Organic photovoltaics: a chemical approach†

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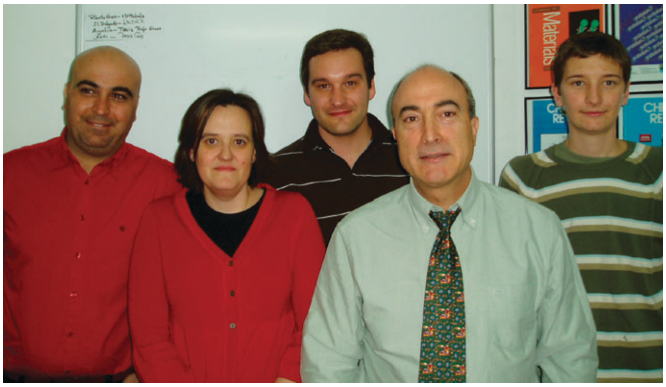
The design of new organic functional molecules able to harvest sun light and efficiently undergo photon to current energy conversion processes is at the forefront of chemical challenges. In this review, the fundamental contribution of chemistry to the multidisciplinary field of organic photovoltaics is presented in a systematic way through the wide variety of organic compounds synthesized to be successfully used in photovoltaic devices.

Introduction

Energy is currently the most important problem facing mankind. The "fire age" in which our civilization has been based from the very beginning is approaching its end. Human beings have been burning a wide variety of materials since early times, and with the advent of carbon-based fossil fuels in the last two centuries, their combustion has become nowadays a major problem due to the huge amounts of carbon dioxide emissions produced all over the world. Because of the resulting pollution, global warming and degradation of the planet, a new era based on non-contaminating renewable energies is currently a priority. In this regard, the Sun, which can be considered as a giant nuclear fusion reactor, represents the most powerful source of energy available in our solar system and, therefore, its use for providing energy to our planet is among the most important challenges nowadays in science. Actually, the energy received from Sun, calculated as 120 000 TW (5% ultraviolet; 43% visible and 52% infrared), surpasses that consumed on the planet over a year by several thousand times.[1]

Photovoltaic (PV) solar cells are currently a hot topic in science, and since the first silicon-based device prepared by Chapin in 1954 exhibiting an efficiency around 6%,[2] different semiconducting materials (inorganic, organic, molecular, polymeric, hybrids, quantum dots, *etc.*) have been used for transforming sun light into chemical energy. Among them, photo- and electro-active organic materials are promising due to key advantages, such as the possibility of processing directly from solution, thus affording lighter, cheaper and flexible all-organic PV devices. Actually, these organic systems have received a lot of attention and a variety of excellent reviews and special issues have recently been published.[3] They are mainly focused on the race to increase efficiency, as well as on those aspects mostly related to the understanding of those essential optical and electronic processes able to transform photon energy into electricity, thus providing a general overview on the state of the art in organic PV solar cells.[4]

Therefore, the aim of this review is to emphasize the contribution of chemistry to this field by covering those aspects related with the nature and properties of the types of compounds used to construct "all-organic" PV devices. Furthermore, the systematic organization of the compounds used for different purposes and tasks in organic solar cells



From left to right: S. Filipone, M.A. Herranz, J. L. Delgado, N. Martín and P.-A. Bouit

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should help the chemical community to think about and to rationalize further alternative compounds which, eventually, result in a better performance of the PV devices.

Thus, this is not a comprehensive review on the chemistry of the so-called "all-organic" or "excitonic" (absorption of light results in the formation of excitons, basically a neutral electron-hole pair) solar cells but, on the contrary, a presentation of the most relevant chemical compounds which currently define the different classes of "all-organic" PV cells. Thus, we have organized this review in four main parts: (i) Basic processes in organic solar cells; (ii) Bulk-heterojunction plastic solar cells based on semiconducting π-conjugated polymers and fullerenes; (iii) Molecular bulk-heterojunction solar cells based on π-conjugated oligomers or dyes and fullerenes; (iv) Other carbon nanostructures, namely endohedral fullerenes and carbon nanotubes (CNTs). Actually, the presence of pristine fullerenes (C_{60} and C_{70}), or most commonly a fullerene derivative (namely PCBM: 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61}), is a common feature in sections (ii) and (iii). Therefore, it is not surprising that there has been recent interest in other available related carbon nanostructures, such as endofullerenes and CNTs, which is covered in (iv).

(i) Basic processes in organic solar cells

Organic solar cells are constituted by semiconducting organic materials formed by contacting electron donor and acceptor compounds (p/n type). A further improvement in the construction of organic photovoltaic devices (OPV) consists on the realization of interpenetrated networks of the donor and acceptor materials. In such bulk heterojunction (BHJ) solar cells, the dramatic increasing of the contact area between the D/A materials leads to a significant increase of the number of generated excitons as well as their dissociation into free charge carriers and hence on the power conversion efficiency (Fig. 1).

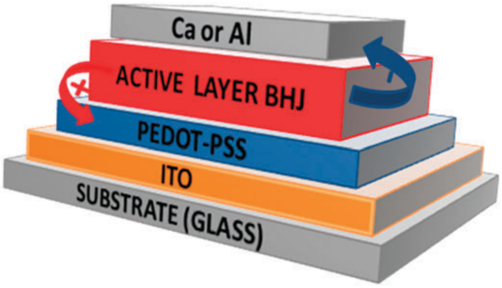

Fig. 1 Basic chemical components for a typical organic photovoltaic (OPV) solar cell.

Transformation of solar energy into electricity occurs through a series of optical and electronic processes which basically involves: (i) optical absorption of sun light and formation of the exciton; (ii) exciton migration to the donor–acceptor interface; (iii) exciton dissociation into charges (electron and holes), and (iv) charge transport and collection at the electrodes. All these steps are not totally understood at present and a number of research groups are currently dedicated to unravelling essential aspects in the search for better energy transformation efficiencies.[5] In contrast to inorganic semiconductors, which upon light excitation form free electrons and hole carriers, organic compounds form excitons whose dissociation into free carriers is not straightforward. Due to their low dielectric constants, it needs to reach the donor–acceptor interface to dissociate into free charges; the driving force for this exciton dissociation being provided by the energy difference between the molecular orbitals of the donor and acceptor.

The transport of the thus generated free charges toward the electrodes represents another important issue. Organic materials typically show charge carrier mobilities significantly lower (around 10^{-5} to 1 $cm^2\ V^{-1}\ s^{-1}$ ranging from amorphous to crystalline materials) than those of inorganic semiconductors

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(around 10^2–10^3 cm^2 V^{-1} s^{-1}). Since charge carrier mobility is strongly dependent on the molecular organization of the material, in order to achieve better efficiencies, a good control on the morphology of the donor–acceptor materials at a nanometre scale is necessary. Furthermore, an efficient charge carrier mobility is essential to prevent charge recombination (geminal or bimolecular) processes which result in lower energy conversion efficiencies.

In summary, an appropriate choice of the donor and acceptor materials is critical to ensure a good match between them in terms of optical, electronic and morphological properties, which eventually determine the effective photocurrent and performance of the PV device. Therefore, the rational design of new materials able to improve some specific demands within the PV device is critical for the successful development of competitive solar cells. In the following sections, we will discuss those materials mainly used in the preparation of "all-organic" solar cells according to their chemical nature and composition.

(ii) Bulk-heterojunction "plastic" solar cells

The term "plastic solar cells" has been coined for those photovoltaic devices using polymers in their constitution. Thus, although a variety of donor and acceptor polymers have previously been used for constructing PV devices, the highest efficiencies have been achieved by mixing electron donor polymers with fullerenes as acceptors. Polymer:fullerene (BHJ) based solar cells[4a,6] are considered suitable candidates to obtain low-cost renewable energy from a large-area, flexible, plastic material.

Fullerenes and their derivatives possess important electronic properties like small reorganization energy, high electron affinity, ability to transport charge and stability, that makes them (see below) one of the best candidates to act as electron acceptor components in BHJ photovoltaic PV devices.[4,7] On the other hand, MDMO-PPV {poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)]-1,4-phenylenevinylene} and P3HT [poly-(3-hexylthiophene)] have been by far the most studied π-conjugated polymers as donor components in BHJ devices. Actually, both polymers have been thoroughly studied from a morphological and electronic standpoint to form BHJ devices by mixing with fullerene derivatives, namely PCBM (**19**, Fig. 4). In fact, the best fullerene/polymer combination has been obtained with PCBM/P3HT(regioregular) mixtures, reaching energy conversion efficiencies in the range of 5%.[8]

In the following, we will briefly describe the most relevant achievements both in the chemistry of polymers as well as on the fullerene chemical modifications for PV purposes.

(a) Polymers for BHJ photovoltaics

Polymers endowed with fullerenes is a broad interdisciplinary field of interest for a variety of purposes.[9] However, photovoltaics are among the most realistic applications for polymer/fullerene blends.

The chemistry of π-conjugated polymers has been focused on tuning their energy (HOMO and LUMO) levels in order to have a good control on the band gap of the polymer. This is a key issue to modulate the light harvesting properties of the polymer [low band gap polymers (lower than 1.5 eV) absorb in the visible region] as well as the right energy match with the acceptor moiety which, eventually, controls the open circuit voltage (V_{oc}) values, and hence the cell power conversion efficiency.

Since π-conjugated polymers constitute a specific field in their own right, we will discuss the trends currently followed in polymer chemistry to improve the performance of the "classical" MDMO-PPV and P3HT. Some of the most relevant polymers synthesized so far are shown in Fig. 2. All of them involve the use of alternating donor and acceptor moieties within the polymer backbone since they allow a fine tuning of the band gap of the polymer, as well as an improvement of planarity and hence of the mobility of the charge carriers. Thus, a variety of soluble electroactive carbo- and heterocyclic derivatives such as fluorene, thiophene, cyclopentadithiophene and carbazole have been used as electron rich units, whereas benzothiadiazole and thienopyrazine have recently been used as the electron poor units.

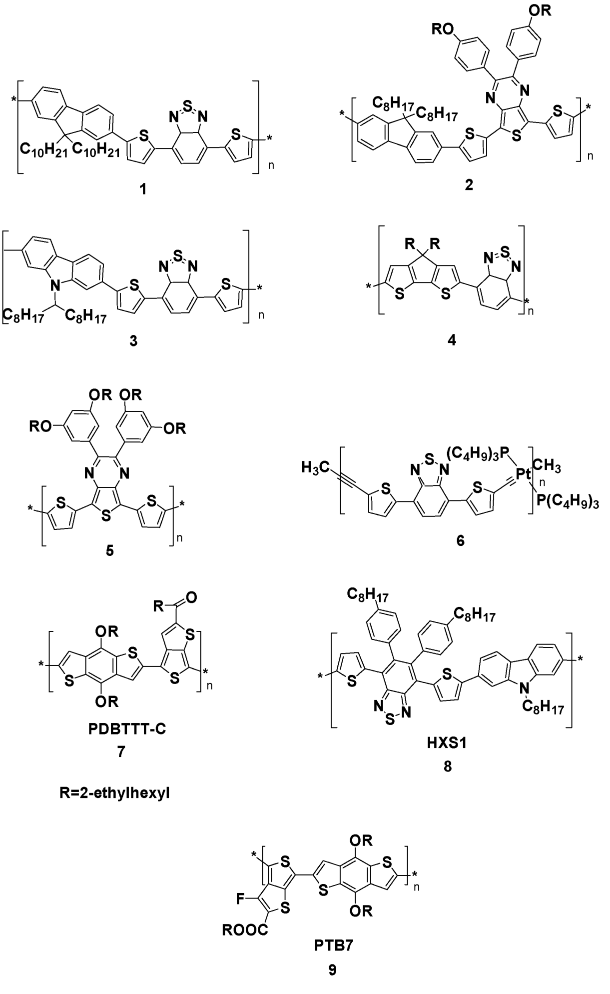
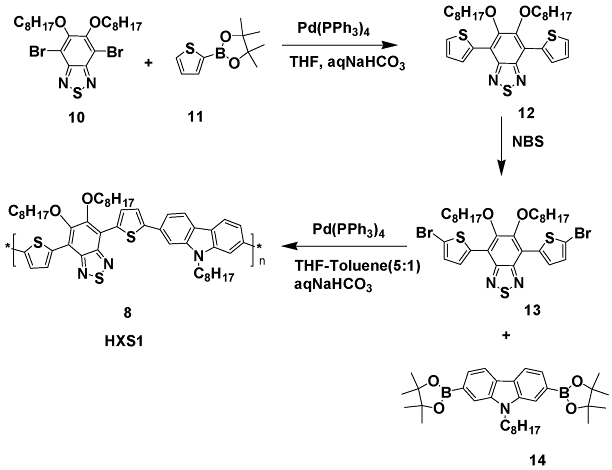


Fig. 2 Representative polymers for PV devices: (**1**) poly[9,9-didecane-fluorene-alt-(bisthienylene) benzothiadiazole],[10] (**2**) APFO-Green 5,[11] (**3**) poly[*N*-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′di-2-thienyl-2′,1′,3′-benzothiadiazole)],[12] (**4**) poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta-[2,1-b;3,4-b2]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)],[13] (**5**) poly-{5,7-di-2-thienyl-2,3-bis(3,5-di(2-ethylhexyloxy)phenyl)thieno[3,4-b]-pyrazine},[14] (**6**) platinum(II) polyyne polymer,[15] (**7**) PDBTTT-C,[16] (**8**), HXS1[17] (**9**) PTB7.[18]

Among the different electron donor polymers prepared so far, we want to focus on a variety of polyfluorene copolymers prepared by Andersson *et al.* known as APFO (alternating polyfluorene copolymers) (**2**), which have allowed a good control of the band gap, covering the solar spectrum up to 1000 nm. Power conversion efficiencies over than 4% have been demonstrated with APFOs in blends with PCBM.[19]

Typically, π-conjugated polymers are endowed with flexible lateral chains to improve their solubility. However, in many cases the side chains prevent the polymer backbones from close packing. Recently, a planar polymer conformation has been achieved in polymer poly(2-(5-(5,6-bis(octyloxy)-4-(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-octyl-9*H* carbazole, HXS-1) bearing two octyloxy chains on the benzothiazole ring and an octyl chain on the carbazole ring. The synthesis of HXS-1 is shown in Scheme 1 to illustrate the synthetic strategy followed for the preparation of this kind of polymer. Thus, the coupling reaction of 4,7-dibromo-5,6-bis(octyloxy)benzo-2,1,3-thiadiazole (**10**) with 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**11**) using $Pd(PPh_3)_4$ as the catalyst precursor and aqueous $NaHCO_3$, and THF as solvent, led to compound **12** in moderate yield. Bromination of **12** with *N*-bromosuccinimide afforded **13** whose further Suzuki–Miyaura polycondensation with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-octyl-9*H*-carbazole (**14**) using $Pd(PPh_3)_4$ as the catalyst precursor in a biphasic mixture of THF–toluene (5 : 1)/aqueous $NaHCO_3$ formed polymer HXS1 as a black solid in good yield.[17]

Semiconducting polymers based on alternating thieno-[3,4-b]thiophene and benzodithiophene units such as **7** and **9** show an excellent photovoltaic behaviour. The stabilization of the quinoid structure from the thieno[3,4-b]thiophene moiety leads to remarkable low band gap polymers (around 1.6 eV). A further optimization has been achieved with the new PTB7 in which the presence of the fluorine atom leads to a lower HOMO level, thus enhancing the V_{oc} parameter. With an average molecular weight around 97.5 kDa and a polydispersity index of 2.1, this soluble polymer exhibits a strong absorption from 550 to 750 nm. Interestingly, by blending this polymer with $PC_{71}BM$, which nicely complements the absorption in the visible range, it has been possible to prepare a PV device exhibiting an energy conversion efficiency of 7.40%. This value represents the highest efficiency reported so far for a polymeric solar cell.[18]



Scheme 1 Synthesis of polymer HXS1.

Since the development of new π-conjugated donor polymers for improving the efficiency in BHJ photovoltaic devices is currently a broad and very active field, out of the scope of this general presentation, for further details the reader is referred to some of the excellent monographs currently available in the literature.[20]

(b) Chemically modified fullerenes for BHJ photovoltaics

The most widely used configuration of polymer solar cells is based on the use of a fullerene derivative as the acceptor component. Indeed, fullerenes have been demonstrated to be the ideal acceptor because of their singular electronic and geometrical properties and for the ability of their chemically functionalized derivatives to form a bicontinous phase network with π-conjugated polymers acting as electron conducting (n type) material.

A variety of chemically modified fullerenes were initially synthesized for blending with semiconducting polymers (namely PPV derivatives) and to prepare photovoltaic devices. These fullerene derivatives were covalently linked to different chemical species such as electron acceptors,[21] electron donors,[22] π-conjugated oligomers,[23] dendrimers,[24] *etc.* (Fig. 3). However, in general, the obtained blends resulted in PV devices exhibiting low energy conversion efficiencies.[25]

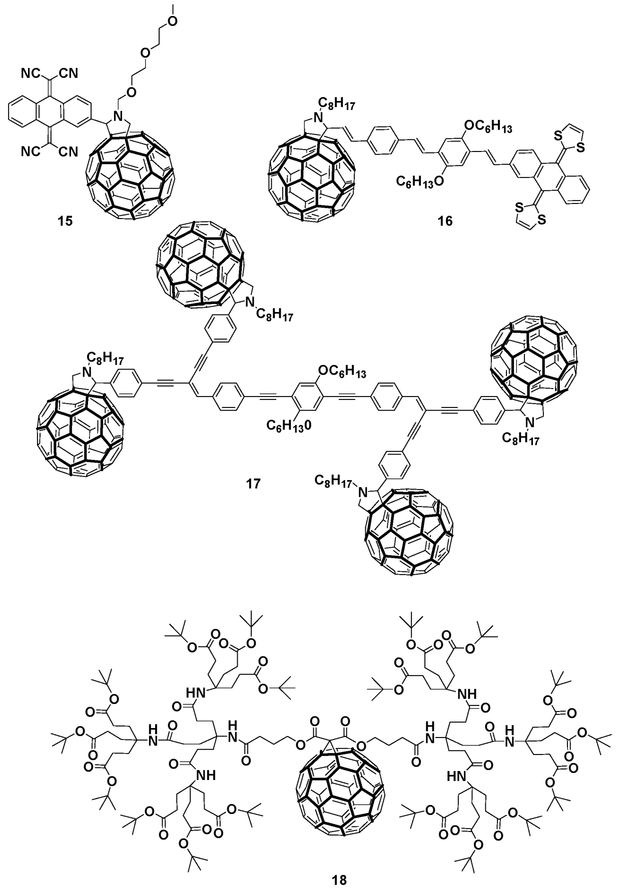
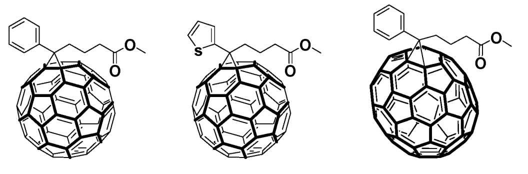


Fig. 3 Some examples of modified fullerenes bearing different organic addends (**15–18**) used to prepare photovoltaic devices.



19 (PCBM) **20 ([60]ThCBM)** **21 ($PC_{71}BM$)**

Fig. 4 PCBM and other representative PCBM analogues involving a thienyl group ([60]ThCBM) or a [70]fullerene ($PC_{71}BM$).

The best known and most widely used fullerene derivative as acceptor for PV devices is [6,6]-phenyl-C_{61} butyric acid methyl ester **19** (PCBM), firstly prepared by Hummelen and Wudl in 1995.[26] Since its first reported application in solar cells,[27] it has been by far the most widely used fullerene, being considered as a benchmark material for testing new devices.

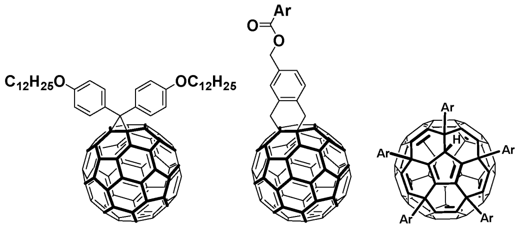
This has led to the synthesis of many other PCBM analogues (**20**, **21**)[28] in an attempt to increase the efficiencies of the cells by improving the processability, the stability or PV parameters, such as the open circuit voltage (V_{oc}) by rising the LUMO energies of the fullerene acceptor (Fig. 4).

In this regard, only small shifts (<100 meV) of the LUMO level have been obtained by attaching a single substituent on the fullerene sphere, even by using electron-donating groups. In contrast, significantly higher V_{oc} values have been achieved through the polyaddition of organic addends to the fullerene cage (~ 100 meV raising of the LUMO per saturated double bond). Recently, an externally verified power-conversion efficiency of 4.5% has been reported by Hummelen *et al.* employing a regioisomeric mixture of PCBM bisadducts as result of an enhanced open-circuit voltage, while maintaining a high short-circuit current (J_{sc}) and fill factor (FF) values.[29]

The cyclopropanation reaction of larger fullerenes to form PCBM analogues is more complex than for C_{60}. Indeed, the lower symmetry and the presence of more than one reactive double bond is often responsible for the formation of regioisomeric mixtures. Nevertheless, the loss of symmetry of C_{70} induces a stronger absorption, even in the visible region. As a result, $PC_{71}BM$[30] is considered a suitable candidate for more efficient polymer solar devices. Moreover, such devices showed the highest verified efficiency determined so far in a BHJ solar cell, with an internal quantum efficiency approaching 100%.[31] Analogously, $PC_{84}BM$,[32] has been obtained as a mixture of three major isomers. The stronger electron affinity and the diminished solubility gave rise, however, to poor power conversion efficiencies.

Although the PCBMs are the acceptors that guarantee the best performance at the moment, it does not mean that they are necessarily the optimum fullerene derivatives. Therefore, a variety of other fullerene derivatives[33] have been synthesized in order to improve the device efficiency or to achieve a better understanding on the dependence of the cell parameters from the structure of the acceptor.

Among the different modified fullerenes prepared so far, diphenylmethanofullerene **22** (DPM12) prepared by Martín *et al.* is another successful type of methanofullerene endowed with two alkyl chains to drastically improve the solubility of the acceptor in the blend and reaching efficiencies in the range of 3% (Fig. 5). Although the LUMO energy level for DPM12 is the same as that for PCBM, an increase for the V_{oc} of 100 mV for DPM12 over PCBM has been observed.[34,35] This is currently an important issue for improving the design of future fullerene-based acceptors.



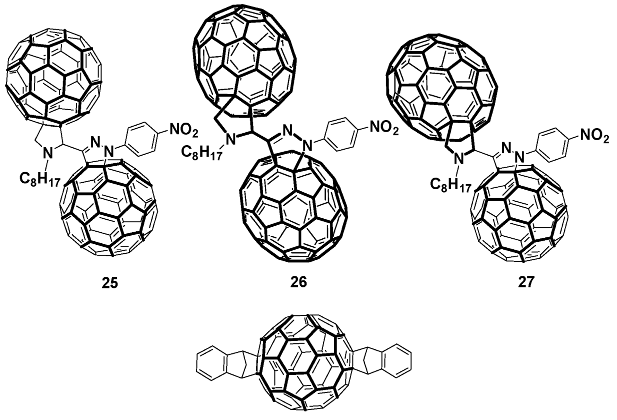
22 (DPM) **23** **24**

Fig. 5 Different modified fullerenes used as successful acceptors for PV devices.

Devices based on dihydronaphthylfullerene benzyl alcohol benzoic ester (**23**) synthesized by Fréchet *et al.* reported one of the highest power conversion efficiencies (PCE) (up to 4.5%) for a non PCBM based polymer–fullerene solar cell.[36]

An alternative molecular approach to control both the length scale of polymer/fullerene phase segregation and the electron mobility in the fullerene network is based on the use of a self-assembly fullerene shuttlecock derivative (**24**), able to form a one-dimensional wirelike domain within the active layer.[37]

Although fullerene dimers are known to exhibit low solubilities,[38] recently a series of soluble homo (**25**: C_{60}–C_{60} and **26**: C_{70}–C_{70}) and heterodimers (**27**: C_{60}–C_{70}) formed from C_{60} and C_{70} derivatives have been prepared and explored as less-known acceptors for PV devices.[39] The synthesis of these pyrrolidino–pyrazolino fullerene dimers has been carried out in a straightforward manner from the formyl-containing pyrazolino[60] or [70]fullerene,[40] which is used as the aldehyde component in the subsequent pyrrolidine formation by 1,3-dipolar cycloaddition of the respective azomethyne ylide with the fullerene.[41] As expected, [70]fullerene dimers showed better absorption in the visible spectrum than the analogues of [60]fullerene. Interestingly, non-optimized BHJ solar cells formed by blending with P3HT exhibited quantum conversion efficiencies of 37%, with a PCE of 1.0% (Fig. 6).



25 **26** **27**

28

Fig. 6 Homo- and hetero-dimers of C_{60} and C_{70} (**25–27**) and bis-cycloadduct **28** bearing two indene units.

A remarkable bis-adduct fullerene derivative formed by two indene units covalently connected to the fullerene sphere of C_{60} (**28**) has recently been reported by Hou and Li.[42] Interestingly, the presence of two aryl groups improves the visible absorption compared to the parent PCBM, as well as its solubility (> 90 mg ml^{-1} in chloroform) and the LUMO energy level, which is 0.17 eV higher than PCBM. Surprisingly, PV devices formed with P3HT as the semiconducting polymer revealed PCE values of 5.44% under illumination of AM1.5, 100 mW cm^{-2}, thus surpassing PCBM which afforded an efficiency of 3.88% under the same experimental conditions.

A major drawback in the synthesis of bis-adducts of fullerenes is that the products formed consist of a mixture of regioisomers which are not separated because of the experimental difficulties. This fact, however, does not seem to have a strong influence on the PV parameters and power conversion efficiencies. Nevertheless, from a chemical viewpoint, the synthesis of isomerically pure bis-adducts and multiadducts of fullerenes is still an open question which should be properly addressed by the chemical community.

Although some of the fullerene derivatives prepared so far exhibit good performances in PV devices, the synthesis of new fullerene derivatives with stronger visible absorption and higher LUMO energy levels than PCBM is currently a challenge for all those chemists engaged in the chemical modification of fullerenes for PV applications.

(c) Double-cable approach for BHJ photovoltaics

This strategy is based on the appendage of the acceptor moiety to the π-conjugated polymeric skeleton with the aim to maximize the interface between the two active components, thus preventing the phase separation between them. At the same time, such an approach is expected to promote an efficient charge transport to the electrodes through a nanoscale homogeneous distribution of the domains of the donor and the acceptor in the blend.

The first example of a PV cell prepared by using the double-cable approach was carried out by spin coating from poly(*p*-phenylenevinylene) and poly(*p*-phenyleneethynylene) covalently connected to methanofullerene units. The resulting photovoltaic parameters (V_{oc} = 0.83 V; J_{sc} = 0.42 $mAcm^{-2}$; *FF* = 0.29 under AM1.5 conditions) appeared to be quite promising.[43]

Interestingly, the realization of effective double-cable polymers brings the p/n heterojunction to the molecular level, thus allowing better control from a chemical viewpoint.[44] However, to date, and despite the beauty of this chemical design, double-cable polymers[9b,11c,45] have yielded poor energy conversion efficiencies. One of the reasons to account for this finding has been the low fullerene loading of the material. Therefore, new polymers have been synthesized such as PTF (**29**) or PBTC-F (**30**) with a higher fullerene content (up to 63 wt%) (Fig. 7). Other studies involving polythiophenes followed this one, with slightly better performances and efficiencies around 0.60%.[46]

An interesting alternative approach is based on the use of well-defined rod-coil block copolymers consisting of P3HT donor and C_{60} acceptor chromophores (P3HT-*b*-P(S_xA_y)-C_{60}) (**31**) as "surfactant". The control of the interface morphology of the P3HT:PCBM donor–acceptor phase domains within the composite resulted in an improvement of the efficiency with respect to the analogous solar cell fabricated without the "surfactant".[47]

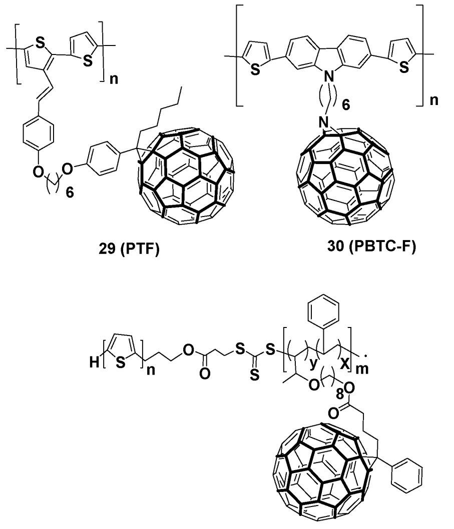


Fig. 7 Some representative examples of fullerene-containing polymers used for the double-cable approach.

(iii) Molecular bulk-heterojunctions

Despite the outstanding results obtained from BHJ solar cells formed from fullerenes and polymers, the use of commercially available P3HT displays a number of troubles associated to its synthesis, purification, and inherent electronic properties.[48] Factors such as polydispersity, regioregularity and molecular weight have a strong influence on the final performance of the photovoltaic device, which indicates that the control over P3HT structure and purity is an important issue for controlling organic photovoltaics. Concerning its electronic properties, it has been calculated that P3HT can only absorb 46% of the available solar photons,[49] owing to a bandgap of 1.90 eV and a relatively narrow absorption band. A promising solution to overcome these limitations could be the use of soluble small conjugated molecules instead of polymers. This strategy would avoid the above mentioned structural problems inherent to polymers, and allow the use of several well-defined small molecules whose electronic properties can be tuned by chemical synthesis, in order to obtain a better photovoltaic performance. Following this approach, in the last years, a number of molecules[48] such as oligomers, dendrimers, dyes and porphyrins have been used as molecular donors blended with pristine [60]fullerene or [60]fullerene derivatives, in order to prepare new and efficient photovoltaic devices.

(a) Conjugated oligomers and dendrimers as donors in BHJ-PV devices

The synthesis and study of new organic monodisperse π-conjugated oligomers is a hot topic in photovoltaics.[50] Oligothiophenes are among the most promising oligomers,

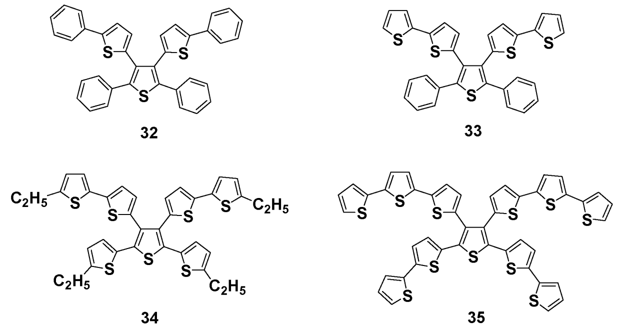


Fig. 8 Chemical structures of four X-shaped oligothiophenes.

due to their exceptional electronic properties and easy tuning of their properties by introducing functional substituents. Several substituted oligothiophenes have been described and studied for organic photovoltaics. However, most of them show a planar geometry, which tends to aggregate due to π–π stacking interactions. Sun *et al.*,[51] described recently the preparation of new X-shaped oligothipohenes (**32–35**) as electron donors in BHJ-PV devices blended with PCBM (Fig. 8). The authors observed that both the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) are highly dependent on the oligothiophene chain length. While increasing the number of oligothiophene rings, the absorption was red-shifted and broadened, therefore the light harvesting properties and the PCE increase from 0.008% to 0.8%.

Another interesting family of thiophene-based compounds has been recently described by the group of Nguyen,[52] namely diketopyrrolo-pyrrole (**36**) (Fig. 9). These appealing compounds are low bandgap well-defined molecules that display intense absorption bands between 500–700 nm. Blends of diketopyrrolo-pyrrole (**36**) and $PC_{71}BM$ were prepared in different ratios and the results revealed the highest efficiency described so far for a molecular bulk heterojunction (PCE of 4.4%).

Using polythiophene-based oligomers and C_{60} derivatives tailored by complementary supramolecular building blocks, Bassani *et al.*[53] built self-assembled devices based on hydrogen bonding. The better efficiency of this device compared with the efficiency obtained for pristine C_{60}, was ascribed to the higher molecular order; which shows the crucial role that supramolecular chemistry can play for the optimization of PV devices. On the other hand, conjugated dendrimers constitute a new kind of well-defined molecular materials with monodisperse structures which are highly controllable due to precise synthetic approaches. In this context Ma *et al.*,[54] have reported on the photovoltaic properties of BHJ-PV devices prepared with blends of PCBM and various generations of dendritic oligothiopenes (DOTs) bearing from 9 to 90 thiophene units (Fig. 10). Owing to the lower HOMO levels of the DOTs, the devices showed remarkable V_{oc} values (0.93–1.06 V), which are higher by 0.3–0.4 V in comparison with P3HT-PCBM. Other photovoltaic parameters like J_{sc} and external quantum efficiency (EQE), showed a different trend, being their values increased with increasing size of the DOT. These photovoltaic parameters lead to a maximum power conversion efficiency of 1.72% for compound **38**, which is composed by 42 units of thiophene.

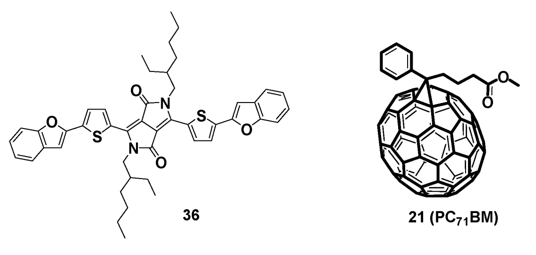


Fig. 9 Chemical structures of DPP(TBFu)$_2$ and C_{71}-PCBM.

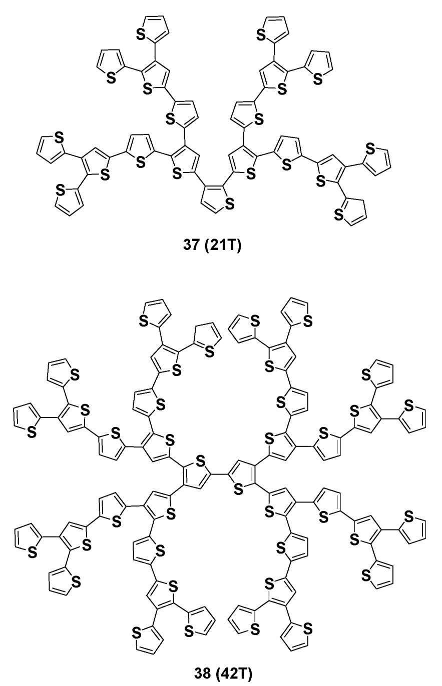


Fig. 10 Chemical structures of the DOTs containing 21 and 42 thiophene units.

(b) Organic dyes as donors in BHJ-PV devices

Following the use of monodisperse and well defined molecules for the preparation of BHJ-PV devices, in the last years a new and interesting approach has emerged in the photovoltaic field. Organic dyes are single molecules which display high absorption extinction coefficients and electronic properties which can be easily tuned by chemical synthesis. Roquet *et al.*[55] have described the synthesis of triphenylamine (TPA) based compounds (**39–41**) (Fig. 11) bearing several units of dicyanovinylene. Photovoltaic studies on these compounds blended with C_{60} in bulk and bilayers heterojunctions reveal a high value of V_{oc} in the BHJ-PV devices due to their high oxidation potential. Owing to an intramolecular charge transfer band from the TPA core to the dicyanovinilene acceptor groups, and to the above mentioned high V_{oc}, an improvement of the power conversion efficiency was observed, while the number of dicyanovinylene acceptor units increase in the molecule (0.49–1.17%).

Kronenberg *et al.*,[56] have recently described the photovoltaic study of blends of merocyanines and PCBM. These dyes

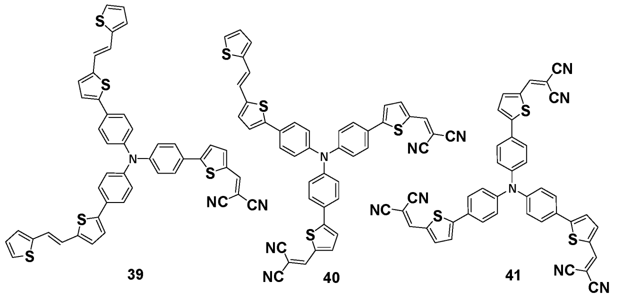


Fig. 11 TPA derivatives bearing one or more dicyano-vinylene groups.

exhibit intense absorption bands (ε up to 1.4×10^5 M^{-1} cm^{-1}) at different wavelengths in the visible spectral region. For several merocyanine dyes (**42**) power conversion efficiencies around 1% were obtained under standard AM 1.5 conditions. However, the best performance was obtained for MD 304 due to a higher J_{sc} value (6.3 mA cm^{-2}) and a V_{oc} of 0.76 V which lead to a PCE of 1.74%.

In order to harvest light in the NIR region, where almost 50% of the sunlight power is displayed, Silvestri *et al.*[57] described the synthesis of two new squaraine derivatives (**43**, **44**) (Fig. 12) displaying intense absorption from 700 nm to 800 nm in solution. Photovoltaic studies of blends of these dyes with PCBM revealed a power conversion efficiency up to 1.3%. To the best of our knowledge this is the first efficient device prepared using NIR light harvesting molecular dyes. In order to improve the efficiency of squaraine/PCBM based BHJs, Mayerhöffer *et al.*[58] studied the charge carrier mobility of a series of squaraine dyes bearing a dicyanovinyl unit, preparing OFET devices. The authors showed that the most efficient photovoltaic device (PCE = 1.79%, J_{sc} = 12.6 mA cm^{-2}) presented good hole-carrier mobility. This remarkable PCE value was attributed to well packed domain of squaraine and PCBM. Besides, the introduction of the dicyanovinyl moiety favorably changes the absorption properties of these squaraine dyes and, therefore, the capability to harvest solar energy. This study illustrates nicely the importance of tuning both absorption properties and morphology in molecular BHJ cells, as has previously been shown with polymer-based devices.

Borondipyrromethene (bodipy) dyes (**45**, **46**) are another kind of organic dye widely used for their outstanding absorption and fluorescence properties in the visible range. Rousseau *et al.*[59] took advantage of the ease of chemical modification on the bodipy core to tune the optical properties of the dyes, and reached 1.3% efficiency in bodipy:PCBM BHJ devices (Fig. 13). Using the same family of dyes, these authors[60] built BHJ devices with both bodipy donors, which display complementary absorption properties in the visible range (λ_{max1} = 590 nm, λ_{max2} = 675 nm). This strategy has solved the problem of the narrow absorption of these organic molecular dyes. An efficiency of 1.7% has been described with this multidonor BHJ, which represents an increase of 0.4% compared to the best efficiency described with a single bodipy donor. This significant increase nicely illustrates the importance of harvesting sunlight in the whole solar spectrum in order to obtain more efficient photovoltaic systems.

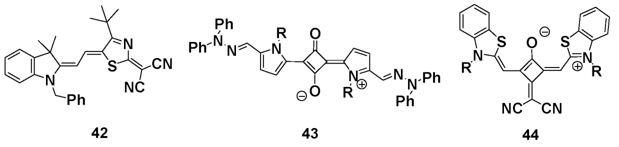


Fig. 12 (**42**) Merocyanine MD 304; (**43** and **44**) squaraine derivatives used for preparing PV devices by blending with PCBM.

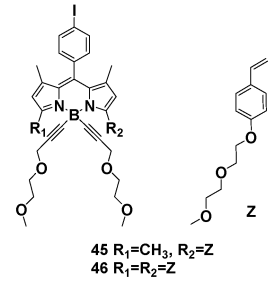


Fig. 13 Bodipy dyes used for PV devices by blending with PCBM.

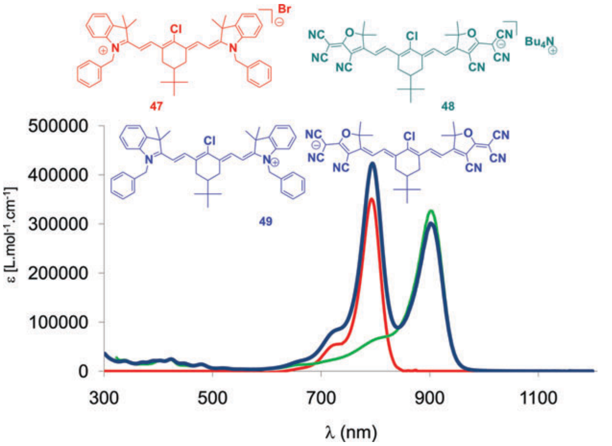


Fig. 14 UV-vis spectra and structures of the cyanines blended with PCBM for PV devices.

Using a similar strategy, we have described a new organic salt (**49**) by association of two NIR absorbing cyanine dyes (**47**, **48**), which exhibits a good solubility in organic solvents (Fig. 14).[61] As a result of the combination of the two cyanines, the complex is able to absorb light in a broad range of the solar spectrum (650–950 nm) displaying outstanding light harvesting properties in the NIR region with giant extinction coefficients. In preliminary experiments, the sun to power conversion efficiency obtained for the cyanine–cyanine complex:[60]PCBM (PCE = 0.4%) was higher than the efficiency observed for blends of PCBM:cyanine-**47** or PCBM:cyanine-**48**. This result indicates that the new dye is an appealing system for further studies as a light harvester for photovoltaics.

(iv) Organic solar cells with innovative carbon nanostructures

As mentioned above, one of the fundamental limitations of OPV device PCEs has been the molecular orbital offset between the available donor and acceptor materials.[4] Toward this goal, new acceptor materials systems are being designed and synthesized to optimize the donor/acceptor energy levels in order to increase the device photovoltage. From the variety of nanoscale size shapes with fascinating properties that carbon is able to provide,[62] carbon nanotubes (CNTs)[63] and endohedral fullerenes[64] are of current interest because of their promising applications in next-generation organic photovoltaics, due to their outstanding intrinsic electronic properties.

(a) Endohedral fullerenes

Novel acceptor materials with LUMO energies closer to that of the donor, such as the derivatives of metalloendohedral fullerenes $M_3N@C_{80}$, where the choice of metal (M = Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) allows the fine tuning of the LUMO levels as well as the absorptive coefficients of the fullerene species, offer the possibility of considerably increasing the PCE of OPV devices.

In preliminary investigations, $Sc_3N@C_{80}$ and $Y_3N@C_{80}$ were shown to be applicable as part of electron-donor/acceptor systems in combination with powerful donors such as ferrocene[65] or π-extended tetrathiafulvalene[66] derivatives (exTTFs) (Fig. 15) (**50** and **51**, respectively). The photophysical investigations revealed a significant stabilization of the radical ion pair state of $Sc_3N@C_{80}$-ferrocene when compared to an analogous C_{60}-ferrocene dyad.[64]

These encouraging results have recently been complemented with the preparation of BHJ based solar cells involving a $Lu_3N@C_{80}$ fulleroid modified with a phenyl butyric acid hexyl ester (**52**, PCBH) solubilizing group and blended with P3HT.[67] In photophysical experiments, the efficient charge transfer between P3HT and the $Lu_3N@C_{80}$-PCBH were confirmed. The optimized P3HT/$Lu_3N@C_{80}$-PCBH active layer morphology has resulted in OPV devices with V_{oc} values as high as 890 mV (260 mV above reference devices made with C_{60}-PCBM) and a similar photocurrent and fill factor compared to P3HT/C_{60}-PCBM reference devices (Fig. 16). The higher overall PCE (4.2%) of the devices fabricated is attributed to a better positioned LUMO level that captures most of the energy associated with each absorbed photon.[46] Further investigations, considering comparative analysis of the film absorption and X-ray diffraction, indicate that the optimized blend ratio in a P3HT matrix differs from a molecular equivalent of an optimized P3HT/C_{60}-PCBM active layer, and this is related to the physical differences of the C_{80} fullerene.[68]

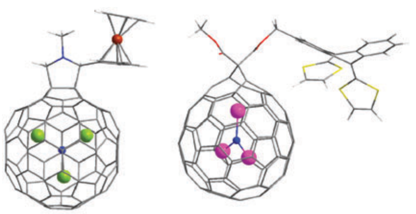


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Fig. 15 Optimized structures of a ferrocenene-I_h-[5,6]-$Sc_3N@C_{80}$ fulleropyrrolidine (**50**) (left) and the down isomer of an exTTF derivative of [6,6]-I_h-$Y_3N@C_{80}$ (**51**) (courtesy of Prof. J. M. Poblet).

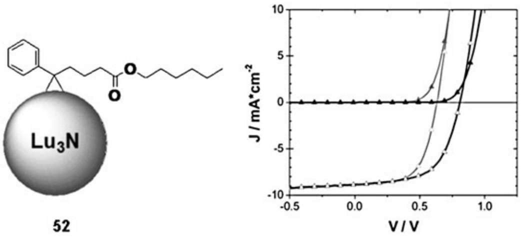

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Fig. 16 $Lu_3N@C_{80}$-PCBH (**52**) and current-voltage characteristics of P3HT/$Lu_3N@C_{80}$-PCBH (black) and P3HT/C_{60}-PCBM (grey). Solid triangles indicate the dark *J–V* curves and open triangles indicate the devices *J–V* curve under solar simulated illumination. Reprinted from ref. 67 with permission from Wiley-VCH.

Although additional investigations are necessary in the near future, the potential of endohedral metallofullerene species to enable optimized OPV devices is certainly very promising.

(b) Carbon nanotubes (CNTs)

Since their discovery, CNTs have been a constant source for scientific motivation and in recent years have emerged as an outstanding class of carbon in OPVs.[69] The most important strategies for implementing CNTs in OPV devices consider the incorporation of single-walled carbon nanotubes (SWCNTs) in dye-sensitized solar cells (DSSC), their combination with semiconducting nanoparticles in quantum dot sensitized solar cells (QDSCs), or the preparation of polymer solar cells by blending CNTs with different organic polymers. Since the important class of DSSC[70] is out of the scope of this work, in this section we will mainly focus on those recent achievements within the two following type of cells:

(i) Quantum dot/CNTs solar cells. Recently, hybrid nanocomposites consisting of CNTs and quantum dot (QD) heterostructures have emerged as excellent candidates for the fabrication of a novel class of PV devices because the nanoscale architectures play a very important role in improving the device performance of PV cells.[71,72]

In a recent example, PV cells were fabricated utilizing hybrid nanocomposites with side-wall attached ZnSe coated CdSe QDs on the surface of oxidized multi-walled carbon nanotubes (MWCNTs). The *I–V* characteristics of Al/(CdSe/ZnSe) QD-SWCNT hybrid conjugate/PEDOT:PSS/ITO PV cells were investigated under illumination with an ultraviolet (UV) lamp (6W, 365 nm)[73] and the estimated PCE was 0.34%. Considering the very large energy barrier between CdSe/ZnSe QDs and PEDOT:PSS, the performance of the PV cell is expected to be enhanced with structure optimization.

(ii) CNTs in polymer solar cells. CNTs have been usually incorporated into active layers of polymer solar cells by the dispersion of CNTs in a solution of an electron-donating conjugated polymer, such as polythiophene or poly(*p*-phenylenevinylene) (PPV) derivatives, and spin-coating the composites onto a transparent conductive electrode, typically ITO, covered with a hole-blocking layer.[74]

Friend *et al.* described the first investigation on the electronic properties of the composite formed by MWCNTs and PPV derivatives.[73a] On the other hand, Kymakis *et al.* demonstrated an increase in the cell performance by blending

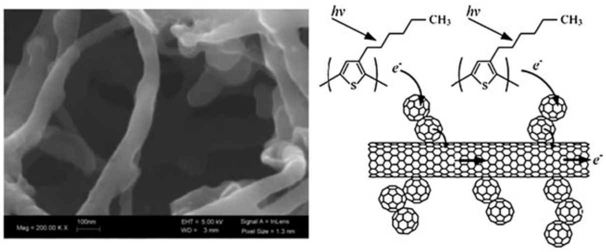

Fig. 17 SEM image of the C_{60}-complex prepared by microwave irradiation. The photoinduced charge separation at the polymer-C_{60} interface is followed by electron transfer from C_{60} to SWCNTs. The SWCNT network provides a direct path for faster electron transport towards the electrode. Reproduced from ref. 75 by permission of The Royal Society of Chemistry.

poly(3-octylthiophene) (P3OT) with only 1 wt% of SWCNTs.[73b] Since their pioneering work, many groups have exploited NTs in bulk heterojunction solar cells.[48,73c,75] However, the power conversion efficiencies of polymer-CNT solar cells are as high as *ca.* 1%, which is much lower than typical values of high-performance bulk heterojunction solar cells (3–6%) with a combination of π-conjugated polymers and fullerene derivatives including PCBM[26] or DPMs.[34,35]

When blending CNTs with different polymers, one of the major issues is to properly disperse the CNTs within the polymer matrix. In this sense, the addition of appropriate functional groups to the CNTs may result in a form compatible with the conjugated polymer. To this end, a C_{60}-SWCNT complex has recently been synthesized *via* a microwave induced functionalization approach and used as component of the photoactive layer in a bulk heterojunction photovoltaic cell (Fig. 17).[76] When compared to a control device with only C_{60} and P3HT, the addition of SWCNTs resulted in an improvement of both J_{sc} and FF, with power conversion efficiency, by as much as 78%.[77]

In recent years, several groups have investigated the possibility of using CNTs as a flexible replacement for ITO,[78] since high quality ITO is expensive due to the resource constraint of indium. In addition, ITO is not compatible with roll-to-roll fabrication processing in contrast with today's market requirements for a fully printable solar cell. For example, Rowell *et al.* demonstrated that SWCNTs based hole-collecting electrodes show well above 80% of the performance of classical ITO electrodes, and allow a significant higher bending stress than ITO based plastic substrates.[77a] Thus, corrected power conversion efficiencies of 2.5% were presented and the slight power loss in comparison to test devices using ITO contacts was mainly attributed to the increased serial resistance.

In order to improve the practical applications of CNTs in OPV devices, several aspects need to be considered: reduced photogeneration, hole blocking, charge recombination pathways, solubility and, which is probably the major challenge, the selective preparation of semiconducting SWCNTs of appropriate bandgaps. The hole blocking in the PV cells arises from the presence of metallic nanotubes in the SWCNTs, which enhances recombination due to their lack of direct bandgap, while the presence of low bandgap semiconducting SWCNTs could limit the maximum voltage which is obtained in the cells.[79] In this sense, in the past year important improvements have been reported towards the selective separation of semiconducting *vs.* metallic CNTs by means of chemical functionalization[80] or microwave irradiation.[81]

Conclusions and outlook

The most significant organic compounds prepared so far to be used in all-organic solar cells have been presented in a systematic way. Bulk heterojunction plastic solar cells consisting of a semiconducting electron donor π-conjugated polymer and a fullerene as the acceptor moiety are currently the most promising devices for practical applications. The most remarkable achievements in π-conjugated polymers have been presented, as well as those modified fullerenes which, by blending with the appropriate polymers, have afforded the best energy conversion efficiencies reported so far, reaching values as high as 7.4%.

Covalently connected π-conjugated polymer–fullerene, forming the so-called double-cable approach, represents an elegant methodology to prepare new materials which, up to now, has afforded comparatively very low energy conversion efficiencies.

Molecular bulk heterojunctions represent an interesting alternative to the use of polymers for the preparation of PV devices. These compounds have been classified in those systems formed by π-conjugated oligomers or dendrimers and fullerenes, and the most recent dyes blended with fullerenes.

Other carbon nanostructures, such as endohedral fullerenes and carbon nanotubes, are promising materials for PV devices. Although so far only a couple of examples are known of PV devices involving endofullerenes, the high energy conversion efficiency (4.2%), similar to that found for the efficient [60]PCBM make these materials good candidates for further studies. Obviously, the main problem of these endofullerenes is currently related with their availability on a larger scale.

Regarding the use of CNTs, it is important to note that the fate of these carbon nanoforms for PV devices depends primarily on the separation of the metallic and semiconducting types of CNTs which are typically mixed in the commercially available materials. Although still low efficiencies have been reported with CNTs, the huge potential of these carbon allotropes makes them very appealing in this field.

A most important matter in all the above materials for improving the cell performance is the precise control of the energy levels of donor and acceptor components as well as the network morphology to maximize the mobility of the charge carriers. In this regard, the realization of nano-structured materials by means of bottom-up supramolecular organization is currently in its infancy[82] and, therefore, more work is need for improving the materials used for PV applications.

In summary, organic solar cells are called to play an important role for satisfying the increasingly energy demands of our society. Because of their features of low cost, flexibility and lightness, these new PV cells—which should nicely complement the commercially available silicon cells—are very appealing for a variety of new practical purposes. The outstanding achievements obtained so far put these solar cells closer to the market.

Acknowledgements

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