Unit 1 “Quantitative evaluation of template effects in macrocyclization reactions”

Co-ordinator: Prof. Paolo Mencarelli

Abstract
The template effect plays an important role in the syntheses of macrocyclic compounds. We prepared a suitable acyclic precursor that leads to the formation of the tetracationic cyclobis(paraquat-p-phenylene) and studied the template effect of electron-rich organic guests, based on the 1,4-dioxybenzene, 1,5-dioxyanaphthalene, and tetraphthalvalene units, bearing side-chains of different length. Depending on the structure of the guest, [2]pseudorotaxanes, [2]rotaxanes, and [2]catenanes are obtained upon the ring closure reaction. We have replaced the 4,4’-bipyridinium unit with the 2,7-diazapyrenium unit, and investigated the effect of different guests. The results indicate that formation of tetracationic aromatic cycles templated by aromatic donors greatly benefits from the use of extended π surfaces. We are now working on another acyclic precursor in which the 1,4-phenylene spacer is replaced with the longer 4,4’-byphenylene unit. With this new precursor, the study of the template effect of bigger guests will be possible.

Unit 2 “Enzymatic and biomimetic oxidation reactions”

Co-ordinator: Prof. Carlo Galli

Abstract
The role of electron transfer processes in the oxidation of N,N-dimethylanilines and aromatic sulfides promoted by nonheme-iron complexes have been investigated. The hydrogen atom transfer (HAT) reactions from phenolic antioxidants to short-lived N-oxyl radicals may represent a tool for evaluating their radical scavenging ability and we proposed that this reaction involves a charge transfer from a π-stacked conformation of phenolic and aminoxyl radical aryl rings. A change of regioselectivity in the HAT process from tertiary amines, useful for synthetic applications, is observed in acidic medium with reactions occurring from the less activated positions. Selective oxidation of natural products to obtain fine chemicals and bioactive compounds can be accomplished in the oxidation of methylated catechins by laccase/1-hydroxybenzotriazole systems. Functionalization of the C-2 or C-4 positions occurs depending on the structural features.

Unit 3 “Supramolecular metallocatalysts”

Co-ordinator: Prof. Antonella Dalla Cort

Abstract
The calixarene moiety has been widely exploited as a convenient molecular platform for the connection of recognition and catalytic units in efficient metallocatalysts with transacylase and nuclease activity. High level of cooperation between active units has been also achieved with functionalized polymer brushes grafted onto silica nanoparticles and in functionalized self-assembled monolayers on Au nanoparticles. Nonheme iron complexes containing imine ligands were easily prepared by one-pot assembly of cheap and commercially available starting materials. These complexes effectively catalyzes the oxidation of a number of non-activated C-H bonds by H2O2 with high turnover numbers and good selectivity.

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We have developed potential catalytic system based on metal-salophen complexes. Their catalytic activity is on the way to be tested.