



An acrylated fullerene derivative for efficient and thermally stable polymer solar cells



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ABSTRACT

The continuous microstructure evolution occurring in active layers of polymer-fullerene solar cells is one of the main causes for their device instability. With aim to tackle it, this work developed a new polymerizable fullerene acceptor, [6,6]-phenyl-C₆₁-butyl acrylate (PC₆₁BA). It was found that PC₆₁BA has similar light-absorption properties and HOMO and LUMO energy levels as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), and can be converted into insoluble oligomers upon heating at 150 °C. Polymer-fullerene solar cells using poly(3-hexylthiophene) (P3HT) as donor and PC₆₁BA as acceptor exhibited an optimized efficiency of 3.54%, the performance comparable to P3HT/PC₆₁BM cells (optimized efficiency: 3.70%). But, the former possess much better thermal stability than the latter owing to aggregation suppression by the polymerized PC₆₁BA. These results indicate that PC₆₁BA, unlike most previous reported, is a unique polymerizable fullerene derivative that can be used alone as acceptor to achieve both efficient and thermally stable polymer solar cells.

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Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted considerable attention owing to their advantages of light weight, flexibility, adaptability to low cost solution processing and large area device fabrication. With great success in material innovation and device engineering in the past decades,¹ PSCs have achieved a significant progress with power conversion efficiency (PCE) record raised from 3–5% in 2000s^{1,2} to nowadays over 10%.^{1,3} Although such efficiency level is needed to be further improved for their real use, it is appropriate to pay attention on device stability issue at the same time.⁴

According to light-to-electric conversion mechanism, a BHJ active layer is generally composed of a physical blend of electron donor (D) and acceptor (A) materials.¹ In order to provide a large D/A interface for efficient exciton dissociation (or charge separa-

tion) and meanwhile the transportation pathways for both hole and electron charge carriers, a bi-continuous interpenetrating D/A biphasic microstructure should be formed in the active layer. Moreover, their domain widths are better to keep in the same magnitude of exciton effective diffusion length (10–20 nm) for a high exciton migration efficiency. Although it is still known little about what governing microstructure formation for a physical blend of two materials and how to precisely control their formation, a number of PSC systems have achieved nearly ideal configuration after careful optimization on device fabrication parameters and procedures, including donor/acceptor ratio, processing solvent and temperature, additives, concentration, spin-coating rate, thermal annealing, solvent vapor annealing, standing alone, and so on, and thus endowed them with high performance.^{1–3} Since no specific factors and interactions are engaged to hold blend components still, the so-formed nanoscale phase-separated microstructures are not thermally stable, and absolutely continue to evolve into large phase separation. And even in many reported cases, large aggregates were clearly naked identified when their active layers were subjected to thermal treatment.⁵ Therefore, such microstructure evolution occurring in PSC active layers mostly leads to reduction on the size of D/A interface, destruction on the hole and electron

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transportation networks, and thus degradation on device performance. In fact, this is a major immanent reason accounting for the instability issue of PSCs, which is different from chemical degradation factors caused by material instability and the invasion of oxygen and moisture.

In order to address it, a strategy has been proposed in the past to utilize crosslinkable photovoltaic materials for BHJ active layers.⁶ After desired microstructure is achieved by means of all applicable techniques and methods, crosslinking reaction is initiated and performed to “lock” or “freeze” active layer components, and thus avoid or retard further phase separation and stabilize the obtained microstructure. This strategy has been widely applied in polymer donor materials, firstly on poly(3-hexylthiophene) (P3HT)^{5–7} and later on donor-acceptor (D-A) conjugated polymers.^{6,8} Therefore, a great number of crosslinkable polymer donors having vinyl, bromo, oxetane, or azide functionality on part of their side chains were synthesized and found they can more or less improve device thermal stability. More recently, we also demonstrated the combination of this strategy with the present known high performance D-A polymers can produce crosslinkable donor materials for PSCs with both high efficiency and long-term stability.⁹ However, in these works, acceptor molecules (PC₆₁BM in the most cases) still kept movable since no crosslinking took place on them. In order to fix acceptor component, it is necessary to develop crosslinkable/polymerizable fullerene acceptor materials at the meantime. However, compared with a large number of crosslinkable donor materials, only a few works were focused on acceptor materials. For example, an epoxide-functionalized fullerene acceptor, PCBG, was reported in 2005.¹⁰ Solar cells based on P3HT/PCBG displayed an initial efficiency of >2%, but strong degraded upon heating at 140 °C for several minutes. In 2010, Hsu, Chen, and their coworkers developed a [6,6]-phenyl-C₆₁-butyric styryl dendron ester (PCBSD) having a dendron shape with two styryl crosslinkers.¹¹ It was firstly used as for fabrication of cross-linked interlayer,^{11,12} and later as additive to P3HT/PC₆₁BM active layer,¹³ both achieving improved device efficiency and stability. But, it was never used as acceptor material alone to combine with donor material for PSCs. In 2013, Chen et al. reported a vinyl-terminated fullerene derivative, PCBD, and used it in combination with vinyl-modified D-A donor material, PBDTTT-V, for inter-cross-linked solar cells.^{8c} Device based on PBDTTT-V/PCBD exhibited a much better stability than PBDTTT-V/PC₆₁BM. The former cell had smaller initial device efficiency than the latter (2.5% vs. 3.3%). Later in 2014, two azido-functionalized fullerene derivatives were reported and also used as a second acceptor material to P3HT/PC₆₁BM blend.¹⁴ More recently, Bucknall et al.

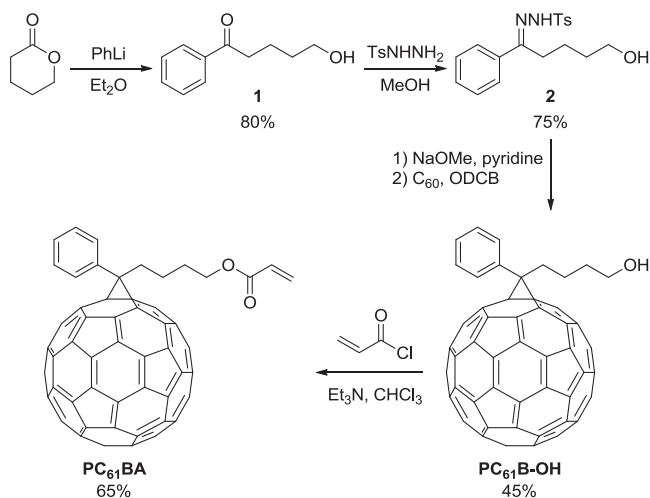
reported a benzocyclobutene-attached fullerene material.¹⁵ Although the device based on it and P3HT displayed a good stability, its initial efficiency was only ~1.2%. Therefore, the polymerizable or crosslinkable fullerene derivative, which can not only greatly improve device stability but also compete with PC₆₁BM in device efficiency as acceptor component alone, has not yet been developed so far.

Analyzing the chemical structures of the above reported crosslinkable or polymerizable fullerene materials, one can find that all of them were prepared from PC₆₁BM, which was hydrolyzed into carboxylic acid firstly and then reacted with corresponding crosslinker unit-containing reagents. This may be the reason that the obtained new fullerene materials showed inferior device efficiency than PC₆₁BM. Therefore, in this study, we propose a new synthetic strategy for polymerizable fullerene materials and obtained an acrylated fullerene derivative, [6,6]-phenyl-C₆₁-butyl acrylate (PC₆₁BA) (Scheme 1). Since it has similar molecular size and shape as PC₆₁BM, it is expected to display comparable device efficiency as PC₆₁BM. Meanwhile, the acrylate functionality could enable its *in-situ* polymerization by means of thermal activation and thus achieve high device stability.

Results and discussion

The Synthesis of PC₆₁BA followed the similar method for PC₆₁-BM,¹⁶ which is outlined in Scheme 1. Starting from lactone, a δ -hydroxyl phenyl ketone **1** was obtained in a yield of 80%. After refluxing with *p*-toluenesulfonyl hydrazide in MeOH, it converted into **2**, an important tosylhydrazone intermediate for 1,3-dipolar addition of fullerene. Afterwards, compound **2** was first treated with MeONa in pyridine to produce the active diazo intermediate and then added with C₆₀ *o*-dichlorobenzene (ODCB) solution, affording PC₆₁B-OH, a hydroxyl-functionalized fullerene derivative, in a yield of 45%. After esterification with acryloyl chloride in the presence of Et₃N, the final product, PC₆₁BA, was obtained in a yield of 65%. Both PC₆₁B-OH and PC₆₁BA are readily soluble in chlorinated solvents, such as chloroform, chlorobenzene, ODCB etc. Their structures were unambiguously identified by ¹H and ¹³C NMR spectroscopy, mass spectroscopy and elemental analysis, as shown in Supplementary Material.

Thermogravimetric analysis (TGA) found that PC₆₁BA possesses a good thermal stability in N₂ atmosphere with a 5%-weight-loss temperatures (*T*_d) of 452.1 °C (Fig. 1a). In differential scanning calorimetry (DSC) as shown in Fig. 1b, it was found that a broad exothermic peak starting around 170 °C and reaching its apex at 182 °C appeared in the 1st heating process. Since acrylated monomers are well known to be easily self-polymerized by means of heat activation, we suspected this exothermic peak is associated with self-polymerization of PC₆₁BA. In order to confirm it, PC₆₁BA was heated at 150 °C and found its 63.5% part became insoluble in chloroform. This proves our suspicion and indicates that PC₆₁BA can undergo self-polymerization upon heating. Besides this exothermic peak, a sharp endothermic peak at 233.6 °C, a small endothermic at 247.2 °C, and a very broad exothermic peak in the temperature region of 240–300 °C were also viewed in the 1st heating trace of DSC. Although their assignment are not understood at present, the former endothermic peak may originate from the melting phase transition of the survived PC₆₁BA that had no time to undergo polymerization during the rapid heating process, while the broad exothermic peak may come from the polymerization of those remained PC₆₁BA and further convert into higher molecular weight polymers. After first heating process, no obvious peaks were found in the 1st cooling process and the 2nd heating-cooling cycle of DSC except glass transition peaks around 238 °C in the cooling process while around 248 °C at heating process.



Scheme 1. Synthesis of PC₆₁BA.

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