Matériaux biohybrides nanostructurés pour l’oxydation électro-catalytique en milieu aqueux par activation du dioxygène.

Nanostructured bio-hybrid materials for electro-catalytic oxidations in aqueous media with molecular oxygen.

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Amid increasing concerns related to chemical hazards, pollution and sustainability, catalytic reactions offer much promise since they promote selective transformations at low temperature and without the need of excess reagents.

As a new strategy for sustainable catalysis, we propose to combine the expertise of the AFFOND and BIOCE teams from the LCBM laboratory with aim to develop new nanostructured bio-hybrid materials for the electro-catalytic oxidation of sulphides in aqueous medium.

HET-s(218-289) is the prion forming domain (PFD) of a fungal prion protein which is capable of self-organizing into amyloid fibrils with a high degree of structural homogeneity, and to do so in a reproducible way. The structure of the obtained fibrils is known with atomic resolution, thus enabling the rational design of biomaterials via selective functionalization of the starting protein. The AFFOND team discovered that amyloid fibrils are obtained even after fusion of HET-s(218-289) with a Rubredoxin (Rd), i.e. a small iron-sulphur protein found in various sulfur-metabolizing bacteria (Figure 1a-b). Furthermore, it was found that the resulting fibres can act as protein nanowires by forming a gel layer onto an electrode and by efficiently transferring electrons from the electrode to the gel matrix.

![Figure 1](image)

4 Forge V. and coll. Submitted.
We now propose to use the fusion protein Rd-HET as a self-assembling module for the design of new functional nanomaterials via a bottom-up manufacturing approach in aqueous solution. Initially we will focus on the construction of bioinspired artificial monooxygenases immobilised onto amyloid nanofibers of different morphology (single/triple strand, bundle, and mesh). To this end, a mononuclear copper complex capable of catalysing the oxidation of organic substrates will be conjugated to a free cysteine naturally present on the Rd domain of the fusion protein. As a result, the catalytic centre will be less than 8 Å away from the redox centre of Rd, thus allowing an efficient electron transfer between the two. The redox potential of the couples involved are thermodynamically compatible ($E_{\text{vs. ENH}} = +0.42\text{V}$ for Cu$^{2+}$/Cu$^{+1}$ of the catalyst, $E_{\text{vs. ENH}} = +0.05\text{V}$ for Rd) and well characterized.

The catalytic cycle involves the reaction of the Cu (I) centre with molecular oxygen O$_2$ to give an oxidizing peroxo species (Figure 1c). Upon substrate oxidation, the resulting Cu(II) centre has to be reduced to its initial state in order initiate a new cycle. At present, the reduction process is carried out by a sacrificial electron donor in solution. In our strategy, the latter will be replaced by the electrons from an electrode via the iron-sulphur centre of Rd domains. **The whole process will thus be an electro-catalytic oxidation at controlled potential.**

The PhD candidate will initially investigate oxidations with a bimolecular catalytic system, then with the copper complex bioconjugated with Rd-Het, and finally with the nanostructured fibres. He/she will then study the influence of the nanomaterial morphology on the effectiveness of the process and develop new strategies for controlling the self-assembly of the material. If successful, the same approach will be then extended to iron and manganese complexes capable of activating O$_2$ for the oxidation of other substrates.

**Mots-clés:** Nanomatériaux, auto-assemblage, bio-inspiré, électro-catalyse, enzyme artificielle.

**Profil du candidat souhaité** : Chimiste ou physico-chimiste avec un gout pour le détail, le travail expérimental en équipe et les projets multidisciplinaires.

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**Equipe de recherche/Research team**: **AFFOND - Amyloid Fibres: From Foldopathies to NanoDesign**.

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