Efficient PV blends comprising more than two semiconductors

Lacramioara Popescu,² Patrick van 't Hof¹, Floris Kooistra², David Kronholm¹, Alexander B. Sieval¹, and Jan C. Hummelen²*

1. Solenne BV, Zernikepark 12,9747 AN Groningen, The Netherlands. (www.solennebv.com) 2. Molecular Electronics, Zernike Institute for Advanced Materials and Stratingh Institute of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: j.c.hummelen@.rug.nl

The intensity of R&D on solar cells based on the bulk heterojunction principle is rapidly increasing during the last 5 years. Much progress has been reported lately on especially bulk heterjunction cells based on the combination of conjugated polymers and fullerene derivatives. The two main forces that drive this upcoming technology is the promise of low cost and possibility of mass production. Verified record cell efficiencies up to 5.4% have been reported now. While new low bandgap polymers are being developed rapidly and investigated intensely nowadays, the combination of regioregular poly(3-hexylthiophene) (rr-P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methano[60]fullerene ([60]PCBM, or simply PCBM) is still the present day work horse for many 'plastic PV'R&D groups.

Very little has been published on the potential of the cost aspect of future mass production of plastic PV devices (of whatever kind). The cost of production of the two components of the PV active layer, i.e. the donor and acceptor materials, should definitely be relatively low compared to the total cost of the device. Since new and improved donor materials are being developed steadily, it is quite hard to make a good assessment of the cost aspect of the donors, at the moment. This does not seem to be the case of the acceptor component. Some alternative fullerene acceptors have been described more recently, but very little research seems to indicate (at least up to now) that acceptors outside the fullerene realm are true competitors. Hence it is of great importance for the field to investigate and optimize the cost and availability aspects of fullerenes and their derivatives, and to assure that even up to a terawatt/year production this technology would indeed be feasible from the materials point of view. The basic atom ingredient carbon, like its classical counterpart silicon, is readily available. Independent of the production method, fullerenes are always formed as a mixture of carbon cages C_n with n = 60, 70, 76, 78, 84, and many other 'higher'fullerenes. Isolation and purification of C_{60} (by far the most abundant fullerene) or C_{70} (the second in abundance) from mixed fullerenes remains a costly procedure, but it is more feasible to separate these two fullerenes from the higher ones.

In the cost analysis of the fullerene derivatives commonly used in plastic PV, such as [60]PCBM, the fullerene raw material is at present the largest driver of final cost of the derivative. The high price of single component fullerenes C_{60} and C_{70} is due to the high price of separation and purification, which is clearly seen by comparing the cost of pure fullerene grades to the as-produced "raw" fullerene grades, which are mixtures primarily of C60 and C70. Since the composition of the active layer is typically at least half fullerene derivative for this type of plastic PV, there is a large incentive in final device cost-savings to minimize fullerene purification as much as possible.

To simply mix two semiconductors, as is routinely done in making bulk heterojunction active layers from a p-type and an n-type molecular material, was a first paradigm shift in (molecular) PV research.^{1,2} Next, we successfully introduced [70]PCBM, as a mixture of constitutional isomers and stereoisomers of fullerene monoadducts, as an n-type material with much stronger absorption in the 400-700 nm range than [60]PCBM.³ We have now taken it one step further and mixed the *two* different types of n-type semiconductors [60]PCBM and [70]PCBM (of which one as a mixture of isomers, in this case) to act together as the n-type material in combination with a donor material, here rr-P3HT. It should be noted that [60]PCBM and [70]PCBM have a close to identical first reduction potential and the onset of their optical absorption is also identical (~ 695 nm). Hence, both the HOMOs and LUMOs of these molecular semiconductors are (close to) identical. From this point of view, a mixture of these two semiconductors can give rise to a rather smooth electronic landscape, in principle. [60]PCBM and [70]PCBM do have very different solubilities and precipitation behaviors as pure components, but blends of the two surprisingly do not seem to affect morphology and complicate the processing conditions for devices. Simply replacing the n-type with the [60]PCBM/[70]PCBM mixture with no change in processing conditions or device parameters results in identical device performance within normal variation. We also show this concept generalizes to other fullerene derivative types, and in devices where [70]derivatives shows improved performance, [60]derivative and [70]derivative blends appear to offer enhanced performance in proportion to the amount of [70]derivative in the blend.



Mean V_{OC} and η values of P3HT:acceptor (1:1w/w) solar cells as a function of the weight percentage of [70]PCBM in the acceptor mixture (given by [60]PCBM:[70]PCBM). The 95% Tukey HSD confidence intervals are shown for all means.

References

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