PhD Thesis Proposal Form
China Scholarship Council (CSC)

FIELD
Chemistry

Thesis subject title : **Self-assembled Semiconducting Nano-Platelets for Opto-Electronic Applications**

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- Thesis proposal (max 1500 words):

Colloidal nanocrystals are thought to be a cheap viable alternative to epitaxy grown III-V semiconductor compounds. These nanoparticles are synthesized in solution and offer several advantages such as low cost, solution processability and easy deposition on large scale, potentially flexible, substrates. However, their outstanding size dependent physical properties will be beneficial for real-world applications only if it is possible to orient them one with respect to each other with a long range positional and orientational order. This challenge is all the more crucial in the case of anisotropic nanoparticles since their coupling and interactions are strongly orientation dependent. We want to address this challenge in the case of colloidal semiconducting nanoplatelets (NPL), a new class of particles with potentially game-changing optical properties that have recently emerged (figure 1.A.)
These nanoparticles are the two-dimensional equivalent of quantum dots with far superior optical properties. Since quantum confinement occurs only along the dimension perpendicular to their atomically controlled thickness, the excitonic features are extremely sharp. In the case of CdSe, large binding energies provide these NPL with outstanding optical properties such as giant oscillator strength, very fast recombination rates and large cross sections. A key feature is the ultra-fast Forster Resonance Energy Transfer (FRET) occurring at the nanoscale between NPL. FRET is particularly fast in the case of nanoplatelets and, more importantly, it is faster than Auger recombination which plagues quantum dots performances in devices Hence, whereas biexcitons usually recombine in 50 to 100 ps in a non-radiative fashion, FRET occurs at the pico-second timescale in NPL. This opens up interesting perspectives in engineering exciton flow in assemblies of NPL (figure 1.B.). Recently, continuous wave room temperature lasing has been demonstrated in NPL and very low lasing

threshold achieved without the self-assembly being optimized To sum-up, NPL are an extremely promising system with already demonstrated applicative relevance. **However, for mastering the FRET-assisted exciton flow, organizing these NPL orderly in a three-dimensional fashion remains the main road-block. FRET is a near field energy transfer which depends strongly on the orientation of the transition dipole between the donor and the acceptor and on the distance between them. Hence, the spatial organization of the interacting particle is decisive.**
Previously, we have shown that it was possible to obtain larger structures composed of stacked NPL through a delicate control of the interaction between NPL. However, these original polymer-like structures (figure 1.C.) are made of only one type of NPL and only face-to-face stacking was achieved. We want to build on these first results to expand the self-assembled structures library made with these building blocks. For example, we would like to produce binary assemblies alternating two different types of NPL with different thicknesses in order to enhance the FRET exchange between donor and acceptor NPL. Edge to edge tiling in monolayers would be of interest for device scale self-assembly (figure 1.D).
The objective of this thesis proposal is to produce three dimensional assemblies composed of one or two types of NPL where the position and orientation of the particles are precisely tuned. The optical properties of these assemblies will be studied in the perspective of their adoption in optoelectronic devices.

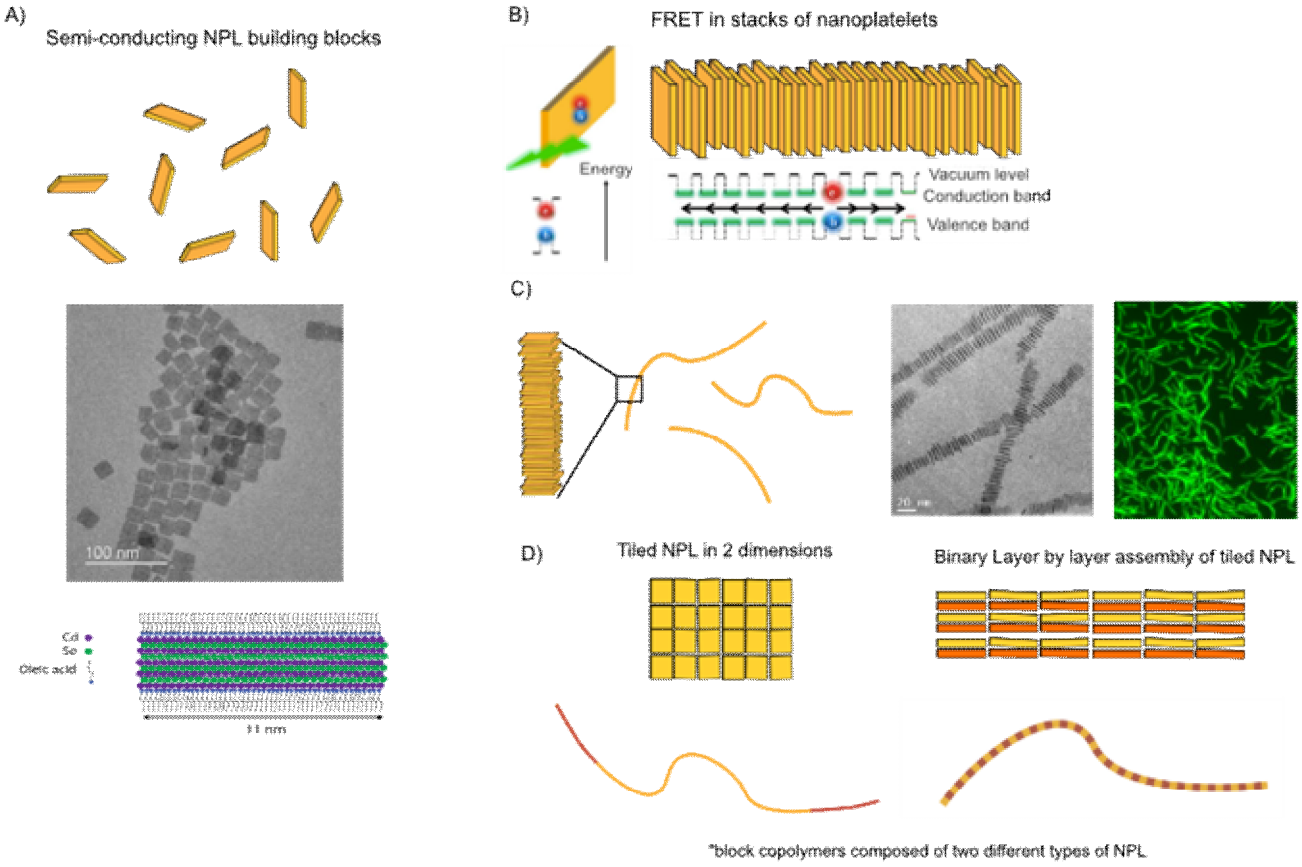

Figure 1: A) Semi-conducting Nanoplatelets: schematic representation of their orientation in solution, TEM image, atomic structure with the ligand brush at the surface. B) FRET and excitonic flow in stacks of nanoplatelets following the absorption of a photon, C) previous results of the PI on the self-assembly of NPL into living polymer \cite{jana_cdse_2016}. D) target self-assembled structures which will be studied in this proposal. The two colors represent two sorts of NPL with different emission properties.

Our previous experience and an extensive review of the literature make us hypothesize that this challenge can be overcome if two main bolts are unlocked. First, the interaction between nanoparticles at the nanoscale differs significantly from their colloidal micron-size counterpart We speculate, in line with recent simulations that they are dominated by ligand-ligand interactions which make their functionalization pivotal. Second, self-assembly in these nanoscale systems is an out-of-

equilibrium process and trapped kinetically stable states can subsist over experimentally observable time-scales. This necessitates monitoring of all the steps from the synthesis to the self-assembly using adapted techniques and particular consideration of drying and/or destabilizing kinetics.
With these issues in mind, we will carry out this research program in four intertwined steps: 1) synthesis and purification of well-defined colloidal NPL with controlled thickness, lateral dimensions and surface functionalization. Two different systems will be studied. First, CdSe NPL on which we already have obtained results. Second, perovskite NPL show great promises and are amenable to the same research framework. We will particularly investigate the surface chemistry and the ligand organization at the surface. 2) Thermodynamic study of the interaction between NPL using colloidal stability studies, osmotic pressure measurement and light/X-ray scattering measurements. 3) Out-of-equilibrium self-assembly of the NPL using various strategies such as microfluidics evaporation, layer-by-layer assembly at liquid-air interface. We will use *in situ* synchrotron based techniques and electron/optical microscopy to assess the self-assembly in real time. 4) Optical properties of the assemblies. We will measure the fluorescent lifetime and emission spectra of the assemblies as a function of their shape/composition and spatial arrangement. The lasing thresholds of the obtained material will also be investigated.
We have designed the project so that it presents an overall low level of risk. Since previous results have already been obtained on the self-assembly of CdSe NPL, step 4 on the optical properties can be started at the beginning of the project without the risk that well-defined assemblies are never obtained. The main risk is that the optical properties are not much affected by the self-assembly but we believe that this prediction stands on physical arguments sound enough for these issues to be investigated. Finally, the fact that we will investigate two systems (CdSe and perovskites) with different degrees of maturation lowers the risk of the project but also magnifies the potential impact.

- Publications of the laboratory in the field (max 5):

1. S. Jana, P. Davidson, B. Abécassis CdSe Nanoplatelets living polymers ***Angew. Chem. Int. Ed.*** 55(32), 9371-9374, 2016

2. B. Abécassis. Three-dimensional self assembly of semi-conducting colloidal nanocrystals: from fundamental forces to collective optical properties**.,** ***ChemPhysChem*** (invited mini-review), 17, 5, 618ï 631, 2016.

3 Real Time in situ probing of high temperature quantum dots solution synthesis
B. Abécassis, C. Bouet, C. Garnero, D. Constantin, N. Lequeux, S. Ithurria, B. Dubertret, B. R. Pauw, D. Pontoni. ***Nano Letters***, 15, 2620, 2015

4. S. Jana, T. Phan, C. Bouet, M.D. Tessier, P. Davidson, B. Dubertret, B. Abécassis, Stacking and colloidal stability of CdSe nanoplatelets, ***Langmuir***, 31, 10532ï 10539, 2015.

5. B. Abécassis, M.D. Tessier, P. Davidson and B. Dubertret, / Self-assembly of CdSe nanoplatelets into giant micromete-scale needls emitting polarized light, ***Nano Letters***, 14, 710-715, 2014.

- Joint Phd (cotutelle) : NO
- Co-directed PhD : NO

- Interest of the Joint Phd for the French codirector, for his/her laboratory, for ENS de Lyon.
  The proposed PhD subject is of great interest for the French codirector and more broadly for his laboratory and ENS Lyon. As a matter of fact, the supervisor has arrived recently (September 2016) in ENS Lyon, after having passed his habilitation thesis and is setting up a research team dedicated to semiconductor nanocrystals with two main aspects: their self-assembly into larger scale superstructures and the elucidation of their formation mechanism using in situ techniques. The PhD subject deals with the first priority and will enable the supervisor to start this new theme in ENS Lyon. This PhD funding is thus a great opportunity to give momentum to the start of this new research direction within the materials group in the Laboratoire de Chimie. Also, this research proposal will bring together three scientists who arrived recently at the Laboratoire de Chimie in ENS-Lyon (B Abécassis, N. Lascoux who will be in charge of the optical characterization and A. Désert who will take the lasing part of the project in charge) and hence facilitate their integration through working together on an innovative research program. The project will bring together new semi-conducting nanomaterials with outstanding optical properties, the experience of the PI in the self-assembly of these systems and the expertise of the group in the optical properties of functional materials.

Date : 30/01/2017

Signature of the PhD director | Name and signature of the Laboratory director

Benjamin Abécassis