PhD contract offer

Subject: Green synthesis of thiazolo[5,4-d]thiazoles and their applications

General information

Workplace: LCP-A2MC – Metz, Université de Lorraine
Type of contract: PhD contract
Contract period: 36 months
Expected date of employment: October 2024
Proportion of work: Full time
Remuneration: Around 1 700€ / month (possibilities of teaching mission => around 2 000€/month))
Desired level of education: Master degree in organic chemistry.

Key words

Organic synthesis, green chemistry, heterocycles

Skills

- The candidate must have a Master degree in organic chemistry (general score **up to 12/20**) with a strong theoretical and practical knowledge in organic chemistry. The candidate should be familiar with usual purification and characterization techniques of organic compounds (NMR, IR, HRMS, UV-vis,…).
- Taste for practical work
- Good knowledge of French and/or English (oral and written) is required.
- As an enthusiastic researcher, the candidate must be curious and open to work in a multi-disciplinary environment.

Work context

The PhD position will take place at the LCP-A2MC (Laboratoire de Chimie et Physique, Approche Multi-échelles des Milieux Complexes) in Metz, in the “Green Chemistry and Environment” group. Complementary informations related to our research interests could be found on our laboratory website (https://lcp-a2mc.univ-lorraine.fr/).The candidate will have access to a standard and secured working place (1 bench / person) dedicated to organic synthesis. Furthermore, he/she will benefit from our synthetic (microwave and ultrasonic facilities, etc.) and characterization platform (NMR, IR, UV-vis, etc.) as well as our national/international collaborations. The PhD work will be supervised on a daily basis by Pr. Stéphanie Hesse and Dr. Jean-François Longevial. The project global progress will be evaluated on a monthly basis. Moreover, a thesis monitoring committee will be held each year. In addition to the proposed research work, the candidate will also benefit from multidisciplinary teaching, lectures and training provided by the Université de Lorraine doctoral school “Chimie-Mécanique-Matériaux-Physique (C2MP)” as well as the ones organized within our laboratory.

Application (before April the 15th)

Applicants are invited to send :
☐1 resume, ☐1 cover letter, ☐diploma copies along with scores details (M1 and M2), ☐1 recommendation letter from the M2-internship supervisor to: Stéphanie HESSE : stephanie.hesse@univ-lorraine.fr and Jean-François LONGEVIAL : jean-francois.longevial@univ-lorraine.fr

Research project

Materials containing thiazolo[5,4-d]thiazoles (TzTz) possess interesting properties in the field of organic electronics. These TzTz patterns are used in optoelectronic devices such as organic light emitting diodes [1] (OLEDs) or organic solar cells. [2] In fact, in recent years, these derivatives have become increasingly popular, resulting in an increased number of publications related to their various application potential.

TzTz are characterized by a rigid and coplanar bicyclic system forming an extended and electro-deficient electronic system. They generally feature good photochemical stability and above average fluorescence quantum yields. Therefore they are used for example for bio-imaging [3] as chemo-sensitive probes [4] or as electrochromic devices. [5]. TzTz can also be original ligands in coordination chemistry. [6]

Thiazolo[5,4-d]thiazole synthesis is relatively easy and obtained by double condensation between dithiooxamide and various aromatic aldehydes under oxidizing conditions. However, these reactions are almost systematically carried out in toxic solvents such as DMF or nitrobenzene at high reaction temperatures and times. [7] The use of these toxic solvents is a major barrier to the development of TzTz in a context of sustainable development.

Biomass solvents and deep eutectic solvents are the target of many concurrent efforts by industry and academic research. [8] Among them, NADES (Natural Deep Eutectic Solvent) are currently the most promising due to their simple and inexpensive production often derived from bio-based products. [9] The “Green Chemistry and Environment” team of LCP-A2MC is working on the transposition of heterocycle syntheses into NADES. Recently, we have shown the interest of NADES L-Proline:Glycerol (Pro:Gly) (1:2) in Knoevenagel reactions and 5-arylidenerhodanines synthesis. [10a] This synthesis is fast (1h at 60°C), easy, catalyst-free and durable because no conventional organic solvent is used. The expected compounds are recovered by simple filtration after hydrolysis and no further purification is necessary.

Consequently, our first objective is to develop an eco-responsible synthesis of symmetric TzTz (using green solvents, activations by ultrasound or microwave, no or little purification). We will thus be able to develop a chemical library of new molecules. An emphasis will be dedicated to the synthesis of symmetrical bio-sourced TzTz in NADES that will be tested for their photophysical properties. Particular attention will then be paid to asymmetric systems with an evaluation of the effects of various electrodonor/acceptor groups. In any case, we will work in a global green chemistry approach

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[9] K. Sreekumar et al. *Soft Matter* **2022,** 18**,** 2695. DOI : 10.1039/d1sm01797g
[10] (a) **S. Hesse** *Beilstein JOC* **2023**, 1537. https://doi.org/10.3762/bjoc.19.110 (b) **S. Hesse**, J. Hertzog, S. Rup-Jacques *J Het Chem* **2023**, soumise