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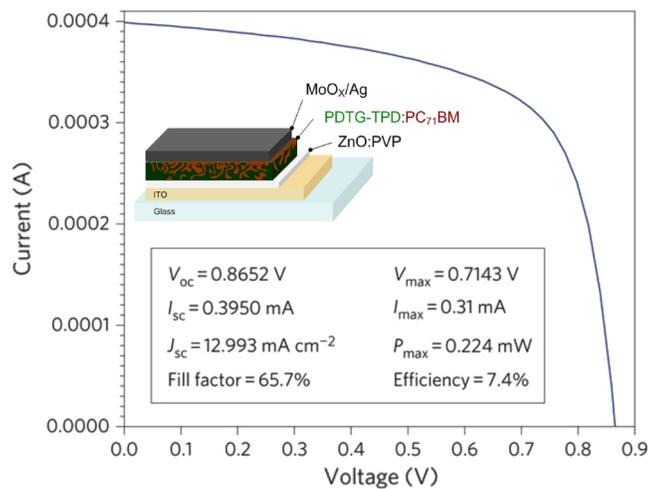
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# Inverted Polymer Solar Cells

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**Abstract:** Inverted bulk heterojunction polymer solar cells have become the preferred device architecture for roll-to-roll (R2R) processing, which allows large area devices to be fabricated on flexible substrates. Significant improvements in inverted solar cell performance have been made with novel photovoltaic polymers, along with optimized blend morphology and improved carrier extraction materials. For the first time, inverted polymer solar cells display their potential for low-cost R2R processing with power conversion efficiencies exceeding 8%.

**Index Terms:** Polymer solar cells, inverted structure, zinc oxide.

Polymer solar cells are attractive for next-generation photovoltaics due to their potential for low-cost roll-to-roll (R2R) processing onto flexible substrates. While the stability of polymer solar cells has been a concern in the past, Konarka has recently demonstrated that their cells have passed the critical lifetime aging tests according to IEC 61646, indicating that device stability does not appear to be an issue [1]. Because of the large exciton binding energy of organic materials, polymer photovoltaic (PPV) cells are excitonic devices wherein photogenerated electron-hole pairs are separated at the interface of an electron donating polymer and an electron accepting fullerene derivative by effective force [2], [3]. The photoactive layer consists of a polymer:fullerene blend which forms a bulk heterojunction (BHJ) [4], [5] resulting in an interpenetrating network of donor and acceptor phases, allowing dissociated holes and electrons to transport separately in the corresponding phases. To efficiently collect the photogenerated carriers, carrier extraction layers are inserted between the active BHJ layer and the electrodes.

The efficiency of PPV cells is determined by the molecular and morphological structures of the photoactive materials, wherein conjugated donor-acceptor polymers are of interest due to the tunability of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels to engineer their electronic and optical properties [6]–[15]. This bandgap engineering of donor-acceptor moieties not only controls the bandgap energy to optimize light harvesting but also allows for favorable energy alignments to achieve high open circuit voltages ( $V_{OC}$ ) and efficient exciton dissociation as well. By controlling these donor and acceptor energy levels, numerous groups have demonstrated significant advances in device performance. For example, the combination of dithienosilole and thienopyrrole-4,6-dione (PDTs-TPD) results in a low bandgap (1.73 eV) polymer with a low-lying HOMO level (−5.57 eV), and the resulting PPV cells

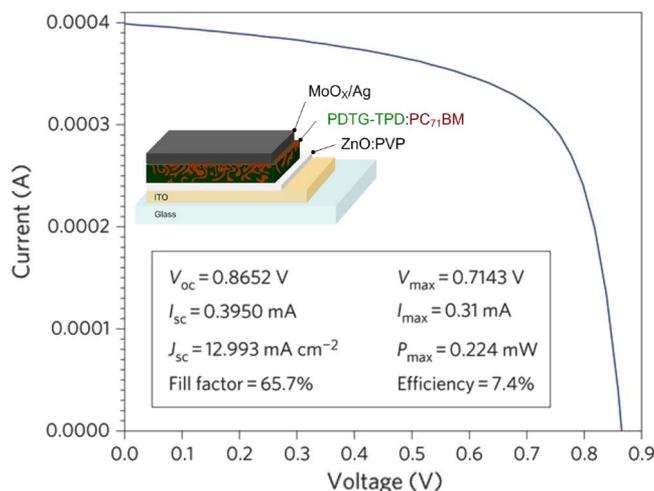


Fig. 1. Certified efficiency of PDTG-TPD: PC<sub>71</sub>BM cell with the inverted device structure. The figure is modified from [19].

give a high photocurrent ( $J_{SC}$ ) while maintaining high open circuit voltages to realize high power conversion efficiencies (PCEs). When blended with [6,6]-phenyl-C71 butyric acid methyl ester (PC<sub>71</sub>BM), these PDTG-TPD polymer solar cells with an optimized BHJ morphology exhibited a PCE exceeding 7% [16]. Replacing the silicon bridging atom with germanium in the donor unit, a dithienogermole-based polymer with a bandgap of 1.69 eV and a slightly higher HOMO level was also realized, and a further enhancement in device performance was observed [8].

Achieving well-controlled nanoscale BHJ morphology is critical to the performance of PPV cells. Solvent additives provide a means to alter the miscibility of the donor and acceptor materials to control the nanoscale morphology [14], [17]. Such a strategy enables the formation of interpenetrating nanosized domains of the conjugated donor-acceptor polymers and PC<sub>71</sub>BM without the requirement of high temperature annealing processes, and solvent additives become a vital component to many donor-acceptor systems. In this, high carrier mobilities were achieved even without the presence of visible crystalline domains in the polymer: PC<sub>71</sub>BM composites. Unlike earlier donor-acceptor polymers, which suffer from recombination limited photocurrent [18], solvent additive assisted morphology control leads to high fill factors and high external quantum efficiencies in BHJ solar cells [8], [16], [19], [20]. Using this approach, a substantial enhancement in device efficiency has been demonstrated by various groups [8], [16].

While PPV cells are fabricated by solution processing, the viability to employ a R2R manufacturing process is determined by the device geometry used. In a conventional PPV cell, a top low work function metal is required for efficient electron collection while conducting polymers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) serve as the bottom anode interlayer for efficient hole extraction. In order to deposit the top electrode, vacuum thermal deposition is required, and this process is not compatible with R2R processes. In contrast to conventional cells, low work function metals are not necessary in inverted cells since a metal oxide electron extraction layer along with the bottom ITO electrode is used as a bottom cathode as shown in the inset of Fig. 1. For the top anode, metal oxides have also been used as hole extraction materials. Specifically, thermal evaporated MoO<sub>3</sub> has now become a standard material for the hole extraction layer in inverted devices fabricated in research laboratories [8], [20]–[22]. More recently, solution processed MoO<sub>3</sub> [23] and Ni<sub>x</sub>O [24] have also been used in conventional polymer solar cells with good performance and these solution processed oxides can potentially be used in the inverted cells. Using these metal oxides as the charge extraction interlayer along with a top printed silver electrode, this device architecture is more compatible with the one used in the R2R printing process. The first inverted polymer solar cell was reported in 2006 [25]. Since then, a variety of

materials have been used as hole and electron transporting layers, and the efficiencies are, in general, lower than those of the conventional cells with a bottom anode. The highest efficiency reported in 2010 was 6.1%, which is a record value demonstrated with the poly[[9-(1-octylonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT): PC<sub>71</sub>BM system when MoO<sub>3</sub> and ZnO were used for hole and electron extraction, respectively [22]. However, most inverted cells have inferior device performance compared with their counterparts fabricated with a conventional geometry.

The poor performance of the inverted cells can be attributed to the quality of the charge extraction materials. Specifically, high density defects are present in solution processed ZnO films and they contribute to the loss of photocurrent. Modifications of solution processed ZnO films have been shown to be effective to improve the device efficiency. For example, it was shown that a thin layer of C<sub>60</sub> on top of ZnO nanoparticles (NPs) helped to improve the morphology of the subsequently spin-coated polymer:fullerene layer, and significantly enhanced the  $J_{sc}$  and PCE (4.9%) of inverted poly(3-hexylthiophene) (P3HT): PC<sub>71</sub>BM cells [21]. This surface modification of ZnO in the inverted cells has led to PCEs comparable with the best conventional cells. The ideal solution processed ZnO films should be of low defect density and have good electric coupling with the BHJ layer. For example, the uniformity of the sol-gel derived ZnO film can be improved when the precursor is blended with an insulating polymer matrix. However, the surface of the as-spun ZnO film becomes polymer rich, and the insulating layer forms a barrier for electron extraction. Treating the ZnO-polymer composite layer with UV-ozone improves the electric coupling and enhances the PCE of inverted PDTG-TPD: PCBM cells to 8.1%. This is the first report of inverted polymer cells with efficiency exceeding 8%. The Newport certified results are shown in Fig. 1 [20].

In summary, high efficiency inverted PPV cells have been demonstrated, which illustrates the viability of PPV for R2R processing and the potential for low-cost light harvesting.

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