Polymer solar cells based on diphenylmethanofullerenes with reduced sidechain length $\dagger\ddagger$

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Diphenylmethanofullerenes (DPMs) show interesting properties as acceptors in polymer bulk heterojunction solar cells due to the high open circuit voltages they generate compared to their energy levels. Here we investigate the effect of reducing the alkane sidechain length of the DPMs from C_{12} to C_6 in the properties of the solar cell. This change leads to an increase in the electron mobility, thus allowing for a lower fullerene content, which in turn results in an increase in the short circuit current and, finally, in an increase in the efficiency of the device (from 2.3 to 2.6%) due to the higher concentration of the more absorbing polymer in the film. Atomic force microscopy images and external quantum efficiencies suggest the absence of crystallization of the fullerene to be at the origin of the slightly reduced performance of DPMs *versus* the standard fullerene [6,6]-phenyl- C_{61} -butyric acid methyl ester, implying that higher efficiencies could be possible with this class of fullerenes.

Introduction

The performance of polymer solar cells has grown steadily over the last decade¹ resulting in devices with power conversion efficiencies over 6% for a number of different polymeric donor materials.² Remarkably, the diversity of the used acceptor materials is extremely small. Even though other acceptors such as n-type polymers³ or inorganic materials⁴ show promising results, the small molecular weight material [6,6]-phenyl-C₆₁-butyric acid methyl ester [60]PCBM⁵ (or its more absorbing alternative [70]PCBM)⁶ has shown superior properties in terms of charge carrier transport, charge separation efficiency and the possibility of creating the ideal morphology in these types of solar cells. Thus, virtually all recorded efficiencies have been obtained by optimizing the donor material with respect to the properties of PCBM. Recently however, an alternative route towards higher efficiencies was demonstrated by modification of the fullerene acceptor material. Since the open circuit voltage of a bulk heterojunction solar cell is ultimately limited by the difference in energy between the HOMO of the donor and the LUMO of the acceptor, modification of the latter should result in a very direct increase in performance due to an increase in the output voltage.7 Examples, such as the use of fullerene bisadducts⁸ and endohedral⁹ fullerenes show the viability of such an approach. Given the above mentioned relation between the acceptor LUMO level and the open circuit voltage, results obtained using

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1,1-bis(4,4'-dodecyloxyphenyl)-(5,6) C_{61} (DPM-12) as acceptor can be seen as a remarkable exception.¹⁰ Here, an increase in the open circuit was observed compared to the standard PCBM, despite the fact that DPM-12 has a similar LUMO level. The power conversion efficiencies obtained using this novel acceptor material however are slightly lower compared to PCBM due to a reduced short circuit current. The probable origin of this reduced current lies in the lower charge transport properties of DPM-12 leading to a rather high volume ratio of the (less absorbing) acceptor material in optimized devices. Furthermore, this lower charge carrier mobility of DPM-12 may be related to the rather long C_{12} side chains of the molecule. In order to check this point, we report here the use of a diphenylmethanofullerene with a shorter (C_6) alkane sidechain (DPM-6) as the acceptor material in polymer solar cells.

Results and discussion

Synthesis

The synthesis of DPM-6 has been carried out in three synthetic steps from commercially available 4,4'-dihydroxybenzophenone (1). Thus, reaction of dihexyloxybenzophenone hydrazone (3) prepared from dihydroxybenzophenone (2) – reacted with [60]fullerene under basic conditions (Bamford–Stevens reaction) in refluxing *o*-DCB – afforded DPM-6 in moderate yield, according to the procedure described in the literature for related compounds (Scheme 1).¹¹

Cyclic voltammetry experiments carried out on DPM-6 in *o*-DCB/MeCN (4 : 1) at room temperature showed three reversible reduction waves at -1.084 V, -1.481 V and -1.996 V *vs* ferrocene, similar to the values found for PCBM ($E_1 = -1.077$ V, $E_2 = -1.469$ V, $E_3 = -1.980$ V). These data confirmed similar LUMO energy levels for both fullerene acceptors. (Fig. 1)

Photovoltaic devices

DPM-6 was tested for its use as the acceptor in combination with the well-known semiconducting polymer poly(3-hexylthiophene)

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Fig. 1 Cyclic voltammetry [V *vs* Ag/AgNO₃] of DPM-6 (\cdots) and PCBM (-). Working electrode: GCE; reference electrode: Ag/Ag⁺; counter electrode: Pt; supporting electrolyte: 0.1 M Bu₄NClO₄; scan rate: 100 mV s⁻¹; solvent: *o*-DCB/MeCN (4 : 1 v/v).

(P3HT). For comparison, P3HT : PCBM devices were fabricated in parallel. The optimal polymer to fullerene ratio of the active layer blend depends on a large number of factors, including the charge transport and absorbing capabilities of both materials and the blend morphology. For P3HT : PCBM a ratio of 1 : 1 has been shown to be optimal, due to the balance in the charge transport of the two materials and the phase separated nature of the materials after thermal or solvent annealing (in contrast to for example the PPV : PCBM blend, which shows a complicated mixture of pure fullerene and blended regions). As stated above, the previously reported P3HT : DPM-12 devices used a polymer : fullerene ratio of 1 : 2 in the blend, likely originating from the poorer transport capabilities of the fullerene. From a light harvesting point of view, such a large fullerene content is undesirable, due to its lower extinction coefficient. When reducing the sidechain length from C_{12} to C_6 a different behavior is observed. Here a polymer : fullerene ratio of 1 : 1 is optimal. Figs 2 and 3 show the current density (J) to voltage (V) characteristics and external quantum efficiencies (EQE) of a typical P3HT : DPM-6 cell together with a reference P3HT : PCBM cell, both with a blend ratio of 1:1. Table 1 lists all the relevant parameters of



Fig. 2 Current density (J) vs voltage (V) characteristics for a P3HT : PCBM (black squares) and P3HT:DPM-6 (red circles) solar cell.



Fig. 3 The external quantum efficiency (EQE) for a P3HT : PCBM (black squares) and P3HT:DPM-6 (red circles) solar cell.

the devices, including the data obtained from a device with a suboptimal P3HT : DPM-6 weight ratio of 1:2 and the previously published result from a P3HT : DPM-12 device. The efficiencies obtained with DPM-6 (2.6%) are superior to the previous results of DPM-12 (2.3%), mainly due to the higher short circuit current. This higher short circuit current can be directly related to the lower optimal weight ratio of DPM-6 in the blend compared to DPM-12. In order to understand why less fullerene content is required for optimal device performance in DPM-6 based devices, mobility measurements were performed.

Mobility measurements

A high charge carrier mobility of donor and acceptor material is of vital importance for charge generation and extraction in solar cells. Previously, 40-fold reduced mobility of DPM-12 compared to PCBM was observed.¹⁰ In order to determine the charge carrier mobility of DPM-6, electron single carrier devices were made by sandwiching a pure DPM-6 layer in between a PEDOT : PSS anode and a barium silver cathode.¹² The deep lying HOMO level (6 eV) ensures that no holes are injected from the PEDOT : PSS anode (5.2 eV work function) and only

Table 1 The solar cell characteristics

Blend	Weight ratio	$V_{\rm oc}/{ m V}$	$J_{ m sc}/ m mA~ m cm^{-2}$	FF (%)	Max EQE (%)	Intensity/W m ⁻²	PCE (%)
P3HT : PCBM	1:1	0.64	9.72	59	59	1200	3.1
P3HT : DPM-6	1:1	0.69	8.47	50	60	1200	2.6
P3HT : DPM-6	1:2	0.60	3.04	58	30	1200	1.0
P3HT : DPM-12 ^{<i>a</i>}	1:2	0.65	4.7	58	54	800	2.3
P3HT : DPM-12"	1:2	0.65	4.7	58	54	800	2.3

Taken from ref. 10.



Fig. 4 Current density (J) vs voltage (V) corrected for the built-in voltage ($V_{\rm bi}$) of a DPM-6 electron only device (symbols), fitted using eqn (1) (red line).

electron transport is measured. The J-V characteristics of the devices (see Fig. 4) show a quadratic dependence, typical for space charge limited current, allowing the charge carrier mobility (μ) to be determined by using:¹³

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \tag{1}$$

An electron mobility of $6 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ was found, which is 3 to 4 times lower than that obtained for PCBM using identical methods.12 Even though this value is slightly lower compared to PCBM it is in the same order as the hole mobility observed in annealed P3HT, ensuring balanced transport between electrons and holes and hence explaining the 1:1 optimal weight ratio of P3HT : DPM-6.

Comparison between DPM-6 and PCBM

Despite the increased performance of DPM-6 over DPM-12, PCBM is still the superior acceptor when combined with P3HT. The lower power conversion efficiency of DPM-6 is mainly caused by a lower short circuit current. From the EQE measurements it is observed that the maximum quantum efficiency for both acceptors is identical, yet PCBM cells show a more pronounced shoulder at higher wavelengths. This additional shoulder has been shown to originate from an increase of the polymer crystallinity after thermal or solvent annealing.¹⁴ In fact, the phase separation and subsequent crystallization of both polymer and fullerene is the main cause of the large increase in device performance upon annealing of P3HT : PCBM solar cells.15

Annealing effect of pure fullerene films

In order to get a first indication of the effect of a thermal treatment on the P3HT : DPM-6 blend, we have obtained atomic force microscopy (AFM) images of layers of the pure fullerene materials before and after annealing. PCBM layers are known to form large, needle-like structures after thermal treatment, which



Fig. 5 AFM images of a pure PCBM film, as-cast (left) and annealed at 150 °C for 1 h (right).



Fig. 6 AFM images of a pure DPM-6 film, as-cast (left) and annealed at 150 °C for 1 h (right).

indicates at least partial crystallization of the material.¹⁶ Indeed, we observe the formation of these structures, as indicated in Fig. 5.

For DPM-6 however, no significant change in the surface morphology was found when annealing up to 150 °C (see Fig. 6). Since we observe no signs of crystallization of the pure material, it is unlikely DPM-6 will do so in the blend of polymer and fullerene. These results indicate further optimisation of the processing conditions, such as a higher annealing step or going to other (mixed solvent) spin casting solutions, can lead to a better morphology and hence device performance. The amorphous nature of these cells, conversely, might result in an enhanced thermal stability, since ongoing crystallization and phase separation will lead to a deteriorated device performance.¹⁷

Open circuit voltage

Similar to the original work with DPM-12, DPM-6 devices generate a significantly higher open circuit voltage compared to PCBM. In fact, the open circuit voltages typically reached with DPM-6 of 0.69 V is 0.04 V higher compared to the initial work with DPM-12. In this work, however, no low work function interlayer at the cathode was used, as can be seen by the low open circuit voltage of 0.55 V of their PCBM : P3HT reference device *vs* literature values of around 0.6 V.¹ Additionally, besides the typically reached open circuit voltages of 0.69 V, in some cases voltages as high as 0.73 V were observed. A detailed analysis of these high open circuit voltages using impedance spectroscopy will be published elsewhere.¹⁸

Conclusions

A diphenylmethanofullerene with a C_6 sidechain on the benzene ring has been synthesized and used in polymer fullerene bulk heterojunction solar cells. Due to the higher electron mobility compared to previous DPMs with C_{12} sidechains, less fullerene content is needed for proper device operation, resulting in a higher short circuit current and device performance. The lower performance vs PCBM is explained by the lower tendency of the fullerene to crystallize and phase separate. It is therefore not unlikely that a further optimization of the processing conditions, such as a higher annealing step or different (mixed) spin casting solutions may result in an improved morphology and hence efficiencies, even surpassing those obtained in PCBM devices due to the higher achievable open circuit voltage of DPM-6. Furthermore, an enhanced thermal stability is expected, due to the more amorphous nature of the active layer, making this fullerene a possible candidate as the acceptor in high performance polymers that do not require any thermal annealing.¹⁹

Experimental details

Details on the materials synthesis as well as the material characterization is presented in the ESI.‡ Pre-patterned ITO-covered glass substrates were first cleaned using soap water, demineralized water, propanol and an UV-ozone treatment. Subsequently, a layer of PEDOT/PSS (Bayer AG) was spin-coated under ambient conditions onto the cleaned substrates and the layer was dried by annealing the substrate for 30 min at 150 °C.

For solar cells, the blend of either P3HT : PCBM or P3HT : DPM-6 was spincoated from chlorobenzene resulting in layer thicknesses of around 200 nm. After a thermal annealing step at 135 °C for 20 min, the devices were completed by thermal evaporation of a 5 nm barium/70 nm silver top contact under vacuum (2×10^{-6} mbar) using a vacuum chamber integrated into an inert atmosphere glovebox (1 ppm O₂ and <1 ppm H₂O).

For electron-only devices, a pure layer of DPM-6 was spincoated from chlorobenzene resulting in a layer thickness of 120 nm. Devices were finished with identical cathodes as the solar cells.

All the devices were fabricated in air up to the spincoating of the active layer, after which the samples were transferred to a N_2 filled glovebox. Evaporation of the top contact and device characterisation was carried out in the same glovebox system. The solar cells were illuminated by a white light halogen lamp in combination with interference filters for the EQE and J-V measurement. An estimation of the short-circuit current density (J_{sc}) under standard test conditions was calculated by convolving the EQE spectrum with the AM1.5G reference spectrum, using the premise of a linear dependence of J_{sc} on light intensity. The estimated illumination intensity (1200 W m⁻²) for the cells under study was taken from the ratio of the measured and calculated J_{sc} . Current–voltage characteristics of the solar cells and electron only devices were recorded using a Keithley 2400 SourceMeter.

The AFM images were performed on layers spincast on glass substrates in tapping mode (AFM Multimode, Veeco) under ambient conditions, using silicon cantilevers (Veeco Probes) with a force constant of about 40 N m⁻¹ and a resonance frequency of around 320 kHz. WSxM software was used for the image analysis.²⁰

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