Stabilizing polymer-based bulk heterojunction solar cells via crosslinking

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Abstract

The active layer of a polymer photovoltaic cell is mainly based on a blend of two components: a semiconducting polymer (electron donor) and a fullerene derivative (electron acceptor) to form the bulk heterojunction (BHJ). To offer optimum photovoltaic performances, the morphology of this layer has to be very carefully controlled at the nanoscale. The materials of the BHJ require specific phase segregation enabling the optimum photogenerated exciton diffusion and dissociation, and also to ensure pathways for charge carriers to electrodes. However, such a specific morphology is thermodynamically unstable over time and phase segregation occurs with thermal cycling under solar operating conditions inducing a decrease of solar cell efficiency. This review reports on the recent progress towards obtaining a stable optimized BHJ morphology and improved efficiency stability, using different chemical routes for crosslinking the organic semiconductors.

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Keywords: photovoltaic; polymer; fullerene; crosslink; morphology; stability

INTRODUCTION

Organic photovoltaic (OPV) cells have attracted a tremendous amount of interest during the last decade. Being able to produce low-cost, large-area, printed OPV modules is indeed a major challenge to answer renewable energy needs. In order to commercialize this technology, three conditions have to be met: a satisfactory power conversion efficiency (PCE); a proven cost-effective method of manufacturing; and a long-enough lifetime of modules under operating conditions. Around a thousand scientific publications are currently published every year on OPVs. Most of them deal with the development of new materials and new device architectures to improve the PCE as the main work-horse of the community. While the highest PCE of 9.2% was described in 2012,1 the stability of devices is not ensured yet and is still a subject of research that needs to be further improved in the future.

It is now recognized that the stability of OPV cells suffers from three main failure mechanisms even with a high-performing encapsulation. Firstly, there are multiple interfacial issues since these devices are made of stacks of layers to be carefully controlled at the nanometre scale. Electrodes can be sensitive to oxidation and interlayer atoms can also diffuse into the active layers. For example, we recently demonstrated that atoms of Mo, O and Ag can diffuse from the top layers of MoO3/Ag into the active layer upon thermal stresses leading to reduced performances.2 Secondly, organic polymer semiconductors suffer from photodegradation under exposure to sunlight. Indeed it is well known that one major problem associated with the application of polymers in general is their instability to weathering.3,4 The photoactive materials used in polymer solar cells are conjugated polymers, in which π-electrons are highly delocalized with consequent electro-optical properties such as solar light absorption. The direct absorption of UV–visible light by the chromophores of the polymer matrix may be responsible for direct photochemical reactions. It has been evidenced that, under the impact of light, aromatic polymers can undergo various reactions without involvement of oxygen, such as rearrangement, chain scissions or crosslinking.5 Those reactions provoke the breaking of the conjugated backbone, resulting in a loss of π-electron conjugation.6,7 As a result of polymer photobleaching, the device performances of organic solar cells are reduced. Finally, the morphology of the polymer–fullerene bulk heterojunction (BHJ) composing the active layer appears to be not stable thermodynamically. To achieve efficient devices, the phase segregation between these materials has to be tuned to form a bi-continuous network with domain sizes of the order of magnitude of the exciton diffusion lengths (below 20–30 nm). However,


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The main topic of this review concerns the specific point of how to stabilize the BHJ at the nanoscale. There are multiple techniques under development to stabilize the BHJ and consequently improve performance stability: the use of ternary blends with compatibilizers such as block copolymers, amorphous fullerene derivatives, high glass transition temperature polymers, thermocleavable polymers, specifically designed donor–acceptor systems with enhanced interactions, functionalized side-chains on the polymer or crosslinkable materials. This mini-review focuses specifically on the crosslinking approaches for OPV cells, since a state of the art already exists for organic light-emitting diodes. During the last decade there have been numerous investigations of the use of crosslinkable materials in OPV cells. Crosslinking consists of branching molecules one to the other by covalent bonding using specific materials or various stimuli (temperature, UV light, photoinitiator, etc.), and is promoted in the solid-state BHJ during device fabrication to freeze the morphology in its optimized form.

Various crosslinking approaches can be considered since the BHJ is composed of two materials, an electron-donating polymer (D) and electron acceptor (A). One can crosslink the donor to the donor (D–D), the donor to the acceptor (D–A) or the
acceptor to the acceptor (A–A). These three approaches are illustrated in Fig. 2 and are successively developed in this review.

Among the various crosslinking technologies developed so far, Fig. 3 shows the functions that have already been employed in organic electronics and more specifically in OPVs. The choice of functional group has to be made in accordance with the crosslinking external stimulus that should be compatible with the conditions of device fabrication. For example, the use of sol–gel chemistry implies activation by the presence of acid, base, fluoride or the activation of photogenerated acids by UV light stress. Epoxide and oxetane groups are also known to require a photoinitiator or acid initiator for further thermal or photo-crosslinking. Some other crosslinking functions are activated by UV light at various wavelengths, such as bromide, azide, anthracene or cinnamate. Azide groups can also promote crosslinking reactions upon thermal annealing, as well as alkenyl, diethynyl or styrene groups. In any case, the crosslinking stimulus must be compatible with the solar cell fabrication process without affecting or degrading other layers. Furthermore, it is necessary to develop techniques that will be easily transferable to large-scale, large-area manufacturing.

**CROSSLINKING DONOR TO DONOR (D–D APPROACH)**

In this approach, the crosslinkable functions are generally attached on the lateral chains of a conjugated backbone. The modified monomer can be used in a homopolymer, but is generally used as a comonomer to randomly disperse the crosslinkable functions along the conjugated backbone, given that a few percent are sufficient to create an insoluble network while retaining the structuration of the polymer. The crosslinked network may thus hinder the diffusion of PCBM in the BHJ. The polymers described in the framework of this approach are presented in Fig. 4.

One of the first demonstrations of an efficient crosslink reducing the formation of PCBM crystals (after thermal annealing at 150 °C for 2 h; Fig. 5) was described by Miyanishi et al. The stabilization of the BHJ during annealing time was achieved using poly[3-(5-hexenyl)thiophene] (P3HT) in which the crosslinkable function was an alkenyl group (Fig. 4). The PCE of these devices showed a smaller decrease (from 3.03 to 1.74%) than for non-crosslinked P3HT (3.11 to 1.00%) after 10 h at 150 °C, even if the formation of PCBM crystals was not completely avoided.

A strategy using bromine-functionalized P3HT (P3HT-Br; Fig. 4) copolymers crosslinked using UV treatment at 254 nm was reported by Kim et al. Devices prepared with the crosslinked P3HT-Br in blends with PCBM exhibited an absence of PCBM crystals (after 24 h at 150 °C) and an improved PCE stability, even after 2 days at 150 °C, due to the stabilization of the BHJ (Fig. 6). High stability with an average PCE of 2.2% was also observed for bilayer devices fabricated with P3HT-Br-10:PCBM.

This Br-involving method was also applied by the same team to a donor–acceptor copolymer (low-bandgap polymer) based on N-alkylthieno[3,4-c]pyrrole-4,6-dione (Fig. 4). The crosslink was optimized for an amount of 16% mol of bromine for this comonomer using UV treatment (254 nm), but was not possible by thermal annealing. While the non-crosslinked BHJ exhibited...
A decrease of PCE from 5.6 to 4.0 % after 72 h at 150 °C, the crosslinked BHJ showed an increase from 3.3 to 4.6% for the same ageing treatment, yielding the highest PCE obtained so far with crosslinked p-type polymers. Very recently analogues of poly(cyclopentadithiophene-alt-benzothiadiazole) (Fig. 4), with an alkenyl group modified or not by anisole or bromobenzene, were used by Waters et al. in solar cells. The crosslink was promoted by high-temperature annealing (260 °C), which could be a problem in some cases due to possible degradation of the poly(3,4-ethylenedioxythiophene) (PEDOT):polystyrenesulfonate (PSS) layer and the impossibility of using polymer substrates, but allowed an improvement of hole mobility. The initial PCEs obtained for non-crosslinked and crosslinked polymers were nearly identical (3.88 and 3.65%, respectively), but the half-life was increased by 45% in the latter case (for encapsulated devices illuminated at AM1.5).

Another important class of crosslinkable function is represented by azide groups. The crosslinking of such functionalized polythiophenes was achieved with a high-temperature treatment (above 185 °C) and was first demonstrated by Murray et al. in 1996. Azides are versatile functions that can promote crosslinks between donor polymer chains upon UV irradiation or promote cycloaddition reaction with PCBM with a thermal treatment at 150 °C (more details are given in the next section) (Fig. 7). In that study, UV irradiation allowed the first demonstration of a solvent-resistant organic transistor, without disrupting the molecular ordering and charge transport. The thermal treatment allowed the stabilization of the OPV BHJ with PCBM, even after 40 h annealing at 150 °C. Nam et al. described another use of P3HT-N₃ to crosslink the BHJ using UV light, still with improved thermal stability of OPV performance.

Crosslinked polyfluorene-alt-bithiophene) conjugated polymers bearing oxetane functions were prepared by Charas et al. and were activated with a photo-acid generator in the presence of UV light (Fig. 4). This allows patterning for various organic electronic applications. Using this technique, nanostructured donor–acceptor interfaces with the formation of columnar-grain films were prepared for OPV cells using a similar polymer, F8T2Ox1 (Fig. 4). The oxetane strategy has also been recently successfully applied by the same team to a P3HT-based polymer (P3HT-Ox10;
Figure 4. Examples of some functionalized side-chain semiconducting polymers: poly[3-(5-hexenyl)thiophene] (P3HNT); bromine-functionalized P3HT (P3HT-Br); azide-functionalized P3HT (P3HT-N₃); oxetane-functionalized polymer; bromine-functionalized N-alkythieno[3,4-c]pyrrole-4,6-dione (TPD-Br); poly(cyclopentadithiophene-alt-benzothiadiazole) (Cr-PCPDTBT); F8T2Ox1; P3HT-Ox10; PTcbpTT; and bromine-, azide- and vinyl-functionalized poly(benzo[1,2-b:4,5-b’]dithiophene-alt-thieno[3,4-b’]thiophene) (PBT).
A recent study by Carlé et al. reports a comparative use of bromine-, azide-, alkenyl- and oxetane-functionalized polymers for solar cells. In all cases, more or less insoluble polymers were obtained evidencing the efficiency of crosslinking. However, that study does not provide any absolute PCE value, so the stability curves plotted with normalized PCE could be speculative depending on the initial PCE achieved with each of these compounds. A similar study was very recently reported by Chen et al. with the aim of comparing vinyl, bromine and azide photo-crosslinkable groups grafted on the low-bandgap conjugated polymer poly(1,2-b;4,5-b’)-dithiophene-alt-thieno(3,4-b)-thiophene (PBT; Fig. 4). The initial PCEs are very close (between 2.5 and 2.7%) and then decrease differently depending on the crosslinking group. Probably due to different crosslinking mechanisms (induced by UV light at 254 nm), it was shown that solar cells based on PBT-Br and PBT-N3 exhibited more thermally stable device performance (after annealing at 150 °C for 12 h) by maintaining 78 and 66% of their initial PCE values, respectively, whereas PBT-vinyl-based device retained only 51% of its initial PCE value. These results are in accordance with the morphology observed in optical microscope images of thin films from blends of different PBT-based polymers with PCBM (Fig. 8), showing that bromine is the most efficient crosslinking group to limit the formation of PCBM crystals.

In the various examples presented in this section, crosslinked polymers retain molecular packing and good mobilities, without degrading optical and electrical properties, and allow a certain stabilization of OPV performance upon thermal annealing in the case of bromine and azide compared to non-crosslinked material. Bromine groups were also applied to maintain the ordered nanostructure of liquid-crystalline conjugated materials (polythiophene functionalized with mesogenic cyanobiphenyl) with UV treatment, as reported by Li et al. The stabilization by crosslinking improved the obtained PCE from 0.5% (non-crosslinked) to 1.2%. Another example of crosslink chemistry was shown by Ouhib et al. using diblock copolymers functionalized with acrylates to improve PCE stability with annealing time. Solar cells prepared with the crosslinked copolymer retained more than 85% of initial PCE after
165 h at 110 °C compared to 65% for P3HT under the same conditions. However, in this case, the crosslinked network of polythiophene did not fully prevent the formation of PCBM crystals (after 40 h at 110 °C).

With this approach, it is possible to use various functions to promote crosslinking reactions. Some of them can be promoted under mild conditions, with thermal or UV treatment. Moreover, some of them such as bromine or vinyl groups can be introduced on lateral chains without markedly affecting the molecular packing of polythiophenes. Copolymerization of usual monomers with comonomers bearing crosslinking functions allows control of crosslinking moieties that is critical to achieve optimal performances. However, while the donor–donor crosslink approach improves performance stability over time, it does not completely hinder the formation of PCBM crystals.

**CROSSLINKING DONOR TO ACCEPTOR (D–A APPROACH)**

With the objective of preventing the formation of micrometric PCBM crystals, various strategies have been investigated. As already mentioned, the formation of a donor–donor reticulated network slows fullerene diffusion in the active layer resulting in an increase of thermal stability of optoelectronic devices. However, a completely frozen morphology cannot be achieved yet. In this...
context, it appears that linking the acceptor to itself (A–A) or to the donor polymer (D–A) could be more effective against macrophase separation. In this case, the links (A–A or D–A) can be realized after deposition and optimization of the BHJ.

As mentioned above, Kim et al. have developed an original approach to achieve thermally stable organic electronic devices by introducing an azide crosslinkable group into a polythiophene backbone. The azide function offers the possibility to crosslink following two chemical pathways (Fig. 7) depending on the stimuli used. On the one hand, the azide could be photochemically decomposed into a molecule of nitrogen and a highly reactive nitrene function. In this case, the generated nitrene radical could react without any selectivity with the donor polymer (D–D crosslinking) and with the acceptor (fullerene derivative, D–A crosslinking). On the other hand, the azide function could thermally (at low temperature) and selectively react with the fullerene derivative through 1,3-dipolar cycloaddition to give triazolino(4′,5′:1,2)fullerenes and subsequent transformation at higher temperature into the respective azafulleroids and/or aziridinofullerenes with extrusion of nitrogen molecules (D–A crosslinking). In the latter case, no reaction could occur between the azide backbone and the donor backbone. The concept was demonstrated through the synthesis of polythiophenes bearing azide groups attached to the end of the alkyl chain (P3HT-azole). Even if azide-functionalized P3HT derivatives were first described by Murray et al., Kim et al. developed a straightforward approach by reaction of a halogenated side chain with sodium azide using 18-crown-6. Thermal treatment at 150 °C of P3HT devices containing 15% of P3HT-azole10 copolymer with PCBM as the electron acceptor resulted in the reaction of the azide group with the fullerene. As a consequence, the BHJ of solar cells containing 15% of P3HT-azole copolymers showed an average efficiency higher than 3.3% after 40 h annealing at 150 °C. This enhanced stability is due to a compatibilizer that forms in situ at the P3HT–PCBM interface and suppresses macrophase separation (Fig. 9).

Gholamkhass and Holdcroft developed new copolymers based on P3HT and polystyrene blocks using azide functions introduced on the polystyrene block (Fig. 10). BHJ devices were fabricated from azide-functionalized graft copolymer possessing a graft-chain density of 1% (n = 0.01) and PCBM. As in the previous example, a thermal stimulus helps trigger a solid-state reaction between the azide groups attached to the copolymer and PCBM.

As a consequence, films were insoluble and the morphology was stabilized, as evidenced by limited growth of macroscopic crystals of PCBM over time (Fig. 11(a)). Photovoltaic devices prepared from these stabilized layers exhibited 1.85% PCE which dropped to 0.93% over 3 h at 150 °C, whereas PCE of regular P3HT/PCBM devices, initially 2.5%, dropped to 0.5% over the same period (Figs. 11(b) and (c)).

By functionalizing a conjugated polymer, still at the end-functionalization of the polymeric chains, Khiev et al. recently reported an unprecedented approach. Indeed, the use of P3HT end-capped with anthracene (P3HT-A) in a blend with PCBM was demonstrated to morphologically stabilize BHJ solar cells. Using a simple UV-curing step, the P3HT-A chain reacted with PCBM fullerene via a [2 + 2] cycloaddition and stabilized the blend (Fig. 12). Optical microscopy images showed a decrease of the formation of PCBM crystals as a result of using P3HT-A when UV treatment (365 nm) was performed before thermal annealing. Even if the effects of UV treatment durations on the current–voltage curves were difficult to explain, an important result stands on the fact that the device performances obtained were not reduced after different UV treatments.

The D–A strategy was principally addressed according to the functionalization of P3HT with crosslinkable functions able to react with the PCBM. In this case, the chemistry is straightforward since only the polymer needs to be synthesized. However, very few functions are able to react specifically with PCBM. In particular, concerted additions of an unsaturated system (azide or diene) through [1,3] dipolar or [4 + 2] cycloaddition to the fullerene could only be envisaged. Nevertheless, this approach may be applicable to all types of fullerene derivatives (PC70BM, PC71BM, indene-C60 bisadduct (IC60BA), etc.).

CROSSLINKING ACCEPTOR TO ACCEPTOR (A–A APPROACH)

The stabilization of the BHJ nanomorphology could also be achieved by realizing a crosslinking process from a conveniently functionalized acceptor fullerene derivative. With the aim of reducing phase separation and clustering of fullerenes in the BHJ, thus reducing the donor–acceptor interfacial area, various strategies were proposed involving grafting thermally crosslinkable groups on the fullerene moiety. To our knowledge, acetylenic, styryl, epoxide, oxetane and silyl groups have now been introduced on the fullerene C60 core (Fig. 13).

Two examples of fullerene derivatives bearing diacetylene groups were developed in the search for a thermal crosslinking process. Compound F2D (Fig. 13) was used by Markov et al. in a PPV derivative–poly(F2D) bilayer structure to form an immobilized electron acceptor layer by thermal polymerization, and another polymerizable derivative composed of four butadiyne subunits was reported by Nierengarten and Setayesh for stabilizing BHJ solar cells. In the latter case, morphological changes were observed in a poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)]–PPV/fullerene film occurring during thermal treatment at 100 °C for 2 h with clear indication that crosslinking of this fullerene derivative was able to stabilize the BHJ.

In devices incorporating P3HT donor and C60-butyric acid glycidol ester (PCBG) acceptor described by Drees et al., the crosslinking of glycidyl ester in PCBG was induced by adding small amounts of the soluble Lewis acid tris(pentafluorophenyl)borane as mild initiator and by heating the sample for up to 1 h at 140 °C. A partial ring-opening polymerization was suggested from infrared spectral studies which showed the disappearance of epoxy ring absorption bands leading to short oligomer chains. While transmission electron microscopy (TEM) images of P3HT:PCBM blends showed a strong morphology change with phase separation into large dendrite-like aggregates, P3HT:PCBG films remained ‘clear’ indicating no large phase separation because of efficient thermal crosslinking process (Fig. 14). Nevertheless, an unusual degradation of the current–voltage curve was observed during this thermal treatment while the short-circuit current and the open-circuit voltage remained unchanged. An incomplete crosslinking process was suggested to be responsible for this phenomenon.

In order to avoid oxidation of the metal cathode and to suppress the use of PEDOT:PSS layer in conventional devices, Cheng et al. developed an efficient approach based on inverted solar cell structures in which an inorganic metal oxide (TiO2 or ZnO) layer was inserted between the indium tin oxide (ITO) and the active layer. Considering that surface hydroxyl groups on metal oxide are known to act as efficient electron donors, it was suggested that oxygen could be replaced by a small molecule such as azide. The success of such an approach would depend on the ability to stabilize the BHJ, which is not the case for the above examples.

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traps, the introduction of an additional n-type fullerene inter-row between both ITO and active layers might improve the device performance. Two oxetane-functionalized fullerene derivatives, [6,6]-phenyl-C$_{61}$-butyric oxetane ester (PCBO) and [6,6]-phenyl-C$_{63}$-butyric oxetane dendron ester (PCBOD), were synthesized in order to demonstrate that the oxetane functionality can anchor onto the TiO$_x$ surface through a cationic ring-opening reaction using a catalytic amount of photo-acid generator upon UV irradiation and thermal treatment. Hydroxyl groups on metal oxide can serve as nucleophiles to open the ring of protonated oxetane, thereby forming a monolayer modifier by covalent bonding (Fig. 15).

Using the self-assembly properties of PCBO and PCBOD on TiO$_x$ surface, an inverted BHJ device showed an impressive PCE of 4.1%, whereas the reference device without this monolayer exhibited a PCE of 3.6%. Improvement of exciton dissociation, reduction of charge recombination, decrease of interface contact resistance and passivation of surface electron traps at the interface of TiO$_x$ were proposed as combined effects for this increase of efficiency. The acceptor PCBOD, containing two oxetane groups, was also capable of self-assembling on the TiO$_x$ surface and a corresponding device incorporating this crosslinked PCBOD interlayer showed a highest PCE of 4.5% which represents 26% enhancement over the reference device. The advantages of both self-assembly and crosslinking in a single fullerene-based molecule were then demonstrated.

The same group developed recently a crosslinkable fullerene material, bis(2-(trichlorosilyl)propyl) malonate C$_{60}$ (TSMC), functionalized with two trichlorosilane groups. Because of an easy hydrolysis of the trichlorosilyl moieties to produce polysiloxane, the TSMC acceptor could be self-assembled and crosslinked on a TiO$_x$ surface by simple spin-coating without the aid of irradiation or post-thermal treatment (Fig. 16). The generation of a self-assembled and crosslinked TSMC layer was shown in particular to lead to an efficient passivation of hydroxyl groups on the TiO$_x$ surface and to form a nanostructured surface. This strategy was applied in the fabrication of P3HT:PC$_{61}$BM- and PDITTDTBT:PC$_{71}$BM-based inverted devices (Fig. 16). These solar cells showed 22 and 35% improvement of efficiency, respectively, over a device without the self-assembled crosslinked TSMC layer.

Cheng and co-workers synthesized a PC$_{61}$BM-based fullerene derivative that contains a small dendron bearing two thermally crosslinkable styryl groups (PCBSD). Crosslinking of this PCBSD acceptor was carried out by heating at 160 °C for 30 min yielding a robust thin film of crosslinked PCBSD (C-PCBSD). Incorporated as an interlayer in P3HT:PC$_{61}$BM or P3HT:IC$_{60}$BA multilayer inverted devices, remarkable PCE values of 4.4 and 6.2% were obtained, respectively, with an improvement of all photovoltaic parameters, thus corresponding to improvements of 20% for P3HT:PC$_{61}$BM and 23% for P3HT:IC$_{60}$BA model devices. Superior air stability was noted indicating that the C-PCBSD interlayer

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Figure 9. (a) Structure of P3HT-azide10. (b) Efficiencies of P3HT/PCBM devices containing 0, 10 or 15% of P3HT-azide10 copolymer during thermal annealing at 150 °C with PCBM as the electron acceptor. (c) Current-voltage curves of 0 and 15% P3HT-azide10 devices with initial (3h) and long-term (40h) thermal annealing. (Reprinted (adapted) with permission from Kim et al. Copyright 2012 American Chemical Society.)

Figure 10. Stabilization of nanomorphology by solid-state reaction of PCBM with azide-functionalized graft copolymer possessing a graft-chain density of 1% (n = 0.01). (Reprinted (adapted) with permission from Gholamkhass and Holdcroft. Copyright 2010 American Chemical Society.)
Figure 11. (a) Optical microscope images of 4/PCBM (refer to Figure 10) blend (50:50) before (A) and after (B) 1 h treatment at 150 °C and of P3HT/PCBM (50:50) blend before (C) and after (D) thermal treatment (1 h at 150 °C). Scale bar: 100 μm. The inset in (D) shows an expanded view (scale bar: 8 μm). (b) Current–voltage characteristics of 4/PCBM (40:60 w/w): as-cast (●), thermally reacted (○) and dark current (□). (c) PCE as a function of annealing time for P3HT/PCBM (●) and 4/PCBM (○) devices with 40:60 wt% ratios.41 (Reprinted (adapted) with permission from Gholamkhass and Holdcroft.41 Copyright 2010 American Chemical Society.)

Figure 12. Left: schematic of P3HT-A, photochemical anthracene dimerization and reaction between anthracene and PCBM in a [2 + 2] cycloaddition. Right: optical microscope images of P3HT-A:PCBM layers after thermal annealing at 150 °C during 2 h (a) without UV treatment and (b) with UV treatment (365 nm) prior to annealing.42 (Reproduced by permission of the Royal Society of Chemistry.)

plays a significant role in increasing the lifetime of an unencapsulated device after exposure to air under ambient conditions (Fig. 17).

To extend the effects of the C-PCBSD interlayer on solar cell efficiency, a P3HT:IC60BA upper layer was then deposited on a C-PCBSD bottom layer with vertically oriented nanorods with the aim of creating a well-organized nanostructured interface. A marked increase of PCE reaching 7.3% was achieved and the device exhibited a marked ambient and morphological stability.51 The results of this A–A approach are currently limited to the functionalization of fullerene C60 with chemical moieties (acetylenic, styryl, epoxide, oxetane and silyl groups) able to polymerize under thermal or photochemical stress or acid initiation. This strategy proved to be effective for creating crosslinked networks with suppression of fullerene crystallites in the blends resulting in interesting stabilization of solid-state morphology. The major drawback lies in the few available polymerizable groups and the subsequent control of the crosslinking process. To date, no example of a crosslinkable group grafted on the fullerene moiety prone to react with C60 itself has been reported in the literature. Interest should be in the formation of blends of some diads, triads or oligomeric structures with the aim of avoiding the proximity of fullerenes. However, the investigation of this strategy should be limited due to the reactivity of fullerenes as electro-deficient alkenes which involves essentially cycloaddition reactions under thermal or photochemical activation.

To generate a mixed network of donor and acceptor, photo-crosslinking was investigated by Zhu et al.52 with the reaction of polythiophene end-capped with epoxide groups and PCBG as an epoxide-functionalized PCBM-based derivative (Fig. 18). This process was initiated by the addition of catalytic amounts of photoinitiator. The thermal stability of P3HT/PCBM (1.67 to 0.85%) and P3HT/PC61BG (1.72 to 0.86%) solar cells was found to be quite similar after 150 min at 120 °C, while the addition
Similarly, a very recent article reports the use of both donor and acceptor materials functionalized with vinyl groups to crosslink on the donor and/or acceptor, so this is an example of the three linking approaches together. The donor material was a low-bandgap copolymer based on benzothiophene and thienothiophene (PBDTTT-V) and the acceptor a fullerene derivative (PCBD), as shown in Fig. 19. Different blends were considered: the vinyl-functionalized donor with the classic PCBM, the corresponding electron-donating copolymer without vinyl groups with PCBD instead of PCBM and a blend with both vinyl-functionalized materials. These experiments showed that crosslinking reactions occurred between polymer chains leading to an insoluble film. When PCBM was used, it could washed off the active layer, but this was not the case when PCBD was used, indicating a reaction between fullerene molecules. The most efficient improvement in stability of device performance was obtained when both vinyl-functionalized materials were used, as shown in Fig. 19, where 79% of initial efficiency was retained after 8 h at 150 °C.

Optical microscope images confirmed that fewer crystals are formed compared to PBDTTT-V:PCBM, but fewer than with the non-functionalized materials.

This strategy involving combining the D–D, A–A and A–D approaches has the significant advantage of being more general and more versatile even if time-consuming chemistry is required since both acceptor and donor need to be functionalized. Thus, only a few examples have been reported. Nevertheless, by selecting appropriate functions, this approach may be developed in the future.

To conclude, the three approaches, D–D, D–A and A–A, gave successful results for the stabilization of morphology and the stability of performance over time. However, the different approaches are not equivalent in terms of these parameters. D–D crosslinking usually leads to the poorest stability of the morphology as the diffusion of PCBM is not retained and crystals are observed after long periods of thermal annealing. In contrast, crosslinking between acceptor molecules stabilizes the morphology, but with the trade-off that there is less choice of functions available to perform reactions onto fullerenes.

Figure 13. Crosslinkable fullerene derivatives bearing diethynyl, silyl, epoxide, oxetane or styrene functionalities.

Figure 14. (a) TEM images of P3HT:PCBM (left) and P3HT:PCBG (right) films after annealing at 140 °C for 1 h. (b) Current–voltage curves (AM 1.5 simulated, 80 mW cm⁻²) of P3HT:PCBG device post-treatment and after additional thermal treatment (10 min at 140 °C). (Reproduced from Drees et al. with permission from the Royal Society of Chemistry.)
CROSSLINKERS IN POLYMER–FULLERENE BLENDS

The crosslinking approaches previously reviewed all require the synthesis of crosslinkable donor and/or acceptor semiconductors. Such a material preparation can be costly. These materials may also become unstable upon storage and during OPV processing steps because they are crosslinkable and contain reactive moieties. Another route to stabilize the BHJ may be the use of crosslinkers, i.e. molecules used as additives, in blends of semiconductors. This pathway leads to versatility, being applicable to multiple semiconducting polymers. This aspect is of great importance since the development of OPV-designed high-efficiency materials is attracting an increasing amount of interest. In this context, the stabilization strategy has to be applicable to future materials.

Very few examples of crosslinkers have been used in BHJ solar cells so far. Ryu and Jang\textsuperscript{54} incorporated an acrylate-based photo-curable crosslinker with a photoinitiator (Fig. 20) into P3HT:PC\textsubscript{71}BM blends. A slight increase of the device performance was observed (from 3.09 to 3.43\% or 3.23\% with 1 or 2\% of crosslinker, respectively) as a result of the crosslinker, but no stability analysis was reported in that study.
Figure 17. Normalized PCE as a function of time for devices A ([ITO/ZnO/C-PCBSD/P3HT:PCBM (1:1 w/w)/PEDOT:PSS/Ag]) and B ([ITO/ZnO/P3HT:PCBM (1:1 w/w)/PEDOT:PSS/Ag]) stored for 35 days in air under ambient conditions.50 (Reprinted (adapted) with permission from Hsieh et al.49 Copyright 2010 American Chemical Society.)

Figure 18. Schematic of D–A crosslinking process occurring between epoxide-based polythiophene and PCBG derivative.

He et al.55 described the use of the crosslinker octane-1,8-diyl bis(1,4-dihydrobenzo[d][1,2]oxathiine-6-carboxylate 3-oxide) (OBOCO; Fig. 21). This small molecule was used as an additive in P3HT:PCBM for crosslinking fullerenes through a heat-triggered Diels–Alder reaction. By adding 5 wt% OBOCO (optimized percentage) into the OPV ink, devices showed significantly improved thermal stability compared with the untreated cells (after 4 days at 150 °C). The PCE for the device with 5% OBOCO decreases from 2.77 to 1.72% (by 38%) and that without OBOCO from 2.74 to 0.78% (by 72%). By adding 5% OBOCO into the active layer, heat-promoted fullerene aggregation was markedly inhibited, leading to significantly enhanced thermal stability of the optimal film morphology.

In terms of versatile crosslinkers for organic semiconductors, a sterically substituted bis(fluorophenyl azide) (s-FPA) has been developed56,57 which demonstrated remarkable crosslinking capabilities. This compound added in minor amounts (a few weight percent) was able to crosslink polymer chains on their alkyl side chains using a deep-UV trigger (Fig. 22). Researchers have been developing such bis-azide crosslinkers for many years58,59 because...
the UV dose required to trigger this chemistry is low and does not affect electronic and photonic properties of semiconducting polymers.

Png et al.\textsuperscript{56} applied this crosslinking strategy with success to various types of organic electronic devices in organic light-emitting diodes with crosslinking of the emitting layer without affecting electroluminescence properties. The interlayers were efficiently crosslinked exhibiting easy multilayer solution processing to avoid dissolution of bottom layers by the solvent used to coat top layers. Transistors were also shown to be unaffected by this crosslinking procedure. In terms of solar cells, however, s-FPA was not used in polymer–fullerene blends. Solar cells were prepared by backfilling with PCBM a pre-patterned crosslinked polymer layer based on OC\textsubscript{10}C\textsubscript{10}-PPV. Patterning was achieved using non-crosslinked phase-directing agents, further developed from the polymer template before backfilling with fullerene derivatives.

Recently, and almost simultaneously, the same team of Ho and co-workers as well as that of Meredith and co-workers used s-FPA as a crosslinker in P3HT sub-layers backfilled with PCBM.\textsuperscript{50, 61} In both studies, highly efficient OPV cells were produced. Backfilling with PCBM such a nanotemplated polymer network may be suitable for large-scale manufacturing. However, as evidenced in both studies, the resultant BHJ remains sensitive to temperature. The fullerene molecules are here not locked in the nanostructured polymer template. As a consequence, such a BHJ may not be more stable over time and temperature under operating conditions.

The crosslinking approach has been used to prepare nanostructured donor–acceptor interfaces in photovoltaic cells. Indeed, poly(fluorene-alt-bithiophene) functionalized with oxetane groups blended with polystyrene, in the presence of a photo-acid generator, could be crosslinked via UV light and thermal treatment after deposition.\textsuperscript{34} Surface patterning by removal of polystyrene left a columnar nanostructure (250 nm in diameter) that could be further filled with PCBM. However, devices prepared in this way presented lower PCEs than that of usual BHJ. Finally, \textit{in situ} n-doping and crosslinking of semiconducting polymers as efficient insoluble electron-transporting materials for inverted polymer solar cells was achieved using a crosslinker similar to s-FPA, namely bis(perfluorophenyl azide).\textsuperscript{62} We recently developed a universal methodology based on a novel bis-azide-based crosslinker able to stabilize any kind of polymer–fullerene blend using thermal crosslinking of fullerene molecules \textit{in situ} after completion of the optimized BHJ morphology. This technique enabled
one to thermally stabilize solar cell efficiency of devices based on P3HT:PC_{71}BM as well as of devices based on highly efficient state-of-the-art low-bandgap polymers blended with PC_{71}BM.

**CONCLUSIONS AND PERSPECTIVES**

Particular attention has been devoted in recent years to the development of new donor and acceptor semiconducting materials, the establishment of relationships between molecular structure and thin-film morphology, photophysical and photovoltaic properties, and also the elaboration of new device concepts such as the BHJ photoactive layer to enhance the efficiency of organic solar cells. Among the various organic materials designed and synthesized by chemists, fullerene derivatives are still the most popular and efficient acceptor materials used in these devices. But their propensity to phase-segregate and to form crystallites in the active layer is one of the major problems responsible for nanometric morphology instability and reduction in efficiency of devices. This review was devoted to the strategy for crosslinking materials as a powerful method to overcome this drawback. The different approaches for crosslinking polymer and/or fullerene materials were reviewed, showing that each of them presents advantages and drawbacks. In the D–D approach the degree of reticulation can be controlled to allow the structuring of the polymer. Various functions are possible to promote this reaction in the solid state using thermal or UV treatment. The latter is the most interesting, as the crosslinking step can be disconnected from the thermal annealing necessary to optimize the morphology. However, in most cases, PCBM crystallization is not completely eliminated. In the D–A approach, the stabilization of the morphology is improved, and the link to the acceptor can be controlled via the amount of introduced functions. However, the method is limited by the choice of functions available to enable reaction of donor with fullerene. The same remark can be made about the A–A approach. Moreover, control of addition to fullerenes is important to retain electron-accepting properties. The A–A approach appears to be the most efficient for inhibiting PCBM crystallization upon thermal stress.
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