

EXPLORING THE PROMISCUITY OF LMRR AS A SCAFFOLD FOR ARTIFICIAL METALLOENZYMES

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Artificial metalloenzymes (ArMs) have been proven to be a valuable concept for enantioselective catalysis. ArMs aim to achieve the high activities and selectivities characteristic of natural enzymes, but expanding the scope acceptance of reactions and substrate by combining it with transition metal catalysis.

A few key aspects on the design of an artificial metalloenzyme have to be taken into account:

- The bioscaffold to be used (usually DNA or protein) provides the second coordination sphere and the chirality responsible for the enantioselectivity.
- The transition metal complex which forms the first coordination sphere of the substrate and gives access to a broad range of reactions.
- The method used to introduce the metal complex into the scaffold. This can be achieved by supramolecular, covalent, dative anchoring and in vivo incorporation of unnatural amino acids approach.

By changing these features we can take profit from the promiscuity of LmrR and use the Arms to catalyse different reactions. Here, we present the developments towards two ArMs based on the same protein scaffold (LmrR, a transcriptional regulator in *Lactococcus lacti*). Changing the method to anchor the metal complex into the scaffold we can access different reactions. Via the supramolecular approach we catalyse carbene transfer reaction and using the in vivo incorporation of unnatural amino acids we are able to catalyse the addition of a water molecule into a double bond.