IEF – Final Report

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Final Publishable Summary

Practical aspects of **spintronics**, and especially **quantum information processing** (QIP), are currently hindered because of the lack of suitable materials. The research project titled "Transition Metals in Carbon Nanostructures" has involved two different tasks, which are intended to solve existing problems producing a new class of hybrid metal-carbon nanomaterials with exploitable properties.

The *first task* of this project has focused on the **organization of electron-spin and optically active endohedral fullerene molecules X@C$_n$** (where X is an atom or cluster incarcerated in the fullerene, and *n* is a number of carbon atoms in the fullerene cage) **on surfaces and the investigation of functional properties of the obtained nanoscale architectures**. In this case, the fullerene cage serves as "nano-container" which facilitates the incorporation of individual endohedral atoms with interesting optical and magnetic properties within supramolecular architectures. However, fullerene cages tend to have relatively isotropic exteriors owing to their spherical shapes, and so precise control of their positions and orientations can be difficult to achieve. An attractive approach for solving this problem is through chemical functionalisation of fullerene cages. This would allow for control over the orientation of the molecules *via* well-defined chemical bonding or highly directional non-covalent interactions. Thus, endohedral fullerenes functionalised with an appropriate chemical group could be able to form spontaneous molecular monolayers on surfaces. This strategy has been the main research vector for the formation of 2D arrays of these molecules at the nanoscale.

There has been two central aims for the first task: i) Development of suitable methods for the controlled assembly of empty fullerenes on gold surfaces and ii) Transfer of the successful strategies utilised for empty fullerenes to magnetic and optically active endohedral fullerenes. The research program inside this task has been developed in three stages:

A) Controlled assembly of sulphur functionalised fullerenes in 2D molecular arrays.

The research has been focused on studying the effects that the anchoring/spacer group attached to the fullerene cage has upon the molecules ability to form well-packed and highly ordered fullerene-terminated self-assembled monolayers (SAMs) on surface to create 2D arrays models for quantum information processing (QIP) applications. Hexagonal closed pack arrays of pristine fullerenes are formed invariably as fullerene-fullerene and fullerene-substrate interactions are typically governed by low directional van der Waals forces. Here, chemical modification of fullerene exteriors has been

utilised to address the lack of structural diversity of fullerene 2D arrays. For the first time the formation of square and rectangular 2D arrays has been reported for fullerene assembly.

B) Controlled deposition of functionalised fullerenes on the pores of molecular networks.

Previous studies show C_{60} heptamers trapped within the hexagonal pores of a 3,4,9,10-perylene tetracarboxylic diimide (PTCDI)/melamine network. To control the deposition of C_{60} molecules the pore size and shape of this honeycomb network can be varied by using analogues of PTCDI. Here, the size/conformation of the group attached to the fullerene cage is utilised to tune the number of fullerene molecules absorbed onto the pores of the 2D hydrogen-bonding network. This sort of size-selective trapping of C_{60} could serve as a platform for future nanotechnologies, such as molecular memory devices.

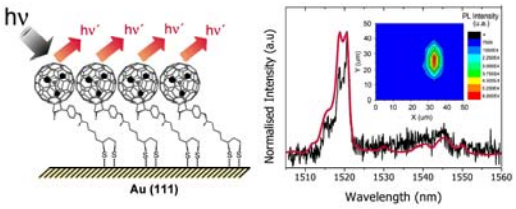

Fig 1. Schematic representation of bonding of the dithiolane group to the Au-surface and PL properties.

C) 2D self-assembled monolayers of S-functionalised endohedral metallofullerenes.

Synthetic strategies developed for empty fullerenes has been successfully transferred to endohedral fullerenes in order to control the assembly of these electron-spin and optically active molecules on surfaces and study functional properties of the obtained nanoscale architectures (Fig. 1). For the first time methods for the attachment of sulphur-containing group to endofullerenes have been reported, and the functional optical/ magnetic properties were retained after the functionalisation.

The *second task* of this project involved the **use of tubular carbon nanostructures as 1D containers for the assembly of nanoscale functional** units such as functionalised endohedral fullerenes, molecular magnets and magnetic nanoparticles, which will be the basic components for the next-generation of electronic and spintronic devices. One particular challenge in the development of such devices is the coupling of the nanoscale units to the macroscopic world, which is essential for read and write purposes. Tubular carbon nanostructures with one macroscopic and two nanoscopic dimensions provide an excellent means to achieve this coupling, yielding a new type of hybrid nanostructure that combines all the key properties, such as magnetic bistability, of the guest-molecules with the functional properties of the host-nanotube, such as high electric conductivity and thermal stability. This breakthrough also paves the way for the construction of ultra high-density magnetic data storage devices.

In this task, interactions between molecules or nanoparticles and nanotubes or nanofibers have been studied, and a general methodology for the confinement of these nanoscale units within the tubular carbon nanostructures has been developed. The structural and functional characterization of two different types of hybrid materials has been investigated:

A) Peapods of functionalised metallofullerenes in single-walled carbon nanotubes (SWNTs).

SWNTs have been used as transparent-test tubes for imaging 1D-arrays of functionalised metallofullerenes for the first time at the atomic scale by low energy AC-HRTEM (Fig. 2). Structural information about the relative position of the functional group and endohedral atoms has been obtained simultaneously. The unique ability of nanotubes to act not only as inert containers, but also as efficient templates for a new form of carbon materials has also been explored using electron beam radiation to trigger the chemical transformation of the inserted materials giving rise to a new form of hybrids that otherwise would not exist.

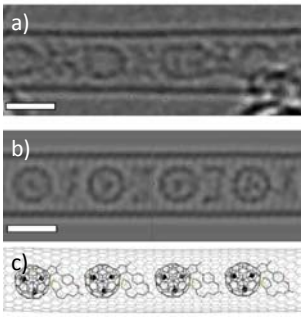

Fig 2. a) Experimental AC-HRTEM image, b) simulated image and c) structural diagram of peapods (scale bar = 1nm).

B) Magnetic quasi-1D arrays in multi-walled carbon nanotubes and carbon nanofibers.

The research has been focused on the use of carbon nanotubes and carbon nanofibers as containers for magnetic quasi-1D arrays. Preformed magnetic nanoparticles and magnetic polynuclear metal clusters, such as single-molecule magnets, have been used for the fabrication of such magnetic arrays. The structural packing of the magnetic nanoscale units inside the internal cavities has been investigated by TEM and correlation between structure and properties has been established. These magnetic compounds can be used as magnetic probes for understanding the effects of carbon nanotubes on the electron-spin properties of magnetic molecules and *vice versa*. Magnetic and electrical measurements in the hybrid materials have been carried out to investigate these effects.