DESIGN AND SYNTHESIS OF COVALENT SYNTHETIC CARBON ARCHITECTURES BASED ON CARBON NANOTUBES AND GRAPHENE

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Nowadays, synthetic carbon nanostructures (SCAs) such as carbon nanotubes (CNTs) and graphene (GR) have raised a huge interest due to its outstanding properties, in example its extended planar aromatic π-system and architectural flexibility. In fact, these materials represent one of the most promising candidates for future applications in material science since these SCAs can be used as building blocks to develop new functional hybrid architectures with enhanced properties, due to the combination with different electroactive counterparts by means of either non-covalent or covalent functionalization.

Considering the possibilities of SCAs, this thesis deals with the electronic modification of SCAs by means of covalent functionalization in order to extend the SCAs' functionalization knowledge and also to obtain new architectures with high stability and strong electronic communication between the different moieties. In this regard, this thesis work is divided in two chapters:

Chapter 1 involves the functionalization of carbon nanotubes with different electroactive units such as porphyrins (P) and phthalocyanines (Pcs) to design a new series of Donor-Acceptor (D-A) architectures. In this sense, single-walled carbon nanotubes (SWCNTs) of different chirality and double-walled carbon nanotubes (DWCNTs) were covalent decorated through a smart combination of Tour reaction and Sonogashira C-C coupling. With the aim of studying the influence of the nature or the relative orientation of the attached group, different porphyrins and phthalocyanines were linked in a deep independent analysis. The obtained functionalized materials were fully characterized by the common techniques used on this kind of materials, confirming the covalent decoration. Additionally, the existence of electronic communication between carbon nanotubes and electroactive units (P and Pcs) were found by optical and electrochemical studies. Finally, we studied the scope of the regioselectivity of the Pauson-Khand reaction in carbon nanotubes by theoretical and experimental studies.

Chapter 2 is centered on covalent functionalization on graphene material. In addition, chemical derivatization of [Li+@C60](PF6) endohedral metallofullerene has been exploring via 1,3-dipolar cycloaddition by the first time. Several graphene and doped graphene (nitrogen and boron) architectures have been prepared using different approaches according to the starting graphene material nature. In this sense, pristine graphene was functionalized via a combination of Tour reaction and esterification, nitrogen-doped graphene N(G) through N-alkylation directly or in combination with "click" chemistry, and in the case of boron-doped graphene B(G) exploiting Lewis acid-base reactions. The resulting hybrid architectures were studied thoroughly by a set of characterization techniques. Optical and electrochemical studies revealed the electroactive and photoactive behave of materials. Additionally, variation of the Hall Voltage were measured for doped-graphene functionalized materials, according to their functionalization degree and to the electronic nature of the organic attached group.