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Cross-linkable azido C₆₀-fullerene derivatives for efficient thermal stabilization of polymer bulk-heterojunction solar cells†

Aurel Diacon,a,b Lionel Derue,a Clémence Lecourtier,b,c Olivier Dautel,d Guillaume Wantz*bd and Piétrick Hudhomme*a

Original [60]PCBM-inspired fullerene derivatives bearing an azido functional group were synthesized. By incorporating an optimized quantity of this thermal cross-linker additive in the P3HT:[60]PCBM photoactive layer, an impressive stabilization of the bulk-heterojunction morphology at its optimal photovoltaic performance was achieved.

Polymer:fullerene-based bulk-heterojunction (BHJ) solar cells have attracted widespread interest in academic and industrial communities leading nowadays to one of the hottest fields of research.1–3 This particular attention is due to the high potential of organic solar cells which presents the advantages of low cost, light weight and processability on flexible substrates4 with new market areas.7,8 The BHJ concept based on an interpenetrating network between the electron donor and acceptor materials offers an efficient strategy to maximize the interfacial area.6 The choice of these materials and the control of the blend morphology are determinant parameters that govern the physical interaction inside the BHJ affecting the whole photocurrent process. While extensive studies have been aimed at designing optimal conjugated polymers as electron donors, fullerenes were rapidly considered to be the ideal acceptors for BHJ based devices thanks to their photophysical and electrochemical properties combined with their high electron mobility.10–12 Since the advent of [6,6]-phenyl-C₆₁-butyric acid methyl ester ([60]PCBM),13 the blend of poly-(3-hexylthiophene) (P3HT) and [60]PCBM has been the most widely investigated with a reproducible power conversion efficiency (PCE) approaching 5%.14 Besides the need for a high PCE, the stability of organic solar cells constitutes a limiting parameter for attaining large scale commercialization.15,16 Improvements of the active layer nanomorphology were obtained with an appropriate annealing treatment17 and/or the addition of a processing additive.18,19 During thermal annealing, both the polymer and [60]PCBM crystallize to form a nanoscale interpenetrating network, but this morphology is not thermally stable since each partner thermodynamically prefers to phase separate. Particularly, it is well-established that [60]PCBM forms crystalline domains in the films, resulting in a significant decrease of the long-term solar cell performance.20 Consequently the control of the nanostructure and the stability of the polymer:fullerene network morphology are the most important challenges in BHJ solar cell development.21,22 Chemical strategies now explored to freeze this nanomorphology are based on the utilization of fullerene-containing nucleating agents which allow to control the crystallization process of [60]PCBM,23 or cross-linking reactions which are investigated to increase the lifetime of the device by locking the morphology thus hindering the phase separation.24 Previous efforts have focused on cross-linked polymers,25–30 small molecules,31,32 and only very few examples are using cross-linked polymer-fullerene complexes33 or cross-linked fullerenes. In this last topic, interesting approaches were reported to modify [60]PCBM with the introduction of epoxide14 or styryl25–38 cross-linkable groups and to apply these n-type materials by replacement of [60]PCBM in the active layer. The cross-linking phenomenon induced by the epoxide group was shown to be incomplete by addition of a Lewis acid initiator or heating at 140 °C, whereas the corresponding process with the styryl group occurred at 160 °C. Another strategy was investigated by working with a [60]PCBM derivative bearing an oxetane group as an electron extracting interlayer for improving the device performance.39

In this study, we successfully developed an original and powerful approach to introduce an azido cross-linkable group
onto a [60]PCBM-based system (Scheme 1). The key point of this innovative strategy was to develop a straightforward synthesis of highly soluble cross-linkable PCBM-based derivatives in order to limit the modification of the morphology in common organic solar cells. Taking advantage of the highly well-known reactivity of the azido group towards C60, an efficient cross-linking process was attained during the thermal annealing treatment resulting in an enhanced stability with suppression of macrophase separation.

[60]PCBM was synthesized from a commercial fullerene C60 according to the literature procedure, then hydrolyzed into [60]PCBA. Considering that the reaction of the azido group onto C60 was susceptible to occur at a temperature up to 50 °C, a one-step synthetic strategy was driven using an esterification with 3-azidopropan-1-ol or 6-azidohexan-1-ol under activation conditions with N-(3-dimethylaminopropyl)-N-ethylcarbodiimide (EDC) in the presence of 1-hydroxybenzotriazole (HOBt) and 4-4-N,N-dimethylaminopyridine (DMAP). Corresponding azidofullerenes [60]PCB-C3-N3 and [60]PCB-C6-N3 were purified by chromatography on silica gel using CH2Cl2/pentane (7/3) as the mixture of eluents and isolated in 80% yield (Scheme 1). Both compounds were immediately dissolved in 1,2-dichlorobenzene at the concentration of 40 mg mL−1 and kept at 4 °C, which resulted in an enhanced stability with suppression of macrophase separation.

This cross-linking temperature appears to be close to that used for the annealing of P3HT:[60]PCBM films. The DSC analysis of P3HT and [60]PCB-C6-N3 in a physical mixture revealed an exothermic peak during the first heating cycle and no modification of P3HT crystallization temperature. This could be interpreted as a selective reaction of the azido group towards the fullerene moiety. Thus, a fast cross-linking reaction could effectively freeze the BHJ morphology, without causing any degradation due to the reaction between fullerene derivatives.

The effect of such cross-linkable materials on the BHJ morphology was studied on the P3HT[60]PCBM blend used as a model. After deposition on glass/ITO/TiOx (Fig. 1a), thermal annealing at 150 °C for 24 h induced the formation of many dendrites, characterizing severe aggregation by crystallization of [60]PCBM (Fig. 1b). In contrast, the blend with P3HT[60]PCB-C3-N3 or P3HT[60]PCB-C6-N3 showed a homogeneous film (Fig. 1c and d). This result could be explained from the fullerene cross-linking phenomenon inhibiting the macrophase separation.

Nanoscale imaging using atomic force microscopy (AFM) further demonstrated that the typical fibrillar structure of the non-aged P3HT:[60]PCBM layer (Fig. 2a) completely changed after 24 h at 150 °C (Fig. 2b). However, the addition of an optimized content of the [60]PCBM-C6-N3 cross-linker in the P3HT:[60]PCBM:[60]PCB-C6-N3 (1 : 0.8 : 0.2 weight ratio) blend enabled the stabilization of the morphology (Fig. 2c and d). BHJ solar cells based on composite films of P3HT[60]PCBM, P3HT[60]PCB-C6-N3 and P3HT[60]PCBM:[60]PCB-C6-N3 mixtures were fabricated with an inverted device structure of ITO/TiOx/BHJ/MoO3/Ag and characterized on a AM1.5 solar simulator set at 100 mW cm−2 (S.I.). When [60]PCB-C6-N3 was used as the only acceptor in devices in place of [60]PCBM, then PCE was dramatically reduced after thermal ageing at 150 °C

Scheme 1 Synthesis of azidofullerenes [60]PCB-C3-N3 and [60]PCB-C6-N3.
during 24 h (S.I.). This could be explained by a non-controlled multiple functionalization of fullerene. Such formation of multi-adducts could inhibit acceptor properties of the fullerene phase in the BHJ with decrease of the electron mobility.

Consequently, [60]PCB-C6-N3 was then used as an additive together with [60]PCBM to form a P3HT:[60]PCBM:[60]PCB-C6-N3 ternary blend. The concentration of [60]PCBM-C6-N3 was carefully optimized and the 1 : 0.8 : 0.2 weight ratio for P3HT:[60]PCBM:[60]PCB-C6-N3, respectively, provided the best stabilization without affecting initial performances (S.I.). The current–voltage ($J$–$V$) curves of these solar devices are plotted in Fig. 3 and the relevant photovoltaic characteristics are listed in Table 1. Pristine devices exhibited similar performance, indicating that the incorporation of the azido cross-linker in addition to the [60]PCBM-type acceptor did not significantly affect the PCE of solar cells. Whereas the PCE of P3HT:[60]PCBM devices decreased rapidly upon annealing at 150 °C to attain 1.4% PCE after 24 h, the devices with a cross-linker stabilized their efficiency at 2.8%. This stabilized efficiency remains even during 24 h (S.I.).

![AFM phase images](image1)

**Fig. 2** AFM phase images of P3HT:[60]PCBM (1 : 1 weight ratio), (a) after solvent annealing not thermally treated and (b) after thermal ageing at 150 °C for 24 h the nano-sized domains are totally destructed. AFM phase images of P3HT:[60]PCBM:[60]PCB-C6-N3 (1 : 0.8 : 0.2 weight ratio) are shown in (c) after solvent annealing not thermally treated and (d) after thermal ageing at 150 °C for 24 h. Nano-domains of P3HT and of PCBM are preserved thanks to the cross-linker. All image sizes are 2 × 2 µm².

![J-V curves](image2)

**Fig. 3** $J$–$V$ curves of P3HT:[60]PCBM solar cells (black symbols) and after 24 h of thermal ageing at 150 °C (red symbols). $J$–$V$ curves of P3HT:[60]PCBM:[60]PCB-C6-N3 (in a 1 : 0.8 : 0.2 ratio, respectively) solar cell pristine (blue symbols) and after 24 h of thermal ageing at 150 °C (green symbols).

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<th>Table 1 Photovoltaic characteristics of solar cells</th>
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<td>P3HT:[60]PCBM (1 : 1 weight ratio) Pristine</td>
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<td>P3HT:[60]PCBM (1 : 1 weight ratio) 24 h @ 150 °C</td>
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<td>P3HT:[60]PCBM:[60]PCB-C6-N3 Pristine (1 : 0.8 : 0.2 weight ratio)</td>
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<tr>
<td>P3HT:[60]PCBM:[60]PCB-C6-N3 24h @ 150 °C (1 : 0.8 : 0.2 weight ratio)</td>
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after longer thermal treatments. One can note the increased $V_{oc}$ after thermal treatment which is in agreement with the formation of fullerene bis- or tris-adducts raising directly the LUMO energy level of [60]PCBM. The optimization using a 0.2 : 0.8 weight ratio for [60]PCB-C$_6$N$_3$ and [60]PCBM, respectively, could suggest here a controlled formation in the photoactive layer of some bis-adducts or tris-adducts that are reported to present an increased $V_{oc}$ in P3HT-based solar cells.\cite{47, 51}

Conclusions

The approach described here provides a powerful tool to efficiently enhance the stability of P3HT-[60]PCBM-based organic solar cells using the addition of a cross-linkable azido functionalized fullerene derivative. This compatibilizer effect drastically suppresses the formation of [60]PCBM crystals in the BHJ and macro-phase separation leading to an extremely stable morphology and devices. The proposed acceptor-acceptor cross-linking strategy using the azidofullerene derivative provides a versatile tool to overcome the morphology instability for the fabrication of more stable fullerene-based solar cells. These fullerene materials can now be expected to be universally applied as additives and morphology stabilizers in all kinds of fullerene-based BHJ solar cells.

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