ADSORPTION AND CYCLO-DEHYDROGENATION OF POLYCYCLIC AROMATIC HIDROCARBONS ON Pt SURFACES: TOWARDS THE SYNTHESIS OF HETEROFULLERENES

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Controlled synthesis of fullerenes and heterofullerenes on surfaces is a preceding step towards the development of a true fullerene-based molecular electronics. Given the limitations of the current preparation techniques based on graphite vaporization, new methods are required for the rational, size-controlled synthesis of fullerenes, heterofullerenes, and endohedral fullerenes.

Here we report a highly efficient (<100%) dehydrogenation mechanism leading to the formation of fullerene C_{60} and for the first time triazafullerene $C_{57}N_3$ in a one-step from their corresponding planar polycyclic aromatic precursors by a surface catalysed process [1]. We have visualized the whole process by in-situ Scanning Tunneling Microscopy (STM) and X-Ray Photoemission spectroscopy (XPS). The cyclodehydrogenation has been confirmed by the thermal desorption of HD and D_2 from hexadeuterated 1-d6 precursors, and by the mass-spectrometric detection of C_{60} in the platinum-catalysed dehydrogenation. First principles DFT calculations have been used to follow the whole process.

The process is catalysed by reactive substrates, as Pt, which favours strong surface-molecule interactions. We have thoroughly studied with STM and large-scale DFT calculations (using both efficient local orbital basis methods FIREBALL [2] and OPENMX [3] and standard plane-wave approaches like VASP [4]) the interaction of the polycyclic planar precursors with different surfaces. Particularly, we have found that this system has the capability to induce a local separation of the chiral molecular species induced upon surface adsorption. The number of established bonds between the substrate and molecule seems to play a key-role in the properties of the system.

The mechanism we describe opens the door to size-controlled production of fullerenes and heterofullerenes, it could allow the encapsulation of different atomic and molecular species to form endohedral fullerenes and to the formation of different carbon-based nanostructures, such as graphene or doped graphene, which nowadays are not readily available on surfaces by other methods.

References:

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