A new material for high-performance solar cells

David Kronholm and J. C. (Kees) Hummelen

Adding multiple substituents to a fullerene-derived n-type semiconductor raises the efficiency of plastic photovoltaic devices.

Concerns about climate change and rising fuel costs are driving a search for cheap, widely available photovoltaics to harness solar energy. Organic photovoltaics offer the potential to greatly decrease the cost and availability of photovoltaic energy due to lower material and manufacturing costs. The certified power conversion efficiency (PCE) of state-of-the-art plastic solar cells is 4–5%. While this is adequate for the first commercial applications, developers are aggressively seeking to increase the PCE to allow for a broader market.

The best-performing organic photovoltaic device architecture uses the so-called bulk heterojunction configuration (see Figure 1), which consists of a polymer electron donor (p-type) and fullerene-derivative electron acceptor (n-type) mixture in the active layer. Improving the properties of the p-type and n-type materials are key areas of research and development for increasing the PCE. With optimal materials the performance of plastic solar devices could theoretically approach the best silicon devices.

In terms of new materials development, most of the focus has been on improving the electronic properties of the electronic polymer p-type. While several new generations of polymer p-types have provided advances over the last 10 years, the n-type used in state-of-the-art systems over the last 12 years has almost exclusively been methanofullerene phenyl-C_{61}-butyric-acid-methyl-ester ([60]PCBM). Only the related molecule [70]PCBM, which has a higher optical absorption, provided any significant improvement, but only for a previous, now outmoded, generation of polymer p-types. Various fullerene derivatives have been tested, but until now no improvement has been seen with the modern p-types, poly-(3-hexylthiophene) (P3HT) or the newer generation of low-bandgap conducting polymers.

Various strategies have been tried to improve performance of the fullerene derivative n-type, with varying degrees of success: increasing the optical absorption, improving solubility, improving miscibility with the p-type, and increasing the energy level of the lowest unoccupied molecular orbital (LUMO). It has been shown that the open circuit voltage (V_{OC}) of the solar device is a function of the energy gap between the highest occupied molecular orbital (HOMO) in the donor and the LUMO in the acceptor. As a result, increasing the LUMO in a wide range of donors could could significantly increase V_{OC} when they are paired with P3HT and other acceptor polymers of similar properties. Significant increases in PCE could result.

We previously used electron-donating groups to influence the electronic properties of the fullerene cage, and this confirmed that a raised LUMO in the acceptor improves V_{OC}. However, the change in the LUMO is small, and problems arise in fabrication of good devices due to poor solubility. A much more effective approach is to raise the LUMO by altering the fullerene cage by adding multiple substituents directly to it. Figure 2 shows one form of bis-[60]PCBM, which has two substituents added to
Figure 2. The chemical structure of bis-[60]PCBM.

the fullerene cage. Different forms, or regioisomers, are possible, when the substituents are attached to the fullerene at different sites or regions relative to each other. bis-[60]PCBM is formed as a mixture of regioisomers and is used as such.

Table 1 summarizes a few key properties of bis-[60]PCBM compared to [60]PCBM. The LUMO of bis-[60]PCBM is 100meV higher than [60]PCBM as determined by cyclic voltammetry, a significant increase. Electron mobilities as measured in field effect transistors (FETs) fabricated from pure bis-[60]PCBM films are less compared to [60]PCBM, though still high enough compared to the hole mobility of the p-type to cause no significant difference in the device current.

Importantly, bis-[60]PCBM also is highly soluble in aromatic solvents, an order of magnitude more soluble than [60]PCBM, so processing is convenient for fabrication of solar cell devices. bis-[60]PCBM was used as a substitute for [60]PCBM in devices based on the well-known P3HT:acceptor configuration. Optimal conditions were obtained by using slightly more n-type in the blend at slightly thinner film thickness. Otherwise, processing conditions were the same, i.e., o-dichlorobenzene was used in combination with thermal annealing. The resulting optimized devices gave a certified (Energy Research Centre of the Netherlands, ECN) efficiency of 4.5% compared to 3.8%, which is among the highest public certified efficiencies recorded for a P3HT organic solar device.

The broad commercial viability of organic solar cells demands increased performance in terms of PCE. So far, these increases are being driven by improvements in materials properties. Organic electronics offer the advantage of a wide variety of techniques, and materials are available, providing opportunities for improvement. With the present approach we have finally succeeded in altering the electronic properties of the n-type sufficiently for a significant improvement in device performance. Similar performance increases are expected for other polymers, and in principle the same ~20% improvement is possible. Importantly, the processability and ease of synthesis of the commonly used [60]PCBM has been preserved, and bis-[60]PCBM may even offer additional advantages in larger-scale printing due to its greatly increased solubility.

Table 1. Comparison of the key properties of [60]PCBM and bis-[60]PCBM.

<table>
<thead>
<tr>
<th>Property</th>
<th>[60]PCBM</th>
<th>bis-[60]PCBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE in P3HT device</td>
<td>3.8%</td>
<td>4.5%</td>
</tr>
<tr>
<td>1st red. potential</td>
<td>−1.08eV</td>
<td>−1.18eV</td>
</tr>
<tr>
<td>FET mobility</td>
<td>$2 \times 10^{-7}$ m$^2$/Vs</td>
<td>$7 \times 10^{-8}$ m$^2$/Vs</td>
</tr>
</tbody>
</table>

Author Information

David Kronholm
Solenne BV
Groningen, The Netherlands
http://www.solennebv.com

David Kronholm is managing director and cofounder of Solenne BV, formed in 2005. He received his PhD in chemical engineering from the Massachusetts Institute of Technology in 2000, and is the author of several patents in the area of fullerenes and organic electronics.

J. C. (Kees) Hummelen
Zernike Institute for Advanced Materials and Stratingh Institute of Chemistry
University of Groningen
Groningen, The Netherlands

Kees Hummelen is professor of chemistry and advanced materials. He is also chief scientist and cofounder of Solenne BV.
References