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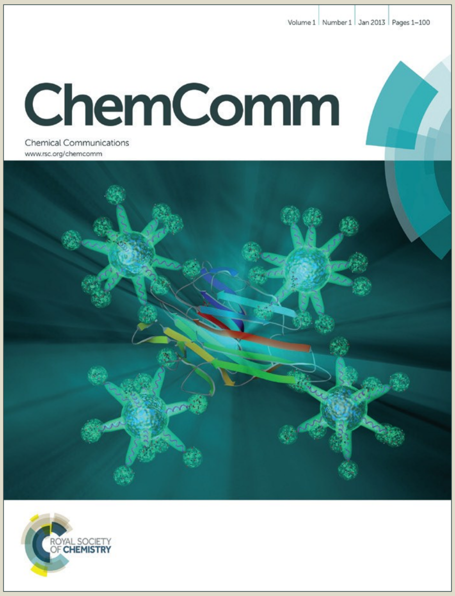

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Photochemical *Site*-selective Synthesis of [70]Methanofullerenes

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Methanofullerenes such as the well-known [70]PCBM are commonly synthesized under harsh conditions to obtain the product as a mixture of *site*-isomers (namely α, β and minor γ) due to the D_{5h} symmetry of C_{70} cage. We report the first *site*-selective synthesis of [70]methanofullerenes under light irradiation and low temperatures, thus avoiding time-consuming and highly expensive HPLC separations. Pure major *site*-isomers α-[70]PCBM and α-[70]DPM have been thus efficiently prepared including the crystal structure of 5b. Photovoltaic preliminary results revealed a slightly beneficial performance for the α-pure [70]PCBM *site*-isomer devices.

Polymer-based plastic solar cells have emerged in the last decade as a low-cost complement/alternative to the classical silicon photovoltaic devices. The main approach to improve the photo-conversion efficiency in organic solar cells is based on a Bulk Heterojunction (BHJ) architecture, in which the donor-acceptor interaction at the interface is maximized.[1] Fullerene derivatives, such as the well-known [60]PCBM ([6,6]-phenyl C_{61} butyric acid methyl ester),[2] and diphenylmethano[60]fullerene [60]DPM,[3] have been extensively used as electron acceptor materials in BHJ due to their exceptional optoelectronic properties.[4,5] Higher fullerenes such as C_{70}, display better light absorption in the visible region of the solar spectrum than [60]fullerene derivatives resulting in higher photocurrent (J_{sc}).[6] For instance, the J_{sc} value of [70]PCBM is 50% higher when compared to its [60]PCBM analog.[7,8] Other higher fullerenes, namely [84]PCBM, showed a low solubility and significantly lower conversion efficiencies.[9]

Many efforts have been made to improve the Power Conversion Efficiency (PCE) of organic photovoltaic devices (OPVs). Materials properties such as light absorption, HOMO-LUMO energy levels, nano-morphology and segregation degree, just to name a few, are strongly related with the efficiency of the device.[10] On the other hand, there are several examples of fullerene bisadducts in which some regioisomerically pure derivatives exhibited higher PCE values than those of the corresponding isomeric mixtures.[11] Thus, control on the isomeric purity of the involved photo and electroactive materials may be crucial to enhance a suitable molecular organization of the photoactive layer in the device.[12] However, there are not many examples that illustrate the correlation between morphology and device performance. One of the reasons for the shortage of these studies is the lack of straightforward and selective methods affording isomerically pure compounds.

Controlling the morphology of the devices fabricated with [70]fullerene derivatives is a challenge because only a few synthetic methods lead to isomeric pure C_{70} derivatives.[13,14] Unlike C_{60}, C_{70} cage is constituted by four non-equivalent double bonds (namely: α, β, γ and δ; Figure 1) which should, in principle, lead to four *site*-isomers that could be isolated only by tedious and time-consuming HPLC techniques.[15] Thus, most of the C_{70} based OPV devices are typically formed by an isomeric mixture of C_{70} derivatives in which usually the α and β *site*-isomers are the most abundant with tiny amounts of the γ isomer.[16]

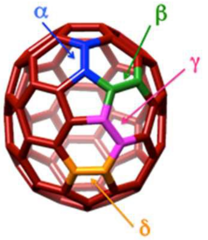

Figure 1. Drawing of pristine C_{70} indicating the four different double bonds (α, β, γ, δ).

Here, we report for the first time a new methodology to obtain methanofullerenes, ([70]PCBM and [70]DPM derivatives) with a high control of the *site*-selectivity under mild conditions. In addition, we describe for the first time the X-ray structure of a [70]DPM derivative (the α-*site*-isomer **5b**).

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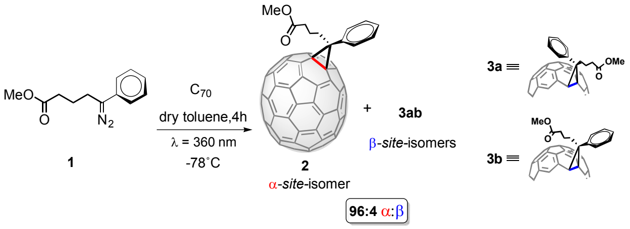
The classic procedure to obtain methanofullerenes such as [70]PCBM is based on the Bamford-Stevens reaction and has previously been reported by Hummelen *et al.*[16] This reaction involves the generation *in situ* of a diazocompound by thermolysis of tosylhydrazone with alkali salts. The subsequent addition to C_{70} leads to a mixture of two *site*-isomers (75:25, α:β).[16] Since this procedure is carried out under drastic conditions, that is, strong bases and refluxing *ortho*-dichlorobenzene (*o*-DCB), it is not considered a suitable method to reach isomeric purity. In addition, the purification of the *site*-isomers from the reaction crude is not possible by silica gel chromatography, and only by using time and solvent-consuming HPLC separation it is possible to isolate the α from the β *site*-isomer.

The lack of a selective synthetic method able to discriminate between *site*-isomers encourages us to develop a new and unprecedented methodology based on light irradiation under mild conditions, thus having a control on the *site*-selectivity.

Synthesis of Pure α–[70]PCBM. The tosylhydrazone PCBM precursor was transformed in the corresponding diazocompound derivative in order to take advantage of the milder conditions offered by fullerene photochemistry (see S. I page 2S).[12,17]

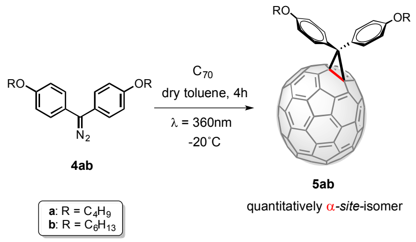
A solution of C_{70} and the alkylaryl-diazocompound **1** in dry toluene was irradiated at λ= 360 nm at -78°C for 4 hours to afford compound **2** (α-*site*-isomer) as main product together with 0a small amount of **3** (β-*site*-isomers). The monoadducts were isolated from unreacted C_{70} and bisadducts by silica gel column chromatography (Scheme 1).

Scheme 1. Selective synthesis of α–[70]PCBM by photochemical reaction.



The isomeric purity was determined by NMR and HPLC resulting in a α:β ratio of 96:4 (Figure S13). As expected, *site*-isomer **2** was obtained as an enantiomeric mixture whereas *site*-isomer **3** is formed by two different diastereo-isomers (**3a** and **3b**), depending on the orientation of the ester group on an equatorial (**3a**) or polar (**3b**) position on the fullerene cage[15] (Scheme 1).

Synthesis of Pure α–[70]DPM. To analyze the scope of this new methodology, the reaction was also carried out with diaryl-diazocompounds. These compounds are highly reactive and have been shown to behave differently to the alkylaryl-diazocompounds.[12,17] When diazocompound **4** was irradiated at 360 nm in the presence of C_{70}, the α-*site*-isomer **5** was exclusively formed (Scheme 2).



Scheme 2. Selective synthesis of α-*site*-isomer **5** by photochemical reaction.

Diphenylmethano[70]fullerenes ([70]DPMs) (**5ab)**, were also characterized by those standard techniques used for **2** and **3**. The selectivity of this reaction was determined by HPLC and NMR spectroscopy. As expected, diazocompound **5** is more reactive than the PCBM precursor alkylaryl-diazocompound **1**, and only -20°C (instead of -78°C) was low enough to reach an excellent selectivity, 100% of α-*site*-isomer (**5ab**), whereas the corresponding β-*site*-isomers (**6ab**) were not observed (Figure 2).

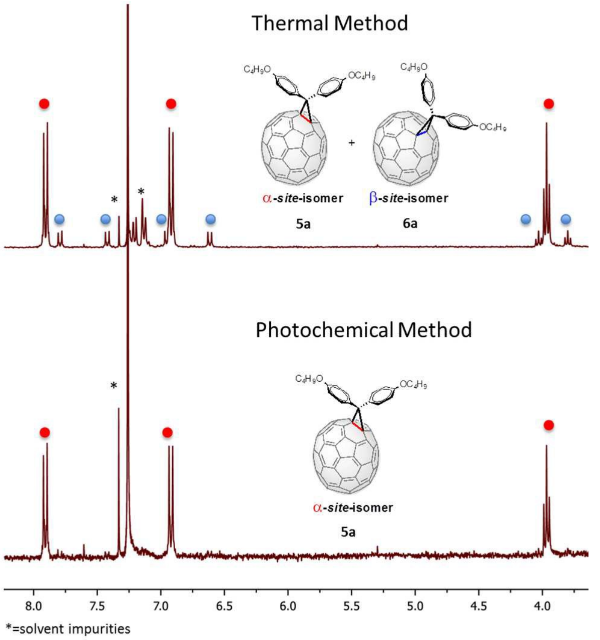


Figure 2. ^1H-NMR (300MHz, 298K, $CDCl_3$) spectra of compounds **5a** (α-*site*-isomer, red) and **6** (β-*site*-isomer, blue) obtained by the classical thermal treatment (top, ratio α:β, 75:25) and by the new photochemical method (bottom, 100% α-*site*-isomer).

In contrast to the β-*site*-isomers, the ^1H-NMR spectra of compounds **5ab** exhibit only one set of signals evidencing the plane of symmetry across the α-bond.

Cyclic Voltammetry Studies. The electrochemical properties of products **2**, **3** and **5** were studied by cyclic voltammetry using *o*-DCB/MeCN (4:1) as solvent at room temperature and

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tetrabutylammonium hexafluorophosphate as the supporting electrolyte (Figure 3).

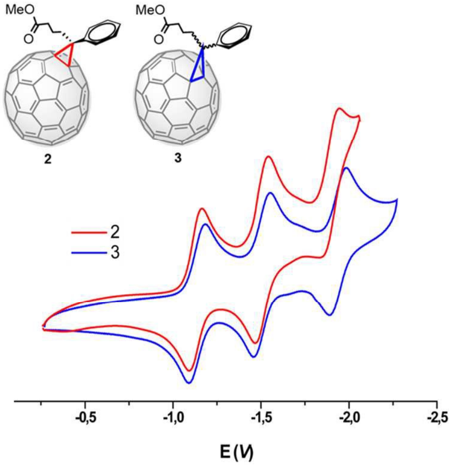

Figure 3. Cyclic voltammetry of products **2** and **3**.

As expected, the first reduction potential of all monoadducts [**2**, **3**, **5a** and **5b** ($E_1^{1/2}$ = -1.13, -1.14, -1.13 and -1.13V, respectively)] were approximately 130mV higher than that observed for pristine C_{70} ($E_1^{1/2}$ = -1.00V). Interestingly, both isomers exhibit the same first reduction potential values within the experimental error. As it is well-known, the LUMO level is directly related with the V_{oc} parameter, which is directly correlated with the cell efficiency. In table S1 the values of the reduction potential values observed for the pure compounds and their respective isomeric mixtures are shown (see S.I).

OPV Device Performance. As preliminary results, some devices were fabricated from pure α-[70]PCBM isomer which was obtained from the product mixture (α:β, 96:4) by HPLC. For comparison purposes, the commercially available isomeric mixture (Solenne, with an isomer composition of 83% α and 17% β according to HPLC measurements) was used for the device fabrication. The two sets of comparison are given in Figure 4 and Table 1. As expected, the devices fabricated from pure α-[70]DPM6 exhibited lower efficiency values than those obtained for pure α-[70]PCBM (see S.I.).

Figure 4. *J-V* graphs for pure α-[70]PCBM (red) and Solenne isomeric mixture (black).

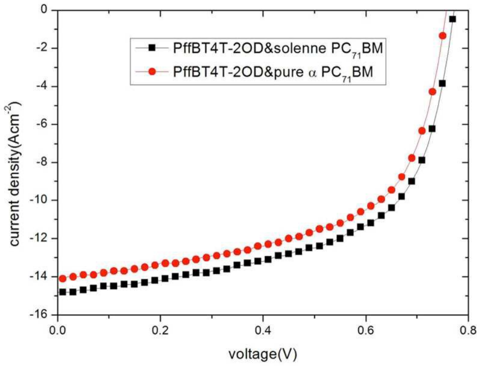

Table 1. Average PCE% reached in a polymer:fullerene BHJ solar cell using pure α-[70]PCBM isomer and a commercially available isomeric mixture. Polymer Y5: PffBT4T-2OD

Active layer	V_{oc}(V)	J_{sc}(mAcm^{-2})	FF(%)	PCE (%)	Best PCE(%)
Y5/ α[70]PCBM	0.78±0.07	14.83±0.91	0.57±0.03	6.63±0.72	7.96
Y5/ Solenne [70]PCBM	0.76±0.01	14.62±1.10	0.57±0.04	6.45±0.66	7.65

For the blend, the PffBT4T-2OD polymer was used, which is one of the most successful polymers, reaching solar energy conversion efficiencies as high as ~10% in polymer:fullerene bulk heterojunction solar cells.[18] In this study, the devices were fabricated from PffBT4T-2OD with two different [70]PCBM fullerene samples. The first one was the [70]PCBM mixture from a commercial source (Solenne) and the second one was pure α-[70]PCBM *site*-isomer from this study. The average efficiency was calculated from three batches of devices from three days. Comparing the pure α-*site*-isomer with the mixture of *site*-isomers, no significant difference in the photovoltaic parameters was observed. Thus, the studied systems showed a remarkable V_{oc} as well as J_{sc} values, with PCEs of 6.45 % for the commercial sample (Solenne) and 6.63 % for the pure α-[70]PCBM *site*-isomer. Although more studies mostly involving aspects of the materials used such as morphology, crystallinity, isomeric ratio in the blend and the polymer/fullerene ratio, as well as other fabrication device conditions are needed, the only conclusion at this stage is that based on the above experimental evidences, the use of pure α-*site*-isomer produces a slight but persistent benefit on the device performance. These experimental findings are also supported by the integrated current for the EQE for PffBT4T-2OD/α-[70]PCBM when compared with that of Solenne mixture (14.72 vs 14.03, see S.I.).

X-Ray Crystallographic Characterization. α pure monoadduct **5b** was unambiguously characterized by single crystal X-ray diffraction. The structure was solved in the monoclinic $P2_1/c$ and the asymmetric unit contains a formula unit ($C_{95}H_{34}O_2$) as depicted in Figure 5a and S18. The C_{70} moiety displays a high degree of disorder, as is usual in this type of compounds, and there is also some disorder in the terminal carbon atoms from the two alkyl chains. Details of the data collection and refinement can be found in the Supplementary Information. There is a supramolecular C-H•••O interaction between neighbour molecules in the [001] direction that yields 1D chains (Figure 5b). On the other hand, a π-π interaction is also present between the bottom C_6 rings (defined by atoms C53F, C54F, C55F, C56F, C67F and C68F) in the C_{70} fullerene. These rings are completely parallel and located at a distance of 3.199 Å, with their centroids displaced from each other and separated 3.807 Å. Each pair of molecules displaying this interaction are related by an inversion centre from the ones

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located in the middle of the *b* and *c* cell vectors (see Figure S20).

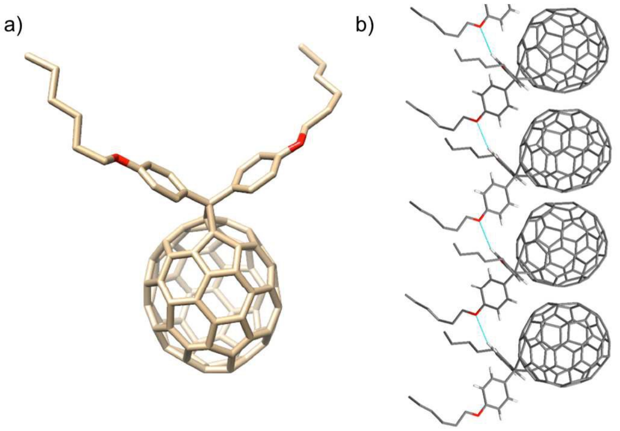

Figure 5. a) Molecular plot of compound **5b** b) Detail of the hydrogen bonds in the solid state structure of **5b**. These supramolecular interactions yield chains in the [001] direction.

Conclusions

We have successfully prepared, isolated, and characterized [70]fullerene derivatives with a remarkable high isomeric purity in two different systems, namely α-[70]PCBM and α-[70]DPM (including the X-ray structure of the α- derivative, compound **5b**). This new synthetic methodology to achieve selectively α-*site*-isomers is carried out under mild conditions using photoactivation. This unprecedented approach avoids time- and solvent-consuming HPLC separations that are usually employed to obtain these products. As it should be expected, the isomerically pure system may affect the morphology and, therefore, the performance of the devices. According to our preliminary results, pure α-[70]PCBM and its isomeric mixture obtained from commercial sources (Solenne) were tested in BHJs solar cells showing a slightly beneficial influence in the final device efficiency.

Acknowledgments

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‡ Procedures, characterization, solar cells fabrication and crystallographic data are included in the supporting information.

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