Cite this: *Chem. Commun.*, 2015, 51, 1128

Received 13th October 2014,
Accepted 24th November 2014

DOI: 10.1039/c4cc08094g

www.rsc.org/chemcomm

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

Werther Cambarau,^a Urs F. Fritze,^b Aurélien Viterisi,^{*a} Emilio Palomares^a and Max von Delius^{*b}

We report the synthesis of a solution-processable, dodecyloxyphenyl-substituted azafullerene monoadduct (DPC₅₉N) and its application as electron acceptor in bulk heterojunction organic solar cells (BHJ-OSCs). Due to its relatively strong absorption of visible light, DPC₅₉N outperforms PC₆₀BM 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 (PC₆₀BM and PC₇₀BM) 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,e,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 C₆₀, 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 C₇₀, whose oval shape is responsible for an increase in J_{SC} in comparison with C₆₀ derivatives. However, the increase in absorption of C₇₀ 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 PC₆₀BM and PC₇₀BM 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 PC₆₀BM (increased V_{OC}) is a result of the bisadduct's LUMO position. Here we report the synthesis of a solution-processable azafullerene monoadduct, **DPC₅₉N**, which in BHJ-OSCs exhibits the characteristics expected from an increased absorption of visible light (higher J_{SC} and EQE in comparison with PC₆₀BM). Based on the results presented herein, we believe that azafullerenes with optimum solubility and LUMO energy levels could be a viable alternative to PC₆₀BM.

Our synthesis of **DPC₅₉N** is shown in Scheme 1. Parent fullerene C₆₀ was transformed into cage-opened ketolactam **1** in two steps following a protocol published previously by Wudl.⁸ From this stable intermediate, target compound **DPC₅₉N**, 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 **DPC₅₉N** is soluble in most organic solvents

Scheme 1 Synthesis of azafullerene monoadduct **DPC₅₉N**. Reaction conditions: (i) C₆₀ (6.94 mmol, 2.0 equiv.), MEM-azide (3.52 mmol, 1.0 equiv.), ODCB, 150 °C, 60 min. (ii) *hν*, 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.

^a Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, Tarragona 43007, Spain. E-mail: aviterisi@iciq.es

^b Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Department of Chemistry and Pharmacy, Henkestraße 42, 91054 Erlangen, Germany. E-mail: max.vondelius@fau.de

† Electronic supplementary information (ESI) available: General experimental procedures, spectroscopic data, fabrication and characterisation of devices. See DOI: 10.1039/c4cc08094g

(e.g. $>10 \text{ mg mL}^{-1}$ in dichloromethane), alleviating the need for further derivatization. Notably, the high solubility of **DPC₅₉N** 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 **PC₆₀BM** and **DPC₅₉N** both in solution and in thin films. **DPC₅₉N** clearly absorbs more light than **PC₆₀BM** 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 **DPC₅₉N** 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 **DPC₅₉N**, which is identical within error with the LUMO energy of **PC₆₀BM** (-3.59 eV obtained under identical experimental conditions; see ESI†).

With these promising characterization data in hand, we turned our attention towards fabricating BHJ-OSCs based on azafullerene **DPC₅₉N**. P3HT was chosen as the donor polymer, and solar cells were fabricated with both **DPC₅₉N** and **PC₆₀BM** 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

Table 1 $J-V$ parameters (averages)^{a,b}

Acceptor	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
DPC₅₉N	7.92 ± 0.28	0.568 ± 0.009	50 ± 1	2.24 ± 0.09 (2.42)
PC₆₀BM	7.23 ± 0.48	0.615 ± 0.008	58 ± 2	2.57 ± 0.13 (2.70)

^a Light intensity: 100 mW cm^{-2} . Donor/acceptor ratio: 1:1. Solvent: chlorobenzene. Active layer thickness: 80 nm. ^b Average values $\pm$ standard deviation (the number of devices was 12 for **DPC₅₉N** and 11 for **PCBM**). The best PCEs are provided in parentheses.

P3HT:**DPC₅₉N** 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:**PC₆₀BM** devices. The $J-V$ characteristics of the best-performing devices are shown in Fig. 2, and the relevant parameters reported in Table 1.

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 **DPC₅₉N** has a tendency to form aggregates in the processed films,¹¹ 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,¹² observed in **DPC₅₉N** devices in respect to the **PC₆₀BM** reference (Fig. 3).

Despite these losses, **DPC₅₉N** devices show a highly promising increase of roughly 0.7 mA cm^{-2} in J_{SC} in respect to the **PC₆₀BM** reference. J_{SC} values are in excellent agreement with those calculated by integrating external quantum efficiency (EQE) over the whole solar spectrum. As seen in the EQE spectrum (Fig. 4), the EQE value of the **DPC₅₉N** 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 **DPC₅₉N** 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 **PC₆₀BM**.

Fig. 1 UV-Vis spectra of **DPC₅₉N** (solid line) and **PC₆₀BM** (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).

Fig. 2 (a) Experimental LUMO energy levels of **PC₆₀BM** and **DPC₅₉N** derived from cyclic voltammetry carried out under identical conditions. (b) Solar cell device structure employed in this study.¹⁰

Fig. 3 $J-V$ characteristics of best-performing P3HT:**DPC₅₉N** and P3HT:**PC₆₀BM** reference devices.

Fig. 4 EQE spectra of best-performing P3HT:DPC₅₉N and P3HT:PC₆₀BM reference devices.

In conclusion, we have described a concise synthesis of a discrete, solution-processable azafullerene derivative, **DPC₅₉N**, for application in BHJ-OSCs. We demonstrated that the azafullerene core provides for enhanced light absorption in the visible region compared to PC₆₀BM without affecting the frontier orbital energies. Our data suggests that the enhanced light absorption leads to an increase of *ca.* 10% in J_{SC} in comparison with reference devices made from PC₆₀BM. This is, to the best of our knowledge, the first example of short circuit enhancement from an azafullerene derivative in respect to PC₆₀BM in BHJ-OSCs. Studies on the synthesis of second-generation azafullerenes with improved J_{SC} and V_{OC} are underway in our laboratories.

M.v.D. thanks the Daimler foundation (postdoctoral grant 32-12/13), the Fonds der Chemischen Industrie (Liebig fellowship Li 191/01) and the Deutsche Forschungsgemeinschaft (Emmy-Noether grant DE-1830/2-1) for financial support. E.P. acknowledges financial support from ICIQ, ICREA, the Spanish MINECO for support through Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-0319), and the EU for the ERCstg Polydot.

Notes and references

- (a) C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia and S. P. Williams, *Adv. Mater.*, 2010, **22**, 3839; (b) C. Deibel and V. Dyakonov, *Rep. Prog. Phys.*, 2010, **73**, 096401; (c) W. Cai, X. Gong and Y. Cao, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 114;

- (d) H.-L. Yip and A. K. Y. Jen, *Energy Environ. Sci.*, 2012, **5**, 5994; (e) P. M. Beaujuge and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2011, **133**, 20009; (f) J. L. Delgado, P. A. Bouit, S. Filippone, M. A. Herranz and N. Martin, *Chem. Commun.*, 2010, **46**, 4853; (g) S. J. Kang, S. Ahn, J. B. Kim, C. Schenck, A. M. Hiszpanski, S. Oh, T. Schiros, Y.-L. Loo and C. Nuckolls, *J. Am. Chem. Soc.*, 2013, **135**, 2207; (h) Y. Morinaka, M. Nobori, M. Murata, A. Wakamiya, T. Sagawa, S. Yoshikawa and Y. Murata, *Chem. Commun.*, 2013, **49**, 3670; (i) P. Zhang, C. Li, Y. Li, X. Yang, L. Chen, B. Xu, W. Tian and Y. Tu, *Chem. Commun.*, 2013, **49**, 4917; (j) A. J. Heeger, *Adv. Mater.*, 2014, **26**, 10; (k) K. A. Mazzio and C. K. Luscombe, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/c4cs00227j; (l) B. C. Schroeder, Z. Li, M. A. Brady, G. C. Faria, R. S. Ashraf, C. J. Takacs, J. S. Cowart, D. T. Duong, K. H. Chiu, C.-H. Tan, J. T. Cabral, A. Salleo, M. L. Chabinyc, J. R. Durrant and I. McCulloch, *Angew. Chem., Int. Ed.*, 2014, **53**, 12870.
- M. T. Dang, L. Hirsch and G. Wantz, *Adv. Mater.*, 2011, **23**, 3597.
- (a) C.-Z. Li, H.-L. Yip and A. K. Y. Jen, *J. Mater. Chem.*, 2012, **22**, 4161; (b) B. Walker, C. Kim and T.-Q. Nguyen, *Chem. Mater.*, 2011, **23**, 470; (c) A. Mishra and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2012, **51**, 2020; (d) Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245; (e) Y. He and Y. Li, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1970; (f) Y. Li, *Chem. – Asian J.*, 2013, **8**, 2316.
- (a) Y. He, H.-Y. Chen, J. Hou and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 1377; (b) G. Zhao, Y. He and Y. Li, *Adv. Mater.*, 2010, **22**, 4355; (c) Y. He, G. Zhao, B. Peng and Y. Li, *Adv. Funct. Mater.*, 2010, **20**, 3383.
- M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem., Int. Ed.*, 2003, **42**, 3371.
- O. Vostrowsky and A. Hirsch, *Chem. Rev.*, 2006, **106**, 5191.
- Z. Xiao, D. He, C. Zuo, L. Gan and L. Ding, *RSC Adv.*, 2014, **4**, 24029.
- (a) C. Bellavia-Lund, R. González, J. C. Hummelen, R. G. Hicks, A. Sastre and F. Wudl, *J. Am. Chem. Soc.*, 1997, **119**, 2946; (b) M. von Delius, F. Hauke and A. Hirsch, *Eur. J. Org. Chem.*, 2008, 4063.
- (a) B. Nuber and A. Hirsch, *Chem. Commun.*, 1998, 405; (b) F. Hauke and A. Hirsch, *Tetrahedron*, 2001, **57**, 3697; (c) G. C. Vougioukalakis, M. M. Roubelakis and M. Orfanopoulos, *J. Org. Chem.*, 2010, **75**, 4124; (d) R. Neubauer, F. W. Heinemann, F. Hampel, Y. Rubin and A. Hirsch, *Angew. Chem., Int. Ed.*, 2012, **51**, 11722.
- The nitrogen atom in azafullerenes is not measurably basic, due to delocalisation of electron density into the fullerene framework (see ref. 6). As such, residual acid in PSS is not expected to have an impact on device efficiency.
- T. A. Bull, L. S. C. Pingree, S. A. Jenekhe, D. S. Ginger and C. K. Luscombe, *ACS Nano*, 2009, **3**, 627.
- Our group and others have shown that differences in nano-morphology, density-of-states and non-geminate recombination kinetics can translate into differences of V_{OC} , even for acceptors with identical LUMO levels. See for example: (a) A. Sánchez-Díaz, M. Izquierdo, S. Filippone, N. Martín and E. Palomares, *Adv. Funct. Mater.*, 2010, **20**, 2695; (b) G. Garcia-Belmonte, P. B. Boix, J. Bisquert, M. Lenes, H. J. Bolink, A. La Rosa, S. Filippone and N. Martín, *J. Phys. Chem. Lett.*, 2010, **1**, 2566; (c) D. Fernández, A. Viterisi, J. W. Ryan, F. Gispert-Guirado, S. Vidal, S. Filippone, N. Martín and E. Palomares, *Nanoscale*, 2014, **6**, 5871.