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Purification and electronic characterisation of 18 isomers of the OPV acceptor material bis-[60]PCBM†

W. Shi,[a] X. Hou,[a] T. Liu,[a] X. Zhao,[a] A. B. Sieval,[b] J. C. Hummelen[c] and T. J. S. Dennis*[a]

The as-produced isomer mixture of the organic photovoltaic device acceptor material bis-[60]PCBM has been purified into its constituents by peak-recycling HPLC, and those individual isomers were characterised by UV-Vis absorption spectroscopy and cyclic voltammetry. A total of 18 isomers were purified from the mixture to a standard exceeding 99.5% with respect to other isomers. The HOMOs, LUMOs, and HOMO–LUMO gaps of the purified isomers vary from −5.673 to −5.444 eV, −3.901 to −3.729 eV, and 1.664 to 1.883 eV, respectively. We also find a correlation between HPLC retention time and the relative positions of the addends; in that generally the closer the addends are to each other the longer the retention time of the isomer, and *vice versa*.

Bulk heterojunction organic photovoltaic ("OPV") devices comprise a blend of a polymer donor and a fullerene-based acceptor. Fullerene derivatives have many properties that make them ideal acceptors: spherical shape, excellent miscibility with the acceptor polymer, a tendency to aggregate, and favourable electron affinity.[1,2] Although there has been a considerable advance in OPV performance over the past decade with considerable improvements in the donor polymer, the acceptor material remains primarily the fullerene derivative phenyl-C_{61}-butyric acid methyl ester ([60]PCBM). Empirically, the energy difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor scales linearly with the OPV open circuit voltage (V_{OC}) under standard conditions.[3–10] As such increasing the LUMO of the fullerene acceptor in principle leads to a higher V_{OC}. An effective method of increasing the LUMO is to add electron pushing functional groups to the fullerene cage.[9] A bisadduct of [60]PCBM, bis-[60]PCBM, has proved successful in this respect.[11,12] The additional addend results in an increase in the acceptor LUMO of about 100 meV[13] (compared to that of [60]PCBM), leading to a significant increase in the power conversion efficiency (PCE).[14] However, the increase in PCE is not as high as expected from the increase in V_{OC}. This is because, unlike [60]PCBM, bis-[60]PCBM exists as a mixture of many isomers, which leads to morphological and energetic disorders in the OPV active layer with a degrading effect on the current.[13] Fabricating devices from isomer-pure samples may remove these disorders. Furthermore, such samples would facilitate the fabrication of devices with substantially higher LUMOs than the ensemble average (and thereby substantially higher V_{OC} values). Hence, using isomer-pure samples may lead to both a higher voltage and a higher current. We present the separation of the as-produced bis-[60]PCBM isomer mixture into 18 constituent isomers by peak-recycling high performance liquid chromatography (HPLC) together with their electronic characterisation by UV-Vis spectroscopy and cyclic voltammetry.

Purification:‡ the purification was performed using a multi-stage, multi-column HPLC process, primarily in the peak-recycling mode. However, the initial separation ("Stage 1") into rough fractions was performed in the normal single-pass mode.

The Stage 1 single-pass HPLC chromatogram of the isomer mixture on the silica column (Fig. 1) indicates that the mixture can be readily separated to the baseline into 7 fractions ("F1–F7"). This is consistent with that previously reported for partial separation within the collaborating group.[15] Fractions F1, F4, F6 and F7 appear as a single peak, whereas the others indicate the presence of multiple sub-fractions.

The fractions with only a single peak were separately concentrated and re-injected into the HPLC, this time in the peak-recycling mode. In all cases, after 5 cycles the HPLC profile was typical of a single component peak, from which we conclude that F1, F4, F6 and F7 each comprises a single isomer. The purification of F2, F3 and F5 proved to be somewhat more complicated. Subsequently, we shall describe in detail the method of purifying F3 into its constituent isomers. After which we shall give a simpler description of the purification of F2 and F5 (of which the reader can follow using the principles gathered from the purification of F3).

[a] *School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London, E1 4NS, UK. E-mail: j.dennis@qmul.ac.uk*
[b] *Solenne BV, Zernikepark 6, 9747AN, Groningen, The Netherlands*
[c] *Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials University of Groningen, Nijenborgh 4, 9747AG, Groningen, The Netherlands*

† Electronic supplementary information (ESI) available: A complete set of HPLC chromatograms of each of the 18 isomers and the UV-Vis absorption spectra and cyclic voltammograms of all 18 purified isomers. See DOI: 10.1039/c6cc07820f

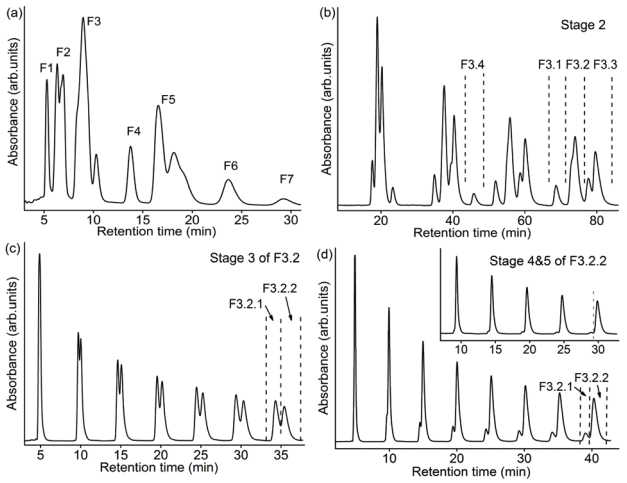

Fig. 1 The complete purification method for fraction F3.2.2 from the isomer mixture: (a) Stage 1 single-pass HPLC profile showing the partial separation of the isomer mixture; (b) Stage 2 peak-recycling for F3; (c) Stage 3 for F3.2; (d) Stages 4 and 5 (inset) for F3.2.2, after which the residual of any other isomer was finally removed.

Fig. 1(b) shows the Stage 2 (peak recycling) HPLC profile of F3 on the silica column. On the first cycle the fraction is partially resolved into 4 sub-fractions ("F3.1–F3.4"). After the 2nd cycle the separation had developed such that sub-fraction F3.4 was resolved from the others to the baseline; hence, it was collected on this cycle. By the 4th cycle, F3.1, F3.2 and F3.3 were all resolved to the baseline and separately collected. However, it is apparent that on the 4th cycle F3.2 has a shoulder on its low retention time side and F3.3 is partially resolved into two peaks. A 7-cycle Stage-3 purity test for both F3.1 and F3.4 indicated that they each comprised a single isomer.

The Stage 3 separation of F3.2 into its components on the silica column proved problematic owing to the lack of resolution of the components. Experimentation with other columns in our laboratory showed that F3.2 separates relatively easily on a 5PBB column (Fig. 1(c)) despite it having about half of the retention time compared to the silica column. By the 2nd cycle, the fraction shows two partially resolved peaks ("F3.2.1 and F3.2.2") of near-equal intensity, and by the 7th cycle the two peaks are resolved half way to the baseline. Although reasonable, but not full, resolution was achieved after 7 cycles, full resolution could not be achieved by continuing to recycle beyond that point. Hence, the partially purified F3.2.1 and F3.2.2 were taken separately off the column by cutting at the minimum between the two peaks on the 7th cycle. Once all of F3.2 was purified to this state, the two fractions were each concentrated to about 50% of a saturated solution, and each subjected to a further recycling HPLC treatment (Stage 4). Fig. 1(d) shows the Stage 4 recycling chromatograms for F3.2.2. It can be seen that again there are two fractions, and that the amount of F3.2.1 remaining after Stage 3 was greatly reduced. Unfortunately, full purification was still not achieved by the 7th cycle on Stage 4 and 5th stage (Fig. 1(d) inset) was required. The purification of F3.2.1 was achieved in a manner analogous to that of F3.2.2 on the 5PBB column. The purification of F3.3 followed a similar multi-stage recycling process to that for F3.2. However, for these isomers a 5PYE column proved to be more effective.

By following a similar process to that for the purification of F3 into its 6 constituent isomers, F2 was separated into 4 isomers ("F2.1.1, F2.1.2, F2.2 and F2.3"). The silica column was used throughout the purification of F2. This is because the short retention times made the other columns less amenable to peak-recycling. F5 also consisted of 4 isomers ("F5.1, F5.2.1, F5.2.2 and F5.3"), with F5.1, F5.2 and F5.3 being separated from one another using the 5PBB column followed by the separation of F5.2.1 and F5.2.2 on the 5PYE column. A flow chart for the full purification process is given in Fig. 2, and a complete set of HPLC profiles for all stages of the purification, including purity tests for each of the 18 isomers, is provided separately in the ESI.†

C_{60} has 30 double bonds, and with the first PC_1BM addend of bis-[60]PCBM bridging the 1, 9 bond (by default), the other group may add across any of the remaining 29 double bonds. In addition, since PC_1BM has two different groups on the cyclopropa-bridge (*i.e.*, [60]PCBM has C_s, not C_{2v} symmetry), the 2nd addend may add in either of two orientations relative to that of the 1st addend. Hence, there are nominally 58 cyclopropa-fullerene isomers of bis-[60]PCBM. However, the high symmetry of the C_{60} molecule and the chirality of many of the isomers reduce the number of effective isomers to 21 separable isomers, on symmetric columns.

Of these, 18 isomers were found in the isomer mixture. That 3 isomers are missing is to be expected. This is because the 3 *cis*-1 isomers, in which the two addends add across adjacent double bonds of the fullerene cage, would have their formation inhibited on steric grounds. Therefore, it seems that, apart from three sterically hindered isomers, the isomer mixture contains all possible dicyclopropa-fullerene isomers. Peak integration analysis of the resulting HPLC profiles indicated that the relative abundances of the isomers vary over not much more than one order of magnitude (ranging from 1.2% to 15.6%). The relative abundance of each individual isomer is given in Table 1.

Electronic characterisation: cyclic voltammograms§ and the UV-Vis absorption spectra¶ of all 18 isomers are given in the ESI.† The LUMO energy levels determined by cyclic voltammetry, the optical HOMO–LUMO gap (E_g) determined by UV-Vis absorption spectroscopy and the HOMO (determined by LUMO – E_g) levels of the 18 isomers are shown in Fig. 3. They are presented in order of increasing HPLC retention time. For comparative purposes our measured analogous data of the mono-adduct [60]PCBM and the bis-[60]PCBM isomer mixture, which are consistent with those presented in the literature,[14,16] are also given. The LUMO energy

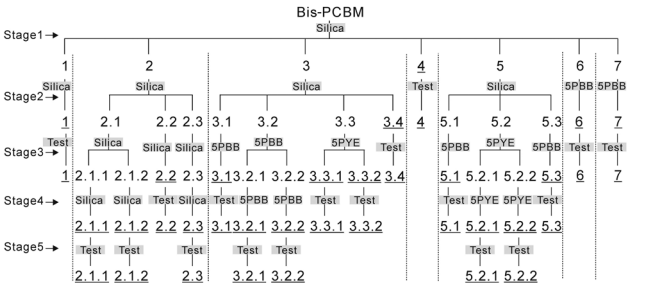

Fig. 2 Flow chart for the complete purification of all 18 isomers, the column used is shown for each stage.

Table 1 The relative abundances of each of the 18 isomers of bis-[60]PCBM

Isomer	F1	F2.1.1	F2.1.2	F2.2	F2.3	F3.1
Abundance (%)	6.7(1)	1.2(2)	7.5(1)	4.4(1)	6.3(1)	3.0(1)
Isomer	F3.2.1	F3.2.2	F3.3.1	F3.3.2	F3.4	F4
Abundance (%)	7.0(1)	7.5(1)	3.4(1)	10.4(1)	1.8(2)	6.2(1)
Isomer	F5.1	F5.2.1	F5.2.2	F5.3	F6	F7
Abundance (%)	15.6(1)	2.3(2)	5.4(1)	3.2(1)	5.2(1)	1.4(2)

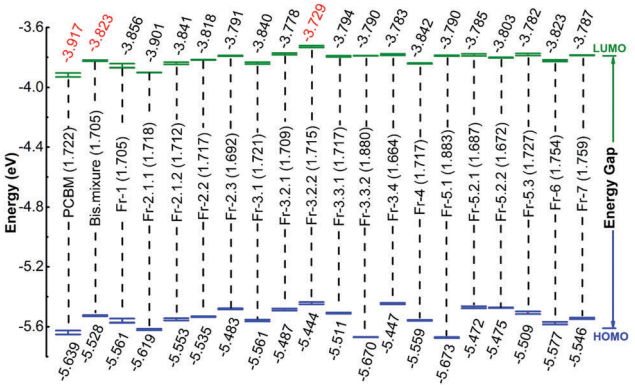

Fig. 3 The HOMO, LUMO and E_g values (in eV) for each of the 18 isomers of bis-[60]PCBM, together with our measured values for the isomer mixture and [60]PCBM.

levels of bis-[60]PCBM range between −3.901 eV and −3.729 eV. In comparison with the LUMO of the mono-adduct (−3.917 eV), the LUMOs of all 18 isomers of bis-[60]PCBM are higher. The increase in the LUMO varies between 16 meV and 188 meV, (F2.1.1 being the lowest and F3.2.2 the highest). Furthermore, 12 of the 18 isomers have LUMO energy levels that are above the quasi-LUMO level (−3.823 eV) of the isomer mixture. From the UV-Vis spectra, E_g varies between 1.664 eV and 1.883 eV (F3.4 and F5.1 being the smallest and the largest, respectively). The HOMO levels of the isomers range between −5.673 eV for F5.1 and −5.444 eV for F3.2.2. This range is reasonably consistent with the calculations of the HOMO energies at the B3LYP/6-31G(d) level of theory for a representative subset of 7 of the isomers by Frost *et al.*,[17] which range from −5.612 to −5.432 eV. However, although the calculated HOMOs are within the range of the experimental values, the calculated range (180 meV) is somewhat narrower than the experimental range (229 meV).

Hirsch and co-workers have purified several bis-adducts of C_{60}, structurally identified them and recorded their UV-Vis absorption spectra.[18] A comparison of their UV-Vis spectra with ours shows very clear similarities such that we may tentatively assign our spectra, and thereby the HPLC fraction, to each of the 7 bond types. For example, the equatorial, *e*, isomers from ref. 18 show a pronounced sharp peak at about 420 nm, a broad and somewhat more intense peak at about 500 nm, and a smooth tail with a relatively low-wavelength onset. By reason of the asymmetry about the bridging carbons of bis-[60]PCBM, we expect two isomers to have these traits, and indeed they are found in two HPLC fractions: F3.3.2 and F5.1. Not only do the spectra of these two fractions have the abovementioned traits, they are also very similar to each other, and yet distinctly different from the other spectra. Furthermore, the *e* isomers were found by Hirsch *et al.* to be the most abundant of their bis-adducts,[18,19] and of our fractions, F3.3.2 and F5.1 are considerably more abundant than any other. Hence, we may with some confidence assign F3.3.2 and F5.1 to being the two equatorial isomers of bis-[60]PCBM. The spectra of the *trans*-2 isomers from ref. 18 have a shoulder near 410 nm, a pronounced sharp peak near 420 nm, a broad but this time less intense peak at about 500 nm, a bumpy tail with several weak peaks between 600 and 700 nm, and a relatively high-wavelength onset. This time we expect the three isomers of bis-[60]PCBM to have these traits and find them in the spectra of only three fractions: F1, F2.1.2 and F3.1. As with the two *e* isomers, the spectra of these three fractions have the appropriate traits, are very similar to each other, and are distinctly different from the other spectra. By similar analyses all other isomers may be readily assigned to their bond-type. Those assignments are given in Fig. 4.

Based on these assignments, there is an apparent correlation between HPLC retention time and the relative positions of the two addends. The *trans*-1 and *trans*-2 isomers tend to elute first, followed by *trans*-3 and *trans*-4, then the equatorial isomers, and finally, *cis*-3 comes off the column before *cis*-2. However, this order is not strictly adhered to. The reason for the close but non-strict adherence is likely to stem from the asymmetry of the PC_1BM addends. Apart from the two *trans*-1 isomers, the asymmetry results in two distinguishable bonds of each bond type, depending on whether the 2nd addend is closer to the phenyl or the methyl butanoate group of the 1st addend. An additional contribution to the non-strict adherence comes from most bond types giving two orientations of the two attends relative to each other. It seems that deviations from the trend are greater as the 2nd addend approaches the equator. Notwithstanding this, there is a clear trend in the abovementioned direction; from which we conclude that in general for this type of bis-adduct, the closer the two addends are to each other the longer is the retention time of that isomer on the columns used (silica, pentabromobenzyl, and pyrenylethyl).

Near room temperature kT is about 26 meV. Hence, within the fullerene phase of a bulk heterojunction OPV, if the LUMO

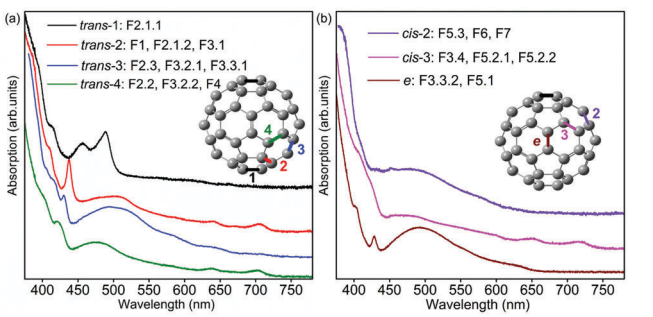

Fig. 4 Representative UV-Vis spectra for each of the 7 bond types in bis-[60]PCBM. In each case, the spectrum is that of the first isomer in the list, but is typical of the others.

levels of neighboring bis-[60]PCBM isomers differ by more than 26 meV, there is the potential for the lower LUMO isomer to act as an electron trap. This is particularly so at low current densities. Of the 18 isomers the first two in order of HPLC retention time (F1 and F2.1.1) are of concern in relation to full mixture-based OPV devices. This is because they are the only isomers outside this range: at 33 meV and 78 meV below the average, respectively. These two isomers may be easily removed *via* a simple single-pass HPLC treatment. However, as single pass HPLC is a necessary requirement to remove potential traps, it would be better to make OPV devices from the individual fractions, as a cheaper alternative to using individual isomers. For example, an OPV device based on only F5, which represents 27% of the mixture, is likely to result from an increase in both the voltage and the current when compared to those made with the as-produced mixture. We say this for three reasons. Firstly, the average LUMO level of F5 is 33 meV above that of the mixture, which should result in a higher V_{OC}. Secondly, the variation of the LUMOs of all four isomers of F5 is 21 meV, which is well below the 26 meV of thermal energy available to the system at room temperature, and hence should improve the current by reducing energetic disorder and potential traps. Thirdly and finally, the reduction in the number of isomers (from 18 to 4) is likely to result in an improved morphology of the fullerene phase within the active layer, and thereby further improved the device current. That a reduction in the number of isomers results in an improved morphology within the fullerene phase was demonstrated by Bouwer *et al.*[13] The same arguments can be made for F3 (at 33% of the mixture with an average LUMO 50 meV above that of the mixture), provided the low LUMO initial sub-fraction F3.1 is dropped out before collection.

The OPV acceptor bis-[60]PCBM was purified into its 18 constituent isomers using the peak-recycling HPLC method, each to a purity exceeding 99%.The UV-Vis spectra and cyclic voltammograms demonstrate that each of the isomers exhibits different electronic properties. Their HOMO, LUMO and HOMO–LUMO gaps range from −5.673 to −5.444 eV, from −3.901 to −3.729 eV, and from 1.664 to 1.883 eV, respectively. The LUMO levels of the majority of the isomers are above that of the isomer mixture, and hence, OPV devices based on each of those isomers are predicted to have a V_{OC} value higher than that of present devices based on the mixture (with F3.2.2 being the most promising at 94 meV above that of the mixture and 188 meV above that of [60]PCBM). Furthermore, with the removal of energetic and morphological disorder associated with the normal mixture of bis-[60]PCBM isomers, it is also predicted that OPV devices based on all of the isomers will have better charge carrier transport properties, and thereby potentially higher currents than those based on the mixture. Based on comparisons with known UV-Vis absorption spectra of analogous materials purified and identified by others,[18,19] we conclude that there is correlation between the HPLC retention time and the relative positions of the addends; in that generally the closer the addends are to each other the longer the retention time of the isomer, and *vice versa*.

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Notes and references

‡ Japan Analytical Industries LC908 peak recycling HPLC; waters 5 mm silica column (19 mm i.d. × 150 mm); Cosmosil (Nacalai Tesque) 5PYE column (20 mm i.d. × 250 mm) or a Cosmosil (Nacalai Tesque) 5PBB column (20 mm i.d. × 250 mm) was used as per Fig. X; toluene eluent, flow rate = 18 mL min^{-1}.

§ Autolab potentiostat galvanostat: scan rate = 10 mV s^{-1}; electrolyte solution = 1 : 4 by volume acetonitrile : 1,2-di-chlorobenzene solvent containing the bis-PCBM isomer at a concentration of 0.1 mg mL^{-1} together with $(n\text{-Bu})_4BF_4$ (0.1 M); ferrocene internal standard; glassy carbon working electrode, platinum mesh counter electrode and a non-aqueous Ag/Ag^+ reference electrode; constant nitrogen purge.

¶ Shimadzu UV-2600 spectrophotometer: range, scanning rate, step size and path length were 325–800 nm, 30 nm min^{-1}, 0.2 nm, and 10 mm, respectively.

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