P3HT:PCBM, Best Seller in Polymer Photovoltaic Research

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In the field of polymer-based photovoltaic cells, poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C$_{61}$ (PCBM) are, to date, the most-studied active materials around the world for the bulk-heterojunction structure. Various power-conversion efficiencies are reported up to approximately 5%. This Research News article is focused on a survey of the tremendous literature published between 2002 and 2010 that exhibits solar cells based on blends of P3HT and PCBM.

Organic photovoltaic solar cells (OPVs) based on solution-processed bulk-heterojunctions (BHJs) of semiconducting polymers have been a world-wide growing field of interest as a source of renewable energy since their discovery in 1995.[1] Semiconducting polymers enable the fabrication of solar cells with several potential advantages, such as light weight, flexibility, and low-cost manufacturing, as well as large-area feasibility. There has been a tremendous number of scientific papers published in the field of OPVs since their discovery, with more than 1953 publications in the year 2010 alone (Source: Scifinder, Jan. 2011; keywords "organic solar cells"). One can also find numerous recent extended reviews on OPVs.[2–7] Among all of these scientific reports, the most-prominent reported material system in BHJs is the mixture of poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-[6,6]C$_{61}$ (P3HT:PCBM) (**Figure 1**). Published between 2002 and 2010, 1033 publications can be found that deal with the bulk-heterojunction based on P3HT:PCBM (Source SciFinder Jan. 2011; "P3HT" and "PCBM"). In this survey, 579 of these papers, that report operating photovoltaic cells with their respective power-conversion efficiencies (PCEs), have been successfully collected and analyzed. **Table 1** shows the increasing amount of research published on P3HT:PCBM per publication year. For each of these papers, the maximum reported PCE value is displayed in Figure 1, which also exhibits a histogram of the distribution of the PCEs. Despite the enormous research effort that has been expended on the improvement of solar cells, with the first P3HT:PCBM cells possessing a PCE of 2.8%,[8] the average efficiency (Table 1) had only slightly increased up to 3% in 2010. Whatever the year of investigation, one can still find papers relating efficiencies of a wide range of values: for example, in 2010, low efficiencies of less than 0.5% were reported, as well

as efficiencies above 4%. The PCE distribution (Figure 1) clearly shows the reasonable capability of the P3HT:PCBM blend. Most PCE values have been found as being between 3% and 4%. More precisely, the main population of publications, with more than 50 items, exhibits efficiencies between 3.8% and 4%. Now, one could expect that P3HT:PCBM-based cells could be improved up to such a value due to the fact that these materials are well known; nonetheless, there are still discussions as to how to reach this goal rapidly without processing hundreds of cells. Due to the complexity of the polymer chemistry, materials science, device engineering, and device physics involved, extended studies on P3HT:PCBM will be continued in the coming years in order to explore these model materials until the next generation of materials become easily commercially available.

Reporting the power-conversion efficiency accurately is not trivial. Scientists are required to use a standard light source (called a solar simulator) that contains adequate filters, such as the air-mass coefficient of 1.5 (AM1.5D for direct and circumsolar, and AM1.5G for global solar irradiation) to simulate indoor, calibrated solar irradiation, in order to investigate solar cells. Solar simulators are generally based on xenon arc lamps but some suppliers offer solar simulators with tungsten, mercury or metal halide lamps. The role of the filters is to minimize the mismatch between a solar simulator's and the sun's spectra. As a consequence, all solar simulators do not necessary give identical light spectra. Equally, the incident-light power also needs to be monitored and controlled continuously during experiments and bulb ageing. Various irradiance meters are available, such as bolometric or thermopile detectors and calibrated photodiodes. Generally, the standard light-input power used is 100 mW cm^{-2}. Among the 579 papers screened in this survey, more than 77% of them report solar cells tested with AM1.5 light power of 100 mW cm^{-2}. Rare are those in which the light-source nature and power were not specified. In order to homogenize the results published in the literature and avoid suspicion on a record-breaking efficiency, we encourage authors to read carefully a paper published by Prof. Yang Yang and coworkers[9] and the note "Reporting Solar-Cell Efficiency" published in 2008 *in* "Solar Energy Materials and Solar Cells".[10]

Most devices are built on indium tin oxide (ITO) on glass sheets. Only a few papers deal with devices built on ITO on flexible substrates such as poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN) or polyethersulfone (PES). ITO is chosen thanks to its transparency in the visible range and its relatively good electrical conductivity. Because of the ITO resistivity, commonly between 10 to 20 Ω/square, the active surface area, as well as the shape of the PV-cell design, are of importance and can dramatically influence the

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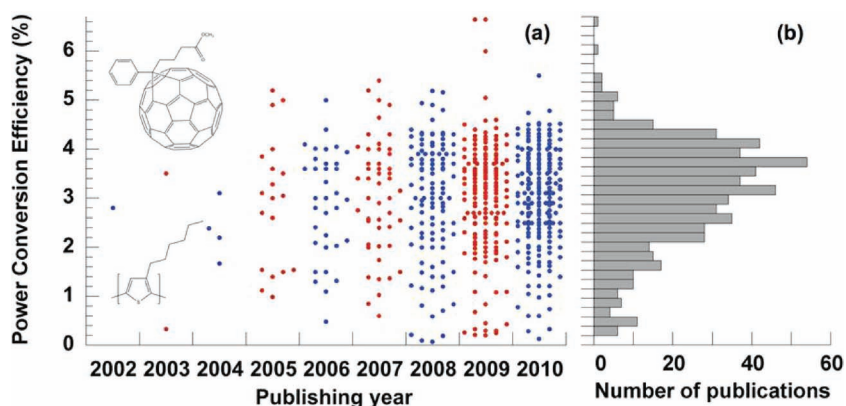
Figure 1. a) Power-conversion efficiencies of the P3HT:PCBM-based solar cells reported in each of the 579 publications screened in this survey. Each dot corresponds to the maximum PCE value reported in each publication The inset shows the chemical structures of P3HT and PCBM. b) The overall distribution of PCE values from 2002 to 2010.

performance.[11–14] As a consequence, not only the light source, but also the surface area of the photovoltaic cells is critical. Most of the analyzed publications report lab-scale PV cells with an active area between 5 and 15 mm². To date, the highest, twice-reported efficiency of P3HT:PCBM is over 6.5% by Lee et al. in 2009.[15,16] They investigated very-small PV cells with an active area of 1.5 mm × 1.5 mm. Conversely, only a few papers have reported a large active area of more than 1 cm² because manufacturing large-area devices requires the use of appropriate deposition techniques such as blade-coating, also know as Doctor Blade,[17–19] screen-printing,[20] roll to roll[21] or inkjet-printing.[22–24] Not only the active area, but also the irradiance methodology is of importance. It has been demonstrated that the use of a shadow mask with an aperture smaller or equal to the active area of the PV cell avoids overestimation of the current density.[13]

Ultimately, the best way to avoid mistakes in publishing the power-conversion efficiency of PV cells is to certify the results by sending the devices to one of the certification institutes such

Table 1. P3HT:PCBM bibliographic data extracted from the literature.

Year	Number of papers[a]	Papers mentioning PCE[b]	Average PCE [%]
2002	1	1	2.8
2003	4	2	1.9
2004	13	4	2.3
2005	31	19	2.9
2006	72	34	2.9
2007	79	47	3.1
2008	177	106	3.0
2009	267	161	3.0
2010	388	205	3.0
2002-2010[c]	1032	579	-

[a]Source SciFinder, January 2011, references containing both "P3HT" and "PCBM". [b]Papers mentioning power - conversion efficiencies analysed in this study. For complete list of publications, see Supporting Information. [c]Total numbers for papers published between 2002 and 2010.

as the National Renewable Energy Laboratory (NREL) (USA), the Fraunhofer Gesellschaft Institut für Solare Energiesysteme (FhG-ISE) (Germany) or the National Institute of Advanced Industrial Science and Technology (AIST) (Japan). To do so, one needs to encapsulate the devices and make sure no degradation will affect the efficiency during such an ageing. Of the 579 papers analyzed here, only a few publications mention a certification.[25–29] A recent review by Brabec et al. shows most of the NREL certificates achieved on OPV materials.[4] The certified cells based on P3HT:PCBM, by Plextronics, Konarka and Sharp, gave PCEs between 3.5–4%, (i.e., curiously in the same range of PCE as the maximum population found on the histogram of Figure 1).

In the case of perfect, standardized PV-cell characterization, in terms of light source and device area, the huge variability in reported efficiencies should be due to the material properties and the process reproducibility. Fundamentally, the purity of the organic materials and solvents is an issue; for example, various grades of PCBM can be supplied with a purity from 95% to 99.9%. The impact of the purity has not been clearly studied for published PV performances yet, mainly because the molecular weight, the polydispersity and the impurities can vary from batch-to-batch and thus from suppliers. Furthermore, it's still difficult to identify down to the ppm range the exact nature of the impurities. Oligomers, monomers and subproducts can be found at low amounts in so-called purified P3HT material because purification of organic compounds is difficult and it is not hard to certify ppb, or even ppm, contents. Metal residues coming from catalysts can be found in P3HT at levels from 1 to 200 ppm. All of these impurities do affect the charge-carrier transport and recombination rates.[30,31]

On the one hand, numerous investigations relate that the higher the regioregularity, the better the crystallinity and the higher the charge-carrier mobility.[32–34] On the other hand, recently, it has been shown that a too-high regioregularity may be an issue. Authors have demonstrated that decreasing the regioregularity leads to polymer-fullerene composites with superior thermal stability by lowering the driving force for the P3HT crystallization.[35,36] **Figure 2**c shows the power-conversion efficiency reported as a function of regioregularity between 2002 and 2010 (only a few papers mentioned the regioregularity). From this data, in the range 90–98% regioregularity, no significant effect is displayed on the performance of PV cells.

The molecular weight of P3HT is also a crucial parameter. The weight-average molecular weight (M_w) is controlled by the preparation technique and monitored by gel-permeation-chromatography (GPC). It has been demonstrated that P3HT in the solid state with a high M_w shows a periodic lamellar structure consisting of crystalline lamellae separated by amorphous interlamellar zones.[37] These amorphous zones seem useful for charge transport because the higher the molecular weight, the higher the hole mobility in pure P3HT.[38–40] Figure 2a shows the efficiency of the reported PV cells as a function of M_w (full circles) and number-average molecular weight M_n
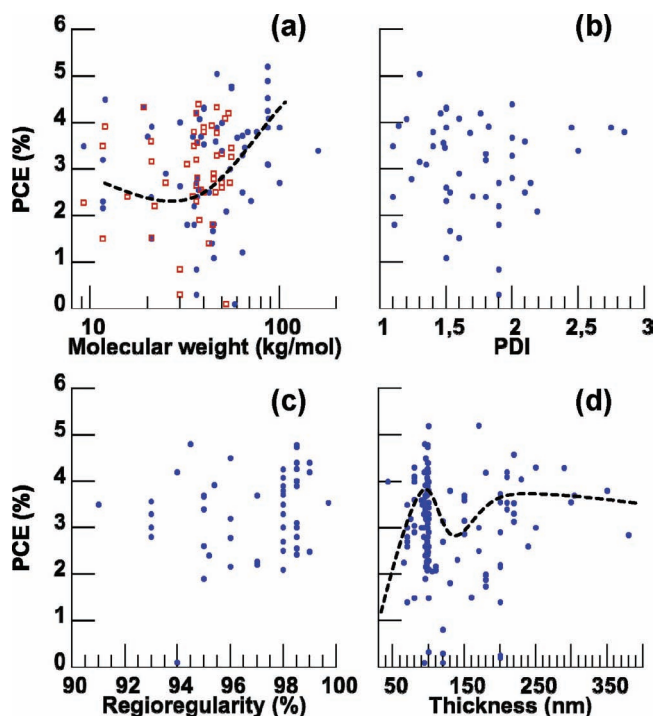
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Figure 2. a–d) Power-conversion efficiency as reported in the literature from 2002 and 2010 with corresponding parameters: molecular weights M_w (full-circle) and M_n (empty squares) (a); polydispersity (b); regioregularity (c); thickness of the P3HT:PCBM active layer (d). The dashed lines are guidelines for the eye.

Figure 3. a) PCE as a function of common solvents used in the literature: chloroform ($CHCl_3$), toluene (T), xylene, chlorobenzene (CB), o-dichlorobenzene (ODCB), and tetrahydronaphthalene (THN); "others" denotes solvents mixtures, the use of solvent additives or an unspecified solvent. b) Survey of PCE as a function of P3HT:PCBM weight ratio. c) Annealing temperature found in the literature, annealing before (Pre) or after (Post) electrode deposition. d) Thermal annealing times.

(empty squares). Due to the discrepancy in PCE, the effect of the molecular weight on performance is not clearly displayed. The trend of increased efficiency with increasing molecular weight is, however, perceptible in Figure 2a. Figure 2b shows a survey of efficiency versus P3HT polydispersity (PDI). From this review, the PDI does not significantly affect the overall performance.

The device architecture affects the overall efficiency of OPV cells. The mostly used stack of layers is the so-called "direct structure" on glass: ITO/hole-transport layer (HTL)/ P3HT:PCBM/electrode. The HTL, which also acts as an electron-blocking layer, is generally made of a solution-processed conducting polymer such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS), even if more-recent papers have exhibited other promising materials of interest, such as MoO_3. In a direct-structure, the top electrode (anode) must consist of a relatively low-work-function metal such as Al, Ca or LiF/ Al. Introduced in 2005, inverted structures have attracted much attention because of their air-stability.[41–44] The basic inverted structure is ITO/electron-transport layer (ETL)/P3HT:PCBM/ HTL/electrode. The ETL acts as a semipermeable membrane that prevents hole transport to the bottom electrode. Metal oxides such as TiO_2, TiO_x, ZnO, AZO or Cs_2CO_3 are generally the most-used materials. Correspondingly, the hole-transport layer (HTL) is typically PEDOT-PSS, but V_2O_5 or MoO_3 are also commonly used in inverted structures.[45] Similar initial power-conversion efficiencies can be obtained on the direct and inverted structures,[46] but the architecture of the device's layer composition and thickness strongly affects the efficiency. In
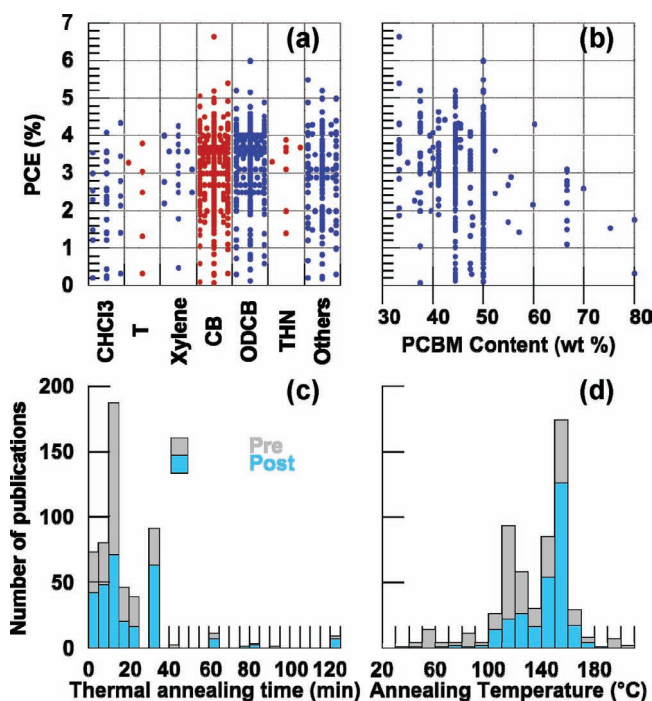
this survey, only 15% of publications were related to inverted structures. However, inverted structures will probably become the dominant geometry in the next few years due to their air-stable properties.

In BHJs, the weight ratio between the P3HT and the PCBM significantly affects the efficiency of solar cells. The P3HT:PCBM power-conversion efficiency is governed by phase separation between the two materials in the solid state. The phase diagram clearly shows how the morphology is affected by the composition ratio.[47,48] From our survey, most authors have used a P3HT:PCBM weight ratio of 1:1 (**Figure 3**a). Many authors also used a weight ratio of 1:0.8, ensuing the promising results displayed by Ma et al. and Reyes-Reyes et al. in 2005.[49,50] Anyhow, according to numerous studies on ratio effects, it is generally advised that P3HT:PCBM be used in a weight ratio between 1:0.8 –1:1 (i.e., with a small excess of P3HT).[51] According to the results presented in Figure 3b, no clear demonstration can be highlighted as to the effects of the ratio, whereas many papers deal with this effect. Actually, the dispersion of the results in the literature reflects the difficulty of having standard materials, the characterization set-up, and also of controlling the phase separation between the P3HT and the PCBM.

The thickness of the P3HT:PCBM active layer is of great importance. P3HT:PCBM enables relatively thick layers, up to 350 nm, to increase light absorption and thus the short-circuit

current of OPV cells without losing much in terms of bulk recombination. However, the use of thin layers down to 50–110 nm also leads to efficient cells thanks to its good absorption coefficient and leads to favoring percolation paths and enhanced charge transport.[52,53] Varying the P3HT:PCBM thickness can be done by working on the deposition parameters and the ink composition. Spin-coated layers can be tuned by playing on spin-speed, spin-time and/or spin-acceleration. Of the 579 papers analyzed in this survey, Figure 2d shows the power-conversion efficiency as a function of the respective thickness. The dashed line is a guide to the eye showing the consistent effect of the thickness. It is important to mention that most of the reported devices were made with thin films with a thickness of approximately 75 nm.

The P3HT:PCBM ink formulation is critical. The solid content of ink drives the viscosity and it has been demonstrated that a varying concentration greatly affects the PV performance.[54] Also, most PV inks can show gelation behaviors due to liquid-state aggregation during the ageing of solutions stored at room temperature.[55] As a consequence, the stirring, storage, and heating temperature of P3HT:PCBM before coating layers are critical; yet, rare are the authors accurately mentioning the ink history.

The key parameter to successfully obtain an optimized phase separation between P3HT:PCBM is to use techniques to anneal solid-state layers and control the morphology using atomic force microscopy (AFM), X-ray diffraction (XRD) and/or transmission electron microscopy (TEM). The most-used annealing technique is the simple thermal annealing of layers after solution-processing. A pristine P3HT:PCBM coating is too intimately mixed to form efficient percolation paths and minimize bulk recombination. Thermal annealing enables the P3HT and PCBM nanodomains sizes to be increased up to optimized values corresponding to the exciton diffusion lengths in each material, which have recently been evaluated to be as low as 3 nm and 30 nm in P3HT and PCBM, respectively.[56] Such a thermal treatment has to be carefully controlled in terms of temperature and duration, such that domains are not overgrown to be too large in size. It is also advised that the heat treatment be performed using a high-quality homogeneous heating plate. Most studies have been done with a thermal-annealing duration from 1–30 min (see Figure 3c) at temperatures from 110 °C to 160 °C (Figure 3d). The optimized duration and temperature strongly depend on the P3HT properties (M_w, PDI and regioregularity), on the P3HT:PCBM weight ratio and on the solvent used.

The PV efficiency is also affected if one thermally anneals the P3HT:PCBM layers before or after the electrode deposition.[57] Approximately half of the publications dealing with P3HT:PCBM have been made with either preproduction or postproduction thermal annealing (Figure 3c, 3d).

Thermal annealing is not necessarily compatible with the use of a flexible substrate, depending on the temperature and on the substrate nature. For large-area, flexible solar cells, room-temperature annealing is feasible using the so-called "solvent-annealing" procedure, consisting of exposing a layer to solvent vapor in order to enable molecular motion and self-reorganization. This can be done after spin-coating the P3HT:PCBM, exposing layers to the same solvent that was used

initially to prepare the P3HT:PCBM ink, or to other solvents, in a closed chamber.[58] In this survey, 20% of the publications report P3HT:PCBM efficiencies obtained using solvent-based annealing. Similar annealing behavior has been achieved using high-boiling-point solvents, enabling a slow drying of layers in a closed, vapor-saturated or open environment, such as using tetrahydronaphthalene (THN) or trichlorobenzene (TCB).[59,60] Also, as mentioned above, playing on the spin-coating spin-speed and spin-time is also used to monitor the solid-state arrangement of P3HT:PCBM. Figure 3a shows the common solvents used in the 579 articles screened here. Chlorobenzene and o-dichlorobenzene are by far the most-used solvents because they are good solvents for both P3HT and PCBM with relatively high boiling points, enabling moderate crystallization of P3HT even without further annealing.

The use of additives in the solvent is studied more and more now to self-organize the optimized phase separation between the donor and the acceptor. For example, additives such as alkylthiols, oleic acid surfactants or di-iodoalkanes are known to help fullerene aggregation because they are better fullerene solvents than polymer solvents.[61–64]

Environmentally speaking, the choice of the solution-processing solvent and additive is an issue. Industrial and governmental regulations recommend solution processing to be done from nontoxic, non-halogenated, non-aromatic solvents if possible. Up to now, non-halogenated solvents are feasible, with THN for example, though non-aromatic solvents have not been deeply studied. Also, complete toxicology-cycle studies have to be carried out around this growing OPV industry.

Thanks to this tremendous amount of literature on P3HT:PCBM, the limitations of this pair of materials have now been clarified.[2] P3HT is a great absorber and shows relatively good charge-transport properties. The short-circuit current of the optimized structure is in the range 8–12 mA cm^{-2}. The fill factor is usually found to be between 0.5 and 0.65. To date, one of the highest fill factors achieved for P3HT:PCBM was recently reported by Lee et al. at 0.74 on thermally post-casting interpenetrated bilayers of P3HT and PCBM.[65] Nevertheless, the highest reported open-circuit voltage (V_{oc}) for the best P3HT:PCBM cells is around 0.66 V.[66] Higher V_{oc} values have been achieved with P3HT using bis-adduct fullerene derivatives such as bis-PCBM or, more recently, indene-C$_{60}$ bisadduct (ICBA), with values of 0.73 V and 0.84 V respectively.[67,68] Because of this limitation, research has been oriented in finding novel electron-donating polymers able to reach higher V_{oc} values with lower HOMO levels, harvesting higher wavelengths in the solar spectra with lower band gaps without losing the driving force for charge separation (i.e., keeping enough splitting between the LUMO levels of the acceptor and the donor). This research has led to numerous so-called low-band-gap polymers designed using rational organic chemistry following these energetic rules.[69] These polymers are mostly alternating copolymers with push-pull motifs and form the so-called "third generation of semiconducting polymers",[70,71] recently leading to power-conversion efficiencies above 6%.[72,73] A strong chemistry effort is required to create the best-performing polymers. Furthermore, for each of these polymers, strong device-engineering research is needed to be able to optimize the solar-cell efficiency. P3HT:PCBM will probably still be

heavily used, especially to demonstrate new concepts of device architectures. Thanks to all the developments discovered using P3HT:PCBM by our growing community of scientists involved in polymer photovoltaics over these last 8 years, one can guess a continuous growth of the efficiency records will continue in the coming years.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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