Experimental report

12/02/2019

Proposal: **5-24-590**

Council: 4/2016

Title: Iron-Phthalocyanine encapsulated inside carbon nanotubes: A structural study of one-dimensional crystal of an organic molecule

Research area: Physics

This proposal is a continuation of 5-32-821

Main proposer: **Ana Carolina LOPES SELVATI**

Experimental team:
Rozenn LE PARC
Jean Louis BANTIGNIES
Ana Carolina LOPES SELVATI

Local contacts:
Viviana CRISTIGLIO
Andrew WILDES

Samples: $C_{32}H_{16}FeN_8$ inside carbon nanotubes

Instrument	Requested days	Allocated days	From	To
D7	8	0		
D16	6	6	29/06/2016	05/07/2016

Abstract:

The structure of the one-dimensional chain of Iron-Phthalocyanine (FePc) encapsulated inside carbon nanotubes is known for room pressure and 7.5 and 14kbar. We propose to study the low pressure range and follow the one-dimensional lattice evolution with applied pressure.

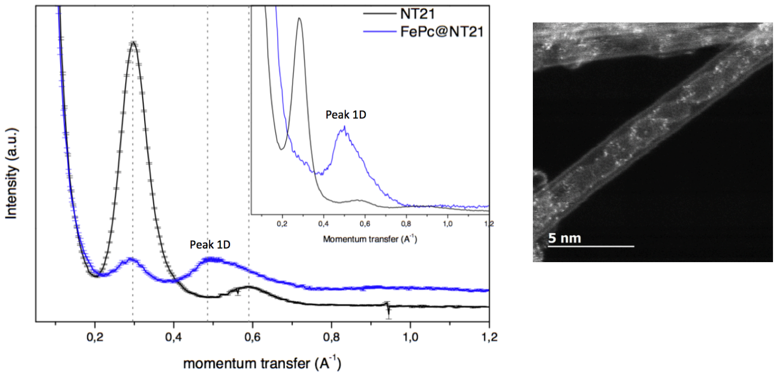

Figure 1: Left - neutron diffraction diagram obtained on D16 at ambient pressure and ambient temperature for a powder of 21 Å diameter single walled carbon nanotubes (NT21, black) and iron phtalocyanine molecules encapsulated inside such tubes (FePc@NT21 bleu); inset same using X-rays. - Right Electron microscopy picture of the hybrid nanotube sample

The experiment 5-24-590 was performed in the period from 29/06/16 to 07/07/16 on D16.

The experimental team was composed of Ana-Carolina Lopes-Selvati (former ILL PhD student), Rozenn LeParc, Viviana Cristiglio, Jean-Louis Bantignies and Stéphane Rols.

About 200 mg of a sample composed of phtalocyanine adsorbed inside 21 Å diameter single walled carbon nanotubes (FePC@NT21) was mixed with deuterated ethanol-methanol. The liquid mixture was injected into the cylindrical core of a TiZr pressure anvil cell. The pressure was increased from RP to reach 0.5, 0.9 and 1.1 GPa, the maximum pressure possible with this apparatus.

Three positions of the detector were necessary to probe the diffraction diagram in the [0.1-1 Å^{-1}] momentum transfer range. An empty nanotube sample was measured at RP and RT. A blank sample (consisting of pure ethanol-methanol inside the TiZr cell) was also measured at different pressures.

A first attempt of increasing the pressure using a CuBe cell revealed unsuccessful. This was due to an imperfect mounting of the soft metal seal. Another attempted was done using a TiZr cell giving less background signal in the small angle range.

The diagram are shown in Figure 2 (Right). Note that the Temperature dependence was also performed on D16 in a previous experiment.

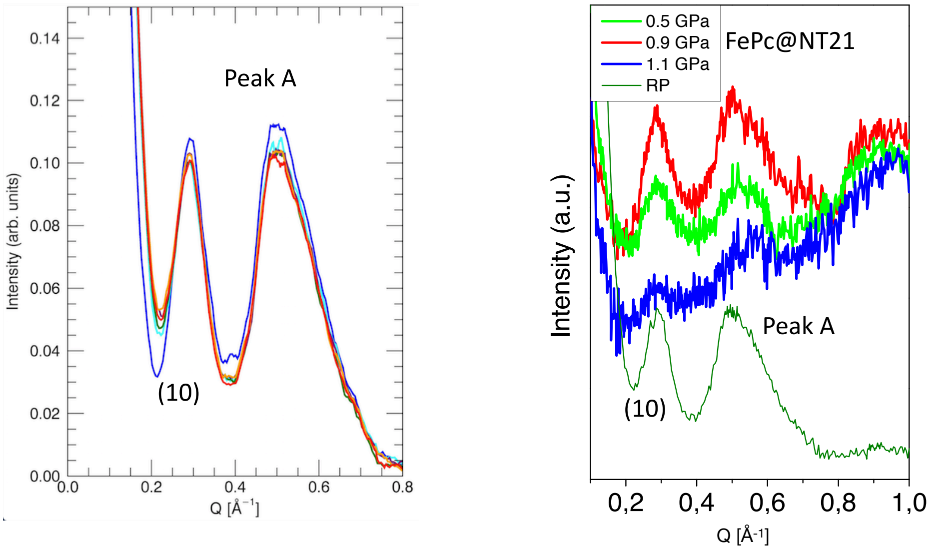

Figure 2: Left - Temperature evolution of the diffraction diagram from 5K (bleu) to 300 K (red). Right: Pressure dependence at 300 K from RP (dark green) to 1.1 GPa (blue)

The diagrams show very weak modification on varying T at room pressure (RP) from 300 K down to 5 K nor on varying P at 300 K from RP to 1.1 GPa. In particular, no modification on the position , nor relative intensity of the (10) and A peaks are observed. The large increase of the background under pressure is due to the increased density of the deuterated ethanol/methanol mixture. One can accept that the variation of temperature alone is insufficient to strongly affect the structure of the inner chain nor the structure of the 2D tube lattice in the absence of e.g. order/disorder phase transition. However, the lack of effects under pressure is surprising. Different effects were expected under applying high pressure:

- a shift of the (10) peak to higher Q due to the decrease of the inter-tube distance and a change of its intensity as the modulation by the form factor is Q dependent.
- a modification of both the profile and the position of peak A resulting from either changing the molecules' relative orientation and/or their separation distance.

Two reasons can be evoked to explain the absence of such effects: a) either there was a leak in the pressure cell which actually prevented the pressure to increase or b) the understanding we have of the diffraction diagram is wrong.

a) We need to redo the high pressure experiment. In order to be able to monitor in situ the pressure we will put a small amount of graphite in order to observe the modification of the (002) reflection under pressure.
b) different analysis are underway using different numerical approaches: atomic MD and homogeneous scattering distribution analysis.