

Campagne 2020 Contrats Doctoraux Instituts/Initiatives

Proposition de Projet de Recherche Doctoral (PRD)

Appel à projet IMat - Institut des Matériaux 2020

Intitulé du Projet de Recherche Doctoral : A Radical Approach to New Organic Light-Harvesting Molecular Materials (RadMolMat)

Directeur de Thèse porteur du projet (titulaire d'une HDR) :

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Unité de Recherche :

Intitulé : Institut Parisien de Chimie Moléculaire (IPCM), Equipe Chimie des Polymères (ECP)
Code (ex. UMR xxxx) : UMR CNRS 8232

ED397-Physique Chimie des Matériaux

Ecole Doctorale de rattachement de l'équipe & d'inscription du doctorant :

Doctorants actuellement encadrés par le directeur de thèse (préciser le nombre de doctorants, leur année de 1^{ere} inscription et la quotité d'encadrement) : 4 co-encadrements de thèse ; 3 Doctorants co-encadrés à 50% actuellement et financés par le CSC : 1 étudiant (Dizheng LIU, Oct. 2016 - Sept. 2020) qui finit + 2 à mi-parcours (Weiwei DU et Haixia LI, Sept. 2018 - Oct. 2022) ; 1 autre doctorant co-encadré à 50% via une bourse du Ministère (Quentin FERNIEZ, oct. 2018 - Nov. 2021).

Co-encadrant :

NOM : **BARISIEN** Prénom : **Thierry**
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Unité de Recherche :

Intitulé : Institut des NanoSciences de Paris (INSP), Equipe Photonique et Cohérence de Spin (PHOCOS)
Code (ex. UMR xxxx) : UMR CNRS 7588

ED564-Physique en IdF

Ecole Doctorale de rattachement : Ou si ED non Alliance SU :

Doctorants actuellement encadrés par le co-directeur de thèse (préciser le nombre de doctorants, leur année de 1^{ere} inscription et la quotité d'encadrement) : 1 étudiante de thèse co-encadrée à 50% (Violette Steinmetz, Oct. 2017 - Sept. 2020).

Cotutelle internationale : Non Oui, précisez Pays et Université :

Description du projet de recherche doctoral (en français ou en anglais)

3 pages maximum – interligne simple – Ce texte sera diffusé en ligne

Proposal's context, positioning and objective(s) :

The global aim of this project is to design, synthesize, probe and understand the electronic properties of a new class of organic polymers with potentially disruptive applications in next-generation light-harvesting materials. By exploiting a unique combination of advanced solid-state chemistry, single molecule quantum optics and time-resolved microscopy, we aim to generate fundamental insights into the ultrafast (fs-ns) quantum mechanical processes that govern light absorption, transport and conversion of energy over nm- μ m length scales in 1D polydiacetylenes (PDAs) [1].

Addressing both important synthesis problematics and outstanding theoretical questions about how excitons and correlated fermions move and interact in low dimensional, under-screened organic (macro)molecular materials [1], the project will also introduce new ways to “manipulate the spins”, opening a route to rationally design a new series of efficient light-harvesting organic materials for desired energy applications, even via harnessing non-classical processes [2].

More precisely, this project will study a new class of topochemically polymerized polydiacetylenes (t-PDAs), i.e. organic semiconductors formed by the in-situ polymerization of diacetylene (DA) monomers in their well-ordered molecular crystals (Fig. 1a-b) [3]. Unlike solution-processed polymer phases whose strong conformational and optoelectronic disorder is the source of many deleterious processes in organic light harvesting devices, topochemical polymerization produces perfectly ordered 1D, pi-conjugated PDAs with electronic (excitonic) properties that can become coherently delocalized over 10s of microns in less than a picosecond after photon absorption (c.f. exciton diffusion lengths of just 1-2nm in typical organic photovoltaic materials) [4]. These outstanding properties were first observed at INSP in 3BMCU-PDAs that are since suggested as ideal structures for exploring how quantum coherent phenomena could lead to more efficient organic semiconductor devices [1,2]. This project takes up this challenge by :

- (1) Synthesizing the first-ever PDAs designed to interact strongly with stable radical groups that will introduce magnetic exchange phenomena into the rich excitonic photophysics of t-PDAs.
- (2) Introducing/developing new methods to resolve ultrafast, single-molecule optics in real-space with unprecedented spatio-temporal resolution.

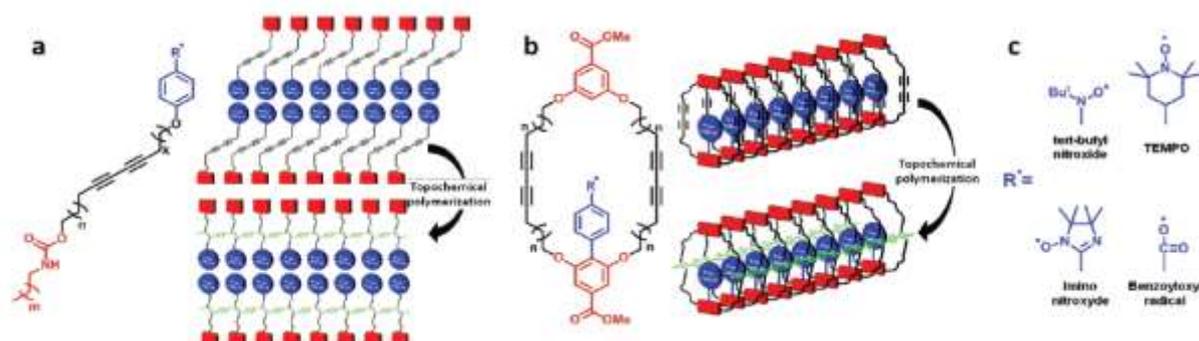


Figure 1 (a) Rod-like DA monomers, multilamellar self-assembly and chain orientation after polymerization. Chain-radical distances controlled by varying “k” repeats in the monomers. (b) Cyclic DA monomer, tubular self-assembly and chain-radical topology after polymerization. Monomer diameters controlled through “n” repeat groups. (c) the stable organic radicals that will be incorporated into the monomers.

Indeed, incorporating organic radicals such as TEMPO (see Fig. 1c), can lead to dramatic effects in small pi-conjugated molecules, including a 100x increase in singlet-to-triplet exciton transition rates [5], an enhanced triplet photon emission and triplet-triplet up-conversion [6], and a linker-dependent triplet deactivation with radical spin polarisation [7]. Engineering “bright triplets » with tunable emission wavelengths would thus be advantageous to reduce loss channels for LEDs and photovoltaics (PVs) [8]. Up-conversion (triplet fusion) could also convert the low energy solar spectrum into wavelengths suitable for PVs [6,9]. However, the effect of exciton/radical interactions on the photophysics of macroscopically extended and defect-free organic semiconductors has yet to be studied.

To sum-up, this project will allow to design and synthesize novel t-PDA structures to investigate spin and magnetic phenomena in extended 1D PDAs, exploring the novel condensed matter behaviors associated with their correlated electronic properties and the possibility of emergent collective effects due to the presence of 1D arrays of radicals next to the PDA chains (magnetism, spin waves, charge density waves). The possibility of magnetic ordering of radicals in the PDA ground state [10], and its manipulation due to strong coupling to optically excited excitons could have applications in ultrafast information storage and processing [11]. Finally, these new extended radical-containing PDA systems should permit the study in unprecedented detail of multiple (many body) excitations and in single chains, which is especially important for improving organic PVs understandings through multiple-exciton generation (singlet fission) [12] and crucial dynamics (binding/separation/ annihilation/spin-dependence) [13].

Skills, Role and Complementarity of the 2 partners :

To achieve these ambitious goals, our complementary consortium provides both complex multi-step synthesis skills at molecular and polymer levels (partner 1) and state-of-the-art theoretical/experimental tools to probe the opto-electronic properties of such materials (partner 2).

Task 1, partner 1, IPCM (D. Kreher, L. Sosa-Vargas, PhD Student to be hired) : Multi-steps synthesis and Self-assembly, photo-polymerization. Dr. D. Kreher will coordinate the project. Together with his colleagues, they have ample experience in the design and synthesis of functional pi-conjugated (macro)molecular materials for opto-electronic applications, in particular 2D and 3D self-organized materials [14]. They will be in charge of the synthesis and characterization of the new radical-containing PDAs. Two novel types of polymer architecture will be fabricated, (1) multilamellar structures and (2) tubular stacks. (1) will be obtained with rod-like diacetylene monomers designed to combine different functional moieties such as free radical, diacetylene and H-bonding units (Fig.1a). Solid-state self-assembly by nano-segregation and hydrogen bonding interactions of such multifunctional elongated molecules drives a multilamellar organization of separate and alternate sublayers of each moiety (Fig. 1a) [15]. The PDA chains will be then obtained by topochemical polymerization of diacetylene units under UV irradiation, creating PDA chains atomically close to a double layer of free radical moieties (Fig. 1a). Importantly, the distance between the free radicals and the polymer chains can be controlled by tuning the spacer length between the diacetylene and radical units in the monomers ('k' in Fig. 1a), allowing a fundamental investigation of the typical length scales of radical/magnetic interactions with the PDA's ground and excited states. Structure (2) will be obtained from cyclic diacetylene monomers containing functional moieties such as free radical, diacetylene and pi-pi stacking units (Figure 1b). Self-assembly under classical noncovalent molecular interactions then leads to supramolecular nanotubes of stacked macrocycles [16], filled by the radical units (Fig. 1b). Topochemical polymerization consequently creates tubular PDA structures (Fig. 1b) where the distance between the free radicals and the polymer chains could be also adjusted by modifying the diameter of the nanotube through tuning the alkyl spacer length separating the diacetylene and pi-pi stacking units (Fig. 1b). Architectures without radical moieties will provide control investigations of purely 'dipolar' interchain energy transfer. The different radical units we will investigate first are shown in Fig. 1c.

Task 2, partner 2, INSP (T. Barisien, A-W. Chin, L. Laurent, PhD Student to be hired): Characterization of the optical and electronic properties of such Materials with new spectroscopy techniques. Dr Thierry Barisien and co-workers have a recognized record of achievements related to theoretical studies and optical spectroscopy of nano-objects (μ -PL, magneto-optics, cryogenic measurements) [8,18], including the first observations of ultrafast μ m-scale coherence and quantum control of luminescence in 3BMCU-PDAs [4,19]. Samples will be prepared as macrocrystals (grown in solution), evaporated monolayered films (oriented through graphoepitaxy [16]), or ultrathin monocrystalline films ($e < 1 \mu\text{m}$, domains area $> \text{mm}^2$) obtained by a recrystallisation technique newly developed by

IPCM (to be published). Thus, following protocols established by INSP's experience with PDAs, reactivity of the monomer assemblies will be probed by exposure of crystals to UV rays and calibrated, using classical absorption spectroscopy, in order to be able to finely adjust the chain density inside the host matrix [16,4]. Luminescence, dichroism, and ultrafast time resolved photoinduced absorption will then allow the evaluation of the crystal quality and provide insights into the excited states structure and dynamics of the chains [17], a prerequisite for the more advanced real-space spectroscopic studies planned. Low temperature transport properties of PDA excitons will also be measured by using a novel approach, excitonic wave packet dynamics being spatially probed in single polymer wires with sub-ps resolution, by using a tightly focused laser pulse. By varying the delay, relative phase and relative position between the probe and generating (pump) pulses, the spatio-temporal dynamics of the wave packet will be unravelled. This type of "scanning" pump-probe with spatially separated excitation and detection has not been implemented before in organic crystals, and is only possible here because of the size of the t-PDAs and high quality films. INSP has also constructed a new magneto-optic cryostat platform that allows single PDA microscopy (μ -luminescence) to be conducted between 3K-300K in B fields from 0-5T. This capability will be instrumental for studying the spin ordering and macroscopic magnetic properties of our new PDA-radical systems.

Adequation with IMAT :

This project is therefore fully in line with the major scientific, industrial and societal challenges of Materials Science, at the interface of chemical engineering and physics, on a subject combining challenges both in optimized syntheses (theme 2) and concerning energy-related issues (topic 2). In addition, this project is completely original, transdisciplinary and at odds with what is currently being watched internationally. This might seem like a risk, but it is a measured risk because of the expertise of the two partners involved who have been maturing this research initiative for several months already, waiting only for financial support and recruitment to initiate this innovative project.

Expected profile of the student :

We are seeking a highly motivated, curious and dynamic student with strong synthetic skills in organic and polymer chemistry, as well as in physics ideally. Good communication skills are required as well, as we are a multicultural, multilingual laboratory.

References related to the project (entries in red denote articles from our consortium) :

[1] Scholes et al., *Nature* 543, 647 (2017); **Gellinas et al., *Science* , 343, 6170, 512 (2014)** ;[2] Bredas et al., *Nature Materials* 16, 35 (2017); Romer et al., *Nature Physics*, 10, 676 (2014); Scholes et al., *Nature Chemistry*, 3, 763 (2011); [3] : Schott, *J. Phys. Chem. B*, 110, 32, 15864 (2006); [4] **Dubin et al., *Nature Physics*, 2, 32–35 (2006)**; [5] Ito et al., *Angew. Chem.*, 53,1 (2014); [6] Han et al., *J. Phys. Chem. Lett.*, 8, 5865, (2017); [7] Chernick et al., *J. Am. Chem. Soc.*, 137, 857 (2015); [8] Becker et al., *Nature*, 553,189 (2018); **J. Ramade et al., *Nanoscale* 10, 6393 (2018)** ; [9] Kerzig and Wenger, *Chem. Sci.*, 9, 6670 (2018); [10] Arantes et al., *J. Phys. Chem. C*, 120, 3289 (2016); Tyutyulkov et al., *Synthetic Metals*, 52, 71, (1992); [11] Mangin et al., *Nature Materials*, 13, 286 (2014); [12] Michl and Smith, *Chem. Rev.*, 110, 6891 (2010); **Bakulin et al., *Nature Chemistry* 8,16 (2016)**; [13] **Bayliss et al. *Phys. Rev. B*, 94, 4, 1 (2016)**; [14] **L. Mazur et al., *Organic Electronics*, 15, 943 (2014)**; **D. Zeng et al., *Macromolecules*, 47, 1715 (2014)**; **Y. M. Xiao et al., *Polymer Journal*, 49, 31 (2017)**; **Tahar Djebbar, et al., *Chem. Mater.*, 23, 4653 (2011)**; **D. Zheng, et al., *Macromolecules*, 47, 1715 (2014)**; **K. J. Lee, et al., *Nature Materials*, 16, 722 (2017)**; **Y. Xiao, et al., *Polymer J.*, 49, 31 (2011)**. [15] Heo et al., *Macromolecules*, 50 , 3, 900 (2017); [16] T. Barisien et al., *Phys. Chem. Chem. Phys.* 18, 12928 (2016) ; [17] Turki et al., *J. Chem. Phys.*, 112, 10526 (2000) [18] Chin et al., *Nature Physics* 9,113 (2013); *Phys. Rev. B*, 93, 7, 075105; (2016); *ArXiv: 1710.01362* (2018); [19] S.A. Zargaleh et al., *Phys. Rev. B* 94, 060102 (2016) ; Holcman et al. *Nano Lett.*, 11, 4496 (2011).