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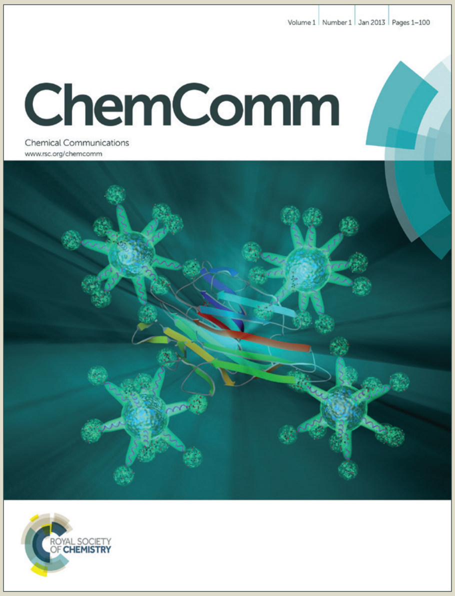

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Reaction of Diazocompounds with C_{70}: Unprecedented Synthesis and Characterization of Isomeric [5,6]-Fulleroids.

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Sara Vidal,[a] Marta Izquierdo,[a] Salvatore Filippone,[a] Fulvio G. Brunetti[a] and Nazario Martín[a,b*]

The synthesis of a variety of PCBM-type [5,6]-fulleroids and their further highly selective photoisomerization to the respective [6,6]-methanofullerenes is presented. Interestingly, the chemical reactivity of [5,6]-fulleroids reveals the same trend (*a* > *b* > *c* > *d*) to that observed for pristine C_{70} ($\alpha > \beta > \gamma > \delta$).

Since their discovery three decades ago, fullerenes have been by far the most used n-type materials in bulk heterojunction solar cells (BHSC) due to their exceptional optoelectronic properties.[1,2,3,4] Higher fullerenes such as C_{70} display improved light absorption in the visible region compared with the most abundant C_{60}, resulting in higher photocurrent values and, therefore, in higher overall power conversion efficiencies. For instance, the well-known [6,6]-$PC_{71}BM$ ([6,6]-phenyl C_{71} butyric acid methyl ester) blended with π-conjugated semiconducting polymers such as MDMO-PPV ([alkoxy-poly(*p*-phenylenevinylene)]) reaches a value of J_{sc}=7.6 mA·cm^2 which means an increase of over 50% when compared to its C_{60} analog.[5,6]

The lower symmetry of C_{70} makes the synthesis of PCBM derivatives more difficult when compared with C_{60}. [70]Fullerene has four different [6,6] reactive bonds and four different [5,6]bonds. The synthetic pathway for preparing PCBM derivatives is based on the Bamford-Stevens reaction, consisting in the thermal treatment of tosylhydrazones with metal alkali salts.[6,7] The diazocompound generated *in situ* from the tosylhydrazone, in the presence of fullerene, affords the respective cycloadducts in both isomeric forms, namely [5,6]-fulleroid and [6,6]-methanofullerenes. This reaction has been one of the most commonly used in fullerenes chemistry in the last decades due to the production of [6,6]-$PC_{71}BM$ for Organic Photovoltaic (OPV) devices. However, much less is known about the [5,6]-open-$PC_{71}BM$ fulleroid obtained in the same chemical reaction. In contrast to methanofullerenes, fulleroids are usually unstable and difficult to isolate. Although the most common method to synthesize fulleroids is the addition of diazocompounds to fullerenes, they are usually formed in low yield together with the [6,6]-methanofullerene derivative as the main product[8] or not formed at all.[9] The mechanism of cycloaddition of diazocompounds to fullerenes has been described by two routes: i) thermolysis of diazocompounds to form carbenes that cycloadd on the [6,6] bonds and form methanofullerenes, and ii) 1,3-dipolar cycloaddition of the diazocompound to fullerene to give rise to a fulleropyrazoline, followed by the extrusion of N_2 to achieve [5,6]-open fulleroids. Usually, thermal treatment or light irradiation transform the kinetically favorable product [5,6]-open fulleroid, to the thermodynamically favored product [6,6]-closed methanofullerene.[10,11]

In the addition of unsymmetrically substituted diazocompounds to the fullerene cage, two stereoisomers are possible for each addition site.

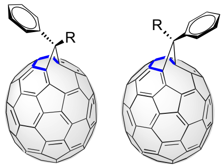

Figure 1. Two possible isomers of [5,6]-fulleroid C_{70} from alkyl-aryl-diazocompounds. Favored [5,6]-isomer contains the phenyl group over the top pentagon ring on C_{70} cage (left).

Thus, the addition of alkyl-aryl substituted diazocompounds, such as the PCBM precursor, to C_{70} preferentially forms the fulleroid isomer in which the aryl group is over the pentagon ring, thus minimizing the stereoelectronic effects (Figure 1).[12,13]

The lack of an efficient methodology to obtain [5,6]-open derivatives is responsible for the scarce studies carried out on these compounds whose properties remain almost unexplored. Here, we report the selective synthesis of three [5,6]-$PC_{71}BM$ fulleroids and three [70]diphenylmethanofullerenes as well as the study of the isomerization process they undergo from the [5,6]-open isomers of C_{70} to the respective [6,6]-closed methanofullerenes.

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[a] Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense de Madrid. Avda. Complutense s/n 28040 Madrid, Spain.
[b] IMDEA–Nanociencia, Campus de Cantoblanco, E-28049 Madrid, Spain.

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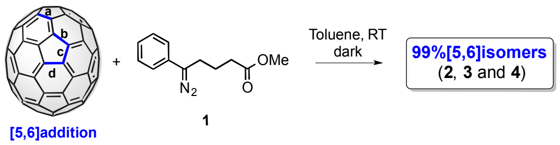
Synthesis of [5,6]-fulleroids 2-4. Diazocompound **1** was prepared from commercially available 4-benzoylbutyric acid previously reported.[6] A solution of **1** and C_{70} in toluene was stirred for 2 minutes in the dark at room temperature (Scheme 1). The reaction crude was purified by silica gel column chromatography using CS_2 as eluent to recover the unreacted C_{70}, and toluene to collect the fulleroid fraction in 86% yield (based on recovered C_{70}) with a ratio fulleroid/methanofullerene 99:1.



Scheme 1. Synthesis of [70]PCBM fulleroids **2-4**.

HPLC analysis of the crude and/or the monoadducts fraction was crucial to determine the number of fulleroid-type isomers obtained in the reaction. The HPLC chromatogram showed three peaks, (compounds **2**-**4**) with analogous UV-vis absorption to that of pristine C_{70}, thus confirming their fulleroid nature; and one small peak corresponding to a α-[6,6]-methanofullerene (compound **5**) (Figure 2a). In this regard, it is important to note that fulleroids and their respective pristine fullerenes share the same π-homo-conjugation (Figure 2b). Another small peak (1.3%) is observed in the chromatogram corresponding to a [6,6]-closed derivative (compound **5**).

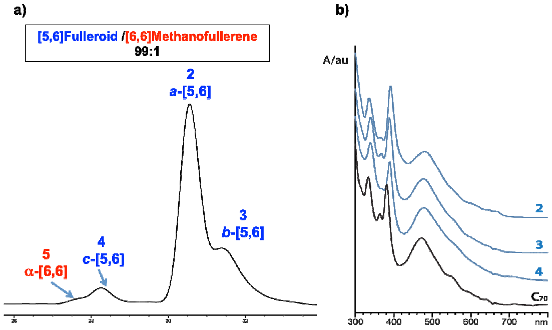
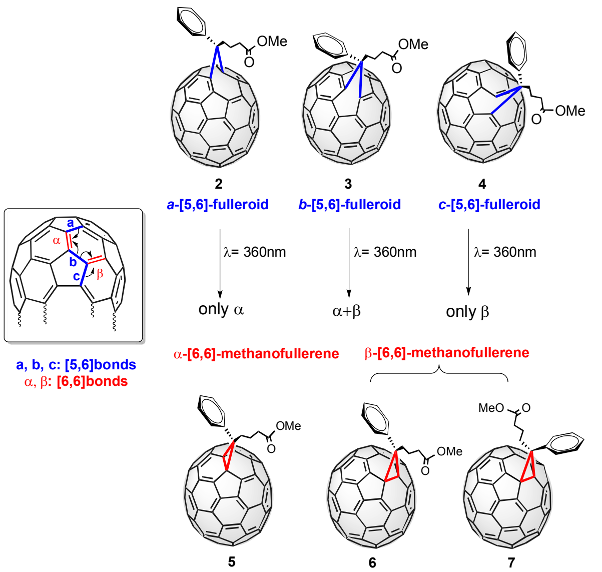


Figure 2. a) HPLC profile of the fraction of fulleroids **2**-**4** after the reaction of **1** and C_{70} in the dark. HPLC column: 5PYE (4,6 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 0.5 ml/min; 320 nm; 25^{0}C). b) UV-vis spectra of fulleroids **2-4** and C_{70} in toluene.

The assignment of each isomer to their corresponding peaks was based on the relative yield (area) showed in the chromatogram. Thus, **2** is the main product, followed by **3** and **4**. The fulleroid fraction containing products **2-4** was characterized by NMR and UV-vis spectroscopy, mass spectrometry and cyclic voltammetry. These experimental techniques confirmed that this fraction is formed unequivocally by fulleroids (pages 4S-6S and 19S, S.I.).

Unlike C_{60} in which all the [5,6] bonds are equivalent, the lower symmetry in C_{70} increases the number of possible PCBM-fulleroid isomers to eight, considering two regioisomers per addition site (*a*, *b*, *c* and *d* sites in Scheme 1).[14] Analogously to the [6,6] bonds (α, β, γ and δ) of C_{70}, the *a* bond, in the pole, is the more strained [5,6] bond with, and should be the more reactive one, followed by *b*, *c* and *d.* Considering that the formation of the isomers with the phenyl group over the hexagon is not favored, the three peaks should correspond to three isomers attached to three different [5,6] bonds, probably *a*, *b* and *c* (Scheme 1). Hence, we considered that the main product should be fulleroid-*a* **2**, followed by fulleroid-*b* **3** and the minor product fulleroid-*c* **4**. It is well-known that fulleroids isomerize to methanofullerenes ([6,6]-closed derivatives) through a di-π-methane rearrangement by the action of light or heat.[11] Thus, three different [6,6]-closed *site*-isomers should be formed after the isomerization process.

When the fulleroids fraction was irradiated at 360nm for 4h at room temperature, the isomerization from fulleroids **2-4** to the [6,6]-PC$_{71}$BM isomers (**5**, **6** and **7,** Scheme 2, Figure S26, S.I.) was quantitative. Despite the three [5,6]-isomers obtained in the reaction (*a*, *b* and *c*), only two [6,6]-*site*isomers (α and β) were observed in a ratio 93:7 (α:β). Since the addend is not symmetric, the β-*site*isomer is composed by two stereoisomers.[15] The UV-vis of compounds **5**, **6** and **7** confirmed that **5** is α-*site*isomer, and **6** and **7** are β-*site*isomers. A plausible explanation of why three [5,6] bonds are isomerized to only two [6,6] bonds can be found in the isomerization tendency of each fulleroid isomer. Fulleroid-*a* **2** can only be transformed into α-*site*isomer; Fulleroid-*b* **3** can be isomerized both to α-*site*isomer and β-*site*isomer, although probably most of the isomerization will progress towards the α-*site*isomer since it is much more reactive. Finally, fulleroid-*c* **4** is the only one able to lead the isomerization to the γ-bond. However, γ-bonds are poorly reactive. Therefore, the isomerization should occur only towards the β-*site*isomer (Scheme 2).



Scheme 2. Isomerization routes from [5,6]-bonds to α- and β-methanofullerenes.

To corroborate these assumptions, each isolated peak was individually irradiated at λ= 360nm. The result was that, in fact, fulleroid-*a* **2** is isomerized exclusively to methanofullene **5** (α-*site*isomer); fulleroid-*b* **3** is isomerized to methanofullerene **5** in 85% and to methanofullerenes **6** and **7** (β-siteisomers) in 15%; and fulleroid-*c* **4** is exclusively isomerized to the β-*site*isomers **6** and **7** (Scheme 2 and Figure 3).

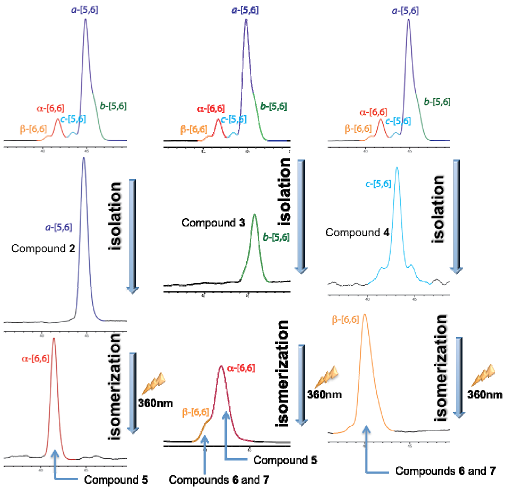
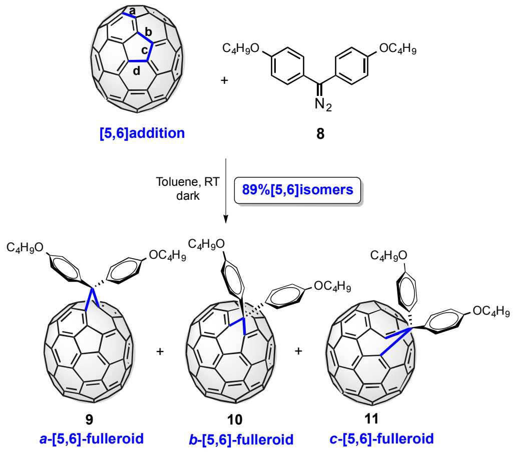


Figure 3. HPLC profiles of the products before and after the isomerization. HPLC column 5PYE semipreparative (10 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 1 ml/min; 320nm; 25^{0}C).

The mechanism and regioselectivity of the formation of [60]fulleroids has previously been explored by Oshima *et al.*[16] In this work, the tendency towards the formation of fulleroids is higher for diazoalkanes than for alkyl-aryl-diazocompounds, being diaryl-diazocompounds those with less tendency of all of them. In 2013, Echegoyen *et al.* reported the extraordinary and unusual reactivity of diazodiaryl compounds in the presence of endofullerene $Sc_3N@I_h$-C_{80}, and the influence of the substituent groups in the *para* position of the aryl group.[17] They found that an electron-donating group in that position favored the formation of the [5,6]-open derivative. To explore the tendency of diaryl-diazocompounds towards the formation of fulleroids on C_{70}, we have synthesized a diaryl-methano bridged fulleroid, namely [5,6]-DPM (**9** and **10**) with an electron-releasing substituent in the *para* position of the phenyl group (OC_4H_9).

Synthesis of [5,6]-fulleroids 9, 10 and 11. Diaryl-diazocompound **8** was prepared from the respective diarylhydrazone **8** by following the standard procedure (supporting information). A solution of 1 equivalent of **8** and C_{70} in toluene was stirred for 2 min in the dark at room temperature (Scheme 3). The reaction crude was purified by silica gel column chromatography using CS_2/hexanes as eluent to recover the unreacted C_{70}, and CS_2 to collect the fraction of monoadducts (mainly fulleroids), in 72% yield (based on recovered C_{70}). The mixture of monoadducts was characterized without any further purification due to the similar polarity and poor stability.



Scheme 3. Synthesis of fulleroids **9**-**11** from C_{70} and diaryl-diazocompound **8**.

Similarly to that found for PCBM derivatives, the analysis by HPLC and UV-vis spectroscopy revealed three peaks corresponding to fulleroids (**9**-**11**) and two small peaks corresponding to [6,6]-closed derivatives (Figure S27, S.I.). Moreover, in contrast to the previous case, the number of possible fulleroids is only four since the addend is now symmetric. The experimental ratio fulleroid/methanofullerene was 89:11. As expected, this ratio resulted lower than the previous case of $PC_{71}BM$. However, it is higher when compared with other related examples using diaryl-diazocompounds.[18] The reason of the pronounced capacity to form fulleroids from diaryl-diazocompound **8** is probably due to the presence of an electron-releasing group in the *para* position of the aryl group which favors the formation of [5,6]-open-derivatives.[17]
The obtained methanofullerene fraction is formed by a mixture of α- and β-*site*isomers in a ratio of 85:15 (α:β). In this case, the addend is symmetric and, therefore, only one β-*site*isomer is found.
The isomerization from the [5,6]-open fulleroids **9**-**11** to the corresponding [6,6]-closed derivatives (**12** (α) and **13** (β)) by irradiation at λ= 360 nm was quantitative (Figure S28, S.I.). The [6,6]-methanofullerenes were formed by a mixture of two *site*-isomers in a ratio of 88:12 (α:β). By analogy to the PCBM derivatives, we assigned compound **9** to fulleroid-*a*, compound **10** to fulleroid-*b*, and compound **11** to fulleroid-*c*.
The fulleroids fraction containing compounds **9**-**11** has also been characterized by the same techniques used for the related compounds **2-4** (Pages 12S-17S, 21S and 22S, S.I.).

Electrochemical properties.
The electrochemical properties of the fulleroids and methanofullerenes reported here have been studied by cyclic voltammetry (CV). It is well known that a saturation of one fullerenic double bond modifies the electrochemical behavior by rising the LUMO energy and the first reduction potential in methanofullerenes is shifted around 80-100mV per saturation towards more negative potentials.[19] In contrast, fulleroid derivatives have the same number of double bonds than pristine fullerene. Thus, the π-homoconjugation in the fullerene cage is not disturbed and the LUMO energy level is not significantly modified.

The cyclic voltammetry of the fraction containing fulleroids **2**, **3** and **4** using *o*-DCB/MeCN (4:1) as solvent at r.t. and $Bu_4N{\cdot}PF_6$ as the supporting electrolyte is shown in Table S1 (Figure S24, S.I.).

As expected, the values of the reduction potential of fulleroids **2**, **3** and **4** ($E_1^{1/2}$: -1,03 V) are similar to those of pristine C_{70} ($E_1^{1/2}$: -1,02 V). However, methanofullerenes **5**, **6** and **7** ($E_1^{1/2}$: -1,13 V) show higher reduction potential values when compared with both fulleroids and pristine C_{70}. The cyclic voltammetry of the DPM derivatives (**9**-**13**) showed similar effects to those presented by PCBM derivatives (**2**-**7**) (Table S1, Figure S25 S.I.). Thus, the CV data nicely confirm the respective fulleroid and methanofullerenes structures, thus supporting the above experimental findings.

In summary, we have carried out the quantitative preparation of less-known [70]PCBM-type [5,6]-fulleroids (**2**-**4**) as well as their analogues of the [70]DPM series (**9**-**11**) which are formed with a high degree of selectivity. UV-vis spectroscopy and CV electrochemical data clearly confirm their [5,6]-fulleroid nature.

As expected, [5,6]-fulleroids are unstable compounds and rapidly undergo a quantitative photochemical isomerization to the respective [6,6]-methanofullerenes. Based on the *site* and stereoisomers obtained for the [6,6]-$PC_{71}BM$ and [70]DPM derivatives, the nature of the precursors [5,6]-fulleroids has been unambiguously assigned. A most appealing experimental finding is that the chemical reactivity of the obtained [5,6]-fulleroids is strongly dependent of the position on the fullerene cage ($a > b > c > d$), thus following a similar trend to that found for the thermal reactivity in pristine [70]fullerene ($\alpha > \beta > \gamma > \delta$).

Despite the instability of the formed [70]fulleroids, their spectroscopy and electrochemical properties have been determined. Furthermore, the CV data unambiguously support their chemical structure based on the high sensibility of the technique.

This study reveals the high and complex reactivity of unsymmetric fullerenes such as C_{70} and confirms the photochemically reactivity of the initially formed [5,6]-fulleroids as a smart and efficient procedure to form thermal and photochemical stable [6,6]-methanofullerenes through a highly selective di-π-methane rearrangement.

Acknowledgments

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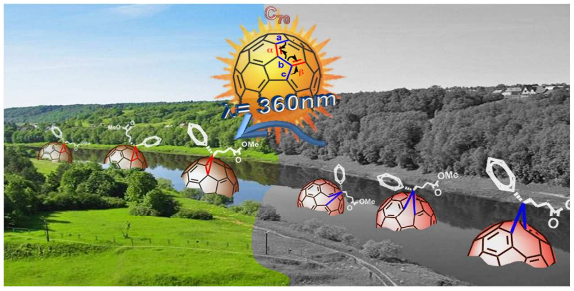

Three new [5,6]-PCBM isomeric fulleroids photoisomerize, in a quantitative and highly selective way, to their respective [6,6]-PCBM methanofullerenes.