

Supplementary Information

Nanostructured organic layers via polymer demixing for interface-enhanced photovoltaic cells

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Supplementary Information S1

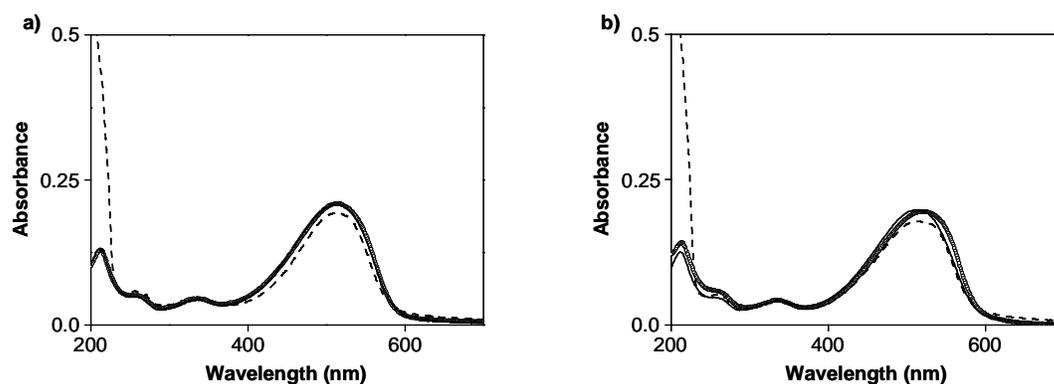


Figure S1. Absorbance spectra of MEH-PPV and MEH-PPV / PS films before and after PS removal. Dashed line, from (a), a blend of MEH-PPV / PS ($M_n = 3000$, 1 : 2 w w⁻¹), (b), a blend of MEH-PPV / PS ($M_n = 70000$, 1 : 2 w w⁻¹) in chlorobenzene. Open circles, of the same films after dipping in cyclohexane solution for 1 minute. Solid line, absorbance spectra of a MEH-PPV-only film, used for comparison. The disappearance of the absorbance at 200 – 250 nm proves the dissolution of PS, the constant absorbance in the 400 – 600 nm range shows that MEH-PPV is not affected by cyclohexane.

Supplementary Information S2

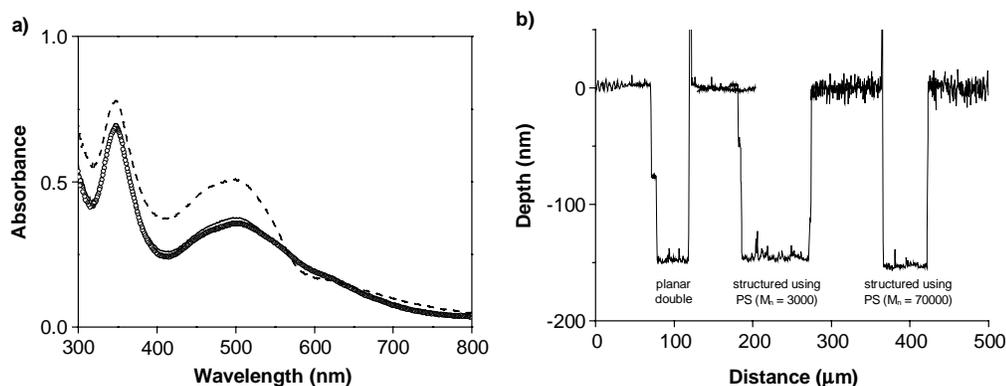


Figure S2. Absorbance spectra and total organic layer thickness of photovoltaic devices. The device structure was ITO / PEDOT:PSS (80 nm) / MEH-PPV / C₆₀ (40 nm) / Al. Measurements were taken in regions without top aluminium cathode. (a), Absorbance spectra using ITO / PEDOT:PSS as the baseline of a planar double layer (solid line), a structured device using PS ($M_n = 3000$) (open circles) and a structured device using PS ($M_n = 70000$) (dashed line). Structured devices were spin-coated from a 1 : 2 w w⁻¹ MEH-PPV / PS blend in chlorobenzene and PS was removed by dipping in cyclohexane for 1 minute. (b) The thicknesses of the organic layers were measured with a profilometer. The constant thickness of ~ 150 nm for all three devices represents the sum of the individual PEDOT:PSS (80 nm), MEH-PPV (~ 30 nm), and C₆₀ (40 nm) layers. The increase in absorbance for the device structured with PS ($M_n = 70000$) points to some light scattering at the surface. This is supported by the AFM cross section shown in Fig. 2Cf, where topographic undulations with dimensions in the range of the wavelength of light are visible.

Supplementary Information S3

Evaluation of electric field effects induced by the rough cathode interface

As we have observed by AFM measurements on structured MEH-PPV layers covered by an evaporated C₆₀ layer, the surface roughness of the MEH-PPV layer determines the surface roughness of the C₆₀ layer. Our best devices used a structured MEH-PPV layer obtained from a blend using MEH-PPV / PS3 (1 : 2 w w⁻¹) in chlorobenzene. Therefore, we have taken these devices to model possible field enhancement effects due to roughness. Since the electric field distribution is governed by the shape of the device electrodes in contact with the organic material, we have taken the roughness of the C₆₀ surface to model the roughness of the aluminium electrode. Typically, the peak-to-valley distance is ~ 5nm and the peak to peak lateral separation is about 50 nm.

To evaluate the effect of a rough cathode interface, a periodic two-dimensional equipotential surface was produced by placing appropriate dipoles in a periodic array and calculating the equipotential surfaces using standard software (Mathematica). At appropriate conditions an equipotential surface having a peak-to-peak distance of 50 nm and a peak-to-valley height of 5 nm can be produced. This surface is taken to represent the electrode surface. At the same time, the equipotential surfaces above the electrode are obtained (Fig. S3-1).

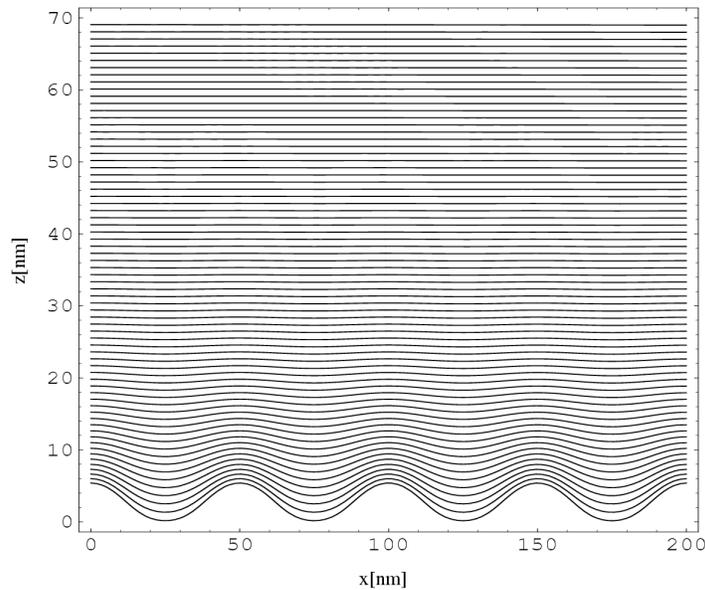


Figure S3-1. Equipotential lines of a two-dimensional array of dipoles being placed in a quadratic lattice with a lattice parameter of 50 nm. The strength of the dipole was adjusted in such a way that there is an equipotential line reflecting the cathode surface roughness in an approximate way.

The electric field in space may then be read from the separation among equipotential surfaces. Fig. S3-1 shows that the electric field is stronger close to hills of the electrode and lower than average in valleys. The relative electric field distribution $F(x,z)/F_0$ can be calculated from the equipotential surfaces of Fig. S3-1. $F(x,z)$ is the field distribution at a given coordinate x on the surface and at a given distance z from the lowest equipotential surface in Fig. S3-1 (representing the cathode surface) while F_0 is the field at infinite z . The relative field strength reaches a constant value after about 20 nm from the electrode surface. Since we are dealing with a linear electrostatic problem, the relative field distribution is independent of the difference in the electrostatic potential between the rough electrode and another flat electrode at a far enough distance z , represented by flat equipotential lines towards the top of Fig. S3-1.

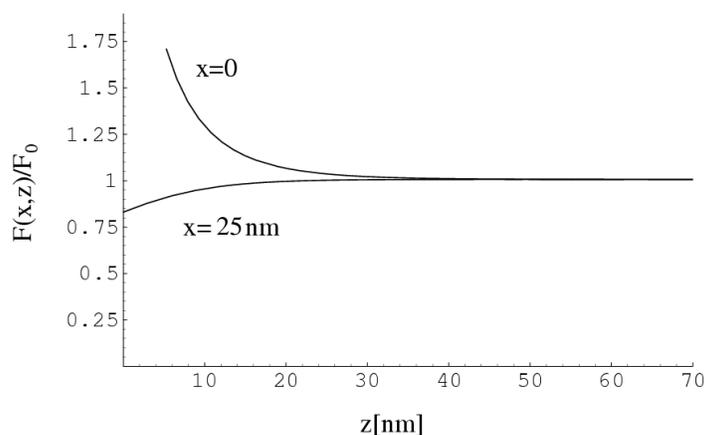


Figure S3-2. Relative field dependence $F(x,z)/F_0$ plotted as a function of distance z perpendicular to the equipotential line representing the cathode surface (lowest lying line in Fig. S3-1).

From this model we can deduce that no field enhancement is present at the organic heterointerface between C_{60} and MEH-PPV situated at 40 nm from the cathode surface. Therefore, we can exclude that better charge separation is induced by a field enhancement effect due to the rough cathode interface. The electric field is enhanced close to the hills of the cathode (about a factor of two at a distance of 5 nm from the electrode), which facilitates electron collection at the aluminium / C_{60} interface. However, since the lowest unoccupied molecular orbital (LUMO) of C_{60} aligns with the Fermi level of the metal [Ohno, T.R. *et al.* C_{60} bonding and energy-level alignment on metal and semiconductor surfaces, *Phys. Rev. B* **1991**, *44*, 13747-13755], it is not likely that electron injection from C_{60} to aluminium is a limiting factor for the current in MEH-PPV / C_{60} photovoltaic cells. Therefore, the rise in performance using the structuring method cannot be attributed to field enhancement effects due to the rough cathode surface.