LABORATOIRE DE CHIMIE DE COORDINATION DU CNRS (UPR8241)
Research team: Molecular design of transition metal pre-catalysts link

PhD position in molecular synthetic chemistry (01/10/2023 – 30/09/2026)

Supervisors: Dr. Dmitry Valyaev (CRCN CNRS), Dr. Vincent César (DR2 CNRS)

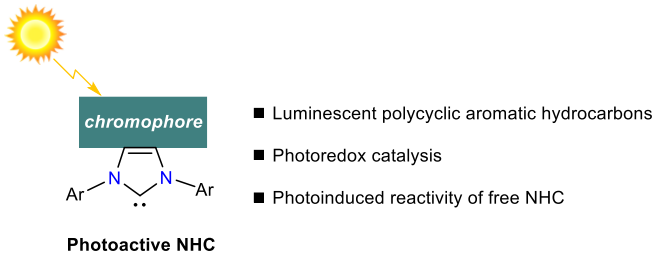
Photoactive *N*-heterocyclic carbenes: Unconventional reactivity, photocatalysis and luminescent materials

Context

Since the beginning of this century, N-heterocyclic carbenes (NHCs) have emerged as gamechanger compounds in modern chemistry. As privileged ligands for transition-metal complexes, NHCs have found multiple applications in organometallic chemistry and catalysis, while their reactivity upon coordination to main-group elements and as organocatalysts has open new research areas.[1] While luminescent NHC-supported complexes have gained great significance over the last decade,[2] the incorporation of a photoactive moiety directly into the scaffold of an NHC remains almost unexplored to date.

PhD objectives

This PhD project, funded by the 'Ministère de l'enseignement supérieur et de la recherche" (MESR), aims at developing unprecedented photoactive NHCs, based on the most classical imidazol-2-ylidene core and whose backbone is functionalized by a photoactive moiety. The latter can be an organic (boron- or phosphorus-based) or an organometallic (Ru- or Ir-based) chromophore and will be installed using the metal-mediated strategy developed in our group.[3] The resulting NHC derivatives will be then exploited as new efficient and tunable classes of luminescent polycyclic aromatic hydrocarbons (proof of concept recently obtained in the frame of the Emergence@INC2022 CNRS program in collaboration with colleagues from ISCR (Rennes) and Ceisam (Nantes)). They will also serve as key building blocks for the development of innovative photoredox catalysts, in which the photosensitizer and the metal-NHC catalytic species are incorporated within the same molecule. Finally, this approach will allow to investigate the photoinduced reactivity of the free luminescent NHCs with the ultimate goal to discover original activation pathways of small molecules and/or inert bonds.



Candidate profile

We are looking for a strongly motivated and dynamic candidate with a solid knowledge in synthetic organic chemistry. Some experience in organometallic chemistry / chemistry of main group elements / photophysical studies will be also appreciated. A good level of autonomy, scientific rigor and communication skills in English is also required. Applications containing a motivation letter and a detailed CV with the name and contact details of two references should be sent to dmitry.valyaev@lcc-toulouse.fr and vincent.cesar@lcc-toulouse.fr.

References:

1) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485.
2) H. Amouri, *Chem. Rev.* **2023**, *123*, 230.
3) a) A. A. Grineva, D. A. Valyaev, V. César, O. A. Filippov, V. N. Khrustalev, S. E. Nefedov, N. Lugan, *Angew. Chem. Int. Ed.* **2018**, *57*, 7986; b) A. A. Grineva, O. A. Filippov, S. E. Nefedov, N. Lugan, V. César, D. A. Valyaev, *Organometallics* **2019**, *38*, 2330; c) A. A. Grineva, O. A. Filippov, Y. Canac, J.-B. Sortais, S. E. Nefedov, N. Lugan, V. César, D. A. Valyaev, *Inorg. Chem.* **2021**, *60*, 4015.

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