Position title: PhD in organic chemistry on material synthesis for thermoelectricity

Characteristics of the Position:

Functions/ features	Doctoral student
Employment type (referens III)	PhD
Category	Organic chemistry
Body	ISP SyMMES
Quotas	100%

Assignment: This PhD. will be in cotutelle between the UMR SyMMES 5819 CEA-CNRS-UGA (Système Moléculaire et nanoMatériaux en Energie et Santé), in the STEP laboratory in Grenoble, France (50%) and in the Chemistry Department from Université Laval, Québec, Canada (50%).

Context and Work Environment

Structure description

On the French side, the SyMMES laboratory aims to develop basic research on themes with strong societal issue: zero-carbon energy, information and communications technology (ICT), biotechnology and human health. The SyMMES explores the design, synthesis and study of architectures and innovative and original functional materials for energy applications. The laboratory is also interested in the reactivity and properties of biomolecules, providing a novel approach to biological questions. The SyMMES hosts around 50 researchers and about sixty non-permanent researchers (students, PhD students and post-doctoral students). In the SyMMES unit, the STEP laboratory is an interdisciplinary team comprising chemists, physico-chemists, electrochemists and physicists. The lab objectives are focused on the control of molecular architectures and complex functionalities, the design of novel performing materials as well as the description and understanding of their physical phenomena at all pertinent length scales.

The main activities are related to the chemical synthesis and the studies of (macro-) molecules (π-conjugated or ionic oligomers and polymers) and nanomaterials (semiconductor nanocrystals and nanowires). These materials are used as the active layer or contact/electrode in (opto-) electronic devices, electrolytes for energy conversion and storage, electrodes for next generation batteries and sensors. The main domains of applications aimed are the new energy technologies (photovoltaics, electrochemical energy conversion and storage, thermoelectrics), organic electronics as well as healthcare and environmental technologies.

On the Canadian side, Pr. Jean-François Morin is a chemistry Professor and Director of the Center for Advanced Materials Research (CERMA). He leads his research group towards the development of new methodologies for the synthesis of organic (semiconductors) and carbon (nanotubes, graphene) nanomaterials. The strategies are oriented towards resolution of problems generally associated with classical synthesis methods towards complex nanostructures. Projects involving both synthesis and characterization are developed.

Team description (N+1 and colleagues): under the authority of Peter Reiss Team composed of 20 agents (15 researchers, 5 technicians and research engineers)

The candidate will be under the authority of Dr. Cyril Aumaître (project holder) and Dr. Renaud Demadrille (thesis director) in Grenoble. He will be integrated to the team composed of 2 technician, 1-2 postdoctoral fellows, 3-4 PhD students and master students. In Québec, he/she will be a member of Morin's research group composed of 10 PhD. students, 2 postdoctoral fellows and under-graduated students. He will be under the supervision of Pr. Jean-François Morin (thesis supervisor).

Position's mission and main activities

Context of the project:

Nowadays, the global climate change is undeniable and a drastic change in our energy consumption from fossil fuels toward non-carbonated energy is mandatory. Renewable energies are highlighted as promising alternatives by using natural resources such as wind power or photovoltaics devices. These technologies are mature and furnish actually a large amount of power to the general electrical grid. However, the electrical influx from these power farms are generally dependent from the weather and the solar cycles (nights and days). Contrariwise, heat energy is present everywhere and at any time. In fact, most of the heat produced by the consumption of primary resources in residential, transportation or industrial sectors is lost in the atmosphere. This considerable amount of wasted energy can be considered as a massive source of unused energy.

Thermoelectricity implies a direct coupling of thermal and electrical energies. By using the Seebeck effect, thermoelectric generators can convert heat to electricity. These devices are using p-type and n-type materials connected thermally in parallel and electrically in series. The thermoelectrical effect occurs when a temperature gradient (ΔT) is applied on both sides, the charge carriers (holes for p-type materials and electrons for n-type materials) diffuse from the hot side to the cold side of the device resulting in the generation of an induced electrostatic potential (ΔV). Generally based on inorganic materials, the utilization of organic thermoelectric materials has been recently investigated. Polymer material properties can be easily tuned, are soluble in various solvents and are cheap to produce. Various polymers have been investigated but often suffers from poor electronic conductivity or high thermal conductivity, which in both cases, is unfavorable for performant thermoelectric materials.

Since the discovery of graphene in 2001, this material have attracted a huge interest thanks to its high carrier mobility and its thermal and chemical stability. Unfortunately, pure graphene materials are not suitable as a thermoelectric material because of its high thermal conductivity. Among the graphene allotropes, graphene nanoribbons (GNRs) are considered as a specific and highly promising class of organic semiconductors thanks to a high electronic conductivity maintained by the rigid π-conjugated backbone of the ribbons, and a reduced thermal conductivity provided by the bandgap opening due to quantum confinement. Nevertheless, Actual GNRs have large bandgaps with uncontrolled HOMO and LUMO levels. Tailoring of these energy levels and their optical properties is currently a major challenge, and the design of the material needs to be finely controlled.

This project aims at the synthesis of novel graphene nanoribbons specially designed for thermoelectric materials working at low temperature (<200°C). This project is targeting the synthesis of new rigid p-type polymers presenting high conductivity and low thermal conductivity. Other parameters such as solubility in organic solvents, high doping content and ease of synthesis are also aimed.

Additionnal references:

D. Miao, M. Daigle, A. Lucotti, J. Boismenu-Lavoie, M. Tommasini, J.-F. Morin, *Angewandte Chemie International Edition* **2018**, *57*, 3588.
D. Miao, C. Aumaitre, J.-F. Morin, *J. Mater. Chem. C* **2019**, *7*, 3015.

E. Yvenou, M. Sandroni, A. Carella, M. N. Gueye, J. Faure-Vincent, S. Pouget, R. Demadrille, J.-P. Simonato, *Mater. Chem. Front.* 2020, Accepted manuscript, https://doi.org/10.1039/D0QM00265H.
O. Bardagot, P. Kubik, T. Marszalek, P. Veyre, A. A. Medjahed, M. Sandroni, B. Grévin, S. Pouget, T. N. Domschke, A. Carella, S. Gambarelli, W. Pisula, R. Demadrille, *Advanced Functional Materials* **2020**, *n/a*, 2000449.

Main activities:

This project is an interdisciplinary project combining chemistry, photochemistry and physics of semiconductor materials. The PhD program will be organized as a *cotutelle* between the French university and Université Laval.

The PhD student will participate in every step of this project from the design of the materials to their studies in devices. This project is mainly oriented to the synthesis of monomers and polymerization via cross-coupling reactions and classical organic synthesis methods. He/she will also be in charge of the characterization of the molecules (NMR, UV-vis, etc.) and will be proposed to use DFT calculations to support the design of the materials.

All the polymerization reactions will be conducted through palladium catalyzed step polymerization such as Suzuki Miyaura, Stille or direct heteroarylation reactions and characterized (SEC, DSC, ATG, NMR, FTIR). Photochemical graphitization will also be investigated through cyclodehydrochlorination reaction. The synthesized materials will be studied in thin films by different surface characterization methods (AFM, KPFM, XRD) in the neutral and doped states.

During his/her contract, the student will have the opportunity to present his/her work in national and international conferences. He/she will also attend to the project meetings and to the writing of the project reports. At the end of the thesis, the student will benefit from a Canadian and a French diploma. The student will have multiple skills in organic synthesis, π-conjugated polymer synthesis and physical characterization.

Restriction or constraints related to the position

Regarding the international and bilateral context of this project, the student will need to speak, write and discuss in English and French. Scientific stays in both countries are mandatory for the project and the candidate must be mobile during the PhD contract.

Desired profile

The candidate should have a master degree in organic chemistry, polymers, or material science. He/she will have to show a real interest in working on a multidisciplinary subject in an international context. A solid knowledge of organic chemistry and pi-conjugated materials are expected and experiences in organic electronics or organic semiconductors should be a strong asset. The candidate must be autonomous in a chemistry laboratory and interested in the renewable energy field. Due to the bilateral context, strong oral and written communication skills are expected with both teams to ensure the continuity of the project.

General information

Applications (CV + letter of motivation+ L3/M1/M2 marks) must be sent to Cyril Aumaitre, Renaud Demadrille and Jean-Francois Morin.

Contact for the questions related to the position:

Cyril AUMAITRE, Research engineer

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