Mimicking biocatalysis for the design of artificial oxygenases based on a versatile protein scaffold

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Catalytic processes are at the forefront of green chemistry development for the safe production of a wide range of chemicals. Among the various approaches, biocatalysis is the most promising strategy but the repertoire of reactions has not yet reached that of (in)organic catalysis. Artificial enzymes fill this gap by enabling abiotic reactions with, in some cases, enzyme catalytic efficiencies[1]. At LCBM, we are involved in the design of artificial metalloenzymes[2] (ArM) for oxidation reactions. Using the NikA protein scaffold, a Ni(II) importer, several chemical transformations were achieved through the incorporation of iron and ruthenium complexes into the protein cavity[3]. This talk will take the audience on a walk through the NikA landscape to present some of the assets of this artificial enzyme. The determination of the 3D-structures of ArM provides crucial information on the factors involved in the stabilization of inorganic catalysts in the protein, the sequence of the chemical steps and the orientation of substrates along the catalytic cycle. Furthermore, the combination of X-ray crystallography with *in silico* approaches allow a better characterization of the interactions between the protagonists forming le ménage à trois, namely the host protein, the catalyst and the substrates[4]. To go further, we took advantages of our knowledge on NikA-based ArM to design novel heterogeneous catalysts using the cross-linked enzyme crystals (CLEC) technology. The NikA-FeL CLEC displayed an outstanding stability for their use in oxidative cleavage of styrenes (< 30,000 catalytic cycles) with good yields (up to 80%)[5].

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