

# SUPPORTING INFORMATION

## On the Dynamics of Additive Migration to Form Cathodic Interlayers in Organic Solar Cells

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Table S1. Fitting parameters of XPS profiles of Al-covered P3HT:PC<sub>71</sub>BM:PEG films that were not-annealed or annealed after Al deposition.

		<i>Not annealed</i>			<i>Annealed after Al deposition</i>		
		C-C\C-H	C-O	O-C=O	C-C\C-H	C-O	O-C=O
<i>0 mg/ml PEG</i>	FWHM [eV]	1.455	1.57	1.583	1.442	1.56	1.656
	Peak intensity [a.u.]	4606	901	631	5184	963	628
	Area	6921.74	1215.97	490.45	7885	1256	487
<i>2 mg/ml PEG</i>	FWHM [eV]	1.404	1.54	1.5	1.41	1.5	1.533
	Peak intensity [a.u.]	4649	1201	607	4353	1654	584
	Area	6896	1560	457	6203	2429	339
<i>5 mg/ml PEG</i>	FWHM [eV]	1.349	1.5	1.68	1.366	1.5	2.02
	Peak intensity [a.u.]	5303	1656	622	5564	1968	672
	Area	7559	2125	447	7899	2610	581

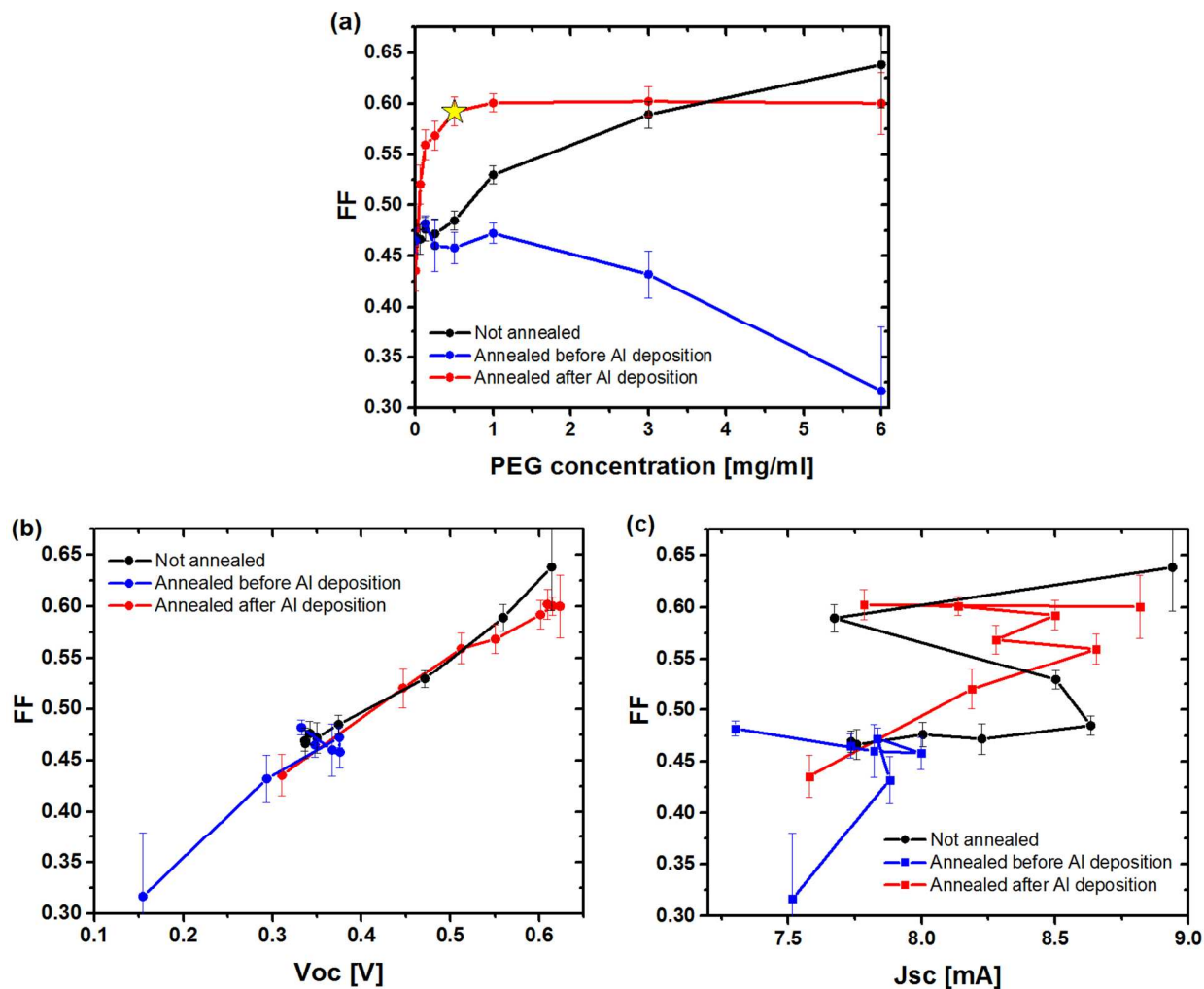


Figure S1. (a) FF as a function of PEG concentration in the processing solution, for devices that were not-annealed (black), annealed before Al deposition (blue), or annealed after Al deposition (red). The FF trends are consistent with Voc trends, and the star highlights the FF saturation point at  $\sim 0.5$  mg/ml PEG, which is also consistent with the Voc saturation. The FF strong correlation with Voc (b), and lack of correlation with Jsc (c) manifest that the device PCE improvement is fully associated with Voc enhancement induced by PEG additive. Therefore, we confine our discussion to the correlation between Voc and the modification of the interfacial composition by PEG additive.

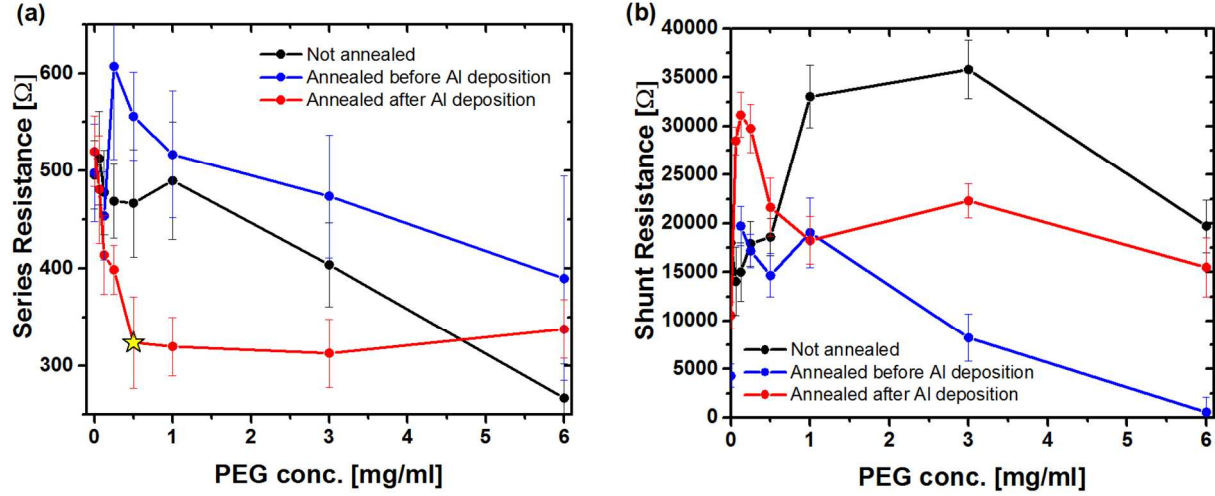


Figure S2. (a) Series resistance  $R_s$ , and (b) Shunt resistance  $R_{sh}$ , as a function of PEG concentration in the processing solution, for devices that were not-annealed (black), annealed prior to Al deposition (blue), or annealed after Al deposition (red). For devices that were not-annealed (black) and devices annealed after Al deposition (red), PEG additive decreases the  $R_s$  and increases  $R_{sh}$ , enhancing the diode ideality. The star highlights the  $R_s$  saturation at  $\sim 0.5$  mg/ml PEG, in good agreement with the saturation obtained for PEG content at the organic/metal interface extracted from the  $V_{oc}$  and FF analysis in the manuscript. For devices annealed before Al deposition (blue) high PEG concentration shorts the device, as evident from substantially decreased  $R_{sh}$  values.

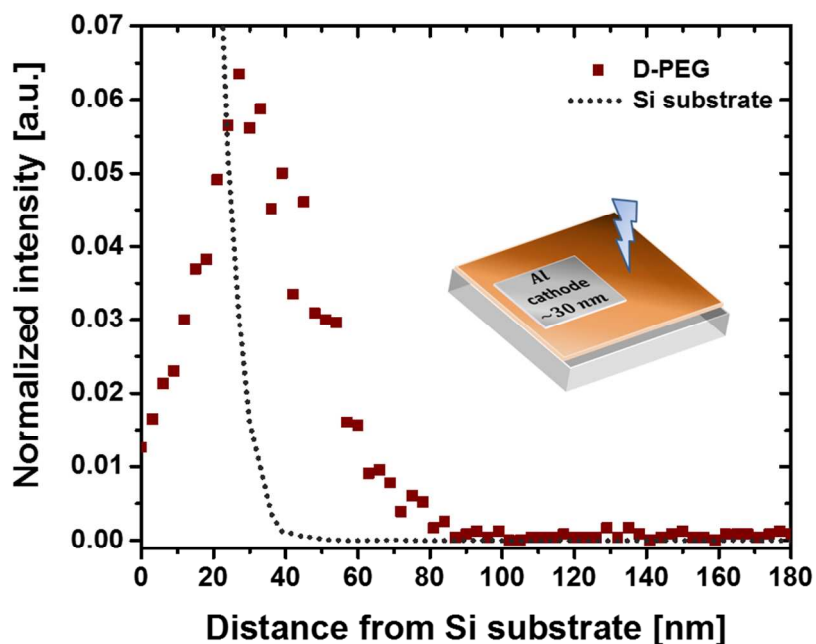


Figure S3. Normalized Dynamic Secondary Ion Mass Spectroscopy (DSIMS) depth profiles of a P3HT:*D*-PEG film with no PC<sub>71</sub>BM, deposited on Si substrate. The normalized intensity of deuterium in the depth profile is directly proportional to the amount of *D*-PEG in that depth. The normalized depth profile shows a single peak of accumulated *D*-PEG near the silicon substrate. The absence of the *D*-PEG doublet observed for all P3HT:PC<sub>71</sub>BM:*D*-PEG films (Figure 6 in manuscript) suggests a PC<sub>71</sub>BM rich phase is responsible of the peak doubling.