Proposition de thèse en chimie bio-inspirée

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The present ARTENOSYN project aims at developing bioinspired artificial systems capable of catalysing important organic reactions in water, under mild conditions and using harmless reactants such as O_2. For this purpose, we are planning to mimic both activities of flavoenzymes, which and capable of catalysing either reduction reactions, by delivering single electrons to a biologic partner, or oxidation reactions, by the reductive activation of O_2; and this with the same flavin cofactors, but located in different protein scaffolds. This project is based on recent interesting results obtained by partner 1, demonstrating that the incorporation of flavin cofactors (FMN) into the local microenvironment of a water soluble polymer (modified polyethyleneimine), can generate an artificial reductase capable of collecting electron pairs from NADH and then delivering single electrons to a redox partner such as manganese(III) porphyrins. Thus, under anaerobic conditions, this system must also be able to deliver single electrons to organic molecules into a locally hydrophobic microenvironment and initiate radical reaction by single electron transfer (SET). Partner 2 is an expert on these radical reactions and a large scope of reactions will be evaluated. Alternatively, under aerobic conditions, the reduced flavin ($FMNH_2$) will react with dioxygen to form organo-peroxo intermediates, which is known to perform oxidation reactions such as Beyer-Villiger, epoxydation or sulfoxidation reactions. The first task of the proposal will be to synthesize libraries of modified polyethyleneimines in order to better understand how their hydrophobicity may influence the kinetic and thermodynamic parameters of the electrons transfer. Then, both radical and oxidation reactions will be thoroughly studied and eventually combined into a tandem system. Finally, chiral polyethyleneimines will also be synthesized by simple derivatization with chiral substituents, in order to perform catalytic asymmetric radical reactions and/or catalytic asymmetric oxidation reactions.

Nous sommes à la recherche d'un candidat pour réaliser un thèse dans notre laboratoire à Orsay (partner 1) dans le cadre d'une ANR collaborative. Il s'agit d'un projet pluridisciplinaire à l'interface entre la chimie bioorganique, supramoléclaire et la catalyse en milieu aqueux. Le candidat devra donc être très ouvert d'esprit, avec de solides connaissances à l'interface chimie/biologie, de façon à développer les flavoenzymes artificielles décrites ci-dessus. Les applications en synthèse organique seront, quant à elles, réalisées en étroite collaboration avec un laboratoire de chimie organique à l'école de Chimie de Mulhouse (partner 2).

informations complémentaires : *Nature Communications* **2015**, 6, 8509