Metallo-supramolecular assembly for application in *green* catalysis.

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Enantioselective catalysis offers many significant advantages over the classical asymmetric *stoichiometric* synthesis. Although it constitutes one of the most appealing strategies while considering economy and environmental issues and thousands of chiral catalysts have been reported, only a few examples have been developed into industrial processes. The main problem in these reactions is the homogenous conditions that reduce their potential applications. The major concern is the need for reusable catalysts as well as to reduce metal product contamination. Many strategies that have been developed to overcome these drawbacks but none of them are yet satisfactory. We propose in the project a different approach to this problem based on the development of <u>self-supported homogeneous</u> <u>catalysts</u>, which can be homogeneous during the reaction but also recyclable at the end of reaction, by means of dynamic equilibria [1].

One general requirement for the reusability of any recoverable catalyst is that the system must be sufficiently stable to maintain the catalytic activity during the recycling process. For this reason the approach that allows the formation of coordination polymer as resting state of the catalytic system is a strategy that warrants this requirement [2]. Thus, the design of suitable polytopic ligands leading to metal coordination polymer with responsive properties will be crucial for the project. Several conceptual schemes will be adopted; two of which are presented below for chiral ditopic bidentate ligands. The system can be completely symmetric by connecting two bidentates ligands (a) or alternatively it can also consist in a bidentate ligand connected to a weak coordinating site (b).



The objective of the thesis will be to develop new chiral and enantiopure ligands using synthetic strategies recently developed in the laboratory [3]. The self-assembly of these ligands in presence of various metal ions to develop metallo-supramolecular polymers will be studied. These objects will then be applied to homogeneous catalysis thanks to the dynamic nature of these systems. The project is therefore interdisciplinary, tackling problems at the interface of organic, inorganic, organometallic and materials chemistry.

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