

A comparison between state-of-the-art ‘gilch’ and ‘sulphinyl’ synthesised MDMO-PPV/PCBM bulk hetero-junction solar cells

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Abstract

To obtain photovoltaic devices based on electron donating conjugated polymers with a higher efficiency, a major breakthrough was realised by mixing the polymers with a suitable electron acceptor, thereby enhancing the rate for photo-induced charge generation by several orders. State-of-the-art organic bulk hetero-junction photovoltaic cells are based on an interpenetrating donor–acceptor network in the bulk to form efficient nanostructured p–n junctions in the organic materials. Devices made with ‘Gilch’ poly(2-methoxy-5-(3',7'-dimethyl-octyloxy))-p-phenylene vinylene, (MDMO-PPV), as an electron donor and (6,6)-phenyl-C₆₁-butyric-acid (PCBM) (a soluble C₆₀ derivative) as an electron acceptor yielded the highest efficiency until now in this class of devices. A power conversion efficiency of approximately $\eta_e \geq 2.5\%$ (electrical power out/incident light power) under AM 1.5 illumination was reported. The ‘gilch’ route is a direct synthetic route. The ‘sulphinyl’ route is a promising, indirect precursor-route towards MDMO-PPV. Due to the non-symmetric monomer, so-called ‘head-to-head’ and ‘tail-to-tail’ additions are excluded to a higher level in comparison to the ‘gilch’ route. This difference between both materials makes them interesting candidates to compare them in the state-of-the-art photovoltaic devices. Preliminary results indicate that the ‘sulphinyl’ MDMO-PPV/PCBM bulk hetero-junction solar cells attain a power conversion efficiency of nearly $\eta_e = 3\%$ (electrical power out/incident light power), have a higher fill factor, incident photon per converted electron value (IPCE) and short circuit current. It is indicated that the observed solar cell characteristics are related to the defect level of the conjugated polymer used. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Applications involving conjugated polymers include light emitting diodes, thin film transistors, sensors and photovoltaic devices [1–5]. This polymeric approach yields in comparison to devices based on small organic molecules a potential to develop a large-scale roll-to-roll production on flexible substrates. The need to develop inexpensive renewable energy sources stimulates the research towards low cost photovoltaic devices. As such, efficient ‘plastic’ solar cells can sustain that

need. Aside from possible economic advantages, polymeric materials possess low specific weight and mechanical flexibility; properties that are desirable for a solar cell. The first conjugated polymeric photovoltaic devices showed efficiencies below 0.01% [6]. The discovery of ultrafast photo-induced electron transfer in a composite of conjugated polymers as donors and buckminsterfullerene (C₆₀) as an acceptor [7] provided a molecular approach to highly efficient photovoltaic conversion. Because the time scale for photo-induced charge transfer is three orders of magnitude faster (<100 fs) [8] than the radiative or non-radiative decay of photo-excitations, the quantum efficiency from donor to acceptor is close to unity [7]. Early devices, based on a conjugated polymer/C₆₀ bilayer, yield monochromatic efficiencies

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of 0.1% [9]. A major increase in efficiency was obtained by blending the conjugated polymer directly with a soluble methanofullerene [10,11]. A large interfacial region is formed. Because any photoexcitation in the composite is within a few nanometers of a donor–acceptor interface, these devices are named as donor–acceptor bulk heterojunction solar cells. Large area (3600 mm²) flexible plastic solar cells based on a blend of alkoxy-PPV (particularly MDMO-PPV) and a soluble fullerene derivative (PCBM), are reported with efficiencies (approx. 1%) equal to similar small area (typically 6 mm²) photovoltaic devices [12], proving the ability for an easy upscaling. It is shown that the power conversion efficiency of an organic photovoltaic cell is dramatically affected by the molecular morphology, caused by the casting conditions [13]. An optimisation of the casting solvent yields an increase in efficiency from 1 to 2.5% by using chlorobenzene instead of toluene for the alkoxy-PPV:PCBM donor–acceptor bulk heterojunction solar cells.

A ‘working-horse’ material used in polymer light emitting diode industries for many years is the alkoxy-poly(*para* phenylene-vinylene) (PPV) derivative: poly(2-methoxy-5-(3',7'-dimethyloxy)-1,4-phenylene vinylene) (MDMO-PPV). MDMO-PPV shows a great performance in various devices, caused by an excellent solubility in many organic solvents. A common synthetic approach, currently used in industry, to obtain MDMO-PPV is a dehydrohalogenation route (the ‘gilch’ route’) [14,15]. Because of the insolubility of many conjugated polymers in common solvents, many useful processing routes are developed. In these so-called precursor polymer routes, a solution processable ‘precursor’ non-conjugated polymer is formed. The conjugated polymer is formed afterwards, by an in situ thermal or chemical treatment of a volatile leaving-group. A well-established representative of this class of synthetic routes is the Wessling precursor route [16–18]. An alternative and promising synthetic approach, by using a non-symmetric chloro-, sulphanyl-substituted monomer, is the ‘sulphanyl’ precursor route [19–21]. It has been shown that the major drawbacks of the Wessling precursor route are overcome by using a non-ionic precursor.

Because of the promising properties of the ‘sulphanyl’ route and the classical use of the ‘gilch’ route in industry, a comparative study between a significant population of ‘gilch’ and ‘sulphanyl’ synthesised MDMO-PPV/PCBM state-of-the-art bulk heterojunction solar cells is presented in this paper.

2. Experimental

For the state-of-the-art solar cells as reported in this paper, poly(2-methoxy-5-(3',7'-dimethyloxy)-1,4-phenylene vinylene) (MDMO-PPV) as an electron

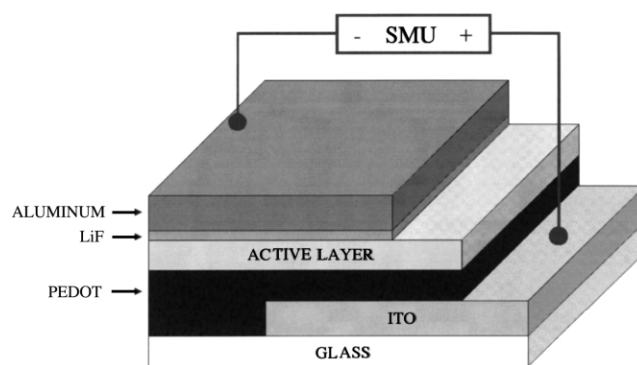


Fig. 1. Schematic representation of the device structure of a state-of-the-art bulk heterojunction solar cell.

donor and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₁ (denoted as PCBM) is used. Both show satisfactory solubility in a large number of organic solvents [22]. The enhanced solubility of PCBM compared to C₆₀ allows a high fullerene to conjugated polymer ratio. A constant ratio PCBM/MDMO-PPV — typical 4:1 by weight is used. To compare the difference in synthetic approach on the photovoltaic performances, devices with different thicknesses of the active MDMO-PPV:PCBM layer were fabricated in an identical manner except for the two types of MDMO-PPV.

The detailed production of these devices, which consisted in all cases of indium tin oxide (ITO)/poly(3,4-ethylene-dioxy-thiophene) (PEDOT)/MDMO-PPV:PCBM/LiF/Al (see Fig. 1) is described elsewhere [23]. The use of a LiF/Al electrode was chosen to provide an ohmic contact between the metal and the organic layer [24,25]. The active layer is applied by spincoating from a solution in chlorobenzene. The variation in thickness is obtained by varying the weight percentage MDMO-PPV in the solvent (typically between 0.5 and 0.2 wt.% of conjugated polymer in chlorobenzene).

A characterisation of the devices is performed under AM 1.5 simulated illumination from a solar simulator (Solar Constant 575 with AM 1.5 filter, K.H. Steuernagel Lichttechnik GmbH). The AM conversion power efficiency ($\eta_{AM\ 1.5}$) of a photovoltaic device is given by Eq. (1).

$$\eta_{AM\ 1.5} = \frac{P_{out}}{P_{in}} = FF \frac{V_{OC} J_{SC}}{P_{in}} \quad (1)$$

$$= \frac{V_{mpp} J_{mpp}}{V_{OC} J_{SC}}$$

In these equations, P_{out} is the output electrical power of the device under illumination; P_{in} is the light intensity incident on the device as measured by the calibrated reference cell; FF is the fill factor; V_{OC} the open-circuit voltage; J_{SC} the short-circuit current density; P_{in} the

light intensity incident on the device, m the spectral mismatch factor that accounts for deviations in the spectral response to that of the reference cell [26]; V_{mpp} the voltage at the maximum power point and J_{mpp} the current density at the maximum power point. For the measurements described in this paper, $P_{\text{in}}=80 \text{ mW/cm}^2$ and $m=0.753$.

The ‘gilch’ route (see Fig. 2(I)) is a direct synthetic route starting from the dichloro-substituted monomer towards the conjugated polymer. The major polymerisation defect is reported to be a tolane-bisbenzyl (TBB) moiety, caused by head-to-head and tail-to-tail additions during polymerisation [27]. The ‘sulphanyl’ route (see Fig. 2(II)) uses an asymmetric chloro-, sulphanyl-substituted monomer. Due to the non-symmetric monomer, it is expected that these effects are excluded to a higher level in comparison to the ‘gilch’ route. Preliminary results are in agreement with this. A characterisation of both materials with various analytical techniques, providing spectroscopic information, thermal results and physico-chemical properties as viscosity behaviour and molecular weight, is reported elsewhere [28].

The described difference, for these in monomer-unit identical materials, makes them interesting candidates to compare them in the state-of-the-art photovoltaic devices as described above.

3. Results

The observed open circuit voltage (V_{OC}) is for all devices identical (0.8 V) and independent from the choice of MDMO-PPV. However, an evaluation of the short circuit current density (J_{SC}) of a significant population of devices with a 100-nm active layer, yields a slightly increased value for the ‘sulphanyl’ devices (4.5 vs. 4.2 mA/cm^2). An increment in fillfactor is also observed when comparing ‘sulphanyl’ versus ‘gilch’ 100

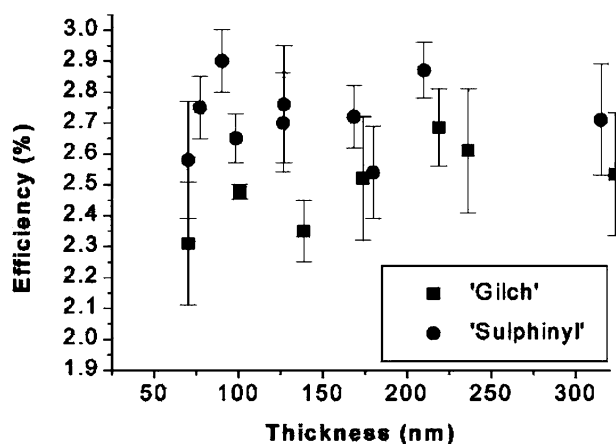


Fig. 3. The power conversion efficiency under AM 1.5 illumination for a significant population (total number of devices=60) of ‘gilch’ (squares) and ‘sulphanyl’ (circles) MDMO-PPV:PCBM bulk heterojunction solar cells.

nm active layer photovoltaic cells (0.62 vs. 0.59). Although these results are close to the limitation of reproducibility, these values are observed for two totally separately prepared batches of a significant population of samples and a trend may be derived. Comparing the AM 1.5 power conversion efficiency an increase of 15% is observed for the ‘sulphanyl’ vs. the ‘gilch’ 100 nm state-of-the-art solar cell (2.9 vs. 2.5%). Evaluating the thickness dependency of the conversion efficiency (see Fig. 3) it is shown that this difference between the ‘gilch’ and ‘sulphanyl’ devices is decreasing with increasing thickness of the active layer. A highly interesting feature of the sulphanyl devices seen in Fig. 3 is their rather expressed thickness independent efficiency. A variation of nearly a factor three in the thickness results in no significant changes of the efficiency. We interpret this behaviour as one of the typical character-

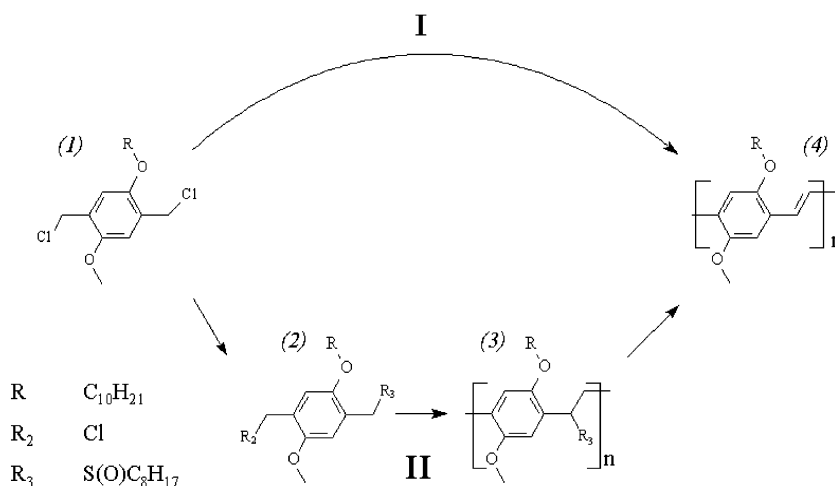


Fig. 2. A schematic representation of the ‘gilch’ (a) and ‘sulphanyl’ (b) synthetic route.

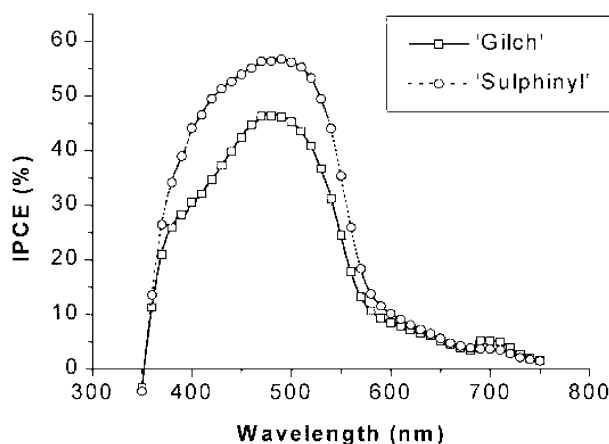


Fig. 4. The incident photon per converted electron ratio (%) (IPCE) as function of the wavelength for a 100-nm 'gilch' and 'sulphinyll' MDMO-PPV:PCBM bulk hetero-junction photovoltaic device.

istics of thin film bulk heterojunction devices, where the photoactive layer comprises a rather low transport mobility but outstanding high life times for the charge carriers.

The incident photon per converted electron ratio (IPCE) as a function of wavelength is presented for a 'gilch' and a 'sulphinyll' MDMO-PPV:PCBM 100 nm bulk hetero-junction solar cell (see Fig. 4).

It is shown that the 'sulphinyll' device is more efficient in converting photons to electrons than the 'gilch' photovoltaic device (a maximum value of 55 vs. 45%). The maximum value is for both devices found at a wavelength of approximately 470 nm. The 'gilch' IPCE curve, the values for the fill factor, short circuit current density, open circuit voltage and power conversion efficiency are in accordance with reported values in literature [13]. Comparing the two synthetic approaches, a lower defect level, caused by TBB moieties is expected for the 'sulphinyll' MDMO-PPV. A lowered trap level, accompanied by an increase in the charge carrier lifetime, would indeed allow us to understand the enhanced performance of the 'sulphinyll' devices. Also, the charge carrier mobility in a disordered medium is affected by inhomogeneous density variations of the hopping sites, as probably induced by electronic defects [29]. Combining these results, our experiments seem to indicate that these two polymers indeed have a different density of electronic defects. Low temperature transport measurements are currently in progress to study and compare the electronic defect densities of the two polymers.

4. Conclusions

A comparison of a significant population of 'sulphinyll' and 'gilch' MDMO-PPV:PCBM state-of-the-art bulk hetero junction solar cells yields an improved photovoltaic characteristic for the 'sulphinyll' device.

The power conversion efficiency (2.9%) is 15% higher than the highest value reported in literature [13]. The higher fill factor and short circuit current indicate an improved charge carrier transport, caused directly or indirectly by the lower defect level of the 'sulphinyll' MDMO-PPV. The detailed mechanism of this observed device improvement and the likely correlation between device performance and defect density are under investigation. A more advanced study concerning more increased and reduced defect levels and morphological issues is in progress. However, these results strongly emphasise the importance of chemistry in the course of developing and improving high class, well-defined and characterised materials for further device enhancement, thereby, contributing a major part of the promising opportunity to develop inexpensive renewable energy sources from bulk heterojunction solar cells.

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