

THESIS TITLE :

Hybrid Nano-Materials Based on Carbon Nanotubes: Elaboration and Study of Their Optical, Electronic and Magnetic Properties

Introduction :

Carbon nanotubes (NT) are tubular structures with nanometer diameter and micrometer length. Since their discovery, there have been extensive researches on these nanomaterials. The one-dimensional structure of single-walled carbon nanotubes renders these materials ideal for optoelectronic applications as they can transport electrons or holes with quasi-ballistic features and as they display optical absorption and near-infrared emission (thanks to van Hove singularities). Furthermore, NT can exhibit metallic or semiconducting character. Therefore, they can be used as promising materials for applications in nano-engineering. In order to make good use of these nanomaterials, it is important to understand and control their physical properties. An efficient way to do that is chromophore encapsulation into host single-walled carbon nanotubes in order to create hybrid nano-systems with tunable optical, electronic and even magnetic properties.

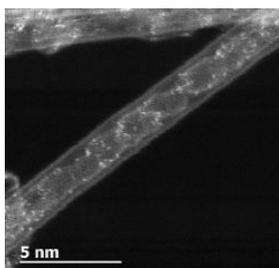


Figure 1: Transmission Electron Microscopy picture of FePc@NT21

Our group, specialized in studies on carbon nanostructures, has recently been interested in the confinement of species such as iodine,¹ quaterthiophene²⁻⁴ or phthalocyanine⁵ molecules (figure 1). Those molecules can absorb from the UV to the red range (700 nm), are either electron donor or acceptor and can display magnetic properties. The physical properties are mainly investigated by Raman and photoluminescence spectroscopies. From Raman measurements, charge transfer from the confined dye to the nanotube can be evidenced. Photoluminescence experiments can demonstrate changes on the emission properties after encapsulation.

The intensities can be increased (Figure 2) or reduced depending on the nature of the confined chromophores (electron donor or acceptor). Therefore, the physical properties can be tuned by molecule confinement into single-walled carbon nanotubes.

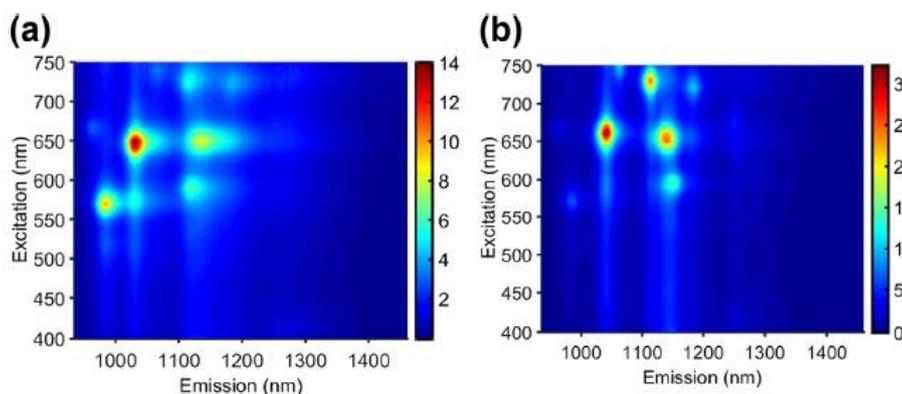


Figure 2: PLE map of empty nanotubes (a) and hybrid systems 4T@NT (b) The scale are not the same for both maps, evidencing a spectacular enhancement of the PL intensity after 4T encapsulation

The main objective of this thesis is the study of the physical properties mainly by Raman and photoluminescence spectroscopies of the different molecules confined into single-walled carbon nanotubes. This involves in particular studying the structural, optical, electronic and the magnetic properties, both at the macroscopic and the

individual scales. Experiments on large-scale facility (ILL, Grenoble, France) are possible. Prior to the study, nano-material synthesis will be done using the vapor phase method.

References:

- (1) Chorro, M.; Kané, G.; Alvarez, L.; Cambedouzou, J.; Paineau, E.; Rossberg, A.; Kociak, M.; Aznar, R.; Pascarelli, S.; Launois, P.; Bantignies, J. L. 1D-Confinement of Polyiodides inside Single-Wall Carbon Nanotubes. *Carbon* **2013**, *52*, 100–108. <https://doi.org/10.1016/j.carbon.2012.09.010>.
- (2) Alvarez, L.; Almadori, Y.; Arenal, R.; Babaa, R.; Michel, T.; Le Parc, R.; Bantignies, J.-L.; Jusselme, B.; Palacin, S.; Hermet, P.; Sauvajol, J.-L. Charge Transfer Evidence between Carbon Nanotubes and Encapsulated Conjugated Oligomers. *The Journal of Physical Chemistry C* **2011**, *115* (24), 11898–11905. <https://doi.org/10.1021/jp1121678>.
- (3) Almadori, Y.; Alvarez, L.; Le Parc, R.; Aznar, R.; Fossard, F.; Loiseau, A.; Jusselme, B.; Campidelli, S.; Hermet, P.; Belhboub, A.; Rahmani, A.; Saito, T.; Bantignies, J.-L. Chromophore Ordering by Confinement into Carbon Nanotubes. *The Journal of Physical Chemistry C* **2014**, *118* (33), 19462–19468. <https://doi.org/10.1021/jp505804d>.
- (4) Alencar, R. S.; Aguiar, A. L.; Ferreira, R. S.; Chambard, R.; Jusselme, B.; Bantignies, J.-L.; Weigel, C.; Clément, S.; Aznar, R.; Machon, D.; Souza Filho, A. G.; San-Miguel, A.; Alvarez, L. Raman Resonance Tuning of Quaterthiophene in Filled Carbon Nanotubes at High Pressures. *Carbon* **2021**, *173*, 163–173. <https://doi.org/10.1016/j.carbon.2020.10.083>.
- (5) Alvarez, L.; Fall, F.; Belhboub, A.; Le Parc, R.; Almadori, Y.; Arenal, R.; Aznar, R.; Dieudonné-George, P.; Hermet, P.; Rahmani, A.; Jusselme, B.; Campidelli, S.; Cambedouzou, J.; Saito, T.; Bantignies, J.-L. One-Dimensional Molecular Crystal of Phthalocyanine Confined into Single-Walled Carbon Nanotubes. *The Journal of Physical Chemistry C* **2015**, *119* (9), 5203–5210. <https://doi.org/10.1021/acs.jpcc.5b00168>.

Scope of the proposed research:

The goal of this thesis is to study the physical interactions taking place in between the confined molecules and the host carbon nanotube and to determine the physical properties of the new smart hybrid nano-systems. The first step will consist in elaborating the hybrid nanotubes. Then, characterization will be mainly performed by Raman and photoluminescence spectroscopies. Preparation of a photo-current device using clean-room technology (photo-lithography, metallic deposition and lift-off) in order to lead photocurrent experiment on encapsulated carbon nanotubes layers. Many other experiments will be performed with collaborating group (Transmission Electron Microscopy with AIST, Japan, x-ray photoemission with faculty of physic, Austria). The experimental work will be supported by calculations performed in collaboration.

Applicant:

This project is adapted for a student with a solid background in photonics, optics or fundamental physics. Prior knowledge of carbon nanotube science is not necessary. The thesis involves substantial experimental work for sample preparation and use of free space optical setup, so skills for experimental work are mandatory. Strong taste for interdisciplinary research and learning new stuff is also essential.

Name of Supervisor :

Laurent Alvarez (laurent.alvarez@umontpellier.fr)