

PCDTBT: en route for low cost plastic solar cells

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Since its inception in 1995, significant advances in the field of bulk heterojunction (BHJ) solar cells have been made and polymeric semiconductors are now considered to be one of the most promising ways to lower the cost of the energy generated by solar cells. Power conversion efficiencies (PCEs) are now reaching the threshold values for commercialisation (9.2% for single-layer BHJ and 10.6% for tandem devices). PCDTBT, a carbazole-based copolymer, is among the most efficient, stable and low-cost materials for BHJ solar cells with a high open-circuit voltage ($V_{oc} \sim 0.90$ V), power conversion efficiency of 7.5% and estimated lifetime of 7 years. PCDTBT surpasses the performance of P3HT (the most studied polymeric material until now) and is now considered as one of the new benchmarks for the development of highly efficient BHJ solar cells.

1 Introduction

Solar energy represents an attractive solution to fulfill our needs regarding green and renewable energy while protecting the environment at the same time. For example, the sun provides in one hour what humanity consumes during one year. However, the large scale development of this technology is somehow limited by the relatively high cost of an installed solar panel. Reports suggest that the cost must be decreased by a factor of 5

to 10 in order to compete with other already known energy sources such as hydropower, nuclear power, wind or fossil fuels (basic research needs for solar energy utilization, USA DOE report 2005). Polymeric semiconductors are considered to be one of the most promising ways to lower the cost of the energy generated by solar cells since they can be easily processed using techniques such as inkjet printing, spin coating, and large scale roll to roll coating techniques.¹ The last five years have witnessed significant advances in bulk heterojunction solar cells with the power conversion efficiency (PCE) reaching 9–10% range and estimated lifetime of 5–10 years.^{2,3} These great advances are mainly fueled by the design and development of

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and poly(thieno[3,4-c]pyrrole-4,6-dione) derivatives for applications in opto-electronics devices such as polymeric electrochromic devices and photovoltaic cells.



Mario Leclerc was awarded a Ph.D. in chemistry from Université Laval, Quebec City, Canada, in 1987, under the guidance of Prof. R.E. Prud'homme. After a short post-doctoral stay at INRS-Energie et Matériaux near Montréal with Prof. L.H. Dao, he joined the Max-Planck-Institute for Polymer Research, in Mainz, Germany, as a post-doctoral fellow in the research group of Prof. G.

Wegner. In 1989, he accepted a position of professor at the Department of Chemistry of Université de Montréal. He returned to Université Laval in 1998 where he has held since 2001 the Canada Research Chair on Electroactive and Photoactive Polymers. His current research activities include the synthesis and characterization of new conjugated oligomers and polymers for applications in micro- and nano-electronics, electro-optics, and genomics.

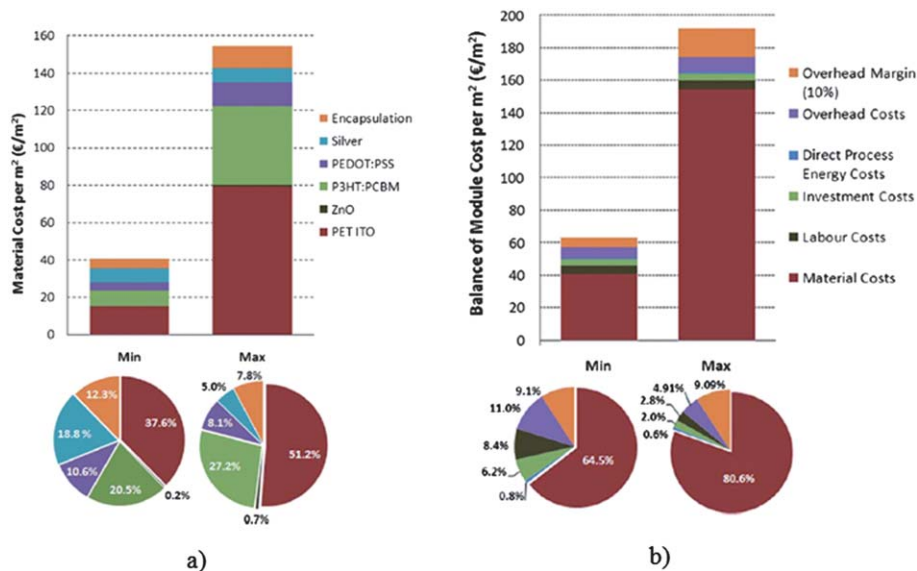


Fig. 1 (a) Estimation of the material costs in polymeric solar cells; (b) estimated costs of polymeric solar cells. Reproduced from ref. 4 with permission from The Royal Society of Chemistry.

new conjugated polymers used as the electron-donating materials in BHJ solar cells. According to the literature, competitive solar electricity from low-cost organic photovoltaics is within reach if efficiencies of *ca.* 7% can be achieved in large area modules and if lifetimes of at least 5 years can be achieved.⁴

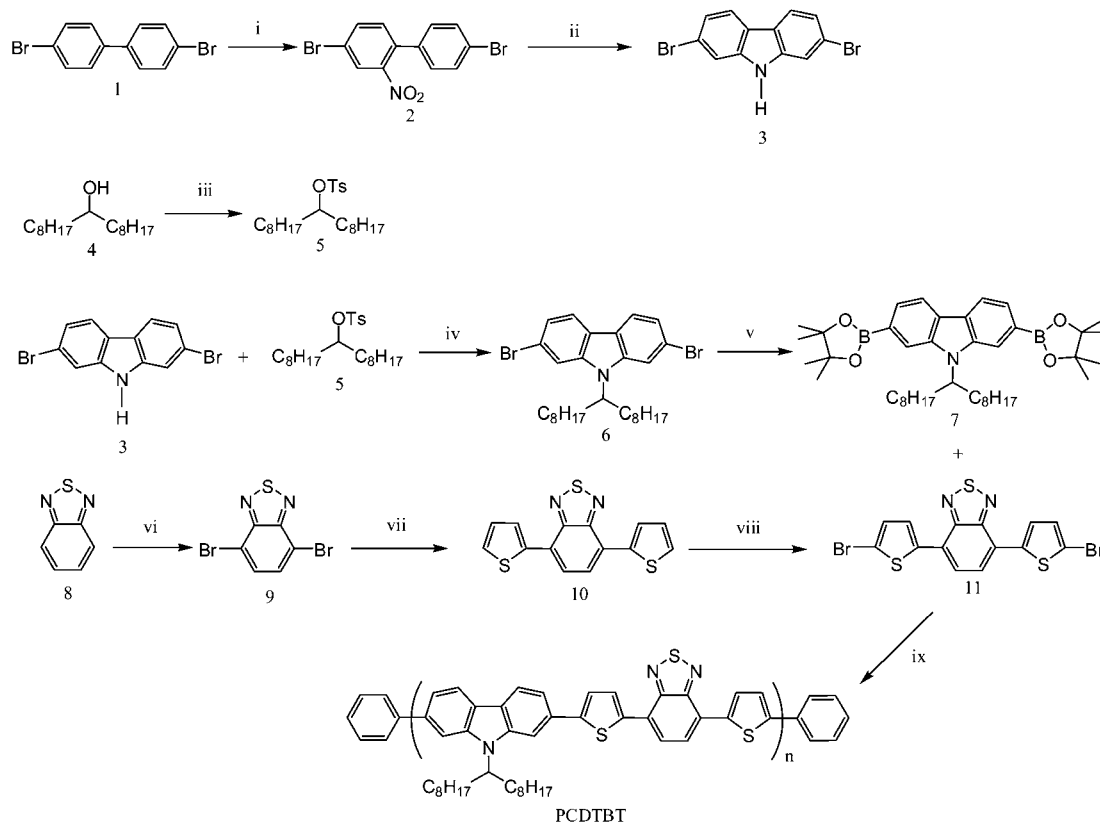
Along these lines and according to Fig. 1a, one can see that the semiconducting materials and the transparent electrode (PET:ITO) contribute to 78.4% of the total material costs. On the other hand, as shown in Fig. 1b, up to 80.6% of the cost of polymeric solar cell modules are related to materials. Therefore, there is plenty of room to bring the cost of organic photovoltaics (OPVs) down by developing low-cost and efficient polymeric materials. PCDTBT (a carbazole-based copolymer) is an efficient and stable material for BHJ solar cells. With a high open-circuit voltage ($V_{oc} \sim 0.90$ V), a power conversion efficiency of up to 7.5% and an estimated lifetime of 7 years, PCDTBT surpasses the performances of P3HT (the most studied polymeric material until now).^{3,5} Together with PTB7 ($V_{oc} = 0.75$ V; $J_{sc} = 17.46$ mA cm⁻²; FF = 69.99 and PCE = 9.2%) and PBDTPD ($V_{oc} = 0.97$ V; $J_{sc} = 12.6$ mA cm⁻²; FF = 70.0 and PCE = 8.5%) PCDTBT can be considered as one of the new standards for highly efficient BHJ solar cells.^{2,6,7}

1.1 Synthesis of PCDTBT

Since the estimated cost of the active materials counts for more than 25% in polymer solar cells, the development of cheap, reliable, reproducible, and scalable synthetic procedures for low-cost polymeric materials is mandatory. Poly[*N*-9'-heptadecan-yl-2,7-carbazole-*alt*-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) was reported for the first time by our laboratory in 2007.⁸ Since then, the preparation of this polymer has been optimized and as shown in Scheme 1, 2,7-dibromocarbazole (3) is now prepared in high yield using two simple steps from commercially available 4,4-dibromobiphenyl.^{9,10} While poly(*N*-alkyl-2,7-carbazole) derivatives generally exhibit

poor solubility and low molecular weights,¹¹ the use of a 9-heptadecan-yl (a secondary alkyl group) side chain on the nitrogen atom of the carbazole unit was a major breakthrough for soluble and high molecular weight poly(2,7-carbazole) derivatives.^{8,12,13} Therefore, 9-heptadecanol (4) is treated with *p*-toluenesulfonyl chloride to give the desired 9-heptadecane *p*-toluenesulfonate (5). The alkylation reaction of 2,7-dibromo-9-carbazole (3) with 9-heptadecane *p*-toluenesulfonate (5) is carried out following a procedure described by Marzoni and Garbrecht and leads to *N*-9'-heptadecan-yl-2,7-dibromocarbazole (6) in high yield.¹⁴ Then, the comonomer 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-*N*-9'-heptadecan-ylcarbazole (7) is prepared using known procedures developed for poly(2,7-fluorene) derivatives.¹⁵

In parallel, 4,7-di(2-bromothien-5-yl)-2,1,3-benzothiadiazole (11) is easily obtained in 3 steps from known procedures.^{16,17} Finally, PCDTBT is prepared using the widely used Suzuki cross-coupling polymerization. In our initial report, high number-average ($M_n = 37$ kDa) and weight-average ($M_w = 73$ kDa) molecular weights were obtained for the fraction of PCDTBT soluble in chloroform.⁸ This fraction was collected after the purification of the crude polymer by successive extraction with acetone, hexane, toluene, and dichloromethane. It is worth noting that the low polymerization yield (23%) combined with tedious purification methods makes no economic sense. However, this PCDTBT batch combined with PC₆₀BM in a bulk heterojunction solar cell (thickness of the active layer 70 nm; solar cell active area 0.90 cm²) led to a short-circuit current (J_{sc}) of 6.92 mA cm⁻², fill factor (FF) of 0.53 (there was a typo in the original version),⁸ high open-circuit voltage (V_{oc}) of 0.89 V and power conversion efficiency of 3.6%. These results drew the attention of both academic and industrial laboratories and several batches of PCDTBT had to be prepared in order to fulfill the numerous requests for collaborations. The optimization of the Suzuki cross-coupling polymerization of PCDTBT was done



Scheme 1 Synthesis of PCDTBT. (i) HNO_3 , $Y = 91\%$; (ii) $\text{P}(\text{OC}_2\text{H}_5)_3$, $Y = 56\%$; (iii) TsCl , Me_3NHCl , Et_3N , $Y = 82\%$; (iv) KOH , DMSO , $Y = 73\%$; (v) BuLi , isopropoxyborolane, $Y = 87\%$; (vi) Br_2 , HBr , $Y = 89\%$; (vii) 2-tributylstannylthiophene, $\text{PdCl}_2(\text{PPh}_3)_2$, $Y = 81\%$; (viii) NBS , $o\text{-DCB}$, $Y = 92\%$; (ix) $\text{Pd}_2\text{dba}_3/\text{P}(o\text{-tolyl})_3$, Et_4NOH 20%, toluene; 3 h, $Y = 90\%$ ($M_n = 20$ kDa; $\text{PDI} = 2.2$).

in order to enhance both the yield of polymerization (soluble fraction) and purification procedures while keeping the molecular weights as high as possible. First, we found that the reduction of the polymerization time from 72 h to 16 h led to an improved polymerization yield (53% for the soluble fraction in chloroform instead of 23%) with no effect on molecular weights.¹² With number-average and weight-average molecular weights of 36 kDa and 55 kDa respectively, this PCDTBT batch combined with PC_{60}BM in a bulk heterojunction solar cell (thickness of the active layer 70 nm; solar cell active area 0.90 cm^2) led to a short-circuit current (J_{sc}) of 6.8 mA cm^{-2} , fill factor (FF) of 0.56, high open-circuit voltage ($V_{\text{oc}} = 0.86\text{ V}$) and power conversion efficiency of 3.6%.¹² Since the processability of these two PCDTBT batches was quite limited due to relatively high molecular weights, we developed an improved synthetic procedure that provides precise control of the PCDTBT molecular weights with enhanced processability.¹⁸ Precise control of the polymerization time (3 h) and simplified purification steps led to reproducible materials with targeted molecular weights in high yields ($\geq 90\%$). According to initial reports on BHJ solar cells, the use of PCDTBT ($M_n \approx 20$ kDa and $M_w \approx 50$ kDa against polystyrene standards in TCB at 135°C) and PC_{60}BM (thickness of the active layer 77 nm; solar cell active area 0.4 cm^2) led to a short-circuit current (J_{sc}) of 9.31 mA cm^{-2} , fill factor (FF) of 0.51, high open-circuit voltage ($V_{\text{oc}} = 0.89\text{ V}$) and power conversion efficiency of 4.15%.¹⁸

1.2 PCDTBT in BHJ solar cells

Following these initial reports, academic and industrial collaborations were established in order to explore the full potential of PCDTBT. Konarka technologies Inc., St-Jean-Photochemicals, University of California at Santa Barbara (Prof. Alan J. Heeger), the National Research Council of Canada (Dr Ye Tao) and us were actively involved in the optimization of BHJ solar cells based on PCDTBT. One of the most interesting features of PCDTBT was reported by Heeger *et al.*¹⁹ Indeed, they demonstrated high-efficiency BHJ solar cells using PCDTBT combined with PC_{70}BM . The processing of the active layer was simple and straightforward, neither thermal annealing nor addition of processing additives were required for achieving a power conversion efficiency of 6.1%.¹⁹ More important was the internal quantum efficiency (IQE) close to 100% implying that every photon absorbed leads to a separated pair of charge carriers and that all photogenerated carriers are collected at the electrodes for an active layer thickness of 80 nm. Another striking feature, which makes PCDTBT one of the most interesting materials, is that PCDTBT is a thermally stable semi-conducting polymer, even more stable than P3HT. Spectroscopic measurements revealed that in air, the $\pi\text{-}\pi$ absorption spectrum of PCDTBT is not affected after exposure to temperatures up to 150°C . Under a N_2 atmosphere, the electronic structure of PCDTBT is stable at temperatures as high

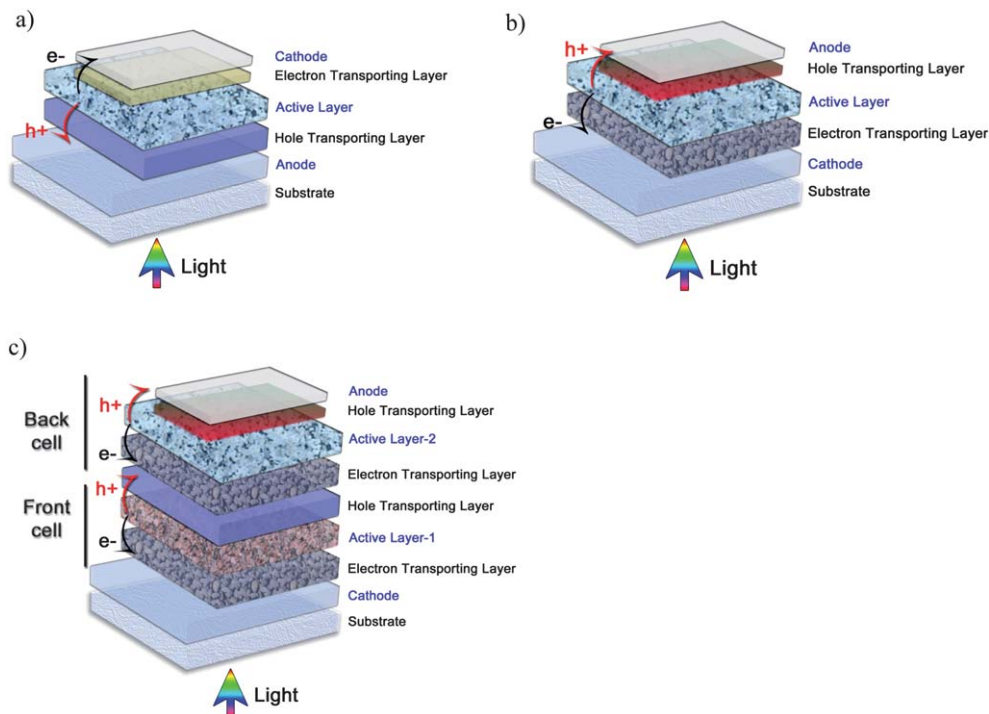


Fig. 2 Configuration of BHJ solar cells: (a) classical (transparent anode, collecting holes), (b) inverted (transparent cathode, collecting electrons) and (c) tandem.

as 350 °C. The stability of both the fully aromatic backbone and mainly amorphous structure of PCDTBT is responsible for the remarkable ability of this material to withstand exposure to high temperatures while the relatively deep HOMO energy level (−5.5 eV) makes PCDTBT inherently stable against oxidation even at high temperatures.²⁰ Moreover, it has been demonstrated that the lifetime of the PCDTBT/PCBM system approaches 7 years, which is, until now, the longest reporting operating life time for a polymer-based solar cell.³

Following these very interesting results, PCDTBT has been the subject of more than 250 publications. Indeed, this promising material has been studied as a polymeric donor in classical, inverted and tandem BHJ solar cells (Fig. 2). On the other hand, numerous photophysical studies probing the exciton formation, relaxation and recombination mechanisms in PCDTBT/PCBM systems were also reported. Such studies are paramount since the recombination mechanism in polymer BHJ solar cells is far from clear and despite extensive research dedicated to polymer solar cells, a general consensus regarding the underlying photo- and device-physics is lacking.^{21–40}

The progression of the power conversion efficiency for PCDTBT-based solar cells is well-known. Upon optimization of both molecular weights of PCDTBT and solar cells processing parameters (thickness of the active layer, electron-acceptor, electrodes, *etc.*) the power conversion efficiency went from 3.6% to 7.5% for classical BHJ solar cells.^{5,8,12} The results for most of the PCDTBT-based BHJ solar cells (classical configuration) are summarized in Table 1.

As discussed earlier, the molecular weight of PCDTBT is a key parameter for high power conversion efficiencies (Table 1). However, since size exclusion chromatography (SEC) is a

relative method to determine molecular weights, comparing molecular weights obtained from a different setup must be avoided. We found that although PCDTBT gives colored but clear solutions in tetrahydrofuran and chloroform, SEC data suggest some aggregation in those two solvents and to get rid of these aggregation problems, the molecular weight of PCDTBT must be measured in trichlorobenzene (TCB) at elevated temperature (110 or 135 °C).⁸ The number-average molecular weight (M_n) of 25 kDa and polydispersity around 2.4 are a good compromise between high power conversion efficiency and processability of PCDTBT. This parameter has to be taken into account for technological transfer from the lab scale to industrial processes.

As shown in Table 1, the acceptor of choice for PCDTBT-based bulk heterojunction solar cells is PC₇₀BM since it improves the light absorption of the active layer in the visible region compared to PC₆₀BM. We found that by changing PC₆₀BM to PC₇₀BM, the short-circuit current (J_{sc}) went from 9.5 mA cm^{−2} (entry 4, PCE = 5.2%) to 10.7 mA cm^{−2} (entry 5, PCE = 5.7%) without any changes in the open-circuit voltage (V_{oc}) and fill factor (FF).⁴¹ Control of the morphology of the PCDTBT/PC₇₀BM blend led to noticeable improvement of device performances with the short-circuit current (J_{sc}) reaching 11.8 mA cm^{−2} and power conversion efficiency reaching up to 7.1% for devices with an active area of 1 cm² (entry 13).⁴⁴ It is interesting to note that this reported power conversion efficiency (7.1%) is close to the one estimated using the theoretical model proposed by Scharber *et al.*⁶⁸

To achieve highly efficient bulk heterojunction solar cells using PCDTBT, the active layer system must be kept very thin (≤100 nm) to ensure sweep-out of carriers prior to

Table 1 Bulk heterojunction solar cells based on PCDTBT

Entry	M_n , kDa	M_w , kDa	PDI	Acceptor	Thickness, nm	J_{sc} , mA cm ⁻²	V_{oc} , V	FF	PCE, %	Active area, cm ²	Ref.
1	37	73	1.97	PC ₆₀ BM	70	6.92	0.89	0.53	3.6	0.90	8
2	36	55	1.54	PC ₆₀ BM	70	6.8	0.86	0.56	3.6	0.90	12
3	n.a.	n.a.	n.a.	PC ₇₀ BM	80	10.6	0.88	0.66	6.1	0.127	19
4	23	55	2.4	PC ₆₀ BM	83	9.5	0.91	0.60	5.2	1.0	41
5	23	55	2.4	PC ₇₀ BM	73	10.7	0.91	0.59	5.7	1.0	
6	10	22	2.2	PC ₆₀ BM	72	7.70	0.79	0.37	2.26	0.4	18
7	17	37	2.2	PC ₆₀ BM	85	8.84	0.89	0.50	3.89	0.4	
8	19	40	2.1	PC ₆₀ BM	77	9.31	0.89	0.51	4.15	0.4	
9	22	64	2.9	PC ₆₀ BM	75	8.86	0.88	0.50	3.92	0.4	
10	19	40	2.1	PC ₇₀ BM	70	10.22	0.89	0.51	4.57	0.4	
11	n.a.	n.a.	n.a.	PC ₇₀ BM	90	12.1	0.90	0.62	6.55	0.16	42
12	36	100	2.75	PC ₇₀ BM	100	10.60	0.87	0.68	6.26	0.0984	43
13	25	64	2.6	PC ₇₀ BM	80	11.8	0.91	0.66	7.1	1.0	44
14	n.a.	n.a.	n.a.	PC ₇₀ BM	90	11.16	0.89	0.65	6.45	0.0984	45
15	n.a.	n.a.	n.a.	PC ₇₀ BM	80	11.61	0.88	0.69	7.1	0.0984	46
16	n.a.	n.a.	n.a.	PC ₇₀ BM	n.a.	11.5	0.879	0.65	6.7	n.a.	47
17	36	100	2.75	PC ₇₀ BM	110	11.95	0.907	0.664	7.2	0.1238	48
18	23	55	2.4	PC ₇₀ BM	80	11.0	0.91	0.61	6.1	1.0	49
19	22.5	32.6	1.45	PC ₇₀ BM	64	8.91	0.78	0.618	4.3	n.a.	50
20	22.5	32.6	1.45	PC ₇₀ BM	70	9.4	0.86	0.606	5.1	0.0212	51
21	65.7	470	7.15	PC ₇₀ BM	120	12.58	0.88	0.612	6.77	0.2	52
22	n.a.	n.a.	n.a.	PC ₇₀ BM	70	11.32	0.88	0.69	6.9	0.12	53
23	n.a.	n.a.	n.a.	PC ₇₀ BM	200	12.09	0.85	0.53	5.4	0.12	
24	13	24	1.8	PC ₇₀ BM	250	13.6	0.88	0.53	6.45	0.12	54
25	n.a.	n.a.	n.a.	PC ₇₀ BM	80	12.1	0.90	0.591	6.5	0.06	55
26	11	59.9	5.44	PC ₇₀ BM	70	12.14	0.91	0.54	6.02	n.a.	56
27	n.a.	n.a.	n.a.	PC ₇₀ BM	70	12.40	0.88	0.68	7.5	0.1176	5
28	n.a.	n.a.	n.a.	PC ₇₀ BM	n.a.	11.98	0.92	0.654	7.21	n.a.	57
29	n.a.	n.a.	n.a.	PC ₇₀ BM	80	6.09	0.84	0.59	5.90	0.16	58
30	n.a.	n.a.	n.a.	PC ₇₀ BM	117	10.18	0.89	0.6403	5.8	0.12	59
31	12.1	26.5	2.18	PC ₇₀ BM	55	10.33	0.86	0.51	4.5	0.048	60
32	n.a.	n.a.	n.a.	PC ₇₀ BM	70	12.0	0.88	0.59	6.27	0.09	61
33	13	24	1.8	PC ₇₀ BM	223	12.79	0.86	0.60	6.60	0.12	62
34	n.a.	n.a.	n.a.	PC ₇₀ BM	50	9.8	0.90	0.58	5.1	n.a.	63
35	n.a.	n.a.	n.a.	PC ₇₀ BM	70	10.17	0.86	0.602	5.26	n.a.	64
36	33	59	1.8	PC ₇₀ BM	70	11.22	0.87	0.665	6.5	0.145	65
37	33	59	1.8	PC ₇₀ BM	150	11.22	0.86	0.520	5.02	0.145	
38	n.a.	n.a.	n.a.	PC ₇₀ BM	80	12.27	0.86	0.67	7.07	0.09	66
39	22.5	32.6	1.45	PC ₇₀ BM	64	9.72	0.86	0.6104	5.10	n.a.	67

recombination since PCDTBT/PCBM devices are characterized by close to Langevin recombination in addition to strong charge trapping.⁵³ Most of the PCDTBT-based BHJ solar cells reported in the literature have the active layer thickness in the right range and, until now, the best device using PCDTBT has been prepared by Heeger *et al.* (entry 27, PCE = 7.5%).⁵ However, the thin photoactive layer limits the absorption of light and thereby the potential for further improvements in solar cells' efficiencies. Moreover, this kind of active layer thicknesses may not be suitable for the commercial yield of the BHJ solar cells fabricated by large-area and solution-based roll-to-roll techniques due to intolerance of thickness variance. To address this issue, thick PCDTBT/PC₇₀BM active layers have been studied (entries 23, 24, 33 and 37). Although the absorption of the incident light was improved using a thicker film (highest J_{sc} values for thick film devices compared to thin films), in all cases, the power conversion efficiencies decreased. For PCDTBT/PC₇₀BM with an active layer thickness of 70 nm (entry 22), short-circuit current

(J_{sc}) of 11.32 mA cm⁻² and Fill Factor (FF) of 0.69 led to a power conversion efficiency of 6.9%. When the thickness of the active layer was increased to 200 nm, a higher short-circuit current of 12.09 mA cm⁻² was obtained but a dramatic drop of the Fill Factor was observed from 0.69 to 0.53 which led to a power conversion efficiency of 5.4%. This significant drop of the Fill Factor (28%) is possibly due to limited charge transport from a non-optimized morphology. Improvement of the nanoscale morphology of thick PCDTBT/PC₇₀BM was achieved using solvent mixtures for the processing of the active layer (entry 24).⁵⁴ By using the trichlorobenzene:chloroform binary system as a solvent, solar cells with a thick active layer of 250 nm were obtained. While the fill factor remains on the low side at 0.53, a short-circuit current of 13.6 mA cm⁻² (the highest reported value for the PCDTBT/PC₇₀BM system) was obtained, leading to a power conversion efficiency of 6.45%.

One major concern regarding the evaluation and comparison of the performance of PCDTBT-based solar cell devices

Table 2 Inverted bulk heterojunction solar cells based on PCDTBT

Entry	M_n , kDa	M_w , kDa	PDI	Acceptor	Thickness, nm	J_{sc} , mA cm ⁻²	V_{oc} , V	FF	PCE, %	Active area, cm ²	Ref.
1	n.a.	n.a.	n.a.	PC ₇₀ BM	n.a.	10.41	0.88	0.688	6.33	0.045	73
2	n.a.	n.a.	n.a.	PC ₇₀ BM	80	9.5	0.89	0.617	6.2	0.16	75
3	13	24	1.8	PC ₇₀ BM	80	10.88	0.88	0.707	6.77	0.12	76
4	n.a.	n.a.	n.a.	PC ₇₀ BM	65	8.76	0.88	0.569	5.48	0.16	77
5	13	24	1.8	PC ₇₀ BM	70	11.2	0.87	0.67	6.53	n.a.	78
6	13	24	1.8	PC ₇₀ BM	80	11.4	0.89	0.65	6.59	0.05	79

reported in the literature is the size of the active area. The efficiency estimation of organic solar cells is dependent on the dimension of the electrode defining the cell area.⁶⁹ The bulk resistance of the indium tin oxide dominates the series resistance of organic solar cells with active areas over 0.01 cm².⁷⁰ Devices with small active areas (0.01 cm²) are usually more efficient as compared to larger devices (1 cm²) due to the reduced electrical resistive loss, enhanced collection efficiency and additional photo-generated carriers in the vicinity of the metal electrode.⁷¹ To limit the measurement errors for power conversion efficiencies, it has been suggested that devices with an active area of at least 0.4 cm² should be used.⁷²

The classical device structure for polymer solar cells is (ITO)/PEDOT:PSS/polymer blend/metal, where a p-type PEDOT:PSS layer is used for anode contact (collecting holes), and a low-work-function metal as the cathode (collecting electrons) (Fig. 2a). Due to intrinsic properties, both the PEDOT:PSS layer and the low-work-function metal cathode are known to limit the device lifetime.⁷³ In order to overcome these instability issues, inverted polymer cells have been developed. For such devices, a high work-function air-stable metal is used as the anode to collect holes and ITO is used as the cathode to collect electrons (Fig. 2b). As compared to the classical structure, the inverted configuration can be fabricated by large-scale and low-cost roll-to-roll manufacturing techniques.⁷⁴ Moreover, this type of configuration is suitable for the fabrication of tandem solar cells, a promising architecture for highly efficient polymeric solar cells. As shown in Table 2, reports on inverted BHJ solar cells using PCDTBT are scarce.

However, a power conversion efficiency of 6.77% was reached for PCDTBT-based inverted solar cells (Table 2, entry 3). With a short-circuit current of 10.88 mA cm⁻², a V_{oc} of 0.88 V and a high Fill Factor of 0.707, these performances exceed those obtained for thick PCDTBT active layers used in classical configurations (Table 1, entry 24 and 33).

It has been proposed that the efficiency of the BHJ-single junction is limited to approximately 10% due to thermalization of hot charge carriers and the lack of absorption of the material

for long-wavelength photons.⁸⁰ A promising approach to improve the power conversion efficiency is the use of tandem solar cells where two different active layers with complementary absorption spectra are monolithically stacked (Fig. 2c). Such devices should enable the fabrication of polymeric solar cells with power conversion efficiencies exceeding more than 14%.⁸⁰ PCDTBT, a polymer with a moderate bandgap (1.8 eV), has been used as the front cell in tandem devices.^{81–84} As shown in Table 3, a high power conversion efficiency of up to 8.90% has been reached.

1.3 PCDTBT stability

As reported earlier, PCDTBT is a thermally stable semiconductor with a promising power conversion efficiency (up to 7.5% for classical BHJ solar cells, 6.77% for inverted structures, and 8.90% for tandem cells). With such advances made on the efficiency front, the lifetime and reliability of PCDTBT-based devices need to be addressed. While modules based on P3HT/fullerene BHJs have shown lifetimes of 5000 h with state-of-the-art encapsulation which translates into the operating lifetime approaching three years, little is known about the stability of other efficient polymeric materials.³ Using an experimental setup developed for the lifetime measurement of P3HT/PCBM BHJs, McGehee *et al.* demonstrated a lifetime for PCDTBT devices that approaches 7 years, which is the longest reported operating lifetime for polymer-based solar cells to date.³ An initial decay of both the V_{oc} and FF for the PCDTBT system was observed during the first 400 h but they remained remarkably stable after the initial efficiency was lost, termed 'burn-in'. McGehee *et al.* suggested that the burn-in degradation is possibly caused by a photochemical reaction in the photoactive layer which creates states in the bandgap of PCDTBT and not by a morphological change in the structural order of the polymer.⁸⁵ Rivaton *et al.* investigated the photochemical behavior of PCDTBT upon exposure to UV-visible light.⁸⁶ They suggested that irradiation stimulated a reorganization of PDCTBT films due to the modification of the 2,7-carbazole building block. The tertiary carbon atom bearing the alkyl side chains has been identified as the weakest link of PCDTBT.

Table 3 Tandem solar cells using PCDTBT as the front cell

Entry	J_{sc} , mA cm ⁻²	V_{oc} , V	FF	PCE, %	Ref.
1	5.8	1.45	0.40	3.3	81
2	4.9	1.67	0.53	4.3	82
3	8.8	1.44	0.59	7.5	83
4	9.58	1.49	0.62	8.90	84

1.4 PCDTBT processing techniques

Spin coating is the most common procedure used for the processing of lab-scale polymer/PCBM BHJs' active layer since it is a precise and reproducible deposition method. However, the limitations are low production rate, small active area and high

production cost since a large amount of material is lost during the process. Moreover, this method is not compatible with roll-to-roll or large area manufacturing. Since PCDTBT is among the most promising materials for polymeric solar cells, solution processes that can be scaled to large-areas, such as spray coating, have been investigated. Until now, a power conversion efficiency of 5.8% has been reported which confirms that spray coating can be a reliable deposition method for polymeric solar cells.^{60,87,88}

Conclusion

Since its first preparation in our laboratory seven years ago, PCDTBT has been one of the most studied alternating copolymers for applications in plastic solar cells. It was the first alternating copolymer to show better performance than P3HT for solar cell applications and these results paved the way to many other important synthetic developments in the OPV field. Moreover, PCDTBT/PCBM blends revealed, for the first time, that the relatively simple BHJ approach can lead to an internal quantum efficiency close to 100%. More importantly, its remarkable properties have been validated in many different laboratories and new investigators can use this polymer as a benchmark to test their new setup or configurations. As written by Dr S. R. Cowan in her Ph.D. Thesis at UCSB⁸⁹ PCDTBT was our *Drosophila melanogaster*, and we were looking forward to the material becoming widely available. High quality PCDTBT is now commercially available (St-Jean-Photochemicals Inc.) and we are therefore confident that this polymer should somehow contribute to set up a viable OPV industry.

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