PhD position (01/11/2023-31/10/2026)

Combining Quantum Dots with NHCs as Exciton Delocalizing Ligands for Boosting their Photocatalytic Activity

Supervision: Dr Vincent César, Dr Dmitry Valyaev ; Co-supervision: Dr Olivier Baslé

Context

Quantum Dots (QDs) have emerged as promising candidates for applications in photocatalysis thanks to their intense and tunable absorption in the visible range, associated with wide quantum confinement-enhanced redox potentials and low photobleaching. Since 2015, the complexity and variety of reported QDs photocatalyzed reactions has been increasing rapidly (e.g. C-C and C-N bond formations) as exemplified by our collaborators.[1] A major limitation to the use of such QDs photocatalyzed reactions in the industry is the unwished process of recombination of charges in photoexcited QDs, which leads to low quantum yields for the reaction, so that its completion requires hours of visible light irradiation.

PhD objectives

This thesis is part of the ANR-funded QDotNHC project (2023-2026). This project aims to improve the photocatalytic efficiency of QDs through enhanced separation and extraction of photoinduced charges from QDs, by grafting advanced N-heterocyclic carbenes (NHCs) as effective exciton delocalizing ligands (EDLs). These NHCs will be engaged in the QDotNHC project to access two new types of QD-NHC nano-objects with efficient charge extraction/separation, namely: *i*) QDs functionalized with redox-active NHC ligands as photogenerated charge extraction channels,[2] *ii*) QD dyads connected by Janus-type bis-NHC ligands (QD1-JanusNHC-QD2).[3] The QDotNHC project brings together three partners with complementary skills:

- Partner 1: CEA-Grenoble IRIG-SyMMES (Dr Vincent Maurel, coordinator). Photocatalysis and QDs
- Partner 2: LCC-CNRS, Toulouse (our team). NHCs and (photo)catalysis
- Partner 3: University of Bern, Switzerland (Prof. Philippe Renaud). Radical organic chemistry.

The PhD student will be based at the LCC and will be in charge of the synthesis of the NHC precursors, of the study of the new NHCs from a molecular point of view and of their grafting onto QDs. Photoredox catalysis is also envisaged. Short stays of 3 months are also planned with partners to acquire expertise in nanochemistry and photocatalysis.

Candidate profile

We are looking for a highly motivated, dynamic candidate with a solid knowledge in organic and organometallic chemistry. Experience in nanochemistry would also be appreciated. A good level of autonomy, scientific rigor and communication skills in English are also required. Applications must be submitted via the CNRS job portal (https://emploi.cnrs.fr/).

References

1. (a) A. Dabbous, E. Colson, D. Chakravorty, J.-M. Mouesca, C. Lombard, S. Caillat, J.-L. Ravanat, F. Dubois, F. Dénès, P. Renaud, V. Maurel, *Chem. Eur. J.* **2023**, *29*, e202300303 doi, (b) E. Colson, J. Andrez, A. Dabbous, F. Dénès, V. Maurel, J.-M. Mouesca, P. Renaud, *Commun. Chem.* **2022**, *5*, 57 doi

2. M. Ruamps, S. Bastin, L. Rechignat, A. Sournia-Saquet, D. A. Valyaev, J.-M. Mouesca, N. Lugan, V. Maurel, V. Cesar, *Chem. Commun.* **2018**, *54*, 7653 doi hal (b) M. Ruamps, S. Bastin, L. Rechignat, A. Sournia-Saquet, L. Vendier, N. Lugan, J.-M. Mouesca, D. A. Valyaev, V. Maurel, V. César, *Molecules* **2022**, *27*, 3776 doi hal

3. 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 doi hal

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