

Characterization by Confocal Laser Scanning Microscopy of the Phase segregation at interfaces in thick films of Organic Blends

S. Lattante,¹ A. Perulli,² M. Anni,¹

¹Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, Italy

²Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Italy

In the last few years it has been well demonstrated, using several complex experimental techniques, that many systems composed of organic blends undergo a vertical phase stratification. In particular the vertical stratification of the prototype poly(3-hexylthiophene) (P3HT) blended with PCBM has been characterized by several experimental techniques, like (just to cite some) UV and X-ray photoelectron spectroscopy (UPS and XPS) [1], X-ray diffraction (XRD) [2], near-edge X-ray absorption fine structure spectroscopy (NEXAFS) [3], all confirming the accumulation of PCBM on the bottom interface and of P3HT at the top interface. Although Confocal Laser Scanning Microscopy (CLSM) can not attain the spatial resolution proper of the above mentioned techniques (in the nm scale), being limited by the diffraction of light, it is nevertheless a simple, time-preserving, diffused and user friendly technique to be exploited for a fast and preliminary check of experimental parameters that can be of importance in designing a particular experiment where a high layer thickness is desirable. For instance the vertical phase stratification in polymer blends is a key parameter to be known in order to properly understand and characterize the physics and behavior of thick organic sensor or planar waveguides: indeed, although very thin organic layers ($\leq 100 \div 200$ nm) are usually requested in devices like bulk heterojunction solar cells [4], in many other application a thick organic layer is on the contrary desirable. For example the ideal thickness of bulk heterojunction organic based photodiodes for image sensing should be $\sim 4 \mu\text{m}$ in order to drastically reduce the reverse bias dark current [5] or to obtain high illuminance detection from ink-jet printed photosensors based on thick ($\sim 1 \mu\text{m}$) luminescent polymer blends [6]: since the usual device structure is the diode-like one where the active layer is sandwiched between two conductor layers, it should be important to know if there is a difference in the blend composition at the interfaces in order to chose the proper top and bot-

tom conductive layers (usually transparent conductive oxides like Indium-Tin Oxide or Fluorine-Tin Oxide and metals like Al or Ag) in order to improve the charge injection/extraction matching the interfaces between the hole (electron) injection/extraction conductive layer with the hole (electron) transporting phase inside the active layer blend. Moreover thick samples are also requested when studying the waveguide-assisted Amplified Spontaneous Emission (ASE) from organic layers composed of luminescent species embedded into polymer inert matrix [7] or lasing effects on thick bilayers [8]: since the optical gain in the waveguide is strongly dependent on the thickness of the active layer and on the overlap between the gain media, the pump laser beam and the electromagnetic field inside the waveguide [9–11], it should be important to know if there is a graded stratification (for instance accumulation on one side of the sample) in the luminescent phase inside the wave-guiding layer.

In this first activity the P3HT:PCBM blend system has been chosen as a standard testing system for the proposed technique, in the form of thick films (range $1 \div 4 \mu\text{m}$) casted onto ultrathin cover glass slides from chlorobenzene solutions with several concentration ratio, both filtering (by a PTFE filter with $0.45 \mu\text{m}$ pore size) and not filtering the initial solutions. The samples have been morphologically characterized by Optical and Confocal Laser Scanning Microscopy with a Nikon Eclipse C1 inverted confocal microscope. Signals were detected simultaneously at 530 ± 20 nm using a bandpass filter and above 770 nm using a high pass filter. The collecting filters have been chosen in order to separate the emission from the two material phases (PL spectra not shown): indeed the 530 nm band pass filter allows to collect the emission generating from the PCBM rich phase only as there is no emission of P3HT below ~ 600 nm, while the 770 nm high pass filter should account mainly for the P3HT rich phase emission.

As an example of the main results, Fig. 1 re-

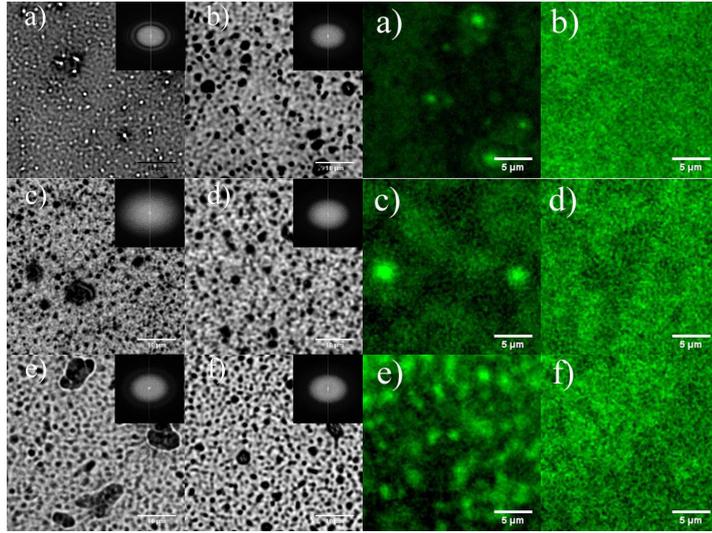


Figure 1. Optical (left) and confocal (right) images of as casted samples: a) and b): 1:1 glass/blend interface and blend/air interface respectively; c) and d): 1:2 glass/blend interface and blend/air interface respectively; e) and f) 2:1 glass/blend interface and blend/air interface respectively (P3HT:PCBM concentration ratio: x:y); insets: calculated 2D FFT. Optical images are $46.08 \times 46.08 \mu\text{m}$ (resolution: $0.09 \mu\text{m}/\text{px}$), Confocal images are $23.04 \times 23.04 \mu\text{m}$ collected @ 770 nm (resolution: $0.09 \mu\text{m}/\text{px}$) (color online)

ports to the left the optical images of the unfiltered samples, along with their two-dimensional Fast Fourier Transform (2D FFT) that has been calculated using the Gwyddion Image Analysis Software [14], while to the right the respective confocal images (collected at 770 nm and above) are reported. Focusing on the optical images, it is clear from the 2D FFT that there is a difference in the texture features between the glass/blend interface and the air/blend interface. The differences are less pronounced for the 2:1 (P3HT:PCBM concentration ratio) sample, indicating that the P3HT phase could be the one that drives the morphological rearrangement of the blend during the solvent evaporation process. The difference between the two surfaces and among the samples can be better analyzed by looking to the averaged radial Power Spectral Density Function (PSDF) [15] of the 2D FFT reported in Fig. 2: while there are little differences in the peak positions in the reciprocal space between air/blend and glass/blend interfaces for the 2:1 sample (main peak at $k = 3 \mu\text{m}^{-1}$ and secondary peaks at $k = 8, 20, 32$ and $39 \mu\text{m}^{-1}$), confirming the hypothesis of a P3HT-driven morphology, a clear peak shift in the lower k range is seen for the 1:1 sample (in particular for the main peak that shifts from 3 to $5 \mu\text{m}^{-1}$) and a more pronounced peak shift for higher k (and shape variation) is seen for the 1:2 samples where the peak at $k = 8 \mu\text{m}^{-1}$, typical of a P3HT-rich phase

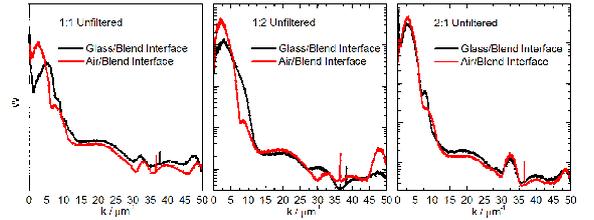


Figure 2. Averaged Radial Power Spectral Density Function for unfiltered samples.

as seen in the 2:1 sample, is only seen for the air/blend interface, indicating a clear variation of morphological composition at the two interfaces. The above considerations can be confirmed by the confocal images at 770 nm channel (reported to the right in Fig. 1) where only the P3HT signal is expected: for the 1:1 and 1:2 sample the signal intensity at the glass/blend interface is weaker than that at the air/blend interface, confirming a P3HT-phase preferential vertical distribution on top of the specimen; the averaged signal intensity is on the contrary less different between the two interfaces for the 2:1 sample. All the above results have been confirmed by the analysis of the images collected at 530 nm (not shown), where the PCBM phase signal is mainly detected at the glass/blend interface. In conclusion, the Confo-

cal Laser Scanning Microscopy has been exploited as a common, simple, fast and user-friendly technique to characterize the prototypical phase composition differences at interfaces of P3HT:PCBM blends with varying mixing ratio. A clear difference in the macroscopic phase content at the bottom and at the top of the samples have been detected, confirming the previous conclusions reported in literature that the PCBM phase has a preferred arrangement on the bottom of the solid film while the P3HT is more diffuse at the top surface. These results are then useful in the preliminary blend morphology characterization field when the phase content at the interfaces is an important parameter to be considered while the thickness of the layer can be or should be of few micrometers. Using the CLSM instead of other techniques like XRD, XPS, UPS, SIMS or Neutron Scattering could indeed allow a fast in-lab checking of the influence of mixing ratio, solvent, annealing and preparation process in a quick few-step experiment.

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