Experimental report

09/02/2016

Proposal: 7-05-455 **Council:** 4/2015

Title: Understanding the grafting of fluorophore molecules on Carbon Nanotubes: a prerequisite for toxicity studies

Research area: Materials

This proposal is a new proposal

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Samples: Carbon nanotubes + Fluorescein
Carbon nanotubes + diamine + cyanine
Carbon nanotubes + cyanine
Cyanine

Instrument	Requested days	Allocated days	From	To
IN1 LAG	4	4	07/12/2015	11/12/2015

Abstract:

The extraordinary physical properties and their 1D morphology of carbon nanotubes (CNTs) has quickly led to many applications in various fields including biology (drug-delivery, scaffolds, imaging, sensors). Use of CNTs always requires their dispersion (de-agglomeration, individualization), obtained by functionalisation, covalent or not (simple adsorption). For covalent grafting, the question of the competition between real grafting and simple adsorption is very relevant and has never been investigated rigorously. This is however a central question, and especially in the field of nanotoxicology and biomedical applications of CNTs: they are for ex. generally tracked inside biological matrices by functionalisation with fluorophores (fluorescence being associated to CNTs). However, fundamental questions are raised as there is no simple evidence that a fluorophore adsorbed on a CNT will stay there forever once inside a cell (molecules with a stronger affinity could lead to desorption of the fluorophore), leading to wrong conclusions. The project aims at using neutrons to identify adsorption sites on CNTs and investigate the ratio between covalent and non-covalent interactions.

The CIRIMAT is working on the Catalytic Chemical Vapour Deposition (CCVD) synthesis of carbon nanotubes (CNTs) for more than 15 years and its expertise in this field is acknowledged at the international level, in particular in relation with double-walled CNTs (DWNTs) and the toxicity of the DWNTs.
The aim of this experiment, which is on the framework of an ILL PhD project, is to characterize (covalent or non-covalent) the interaction between CNTs and model molecules (fluorophores), aiming at answering the following fundamental questions:

(i) What are the adsorption sites in CNTs samples (different surface sites are available)?
(ii) What is the ratio between covalent and adsorbed molecules in the case of a covalent grafting?

This experiment followed the experiment 07-05-432 performed in September 2015 in order to complete and even enlarge the study of the grafting mechanisms occurring during the functionalization process of Double-Walled Carbon NanoTubes (DWCNTs). (See experimental report 07-05-432 for details)
In order to go further and have a better understanding of the covalent and non-covalent grafting mechanisms of fluorofores, we measured in December 5 Samples:

(1) - Spontaneous adsorption of FITC in DWNT, to complete our recent results shown in Fig. 1
(2) - Spontaneous adsorption of streptocyanine onto the DWNT
(3) - Covalent grafting of streptocyanine onto the DWNT
(4) - Pure streptocyanine
(5) - Product of reaction in between the streptocyanine and the linking molecule (Diamine)

The choice of this new fluorophore has been motivated by the presence of two 6-carbon rings which are not parallel to one another and point almost perpendicularly to the carbon chain (see sample 4 in figure 1 below). This particular space conformation of the streptocyanine should not lead to spontaneous adsorption on CNTs, and thus, should bring new information about the non-covalent grafting mechanisms.

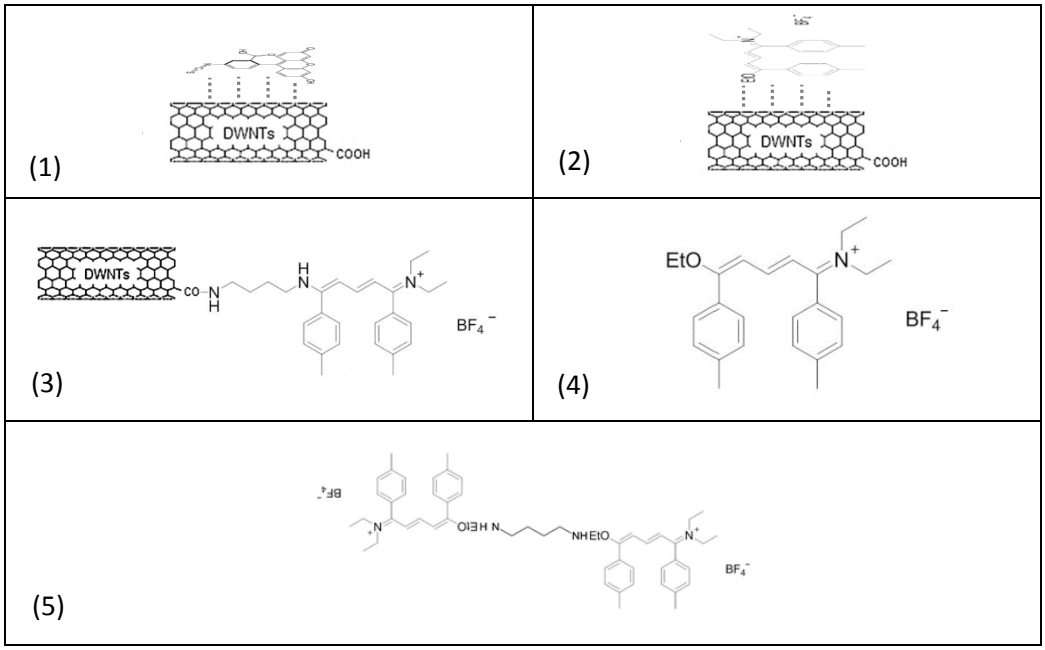

Figure 1: Representation of the five measured samples

The INS spectra obtained in this experiment (see below figure 2 & 3), conjugated with the relevant choice of the five samples above, provided very interesting information about the characteristic vibrational bands

(stretching region) of the covalent grafting occurring at the final step of the functionalization process. These precious information allowed a better understanding of the grafting mechanisms of the streptocyanine onto DWCNTs.

Figure 2 shows a comparison of the Inelastic Neutron Scattering spectra performed on IN1-LAGRANGE of the two different molecules adsorbed on the DWNTs.

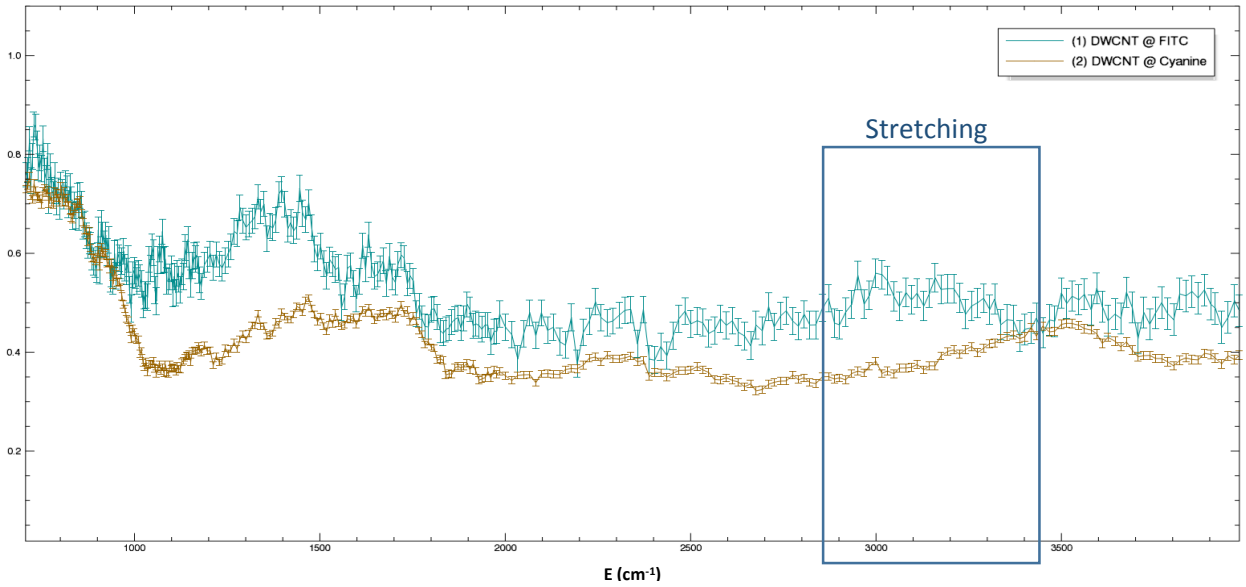

Figure 2: Normalized INS spectra of DWNTs with adsorbed fluorophores

Figure 3 shows a comparison of the INS spectra performed on IN1-LAGRANGE of the references Cyanine based samples and the product of the functionalization process of the Cyanine on DWNTs.

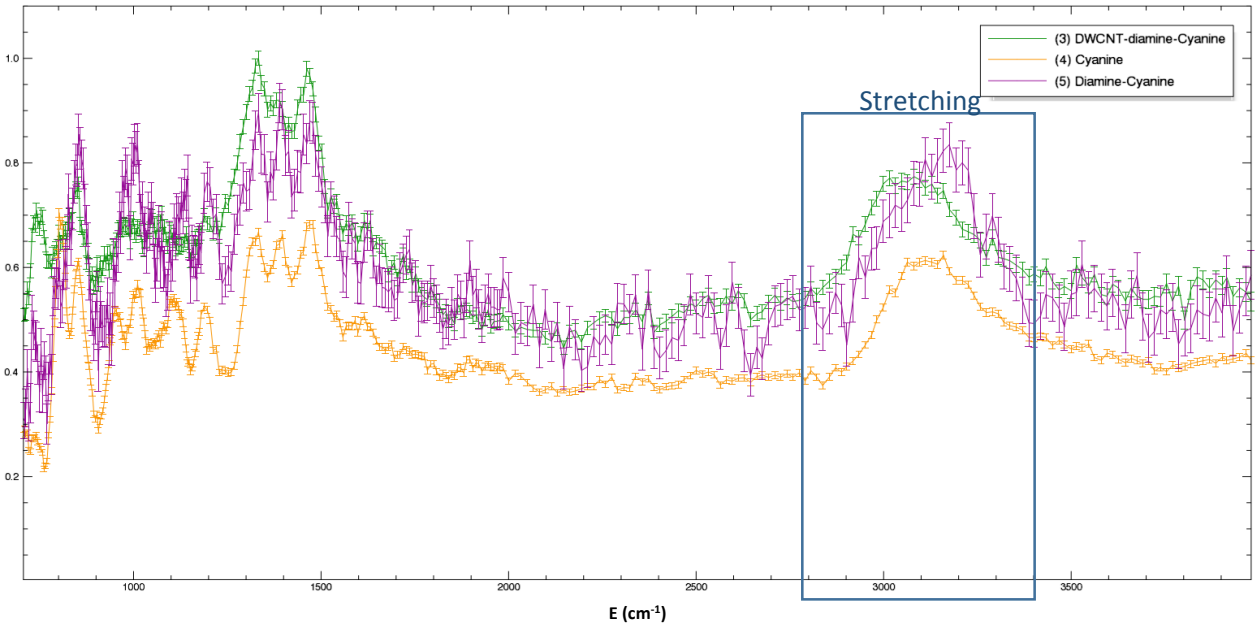

Figure 2: Normalized INS spectra of samples 3 to 5