Structural Identification of 19 Purified Isomers of the OPV Acceptor Material bisPCBM by ^{13}C NMR and UV-Vis Absorption Spectroscopy and High Performance Liquid Chromatography

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ABSTRACT: The molecular structures of 19 purified isomers of bis-phenyl- C_{60} -butyric acid methyl ester ("bis[60]PCBM") were identified by a combination of ^{13}C NMR and UV-Vis absorption spectroscopy, and HPLC retention time analysis. All 19 isomers are dicyclopenta-fullerenes (none are homo-fullerenes). There were 7 isomers with C_1 molecular point group symmetry, 4 with C_5 , 6 with C_2 , 1 with C_{2v} and 1 with C_{2h} symmetry. The C_{2h} , C_{2v} , and all 5 non-equatorial C_1 isomers were unambiguously assigned to their respective HPLC fractions. For the other 12 isomers, the ^{13}C NMR and UV-Vis spectra placed them in 6 groups of two same-symmetry isomers. Based on the widely spaced HPLC retention times of the two isomers within each of these 6 groups, and the empirical inverse correlation between retention time and addend spacing, each isomer was assigned to its corresponding HPLC fraction. In addition, the missing *trans*-1 isomer was found, purified, and characterized.

1 INTRODUCTION

Bis[60]PCBM is easy to synthesize, highly processable, and solar cells based on this material are relatively simple and cheap to fabricate and have high power conversion efficiencies amongst OPVs.¹⁻³ However, it has greater potential in this application because it is synthesized as a mixture of structural isomers which gives both energetic properties⁴ (influencing device voltage), and morphological properties (influencing device current), that may range from poor to excellent. 18 of a possible 19 isomers were recently purified from the as-produced mixture, and the frontier molecular orbitals characterized by UV-Vis spectroscopy and cyclic voltammetry.⁴ Their lowest unoccupied molecular orbitals ("LUMOs") were found to vary from -3.90 to -3.73 eV. As such, the LUMO levels of all 18 isomers are above that of PCBM (-3.92 eV). Furthermore, the LUMOs of 13 of the 18 isomers are above that of the isomer mixture (-3.82 eV).⁴ As the open-circuit voltage (" V_{oc} ") of OPVs scales linearly with the energy difference between the highest occupied molecular orbitals ("HOMOs") of the donors and the LUMOs of the acceptors,⁵⁻¹² OPV devices based on each of those 13 individual isomers will each have a higher V_{oc} than that of present devices based on the mixture. One isomer, with a LUMO *ca.* 100 meV above that of the mixture (and *ca.* 200 meV above that of PCBM), is particularly promising.⁴ The most abundant isomer of bis[60]PCBM has recently been incorporated in a perovskite-based photovoltaic device in pure form.¹³ This device had a high power conversion efficiency of 20.8%, which is substantially higher than similar devices based on

(a) the pristine perovskite or (b) [60]PCBM treated perovskite. Perhaps more importantly, this device yielded a very substantial increase in device lifetime. The efficiency of an unsealed isomer-pure bis[60]PCBM-based device fell by less than 10% after 45 days at 65°C in air; whereas, the efficiency of a device based on [60]PCBM and pristine perovskite-based fell by 30% and 50% during the same period.¹³ Several works on other fullerene bis-adducts have recently appeared in the literature. These have highlighted the effects of fullerene bisadduct regioisomers,¹⁴ single crystals,¹⁵ and on photovoltaic performance.¹⁶

At present, although we now know the frontier energy levels of each purified HPLC fraction,⁴ we do not know which isomer of bisPCBM corresponds to which HPLC fraction. In addition, to draw meaningful conclusions on why some isomers are better/worse than others in terms of OPV device performance we need to know which isomer is being employed in which device; something that again is presently unknown. In this paper, *via* arguments based on a combination of UV-Vis absorption spectra, ^{13}C NMR spectra and HPLC retention times, each of the 19 HPLC fractions is assigned to its corresponding bis[60]PCBM isomer.

This paper will enable those who follow and produce photovoltaic devices based on purified bis[60]PCBM isomers to know which specific isomer is being employed in their devices, and hence, will allow the development of a deeper understanding of energetic and morphological order/disorder within the acceptor phase, and thereby allow the abovementioned meaningful conclusions to be drawn on why some isomers perform better than others.

2 EXPERIMENTAL SECTION

10 g of bis[60]PCBM isomer mixture was synthesized following the method of References 17 and 18. Briefly, 5-oxo-5-phenylpentanoic acid is converted into its methyl ester under reflux with methanol. A tosylhydrazone is then formed by reaction of the ester with p-toluenesulfonyl hydrazine. Finally, the tosylhydrazone is reacted anaerobically with C₆₀ in 1,2-dichlorobenzene, pyridine and sodium methoxide under sodium-vapor irradiation at 85°C to yield the bis[60]PCBM. Twice as much of the tosylhydrazone is used in the final stage compared to that of Reference 17 for [60]PCBM.

The crude bis[60]PCBM mixture was then purified into its constituent isomers by HPLC. The purification followed the method of Reference 4 and the HPLC fractions names used in this paper correspond to those from that reference. Single-pass HPLC was used to divide into mixture into 7 well-resolved components on a silica column (Waters Sunfire 19 mm i.d. × 150 mm). Several components had sub-components which were resolved from each other on a pentabromobenzyl (5PBB) column (Nakalai Tesque Cosmosil 20 mm i.d. × 250 mm) by peak-recycling HPLC. All HPLC work was carried out using a Japan Analytical Industry LC-908 HPLC machine with toluene eluent at a flow rate of 18 ml min⁻¹ and UV detection operating at 312 nm.

The ¹³C NMR spectra were recorded on Bruker AV600 spectrometer, in carbon disulfide solution to which a few drops of benzene-d₆ lock was added (with exception of HPLC fraction F2.3, which was carried out in 1,2-dichlorobenzene-d₄ solution owing to very low solubility in CS₂). In each case, depending on solubility of the isomer, between 1024 and 8192 scans were co-added to produce the final spectrum.

The UV-Vis absorption spectrum of HPLC Fraction F1.1 was recorded on a Shimadzu UV-2600 spectrophotometer: the range, scanning rate, step size and path length were 350 – 800 nm, 30 nm min⁻¹, 0.1 nm, and 10 mm, respectively.

3 RESULTS AND DISCUSSION

3.1 Note on nomenclature and the number of isomers.

There are literally hundreds of structural isomers of bis[60]PCBM. These include cyclopropa-fullerenes bridging double-bonds in fullerenes, homofullerenes bridging double-bonds and homofullerenes bridging single-bonds. However, as will be shown later in this paper, all the isomers are in fact cyclopropa-fullerenes. Hence, this discussion on nomenclature and the number of isomers will be limited to isomers of this type. The trivial name of the mono-analogue of bis[60]PCBM is PCBM, which reflects the parts of the molecule; *i.e.*, phenyl C_n butyric acid methyl ester. However, when the PC₁BM group was added to other fullerenes, *e.g.*, C₇₀ and C₈₄, the name was commonly modified to include the original fullerene in brackets as [60]PCBM, [70]PCBM, *etc.* However, other systems are also in use such as PC₆₁BM in place of [60]PCBM, which can lead to ambiguity and confusion. The ambiguity may be removed by using the IUPAC systematic nomenclature. However, these names can become unwieldy. For example,

[60]PCBM becomes methyl 4-[61-phenyl,3aH'-cyclopropa-1,9-(C₆₀-I_h)[5,6]fullerenyl]butanoate. Extending the trivial name to include two addends on the fullerene was simply achieved by adding the prefix bis to give bis[60]PCBM. However, transforming the systematic name the molecule has complications in that almost all the isomers are chiral, and hence, the positions of the two ligands as well as the stereochemistry (R/S isomerism) about each of the carbons of both bridges needs defining. An example of the name of one of the 36 cyclopropa-fullerene isomers of the bis[60]PCBM isomers is: dimethyl 4'4''-[61(R),62(S)-diphenyl,3aH',3aH''-dicyclopropa-1(S),9(R):49(S),59(R)-(C₆₀-I_h)[5,6]fullerendiyl]dibutanoate. Hence, not only is the systematic name very cumbersome, the amount of branching that would occur before a difference was found would be so hard to keep track of that a computer with code specific to each isomer would be required to reliably determine the stereochemistry. With the problems associated with the systematic nomenclature, a trivial naming system that is as less ambiguous as possible is beneficial.

One system that has gained some popularity for fullerene bis adducts is to refer to position of the 2nd addend relative to the first as *cis*, *trans* or *e* depending on whether the 2nd addend is on the same hemisphere (*cis*), opposite hemisphere (*trans*), or on the equator (*e* for equatorial) relative to the position of the first isomer.¹⁹⁻²¹ This nomenclature gives rise to groupings of symmetrically equivalent bonds into 8 different bond-types – designated *cis*-1, *cis*-2, *cis*-3, *e*, *trans*-4, *trans*-3, *trans*-2 and *trans*-1 in order of increasing distance between the two addends. These 8 bond-types are shown in Figure 1.

There are however, several drawbacks with the *cis/trans* bond-type designations in fullerene derivatives. The first is that it is a non-standard definition. This is because *cis* and *trans* properly refer to cases where two ligands are on the same side (*cis*) or opposite sides (*trans*) of a plane going through a double bond or a ring. A point-in-case would be fullerene bis-adduct with substituted alkene ligands, which could have two different definitions of *cis/trans* within the same molecule. The second problem is that it was developed for symmetric addends, where all isomers are achiral and where all 4 possible *trans*-2 bonds (for example) are symmetrically equivalent, and hence, require just one name. Bis[60]PCBM isomers, and other dicyclopropa-fullerenes in general are asymmetric about the bridge carbon, and hence, generally chiral. Therefore, the 4 *trans*-2 bonds (again for example) in bis[60]PCBM are all distinguishable, requiring additional labelling for each. In this respect it is common for different researchers to use different nomenclature with primes, double primes, triple primes, *etc.*, or *a*, *b*, *c*, *etc.*; all of which are non-standard and ill defined. A third problem is that there are two types of *e* bonds; *i.e.*, horizontal (21,40 and 30,31) and vertical (16,17 and 44,45) equatorial bonds. These are sometimes distinguished as *e'* and *e''*,¹⁹ but again which is which is ill defined.

Herein, we propose an trivial nomenclature that retains the commonly-used bis[60]PCBM, but replaces the *trans*-1, *cis*-2, *etc.*, labels, together with their ill-defined sub-labels for the variants of each bond-type, with the fullerene carbon atom numbering from the IUPAC system.

Figure 1. The 8 bond-types for C_{60} bis-adducts. For symmetrical bis-adducts, except for the sole *trans*-1 bond, there are 4 symmetrically equivalent bonds of each type (left, right and mirrored behind). However, for unsymmetrical bis-adducts, such as bis[60]PCBM, the bond-types on the right are not equivalent to those on the left (indicated by solid and dotted lines); and those behind are, in general, enantiomers of those in front – yielding 4 generally symmetrically inequivalent bonds of each non *trans*-1 type.

With the system proposed here, there is no need to ascertain the stereochemistry. This is because the isomers may be unambiguously distinguished *via* their molecular point-group symmetry, which is both easier to determine and easier to visualize.

Using the IUPAC numbering system, the first addends in bis[60]PCBM bridges the 1,9 bond of C_{60} , by default (indeed it does so in all bis adducts of C_{60}). The *trans*-1 bond of bis[60]PCBM is therefore 52,60. With PC₁BM being asymmetrical about the bridge carbon, the 2nd addend may add in two different orientations relative to the first; yielding two possible *trans*-1 type isomers. These have C_{2h} and C_{2v} molecular point group symmetry. We would propose calling them in the style $(C_{2h})1,9:52,60$ -bis[60]PCBM. However, as mentioned above, the 1st addend bridges the 1,9 fullerene-bond in all isomers of all C_{60} bis-adducts. As such, we propose to omit 1,9: from the name on grounds that the first addend can only be there, and then leave its present implied by the 'bis' prefix. Hence, we shorten this name to $(C_{2h})52,60$ -bis[60]PCBM.

The *cis/trans* nomenclature can also handle the achiral *trans*-1 bond; for example as $(C_{2h})trans$ -1-bis[60]PCBM. However, for the *trans*-2 bond asymmetry and chirality yield 4 distinguishable *trans*-2 bonds in bis[60]PCBM (49,59; 50,51; 53,54, and 55,56), for which the two relative orientations give rise to two isomers in two point groups (C_1 and C_2) *per* bond. Using the point group and the bond type, *e.g.*, as $(C_1)trans$ -2-bis[60]PCBM and $(C_2)trans$ -2-

bis[60]PCBM cannot distinguish all 8 nominal combinations, whereas $(C_{1/2})_{x,y}$ -bis[PCBM], where x,y is 49,59; 50,51; 53,54, and 55,56 as appropriate, easily can.

Turning to the number of isomers, with the first addend bridging fullerenes carbons 1 and 9 by default, there are 29 other double bonds to which the 2nd addend may attach. As the 2nd addend may attach in two orientations relative to that of the 1st addend there are nominally 58 cyclopropa-fullerene isomer of bis[60]PCBM. However, as will be explained in detail below, symmetry reduces this number to 36 physically distinguishable isomers. Many of these isomers have enantiomers, which cannot be spectroscopically distinguished or separated on symmetrical columns. This reduces the number of effective isomers to 22.

All 58 nominal isomers are accounted for in Table 1. The 22 spectroscopically distinguishable isomers are listed in the first column. Interchanging the two addends by reorienting the isomer such that the 2nd addend is at the 1,9 position gives a symmetrically equivalent isomer, which does not generally have the same numbering as the original, but nevertheless is structurally identical to it. These symmetrical equivalents are listed in the 2nd column of Table 1. The isomers in the 2nd column with different numberings to those in the 1st column are not different isomers, but instead represent alternative numberings to those in the 1st column. By convention, the numbering with the lowest initial number is preferred, and hence those in the 2nd column may be disregarded from the isomer count.

The UV-Vis absorption spectra show that the *trans*-1 'polar' isomers and the *e* 'equatorial' isomers each form a group of two similar but distinguishable isomers, and that those for the other bond-types (*trans*-3, *trans*-4, *cis*-3 and *cis*-2) each form a bond-type group with three members.⁴ This observation may be explained by Table 1.

That there are only two isomers involving the *trans*-1 bond was demonstrated above in the discussion on nomenclature. Of the 4 nominal *trans*-2 isomers with C_1 symmetry (*i.e.*, those bridging fullerene carbons 49,59; 50,51; 53,54 and 55,56), 53,54 is identical to 49,59, and hence, 53,54 may be disregarded. Similarly, 55,56 is identical to 50,51, and hence 55,56 may be disregarded. Finally, of the two surviving physically distinguishable isomers, 51,50 is the enantiomer of 49,59, and so 49,59 and 50,51 cannot be distinguished spectroscopically or purified from each other on symmetrical HPLC columns. This reduces the number of spectroscopically distinguishable *trans*-2 isomers with C_1 symmetry to only one - $(C_1)49,59$ -bis[60]PCBM. By similar arguments, all three-membered bond-type groups effectively have only one C_1 isomer.

The three-membered groups have non- C_1 isomers where both have C_2 symmetry or both have C_s symmetry. Taking the C_2 case first, and the *trans*-2 isomers again as our example, all 4 nominal C_2 isomers (again, 49,59; 50,51; 53,54 and 55,56) this time all give the same numbering on exchanging the addends. For example, placing the 2nd addend of $(C_2)49,59$ -bis[60]PCBM at the 1,9 position of the 1st addend yields the same numbering as before - $(C_2)49,59$ -bis[60]PCBM. The result is also the same for $(C_2)53,54$ -bis[60]PCBM. Both *trans*-2 C_2 isomers have enantiomers that also transform onto themselves. Hence, there are two spec-

troscopically distinguishable *trans*-2 isomers of this type; which are (C₂)49,59-bis[60]PCBM and (C₂)53,54-bis[60]PCBM. By similar arguments the *trans*-3 and *cis*-3 bond-type groups will also have two spectroscopically distinguishable C₂ isomers. The *trans*-4, *cis*-2 and *cis*-1 bond-type groups consist of isomers C₁ or C_s symmetry, for which again in each case the 4 nominal C_s isomers give rise to two spectroscopically distinguishable C_s isomers and one spectroscopically distinguishable C₁ isomer.

The 3 isomers involving the *cis*-1 bond-type are not expected to form owing to steric hindrance that is the result of both bulky addends otherwise being attached to adjacent double bonds on the same hexagonal ring on the fullerene. That isomers associated with the *cis*-1 bond do not form has been previously reported for another fullerene bis-adduct.^{19,20} As such, we expect a maximum of 19 spectroscopically-distinguishable isomers of bis[60]PCBM; which as will be shown below, is found to be the case.

The above discussion is chemically interesting because it indicates that all possible cyclopropa-fullerene isomers of bis[60]PCBM are formed, and conversely, that no other types isomers are formed at all. For example, none of the isomers of bis[60]PCBM involve bridging of bonds within 5-membered rings and none of the isomers are homofullerenes. This may be contrasted with [70]PCBM, for example, which also may exist as *ca.* 20 cyclopropa-fullerene isomers, but only three isomers have ever been found.²²

Table 1. All 58 nominal cyclopropa-fullerene isomers of bis[60]PCBM indicating the 22 spectroscopically distinguishable isomers, their symmetrical equivalents, their enantiomers, and the symmetrical equivalents of enantiomers. The equatorial isomers cannot be distinguished by symmetry; but may be distinguished by whether the phenyl attached to carbon 62 is *syn* or *anti* with respect to the addend at carbon 61; or by the about chirality carbon-62, as appropriate.

Isomer	Sym. equiv.	Enantiomer	Sym. equiv.
(C _{2h})52,60	(C _{2h})52,60	--	--
(C _{2v})52,60	(C _{2v})52,60	--	--
(C ₂)49,59	(C ₂)49,59	(C ₂)50,51	(C ₂)50,51
(C ₁)49,59	(C ₁)53,54	(C ₁)50,51	(C ₁)55,56
(C ₂)53,54	(C ₂)53,54	(C ₂)55,56	(C ₂)55,56
(C ₂)34,35	(C ₂)34,35	(C ₂)46,58	(C ₂)46,58
(C ₁)34,35	(C ₁)43,57	(C ₁)46,58	(C ₁)36,37
(C ₂)36,37	(C ₂)36,37	(C ₂)43,57	(C ₂)43,57
(C _s)32,33	(C _s)47,48	(C _s)47,48	(C _s)32,33
(C ₁)32,33	(C ₁)38,39	(C ₁)47,48	(C ₁)41,42
(C _s)38,39	(C _s)41,42	(C _s)41,42	(C _s)38,39
<i>anti</i> (C ₁)16,17	<i>R</i> (C ₁)21,40	<i>anti</i> (C ₁)44,45	<i>S</i> (C ₁)21,40
<i>syn</i> (C ₁)16,17	<i>R</i> (C ₁)30,31	<i>syn</i> (C ₁)44,45	<i>S</i> (C ₁)30,31
(C ₂)13,14	(C ₂)13,14	(C ₂)28,29	(C ₂)28,29
(C ₁)13,14	(C ₁)22,23	(C ₁)28,29	(C ₁)19,20-
(C ₂)19,20	(C ₂)19,20	(C ₂)22,23	(C ₂)22,23
(C _s)3,15	(C _s)26,27	(C _s)26,27	(C _s)3,15
(C ₁)3,15	(C ₁)4,18	(C ₁)26,27	(C ₁)24,25
(C _s)4,18	(C _s)24,25	(C _s)24,25	(C _s)4,18
(C _s)5,6	(C _s)7,8	(C _s)7,8	(C _s)5,6
(C ₁)2,12	(C ₁)5,6	(C ₁)10,11	(C ₁)7,8
(C _s)2,12	(C _s)10,11	(C _s)10,11	(C _s)2,12

3.2 Purification and UV-Vis absorption spectroscopy of the missing *trans*-1 isomer.

Dennis and co-workers recently purified 18 isomers of bis[60]PCBM and characterized of their frontier molecular orbitals (HOMOs, LUMOs and E_{gaps}).⁴ From their UV-Vis absorption spectra, they assigned each isomer to one of 7 expected bond-types (*trans*-1, *trans*-2, *trans*-3, *trans*-4, *e*, *cis*-3 and *cis*-2) with there being two or three members of each of the 7 groups.

These authors also reported that there is an inverse correlation between the HPLC retention time of an isomer and the separation between its two addends; that is, for example, the two *trans*-1 isomers elute early from the silica column (as the 1st and 3rd isomers), whereas the three *cis*-2 isomers elute as the final 3 isomers.⁴ Using the separation between carbon-4 of each of the two methylbutanoate groups as a simple measure of this separation, herein we find that the 4 isomers of bis[60]PCBM with the largest separation between the two addends are the *trans*-1 isomer with C_{2h} symmetry, a *trans*-2 with C₂ symmetry, the *trans*-1 isomer with C_{2v} symmetry and the *trans*-2 isomer with C₁ symmetry. Based on these spacings, we predicted that the missing *trans*-1 isomer should occur with a slightly shorter retention time than the first isomer (HPLC fraction F1) found in Reference 4 (a *trans*-2 isomer that we will later show has C₂ symmetry, which we predicted to be the 2nd isomer to elute from the column). Re-examination of the HPLC profile of the previously reported HPLC fraction F1 revealed a tiny shoulder in the low retention-time side of F1, that had been removed from fraction F1 during its purification, but not further reported. For the present paper, this tiny shoulder was isolated from F1 by peak recycling HPLC.

Figure 2 shows the UV-Vis absorption spectrum of this new HPLC fraction; which has the same color (yellow) as the other *trans*-1 isomer (F2.1.1), and its UV-Vis absorption spectrum is also remarkably similar with that of F2.1.1, while being substantially different from those of all the other isomers.⁴ The onset of its UV-Vis spectrum occurs at 745.2 nm, and indicates a HOMO-LUMO gap of 1.664(3) eV. With the previously reported HPLC fraction F1 consisting of two fractions, fraction F1 is hereby re-designated as F1.2; and the newly discovered *trans*-1 isomer is termed F1.1.

Figure 2. The UV-Vis absorption spectrum of HPLC fraction F1.1. From its onset (insert), the HOMO-LUMO gap is determined to be 1.664 ± 0.003 eV.

3.3 The ^{13}C NMR spectra

The ^{13}C NMR spectrum of the mono-adducted analogue, [60]PCBM, indicates that this species has C_s molecular point group symmetry and that it exists as a cyclopropa-fullerene.¹⁵ The key indicator of this structure is the presence of a doubly degenerate line in the sp^3 region of the ^{13}C NMR spectrum near 80 ppm. This line was assigned to the two symmetrically equivalent 'bridgehead' carbons on the fullerene cage following the cycloaddition (*i.e.*, atoms 1 and 9 of the 1,9,61 cyclopropa ring). These two carbons were originally double bonded on the fullerene cage and thereby sp^2 hybridised. However, upon cycloaddition, these atoms converted to sp^3 hybridisation – becoming part of a cyclopropa-ring (with a commensurate reduction of sp^2 -hybridised carbons on the fullerene cage from 60 to 58).

As will be demonstrated below, the ^{13}C NMR spectra of the purified bis[60]PCBM isomers show that in every case these isomers also possessed lines near 80 ppm and a reduction of sp^2 carbons on the fullerene from 60 to 56 in this case. From this, it is concluded that all 19 isomers bis[60]PCBM isomers are, like [60]PCBM, cyclopropa-fullerenes.

Of the 19 possible isomers, 7 isomers are predicted to have C_1 molecular point group symmetry. These 7 ^{13}C spectra will all have the same general form – consisting of 84 non-degenerate lines; broken into 14 lines in the sp^3 region (15 – 85 ppm) and 70 lines in the sp^2 region (125 – 175 ppm) – albeit with differing values for the chemical shifts for each isomer. Four isomers are predicted to have C_s symmetry, which will each give rise to 44 distinct resonances. These may be divided into 7 doubly-degenerate resonances in the sp^3 region together with 33 doubly-degenerate and 4 non-degenerate lines in the sp^2 region. Six isomers are predicted to have C_2 symmetry and have spectra comprising 7 doubly degenerate sp^3 lines and 35 doubly-degenerate sp^2 lines. The final two isomers are the polar structures, which are predicted to have C_{2v} symmetry (giving rise to 1 4-fold degenerate and 5 doubly-degenerate sp^3 lines, and 15 4-fold degenerate and 6 doubly-degenerate sp^2 lines) and C_{2h} symmetry (1 4-fold degenerate and 5 doubly-degenerate sp^3 lines, and 15 4-fold degenerate and 6 doubly-degenerate sp^2 lines). As will be shown below, these predictions are seen to be correct.

Trans-1 isomers: Although about 10 mg of the new isomer F1.1 was synthesized and purified from the mixture by HPLC, the solubility of this isomer is very low when purified; even in 'high-solubility' solvents for fullerenes – such as 1,2-dichlorobenzene; which gave a pale-yellow solution over precipitated solid; indicating a strong propensity to aggregate. As such, the solubility of F1.1 was not high enough to record a ^{13}C NMR spectrum of it.

Based on characteristic similarities and differences between the UV-Vis absorption spectra of the 18 previously purified isomers, Dennis and co-workers⁴ predicted that HPLC fraction F2.1.1 should involve the 2nd addend bridging the *trans*-1 (*i.e.*, 52,60) fullerene bond (where the first addend bridges the 1,9 fullerene-bond in all isomers by default). However, they were unable to say whether this fraction was the C_{2h} or C_{2v} *trans*-1 isomer. Using the abovementioned methylbutanoate carbon-4 separation

method, we predict in this paper that F2.1.1 is the *trans*-1 isomer with C_{2v} symmetry. This is because, as mentioned in the discussion of the UV-Vis spectrum of F1.1, the separation of the two methylbutanoate groups is greater for the C_{2h} isomer than for the C_{2v} isomer, which would suggest that the C_{2h} isomer should elute from the silica column before the C_{2v} isomer.

The ^{13}C NMR spectrum of F2.1.1, is shown in Figure 3. This spectrum can be broken into two parts (a) resonances between 15 and 85 ppm, and after a gap of about 40 ppm, (b) those between 125 and 175 ppm, which respectively correspond to resonances from sp^3 and sp^2 hybridized carbons. The sp^3 region comprises 6 resonances. Based on typical 'group resonances', the first three lines may be assigned to the $-(\text{CH}_2-\text{CH}_2-\text{CH}_2)-$ part of the ester, with the central carbon corresponding to the resonance at 22.94 ppm, and the two outer carbons giving the two resonances near 34 ppm. These resonances have an integration of 2 because both addends are symmetrically equivalent. The resonance at 44.93 ppm may be assigned to the methyl groups and the resonance at 50.30 ppm to the bridge carbons (bis[60]PCBM carbons 61 and 62). The final sp^3 resonance occurs at 79.92 ppm and has an integration of 4. With all sp^3 carbons of the butyric acid methyl ester group and the two bridge carbons accounted for, this final resonance can only come from the fullerene. It is the presence of this resonance that confirms that this isomer is, like [60]PCBM, a cyclopropa fullerene. As will be seen below, the integration of all the sp^2 resonance from the fullerene is reduced from 60 to 56, which is also consistent with this conclusion. The resonance at 79.92 with integration of 4 is therefore assigned to fullerene carbons 1, 9, 52 and 60 – all of which are symmetrically equivalent for this *trans*-1 isomers.

The first 5 lines in the sp^2 region occur at 128.48, 128.87, 132.45, 137.69 and 137.62, and have integrations of 2, 4, 4, 4, 2. The 4 phenyl resonances should be not far removed from the 128.06 ppm of deuterated benzene, and hence should be four of these 5 resonances. The phenyl ring should give integrations of 2, 2, 4 and 4.

Figure 3. The ^{13}C NMR spectrum of HPLC fraction F2.1.1 of (a) the sp^3 hybridized carbons, and (b) sp^2 hybridised carbons. The pattern of $12 \times 2 + 15 \times 4$ indicated that F2.1.1 can only be the *trans*-1 isomer (C_{2v})52,60-bis[60]PCBM. The off-scale fea-

ture near 128 ppm, in this spectrum and the other spectra in this paper, is due to the benzene-d₆ signal lock.

The resonances at 128.48 and 137.62 ppm each has an integration of 2, with the 128.48 ppm being the slightly more intense. On grounds that phenyl carbon 4 has a hydrogen bonded to it, whereas phenyl carbon 1 is bonded to only carbon atoms. The hydrogen on phenyl carbon 4 will result in that carbon having faster relaxation than phenyl carbon 1, accounting for carbon 4 having a slightly higher intensity than carbon 1. Hence, the resonance at 128.48 and 137.69 ppm are assigned to carbon-4 and carbon-1 from each of the two symmetrically-equivalent phenyl rings. Similarly, the resonances at 128.87 and 132.34 ppm (each with an integration of 4) have slightly greater intensity than the resonance at 137.62, which indicates that these two resonances come from carbons with bonded hydrogen and are therefore the remaining resonances from the phenyl groups. Hence, the resonance 128.87 ppm is assigned to phenyl carbons 3 and 5, and the resonance at 132.45 ppm is assigned to phenyl carbons 2 and 6. The resonance at 137.62 is therefore the first of the fullerene lines.

There then follows a cluster of lines between 138 and 148 ppm, of which 11 have an integration of four, and 4 have an integration of two. When taken with the integration-4 line at 137.21 ppm, these account for the 56 *sp*² resonances on the fullerene cage.

The final resonance occurs at 171.92 ppm and has an integration of 2. This resonance may, again based on 'group resonances, be readily be assigned to the two carbonyl carbons from the symmetrically-equivalent ester groups. As such, all 84 carbons of bis[60]PCBM have been accounted for in this spectrum.

The measured chemical shifts of all the resonances and HPLC fraction assignment are:

Fraction F2.1.1; (C_{2v})52,60-bis[60]PCBM

171.92	146.43	146.34	145.74	145.59	145.55	145.54
144.87	144.51	144.18	144.08	143.92	143.86	141.80
141.52	138.58	137.62	137.69	132.45	128.87	128.48
76.92	51.30	44.93	34.51	34.03	22.94	

Resonances in bold result from 2 symmetrically equivalent carbons within the molecule, whereas, all other resonances result from 4 symmetrically equivalent carbons atoms.

The form of all the spectra of the other 18 isomers follow this general pattern; resonances from the C₃H₆ group (20-35 ppm), followed by the methyl and bridge carbons (45-55 ppm), followed by the bridgehead carbons near 80 ppm in the *sp*³ region; then resonances from the phenyl rings (128-138 ppm), followed the fullerene (137-152 ppm) and finally from the carbonyls (near 170 ppm). As such, the discussions for these isomers will focus on molecular structure identification without discussion of the line assignments.

We may also conclude (by elimination) that the isomer with very low solubility (the newly discovered HPLC fraction F1.1) must be the other *trans*-1 isomer – (C_{2h})52,60-bis[60]PCBM. As mentioned above, this conclusion is confirmed by the UV-Vis absorption spectrum of fraction F1.1 (Figure 1), which is similar with that of the other *trans*-1

isomer (fraction F2.1.1),⁴ but markedly different from the spectra of the other 17 isomers.

Stick diagrams of the isomers corresponding to (a) HPLC fraction F1.1 (C_{2h})52,60-bis[60]PCBM and (b) fraction F2.1.1 (C_{2v})52,60-bis[60]PCBM, are given in Figure 4.

Figure 4. Representations of the molecular structures of (a) (C_{2h})52,60-bis[60]PCBM and (b) (C_{2v})52,60-bis[60]PCBM, which correspond to the 1st and 3rd HPLC fractions (F1.1 and F2.1.1) to elute from a silica column.

Trans-2 isomers: Based on the UV-Vis spectroscopic results from Reference 4 and the contents of Table 1 above, we expect the three *trans*-2 isomers to comprise two C₂ isomers and one C₁ isomer; and to be the 2nd, 4th and 7th HPLC fractions in elution order; *i.e.*, to be F1.2, F2.1.2 and F3.1.

The ¹³C NMR spectra of F1.2, F2.1.1 and F3.1 are shown in Figure 5. The spectra of F1.2 and F3.1 demonstrate that the two corresponding isomers both have C₂ symmetry (as indicated by 42 double intensity lines) and the spectrum of F2.1.2 has C₁ symmetry (84 single intensity lines) – in line with these predictions.

These conclusions are consistent the retention-time order prediction based on the methylbutanoate carbon-4 addend separation method mentioned above in the UV-Vis sub-section. Indeed, this method correctly predicts that 1st and 3rd isomers should be the *trans*-1 isomers with C_{2h} and C_{2v} symmetry respectively; that the 2nd and 7th isomer should both be *trans*-2 isomer with C₂ symmetry and that the 4th eluting isomer is the *trans*-2 isomer with C₁ symmetry; and goes on to correctly predicts the retention time order of 13 of the 19 isomers. There are only three minor imperfect predictions with this method. We say minor because in each of the 3 cases they are only wrong in giving reversed predictions of adjacent isomers in the HPLC profile with retention times that are so close that they required extensive repeated peak-recycling HPLC to separate; *i.e.*, they gave reverse predictions for only a few isomers where those isomers had practically identical retention times.

As only one *trans*-2 isomer has C₁ symmetry, we may unambiguously assign HPLC fraction F2.1.2 to the isomer (C₁)49,59-bis[60]PCBM. The other two *trans*-2 isomers (F1.2 and F3.1) both have C₂ symmetry, and hence have identical forms to their ¹³C NMR spectra (42 double intensity lines – albeit with similar but non-identical chemical shifts). As such, these two C₂ isomers cannot be distinguished from the ¹³C NMR spectra alone. To aid in their identification, these two spectra were simulated at the

B3LYP/6-31G** level of theory using input geometries calculated at the same level.²³ Unfortunately, similarities and differences between the measured chemical shifts of the two *trans*-2 C_2 isomers were not reliably reproduced in the corresponding simulated spectra. Hence, the simulations were unable to usefully distinguish these two isomers. This unreliability was also found in the cases of all the other bond types which had two isomers with the same symmetry.

Figure 5. The ^{13}C NMR spectra of the three *trans*-2 isomers for (a) sp^3 carbons and (b) sp^2 carbons or HPLC fractions (i) F1.1, (ii) F2.1.2 and (iii) F3.1, which are identified as being the isomers $(C_2)49,59\text{-bis}[60]\text{PCBM}$, $(C_1)49,59\text{-bis}[60]\text{PCBM}$, and $(C_2)53,54\text{-bis}[60]\text{PCBM}$, respectively.

However, it is noted that the HPLC retention time order of the three *trans*-2 isomers is $C_2 - C_1 - C_2$. Hence, the two otherwise indistinguishable symmetric isomers within the *trans*-2 groups are widely separated in the HPLC profile. Indeed, as will be demonstrated below, this *symmetric* – *asymmetric* – *symmetric* HPLC elution behavior is observed for all the three-membered groups (*i.e.*, *trans*-3, *trans*-4, *cis*-3 and *cis*-2).

That the isomers of the same symmetry within each bond-type group have widely separated HPLC retention times may be rationalized based on the separation of the two addends. This is because in each case the two symmetric isomers involve different distinguishable bonds (for example, 49,59 and 53,54 for the two C_2 *trans*-2 isomers; and 3,15 and 4,18 for the two C_s *cis*-2 isomers), and hence, the separation of the addends will be different leading to the isomer with the closer addends having the longer HPLC retention time. As such, we assign the C_2 *trans*-2 isomer with the shorter HPLC retention time (F1.2) to the C_2

trans-2 isomer with the greater separation between the two addends – that is, $(C_2)49,59\text{-bis}[60]\text{PCBM}$. Likewise we assign the C_2 *trans*-2 isomer with the longer HPLC retention time (F3.1) to the C_2 *trans*-2 isomer with the shorter addend separation; *i.e.*, $(C_2)53,54\text{-bis}[60]\text{PCBM}$.

The chemical shifts of the three *trans*-2 isomers together with HPLC fraction assignments are listed below. As with all the C_1 isomers, all resonances correspond to an individual carbon atom within the molecule, and as with all the C_2 isomers all resonances originate from a pair of symmetrically equivalent carbon atoms. Where there is a coincidence of resonances the chemical shifts of the two components are listed separately.

Fraction F1.2: $(C_2)49,59\text{-bis}[60]\text{PCBM}$

171.88	150.98	147.91	147.18	146.34	146.32	146.28
145.95	145.58	145.55	145.23	145.16	144.87	144.83
144.52	144.50	144.11	144.01	143.61	142.82	142.64
142.36	142.25	142.15	137.31	136.50	136.43	132.20
132.20	128.66	128.66	78.93	51.34	49.38	34.10
34.06	23.01					

Fraction F2.1.2: $(C_1)49,59\text{-bis}[60]\text{PCBM}$

171.95	171.79	151.85	150.96	147.86	147.27	147.19
146.68	146.49	146.48	146.45	146.28	146.25	146.16
145.96	145.92	145.83	145.68	145.66	145.58	145.51
145.31	145.23	145.21	144.92	144.89	144.78	144.77
144.58	144.49	144.46	144.22	144.07	143.94	143.69
143.61	143.46	142.93	142.76	142.63	142.60	142.56
142.44	142.38	142.15	142.13	142.01	141.79	141.56
141.03	140.58	140.29	139.98	139.43	137.62	137.36
137.29	136.98	136.88	136.63	136.46	132.50	132.50
132.20	133.20	128.89	128.89	128.68	128.68	128.56
128.34	79.17	79.15	78.96	78.92	51.34	51.21
49.48	49.3	34.12	34.06	33.88	23.02	22.74

Fraction F3.1: $(C_2)53,54\text{-bis}[60]\text{PCBM}$

171.82	151.8	147.21	146.87	146.35	146.26	146.04
146.01	145.82	145.80	145.47	145.40	144.98	144.82
144.81	144.43	144.04	143.73	143.44	142.86	142.78
142.53	142.16	141.98	141.09	140.56	139.43	137.31
137.95	136.90	132.52	132.52	128.90	128.90	128.57
78.17	78.91	51.22	49.39	34.14	33.89	22.77

Figure 6 shows stick diagrams of the isomers corresponding to HPLC fraction (a) F1.2, $(C_2)49,59\text{-bis}[60]\text{PCBM}$; (b) fraction F2.1.1, $(C_1)49,59\text{-bis}[60]\text{PCBM}$; and (c) fraction F3.1, $(C_2)53,54\text{-bis}[60]\text{PCBM}$.

Figure 6. Representations of the molecular structures of (a) $(C_2)49,59\text{-bis}[60]\text{PCBM}$, (b) $(C_1)49,59\text{-bis}[60]\text{PCBM}$ and (c) $(C_2)53,54\text{-bis}[60]\text{PCBM}$ which correspond to the 2nd, 4th and 7th HPLC fractions (F1.2, F2.1.2 and F3.1) to elute from a silica HPLC column.

Trans-3 isomers: HPLC fractions F2.3, F3.2.1 and F3.3.1 were predicted to be the three *trans*-2 isomers,⁴ which herein we further predict to consist of two C_2 isomers and one C_1 isomer. The ^{13}C NMR spectra of these fractions are shown in Figure 7.

Figure 7. The ^{13}C NMR spectra, (a) sp^3 carbons and (b) sp^2 carbons, of the three *trans*-3 isomers which correspond to HPLC fractions (i) F2.3, (ii) F3.2.1 and (iii) F3.3.1; and are identified as being isomers (C_2) 34,35-bis[60]PCBM, (C_1) 34,35-bis[60]PCBM, and (C_2) 36,37-bis[60]PCBM, respectively.

The line pattern of the middle and final fractions, F3.2.1 and F3.3.1, have 84 single-intensity lines and 42 double-intensity lines, respectively. As such, they are consistent with this prediction; respectively having C_1 and C_2 symmetry. Hence, like the *trans*-2 case, it is the middle fraction that is the one with C_1 symmetry.

However, like fraction F1.1, fraction F2.3 had low solubility in CS_2 , and had a high propensity to aggregate and precipitate out of solution. F2.3 nevertheless had sufficient solubility in 1,2-dichlorobenzene for a spectrum to be recorded in a reasonable time (8 hours signal averaging).

Unfortunately, this solvent has many lines between 125 and 135 ppm; some of which obliterate the lines corresponding to the phenyl groups in bis[60]PCBM. Nevertheless, this spectrum possesses 7 lines in the sp^3 region (4 lines and from the methylbutanoate group, 2 lines from the bridgehead fullerene carbons and a single cyclopropa-bridge carbon), which can only be consistent with C_2 or C_s symmetry. In the sp^2 region it indicates 28 fullerene carbons and expected and a single carbonyl resonance, which can only be consistent with C_2 symmetry (as this gives half the number of such carbon resonances – all lines must be doubly degenerate). Hence, despite the phenyl lines being obliterated by the solvent, we confidently concluded that F2.3 is indeed the other predicted *trans*-3 isomer with C_2 symmetry. HPLC fraction F3.2.1, the sole *trans*-3 C_1 isomer,

is unambiguously assigned to the isomer (C_1) 34,35-bis[60]PCBM. By similar arguments to those given for the two *trans*-2 C_2 isomers above, the widely separated HPLC C_2 fractions (F2.3 and F3.3.1) may be assigned to (C_2) 34,35-bis[60]PCBM and (C_2) 36,37-bis[60]PCBM, respectively. The chemical shifts of the three *trans*-2 isomers together with HPLC fraction assignments are as follows:

Fraction F2.3: (C_2) 34,35-bis[60]PCBM

172.47	149.63	148.98	148.95	148.34	147.18	146.71
146.25	146.25	146.24	146.23	145.48	145.19	144.43
144.21	144.08	143.87	143.19	143.14	143.10	142.45
141.74	141.51	141.47	141.07	140.42	137.51	137.30
137.01	No Ph.	No Ph.	No Ph.	No Ph.	No Ph.	No Ph.
79.93	79.43	51.06	50.97	33.55	33.44	22.41

Fraction F3.2.1: (C_2) 34,35-bis[60]PCBM

171.87	171.77	150.04	147.73	149.42	149.26	149.05
148.87	148.57	148.25	149.18	148.17	147.41	147.18
147.05	146.93	146.81	146.79	146.70	146.54	146.48
146.53	146.36	146.37	145.79	145.68	145.24	145.08
144.90	144.58	144.55	144.51	144.48	144.47	144.45
144.33	144.16	144.04	143.70	143.67	143.66	143.63
143.55	143.39	143.02	142.89	142.26	142.09	142.03
141.79	141.70	141.40	141.12	141.06	140.67	138.40
138.25	137.92	137.50	137.29	137.09	132.27	132.27
132.17	132.17	128.72	128.72	128.60	128.60	128.44
80.13	80.10	79.56	79.52	51.28	51.27	51.21
51.18	34.18	33.94	33.92	33.83	22.87	22.80

Fraction F3.3.1: (C_2) 36,37-bis[60]PCBM

171.73	150.10	149.40	148.80	148.12	148.05	147.02
146.62	146.56	146.41	146.34	145.77	145.67	145.01
144.74	144.46	144.39	136.63	134.63	143.37	143.12
142.06	142.06	141.31	141.27	140.79	138.57	137.91
137.10	132.29	132.29	130.77	128.74	128.74	128.47
80.11	79.48	51.19	51.19	34.17	33.83	22.80

Figure 8 shows stick diagrams of the isomers corresponding to HPLC fraction (a) F2.3, (C_2) 34,35-bis[60]PCBM; (b) fraction F3.2.1, (C_1) 34,35-bis[60]PCBM; and (c) fraction F3.3.1, (C_2) 36,37-bis[60]PCBM.

Figure 8. Representations of the molecular structures of (a) (C_2) 34,35-bis[60]PCBM, (b) (C_1) 34,35-bis[60]PCBM and (c) (C_2) 36,37-bis[60]PCBM which correspond to the 6th, 9th and 11th HPLC fractions (F2.3, F3.2.1 and F3.3.1) to elute from a silica column.

Trans-4 isomers: The *trans*-4 isomers, which comprise HPLC fractions F2.2, F3.2.2 and F4 are shown in Figure 9. These are predicted here to comprise two C_s isomers (with NMR line pattern 4×1 and 40×2) and one C_1 isomer with pattern 84×1 , which Figure 9 shows to be correct.

Figure 9. The ^{13}C NMR spectra, (a) sp^3 carbons and (b) sp^2 carbons, of the three *trans-4* isomers which correspond to HPLC fractions (i) F2.2, (ii) F3.2.2 and (iii) F4; and are identified as being the isomers $(C_s)32,33\text{-bis}[60]\text{PCBM}$, $(C_1)32,33\text{-bis}[60]\text{PCBM}$, and $(C_s)38,39\text{-bis}[60]\text{PCBM}$, respectively.

They also show that the *trans-4* isomers elute in the order $C_s - C_1 - C_s$ from the silica HPLC column. HPLC fraction F3.2.2, being the sole *trans-4* C_1 isomer, is assigned to the isomer $(C_1)32,33\text{-bis}[60]\text{PCBM}$. As with the previous bond-types, the two same-symmetry isomers are widely spaced in the HPLC profile - as fractions F2.2 and F4, which means that 7 other isomers elute between the two symmetric *trans-4* isomers. As the two addends are further apart in $(C_s)32,33\text{-bis}[60]\text{PCBM}$, this isomer is assigned to F2.2; and thereby, $(C_s)38,39\text{-bis}[60]\text{PCBM}$ with its shorter addend separation is assigned to F4.

Stick diagrams of the three *trans-4* isomers, which correspond to HPLC fractions (a) F3.2, $(C_s)32,33\text{-bis}[60]\text{PCBM}$, (b) F3.2.2, $(C_1)32,33\text{-bis}[60]\text{PCBM}$ and (c) F5.1, $(C_1)30,31\text{-bis}[60]\text{PCBM}$ are shown in Figure 10, and their respective chemical shifts, are as follows (for the C_s isomers, resonances in bold-face result from single carbons within the molecule, whereas, all other resonances result from 2 symmetrically equivalent carbons atoms):

HPLC Fraction F2.2: $(C_s)32,33\text{-bis}[60]\text{PCBM}$

171.64	148.26	147.67	147.31	147.24	146.87	145.92
145.91	145.73	145.61	145.46	145.43	145.34	145.31
145.17	144.65	144.39	144.28	143.41	143.11	143.11
142.49	142.41	142.13	141.98	141.43	141.33	139.32
138.36	137.89	137.56	137.23	134.41	131.97	131.97
128.59	128.52	78.89	78.51	51.31	49.52	34.05
33.92	22.81					

HPLC Fraction F3.2.2: $(C_1)32,33\text{-bis}[60]\text{PCBM}$

171.81	171.66	149.60	148.21	147.62	147.42	147.38
147.27	146.86	146.42	146.22	145.97	145.97	145.85
145.84	145.77	145.70	145.63	145.60	145.60	145.51
154.51	145.48	145.44	145.43	145.29	145.19	145.06
144.32	144.29	143.97	143.57	143.39	143.17	143.17
142.98	142.86	142.55	142.52	142.45	142.33	142.22
142.21	142.19	141.73	141.54	141.51	141.11	139.84
139.48	138.31	137.93	137.79	137.54	137.44	137.44
137.26	135.04	134.72	132.15	132.15	132.12	132.12
130.77	128.74	128.74	128.60	128.60	128.41	128.32
79.02	78.97	78.63	78.44	51.28	15.14	49.64
49.56	34.21	34.09	33.91	33.84	22.83	22.73

HPLC Fraction F4: $(C_s)38,39\text{-bis}[60]\text{PCBM}$

171.87	148.53	148.13	147.33	146.56	146.33	146.17
146.10	145.96	145.83	145.64	145.55	145.51	145.45
145.34	145.05	144.45	143.99	134.54	143.05	142.95
142.46	142.46	142.27	141.82	141.26	139.99	137.87
137.64	137.42	137.31	135.32	132.19	132.19	127.77
128.77	128.44	79.08	78.57	51.22	49.67	34.29
33.84	22.76

Figure 10. Representations of the molecular structures of the *trans-4* isomers: (a) $(C_s)32,33\text{-bis}[60]\text{PCBM}$, (b) $(C_1)32,33\text{-bis}[60]\text{PCBM}$ and (c) $(C_s)38,39\text{-bis}[60]\text{PCBM}$, which respectively are 5th, 9th and 13th HPLC fractions (F2.2, F3.2.2 and F4) to elute from a silica column.

Equatorial isomers: The two *equatorial* isomers are (*syn*)16,17-bis[60]PCBM and (*anti*)16,17-bis[60]PCBM, where *syn* and *anti* refers to the orientations of the phenyl group of the addend bridging fullerene carbons 16 and 17 to the other addend. That is, (*syn*)16,17-bisPCBM has the phenyl group on the 16,17,62 ring oriented towards the PCBM group on the 1,9,61 ring, and the butyric acid methyl ester group oriented away from the other addend; and conversely (*anti*)16,17-bis[60]PCBM has the phenyl group on the 16,17,62 ring oriented away the other PCBM group. These two isomers are each predicted to be either F3.3.2 or F5.1.⁴ The ^{13}C NMR spectra of these isomers are shown in Figure 11.

In this case both isomers are found to have C_1 symmetry, as the ^{13}C NMR spectra of these HPLC fractions each consists of 84 equal-intensity lines. As with other groups with two members of the same symmetry, these two C_1 isomers cannot be distinguished based on the ^{13}C NMR spectra alone. However, based on the separation of the two addends, we assign F3.3.2 to the isomer with the greater separation - (*syn*)16,17-bis[60]PCBM and thereby assign F5.1 to (*anti*)16,17-bis[60]PCBM.

Figure 11. The ^{13}C NMR spectra, (a) sp^3 carbons and (b) sp^2 carbons, of the two equatorial isomers, which correspond to HPLC fractions (i) F3.3.2 and (ii) F5.1. These isomers are identified as being the isomers $(C_1)30,31\text{-bis}[60]\text{PCBM}$, $(C_1)21,40\text{-bis}[60]\text{PCBM}$, respectively.

These names represent a departure from our nomenclature system. This is because the isomers should be named by as the isomer with the lowest initial number. Unfortunately, in this case both isomers would be variants of 16,17-bis[60]PCBM that are distinguished by the relative orientation of the two addends rather than symmetry or bridgehead carbons; which introduces an additional complication into the naming system just for these two isomers. However, this complication may be lifted without introducing any ambiguity by naming them after their respective symmetrical equivalents (as per Table 1), which are distinguishable by their relative bridgehead carbon numbers, and which is consistent with the names of all the other isomers. Hence, we rename (*syn*)16,17-bis[60]PCBM and (*anti*)16,17-bis[60]PCBM as their respective symmetric equivalents $(C_1)30,31\text{-bis}[60]\text{PCBM}$ and $(C_1)21,40\text{-bis}[60]\text{PCBM}$.

Stick diagrams of the equatorial isomers corresponding to HPLC fraction (a) F3.3.2, $(C_1)21,40\text{-bis}[60]\text{PCBM}$ and (b) fraction F5.1, $(C_1)30,31\text{-bis}[60]\text{PCBM}$ are shown in Figure 12, and their respective chemical shifts, are as follows:

HPLC Fraction F3.3.2: $(C_1)30,31\text{-bis}[60]\text{PCBM}$

171.67	171.59	151.94	150.05	148.04	147.99	147.44
147.15	146.92	146.85	146.67	146.66	146.64	146.63
146.60	146.27	146.18	146.12	145.92	145.74	147.73
145.56	145.48	144.91	144.88	144.88	144.85	144.79
144.76	144.75	144.58	144.54	144.53	144.48	144.37
144.33	144.14	144.14	143.99	143.73	143.48	143.29
143.18	143.18	142.52	142.12	142.12	142.01	141.98
141.78	141.37	140.93	140.92	140.18	139.11	138.91
138.17	138.13	137.35	136.64	132.15	132.15	131.78
131.78	128.78	128.78	128.68	128.55	128.51	128.51

80.72	80.67	80.45	79.05	53.69	51.28	51.19
50.97	34.59	33.84	33.84	33.45	22.72	22.68

HPLC Fraction F5.1: $(C_1)21,40\text{-bis}[60]\text{PCBM}$

171.56	171.81	150.90	150.05	147.63	147.58	147.39
147.34	147.16	147.12	146.97	147.84	147.64	146.39
146.33	146.33	146.26	146.17	146.08	145.65	145.61
145.53	145.23	145.12	145.12	144.95	144.92	144.90
144.88	144.83	144.81	144.63	144.60	144.54	144.32
144.48	144.24	144.24	144.09	143.95	143.7	143.54
143.43	143.32	142.28	142.18	142.07	141.91	141.81
141.64	141.43	141.25	141.11	140.66	139.42	139.21
137.88	137.84	137.46	136.89	133.22	132.25	132.25
131.99	131.99	130.76	128.57	128.57	128.38	128.34
80.93	80.86	80.58	79.47	53.99	51.19	51.19
51.05	34.43	33.85	33.78	33.56	22.89	22.78

Figure 12. Representations of the molecular structures of the two equatorial isomer: (a) $(C_1)30,31\text{-bis}[60]\text{PCBM}$ and (b) $(C_1)21,40\text{-bis}[60]\text{PCBM}$, which correspond to the 11th and 14th HPLC fractions (F3.3.2 and F5.1) to elute from a silica column.

Cis-3 isomers: The three *cis*-3 are predicted to comprise two C_2 isomers and one C_1 isomer and to correspond to HPLC fractions F3.4, F5.2.1 and F5.2.2. As with all other groups, the ^{13}C NMR spectra of these fractions, shown in Figure 13, are consistent with these predictions.

The spectra of F3.4 and F5.2.1 both give 42 double-intensity lines (indicating C_2 symmetry) and that of F5.2.2 gives 84 single intensity lines. The elution order represents a deviation from the symmetric – asymmetric – symmetric order of the other isomers; being $C_2 - C_2 - C_1$ in this case. However, this is a very minor deviation; which is because these two isomers, F5.2.1 and F5.2.2, are two adjacent sub-sub-fractions of F5). As such, the C_1 *cis*-3 isomer and the 2nd C_2 *cis*-3 isomer essentially have identical HPLC retention times the silica column.

Based on the considerations above used to assign the other isomers, HPLC fractions F3.4, F5.2.1 and F5.2.2 are respectively assigned to the isomers $(C_2)13,14\text{-bis}[60]\text{PCBM}$, $(C_2)19,20\text{-bis}[60]\text{PCBM}$ and $(C_1)13,14\text{-bis}[60]\text{PCBM}$. Stick diagrams of the three *cis*-3 isomers, which corresponding to HPLC fractions (a) F3.4 $(C_2)13,14\text{-bis}[60]\text{PCBM}$, (b) F3.2.2 $(C_2)19,20\text{-bis}[60]\text{PCBM}$ and (c) F5.1, $(C_1)13,14\text{-bis}[60]\text{PCBM}$ are shown in Figure 14, and their respective chemical shifts, are as follows:

HPLC Fraction F3.4: (*C*₂)13,14-bis[60]PCBM

171.62	147.09	146.81	146.49	145.74	145.65	145.53
145.39	145.38	145.31	145.07	144.92	144.79	144.61
144.57	144.46	144.01	143.79	143.48	142.95	142.94
142.83	142.26	141.51	140.99	149.59	137.81	137.21
136.99	136.85	131.66	131.66	128.56	128.56	128.35
80.32	77.00	51.16	47.29	33.84	33.60	22.50

HPLC Fraction F5.2.1: (*C*₂)19,20-bis[60]PCBM

171.97	146.62	146.44	146.29	145.92	145.65	145.47
145.26	145.21	145.05	144.95	144.86	144.79	144.77
144.69	144.62	143.78	142.89	142.65	141.89	141.20
141.15	141.04	137.83	137.61	137.46	137.08	137.03
133.28	132.29	131.47	130.77	128.71	128.36	128.35
80.30	76.71	51.17	47.89	33.91	33.59	22.50

HPLC Fraction F5.2.2: (*C*₁)13,14-bis[60]PCBM

171.79	171.76	147.39	146.72	146.69	146.51	146.24
146.07	145.86	145.78	145.62	145.59	145.55	145.38
145.36	145.30	145.29	145.27	145.26	145.19	145.11
145.11	144.92	144.91	144.88	144.87	144.74	144.68
144.67	144.63	144.61	144.59	144.37	143.88	143.78
143.77	143.54	143.51	142.96	142.84	142.79	142.71
142.42	141.62	141.43	141.39	141.21	140.87	140.82
140.74	137.89	137.42	137.39	137.39	137.23	137.18
136.88	136.86	132.39	132.17	132.17	132.17	132.17
131.81	128.63	128.59	128.48	138.48	128.48	138.48
80.29	80.02	77.14	75.57	51.24	51.24	47.65
47.53	34.27	33.87	33.53	33.36	22.69	21.93

Figure 13. The ¹³C NMR spectra, (a) *sp*³ carbons and (b) *sp*² carbons of the *cis*-3 isomers, which correspond to HPLC fractions (i) F3.4, (ii) F5.2.1 and (ii) F 5.2.2, and are identified as being the isomers (*C*₂)13,14-bis[60]PCBM, (*C*₂)19,20-bis[60]PCBM, and (*C*₁)13,14-bis[60]PCBM, respectively.

Figure 14. Representations of the molecular structures of the two equatorial isomer: (a) (*C*₂)13,14-bis[60]PCBM, (b) (*C*₂)19,20-bis[60]PCBM and (c) (*C*₁)13,14-bis[60]PCBM, which correspond to the 12th, 15th and 16th HPLC fractions (F3.4, F5.2.1 and F5.2.2) to elute from a silica column.

***Cis*-2 isomers:** The final three isomers to elute from the silica column, F5.3, F6 and F7, are the three *cis*-2 isomers. Their ¹³C NMR spectra, Figure 15, show that these isomers respectively have *C*_s, *C*₁ and *C*_s symmetry (as indicated by their 40 × 2 + 4 × 1 and 84 × 1 line-patterns, as appropriate). Fraction F6, the sole *cis*-2 *C*₁ isomer is assigned to (*C*₁)3,15-bis[60]PCBM. With the two *C*_s isomers, F5.3 and F7, being widely spaced in the HPLC profile, they are respectively assigned to (*C*_s)4,18-bis[60]PCBM and (*C*_s)3,15-bis[60]PCBM (on the established basis that the 4,18 *cis*-2 bond yields an isomer with larger addend separation than does the 3,15 *cis*-2 bond).

Figure 15. The ¹³C NMR spectra, (a) *sp*³ carbons and (b) *sp*² carbons, of the three *cis*-2 isomers, which correspond to HPLC fractions (i) F5.3, (ii) F6 and (ii) F 7, and are identified as being the isomers (*C*_s)3,15-bis[60]PCBM, (*C*₁)3,15-bis[60]PCBM, and (*C*_s)4,18-bis[60]PCBM, respectively.

Stick diagrams of the three *cis*-2 isomers, which corresponding to HPLC fractions (a) F5.3 (C_s)3,15-bis[60]PCBM, (b) F6 (C_1)3,15-bis[60]PCBM and (c) F7 (C_s)4,18-bis[60]PCBM are shown in Figure 16, and their respective chemical shifts, are as follows:

HPLC Fraction F5.3: (C_s)3,15-bis[60]PCBM

172.10 150.92 149.68 **147.69** 147.64 146.93 146.36
146.15 146.05 145.63 145.52 145.45 145.44 144.79
144.80 144.58 144.54 144.44 **143.99** 143.86 143.64
143.58 143.03 151.52 141.43 139.84 137.61 136.41
135.72 135.34 133.77 132.32 132.32 **130.38** 128.69
128.69 128.38 78.14 75.50 51.23 49.65 33.72
33.61 22.94

HPLC Fraction F6: (C_1)3,15-bis[60]PCBM

171.85 171.67 151.83 150.57 150.04 148.91 147.78
147.73 146.61 147.60 146.87 146.36 146.26 146.13
146.08 146.07 146.07 146.06 145.76 145.73 145.55
145.53 145.49 145.49 145.44 145.34 144.97 144.68
144.62 144.55 144.55 144.48 144.47 144.28 144.01
143.98 143.87 143.95 143.94 143.85 143.81 143.80
143.64 142.87 142.82 141.79 141.57 141.53 141.31
139.70 139.15 136.66 136.15 136.09 135.76 135.76
135.68 133.27 133.26 132.31 132.31 131.76 131.76
130.78 128.66 128.66 128.60 128.60 128.45 128.31
78.35 78.23 75.40 74.73 51.28 51.25 49.51
49.14 34.09 33.61 33.42 32.67 23.11 22.55

HPLC Fraction F7: (C_s)4,18-bis[60]PCBM

171.67 151.86 149.37 **147.78** 147.71 **147.55** 146.30
146.15 146.11 145.91 145.57 145.54 145.51 145.37
145.35 144.66 144.48 144.13 144.08 144.04 144.01
143.98 143.57 142.75 141.91 141.39 139.33 136.33
136.00 135.98 132.73 131.51 131.51 **130.77** 129.59
128.44 128.44 78.67 74.65 51.22 49.02 33.7
32.90 22.53

Figure 16. Representations of the molecular structures of the two equatorial isomer: (a) (C_s)3,15-bis[60]PCBM, (b) (C_1)3,15-bis[60]PCBM and (c) (C_s)4,18-bis[60]PCBM, which correspond to the 17th, 18th and 19th HPLC fractions (F5.3, F6 and F7) to elute from a silica column.

The above discussions on the ^{13}C NMR of all 19 isomers are summarized in Table 2, which lists the HPLC fractions of the purified isomers presented in order of increasing retention time. These fractions are aligned with their bond-types, measured ^{13}C NMR patterns, and structure assignments based on the above arguments.

Table 2. Complete isomer assignments to HPLC fractions⁴ based on a combination of (a) isomer-type (from UV-Vis spectra),⁴ (b) ^{13}C NMR line patterns and (c) HPLC retention time.

HPLC Fraction	Bond Type	^{13}C NMR Pattern	Isomer assignment
F1.1	<i>trans</i> -1	10×2 + 14×4	(C_{2h})52,60-bis[60]PCBM
F1.2	<i>trans</i> -2	42×2	(C_2)49,59-bis[60]PCBM
F2.1.1	<i>trans</i> -1	12×2 + 15×4	(C_{2v})52,60-bis[60]PCBM
F2.1.2	<i>trans</i> -2	84×4	(C_i)49,59-bis[60]PCBM
F2.2	<i>trans</i> -4	4×1 + 40×2	(C_s)32,33-bis[60]PCBM
F2.3	<i>trans</i> -3	42×2	(C_2)34,35-bis[60]PCBM
F3.1	<i>trans</i> -2	42×2	(C_2)53,54-bis[60]PCBM
F3.2.1	<i>trans</i> -3	84×1	(C_1)34,35-bis[60]PCBM
F3.2.2	<i>trans</i> -4	84×1	(C_1)32,33-bis[60]PCBM
F3.3.1	<i>trans</i> -3	42×2	(C_2)36,37-bis[60]PCBM
F3.3.2	<i>equatorial</i>	84×1	(C_1)30,31-bis[60]PCBM
F3.4	<i>cis</i> -3	42×2	(C_2)13,14-bis[60]PCBM
F4	<i>trans</i> -4	4×1 + 40×2	(C_s)38,39-bis[60]PCBM
F5.1	<i>equatorial</i>	84×1	(C_1)21,40-bis[60]PCBM
F5.2.1	<i>cis</i> -3	42×2	(C_2)19,20-bis[60]PCBM
F5.2.2	<i>cis</i> -3	84×1	(C_1)13,14-bis[60]PCBM
F5.3	<i>cis</i> -2	4×1 + 40×2	(C_s)3,15-bis[60]PCBM
F6	<i>cis</i> -2	84×1	(C_1)3,15-bis[60]PCBM
F7	<i>cis</i> -2	4×1 + 40×2	(C_s)4,18-bis[60]PCBM

4 CONCLUSIONS

The molecular structures of all 19 purified isomers of the OPV acceptor material bis[60]PCBM have been determined by a combination of UV-Vis absorption spectroscopy, ^{13}C NMR spectroscopy and HPLC retention time analysis. The results show that all 19 isomers are dicyclopropa-fullerenes (and conversely that none are homo-fullerenes involving single bonds, double bonds or a combination of both). With these findings, each purified HPLC fraction was associated with a specific structural isomer. This information is crucial to those who fabricate photovoltaic devices using purified bis[60]PCBM isomers. This is because they can now know which specific structural isomer (rather than merely which HPLC fraction) is being employed in their devices. With this information, photovoltaic devices based purified bis[60]PCBM isomers may now be associated with a specific structural isomer (as opposed to merely the HPLC fraction label), and thereby a deeper understanding of the energetic and morphological order/disorder within the acceptor phase of bulk heterojunction OPVs and the electron extraction layer of perovskite solar cells may be further developed.

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Author Contributions

The manuscript was written through contributions of all authors. TL synthesized the isomer mixture, purified it, performed NMR data acquisition and carried out the data analyses. IA facilitated access to the NMR spectrometer and aided

TL and TJSD in the data analysis. TJSD and IA co-supervised TL, and TL and TJSD wrote the paper. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

[60]PCBM, phenyl C_{61} butyric acid methyl ester; bis-[60]PCBM, bis-phenyl C_{62} butyric acid methyl ester; NMR, nuclear magnetic resonance; UV-Vis, ultraviolet-visible; HPLC, high performance liquid chromatography.

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