Interface Trap States in Organic Photodiodes

Supplementary Information

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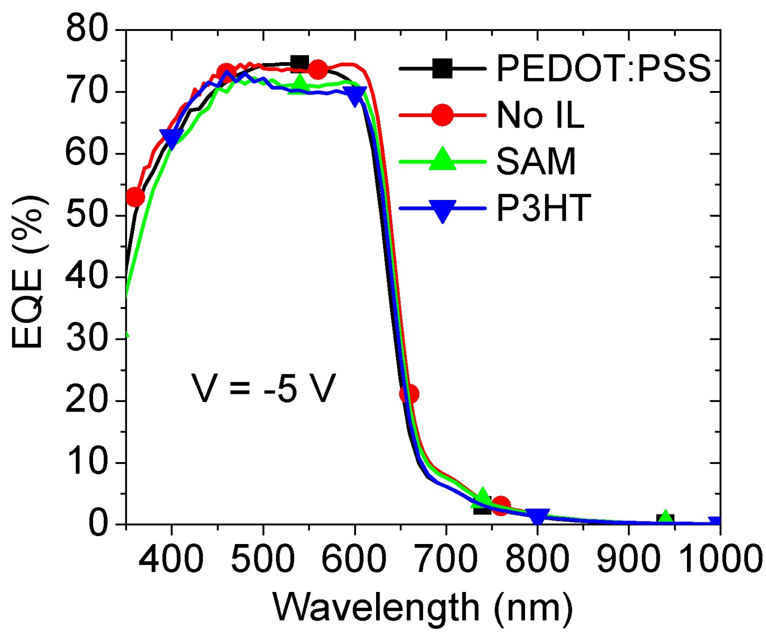
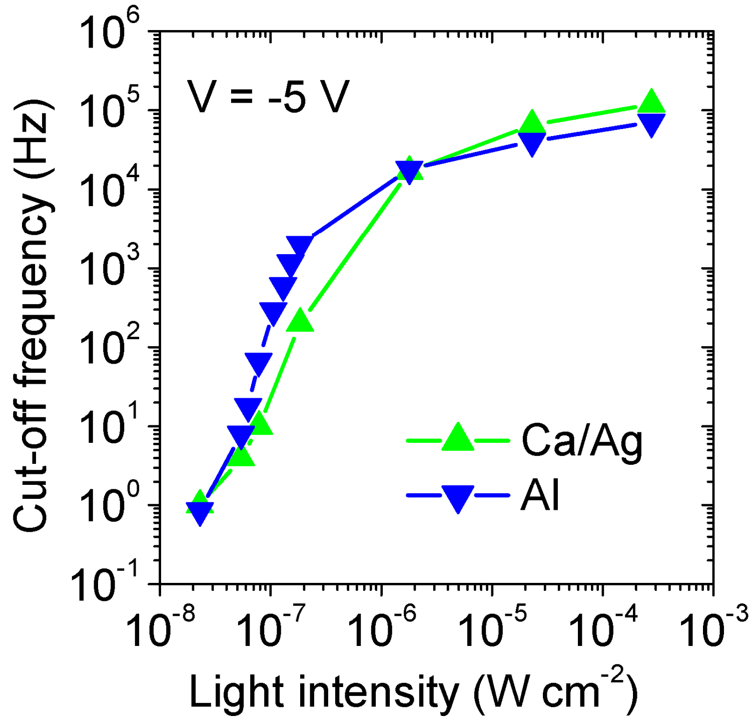
Supplementary Figure 1



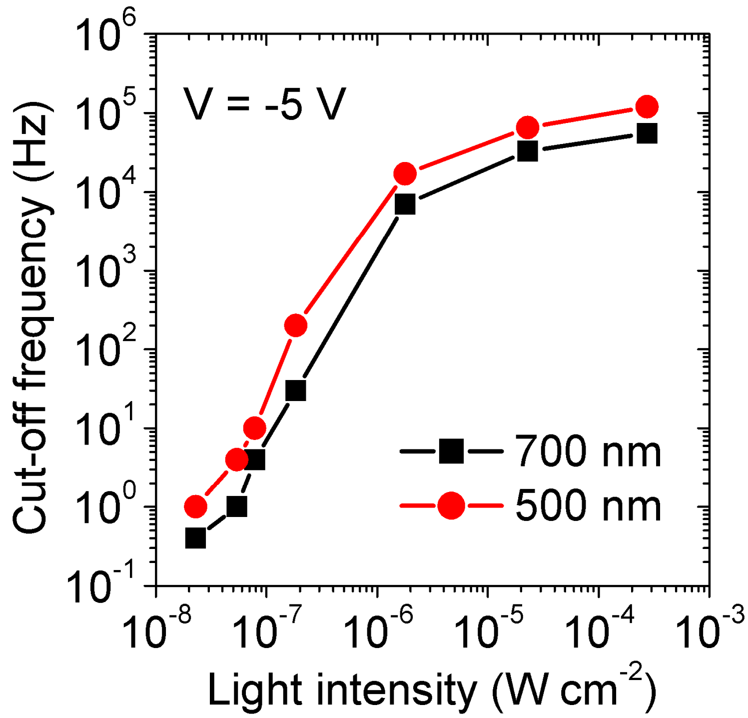
Supplementary Figure 1: *EQE* plot of OPDs with PEDOT:PSS, P3HT and SAM as IL and without IL. Measurements performed at V = -5 V.

Supplementary Figure 2



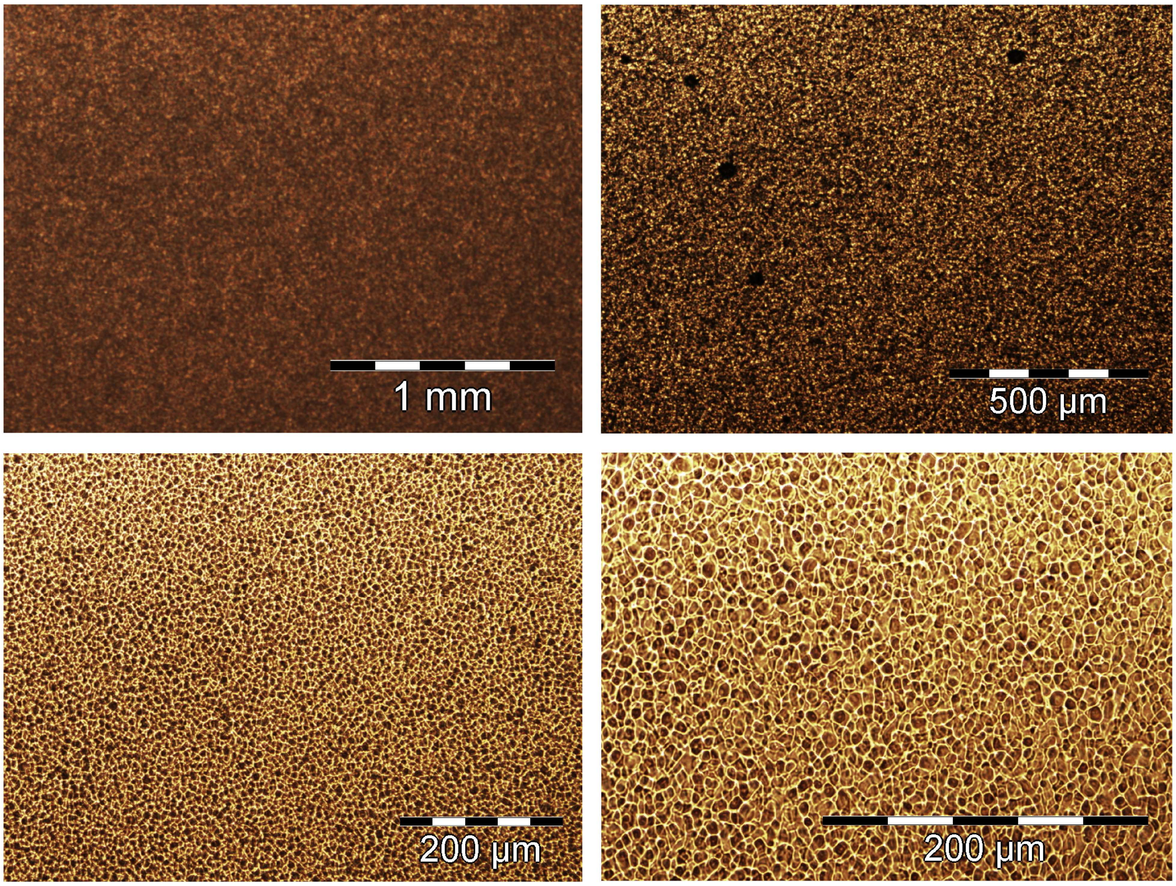
Supplementary Figure 2: Cut-off frequency vs. light intensity of two diodes both with PEDOT:PSS IL, one with Ca/Ag and the second with Al as top electrode. Measurements performed at V = -5 V.

Supplementary Figure 3



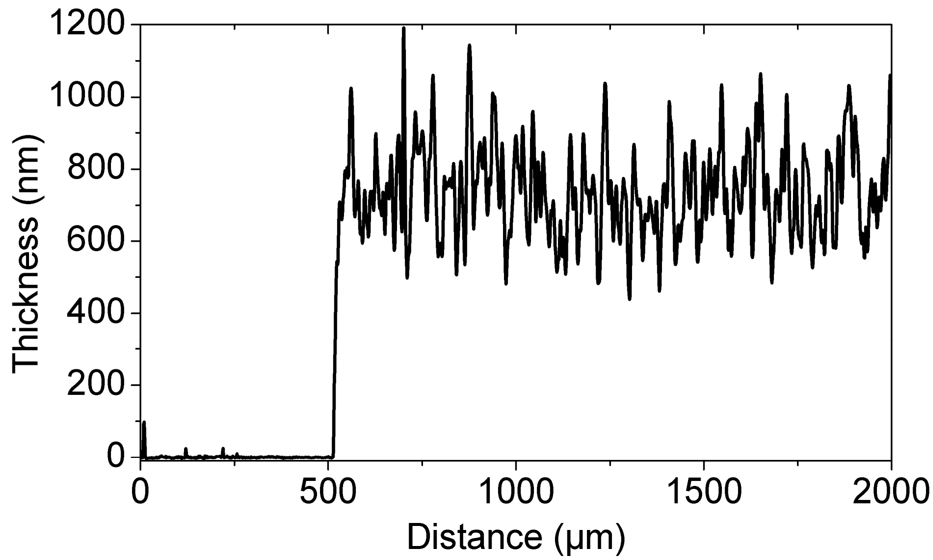
Supplementary Figure 3: Cut-off frequency vs. light intensity of two diodes both with PEDOT:PSS IL, one with 500 nm and the second with 700 nm semiconductor thickness. Measurements performed at V = -5 V.

Supplementary Figure 4



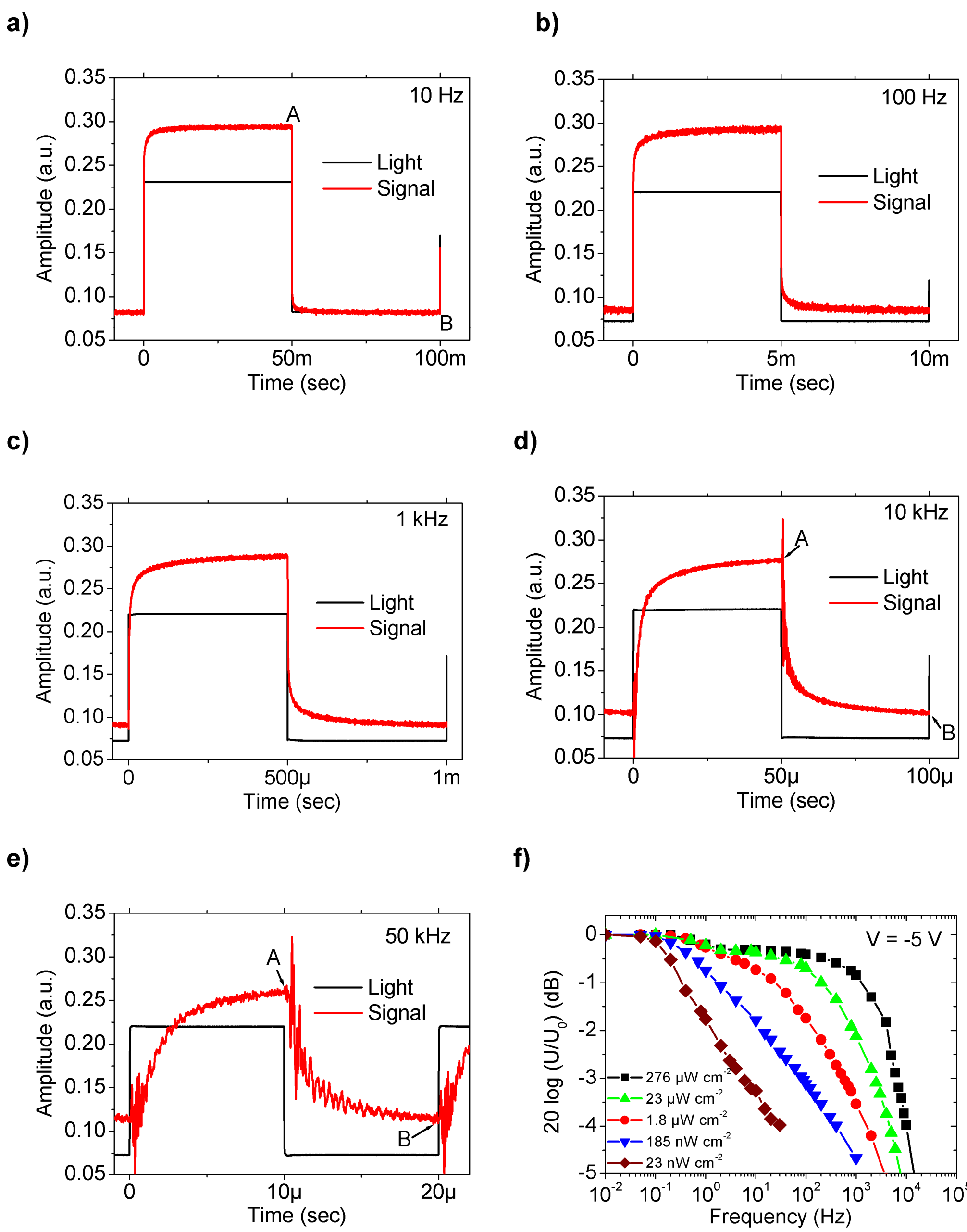
Supplementary Figure 4: Optical microscopic pictures of spray-coated BHJ with ~500 nm thickness at different magnifications. The spray-coating process allows to fabricate thin film stacks with grain sizes of <10 µm and low intermixing of IL and BHJ.

Supplementary Figure 5



Supplementary Figure 5: Exemplary profilometer measurement of a spray-coated BHJ layer with mean thickness of ~700 nm. The best compromise between dark current and EQE values is achieved with mean BHJ thickness of ~500 nm to ~700 nm. Thin layers result in a device with high dark currents due to low resistive paths between anode and cathode while thick layers result in a device with reduced EQE due to charge carriers recombination.

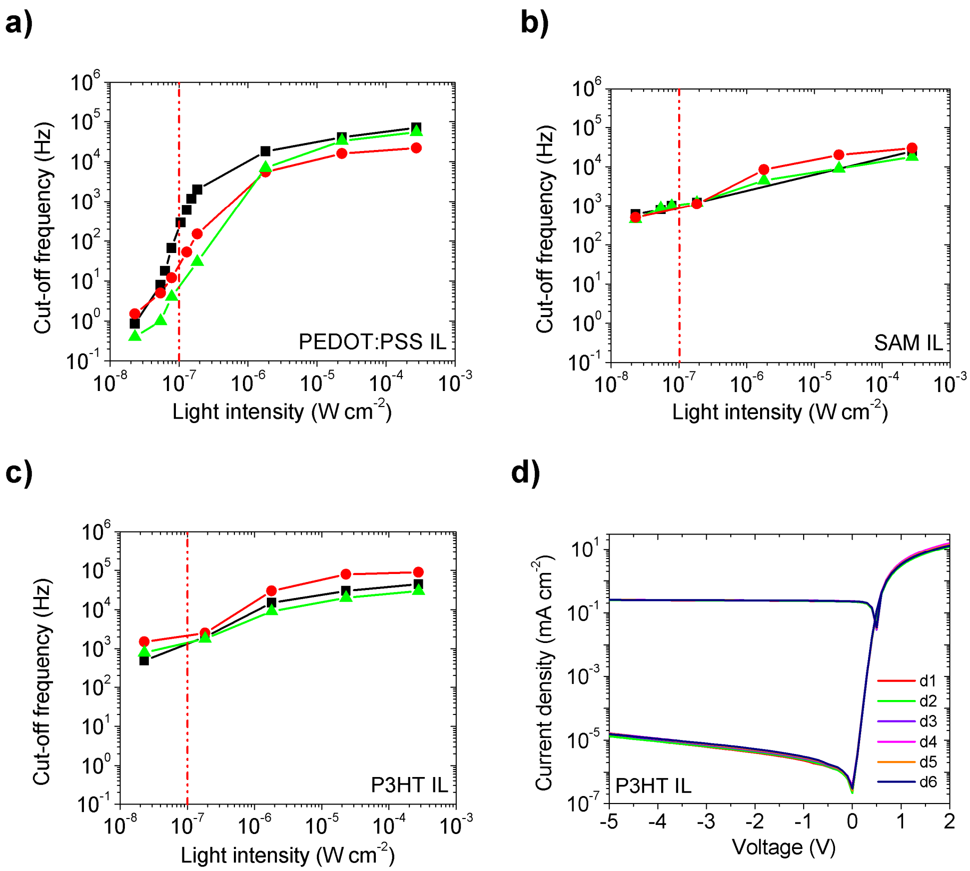
Supplementary Figure 6



Supplementary Figure 6: Dynamic cut-off measurements. Exemplary OPD signal response to a square-shaped light pulse (532 nm @ 60 µW cm^{-2}, 50 % duty cycle) with illumination frequency of a) 10 Hz, b) 100 Hz, c) 1 kHz, d) 10 kHz and e) 50 kHz. With the help of the digital oscilloscope we derived the amplitude differences between the points were the light pulse change (A minus B in the Figure). We varied the square-shape light frequency and for each frequency me measure the A-B amplitude. The measured difference amplitude (U, Fig. f) is then normalized for the difference amplitude at the lowest frequency (U_0). From the U/ U_0 ratio the amplitude Bode plot is extracted. Cut-off frequency corresponds to the cross point between the amplitude Bode plot and the -3dB. For low light intensity a low pass filter (SIM965 Analog filter from SRS, Butterworth filter with 12 dB/oct. slope) is used. Filter cut-off frequency, which is varied according to the measurement range, has always kept at least one decade higher than the light pulse frequency to ensure no amplitude cut-off due to the filter characteristics. The transimpedance amplifier DHPCA-100 from Femto is set with gain of 10^4 V/A for high and medium light intensities. For low light intensities the amplification gain is increased (up to 10^6 V/A for 20 nW/cm^2 light intensities). OPDs are measured with the same settings of the instruments for comparison.

f) Bode plot of a -5 V reverse biased OPD without IL with varying pulsed green light illumination ranging from ~276 µW cm^{-2} to ~23 nW cm^{-2}

Supplementary Figure 7



Supplementary Figure 7: OPD reproducibility. Cut-off frequency measurements at -5 V reverse bias on three OPDs with a) PEDOT:PSS IL, b) SAM IL and c) P3HT IL. The vertical line at 10^{-7} W cm^2 is a guide for the eyes to easily identify the low light intensity regime. d) IV overlap of six 1 cm^2 active area OPDs with P3HT IL processed from different batches.

Supplementary Table 1

	Low power (nW cm^{-2})	**High power (μW cm^{-2})**
Low frequency (Hz)	- Few charge carriers generated - Majority of charge carriers trapped at the interface - Trapped carriers considerably affect the measured diode current	- Large number of charge carriers generated - Carriers exceed the number of trap states at the interface (the upper limit depends on trap parameters and carrier concentrations) - Interface traps are filled without any visible degradation of the photocurrent
High frequency (kHz)	- Time constant of the interface traps determines the cut-off frequency of the device	- Effect of the surface traps is still negligible like at low frequencies - Cut-off frequency is given by the time constant of the volume traps, which are present in a high concentration

Supplementary Table 1: Trap influence on the dynamic response of the OPD.