

Improvement of P3HT:PCBM bulk-heterojunction inverted solar cell efficiency by addition of conjugated arylenedithiol

A. Operamolla,¹ O. H. Omar,² G. M. Farinola,¹ F. Babudri,¹ P. Cosma,¹ S. Lattante,³ A. Perulli,⁴ M. Anni,³ and M. Di Giulio³

¹Dipartimento di Chimica, Università di Bari "Aldo Moro", Italy

²CNR-ICCOM c/o Dipartimento di Chimica, Università di Bari "Aldo Moro", Italy

³Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, Italy

⁴Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Italy

The recent outcomes in the field of polymer solar cells have attracted much interest both on the academic and the industrial point of view. These third generation photovoltaic devices present a great potential in terms of cost, scalability and environmental impact. However, some important issues linked to their fabrication and stability still need to be solved in order to bring this technology to an effective commercialization. Indeed the main drawbacks are mostly related to the need to preserve the active layer from atmosphere components such as water and oxygen, and to the processing techniques adopted in the fabrication process that impact on the nanoscale morphology of the bulk heterojunction. Moreover, shortening of devices lifetimes is observed in the presence of the commonly adopted hole injection layer, PEDOT:PSS, and of low work function metal cathodes [1]. With this respect, solar cells fabricated in inverted geometry present special features in terms of lifetimes with respect to the conventional ones because they take advantage of more stable electrodes. In the inverted structure, illumination of the device is made through the cathode, covered by a modified transparent low work function metal oxide layer, while the anode usually consists of a stable silver thin film [2].

This geometry as well as the well known direct one, needs extensive optimization of the blend

nanoscale morphology. Besides, it benefits at the largest extent from the vertical phase separation demonstrated in P3HT:PCBM blends deposited from solution: during solution deposition, P3HT tends to accumulate at the air surface where silver anode is deposited, while PCBM concentrates at the interface with the hole blocking layer, facilitating holes and electrons extraction. The driving force of the vertical phase separation process is believed to be the difference in surface energy of each component [3]. A morphologically optimized active layer should also possess nanophases of proper dimensions if compared to the exciton diffusion length (10-20nm) and well interconnected between each other to ensure a good percolation path of charges through the blend to the electrodes. This lateral phase separation in polymer blends is affected by several parameters, including kind of solvent, concentration, temperature and solvent evaporation rate. The morphology is strongly dependent on the capability of the donor-acceptor couple to spontaneously self-assemble into separate domains during deposition or after thermal annealing, but it is also possible to control blend morphology by addition of processing additives to the host solvent [4]. Introduction of alkyl thiols, which are bad solvents for P3HT, to P3HT:PCBM solutions as cosolvents can increase the photoconductivity and carrier lifetime of the deposited blend, due to enhanced structural order [5].

In the present work we demonstrate improvement of the performances of an inverted P3HT:PCBM bulk heterojunction solar cell by addition of a small amount of a molecular additive, namely ([1,1;4,1]terphenyl-3,5-diyl)dimethanethiol (TD), bearing two pending benzylthiol groups (Figure 1). This work is meant to demonstrate an innovative idea: a novel class of molecular semiconductors functionalized

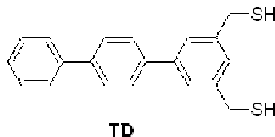


Figure 1. Molecular structure of the ([1,1;4,1]terphenyl-3,5-diyl)dimethanethiol (TD).

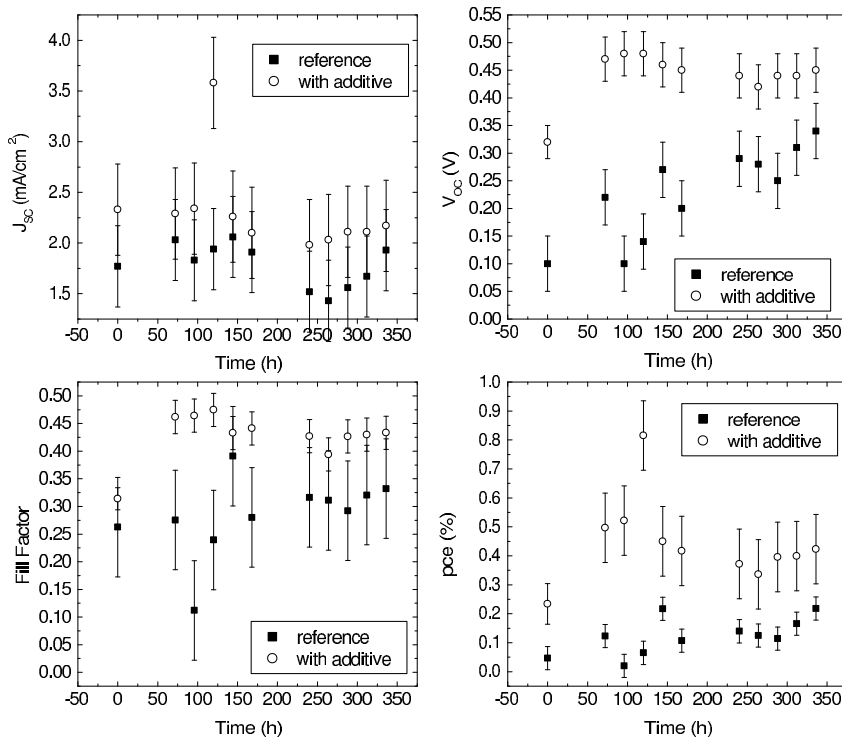


Figure 2. Short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (pce) vs time of considered devices.

with pending thiol (-SH) groups can show photovoltaic properties and enhance the performances of molecular blends, by acting on their morphology and/or photoactivated processes.

TD was prepared according to our previous reports [6–8]. At the end of the synthesis the compound was carefully purified by double recrystallization from hexane:dichloromethane 20:1.

Two bulk heterojunction inverted polymer solar cells were fabricated in air. As cathode, we selected FTO on glass covered by a thin layer of zinc oxide nanoparticles deposited by spin coating. We compared the performances of two active layers: the first one consisting of a mixture of P3HT and PCBM in weight ratio 1:1. The second one had the same composition plus addition of 5% by weight of TD. The Figure 2 reports the short-circuit current density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (FF) and the overall power conversion efficiency (pce) vs time of the devices. The sample prepared with the additive TD shows on the average higher V_{oc} , J_{sc} and FF than the pristine device and consequently doubles the device efficiency from 0.2 (at maximum) for the pristine device to 0.4-0.5%. Such considerable increase in efficiency appears a consequence of the enhancement in J_{sc} and fill

factor as well as V_{oc} : the effects on FF and J_{sc} were observed by other authors after addition of n-octylthiol [9], and could be consequence of reduced recombination within the blend and/or improved electron mobility originated by a more ordered morphology. In our devices, there is also a significant increase in V_{oc} that was not present in other reports, where processing with alkyl thiols generated a loss in the absolute value of open circuit voltage: in our case, though the presence of a material with a lower HOMO level (TD) in the ternary blend could possibly enhance thermalization losses of positive photocarriers [10], the effect can be in any case connected to the presence of our additive, which beyond influencing the blend morphology participates in some way in the charge generation/injection processes operating in the solar cell.

We have demonstrated that adding a few % bw of TD additive improves the overall performance of P3HT:PCBM long term air stable inverted bulk heterojunction solar cells by an inner influence on the active blend morphology. These results open the way to a novel class of organic semiconductors for OPV, which differ from the conventional ones for the functionalization with pending thiol groups. These molecular semicon-

ductors, already of interest in the field of molecular electronics, are able to confer to the processed active layer the capability to self assemble into ordered domains, with the required lateral and vertical phase separation for optimal charge generation and transport to the electrodes.

REFERENCES

1. M. Jrgensen *et al.*, *Adv. Mater.* 24 (2012) 580
2. M. S. White *et al.*, *Appl. Phys. Lett.* 89 (2006) 143517
3. Z. Xu *et al.*, *Adv. Funct. Mater.*, 19 (2009) 1227
4. A. Pivrikas, H. Neugebauer, N. S. Sariciftci, *Sol. En.* 85 (2011) 1226
5. J. Peet *et al.*, *Appl. Phys. Lett.* 89 (2006), 252105
6. A. Operamolla *et al.*, *J. Org. Chem.* 72 (2007) 10272
7. S. Casalini *et al.*, *J. Mater. Chem.* 22 (2012) 12155
8. G. Bruno *et al.*, *Appl. Phys. Lett.* 96, (2010) 133506
9. A. Pivrikas, P. Stadler, H. Neugebauer, N. S. Sariciftci, *Org. Electron.* 9 (2008) 775
10. M. Koppe *et al.*, *Adv. Funct. Mater.* 20 (2010) 338-346.