Supplementary Information

Organic Solar Cells Based on Nanoporous P3HT Obtained from Self Assembled P3HT:PS Templates

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In the Supporting Information, we provide further characterization of the nanostructured films and devices obtained based on these films.

More specifically, AFM depth profiles as well as larger scale AFM images of the nanostructured obtained with 15, 25 and 35 PS wt% are displayed in Figure SI1. With this insight of the structures obtained, we can appreciate in a better way the pore regularity on a larger area.

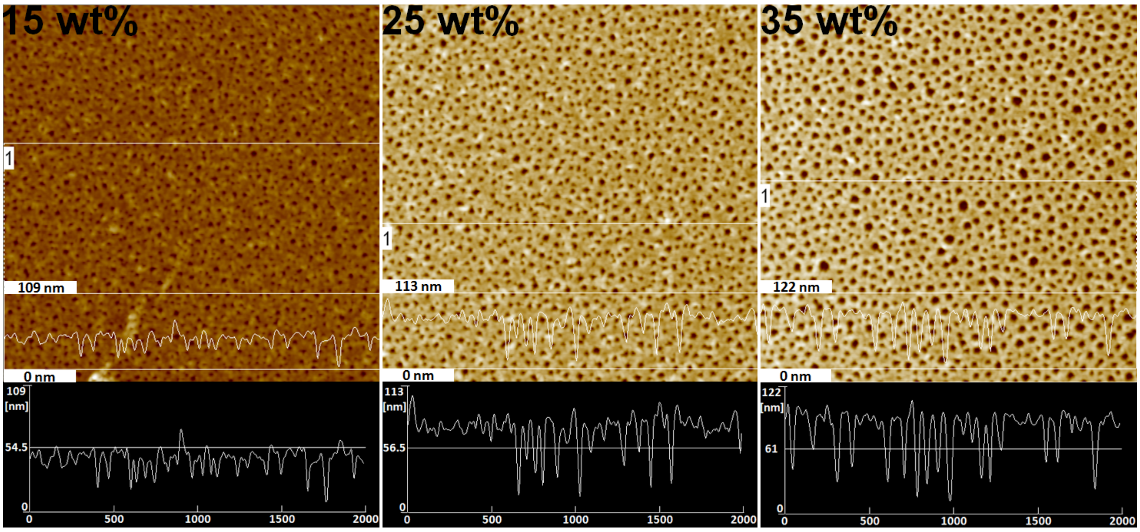

Figure SI1. 20 x 20 μm AFM images of the nanostructures obtained with 15, 25 and 35 PS wt% and their corresponding cross-section profiles.

These structures are obtained specifically with the chosen molecular weights (Mw) for both P3HT and PS. The low Mw P3HT used for the experiments is well adapted for device fabrication but higher Mw P3HT such as the ones used in literature may result in higher performances (reaching up to 3.5% of efficiency in average).[SI1,SI2]

For a better understanding of our choice for the device architecture, more specifically, for the choice of the cathode (only aluminum unlike the calcium/aluminum electrode used in literature),[SI1,SI2] we provide further comparison with the state-of-art of the graded bilayer devices. As can be seen in the main article, our reference device does not display efficiencies as high as 3.5 %. This is related to a few limitations resulting from the use of a P3HT with specific Mw (21 000 g/mol). Unlike the P3HT used in literature (Mw = 45 000 g/mol), we cannot anneal the thin films prior to electrode deposition as this results in much lower efficiencies. P3HT may migrate in the vertical direction through similar pre-annealing and with the low Mw P3HT used in our work, there is a larger probability to observe such migration. Unlike Ca/Al, using only Al allows post-annealing the devices which then exhibit much higher performances than the pre-annealed ones with Ca/Al as the top electrode. We also optimized the post-annealing conditions to get good reproducibility with a post-annealing of 140°C for 10 min. Results using an annealing temperature of 150°C for 10 min demonstrate better device performances for about half the devices but the remaining half display a remarkable decrease in fill factor (FF) leading to lower efficiencies. In Table SI2, we summarize the performances of devices obtained with efficient annealing.

As this work is a proof of concept regarding the influence of the pore dimensions over the device performances, we chose the spin-coating conditions (P3HT:PS blends spin-coated at 1500 rpm for 30s) that provides the widest range of pore dimensions. Furthermore, the use of high boiling point solvents such as dichlorobenzene is known to give better performances but no nanoporous structures are obtained if dichlorobenzene is used as the solvent. Last but not least, in order to fill the pores as much as possible, the optimized conditions for PCBM spin-coating (4000 rpm for 10s) were modified. We choose to spin-coat the PCBM solution in dichloromethane (10 mg/ml) at 2000 rpm for 30s. However, in Table SI2, we find the comparison between both PCBM spin coating conditions.

PS wt%/PCBM spin-coating speed	**Jsc (mA/cm^2)**	**Voc (mV)**	**FF (%)**	**PCE (%)**
0 wt% / 2000 rpm	10.0	591	46.6	2.75
0 wt% / 4000 rpm	9.79	604	50.7	2.99
15 wt% / 2000 rpm	9.09	602	53.8	2.95
15 wt% / 4000 rpm	8.81	610	57.9	3.12
25 wt% / 2000 rpm	10.0	611	54.3	3.32
25 wt% / 4000 rpm	9.26	611	56.4	3.19
35 wt% / 2000 rpm	9.67	619	54.6	3.27
35 wt% / 4000 rpm	8.14	612	59.9	2.98

Table SI2: summary of the device performances obtained under various conditions. All devices are post-annealed at 150°C for 10 min.

As we can observe inTable SI2, the device performances greatly depend on the

PCBM deposition conditions. Theoretically, while the faster spinning condition (4000 rpm) leads to enhanced photovoltaic performances for the low surface roughness P3HT films (up to 15 wt%), the slower spinning condition (2000 rpm) allows a better filling of the porous structures resulting in higher efficiencies for the 25 and 35 PS wt% films. Interestingly, as we can see in Figure SI2, the device performances perfectly follow these trends.

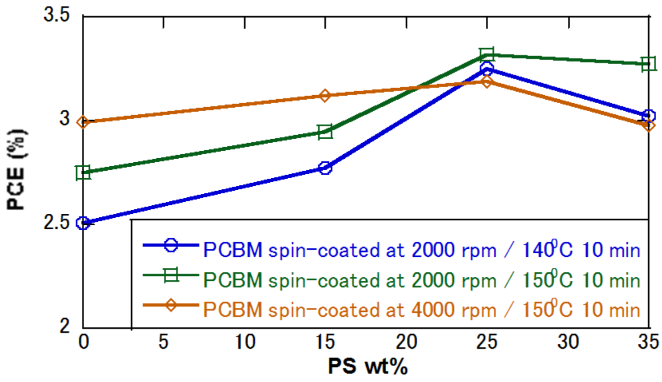

Figure SI2. Evolution of the PCE with increasing PS wt% from device fabricated under various conditions, namely, with PCBM spin-coated at either 2000 rpm (blue and green) or 4000 rpm (red) and the resulting devices annealed at either 140°C (blue) or 150°C (green and red).

Throughout literature on graded bilayer structures, the reproducibility of the results seems to be a major issue (maximum efficiencies of 3.8 % with an average of 3.5 % for similar conditions).[SI1,SI2] In the main text of our work, we focus on obtaining reproducible results (annealing at 140°C for 10 min) and chose the optimized conditions for nanostructured devices. To be able to compare the influence of nanostructures over the device performances, we compare them to devices obtained in the same conditions. However, the optimized nanostructured devices even overcome the performances of the optimized planar devices as the pores obtained (e.g. for the 25 PS wt% films) are partially filled during the spin-coating process.

References (Supporting Information):

(SI1) A. L. Ayzner, C. J. Tassone, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C*, 2009, **113**, 20050–20060.

(SI2) K. H. Lee, P. E. Schwenn, A. R. G. Smith, H. Cavaye, P. E. Shaw, M. James, K. B. Krueger, I. R. Gentle, P. Meredith, P. Burn, *Adv. Mater.*, 2011, **23**, 766-770.