Improving the compatibility of fullerene acceptors with fluorene-containing donor-polymers in organic photovoltaic devices†

Jan-Carlos Kuhlmann,[a] Paul de Bruyn,[bc] Ricardo K. M. Bouwer,[ac] Auke Meetsma,[b] Paul W. M. Blom[b] and Jan C. Hummelen*[ab]

Received 11th May 2010, Accepted 9th July 2010
DOI: 10.1039/c0cc01347a

Fluorene-containing PCBM analogs have been synthesized and tested with a polyfluorene copolymer, PF10TBT, in organic photovoltaic devices resulting in an increase of ~130 mV in the open circuit voltage compared to devices with PCBM as acceptor material.

This communication describes the synthesis and characterization of fluorene-containing phenyl-C_{61}-butyric-acid methyl ester (PCBM) analogs and preliminary results of their use in photovoltaic devices containing the fluorene-bearing polymer, poly[2,7-(9,9-didecylfluorene)-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PF10TBT, Scheme 1: **13**). Power conversion efficiencies (PCE) of up to 4.2% in bulk-heterojunction (BHJ) organic photovoltaic devices (OPVs) of PF10TBT with PCBM as acceptor have been reported.[1,2]

The morphology of the active layer is crucial for highly efficient OPVs. One way to improve the morphology of the active layer is by improving the compatibility of donor and acceptor by increasing their structural similarity. This approach of incorporating groups that are structurally similar to the donor has been reported previously by our group.[3] In this previous work, a thiophene unit was included in the fullerene acceptor to improve the miscibility with polythiophene donors, particularly regioregular poly(3-hexylthiophene) (rr-P3HT). This improved the morphology of the BHJ film after thermal annealing by increasing the ability of the P3HT to form crystalline domains. PCEs of 3.0% were measured in these devices.

Recently a fluorene-copolymer containing polar side groups to improve the chemical compatibility with fullerenes was reported, but this (opposite) approach resulted in slightly lower PCEs as compared to the unmodified copolymer.[4]

In this communication we report on our efforts to improve the compatibility of the fullerene acceptor with fluorene-containing polymers by incorporating fluorene moieties into three different fullerene acceptors, differing by the substituents at the 9-position of the fluorene. We chose the three alkyl chains that are the most commonly used in fluorene-based copolymers: bis-hexyl, bis-octyl and bis-decyl. The resulting 9,9-dialkyl-9*H*-fluoren-2-yl-C_{61}-butyric-acid methyl esters are abbreviated F*n*CBM where *n* is the number of carbons of the alkyl chain. The synthesis of the F*n*CBM series is given in Scheme 1 (described in more detail in the ESI†). The fluorene moiety was dialkylated with the appropriate alkylbromide in dimethylsulfoxide in the presence of potassium hydroxide. Purification with column chromatography (SiO_2/heptane) yielded the products as colorless oils. The dialkylated fluorenes **1–3** were further functionalized by Friedel–Crafts acylation with methyl 5-chloro-5-oxopentanoate. Column chromatography (SiO_2/toluene) yielded the pure keto esters **4–6**. These keto esters were then reacted with tosylhydrazide in toluene under Dean–Stark conditions. Subsequent recrystallisation from hot methanol yielded the tosylhydrazones **7–9** as pale yellow crystals. Standard diazo addition[5] of **7–9** to C_{60} followed by column chromatography (SiO_2/CS_2 to remove unreacted C_{60}, then 1 : 1 toluene/cyclohexane) yielded the pure adducts **10–12**.

Acylation of fluorenes can occur at different positions of the fluorene moiety.[6] Since unambiguous structural proof could not be obtained by NMR spectroscopy, crystal structures were obtained for **7** to confirm the proposed structure (Fig. S3, ESI†).

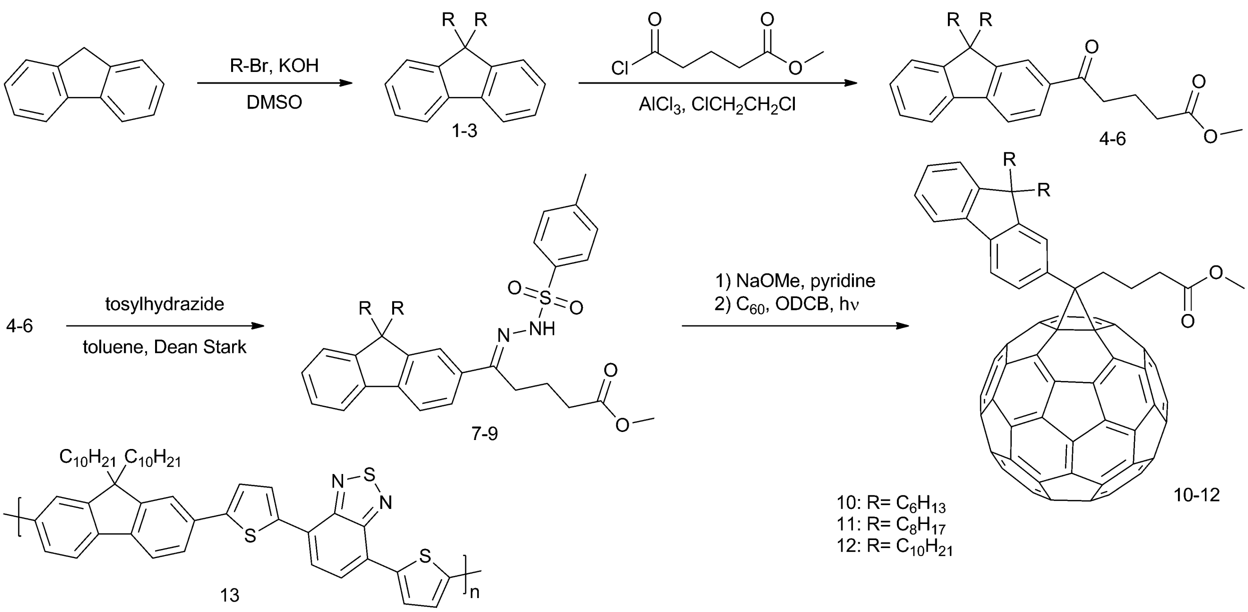
Cyclic voltammetry (CV) of the F*n*CBMs shows only marginal differences (7–16 mV more negative) in the first half-wave reduction potentials as compared to PCBM (Table 1). All reductions were reversible. To evaluate the effect of the fluorene moieties on the performance of OPVs we fabricated a series of photovoltaic devices with the F*n*CBMs as acceptors and PF10TBT as the donor and one device with PCBM as the acceptor for reference. We fabricated these devices by spin-coating PF10TBT and the fullerene acceptor from chlorobenzene solutions on PEDOT : PSS-coated ITO glass substrates and evaporating LiF and aluminium on top of the active layer. In a first series the devices were fabricated with a 1 : 4 polymer : fullerene ratio (by weight). These are the optimal conditions for maximizing PCEs with PCBM but not necessarily the best for the F*n*CBMs. The results obtained from the best of these devices with active layer thicknesses of ~120 nm are summarized in Table 1.

Compared to PCBM, the devices that have F*n*CBMs as acceptor showed increased open-circuit voltages (V_{OC}) of up to 130 mV (for F_8CBM and F_{10}CBM). This increase in V_{OC}, compared to devices comprising PF10TBT : PCBM active layers, cannot be explained by the energy levels of the polymer and that of the fullerene measured with CV. However, it is known that in OPVs comprising PF10TBT : PCBM active layers V_{OC} increases with decreasing concentrations of

---

[a] *Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: j.c.hummelen@rug.nl; Fax: +31 50 363 8751; Tel: +31 50 363 5553*
[b] *Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[c] *Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands*

† Electronic supplementary information (ESI) available: Details on synthetic procedures, solar cells preparation, and crystal structure of compound **7**. CCDC 776856. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc01347a



Scheme 1 Synthesis of fluorene-containing PCBM analogs (F*n*CBMs) and structure of PF10TBT (**13**).

Table 1 Reduction potentials and *J–V* characteristics

Acceptor	$E_{1/2}$,1,red.[a]	Weight ratio *D* : *A*	J_{SC}/A m^{-2}	V_{OC}/V	FF	PCE
PCBM	−1.080	1 : 4	60.63	0.95	0.60	3.46
F$_6$CBM	−1.087	1 : 4	42.45	1.07	0.44	2.02
		1 : 5.1[b]	46.30	1.07	0.45	2.24
F$_8$CBM	−1.086	1 : 4	34.43	1.08	0.39	1.46
		1 : 5.4[b]	40.20	1.08	0.43	1.88
F$_{10}$CBM	−1.096	1 : 4	31.43	1.08	0.39	1.33
		1 : 5.6[b]	33.70	1.08	0.40	1.44

[a] Cyclic voltammetry data. Experimental conditions: Pt working electrode, Ag/Ag+ reference electrode, values are compared to a Fc/Fc+ internal standard, Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte, ODCB/acetonitrile (4 : 1) as the solvent, 10 mV s^{-1} scan rate. [b] Corrected for molecular mass.

fullerene[7] and due to their increased molecular weight (over PCBM), the volume fraction of fullerene is lower in the devices containing F*n*CBMs than in the PCBM-containing reference device. To test this hypothesis, a second series of devices with an adjusted volume fraction of the F*n*CBMs compared to PCBM was prepared. The results obtained are compared to the results from the first series in Table 1. Unexpectedly, the V_{OC} values remain unchanged but the short-circuit current (J_{SC}) and fill factor (FF) values are slightly better. It is commonly accepted that the $V_{OC(max)}$ of OPV devices is linearly related to the energy difference between the HOMO of the donor and the LUMO of the acceptor. However the observed increase of up to 130 mV in V_{OC} without significantly changing the reduction potential of the acceptor shows that other factors influence the V_{OC} as well. A closer look at other acceptors in the literature revealed that the difference in reduction potential, relative to PCBM, is usually equal to the difference in V_{OC} of the actual devices within ±30 mV. Increases in V_{OC} of up to 40 mV higher than the difference in reduction potential were found for some mono-adducts.[8,9] For bisPCBM : P3HT and DPM-12 : P3HT this extra V_{OC} increase is even 50–100 mV, which is remarkable but still considerably lower than that of the donor:acceptor pair reported here.[10–12]

In conclusion we have synthesized three new fluorene-containing analogs of PCBM to improve the compatibility with fluorene-containing copolymers in BHJ-OPVs. Preliminary testing of these new acceptors with PF10TBT resulted in an unexpected increase in V_{OC} of ~130 mV. Further optimization of the device morphology to increase FF and PCE, as well as investigations to unravel the cause of the extra increase in V_{OC} are ongoing.

The work of P. de Bruyn and R. K. M. Bouwer forms part of the research programme of the Dutch Polymer Institute (DPI), project #660 and #524.

Notes and references

1 L. H. Slooff, S. C. Veenstra, J. M. Kroon, D. J. D. Moet, J. Sweelssen and M. M. Koetse, *Appl. Phys. Lett.*, 2007, **90**, 143506.
2 D. J. D. Moet, L. H. Slooff, J. M. Kroon, S. S. Chevtchenko, J. Loos, M. M. Koetse, J. Sweelssen and S. C. Veenstra, *Proceedings of the MRS Fall Meeting*, Boston (MRS, Warrendale, PA), 2006, 974E.
3 L. M. Popescu, P. van't Hof, A. B. Sieval, H. T. Jonkman and J. C. Hummelen, *Appl. Phys. Lett.*, 2006, **89**, 213507.
4 D. Gedefaw, Y. Zhou, S. Hellstrom, L. Lindgren, L. M. Andersson, F. L. Zhang, W. Mammo, O. Inganäs and M. R. Andersson, *J. Mater. Chem.*, 2009, **19**, 5359.

5 J. C. Hummelen, B. W. Knight, F. Lepeq, F. Wudl, J. Yao and C. L. Wilkins, *J. Org. Chem.*, 1995, **60**, 532.
6 S. J. J. Titinchi, F. S. Kamounah, H. S. Abbo and O. Hammerich, *ARKIVOC*, 2008, **13**, 91.
7 D. Veldman, O. Ipek, S. C. J. Meskers, J. Sweelssen, M. M. Koetse, S. C. Veenstra, J. M. Kroon, S. S. van Bavel, J. Loos and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2008, **130**, 7721.
8 S. A. Backer, K. Sivula, D. F. Kavulak and J. M. J. Fréchet, *Chem. Mater.*, 2007, **19**, 2927.
9 C. Yang, J. Y. Kim, S. Cho, J. K. Lee, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2008, **130**, 6444.
10 M. Lenes, G. J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen and P. W. M. Blom, *Adv. Mater.*, 2008, **20**, 2116.
11 I. Riedel, E. von Hauff, J. Parisi, N. Martín, F. Giacalone and V. Dyakonov, *Adv. Funct. Mater.*, 2005, **15**, 1979.
12 Riedel *et al.* (ref. 11) reported an increase of 100 mV in V_{OC}, compared to the V_{OC} of their PCBM : P3HT reference cells (0.55 V). However, optimized PCBM : P3HT devices nowadays show V_{OC} values of 0.58 V or higher.