

Investigation of effect of solvent and annealing on spatial inhomogeneity in inverted all-polymer solar cells

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In this report we present the main results obtained completing the investigation of the correlation between the local PL and the EQE in a regioregular poly(3-ethylthiophene):poly(9,9-dioctylfluorene-co-benzothiadiazole) inverted bulk heterojunction solar cell by laser confocal mapping. The first part of this study is presented in Ref.[1]. In this study the morphology and the local active polymer mixing are changed by depositing the active layer from four different solvents and by thermal annealing. We show that the increase of the solvent boiling point affects the EQE nonuniformity due to thickness fluctuations, the density nonuniformity of rrP3HT aggregate phase, and the blend components clustering. The thermal annealing leads to a general improvement of EQE and to an F8BT clustering in all the samples with local decrease of the EQE.

In the last few years considerable improvements of the device efficiency, stability and manufacturing costs reduction for organic solar cells have been reported. Actually efficiency above 10%, lifetime of several years, and the possibility to obtain energy payback time as low as one day, clearly approach bulk heterojunction organic solar cells to real applications. In order to improve the active material absorption in the visible, to exploit energy level engineering, and to reduce the costs, fullerene free solar cells have been proposed, recently reaching the noteworthy efficiency of 8.4% in triple layer oligomeric structure and 6.47% in all polymer solar cells (APSC). Concerning the device stability, the development of the so called inverted structure has recently demonstrated the possibility to reach high lifetime without the need of encapsulation and high efficiency, as evidenced by the efficiency record of 9.2% in inverted solar cells. The efficiency optimization of bulk heterojunction devices requires the determination of a trade-off between the reduction of average donor-acceptor distance below the ex-

citon diffusion length (typically of about 10nm), necessary to have an efficient charge generation, and the presence of large enough interconnected domains of the two components, to allow efficient charge transport and collection. For this reason, several investigations of the correlation between device efficiency and local active material composition on a submicrometric scale have been performed both in polymer-fullerene and, for analogy, in polymer-polymer solar cells[2].

We recently demonstrated, by confocal Photoluminescence (PL) and External Quantum Efficiency (EQE) mapping, that in polymer:polymer solar cells the local properties of the active material at the nanoscale can show inhomogeneities across the active layer on a much larger scale (up to 100 μm), strongly affecting the charge generation and collection efficiency[1].

The complete work can be found in Ref.[3]. In order to improve the understanding of the correlation between local PL and EQE properties in APSC in this work we investigate rrP3HT:F8BT inverted solar cells deposited under different conditions of the active layer (solvent and thermal annealing), chosen as prototypical APSC.

The combined use of PL and EQE confocal mapping allowed us to observe that the choice of the solvent strongly affects the PL and EQE uniformity causing fluctuations of the active layer thickness, of the rrP3HT and F8BT mixing, of the rrP3HT aggregation state and of the charge collection efficiency. We investigate the statistical distribution of the EQE in the different samples demonstrating that the maximum local EQE is independent of the solvent in non-annealed samples, and that the solvent induced efficiency variations are mainly due to a different large scale homogeneity of the device response. After the thermal annealing a general increase of the EQE is observed, with differences between different samples. Based on the maximum values, we estimate

that the optimization of the large scale morphology and molecular arrangement can result in an EQE improvement between 2.7 and 6.5 times.

We fabricated inverted solar cells with the same composition of the active layer (rrP3HT:F8BT = 60:40 by weight, total concentration of 30 mg/ml) deposited by spin coating from different solvents. The details of the solar cell structure and the different steps on the devices fabrication (substrate cleaning, deposition technique, etc.) can be found in Ref.[1].

The PL and the Photocurrent (PC) mapping were performed as described in Ref.[1]. The PL maps were measured in the range 579 ± 25 nm, close to the F8BT PL peak wavelength and in the low wavelength range of the non aggregated P3HT PL, using a band-pass filter, and above 770 nm using a high pass filter, where only P3HT PL is present. The incident excitation power was $P = 18\mu W$, measured by a power meter placed on the objective focal plane.

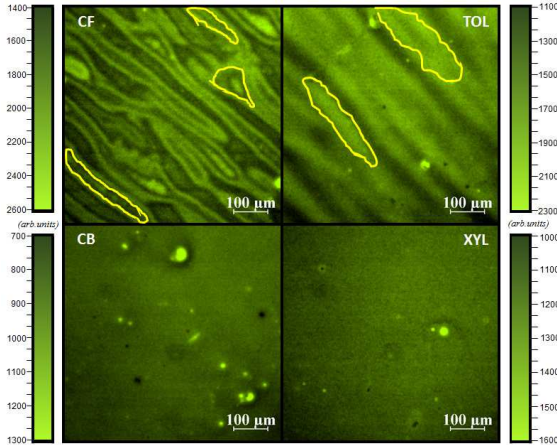


Figure 1. PL maps ($600\mu m * 600\mu m$) at $\lambda=579$ nm of the rrP3HT:F8BT blend before the annealing for the different solvents: chloroform (CF), toluene (TOL), chlorobenzene (CB) and xylene (XYL). Few regions showing the peculiar correlation between PL and EQE intensity, in CF and TOL samples, are evidenced by the yellow contours.

In Fig.1 the PL maps of a $600\mu m * 600\mu m$ region of the active film, with the band-pass filter at 579 ± 25 nm (chosen as example of PL maps), are reported, in order of increasing boiling point of the solvent, respectively chloroform (CF), toluene (TOL), chlorobenzene (CB) and xylene (XYL).

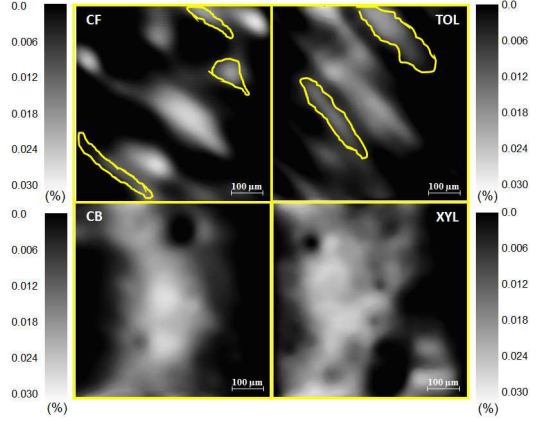


Figure 2. EQE maps of the same regions of Fig.1, for the different solvents before the annealing. Few regions showing the peculiar correlation between PL and EQE intensity, in CF and TOL samples, are evidenced by the yellow contours.

Beyond the progressive improvement of the PL intensity uniformity the main observed results are:

1. CF sample shows evidently non uniform PL maps, with common bright and dark stripes in both detection spectral ranges (bright regions at 579 nm coincide with bright regions above 770 nm);
2. TOL sample shows bright and dark stripes, complementary in the two detection ranges (bright regions at 579 nm coincide with dark regions above 770 nm and viceversa);
3. CB sample shows a rather uniform PL, with some bright spots with a diameter of about $20\mu m$ visible in both detection channels and few smaller spots dark at 579 nm and bright above 770 nm;
4. XYL sample shows the most uniform PL map, with a low density of bright spots in the 579 nm map of about $20\mu m$ diameter, corresponding to dark regions above 770 nm.

The EQE maps of these non annealed films (see Fig. 2) show evident non uniformity, clearly correlated with the PL non uniformity. In particular, the correlation between the PL and EQE non uniformity changes as a function of the used solvent:

1. CF sample reveals elongated portions with high EQE, nearly corresponding to regions with low PL intensity (see regions with yellow contours in Figs. 1 - 2);

2. TOL sample shows wide stripes with high EQE regions coinciding with the low (high) PL regions of the $\lambda > 770nm$ ($\lambda = 579nm$)map (see regions with yellow contours in Figs. 1 - 2);
3. CB and XYL samples show a higher EQE uniformity, with negligible EQE around the bright clusters in the PL maps;
4. almost identical maximum EQE of about 0.030% is observed in all the samples;
5. in all the samples wide regions with negligible EQE are observed, without any regular correlation with PL non uniformity.

Our results are consistent with a uniform composition of the active blend, and with similar local F8BT:P3HT interactions, which should result in uniform charges photogeneration efficiency. On the other hand, the lack of thickness uniformity of the active layer results in thick regions with high PL but low charges collection efficiency, and thus low EQE, and in thin regions with lower PL but higher charges collection efficiency, and thus higher EQE. We observe that all the EQE maps also show wide regions in which the photovoltaic response is not directly correlated to the local PL properties. In particular in several regions of the film strong EQE suppression are observed in absence of evident PL variations (as very evident by comparing the PL and EQE maps in CB and XYL). As the local PL properties are affected by local thickness and composition variation, similar PL properties are the signature of similar local properties of the active film and thus, in particular, similar charge generation efficiency. The evidence of EQE variation in this case are then a signature of local variation of charge collection efficiency, probably related to local variations of the efficiency of charge recombination and charge extraction from the electrodes.

In conclusion, we investigated the possible contributions to large scale inhomogeneity of the local EQE in rrP3HT:F8BT inverted solar cells, evidencing the role of fluctuations of the active layer thickness, of the rrP3HT and F8BT mixing, of the rrP3HT aggregation state, with relative importance determined by the solvent.

We show that the increase of the solvent boiling point modifies the dominant contribution to EQE non uniformity from thickness fluctuations, to non uniform density of rrP3HT aggregate phase, to blend components clustering. The thermal annealing leads to F8BT clustering in all the samples, locally decreasing the EQE.

Moreover we observed that large regions of the samples show negligible EQE, without correlation

to the local PL properties, ascribed to local drastic reduction of charge extraction efficiency.

Finally we showed that the maximum local EQE is independent on the solvent in non-annealed samples, suggesting that all the solvent can locally lead to optimal efficiency and that the solvent induced efficiency variations are mainly due to a different large scale homogeneity of the device response. After the thermal annealing a general increase of the EQE is observed, with differences between different samples. We estimate that the optimization of the large scale morphology and molecular arrangement can result in an EQE improvement between 2.7 and 6.3 times.

Concerning the possible generality of our results also for systems with higher efficiency we suggest that at least in organic solar cells showing efficiency below the actual state of the art, the investigation of the large scale device uniformity can allow the improvement of the understanding of the origin of the low efficiency. In particular polymer-polymer systems could be particularly affected by the features discussed in the paper, at least suggesting to add this kind of studies in works aiming to understand the origin of low efficiencies.

REFERENCES

1. A. Perulli *et al.*, Appl. Phys. Lett 103 (2013) 053305.
2. R. Steyrlleuthner *et al.*, J.Am.Chem.Soc. 134 (2012) 18303.
3. A. Perulli *et al.*, accepted for publication in J. Pol. Sci. Part B: Pol. Phys.