Highly Luminescent (Macro)Molecular Materials Merging Pyridylidenes and Main Group Elements for OLED Applications

Funding program:

Established in 2015, the Nanyang Technological University (NTU) - Sorbonne University (SU) joint PhD degree program provides students with a unique opportunity to explore a thesis project in an interdisciplinary and intercultural environment.

Students in the program will have two main thesis supervisors, one in NTU (Singapore) and one in SU (Paris). Mainly located at SU, the students will have to spend at least 12 months in Taiwan at the NTU partner university.

Upon completion of the degree requirements, the students will be awarded doctorate degrees jointly by NTU and SU.

Candidates interested by this joint project are advised to contact either Dr. Jamal Moussa (SU Associate Prof., French supervisor) or Dr. Rei Kinjo (NTU Prof., Singaporean supervisor) for additional information on the project, as well as admission requirements.

Overview of the project:

This project involves both fundamental and applied chemistry aspects. On one hand, the SU team has recently developed new powerful methodologies of preparation of pyridylidene metal complexes (**Figure 1a**).[1] On the other hand, a variety of p-block elements-based aromatic heterocycles have been developed by the NTU team in these last years (**Figure 1b**).[2]

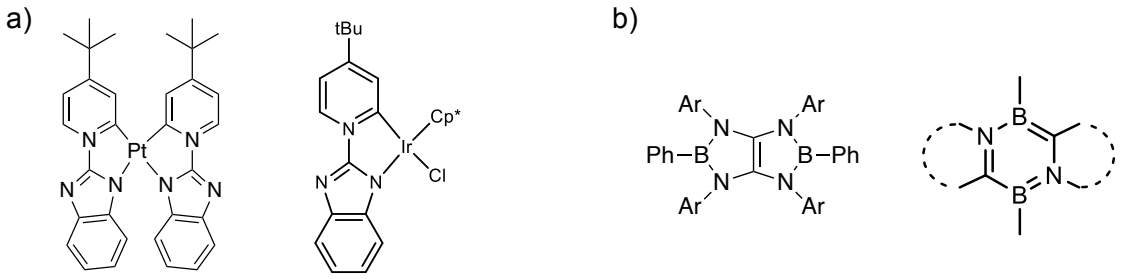

Figure 1: Examples of: pyridylidene complexes of platinum(II) and iridium(III) (a), and boron-containing heterocycles (b).

By combining both research areas, this project aims to develop a new class of compounds incorporating p-block elements into the pyridylidene scaffolds, and elucidate their bonding and structural features as well as their optical properties. Furthermore, the luminescent properties of those compounds will be examined and optimized to give a new type of highly emissive materials suitable for the fabrication of high performance OLEDs (**Figure 2**).

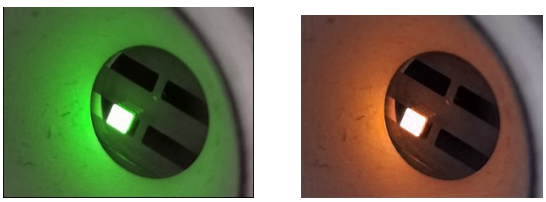

Figure 2: Illustration of expected OLED devices. (Photographs of OLEDs prepared at OPERA laboratory of professor C. Adachi)

(NTU contribution)

(i) Design and synthesis of adapted main group elements.

(ii) Photophysical characterization, structural authentication of the main group elements which will be combined with pyridylidene building blocks.

(ii) Screening of the basic reactivity of the developed compounds.

(Sorbonne Université contribution)
(i) Design and synthesis of pyridylidene building blocks.
(ii) Structural characterization, elucidation of the photophysical & optical properties of the main group elements combined with pyridylidene units as oligomers/polymers.
(iii) Theoretical analysis of the synthesized materials via ab initio calculations performed at both NTU and SU in close collaboration with Dr. Gilles Frison (Laboratoire de chimie théorique, SU).
(iii) The most promising synthesized compounds exhibiting high photoluminescence properties will be used to prepare OLED devices in the laboratory of Prof. Chihaya Adachi (OPERA lab.) at Kyushu University (Japan) in the frame of the CNRS International Research Project "LUX-ERIT" launched in 2023 for 5 years between CNRS-SU and Kyushu University.

Context and positioning of the project:

Pyridylidenes are highly reactive molecules that cannot be handled and used in pure form (**Figure 3**). Thus, there are only few examples of such intriguing molecules described in the literature as metal complexes (less than 50 references).[3] These class of carbenes are better σ-donors than the classical imidazolylidene counterparts and also behave as highly π-acceptor ligands with transition metal centres.[4] We note that there is no report of pyridylidene adduct with main group elements such as boron, silicon or phosphorus indicating a highly synthetically challenging project.

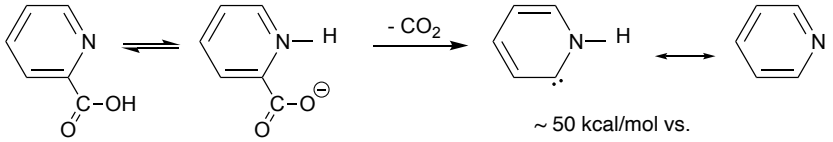

Figure 3: Decarboxylation of 2-picolinic acid leading to the Hammick intermediate pyridylidene that evolves to pyridine.

Incorporation of main group elements generally profoundly impacts the structural and electronic properties of π-conjugated molecules or oligomers/polymers.[5]

Candidate profile:

The candidate should ideally possess a strong background in organic chemistry and/or organometallic chemistry with fundamental knowledge in optical properties (absorption and emission). Skills in polymer chemistry or DFT calculation methods would be a plus. Good skills in English communication are expected, as the candidate will have to interact with French, Singaporean and Japanese researchers.
For more information or, to apply send an e-mail to jamal.moussa@sorbonne-universite.fr and RKinjo@ntu.edu.sg

[1] a) J. Montagu, G. Gontard, J. A. G. Williams, J. Moussa *Eur. J. Inorg. Chem.* **2023**, e202300487; b)
[2] a) K. Ota, R. Kinjo *Chem. Soc. Rev.* **2021***, 50*, 10594; b) K. Ota, R. Kinjo *Angew. Chem. Int. Ed.* **2020***, 59*, 6572; c) L. Zhu, R. Kinjo *Angew. Chem. Int Ed,* **2023***, 62*, e202312949
[3] S. S. Jamil, J. Moussa *Review in preparation*
[4] a) O. Schuster, L. Yang, H.G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445; b) E. Stander Grobler, O. Schuster, G. Heudenrych, S. Cronje, E. Tosh, M. Albrecht, G. Frenking, H.G. Raubenheimer, *Organometallics* **2010**, *29*, 5821
[5] a) Y.-G Shi, J.-W. Wang, H. Li, G.-F. Hu, X. Li, S. K. Mellerup, N. Wang, T. Peng, S. Wang *Chem. Sci.*, **2018**, *9*, 1902; b) A. Sengupta, A. Doshi, F. Jäkle, R. Peetz, *J. Polym. Sci. A: Polym. Chem.* **2015**, *53*, 1707; c) A. W. Baggett, F. Guo, B. Li, S.-Y. Liu, F. Jäkle, *Angew. Chem. Int. Ed.* **2015**, DOI:10.1002/anie.201504822