Increased short circuit current in an azafullerene-based organic solar cell

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We report the synthesis of a solution-processable, dodecyloxyphenyl-substituted azafullerene monoadduct (DPC$_{59}$N) and its application as electron acceptor in bulk heterojunction organic solar cells (BHJ-OSCs). Due to its relatively strong absorption of visible light, DPC$_{59}$N outperforms PC$_{60}$BM in respect to short circuit current (J_{SC}) and external quantum efficiency (EQE) in blends with donor P3HT.

The field of solution-processed bulk-heterojunction (BHJ) solar cells has been widely dominated by fullerenes as electron acceptors.[1] Among these fullerenes, derivatives based on the phenyl-butyric acid methyl ester motif (PC$_{60}$BM and PC$_{70}$BM) have been by far the most commonly used.[2] Numerous alternatives have been published to date,[3] however, only a few structures have led to higher power conversion efficiencies (PCEs) than their methyl ester counterparts.[3a,3e, 4]

For achieving an improvement of PCE by chemical functionalization of fullerenes, chemists have mainly relied on two strategies. First, the HOMO-LUMO level position can be fine-tuned by (multiple) functionalization of C$_{60}$, which in turn can result in an increase in open circuit voltage (V_{OC}).[3f] Alternatively, the symmetry of the fullerene core can be decreased to enhance optical absorption in the visible range of the solar spectrum, thus inducing an increase in J_{SC}.[4c, 5] While the first strategy has been widely adopted, the second strategy has been restricted to the use of C$_{70}$, whose oval shape is responsible for an increase in J_{SC} in comparison with C$_{60}$ derivatives. However, the increase in absorption of C$_{70}$ derivatives is most pronounced in the UV region, therefore limiting the increase in J_{SC} that one can optimally achieve.

In light of these considerations, we wondered whether azafullerenes, a class of fullerenes in which one carbon atom is replaced by a nitrogen atom,[6] could potentially

outperform $PC_{60}BM$ and $PC_{70}BM$ in BHJ-OSCs by having their absorption further shifted toward the visible region of the spectrum.

Only very recently, Gan and Ding described the first BHJ-OSC based on an azafullerene electron acceptor.[7] In this study, the authors transformed an azafullerene monoadduct into a bisadduct (as mixture of regioisomers) to enhance solubility, and the observed improvement in comparison to benchmark $PC_{60}BM$ (increased V_{OC}) is a result of the bisadduct's LUMO position. Here we report the synthesis of a solution-processable azafullerene monoadduct, **DPC$_{59}$N**, which in BHJ-OSCs exhibits the characteristics expected from an increased absorption of visible light (higher J_{SC} and EQE in comparison with $PC_{60}BM$). Based on the results presented herein, we believe that azafullerenes with optimum solubility and LUMO energy levels could be a viable alternative to $PC_{60}BM$.

Scheme 1 Synthesis of azafullerene monoadduct **DPC$_{59}$N**[a]
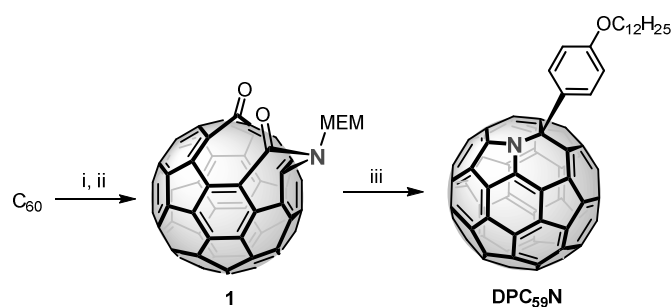
[a] Reaction conditions: (i) C_{60} (6.94 mmol, 2.0 equiv.), MEM-azide (3.52 mmol, 1.0 equiv.), ODCB, 150 °C, 60 min. (ii) hv, air, ODCB, 15 °C, 5-6 h, 13% (two steps). (iii) **1** (70 µmol, 1.0 equiv.), dodecyloxybenzene (700 µmol, 10 equiv.), *p*-TsOH (700 µmol, 10 equiv.), ODCB, 150 °C, 23 min, 37%. MEM: methoxyethoxymethyl; ODCB: 1,2-dichlorobenzene.

Our synthesis of **DPC$_{59}$N** is shown in Scheme 1. Parent fullerene C$_{60}$ was transformed into cage-opened ketolactam **1** in two steps following a protocol published previously by Wudl.[8] From this stable intermediate, target compound **DPC$_{59}$N**, which is dark green in solution, was prepared in one single step in 37% yield.[9]

In contrast to the azafullerene monoadduct prepared by Gan and Ding,[5] **DPC$_{59}$N** is soluble in most organic solvents (e.g. >10 mg/mL in dichloromethane), alleviating the need for further derivatization. Notably, the high solubility of **DPC$_{59}$N** allowed us to fabricate solar cells based on this discrete molecule, and not a mixture of regioisomeric bisadducts, which can be hard to rigorously purify and characterize.

Fig. 1 shows the UV-Vis spectra of PC$_{60}$BM and **DPC$_{59}$N** both in solution and in thin films. **DPC$_{59}$N** clearly absorbs more light than PC$_{60}$BM between 400 and 500 nm, with absorbance coefficients larger by up to a factor of six, a trend we also found in thin films. To obtain a complete picture of the suitability of **DPC$_{59}$N** as acceptor in BHJ-OSCs, a cyclic voltammogram was recorded in 1,2-dichlorobenzene and a LUMO energy of -3.63 eV was calculated for **DPC$_{59}$N**, which is identical within error with the LUMO energy of PC$_{60}$BM (-3.59 eV obtained under identical experimental conditions; see ESI[†]).
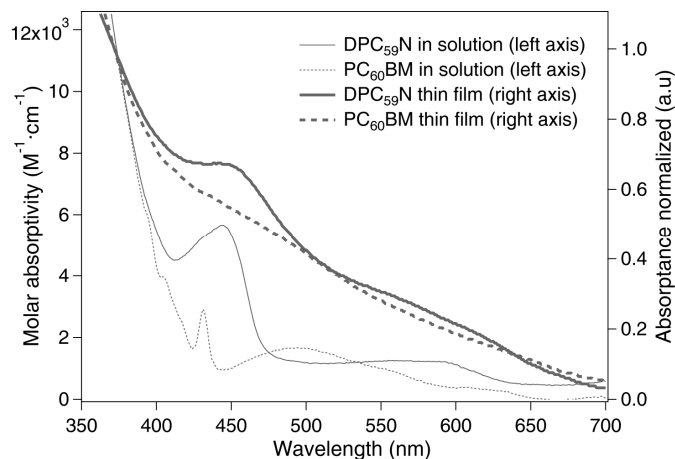
Fig. 1 UV-Vis spectra of **DPC$_{59}$N** (solid line) and PC$_{60}$BM (broken line) in solution (dichloromethane) and in thin films. For better comparison, the spectra of the thin films were normalized at the point of identical molar absorptivity of the two fullerenes in solution (372 nm).

With these promising characterization data in hand, we turned our attention towards fabricating BHJ-OSCs based on azafullerene **DPC$_{59}$N**. P3HT was chosen as the donor polymer, and solar cells were fabricated with both **DPC$_{59}$N** and PC$_{60}$BM for comparison purposes (see Fig. 2 for structure). Devices were fabricated with identical thickness and blend ratio so that any changes in the *J-V* characteristics could be attributed to the absorption difference of the fullerenes. Therefore, devices of P3HT:**DPC$_{59}$N** were first optimized for donor/acceptor (D/A) ratio, active layer thickness and annealing temperature. The optimum parameters resulting from the optimization were then used for fabrication of the reference P3HT:PC$_{60}$BM devices. The *J-V* characteristics of the best-performing devices are shown in Fig. 2, and the relevant parameters reported in Table 1.
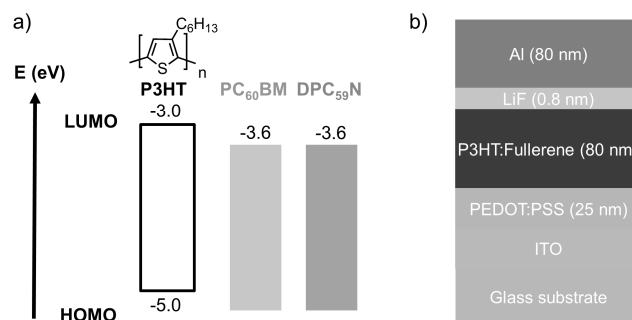
Fig. 2 (a) Experimental LUMO energy levels of $PC_{60}BM$ and **$DPC_{59}N$** derived from cyclic voltammetry carried out under identical conditions. (b) Solar cell device structure employed in this study.

Table 1 *J-V* parameters (averages)[b,c]

Acceptor	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
$DPC_{59}N$	7.92 ± 0.28	0.568 ±0.009	50 ± 1	2.24 ± 0.09 (**2.42**)
$PC_{60}BM$	7.23 ± 0.48	0.615 ± 0.008	58 ± 2	2.57 ± 0.13 (**2.70**)

[b] Light intensity: 100 mW/cm^2. Donor/acceptor ratio: 1:1. Solvent: chlorobenzene. Active layer thickness: 80 nm. [c] Average values ± standard deviation (the sample size was 12 for **$DPC_{59}N$** and 11 for PCBM). The best PCEs are provided in parentheses.

Several solvent systems were assessed in the active layer processing optimisation, resulting in chlorobenzene (CB) offering the best solubility and film homogeneity properties. We noticed however that **DPC$_{59}$N** has a tendency to form aggregates in the processed films,[10] an issue that could be partially addressed by leaving the D/A blend stirring for several days at 50°C before the deposition of the active layer (see ESI† for details). Nevertheless, this aggregation effect is likely responsible for the somewhat lower fill factor (FF), and consequently lower V_{OC} and PCE, observed in **DPC$_{59}$N** devices in respect to the PC$_{60}$BM reference (Fig. 3).
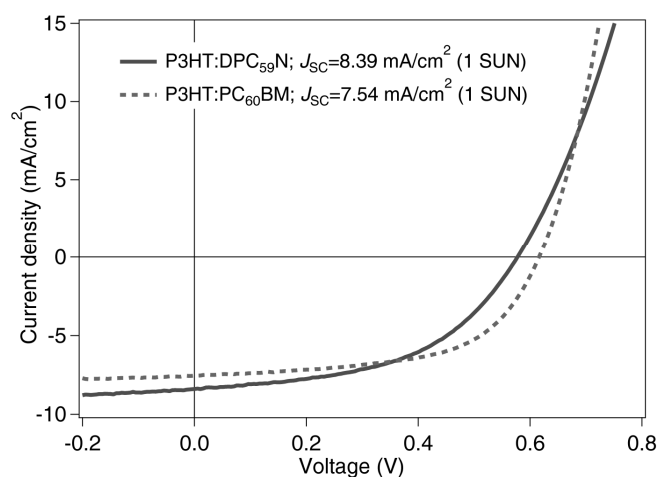

Fig. 3 *J-V* characteristics of best-performing P3HT:**DPC$_{59}$N** and P3HT:PC$_{60}$BM reference devices.

Despite these losses, **DPC$_{59}$N** devices show a highly promising increase of almost 1 mA/cm^2 in J_{SC} in respect to the PC$_{60}$BM reference. J_{SC} values are in perfect agreement with those calculated by integrating cells external quantum efficiency (EQE) over the whole solar spectrum. As seen in the EQE spectrum (Fig. 4), the EQE value of the

DPC$_{59}$N devices show a significant increase in intensity from 360 nm up to 500 nm. This increase peaks at a wavelength of 400 nm, where the difference in EQE between the two devices is higher than 15%. The good match between the absorption spectra of **DPC$_{59}$N** and the area of increased EQE suggests that the enhancement of J_{SC} is due to the azafullerene's stronger absorption of light in the visible region in comparison with PC$_{60}$BM.
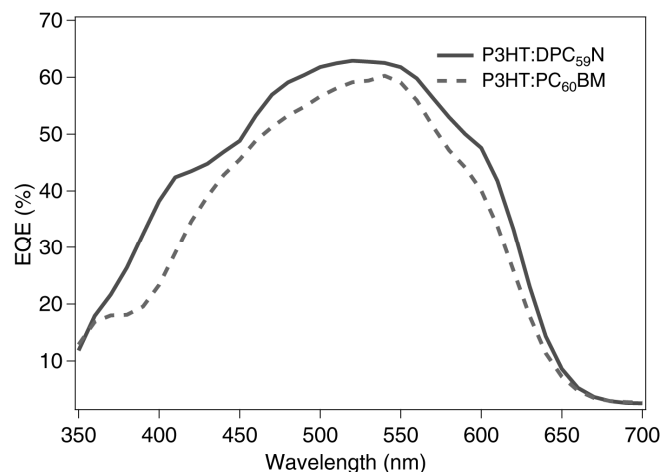

Fig. 4 EQE spectra of best-performing P3HT:**DPC$_{59}$N** and P3HT:PC$_{60}$BM reference devices.

In conclusion, we have described a concise synthesis of a discrete, solution-processable azafullerene derivative, **DPC$_{59}$N**, for application in BHJ-OSCs. We demonstrated that the azafullerene core provides for enhanced light absorption in the visible region compared to PC$_{60}$BM without affecting the frontier orbital energies. Our data suggests that the enhanced light absorption leads to an increase of over 11% in J_{SC} in comparison with reference devices made from PC$_{60}$BM. This is, to the best of our knowledge, the first example of short circuit enhancement from an azafullerene

derivative in respect to $PC_{60}BM$ in BHJ-OSCs. Studies on the synthesis of second-generation azafullerenes with improved J_{SC} *and* V_{OC} are underway in our laboratories.

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Graphical Abstract: