Spatiotemporal Study of Exciton Transport in Oriented Nanocrystal Arrays

iMAT 2023 AAP - Doctoral Research Project Proposal

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2A) SCIENTIFIC CONTEXT OF PROJECT

AIM

The aim of this iMAT PhD project is to reveal fundamental structure–property relationships between the dimensionality of nanocrystal arrays and exciton transport and how it connects to macro-scale optoelectronic device functionality. The approach here is to spatiotemporally probe microscopic exciton transport properties in an advanced nanocrystal-based optoelectronic device configuration that features directed exciton transport. This project combines state-of-the-art topologically-driven assembly of ordered and oriented nanocrystals coupled by conductive ligands with an advanced pump-probe optical microscopy and numerical modeling.

The project consists of four stages that are expected to be feasible in the timeframe of a PhD student:

1. **Finalize a pump-probe optical scattering microscope** capable of spatiotemporally measuring photoexcited exciton transport at microscopic length scales in optoelectronic materials.
2. Optimize the **liquid crystal topology-driven assembly of semiconducting colloidal nanocrystals coupled by conductive ligands** to be suitable for optical microscopy and exciton transport studies**.**
3. Understand the **relationship between array dimensionality and anisotropic exciton transport**.
4. Control **local transport behavior under applied bias** in the ordered nanocrystal arrays.

This project fits both thematic axes of the iMAT AAP 2023: “Défis et Recherche Fondamentale” and “Méthodes, Techniques, Innovation.” Specifically, we will build an **advanced spatiotemporal optical** setup, apply it to **exciton dynamics** in **topologically-induced anisotropic material depositions** in **novel optoelectronic device configurations**, and model transport by **finite element simulations**.

CONTEXT

Motivation. Achieving switchable, directed exciton and phonon transport could revolutionize optoelectronics and phonon logic (Fig 1), but tailored anisotropic transport and dynamic tunability on device-relevant scales remain challenging. Devices made from next-generation materials such as colloidal semiconductor nanocrystals (NCs) are particularly attractive; they offer a cost-effective alternative to epitaxially-grown materials, broad tunability,[1] and enable bottom-up design of hierarchical structures.[2] **It is important to develop controlled assembly of coupled NC arrays to control transport and to simultaneously develop spectroscopic methods that probe the microscopic exciton dynamics to uncover structure–function properties.**

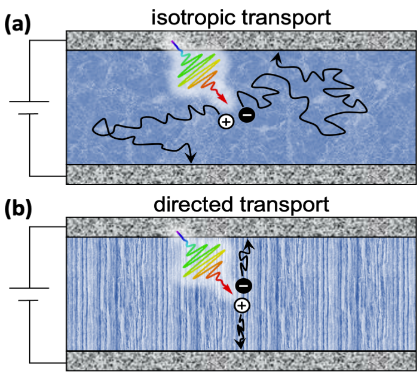

Fig 1. *Cartoon of enhanced efficiency in optoelectronics via directed transport.*

Open Questions. In optoelectronic devices made from solution-processed NCs, isotropic energy transport in self assembled films has been well characterized,[3–5] but several fundamental questions remain about transport in more advanced hierarchical structures. **How do anisotropic assembly and the dimensionality of the NC array impact the exciton transport? Under applied electrical bias in a working optoelectronic device, how does the electric field impact microscopic transport?**

Technical challenge. Probing local exciton dynamics in nanocrystalline materials by optical microscopy (expertise of PI Utterback, INSP) has become well established,[3,6] yet previous studies featured disordered 3D films with insulating ligands. Recently, project PI Lacaze (INSP) used topological defects in liquid crystals as scaffolding to direct NC assembly and achieved several-µm sized ordered and oriented arrays.[7] Moreover, Sosa-Vargas (IPMC) has achieved enhanced electronic coupling in such systems using specially tailored aromatic ligands, in contrast to the typical surface properties of as-synthesized NCs.[11] Spatiotemporal microscopy combined with finite element simulations offers the ideal approach to probe and understand the anisotropic transport within these coupled, ordered and oriented arrays with unprecedented microscopic detail.

SCIENTIFIC APPROACH

We chose to focus on PbS NCs as a model system as they have been widely studied for optoelectronic devices,[8] their self-assembly protocols are understood,[2,3] and exciton hopping in 3D films has been well studied by ultrafast microscopies.[3] Yet microscopic performance bottlenecks in devices remain unclear.

Pump-probe microscopy technique. The principal technique used in this project is stroboscopic optical scattering (stroboSCAT) microscopy. This technique uses a focused pump light pulse and a delayed wide-field probe light pulse to visualize the spatiotemporal evolution of a localized excited population profile through refractive index perturbations (Fig 2). The key observable is the lateral expansion of the exciton profile that yields local transport parameters. A few labs (including work by **PI Utterback**, **INSP**) have demonstrated few-nm "sensitivity" of carrier transport and simultaneous wide-field imaging of sample structure.[4,5,9] After finishing building the setup recently started by Utterback at INSP, the technique will be benchmarked and optimized using single crystal silicon that is well understood.[9]

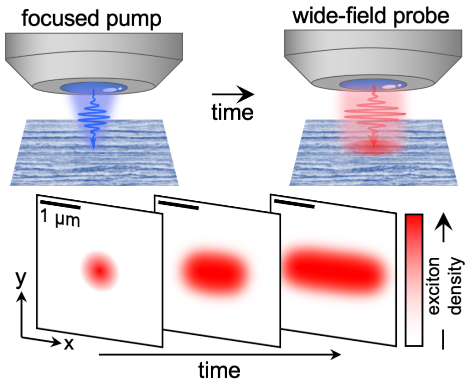

Fig 2. Schematic diagram of stroboSCAT experiment and resulting data of anisotropic exciton distribution expansion.

Assembly of oriented superlattices. Anisotropic assembly of PbS NCs functionalized with semiconducting ligands will be driven by topological defects of liquid crystals. **PI Lacaze (INSP)** previously showed that smectic patterns of 4-n-octyl-4'-cyanobiphenyl (8CB) in presence of ~6 nm gold nanospheres lead to *ordered* and *oriented* 1D NC arrays confined in the linear dislocations and 2D arrays of oriented hexagonally-packed NCs in the ribbon-like grain boundaries (Fig 3).[10] We will assemble such liquid crystal-driven PbS NC arrays on coverslips amenable to optical microscopy. **Sosa-Vargas (IPCM)** will provide aromatic ligands for the NCs that enable the exciton transport by lowering the tunneling barrier compared to the native ligands (Fig 4).[11] Control samples of 3D NC films will be achieved by previously established dropcasting.

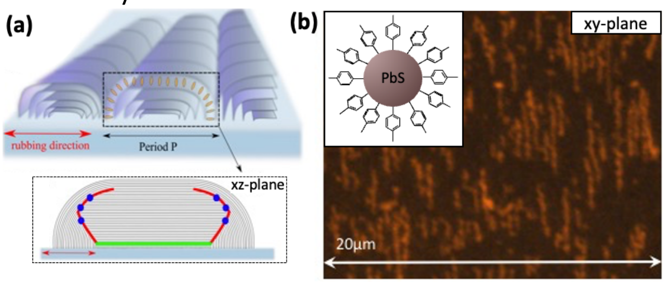

Fig 3. (a) Model of patterns where smectic layers are superimposed and include 1D dislocations (blue) and 2D ribbon-like grain boundaries (green). (b) Ribbons of fluorescent nanocrystals in 8CB 1D patterns on several µm scale.

Impact of dimensionality on anisotropic exciton transport. We will track the lateral spatiotemporal evolution of a photoexcited exciton profile as a function of NC array dimensionality for 1D, 2D and 3D assemblies (Fig 4). We will probe local anisotropy through orientation-dependent mean-squared displacement (Fig 2), correlating to local structure by optical microscopy, AFM and GISAXS.[7,12] Combined with finite element simulations supervised by **Connolly (GeePs)**, we will build a picture of the microscopic parameters that determine excitonic transport anisotropy.[13]

Impact of electric field on directed transport. Finally, we will study the impact of an applied electric field on directed transport in optoelectronic device configurations by performing the same assembly on commercial substrates that have interdigitated electrodes. Preliminary work by PI Lacaze has already demonstrated this fabrication capability. We will track the lateral spatiotemporal evolution of a photoexcited carrier profile driven by an electric field along the NC arrays of varying dimensionality. Device-level current–voltage characteristics will be measured using a source–probe over the course of experiments to correlate microscopic transport to macroscopic current.

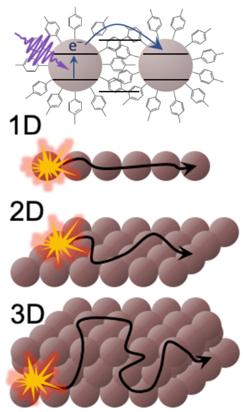

Figure 4. Carrier hopping between NCs and transport vs. dimensionality.

RISKS & FEASIBILITY

This proposal has been designed with the timeline of a single PhD student in mind. The ability of stroboSCAT (expertise of Utterback) to probe carriers in disordered NC films has already been established, and Lacaze and Sosa-Vargas have already obtained oriented assemblies of similar semiconducting NCs with conductive ligands that reach ~10 µm in length. We are thus confident in the ability to assemble oriented PbS NC arrays and to probe their microscopic exciton transport properties. Worst case scenario, this first series of studies alone could constitute a PhD. If the integration of electrodes hinders project's final stage, we will seek collaboration with experts in device fabrication within l'Alliance SU (e.g., Lhuillier at INSP). Alternatively, the semiconducting NCs could be replaced with metallic ones to also study anisotropic thermal transport—another interest of PI Utterback.[4]

SKILLS AND COHERENCE OF TEAM

The proposed project uniquely combines expertise in NC functionalization (**Sosa-Vargas, IPCM**), directed NC assembly (**Lacaze, INSP**), optical microscopy and spectroscopy (**Utterback, just hired at INSP**), and finite element simulations (**Connolly, GeePs**). These advanced skills are normally found in separate fields, but the nature of the scientific questions motivates the first-time collaboration between the PI's of this project. In more detail, Utterback (INSP) has ample experience[4] with the advanced pump-probe microscopy technique stroboSCAT that is to be the basis of the project—a technique performed in only a few labs in the world. Lacaze (INSP) is the leading expert in liquid crystal-driven assembly of NCs and has ample expertise characterizing their structure by GISAXS.[7,12] NCs will be provided by Yoann Prado (IE-INSP). NC functionalization with state-of-the-art conductive ligands is the experience of Sosa-Vargas (IPCM). Connolly (GeePs) is an expert in finite element simulations of transport in optoelectronics, focusing on photovoltaic devices.

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2b) RESEARCH PLAN AND PROVISIONAL CALENDAR

The ***first year*** will consist of finishing and optimizing the stroboSCAT instrument at INSP—Utterback has separate funds for the technique's components (CNRS DIALOG) and has begun building. The design of the microscope is based closely on the original version at UC Berkeley that Utterback has experience on.[4,9] After the student completes the setup, it will benchmarked by applying it to measure the charge diffusion coefficient in silicon wafers and simple NC films that have been well studied in the past.[3,4,9] In parallel, the student will be guided by Sosa Vargas to prepare the NCs with conductive ligands, and by Lacaze to adapt the fabrication procedure of liquid crystal-embedded NC arrays on substrates of microscope slides that are appropriate for optical microscopy. The assembly of oriented arrays will be verified using combined optical microscopy and synchrotron-based GISAXS (Lacaze's experience).

During the ***second year*** the PhD student will perform stroboSCAT measurements on anisotropic arrays of PbS NCs in liquid crystal matrices to directly access local exciton transport properties. They will explore the impact of dimensionality on exciton transport by studying 1D and 2D oriented arrays and 3D arrays. The student will be guided by Connolly to model the transport using SILVACO.

In ***third year*** of the project the student will build off of the work of the second year and move on to the more ambitious sample geometry feature interdigitated electrodes. If the direction of interdigitated electrodes fails too close to the end of the PhD timeline, then the student will return to the system of oriented low-dimensional arrays, but replace the PbS NCs with metal particles (e.g., Au) to study the anisotropic thermal properties of the system—another feasible and rich direction.