PPSM - Soutenance de thèse

12 Novembre 2013- 14h00

Auditorium D. Chemla (bâtiment de l'institut d'Alembert)

Yuanyuan Liao

Directeur de thèse : Robert Pansu

Co-encadrante : Valérie Génot

«Crystals and Nanoparticles of a BODIPY derivative: spectroscopy and microfluidic precipitation»

During this work, we have addressed two aspects of the properties of the fluorescent organic nanoparticles made of Adambodipy: their spectroscopy and their production with controlled sizes. We have produced micro-crystals (100x10x1µm3) by precipitation in solutions of low supersaturation. We have measured their spectroscopy under microscope in the range 380nm to 900nm. The microcrystals are birefringent and dichroic. By adding polarizers on a microscope we have measured their refraction index along the two neutral axes according to the method of Swanepoel.

We have measured the two absorption spectra along the neutral axis. We have calculated these absorption spectra using the model of the dipolar coupling for Frenkel excitons. The amplitude of this coupling has been estimated according to the classic model. But for two particular pairs of the cell, we have compared this estimation with the value that can be deduced from the quantum calculation of a dimer by TDDFT.

The calculated spectra reproduce the dichroism, the spectral broadening of the absorption spectra but not the experimental peak shape probably because our micro-spectrophotometer levels up at high absorbance. The calculated fluorescence spectra predict a polarized transition along the b direction of the cell. The experiment shows two other red shifted bands. The study of their polarization, as well as their fluorescence lifetime allows us to attribute them to defects in the crystal. The spectra of the nanoparticles produced in the second part of this work are not those of crystals. We have been able to reproduce them theoretically by introducing an orientation disorder inside the periodic structure.

The 3D hydrodynamic focusing enables us to produce nanoparticles with controlled size without precipitation of Adambodipy on the wall. We have used the PDMS technology and we the moved to a glass tube approach, in order to avoid the diffusion of fluorescence into the PDMS. By adjusting the flow ratio between the inner organic solution of the dye and outer aqueous solution, we can control the size of the nanoparticle between 100nm and 300nm. The stability of the colloidal suspension is maintained by the surfactant CTACl below the CMC. Indeed above the CMC, the nanoparticles exist together with dyes dispersed in micelles.

We have simulated using COMSOL the precipitation of the nanoparticles. We have introduced in the calculation the hydrodynamic and mutual diffusion of water and ethanol, as well as the diffusion of the Adambodipy. From our studies of the solubility of Adambodipy in water/ethanol mixtures, we have obtained the saturation curve and we have built the supersaturation maps in the micro-device. We have used Fluorescence lifetime imaging microscopy to follow in situ the precipitation process. From the decay collected in different positions can be attributed to the coexistence of three species: the monomers, the nanoparticles and an intermediate species supposed to be the nuclei. The FLIM shows a precipitation in the diffusion area of the two solvents as well as a massive precipitation after a few hundred of millisecond. The FLIM images are very close to the COMSOL predictions.

PPSM
ENS Cachan – 61 avenue du Président Wilson
94235 Cachan Cedex – France
Tél : *+33 1 47 40 53 38 –* ***Fax :*** *+33 1 47 40 24 54*
e-mail : *ahusson@ppsm.ens-cachan.fr*
site web : *http://www.ppsm.ens-cachan.fr*