A series of new, easily synthesized C$_{60}$–fullerene derivatives is introduced that allow for optimization of the interactions between rr-P3HT and the fullerene by systematic variation of the size of the ester group. Two compounds gave overall cell efficiencies of 4.8%, clearly outperforming [60]PCBM which gives 4.3% under identical conditions.

Two decades after the introduction of the bulk heterojunction (BHJ) organic solar cell,\(^2,3\) the evolution of polymer:fullerene organic photovoltaic devices is still continuing at a remarkable pace. New conducting polymers\(^2,3\) and small molecules\(^4,5\) are constantly developed, which give increased power conversion efficiencies (PCE) because of, e.g., improved conductivity, increased light absorption, or optimized band gaps.\(^3,6\) Also, new strategies for solar cells,\(^7\) better insight into the physical processes taking place in the active layer, and other improvements have resulted in significant increases in the PCE. Currently, the best fullerene-based organic solar cells give efficiencies approaching 10\% under AM1.5 illumination.\(^7,5\)

In contrast to the developments mentioned above, it is remarkably quiet on the fullerene front. Many of the newly introduced devices still contain [60]PCBM, the C$_{60}$-derivative that was first used 20 years ago in the original devices,\(^1\) or its C$_{70}$-analogue, [70]PCBM, known for more than 10 years.\(^6\) Since then, only a few other fullerene derivatives have found their way into the worldwide research community, the most prominent examples being bis[60]PCBM\(^0\) and the indene-C$_{60}$ bisadduct ([60]ICBA).\(^10\) Both materials are fullerene bis-adducts, meaning that two addends are bound to the fullerene sphere instead of only one, as is the case in [60]PCBM. Devices containing bis-adducts give higher open circuit voltages ($V_{oc}$), if the donor LUMO level is high enough, because the energy level of the LUMO of the bisadducts is above that of [60]PCBM.

A higher $V_{oc}$ increases the PCE, but it has been found that bis-adducts also have several disadvantages. Quite often, the increase in $V_{oc}$ is accompanied by a decrease in $J_{sc}$ and/or fill factor. As a result, the overall performance of devices containing bis[60]PCBM is often not much better than those containing [60]PCBM, despite an increase of the $V_{oc}$ of ~100 mV.\(^11\) Devices containing [60]ICBA show an even larger increase in $V_{oc}$, but this compound only works well with a few polymers,\(^10\) while giving fairly poor results with many other ones.\(^12\)

Only a limited set of fullerene electron acceptors is currently commercially available. This hinders further improvements of the polymer:fullerene solar cells, in particular because of the limited possibilities to mix-and-match donor and acceptor materials during optimization. The device performance is not only determined by the LUMO and HOMO levels of the organic components, but also by, e.g., the successful mixing of the electron donor and acceptor in the active layer, by molecular interactions between the fullerene and the polymer, and by intermolecular interactions between the fullerenes within the fullerene-rich domains.\(^11\) Therefore, future evolution in the PCE of organic solar cells is predicated on the continued development of new fullerene derivatives.

A few factors should be taken into account when designing new fullerene derivatives for organic electronics, if they are to be generally used in the field. First, the solubility of the derivative in processing solvents should not be too high, or too low. This was clearly demonstrated when a series of [60]PCBM analogues was investigated.\(^14,15\) Second, the starting material, i.e., the reagent that must react with the fullerene, must be easily available on a large scale. Third, it should be easy to purify the targeted fullerene derivative. The latter factors are crucial for commercial large-scale production.

For [60]PCBM, [70]PCBM and bis[60]PCBM, all of the above factors are satisfied, with one exception being the facile synthesis of the starting material. For [60]ICBA the purification of the fullerene derivative is problematic on a large scale, because of the low solubility of [60]ICMA, the mono-adduct that is also formed in the reaction. [60]ICMA can act as a 150 mV deep trap...
in the devices, and therefore must be removed completely to obtain a satisfactory PV device. Expensive purification procedures are necessary to obtain sufficiently pure [60]ICBA.

With the above requirements in mind we have synthesized a series of new fullerene derivatives (Fig. 1) that combine the advantages of [60]PCBM, i.e., good solubility and easy separation, with the higher $V_{oc}$ values that are obtained with the fullerene Diels–Alder adducts [60]ICMA and [60]ICBA, and other similar derivatives.1,2,15,16

The Diels–Alder addition of 1,3-dienes, such as iso-indene, to C60 is a straightforward one-pot reaction.17 The iso-indene is formed in situ from 1H-indene by a [1,2]hydrogen shift at high temperatures.18 Unfortunately, substituted indenes are often not easily synthesized, but indene can react with acrylates in a Michael-reaction.19 The resulting substituted indene can then be reacted with C60, and this reaction was used to prepare the compounds described in this investigation (Fig. 1). The ethyl ester, [60]IPE, and butyl ester, [60]IPB, were prepared directly from C60 and the 3-(1-indenyl) propionic acid esters in 25% and 30% yield, respectively (78 and 71% based on reacted C60). The hexyl ester, [60]IPH, was synthesized in almost quantitative yield by dibutyltin oxide-catalyzed transesterification of [60]IPE with 1-hexanol.20

The three compounds were characterized by NMR, IR, and LC-MS. The $^1$H and $^{13}$C NMR spectra are shown in Fig. S1–S6 (ESI†). The $^1$H NMR spectra show separate signals for all aliphatic hydrogens except those from the alkyll ester moiety, because of the asymmetry of the fullerene derivative. To further study the coupling pattern, a $^3$H–$^1$H COSY spectrum of [60]IPB was measured (Fig. S7, ESI†). For all three compounds, the two hydrogen atoms from the 5-membered ring of the former indene moiety are observed at the same positions in $^1$H NMR spectra: a singlet at 4.93 ppm, and two doublets with $J$ = 10 Hz at 3.63 and 2.81 ppm. In [60]ICMA, the adduct of indene on C60 the same set of three signals is observed, but in a 2 : 1 : 1 ratio.19 This clearly shows that the substituted indenes add to C60 in the same manner as indene itself, thus confirming the structure of the new fullerene derivatives. Importantly, all three compounds have good solubility in solvents commonly used for making organic solar cells. Evidently, the solubility of [60]IPB and, especially, [60]IPH is considerably higher than that of [60]IPE.

Analysis by cyclic voltammetry showed that the LUMO level of these new derivatives is approximately 30 mV above that of [60]PCBM, i.e., at the same level as ICMA (Table S1, ESI†). The first three reductions of the new derivatives are all reversible. The cyclic voltammogram of [60]IPE is shown in Fig. S8 (ESI†).

Next, we prepared polymer:fullerene BHJ devices comprising rr-P3HT and the different fullerene derivatives (i.e., [60]PCBM, [60]IPE, [60]IPB, or [60]IPH) to study the impact of the fullerene structure on the PCE. The active layers were spin coated from solutions with constant polymer:fullerene molar ratio and using identical processing conditions, enabling the direct comparison between the devices (details see ESI†). The current density–voltage ($J$–$V$) measurements can be found in Fig. 2, light and dark curves on a log–log plot in Fig. S10 (ESI†), and the average and maximum solar cell characteristics of 16 devices are summarized in Table 1.

In our hands, the standard processing for rr-P3HT:[60]PCBM BHJs yields an average $J_{sc}$, $V_{oc}$, FF, and PCE of 10.67 mA cm$^{-2}$, 0.595 V, 0.67, and 4.27%, respectively. When increasing the fullerene alkyl ester length from ethyl to butyl to hexyl, we observe both an increase in the $J_{sc}$, $V_{oc}$ and FF from 9.59 mA cm$^{-2}$, 0.605 V, 0.61 to 10.66 mA cm$^{-2}$, 0.647 V, and 0.69 to 10.56 mA cm$^{-2}$, 0.647 V, and 0.68 resulting in an increase in the average PCE from 3.52% to 4.76% to 4.62%, respectively; i.e. devices containing either [60]IPB or [60]IPH have similar $J_{sc}$ and FF relative to P3HT:PCBM, indicating similar charge generation and extraction efficiencies. However, in agreement with the CV results, we find that both [60]IPB and [60]IPH give a 50 mV higher $V_{oc}$ relative to [60]PCBM. This higher $V_{oc}$ leads to an increase in the maximum PCE from 4.40% to 4.97%. This means that both [60]IPB and [60]IPH can be used as a direct

Table 1 | Average $J_{sc}$, $V_{oc}$, FF, and PCE of 10 devices and maximum values in parentheses measured under AM 1.5G illumination

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[60]PCBM</td>
<td>10.67 (10.85)</td>
<td>0.595 (0.598)</td>
<td>0.67 (0.68)</td>
<td>4.27 (4.40)</td>
</tr>
<tr>
<td>[60]IPE</td>
<td>9.59 (9.82)</td>
<td>0.605 (0.610)</td>
<td>0.61 (0.62)</td>
<td>3.52 (3.69)</td>
</tr>
<tr>
<td>[60]IPB</td>
<td>10.66 (10.89)</td>
<td>0.647 (0.647)</td>
<td>0.69 (0.70)</td>
<td>4.76 (4.93)</td>
</tr>
<tr>
<td>[60]IPH</td>
<td>10.56 (11.18)</td>
<td>0.647 (0.647)</td>
<td>0.68 (0.69)</td>
<td>4.62 (4.97)</td>
</tr>
</tbody>
</table>
substitute for [60]PCBM yielding higher efficiencies without the need for extensive device optimization.

An interesting dependence of the $J-V$ characteristics on the length of the alkyl ester appended to the fullerene derivatives is observed. As the alkyl ester length is increased from ethyl to butyl, there is a reduction in the reverse bias slope indicating an enhancement in the charge extraction, resulting in an increase in the $J_{sc}$, $V_{oc}$, and FF, while producing a 35% improvement in the PCE; further increase from butyl to hexyl yields essentially indistinguishable device characteristics. It is likely that this observed correlation between the alkyl ester length and the $J_{sc}$ and FF is due to changes in the interaction between P3HT and the fullerenes (vide infra). These interactions influence the volume fraction of P3HT crystallites, fullerene-rich aggregates, and intermixed phase composition resulting in more efficient charge extraction. Furthermore, the observed increase in the $V_{oc}$ with increasing alkyl ester length can be explained by a concurrent decrease in the charge carrier recombination and decrease in P3HT aggregation. Further increasing the alkyl ester length from butyl to hexyl produces little change in the device efficiency, suggesting that both of these fullerene derivatives fall within the acceptable region of polymer-fullerene miscibilities.

The systematic modification of the alkyl ester length motivates a more detailed investigation of the active layer structure and how it relates to the PCE. An increase in both the $J_{sc}$ and FF is usually linked to changes in the microstructure of the active layer that is formed during the solvent evaporation and subsequent processing. To provide greater detail into influence of the fullerene structure on the active crystallite microstructure, we used grazing-incidence X-ray diffraction (GIXD). The diffraction patterns, collected from samples fabricated from the same solutions and similar processing conditions so as to directly compare with the $J-V$ measurements, exhibit the characteristic diffraction of semicrystalline P3HT with the alkyl stacking reflections centered at 0.39, 0.78, and 1.17 Å\(^{-1}\) (Fig. 3a and Fig. S11, ESI\(^{†}\)). We also observe the characteristic isotropic scattering ring centered at 1.39 Å\(^{-1}\) indicating that, similar to [60]PCBM, the new fullerene derivatives remain disordered within the active layer. Fig. 3a shows a series of radially integrated cake slices from blends of P3HT and [60]IPE (green), [60]IPB (blue), and [60]IPH (orange). As the alkyl ester length is increased we observe a 20% decrease in the area of the first order reflection of the P3HT (determined by the azimuthal area, Fig. 3b). Clearly, the increase of the length of the alkyl ester appended to the fullerene decreases the volume fraction of P3HT crystallites.

The decrease in the volume fraction of P3HT crystallites with increasing fullerene alkyl ester length can be rationalized within the framework of a binary interaction model describing the Gibbs free energy of mixing and the melting point depression of a semicrystalline polymer. Following the relationship established by Flory–Huggins and extended by Nishi–Wang, one should expect that an increase in the enthalpic interaction between the polymer and the fullerene will relate to a decrease in both equilibrium melting point of the polymer within the blend as well as a decrease in the heat of fusion per unit volume (i.e., volume fraction of polymer crystallites observed above).
[60]IPE results from an increased interaction of [60]IPB with P3HT, limiting the “over-crystallization” of the P3HT. The discontinuous change in the J-V characteristics leads us to speculate that the over-crystallization of P3HT and reduced miscibility of the [60]IPE possibly leads to a non-optimal vertical phase separation within the devices, i.e., P3HT-rich cathode interface and/or fullerene-rich anode interface, which limits charge extraction and thus the J_sc and FF. The elucidation of this specific structure–property relationship will be the subject of a future study.

In conclusion, a series of new, easily accessible fullerene derivatives was synthesized that have a LUMO level above that of [60]PCBM. We found that P3HT:fullerene solar cells fabricated with identical protocols gave an increase in Voc of 50 mV relative to the [60]PCBM cells, in agreement with the molecular orbital energy levels quantified by CV. By following identical processing conditions, two of the derivatives matched the J_sc and FF of fully optimized reference devices containing [60]PCBM. Interestingly, the average overall PCE of the cells containing these new compounds was increased from 4.3% (for the [60]PCBM cells) to 4.8%, with maximum values reaching 5%, which approaches the maximum PCE that has been reported for P3HT and [60]PCBM. Furthermore, we found that the interactions between the polymer and the fullerene can be tuned by simple modification of the alkyl ester length. These results show that these new derivatives can be an interesting alternative for [60]PCBM in many polymer:fullerene organic photovoltaic devices. We are currently further exploring the properties of these new materials.

Notes and references