

## Open post-doctoral position Synthesis of $\pi$ -d Conjugated Coordination Oligomers for solar energy

### Context

Organic NIR-absorbers (750-1400 nm) built on molecules having an extensive electrons delocalization in one direction (1D) are of considerable interest from both fundamental and applied points of view. Increasing their width is also extremely appealing because the molecules can now be viewed as two dimensional (2D) graphene nanoribbon heterostructures (GNRs), subject of tremendous works during the last decade. Both are prepared by classical approaches based on the use of standard C-C coupling reactions. Recently, the  $\pi$ -d conjugated coordination strategy emerged and received a major attention as the delocalization of electrons in the  $\pi$ -d systems (over both metals and ligands) improves the stability of the materials and their charged or spin states (upon external input). To the best of our knowledge, the precise control of the length (1D) and width (2D) in  $\pi$ -d conjugated materials remains beyond reach although such a control is needed to obtain (new) specific electronic features inherent to the  $\pi$ -d conjugation.

### Project

The extension of the electrons delocalization is one of the most effective strategy to redshift the absorption bands up to the NIR region. The stepwise access to polynuclear  $\pi$ -d oligomers by coordination chemistry (extension by metal-ligand assembly) encountered so far drastic limitations. We recently described the first synthesis in solution of one dimensional  $\pi$ -d conjugated coordination oligomers by stepwise metalation of a quinonediimine (QDI) **1** (Scheme 1). The possibility of exactly controlling the length (1D) of the oligomers allows the fine tuning of the absorption properties going from the UV to the NIR regions (Fig. 1).

We wish now to extend the  $\pi$ -d conjugation in one direction (1D) and to bring an additional  $\pi$ -conjugation (through the bridge) in the orthogonal direction (2D). To this end, our project is built around two axes.

- 1) The introduction of soluble C-substituents to extend the size of the 1D-chains: our strategy is based on the use of soluble C-substituted QDI ligands with no substituent on the nitrogen atoms which would allow for the oligomerization process going further in solution, while retaining a flat geometry of the chains.
- 2) The two-dimensional extension of the  $\pi$ -d conjugation (2D-frameworks interconnected through bridges) that should provide a faster reduction of the HOMO-LUMO gaps than the ones obtained in structurally equivalent linear 1D molecules.

### References

1. H. Audi, Z. Chen, A. Charaf-Eddin, A. D'Aléo, G. Canard, D. Jacquemin, O. Siri, *Chem. Commun.*, **2014**, 50, 15140.
2. V. M. Santhini, C. Wäckerlin, A. Cahlik, M. Ondráček, S. Pascal, A. Matěj, O. Stetsovyh, P. Mutombo, P. Lazar, O. Siri, P. Jelinek *Angew. Chem. Int. Ed.* **2021**, 60, 439-445.

### Skills

Organic synthesis, coordination chemistry, metal catalyzed coupling reactions

### Informations

Start date: 01/01/2023; funding: ANR; duration: 24 months.

### Application

Detailed CV with a summary of work and two recommendation letters, can be sent by email to Dr. O. Siri at the following address: olivier.siri@univ-amu.fr

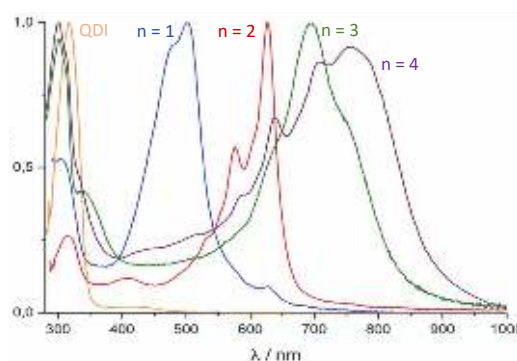
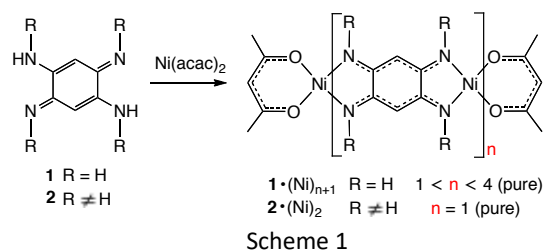


Fig 1. Absorption of oligomers  $1 \bullet (\text{Ni})_{n+1}$  in solution

