The synthesis of a [60]fullerene-benzene building block and its further chemical cycloaddition reaction with graphene has resulted in a new all-carbon hybrid material which has been characterized by TGA, FTIR and Raman spectroscopies, XPS as well as AFM and TEM. Based on computational studies, the formation of both [2+2] and [4+2] cycloadducts on the graphene surface is feasible.

Arynes constitute a family of elusive intermediates whose existence was proposed over a century ago. However, it was not until 1953 when the first experimental evidence of the intermediacy of the parent benzene in a chemical reaction was reported. Since then, a wide variety of synthetic methods on the generation of benzene as well as its use in the construction of sophisticated chemical structures has been reported.

Intensive work has been carried out to prepare a comprehensive family of polycyclic aromatic hydrocarbons using benzene and its derivatives. Nevertheless, the chemical structure of arynes is still a matter of controversy and their structural characterization is an open question since, under certain conditions, a cumulene versus acetylene character has been proposed. In this regard, the on-surface generation and imaging of arynes by atomic force microscopy has recently been reported.

The [2+2] cycloaddition reaction of the highly reactive intermediate benzene with [60]fullerene was firstly reported in 1992 affording, in addition to the expected monoadduct, the formation of bis, tris and tetraadducts. Soon afterwards, the monocrystals obtained from the monoadduct formed in the reaction of 4,5-dimethoxybenzene with C_{60} allowed determining that the cycloaddition process takes place at the (6,6) double bond of the fullerene sphere. Furthermore, it has also been reported the formation of an open cage (5,6) monoadduct stemming from the rearrangement of the previously formed closed cage (6,6) isomer. Interestingly, the reaction of arynes with endohedral metallofullerenes has afforded both (5,6) and (6,6) cycloadducts.

The benzene cycloaddition to other carbon nanostructures such as single wall carbon nanotubes (SWCNT) and carbon nanohorns has also been investigated considering in situ generated benzenes, under classical conditions or by using microwave irradiation. Furthermore, different α-(trimethylsilyl) phenyl triflates have been reacted with multi-layered graphene sheets or using graphene-coated Cu foils under arylene-forming conditions. On both graphene surfaces the cycloaddition occurred under mild conditions and provided stable materials with a good degree of functionalization.

In this communication we report on the synthesis of an unprecedented C_{60}-aryne precursor and its use for the construction of a novel fullerene-graphene nanostructure. As an adequate precursor of such a C_{60}-aryne species we envisioned an α-(trimethylsilyl) aryl trflate covalently linked to the fullerene sphere, which could be synthesized by means of a [2+2] cycloaddition between [60]fullerene and 2,5-bis(trimethylsilyl)-1,4-phenylene bis(triflate) 1. A similar approach, based on the controlled generation of only one of the two possible arylene functionalities from the 1,4-benzodiazepine precursor 1, followed by reaction with an adequate partner, has been previously developed by some of us for the synthesis of other complex polycyclic arylene precursors. The reaction of the novel C_{60}-aryne building block with graphene should afford in a straightforward manner a new covalent all-carbon hybrid which combines two close relatives of the nanocarbon family such as [60]fullerene and graphene.

Bistrflate 1 was prepared in two synthetic steps from hydroquinone. Reaction of bistrflate 1 with C_{60}, carried out under stoichiometric control in order to get the intermediate monoaroyne, resulted in the formation of the fullerene monoadduct 2 (Scheme 1). Thus, a solution of 1 and C_{60} in chlorobenzene was treated with anhydrous TBAF (1.0 equiv,
1M in CH$_3$CN). After purification by column chromatography, monoadduct 2 was isolated in a 21% yield. This cycloadduct was fully characterized (see ESI for details, Figs. S2 and S3), showing the expected aromatic protons at 8.1 and 7.9 ppm in the $^1$H-NMR spectrum as well as the typical singlet (9H) of the TMS group which appears at 0.6 ppm. This new fullerene derivative (2), an aryne precursor endowed with a [60]fullerene moiety, is an appealing new building block (fullerobenzyne, 3) for materials science that could provide access to new molecules and materials by subsequent chemical reactions with a large variety of dienes.

In a first attempt, the o-(trimethylsilyl)aryl trflate 2 was reacted with [60]fullerene and resulted in the formation of fullerene dumbbell 4, although the low solubility of this compound as well as the competitive processes leading to multiadducts formation resulted in a low yield ((see ESI for details, Figs. S5-S7). It is worth mentioning that in that absence of C$_{60}$ or any other diene, fullerobenzyne 3 reacts with itself and the TBAF, providing a complex mixture of compounds based on mass spectrometry (see ESI for details, Fig. S4).

The efficiency of trflate 2 as precursor of the novel fullerobenzyne 3 was further proved through a trapping experiment with furan, a system without the problem of regioselectivity of C$_{60}$. Thus, treatment of 2 with anhydrous TBAF in chlorobenzene using furan as cosolvent, successfully afforded the Diels-Alder adduct 5 in 43% yield (Scheme 2, see ESI for details, Fig. S8).

Scheme 1 Synthesis of monoadduct 2 and fullerene dumbbell 4, via fullerobenzyne 3.

Next, we decided to investigate the functionalization of pristine graphene with fullerobenzyne 3 to obtain hybrid all-carbon nanostructures. Prior to reaction, the pristine graphene material was obtained through exfoliation from graphite in o-DCB under inert atmosphere following Coleman’s procedure toward few-layered graphene (FLG) suspensions with a high degree of purity (Fig. S1). The cycloaddition reaction of FLG with fullerobenzyne was carried out preparing a solution of anhydrous TBAF in dry acetonitrile that was slowly added dropwise to a solution of monoadduct 2 and FLG in dry o-DCB (see ESI for details). The solution was stirred vigorously for 12 h at 40 °C, the solvents removed by filtration and the residue purified by subsequent washing to yield nanoconjugates 6 (Scheme 3) that were fully characterized by using a variety of techniques, namely thermogravimetric analysis (TGA), FTIR, Raman, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and transmission electron microscopy (TEM).

Scheme 3 Cycloaddition reaction of fullerobenzyne 3 and FLG.

A first hint on the covalent attachment of fullerobenzyne 3 to FLG was obtained from TGA under inert atmosphere (Fig. S9). The FLG-C$_{60}$ nanoconjugates 6 present a 28% weight loss, which should correspond to the organic moieties attached on the FLG surface. The organic precursor 2 was also analysed and presented two weight loss contributions and a skeleton remaining intact that could be attributed to the C$_{60}$ itself.

Additional confirmation of the cycloaddition reaction taking place on FLG was obtained by FTIR and Raman spectroscopies. In the FTIR spectrum of FLG-C$_{60}$ (6) are clearly observed the skeletal in-plane vibrations of graphene at 1581 cm$^{-1}$ as well as some vibrational peaks at 2927 and 2854 cm$^{-1}$ that could be due to defects on the structure. Furthermore, the characteristic vibrational peaks of pristine C$_{60}$ are observed at 1455, 1125 and 525 cm$^{-1}$. These peaks were also present in the precursor 2 with slight shifts (Fig. 1).

The Raman spectrum of FLG excited at 532 nm presents three characteristic bands, the D, G and 2D bands centered around 1340, 1565, and 2678 cm$^{-1}$, respectively. Upon formation of the FLG-C$_{60}$ nanoconjugates 6, the intensity on the D band increases due to the rehybridization of the carbon atoms from sp$^3$ to sp$^2$ (Fig. S10). Thus, the I$_D$/I$_G$ ratio growth from 0.17 for FLG to 0.29 for FLG-C$_{60}$ indicating the covalent anchoring of the [60]fullerene moiety in agreement with the previously mentioned TGA weight loss. In addition, the very sensitive to doping effects G band appears – 4 cm$^{-1}$ upshifted for the FLG-C$_{60}$ sample when compared to FLG, which suggests a possible
Electronic interaction between FLG and the electron-acceptor C$_{60}$.

The FLG-C$_{60}$ nanoconjugates 6 were further studied by XPS spectroscopy. The XPS survey spectrum of 6 shows carbon (C 1s) as the main element and an oxygen (O 1s) contribution of 13%, as in the case of the starting FLG, indicating that no extra oxygen atoms were anchored to the graphene surface during the reaction with fullerobenzene (Fig. S11). The high-resolution C 1s core-level spectrum of FLG was composed of the four expected components: photoelectrons emitted from sp$^2$ carbon atoms, sp$^3$ carbon atoms, oxidized carbon atoms in the C=O bonds and the π-π* shake up structure of graphene sheets, respectively (Fig. S12). In the case of FLG-C$_{60}$ nanoconjugates 6, although the contribution from the sp$^3$/sp$^2$ carbon atoms has a similar relative intensity to that of FLG, two new contributions that could be assigned to C 1s shake-up satellite peaks of C$_{60}$ are observed (Fig. 2)."
and the energy barrier to move from the minima at [2+2] to that at [4+2] cycloadduct positions is approximately 0.1 eV. By modelling a step edge on the upper graphene sheet and locating the benzene moiety in the region of the step edge (see Fig. S18 and Table S2), it is found that the value of $E^*$ ([2+2]) increases (i.e. 4.06 eV when located to 2.5 Å from the step edge) and the value of $E^*$ ([4+2]) decreases (i.e. 5.15 eV when located to 2.5 Å from the step edge) from the values found for locations on the basal plane (infinite plane of graphene with no step edge).

Table 1 Binding energies, $E^*$ (eV), and bond lengths, $d$ (Å), for the exothermic cycloaddition reaction of FLG and benzene derivatives.

<table>
<thead>
<tr>
<th>System</th>
<th>$E^*$ ([2+2])</th>
<th>$E^*$ ([4+2])</th>
<th>$d$ ([2+2])</th>
<th>$d$ ([4+2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLG-benzene</td>
<td>3.63</td>
<td>5.67</td>
<td>1.55</td>
<td>1.59</td>
</tr>
<tr>
<td>FLG-fullerobenzene</td>
<td>3.62</td>
<td>5.65</td>
<td>1.55</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Regardless of the covalent connectivity between the $C_{60}$ units and the graphene layer, it is important to note that, to the best of our knowledge, that this is a rather unique case in which the fullerene balls are linked to the graphene in a rigid manner involving two covalent bonds, which provides a regular and homogeneous distance between them.

In summary, we have carried out the synthesis of a new building block (2) that allows to access an elusive arylene endoarded with a [60]fullerene unit (fullerobenzene). The fullerene monoadduct 2, easily obtained from 2,5-bis(trimethylsilyl)phenyl 1,4-bis(triflate), resulted to be an adequate precursor of the novel arylene 3, that efficiently reacts with furan, $C_{60}$ and graphene. The new FLG-$C_{60}$ nanoconjugates 6 have been fully characterized by using a variety of techniques (TGA, FTIR, Raman, XPS, AFM and TEM). All of them nicely support the formation of the new carbon hybrids and reveals the efficiency of the cycloaddition over FLG. Theoretical calculations demonstrate the [4+2] cycloadducts to be the more stable configuration to be formed, although the formation of the [2+2] products cannot be ruled out based on the small difference in energy, which is in accordance with previous theoretical investigations. Based on the remarkable higher reactivity of the fullerene units compared with the graphene layer, work is currently in progress to determine the chemical reactivity and selectivity of the new carbon-based nanoconjugates and their properties as new materials for practical purposes.

Financial support from the European Research Council (ERC-320441-Chiralcarbon), the European Commission (EC) FP7 ITN “MOLESCO” Project No. 606728 and FP7 ICT-2013-FET “PAMS” Project No. 610446, the UCM (GR3/14-910781), the Ministerio de Economía y Competitividad (MINECO) of Spain (Projects CTQ2013-44142-P, MAT2013-46593-C6-6-P, CTQ2014-52045-R and CTQ2015-71936-REDT), the CAM (PHOTOCARBON project S2013/MIT-2841) and FEDER is acknowledged. N. M. thanks the Alexander von Humboldt Foundation. The authors thank Laura Acevedo for the AFM measurements.

Notes and references


21. A similar result was proposed for the cycloaddition of simple benzenes to graphene sheets, see ref. 13.


Table of contents entry

Covalent all-carbon few layer graphene and [60]fullerene conjugates can be easily formed from a versatile [60]fullerene-benzyne building block