**Supporting Information**

# Reproducible, High Performance Fully-Printed Photodiodes on Flexible Substrates Through the Use of a Polyethylenimine Interlayer

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## S1. Characterization of PEI films

S1.1 AFM measurements of PEI films printed on PEDOT:PSS

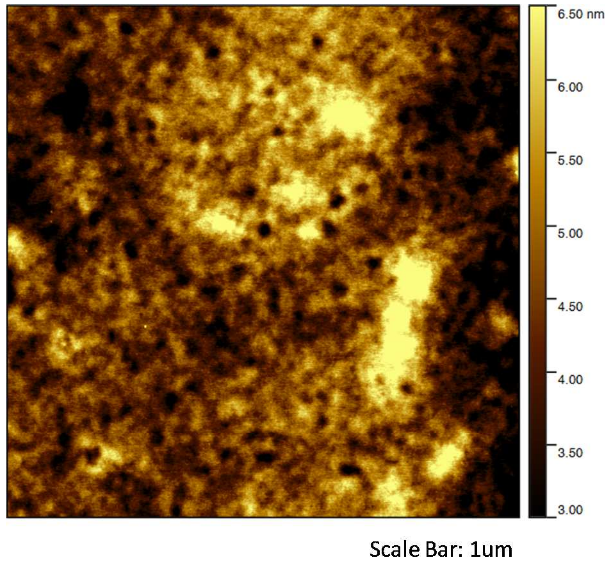


**Figure S1.** AFM measurement of PEIH2O printed film (4 layers, 35 μm drop spacing).

Rougness (rms): 0.940 nm.

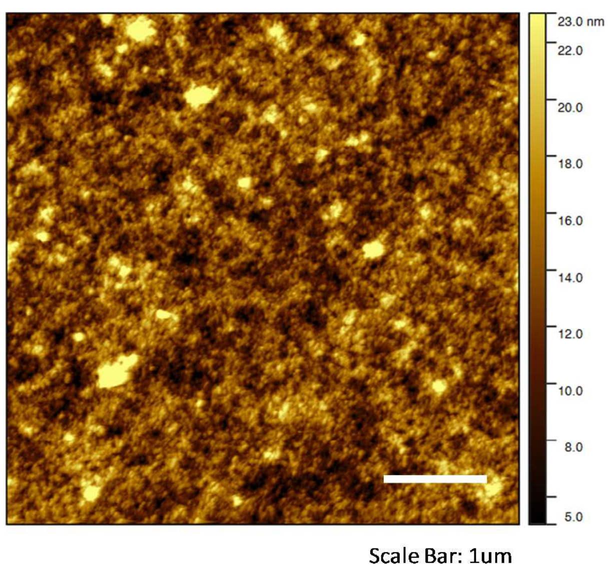


**Figure S2.** AFM measurement of PEI0.2 printed film (2 layers, 35 μm drop spacing).

Rougness (rms): 3.40 nm.

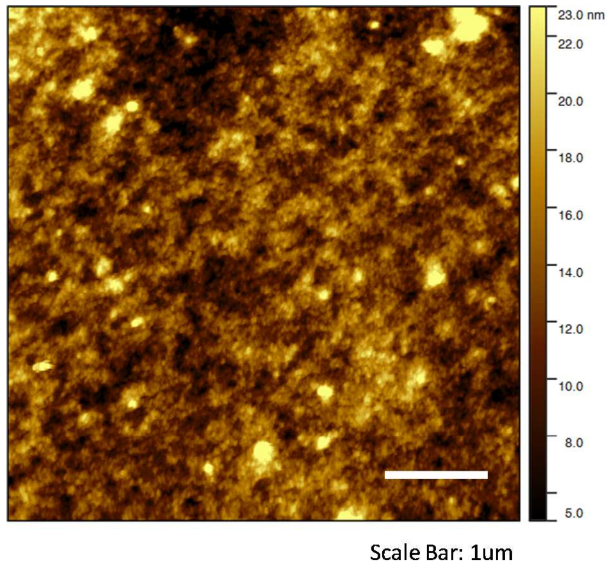


**Figure S3.** AFM measurement of PEI0.3 printed film (2 layers, 45 μm drop spacing).

Rougness (rms): 3.37 nm.

S1.2 Surface profile measurements of PEI films printed on PEDOT:PSS

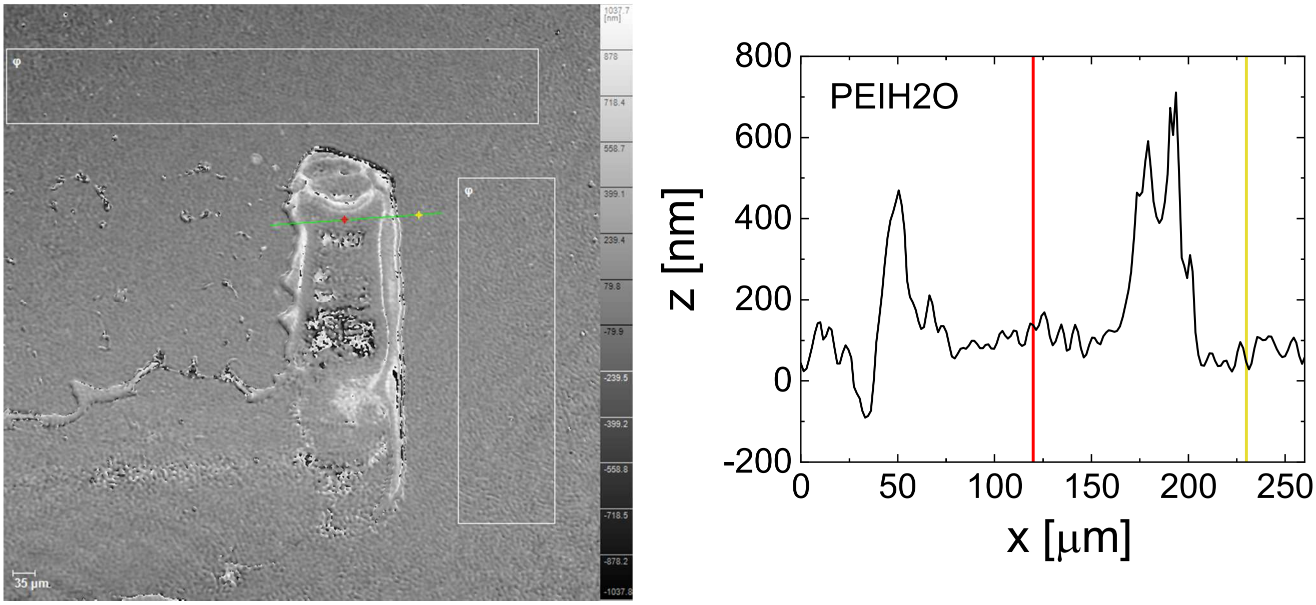


**Figure S4**. Surface profile of PEIH2O printed film (4 layers, 35 µm drop spacing).

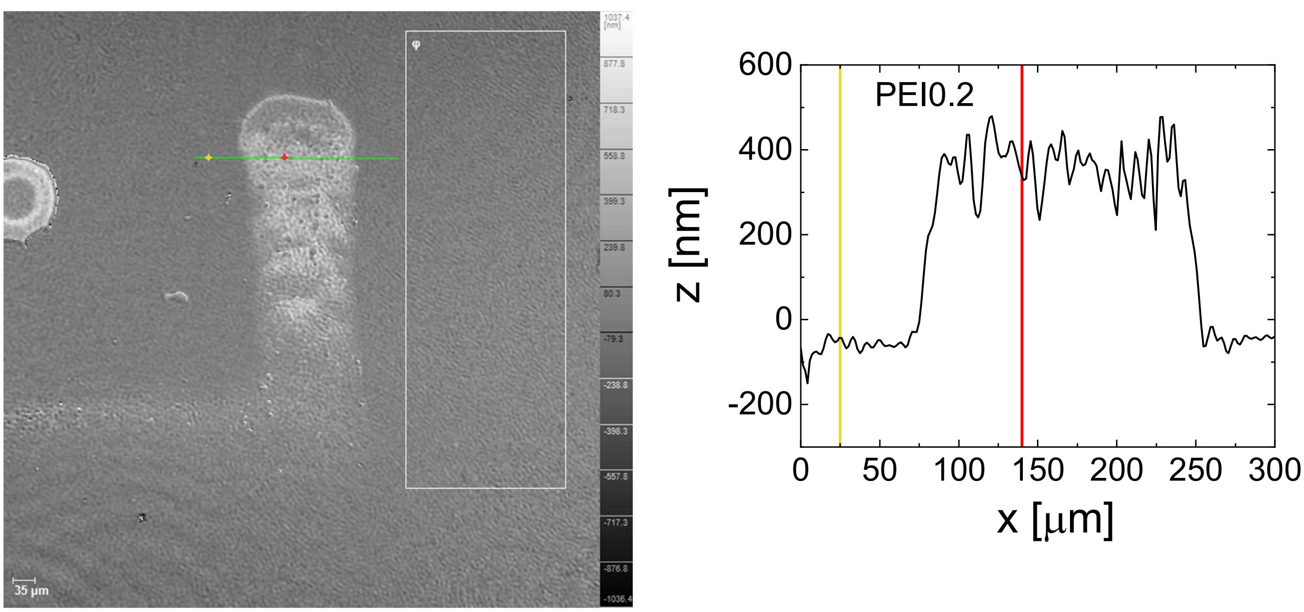


**Figure S5**. Surface profile of PEI0.2 printed film (2 layers, 35 µm drop spacing).

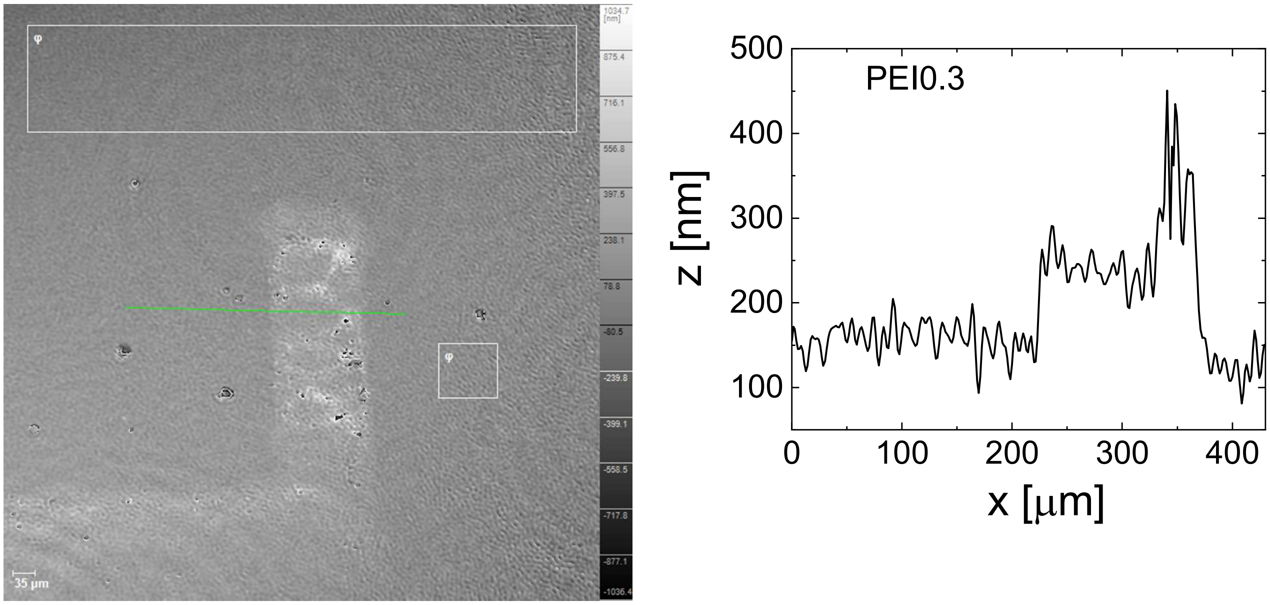


**Figure S6**. Surface profile of PEI0.3 printed film (2 layers, 45 μm drop spacing).

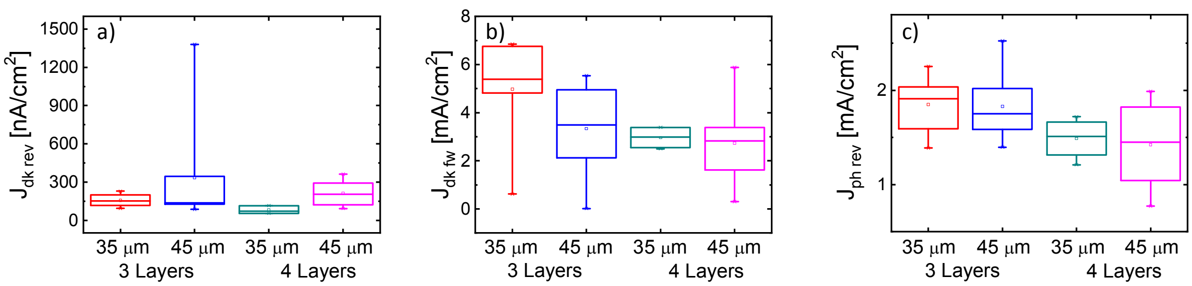


**Figure S7.** Current density boxplots for different combinations of drop spacing and layer number used for PEI interlayer single-solvent ink. Figure S7a: reverse bias (-1 V) current density in dark ($J_{dk\ rev}$). Figure S7b: forward bias (1 V) current density in dark ($J_{dk\ fw}$). Figure S7c: reverse bias (-1 V) photocurrent density ($J_{ph\ rev}$).

**S2. Effect of drop spacing and layer number in PEIH2O ink**

Drop spacing and number of printed layers of PEI are to be optimezed separately for each ink, and they tend to have an effect on device quality, the entity of which depends on the solution composition. This effect on reproducibility of device performance is also found in PEIH2O devices, and is evaluated in terms of reverse bias (-1 V) and forward bias (1 V) current in dark conditions, and reverse bias photocurrent under 1 mWcm$^{-2}$ white light incident power. We compared results obtained varying PEI ink drop spacing between 35 µm, 45 µm or 55 µm and layer number between 1 and 4. Apart from occasionally working detectors, for single and double layer PEIH2O, this resulted in non-rectifying devices, giving $10^7$ nAcm$^{-2}$ at -1 V reverse bias, in dark. This could be due to a deposited material quantity too low to ensure an even coverage of the whole contact surface, leaving quasi-ohmic paths in the vertical stack. Furthermore, 55 μm drop spacing was found to be too high to obtain a uniform deposition, even with a higher number of layers. Passing to 3 or 4 layers, the results shown in the boxplots in Figure S7 were obtained, in terms of current density mean value and dispersion. Devices with 4 layers of PEI and 45 μm drop spacing (colored in pink in the graph) show the worst reverse dark current mean value, over 180 $nAcm^{-2}$, and standard deviation (around 100 $nAcm^{-2}$). The ones with 4 layers and 35 μm drop spacing show a better mean reverse dark current (around 80 $nAcm^{-2}$) with a tighter dispersion, which is less than 50 $nAcm^{-2}$, and also show better reproducibility in forward bias dark current (1 V in the graph) and photocurrent in reverse bias (showed at -1 V). Printing 3 layers with 35 μm drop spacing gives the best rectification ratio (defined as the ratio between dark forward and reverse current evaluated at +1 V and –1 V respectively) and photocurrent over dark current ratio (defined as the ratio between the photocurrent under 1 $mW \cdot cm^{-2}$ white light, and the dark reverse current, both evaluated at -1 V), at the price of a higher reverse dark current mean value. In fact, 3 layer devices have a higher forward current mean value compared to 4 layer ones. This is fairly reasonable, considering that PEI is, in itself, an insulator.

In addition to current measurements, device external quantum efficiency (EQE) was measured. At first, the effect of a different number of layers of PEI on the EQE was evaluated, keeping the drop spacing fixed. Both the graphs in Figure S8, showing average EQE and corresponding dispersion for 3-layer (Figure S8a) and 4-layer (Figure S8b) devices, show values around 90% at 525 nm, which exceed the best fully printed examples in the literature.[1,2] Comparing Figure S8a to Figure S8b, one can conclude that the layer number seems to have just a minor effect on efficiency, apart from slightly higher and less disperse values in 3-layer devices with respect to 4-layer ones. A lower number of layers deposits less material on the contact and favors carrier collection and thus efficiency. In turn, Figure S9a and Figure S9b can give an idea of the effect of a 35 µm drop spacing, versus 45 µm drop spacing, respectively. The collected data sample comes from devices with the same, fixed number of layers (3). The favorable effect of having less material deposited is, again, apparent, with the 45 µm efficiency and value dispersion fairly better than the 35 µm one (average around 100% versus 80%, respectively, at 525 nm). Devices with 3 layers/45 µm spacing, and 4 layers/35 µm have the highest average EQE (over 80% and over 100%, respectively, at 525 nm) with the smallest dispersion (standard deviations under 20% EQE).

EQE values higher than 100%, noticeable in PEIH2O detectors, underline the presence of a photoconductive behavior in these devices. The same phenomenon was also found in P3HT:PCBM photodetectors from a previous work, showing a similar structure, but without being entirely printed, (reference,[3] page 39, section 2.3.6). Furthermore, photoconduction is also found in other P3HT:PCBM based, solution processed and printed detectors.[4,5,6] EQE values lower than 100% in PEI0.2/0.3 do not exclude a similar photoconductive regime for these devices, but with inferior charge collection capabilities at the interface with the functionalized electrode, resulting in lower EQE, as already mentioned.

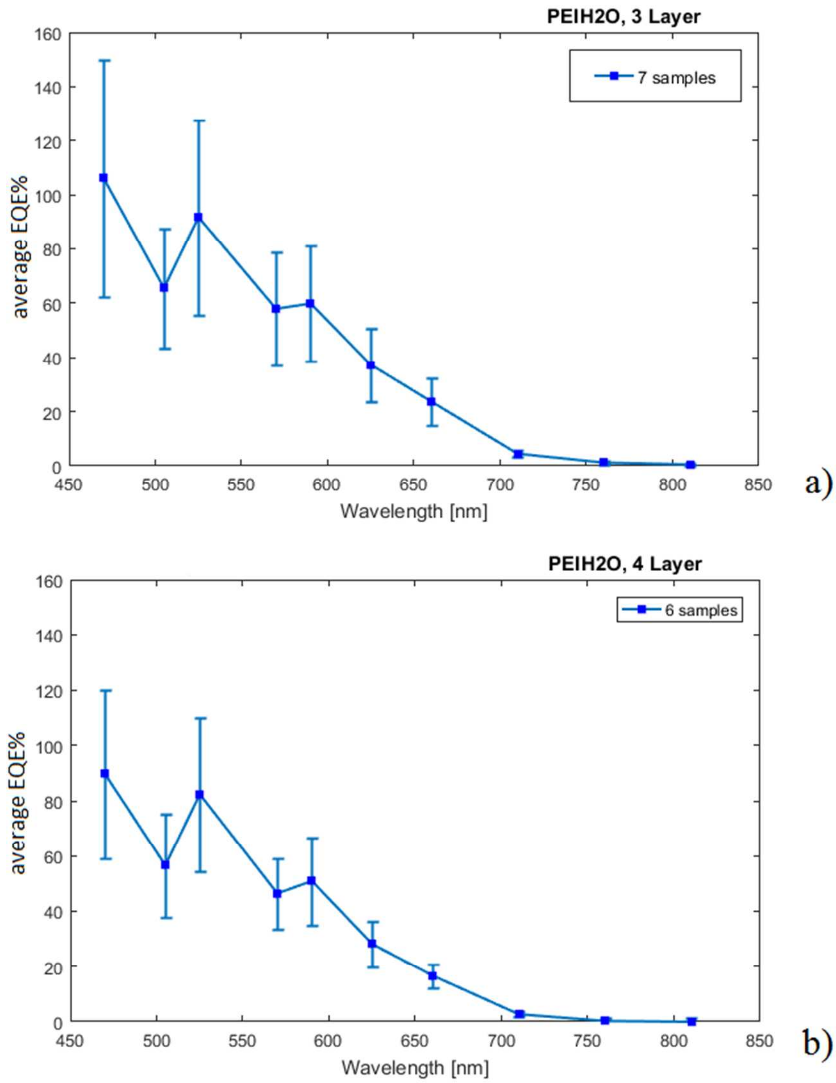


**Figure S8.** Average External Quantum Efficiency and corresponding dispersion from a sample of 7 (Figure S8a) and 6 (Figure S8b) devices, evaluated under 4.3 $mWcm^{-2}$ light power density at different wavelengths for PEIH2O interlayer ink. Figure S8a: devices printed with 3 layers. Figure S8b: devices printed with 4 layers. In both cases, a drop spacing of 35 µm was used for the device interlayer.

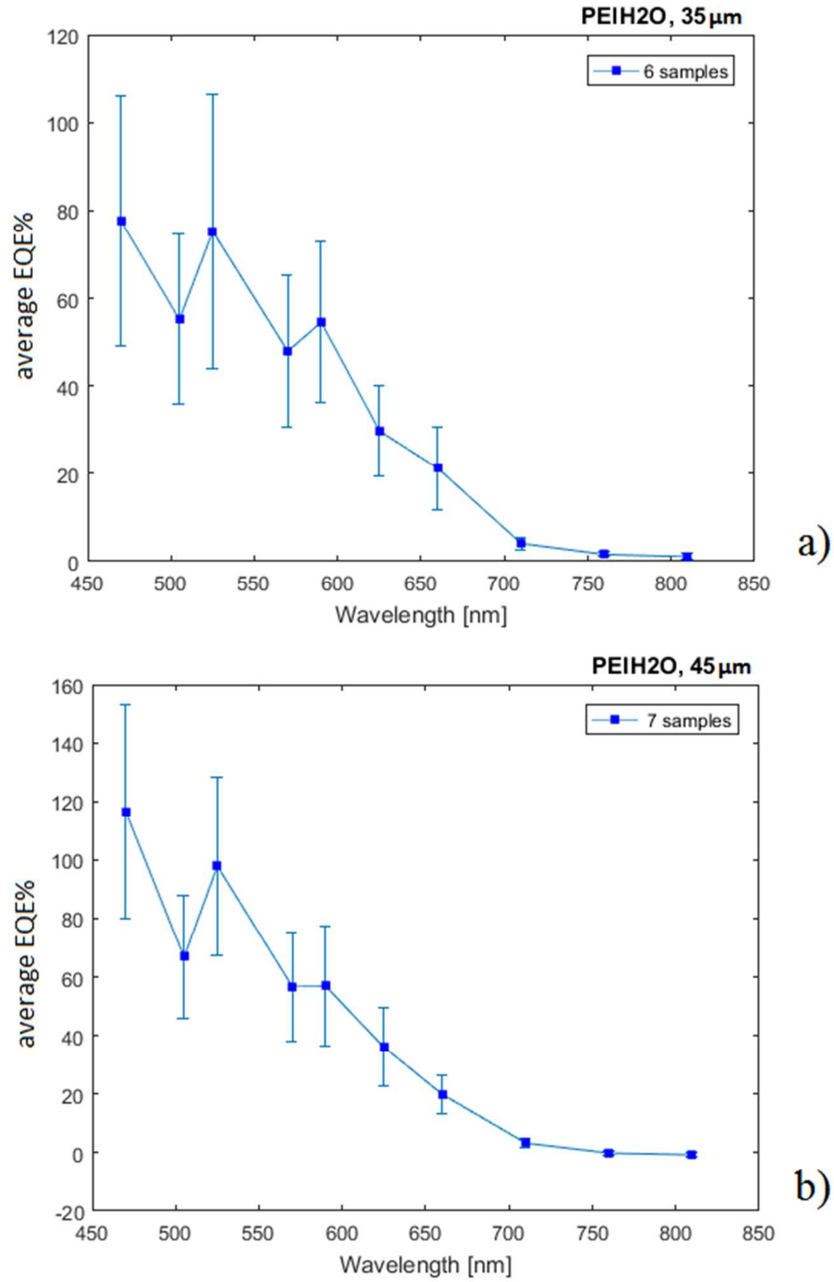


**Figure S9.** Average External Quantum Efficiency and corresponding dispersion from a sample of 6 (Figure S9a) and 7 (Figure S9b) devices, evaluated under 4.3 $mWcm^{-2}$ light power density at different wavelengths for PEIH2O interlayer ink. Figure S9a: devices having a PEI interlayer printed with 3 layers and a 35 µm drop spacing. Figure S9b: devices having PEI printed with 3 layers and a 45 µm drop spacing.

**S3. Confidence intervals for dark current and photo-current in PEI0.3 45μm 2Layers and PEI0.2 35μm 2Layers**

**Table S1**

| | $J_{dk\ rev}$ [nA/cm$^2$] | | |
|---|---|---|---|
| | Lower 90% | Mean | Upper 90% |
| PEI0.3 45μm 2L | 52.56 | 56.93 | 61.24 |
| PEI0.2 35μm 2L | 58.86 | 68.67 | 78.34 |

| | $J_{ph\ rev}$ [mA/cm$^2$] | | |
|---|---|---|---|
| | Lower 90% | Mean | Upper 90% |
| PEI0.3 45μm 2L | 0.96 | 1.02 | 1.08 |
| PEI0.2 35μm 2L | 0.97 | 1.05 | 1.13 |

From data of Fig. 3, we have calculated the 90% confidence intervals (CI) for the mean $J_{dk\ rev}$ and $J_{ph\ rev}$. Focusing on $J_{dk\ rev}$, the two CIs (52.3-61.24 and 58.9-78.3) barely overlap, therefore the conclusion that dark current in PEI0.3 45μm 2L is lower than in PEI0.2 35μm 2L is statistically relevant.

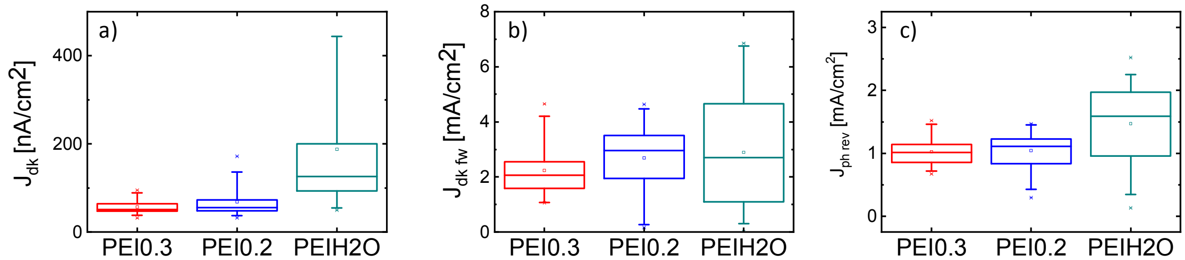


**Figure S10.** Current density comparison boxplots for reverse dark currents at -1 V bias (Figure S10a), forward dark currents at 1 V bias (Figure S10b) and reverse photocurrents at -1 V bias (Figure S10c). Each plot compares results for PEI0.3 (red), PEI0.2 (blue) and PEIH20 (green) solution compositions, considering both 35 µm and 45 µm drop spacings, for a more ink-related evaluation.

**S4. Single solvent and multiple solvent aqueous solutions general comparison**

A more ink-related scenario of comparison between the tested inks, considering for each composition all the combinations of number of printed layers and drop spacings, can start from an examination of the current density boxplots included in Figure S10. It must be stressed that the most important advantage of the multisolvent approach with respect to the single solvent one is the outstanding gain in process yield. The reason for presenting this comparison is to have a general resume of the obtained results. A sample consisting of 34 devices from each ink composition is used to build up a statistical evaluation in terms of current density mean values and dispersion, for reverse (-1 V bias) and forward (1 V bias) current in dark, and reverse (-1 V bias) photocurrent (evaluated under 1 mWcm$^{-2}$ white light incident power as in the previous sections). It is apparent, looking at the reverse current values in dark (Figure S10a) and light

(Figure S10c) that the multiple solvent compositions grant an important improvement in terms of value dispersion and performance reproducibility, at the cost of an inferior photocurrent collection capability. The reverse dark current standard deviation drops from hundreds of $nAcm^{-2}$ to tens of $nAcm^{-2}$, as summarized in **Table 1** of the paper. In turn, single solvent PEI devices have an average photocurrent exceeding 1.5 $mAcm^{-2}$, versus an approximate average of 1 $mAcm^{-2}$ noticeable in PEI0.2 and PEI0.3, which anyway remain less disperse. Limiting the comparison to the two multi-solvent inks, measurements show that PEI0.3 gives better reproducibility, at the expense of lesser performance on the best devices, as one can notice from Figure S10a, S10b and S10c. In fact, PEI0.2 shows excellent results (best case rectification ratio of $10^5$, with reverse dark current density of 37 $nAcm^{-2}$) alternated with poor ones (worst case rectification ratio of $8\cdot10^3$, with reverse dark current density of 127 $nAcm^{-2}$).

The tradeoff, observed in PEIH2O versus PEI0.2/0.3, between reproducibility and photocurrent collection capability is coherent with the results shown in Figure S11, and Figure 4 of the paper on EQE, which in PEIH2O devices is higher at each measured wavelength (around 100% at 470 nm and 90% at 525 nm in PEIH2O, versus 60% at 470 nm and 50-45% at 525 nm in PEI0.2/0.3). Each EQE plot is shown together with the IV characteristic of the corresponding best device in dark and under white light (1 $mWcm^{-2}$). Interestingly, considering interlayers deposited with optimized drop spacing/layer number combinations, PEI0.2/0.3 have a slightly faster time response with respect to PEIH2O ones. Furthermore, an improvement is recorded for the respective standard deviations of the medium (8.69 µs for PEIH2O, 2.57 µs for PEI0.2, 3 µs for PEI0.3) and slow (31.9 µs for PEIH2O, 13 µs for PEI0.2, 17.61 µs for PEI0.3) time constants.

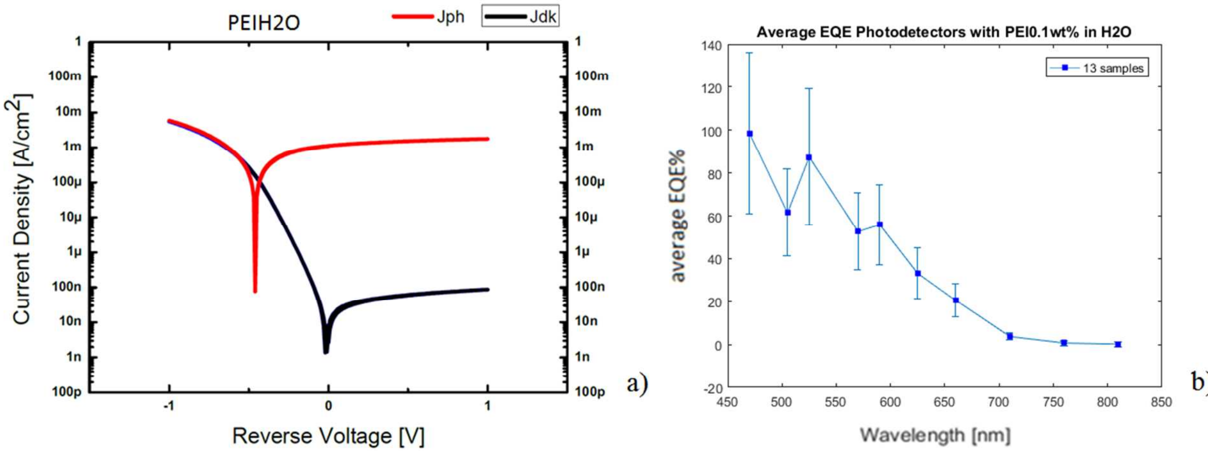


**Figure S11.** Figure S11a: IV plot of the best PEIH2O device, in dark (black curve), and under 1 $mWcm^{-2}$ (red curve). Figure S11b: External Quantum Efficiency, with corresponding dispersion from a sample of 13 PEIH2O devices, evaluated under 4.3 $mWcm^{-2}$ light power density at different wavelengths. Devices included in the sample were taken from all the different drop spacing/layer number combinations that resulted in working detectors, for a more ink-related evaluation. The average EQE is noticeably higher at each evaluated wavelength in devices printed with this ink with respect to multi-solvent printed ones.

## S5. Effect of relative humidity during PEI printing

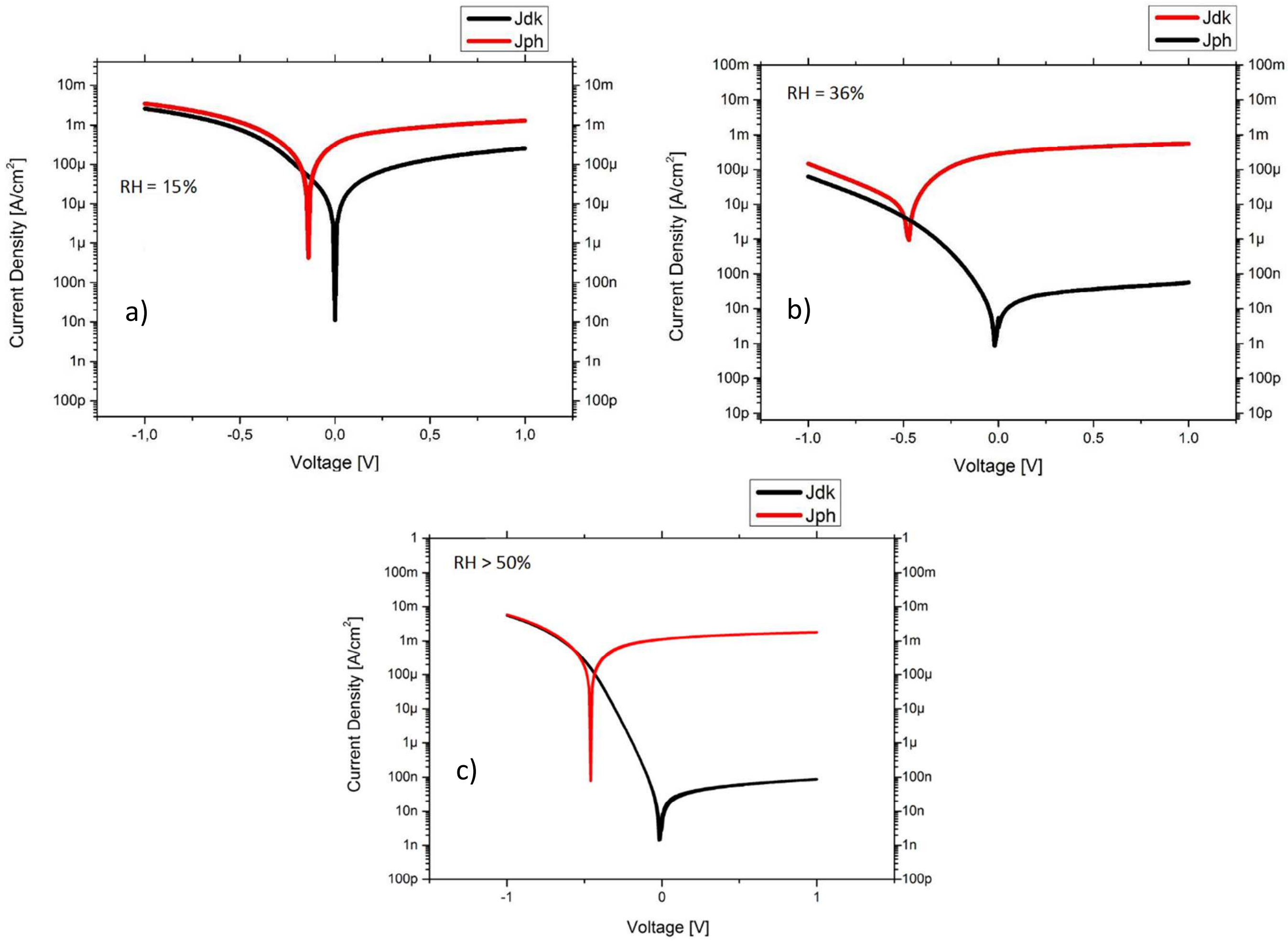


**Figure S12.** Current/voltage characteristic of photodetectors in dark (black curve) and under 1 mWcm$^{-2}$ impinging white light (red curve), measured in nitrogen after a rest period in inert atmosphere of over 24 hours for the device. The photodiodes have an interlayer printed with PEI0.3 ink using optimized parameters (2 layers and 45 µm drop spacing) at 15% relative humidity (Figure S12a), 36% relative humidity (Figure S12b) and relative humidity higher than 50% (Figure S12c). Notice the high reverse currents and poor rectification ratio in Figure S12a, leaving scarce room for light detection, and the gradual improvement towards higher humidity values.

**References**

[1] Pierre, A; Deckman, I.; Lechêne, P. B.; Arias, A. C. High Detectivity All-Printed Organic Photodiodes *Advanced Materials*, **2015**, 27, 6411-6417.

[2] Marcin, K.; Dhez, O.; Pecastaings, G.; Curutchet, A.; Hirsch, L. Long-term stable organic photodetectors with ultra low dark currents for high detectivity applications *Scientific Reports*, **2016**, 6.

[3] Grimoldi, A. Integration of Direct-Written Organic Photodetectors and Organic Transistors: Towards Passive Pixels for Plastic Large-area Imagers *PhD Thesis*, Politecnico di Milano, **2016**.

[4] Grimoldi, A.; Colella, L.; La Monaca, L.; Azzellino, G.; Caironi, M.; Bertarelli, C.; Natali, D.; Sampietro, M. Inkjet Printed Polymeric Electron Blocking and Surface Energy Modifying Layer for Low Dark Current Organic Photodetectors *Organic Electronics*, **2016**, 36, 29-34.

[5] Li, L.; Zhang, F.; Wang, J.; An, Q.; Sun, Q.; Wang, W.; Zhang, J.; Teng, F. Achieving EQE of 16,700% in P3HT:PC71BM based Photodetectors by Trap-assisted Photomultiplication *Scientific Reports*, **2015**, 5, 9181.

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