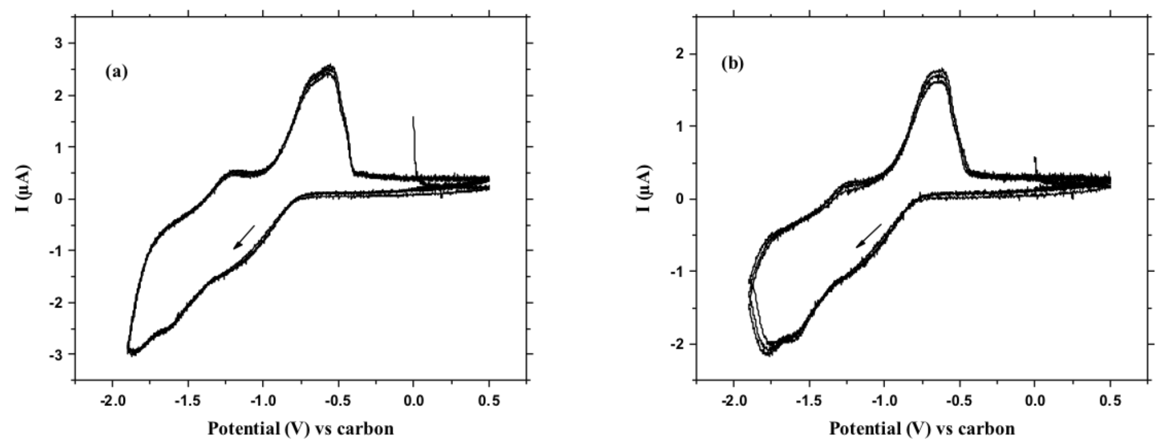

Fig. S4. Cyclic voltammograms in transistor configuration for PCBM films in 4 M [Li][TFSI] in tetraethylene glycol dimethyl-ether (TEGDME), with sweep rates of 100 mV·s^{-1} (a) and 50 mV·s^{-1} (b). The quasi reference electrode is made of high surface area activated carbon. Only the first three cycles are shown.

In 4 M [Li][TFSI] in TEGDME, PCBM electrodes feature, during the forward (cathodic) scan, two reduction processes located at around -1.0 V (shoulder) and -1.6 V (weak peak) at 100 mV·s^{-1} whereas three reduction processes are observable at 50 mV·s^{-1}, located at around -1.0 V (shoulder), -1.6 V (weak peak) and -1.75 V (peak) vs carbon. During the backward (anodic) scan, two anodic processes are observed: one located at around -1.25 V (weak peak), both for 100 mV·s^{-1} and 50 mV·s^{-1}, and another one located at around -0.5 V (peak with shoulder at -0.75 V) for 100 mV·s^{-1} and -0.7 V (*flat* peak), for 50 mV·s^{-1}. It is possible to observe that the voltammograms are less resolved than in the [EMIM][TFSI] and [PYR14][TFSI] cases.

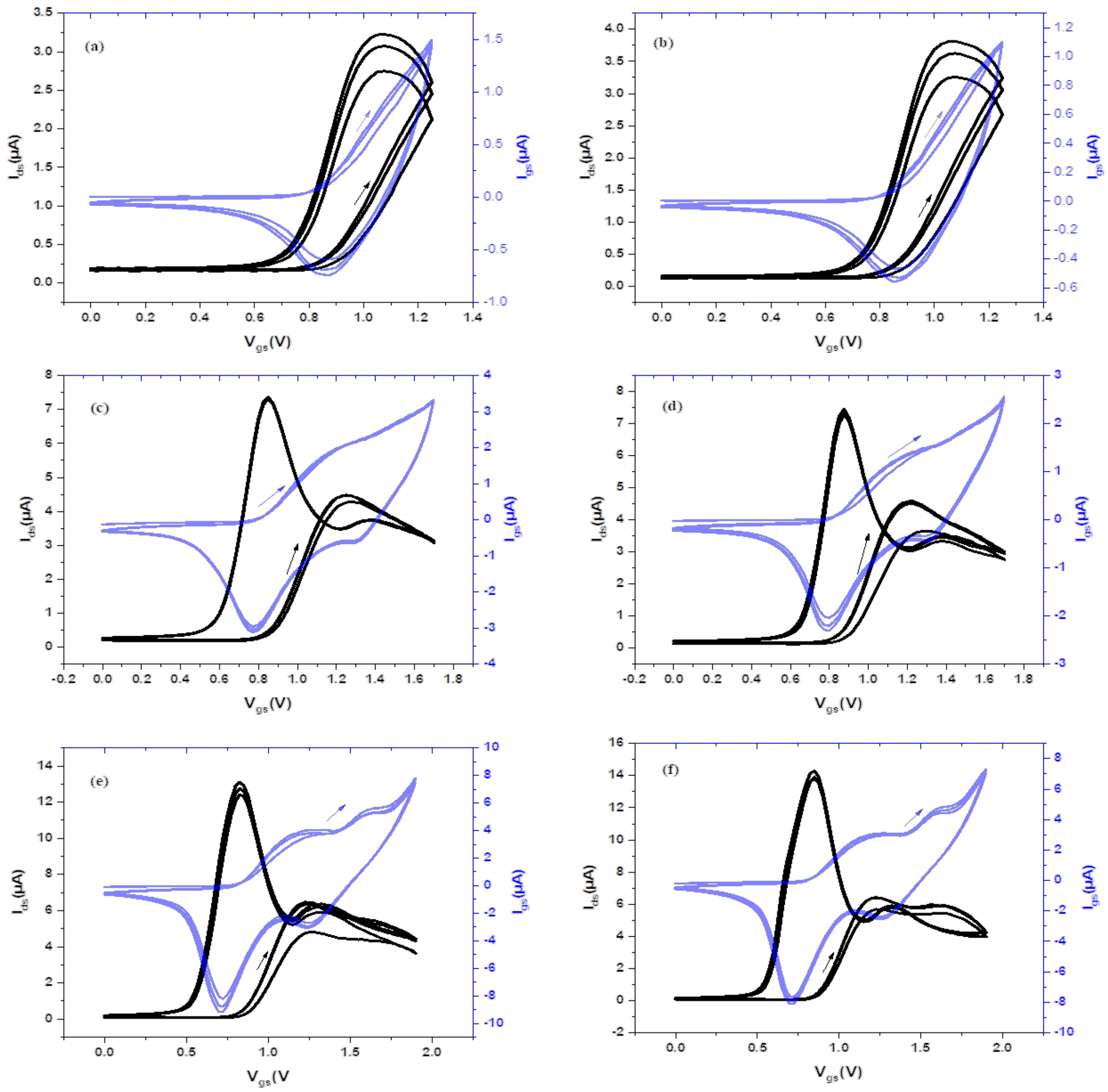

Fig. S5. Transfer characteristics obtained for PCBM transistors gated with 4 M [Li][TFSI] in TEGDME for increasing upper limits of V_{gs}. For (a) (b) the interval is 0 V/1.25 V. For (c) (d) the interval is 0 V/1.7 V. For (e) (f) the interval is 0 V/1.9 V. V_{gs} sweeping rates: (a), (c) and (e) 100 mV·s^{-1}, (b), (d) and (f) 50 mV·s^{-1}.

The linear transfer characteristics for 4 M [Li][TFSI] in TEGDME show that the transistor currents increase with the decrease of the sweep rate, as expected (see main text). For V_{gs} up to 1.25 V, I_{ds} vs V_{gs} plots at 100 mVs^{-1} and 50 mVs^{-1}, show one peak during the backward scan. For V_{gs} up to 1.7 and 1.9 V, during the forward scan, one broad peak is observable both at 100 mV·s^{-1} and 50 mV·s^{-1}. At these two rates, in the backward scan, an intense peak is observable, located at lower potentials with respect to the peak observed during the forward scan. Overall, the behavior of the PCBM transistors gated in 4 M [Li][TFSI] in TEGDME resembles that one of analogous PCBM transistors gated with [EMIM][TFSI] ("bulk" doping as opposed to "surface-confined" doping observed with [PYR14][TFSI], see main text).

Ionic liquid [EMIM][TFSI]						
Scan rate of the electrochemical potential	Potential vs carbon	Current	Potential vs carbon	Current	Potential vs carbon	Current
Cathodic scan (third cycle)						
100mV/s	-0.99 V	-12.9 µA	-1.38 V	-39.8 µA	-1.67 V	-39.7 µA
50mV/s	-1.01 V	-9.2 µA	-1.35 V	-24.86 µA	-1.64 V	-24.75 µA
1mV/s	-0.83 V	-0.28 µA	-1.37 V	-1.52 µA	-1.71 V	-1.35 µA
Anodic scan (third cycle)						
100mV/s	-1.43 V	22.8 µA	-1.1 V	21.5 µA	-0.57 V	19.8 µA
50mV/s	-1.43 V	13.79 µA	-1.1 V	13.78 µA	-0.66 V	11.8 µA
1mV/s	-1.5 V	0.07 µA	-0.98 V	0.76 µA	-0.64 V	0.84 µA
Ionic liquid [PYR14][TFSI]						
Cathodic scan (third cycle)						
100mV/s	-0.99 V	-1.94 µA	-1.35 V	-3.80 µA	-1.62 V	-3.92 µA
50mV/s	-1.04 V	-1.78 µA	-1.37V	-3.55 µA	-1.64V	-3.87 µA
1mV/s	-0.95 V	-0.17 µA	-1.33 V	-0.79 µA	-1.72V	-0.94 µA
Anodic scan (third cycle)						
100mV/s	-1.49 V	1.82 µA	-1. 05 V	2.64 µA	-0.67 V	4.99 µA
50mV/s	-1.51 V	1.88 µA	-1.11 V	2.77 µA	-0.67 V	4.65 µA
1mV/s	-1.58 V	0.24 µA	-1.24 V	0.34 µA	-0.72 V	0.92 µA

Table S1. Cathodic and anodic current peak positions extracted at different scan rates, 100 mVs^{-1}, 50 mVs^{-1}, and 1 mVs^{-1}, for PCBM films in transistor configuration (see main text) in different ionic liquids, specified in the Table.