Experimental report

17/02/2020

Proposal: **5-22-778** **Council:** 4/2019

Title: Fine understanding of hybrid carbon nanotubes using high pressure

Research area: Materials

This proposal is a new proposal

Main proposer: **Laurent ALVAREZ**

Experimental team:
Stephane ROLS
Laurent ALVAREZ
Jean Louis BANTIGNIES
Romain CHAMBARD

Local contacts: Viviana CRISTIGLIO

Samples: iron phtalocyanine @ carbon nanotubes

Instrument	Requested days	Allocated days	From	To
D16	8	6	11/02/2020	17/02/2020

Abstract:

The goal of the experiment we propose is to understand the structuring of iron phtalocyanines molecules when encapsulated inside single wall carbon nanotubes with varying diameter. We propose a high pressure study. The role of pressure is two-fold: on one hand it will allow disentangling the bundle 2D lattice peaks from those associated to the inner chain of molecules, and on the other hand it will allow one to monitor the changes of the inner chain when the molecules are forced to adopt a different packing.

Phthalocyanines are a class of stable, blue-green synthetic pigments which can be synthesized with a variety of metal ions at their center [1]. Within molecular nanotechnology their strong optical absorption is already being exploited in photovoltaic devices containing phthalo-fullerene mixed phases [1]. They also display other useful bulk optical properties including dichroism and luminescence [2] as well the magnetic properties dependent of their structures [3].
In the bulk phase, Iron Phtalocyanines (FePc) exhibits magnetic properties governed by the crystalline structure. In particular, in α-FePc the magnetic moments are strongly coupled into ferromagnetic chains (along b-axis), a weak interchain coupling leads to a molecular ferromagnet below 10K [4]. Restricting FePc assemblies to one dimension raises a variety of exciting issues concerning the modification of the electronic structure and hence to their optical, magnetic and transport properties. We have managed to encapsulate these photoactive molecules inside large diameter (21Å) carbon nanotube [5] (further referred to as NT21, the hybrid system being FePc@NT21). Our XRD investigations tend to indicate that the guest FePc molecules form a linear crystalline structure inside the NT, with a stacking characterised by a tilt angle of ~30° between the nanotube axis and the direction perpendicular to the FePc atomic plane. The XRD diagram of pure NT21 is characterised by a strong diffraction peak at small angle corresponding to a momentum transfer equal to 0.3 $Å^{-1}$. This intense feature represents the (10) reflection on the 2D hexagonal lattice formed from the packing of parallel tubes into bundles. The intensity of this feature is modulated by the form factor of the tubes, so that filling them with molecules, i.e. changing the tube's scattering distribution, is known to strongly damp this feature. Of course, this effect is both dependent on the filling factor, and on the radiation (X-Ray and neutron). The observation of the vanishing of this (10) peak is classically taken as the experimental signature of the filling of the tubes. The structuring of the inserted molecules has been previously associated to a second peak visible in the low Q region around 0.5 $Å^{-1}$ in the FePc@NT21 diagram. The latter, further referred to « peak A » in the following was supposedly attributed to the reflection on the 1D lattice formed by the inner chain of the FePc molecules, with lattice parameter of ~1nm which tend to indicate that the molecules filling up the tube adopted a disordered and diluted state with important tilt angle between the molecules plane and the nanotube long axis.

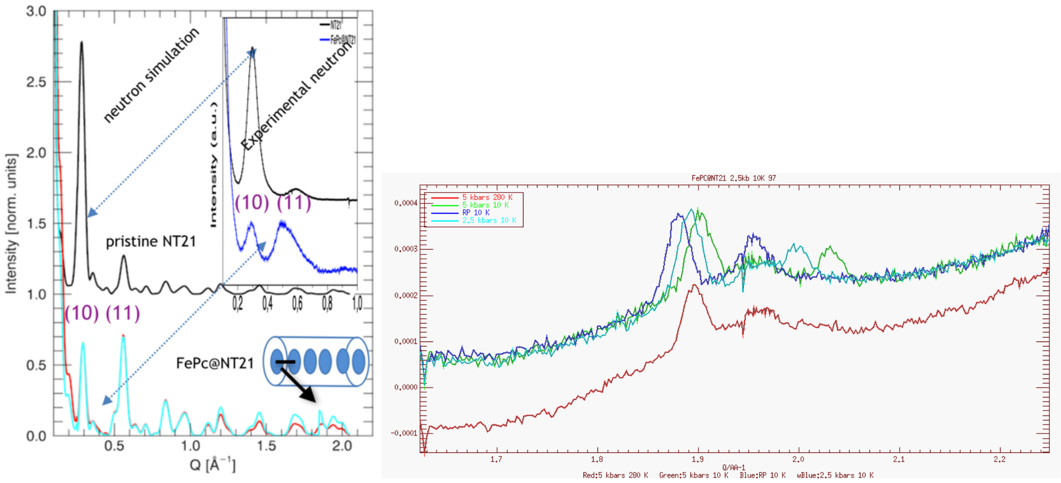

Figure 1: Experimental and simulated X-ray diffraction diagrams (left) and neutrons

However our calculations (see Fig. 1) together with the observation of the absence of any modification of the peak A under high pressure and/or low temperatures (see Exp.Rep.#5-24-590 and [6]) suggested that peak A was actually the (11) bundle feature (calculated at Q~0.55 $Å^{-1}$), the latter being increased when filling the tube with molecules (forma factor effect).

Our team has performed a recent [experiment 5-22-778 performed from 11-17/02/2020 on D16, i.e. less than 1 day before the proposal deadline] which consisted in applying a pressure of 5 kbar (using a 4He gas pressure cell) at high temperature followed by a subsequent cooling at 2K. Below some 40 K, a peak appears at a Q value ~ 2.03 $Å^{-1}$ in perfect agreement with the FePc 1D intermolecular reflection (see Fig. 1, the peak at 1.9 Å^{-1}is the Graphite 002 reflection that we used as a calibrant for pressure). On releasing the pressure at 10 K the peaks shifts down to lower Q, with a value of 1.95 Å^{-1} ⇔ 3.22 Å intermolecular spacing, in very good agreement with the intermolecular spacing found in the bulk phase of FePc.

This observation indicates that under pressure and cooling,

1) it is possible to orient the FePc molecules along the tube axis, with an 1D lattice parameter reaching 3.1 Å at 5 kbar.
2) the orientation remains on releasing the pressure at low T.

At the moment, the following questions remains:

1) what is the minimum pressure to induce ordering (role of pressure / temperature)?
2) is there a (ferro)magnetic ordering of the Fe magnetic moments associated with this transition?
3) is it possible to obtain the ordering on hybrid nanotubes having a smaller diameter

A. We propose to tackle points 1) and 2) on the sample we have studied up to know (FePc@NT21) using D16 for point 1) and D7 for point 2).

- ➔ On D16, we will use the 4He high pressure gas cell inside and orange cryostat. Four pressures will be applied, from 0 to 5 kbars with 5 points in temperatures between 2K and 50 K. This will give 20 points in the phase diagrams for two detectors conditions, i.e. 40 measurements. Considering 1 pressure per day, we ask for 6 days of beam time, including the measurements of empty cell, V and Cd.
- ➔ On D7, we ask for 4 days of beam time in order to detect any magnetic scattering signal in the 0.3 – 4 Å^{-1}range.

B. We propose to tackle points A) by extending the measurements described in A1) on a FePc@NT14 sample. Only the 5 kbars / 2K point will be measured for this sample. An extra day is recquired

In total we ask for 6+1 = 7 days on D16 and 4 days on D7.

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[1] J. C. Swarbrick, et al, Phys. Chem. Chem. Phys., 2010, 12, 9693–9699 ;[2] K. Schulte et al, Adv. Mater., 19, 2007 3312–3316; [3] M. Evangelisti et al, Phys. Rev. B, 66, 2008, 144410;[4] Functional Phthalocyanine Molecular Materials, Jianzhuang Jiang, Springer (2010);[5] L. Alvarez et al. J. Phys. Chem. C 2015, 119, 5203–5210; [6] A. C. Lopez-Selvati, PhD Thesis, 2016