Ecole Doctorale Carnot-Pasteur

Proposition de sujet de thèse

Intitulé français du sujet de thèse proposé : Synthèse et étude des propriétés électroniques de nouveaux composés riches en azote à base de *s*-tétrazine

Intitulé en anglais : Synthesis and electronic properties of novel aza-aromatic based on *s*-tetrazines

Unité de recherche : Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB-UMR CNRS 6302)

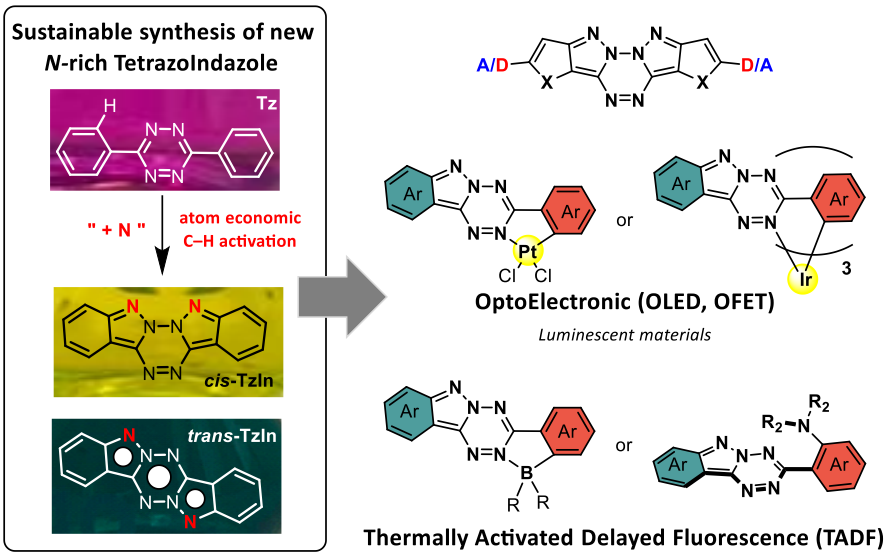
Nom, prénom et courriel du directeur (et co-directeur) de thèse :
Directeur : Pr. Jean-Cyrille HIERSO ; jean-cyrille.hierso@ube.fr
Co-encadrant : Dr. Julien ROGER ; julien.roger@ube.fr

Domaine scientifique principal de la thèse : *Chimie organométallique et catalyse*

Domaine scientifique secondaire de la thèse : *Matériaux moléculaires*

Description du projet scientifique

This project aims at designing new Pi-conjugated heterocycles (Scheme 1) through greener processes (C–H activation) to design materials with potential applications in energy conversion and optoelectronics (photovoltaic applications, OLEDs and OFETs). The program relies on the rational development of synthetic methods based on important **tetrazo[1,2-*b*]indazoles (TzIn)** molecules with high *N*-content based on the *s*-tetrazine core **(Tz)** mastered by our group.[1]



Scheme 1 – Sustainable synthesis of N-rich heteroaromatics based on s-tetrazine scaffold for optoelectronics applications

Since 2015, our group has successfully employed catalysed *N*-directed C–H bond functionalization on nitrogen containing molecules for new applications mainly based on the *s*-aryltetrazines.[2] The corresponding halogenated *s*-tetrazines are key intermediates to reach bulky *s*-aryltetrazines by Palladium-catalysed Suzuki couplings but also for copper-catalysed formation of C–X (X = O, N, S, P)

bond.[3] We also reported a straight one-step selective access to T-shaped and Z-shaped polyaromatics *s*-tetrazines by rhodium catalysis.[4] We recently reported the synthesis of an unprecedented *N*-rich heteroaromatics, namely tetrazo[1,2-*b*]indazole synthesized from fluorinated aryl-*s*-tetrazine by an azidation/intramolecular cyclisation process.[1]

The present project aims to develop innovative *N*-rich heteroaromatics based on *s*-tetrazine scaffold with fluorescence properties (Scheme 1). This new class of molecules can be modified by regioselective functionalization in *ortho*-position of the aryl moieties by relevant transition metals, reagents or functionalizations (Scheme 1).

The PhD project will be conducted in the "Catalysis, Polymers, Coordination and Modelling" CaPCoM team at the ICMUB laboratory in Dijon. The successful candidate will join the team of Dr. Julien ROGER, in collaboration with Pr. Paul FLEURAT-LESSARD and his group (*An assistant-professor will hire in 2026 for the rationalization of luminescence spectrum by DFT calculations*). The project will combine our expertise on C–H bond functionalization by transition metals and mechanism understanding, within a national collaboration with Dr P.-A. BOUIT group (ISC-Rennes).

Bibliography

[1] a) Roger et *al, Angew. Chem. Int. Ed.* **2023**, *62*, e202300571; b) *Dalton Trans.* **2024**, *53*, 10737–10743.
[2] a) Hierso et *al.*, *Angew. Chem. Int. Ed.* **2016**, *55*, 5555; b) Hierso et *al.*, *ACS Catal.*, **2017**, *7*, 8493;
[3] Hierso et *al.*, *Angew. Chem. Int. Ed.* **2020**, *59*, 1149–1154.
[4] Roger et *al.*, *Adv. Synth. Catal.* **2025**, *367*, e70021.

Connaissances et compétences requises :

The candidate should hold a M2 in Molecular Chemistry, and have some knowledge about organic chemistry and organometallic chemistry. This subject is by nature multidisciplinary so that the candidate must be prepared to work in a team and collaborate with specialists from different horizons.