Experimental report

08/02/2016

Proposal: 7-05-432 **Council:** 4/2014

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

Research area: Chemistry

This proposal is a new proposal

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Samples: carbon nanotubes
C20H12O5
carbon nanotubes + diamine
carbon nanotube +diamine + C20H12O5

Instrument	Requested days	Allocated days	From	To
IN1 LAG	4	4	15/09/2015	19/09/2015

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?

Six different samples were chosen for this experiment (figure 1). Three of them were references samples, corresponding to the two different molecules used during the functionalization (1 & 2). While sample 3 is the product of reaction between samples 1 and 2 and acts as a witness of the covalent bonding of the latter ones. This type of bond is looked for in this experiment.

The other three samples were synthetized in the CIRIMAT Toulouse and correspond to three different steps of the functionalization process of Double-walled carbon nanotubes (DWCNTs). The first one was constituted of double-oxidized DWCNTs (4), the second one was DWCNTs with grafted putrescine (1,4-diaminobutane) (5) and the third one, which corresponds to the final step of the functionalization process was made of DWCNTs-putrescine with grafted Fluorescein Isothiocyanate (FITC) (6).

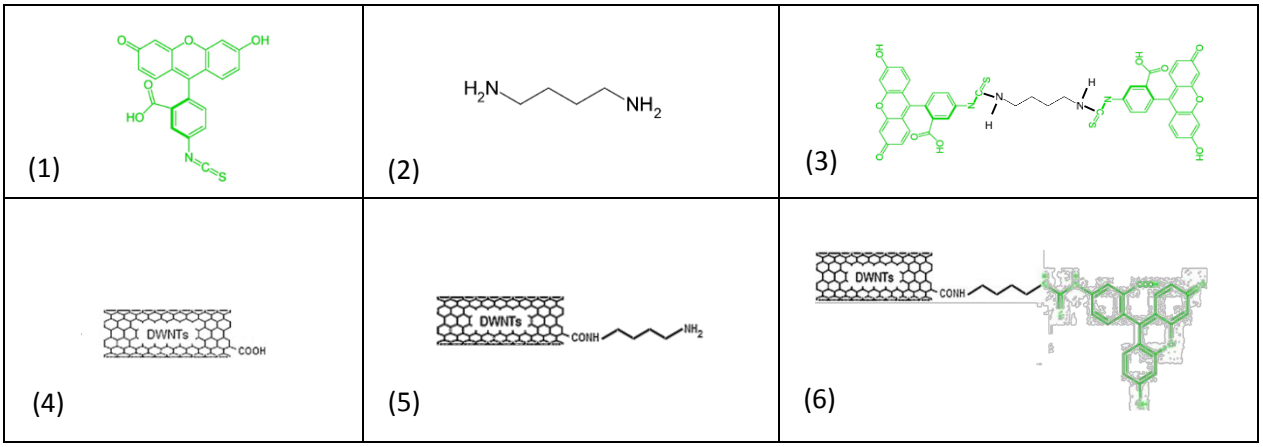

Figure 1: Representation of the six measured samples

The INS spectra obtained in this experiment (see figure 2 & 3 below) provided very interesting information about the characteristic vibrational bands (bending and stretching region) of the covalent grafting occurring in between sample (5) and (6). These precious information allowed a better understanding of the grafting mechanisms of the FITC as well as a primary rough estimation of the functionalization process efficiency by fitting the stretching region.

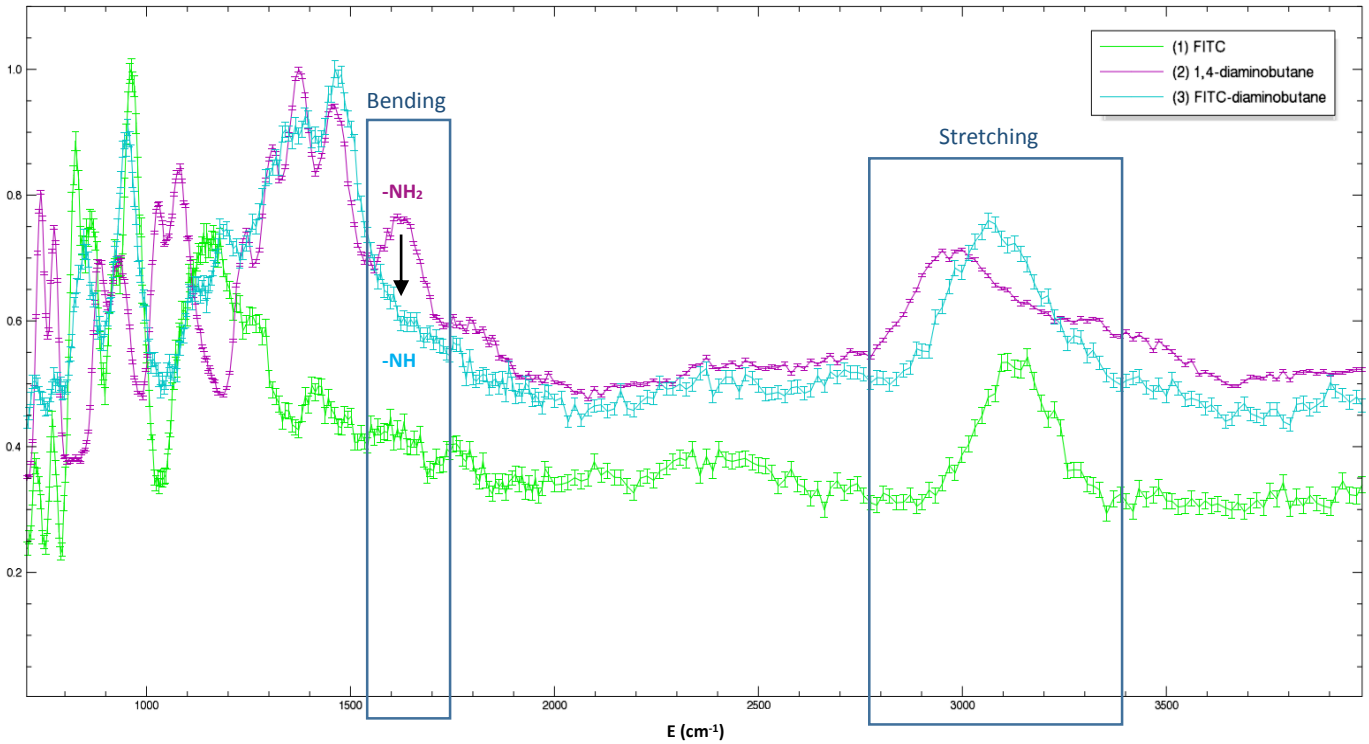

Figure 2: Normalized INS Spectra of the references samples

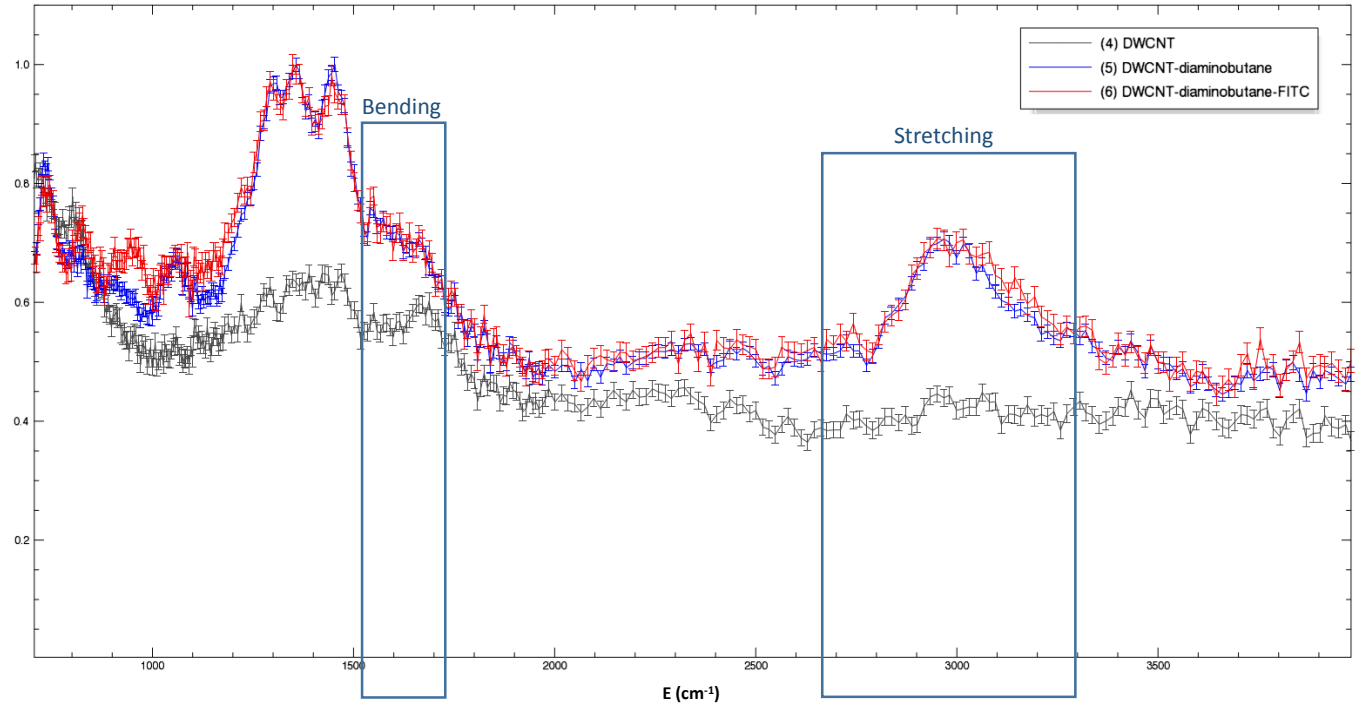

Figure 3: Normalized INS spectra of the DWNTs Samples