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The Use of Tethered Addends to Decrease the Number of Isomers of Bisadduct Analogues of PCBM**

Ricardo K. M. Bouwer[b] and Jan C. Hummelen*[a]

This communication describes the reduction of the possible isomers that are formed upon double cyclopropanation of C_{60} by the use of a bidentate tosylhydrozone in which the reactive groups are linked by an ethylene glycol tether. One of the most widely used electron acceptors in bulk heterojunction organic photovoltaic devices (OPVs) is phenyl-C_{61}-butyric acid methyl ester (PCBM), which dramatically increased the efficiency of early OPVs by enabling the fullerene component to be co-soluble with the (typically polymeric) donor molecule.[1] Since the discovery of PCBM, power conversion efficiencies of more than 5% have been reached in OPVs that use blends of poly(3-hexylthiophene) (P3HT) and PCBM.[2] Recently, significantly higher efficiencies were reached with other polymers.[3] This has been accomplished in part by improving the bulk-heterojunction morphology of the composite films these blends form, but there are two other important factors: 1) the band gap of the polymer, which is important for efficient light absorption[4] and 2) the open circuit voltage (Voc) that the OPV produces. The most direct way to influence the Voc of donor–acceptor-based OPV devices is to alter the offset between the HOMO of the donor and the LUMO of the acceptor. The attachment of electron-donating groups or the saturation of multiple double bonds on the fullerene cage raises the LUMO energy of the resulting fullerene moiety, thereby increasing

Voc without negatively impacting the band gap of the donor (and hence the ability of the OPV device to absorb light).[5]

Previous work from our group has shown that introducing electron-donating groups on the phenyl ring of PCBM yields a small increase in the Voc of OPVs with P3HT as the donor.[6] Recently, higher adducts of PCBM were used to further increase the Voc of P3HT-based OPVs by approximately 100 meV per saturated double bond (i.e., adduct).[7] The drawback to this approach is the concomitant increase in the formation of regioisomers when compared with the synthesis of mono-adducts such as PCBM. Even bis-adducts with two identical, symmetric addends (the functional group that forms a bond to the fullerene cage) can be formed as eight different regioisomers.[8]

Figure 1 C shows these possible regioisomer positions; bonds that are highlighted in bold indicate the two attachment points of the addends. Bis-PCBM (PCBM that has a second identical addend added to the fullerene cage), however, has non-symmetric addends, raising the number of possible stereo- and regio-isomers to 22, of which 15 are discernable in an HPLC chromatogram obtained by using a silica gel column (Figure 1 A). The presence of multiple isomers of bis-PCBM decreases electron mobility in OPVs by reducing the π–π interactions between fullerene cages.[9] Different isomers can also have different reduction potentials[10] and isomers with less-negative reduction potentials than the average will act as (shallow) electron traps.[11] Moreover, the overall morphology of OPVs is negatively impacted by the presence of a mixture of isomers.[9]

Herein, we report our efforts to reduce the number of isomers of bis-PCBM that are formed by the double cyclopropanation of C_{60} by tethering the two addends with an ethylene glycol linker. The eight possible regio isomers of bis-PCBM, depicted in Figure 1 C, exist as a mixture of up to four stereoisomers (depending on the symmetry of the regioisomer); the two methyl esters can point away from each other, towards each other, or one in either direction. The *cis*-1 isomer, however, is sterically prohibited by the bulk of the addends.[8] The number of regioisomers is reduced further by tethering the addends together with a linker that is

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[**] PCBM = Phenyl-C_{61}-butyric acid methyl ester.

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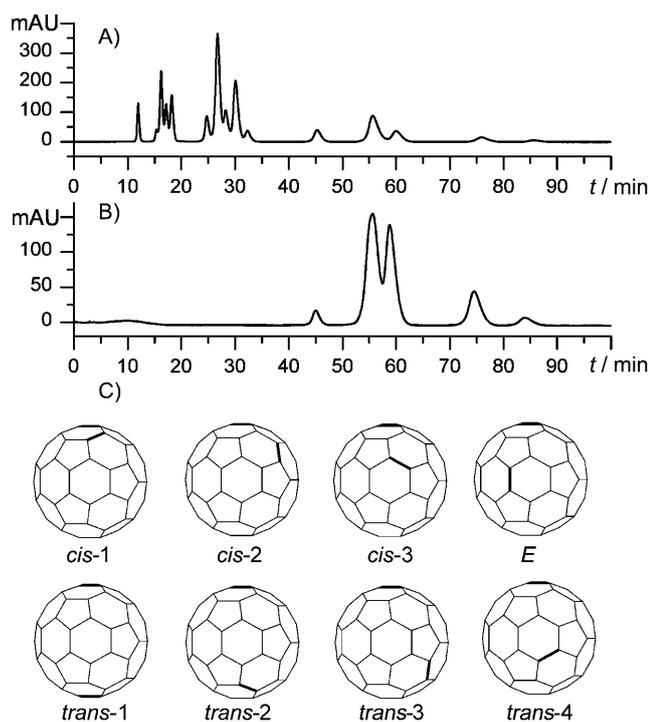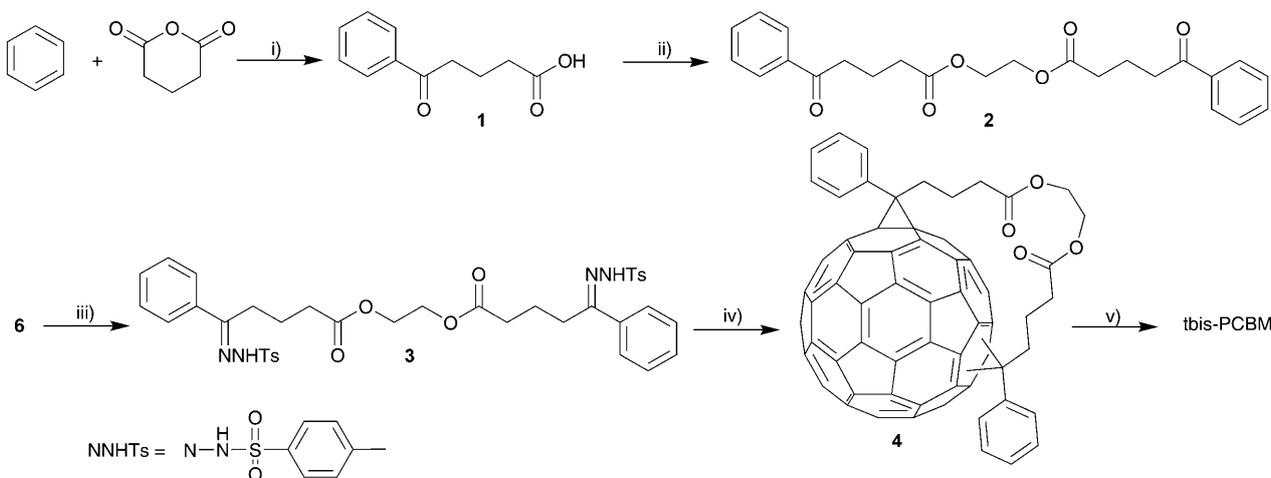
Figure 1. HPLC chromatograms of the mixtures of isomers of bis-PCBM obtained by standard bis-addition (A) and from tethered addends (B) showing that less isomers are present in the latter. C) All possible regioisomers of bis-adducts of C_{60}.

hydrazone addends together. In addition to decreasing the number of possible regioisomers that can form, our approach—which employs diazo additions[13] with asymmetric addends instead of Bingel additions with symmetric ones—reduces the number of possible stereoisomers by restricting the orientation of the ester moiety; only the regioisomers that are close together can have the ester groups pointing in opposite directions due to the short tether.

Scheme 1 shows the synthesis of the ethylene-tethered bis-(4-benzoylbutyric acid tosylhydrazone) 3 and the addition to the fullerene moiety (see the Supporting Information for more details). 4-Benzoyl butyric acid (1) was reacted in a Dean–Stark apparatus with ethylene glycol in the presence of a catalytic amount of concentrated sulfuric acid. The treatment of the resulting ester, 2, with tosylhydrazide in toluene and using a Dean–Stark apparatus afforded the bis-tosylhydrazone 3 in good yield. C_{60} and 3 were then dissolved in *ortho*-dichlorobenzene (ODCB) and heated to 110 °C. The subsequent addition of *t*BuOK induced the transformation of the tosylhydrazone moieties into highly reactive diazo groups, which reacted in situ with C_{60} to give the tethered adducts mixture 4. The crude product was purified by column chromatography (SiO_2/toluene). Compound 4 was readily transesterified to bis-PCBM by methanol in ODCB in the presence of a catalytic amount of concentrated sulfuric acid.

The yield of this tethered double cyclopropanation reaction is not as high as would be expected from the analogous standard bis-PCBM double cylopropanation reaction because of the formation of cross-linked side products and the partial hydrolysis of the tethered ester by trace amounts of hydroxide in the *t*BuOK, resulting in the insoluble acid (carboxylate) analogue of PCBM. However, since fewer isomers are formed, the overall yield of the purified isomer fraction is higher (16% compared with ≈11% without using the tether).

shorter than the distance between every possible combination of two reactive sites on the fullerene cage. Diederich and co-workers[8] used a tether-directed approach for synthesising different regioisomers and substitution patterns in Bingel additions (addition to a fullerene cage by nucleophilic attack[12]) of bis-malonates to C_{60} by tethering them with diol linkers. We applied a similar approach in which ethylene glycol was used to link two 4-benzoylbutyric acid tosyl-

Scheme 1. Synthesis of the ethylene-tethered bis-(4-benzoylbutyric acid tosylhydrazone) 3 and the addition to the fullerene moiety. i) $AlCl_3$, $ClCH_2CH_2Cl$; ii) ethylene glycol, $H^+_{(cat.)}$, toluene, Dean–Stark; iii) tosylhydrazide, toluene, Dean–Stark; iv) C_{60}, ODCB, *t*BuOK; v) MeOH, H^+, ODCB.
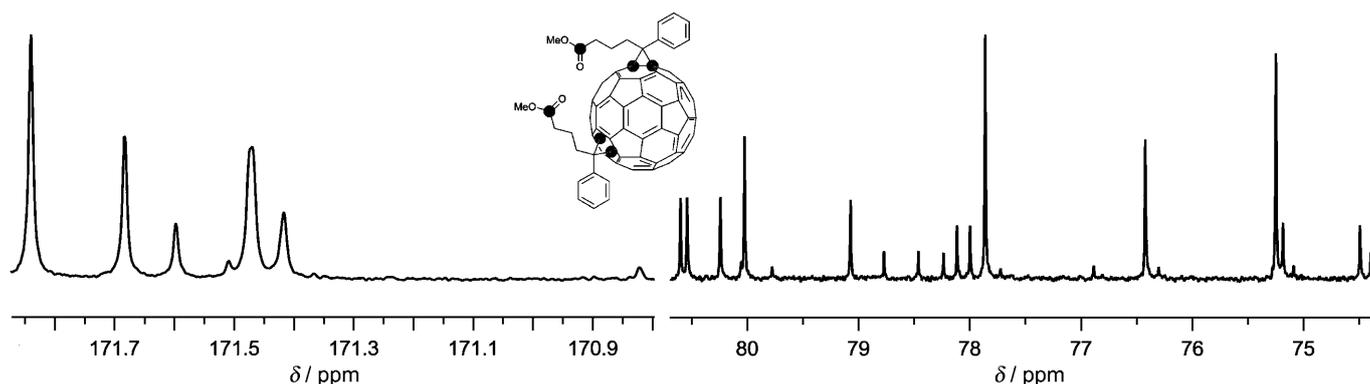
Figure 2. The ^{13}C NMR spectrum of the carbonyl (left) and bridgehead (right) area of the isomers obtained from tethered addends (a colour version of the figure is available in the Supporting Information).

Analysis of the tether-directed bis-PCBM (abbreviated tbis-PCBM) by HPLC revealed that only the isomers leading to the last five peaks of the HPLC chromatogram (Figure 1 B) of the full isomer mixture (i.e., bis-PCBM synthesised by the un-tethered method; Figure 1 A) are formed. However, due to the broadness of the peaks, we cannot state with certainty that these peaks belong to single isomers. High-resolution ^{13}C NMR spectroscopy (Figure 2) showed eight resonances in the carbonyl region at $\delta =$ 171.84, 171.68, 171.60, 171.51, 171.47 (two peaks), 171.42 and 170.82 ppm. If all of the isomers were symmetric, this would correspond to eight different isomers. However, the similar intensities of the peaks at $\delta = 170.82$ and 171.51 ppm are indicative of stemming from a single isomer, as are the peaks at $\delta = 171.42$ and 171.60 ppm. There are similar groupings of intensities in the area $\delta = 73$–81 ppm, where the bridgehead carbon atom peaks are found; two peaks for the symmetric isomers and four for the asymmetric ones.[14] From this analysis, we are tempted to conclude that there are two symmetric and three non-symmetric major isomers. There are also two minor isomers, one symmetric and one non-symmetric, as indicated by resonances for their bridgehead carbon atoms, but not their carbonyl carbon atoms, bringing the total to seven isomers—five major and two minor.

Semi-empirical molecular modelling (PM3, Hyperchem 8.0) of tbis-PCBM isomers reveals that the length of the ethylene tether limits the possible regioisomers to the cis-2, cis-3, E and trans-3 bis-adducts. Including the stereoisomers, there are seven possible isomers; one non-symmetric E isomer (with its second ester group pointing towards the first addend), three cis-2 isomers (two symmetric, both ester groups pointing in the same direction, one non-symmetric, the ester groups pointing in opposite direction), one non-symmetric cis-3 isomer (the ester groups pointing the same way), one non-symmetric trans-3 isomer (with the ester groups pointing towards each other) and one symmetric cis-3 isomer (with both ester groups pointing toward each other). This is in good agreement with the HPLC and ^{13}C NMR spectroscopy data.

In conclusion, the use of an ethylene tether reduces the number of isomers of bis-PCBM that are formed from the double cyclopropanation of C_{60} from 22 to 7 when compared with standard bis-addition. The isomers were identified as seven forms of E, cis-2, cis-3 and trans-3 regioisomers through a combination of HPLC, NMR spectroscopy and molecular modelling. Of these seven forms, five can be considered major isomers. Future efforts will focus on testing the influence of tbis-PCMB on the performance of OPVs, improving the yield of the tethered double cyclopropanation and investigating the influence of other tethers on the product isomer distribution.

Acknowledgment

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[14] Only the *trans*-1 isomer with both phenyl groups pointing in the same direction shows one resonance for the bridgehead carbon atoms due to C_s symmetry caused by the mirror plane through both addends.