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## Investigation of the spatial inhomogeneity of charge generation and collection in inverted all polymer solar cells

A. Perulli $^1$ , S. Lattante $^2$ , A. Persano $^3$ , A. Cola $^3,$  M. Di Giulio $^2$  and M. Anni $^2$ 

<sup>1</sup>Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via per Monteroni, 73100 Lecce, Italy

<sup>2</sup>Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, Via per Arnesano, 73100 Lecce, Italy,

<sup>3</sup>IMM-CNR, Institute for Microelectronics and Microsystems-Unit of Lecce, National Research Council, Via Monteroni, I-73100 Lecce, Italy

In this report we present the main results of the investigation of the correlation between the local PL and the EQE in a regioregular poly(3-exylthiophene):poly(9,9-dioctylfluorene-co-benzothiadiazole) inverted bulk heterojunction solar cell by laser confocal mapping. Further details can be found in Ref.[1]. We show that the charge generation and charge collection are strongly non uniform on a length scale up to 100  $\mu m$ . Our results evidence that organic solar cells optimization requires not only the control of the submicrometric active materials arrangement, but also the control of the large scale device uniformity.

During the last years the performance of bulk heterojunction solar cells has been improved significantly, up to abuot 12%. Thin film photovoltaic cells based on solution processable organic semiconductors have attracted remarkable interest as a possible alternative to conventional, inorganic photovoltaic technologies. This kind of photovoltaic devices based on organic materials presents the following advantages: low weight and flexibility of the PV modules, semitransparency, easy integration into other products, new market opportunities, e.g. wearable PV, significantly lower manufacturing costs compared to conventional inorganic technologies, manufacturing of organic photovoltaic (OPV) in a continuous process using state of the art printing tools, short energy payback times and low environmental impact during manufacturing and operations (Ref.[2]).

In the frame of developing novel active materials for OPV polymer-polymer blends have been proposed as alternative to polymer-fullerene blends as conjugated polymers have a much higher absorption coefficient in comparison to modified fullerenes in the visible range and they are much easier to obtain with well-tuned energy levels. To date a major drawback of all-polymer



Figure 1. Example of confocal microscope map  $(600\mu m * 600\mu m)$  in three dimensions of the photoluminescence (PL, green) and the photocurrent (PC, blue).

systems has been the tendency to form large phase domains (micron-scale), which considerably limits the device performance (Ref.[3]).

In order to optimize the efficiency of the bulk heterojunction organic solar cells (OSCs) great attention as been denoted to the control of the nanoscale intermixing between the components of the active layer. For this reason, similarly to the investigation of polymer:fullerene systems, several studies have been performed to correlate the device performance and the active layer morphology for polymer:polymer systems. To date all the studies on the local properties of OSCs have been performed by mapping device regions up to  $20\mu m * 20\mu m$  which is much smaller than the whole device active surface (about 1mm \* 1mm).

In this work we investigated, by Confocal Laser Scanning Microscopy, the correlation between local radiative recombination and charge extrac-



Figure 2. PL and EQE maps of the rrP3HT:F8BT blend for a sample region of  $600\mu m * 600\mu m$ . (a) F8BT PL map, (b) rrP3HT PL map, (c) EQE map, (averaged EQE  $\simeq 0.35\%$  for exciting wavelength of 488 nm) (Optical resolution is 1.24  $\mu m/px$ ).

tion in a  $600\mu m * 600\mu m$  region of an inverted all polymer OSC based on a blend of regioregular poly(3-exylthiophene) (rrP3HT) and poly(9,9dioctylfluorene-co-benzothiadiazole) (F8BT). The device was fabricated on fluorine-doped tin oxide (FTO) covered glass substrates, cleaned in an ultrasonic bath. A thin layer (~ 80nm) of Zinc oxide (ZnO) nanoparticles (used as an electron selective layer) was deposited by spincoating onto the substrates from a water dispersion. A chlorobenzene solution of a blend of rrP3HT:F8BT = 60:40 by weight (total concentration of 30 mg/ml) were spin-coated onto the ZnO (polymer blend film  $\sim 150nm$  of thickness). Finally, the silver top electrodes ( $\sim 100nm$ ) were thermally evaporated onto the active layer. The device was annealed in air at 150°C for 20 min after the evaporation of Ag.

The PL and the PC mapping was performed by a Nikon Eclipse C1 Confocal Laser Scanning inverted microscope exciting the samples with the 488 nm line of an argon laser. The PL was collected in backscattering configuration through the bottom transparent electrode and detected by a couple of photo-multipliers (PMTs). The PC signal was measured by a low-noise current preamplifier Stanford Research SR570 and was detected under short circuit condition (0V bias applied to the sample). The PL and PC measurements were synchronized pixel by pixel with the laser scanning on the sample ( $46\mu s$  pixel dwell time).

In order to separate the F8BT and the rrP3HT PL the signal was collected in the 579  $\pm$  25 nm range using a band-pass filter and above 770 nm using a high pass filter. The incident excitation power was  $P = 4.3\mu W$ , measured by a power meter placed on the objective focal plane.



Figure 3. Cross-sectional intensity profiles taken from rrP3HT PL and EQE maps (measured along the white arrows in Fig. 2 (b) and (c)). The dashed line indicates the average PL and EQE values, on the whole profile. The arrows evidence regions of complementary PL and EQE, while the lines evidence regions with constant PL and nonconstant EQE.

In fig. 1 we show an example of confocal microscope map  $(600\mu m * 600\mu m)$  in three dimensions of the photoluminescence (PL, green) and the photocurrent (PC, blue).

The typical F8BT PL, rrP3HT PL and EQE maps of a  $600\mu m * 600\mu m$  region (see Fig. 2) clearly show non uniform signals, with photocurrent values of the order of 10 nA. The main features are:

1) the F8BT and rrP3HT PL maps are not complementary indicating that inhomogeneities in these maps are not due to microscopic phase separation of the two polymers;

2) presence, for both polymers, of common regions of high PL intensity with a typical size from 20  $\mu m$  to 200  $\mu m$ . These bright regions show a PL intensity which is about 20 % higher than the surrounding ones (see scale bars in Fig. 2);

3) Clear complementarity of the PL and EQE maps, with low EQE in the high PL regions, and vice versa. The inhomogeneity of the EQE map is characterized by borders sharper than PL maps, with very low EQE regions extending over most of the investigated area.

Since the competition between the optical recombination and the charge transfer/transport mechanism should results in a complementarity between PL and EQE signals, and as the charge generation efficiency depends on the rrP3HT:F8BT intermixing at the nanoscale, the high (low) EQE regions are likely indicative of a submicrometric rrP3HT:F8BT arrangment favorable (unfavorable) for charge transfers, than resulting in low (high) PL intensity.

The observed spatial non uniformity of both signals indicates the existence of regions, on the scale from tens to hundreds of microns, with locally different submicrometric arrangment. This length scale of these non uniformity is higher than the one to date observed by investigating micrometric sample regions. This result suggests that great care has to be used when correlating the overall device efficiency with the microscopic and sub-microscopic features of the active material, unless the film homogeneity on large scale has been checked.

In order to improve the understanding of the correlation between the local PL and EQE we focused our attention on the intensity profile(measured along the white arrows in Fig. 2 (b) and (c)) of both signals (see Fig. 3). The reported profiles clearly show not only regions (evidenced by the arrows) in which the EQE and PL rrP3HT signal are complementary, but also intervals in which the PL signal is almost constant, while the EQE is strongly varying (evidenced by the bars), like the 80  $\div$  240  $\mu m$  and 350  $\div$  480  $\mu m$  ranges.

The observed lack of correlation between the PL and the EQE in several sample regions clearly evidences spatial inhomogeneity of the charge collection efficiency, showing large variations across the sample on a length scale from tens to hundreds of  $\mu m$ .

We can exclude any relevant role of local thickness fluctuation, that would also greatly affect the PL intensity suggesting that the observed results are due to locally different charge recombination rate related to the blend morphology, and/or to local variation of the charge extraction efficiency from the electrodes.

In conclusion, we observe a strong non uniformity of the charge generation and charge collection efficiency due to the existence of large scale domains with locally different rrP3HT:F8BT submicrometric order, indicating that the correlation between the macroscopic device properties and the local active material ones cannot be limited to the sub-micrometric or micrometric scale, as the photovoltaic behaviour of the film can be strongly non uniform on a much larger scale. For this reason in the device optimization great care should be given to the uniformity of both the active layer and of the electrodes for a size scale comparable with the whole device one.

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