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Catalytic applications of molecular machines

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

A molecular level machine is an assembly of discrete number of molecular components which was designed to perform machinelike movements in microscopic scale [1]. In the molecular machines not only the nature of the movement of its component is very important, but also its function must be controlled. For example, the ability to make it repeat its operation in acyclic fashion and timescale needed to complete a full cycle of movement are very important. The concept of molecular level machine is not a new phenomenon. This issue was first mentioned in 1959 by Richard Feynman [2]. The 2016 Nobel Prize in chemistry was awarded to Jean-Pierre Sauvage, Fraser Stoddart and Ben Feringa for their deep researches on designing and synthesis of molecular machines. Molecular machines can be divided into two broad categories: synthetic and biological. In the body, assembles of proteins can play the role of molecular machines. Enzymes such as myosin, kinesin, dynesin and also are linear motors which convert the energy of ATP hydrolysis into mechanical work [3]. A molecular machine works by repeating cycles in molecule. This feature has a good influence in chemical change or reactions such as: acid/base reaction, isomerization, oxidation/reduction processes and complexation/decomplexation [1]. Most of these systems have a rotaxane and catenane portions. A rotaxane have macrocyclic and dumbbell-shaped compounds. The molecular cycle encircles the linear rodlike part of the dumbbell-shaped component. Catenanes are made of several (at least two part) interlocked macrocycles. Although the two parts cannot dissociate from each other but, none of them are covalently linked to each other too (Fig. 1) [4].

In recent years, molecular machines have been widely used in various fields [5]. A number of applications of these systems are shown in below (Scheme 1).

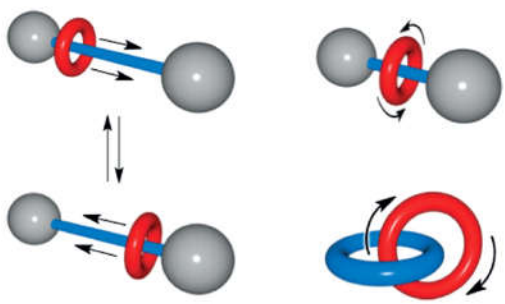
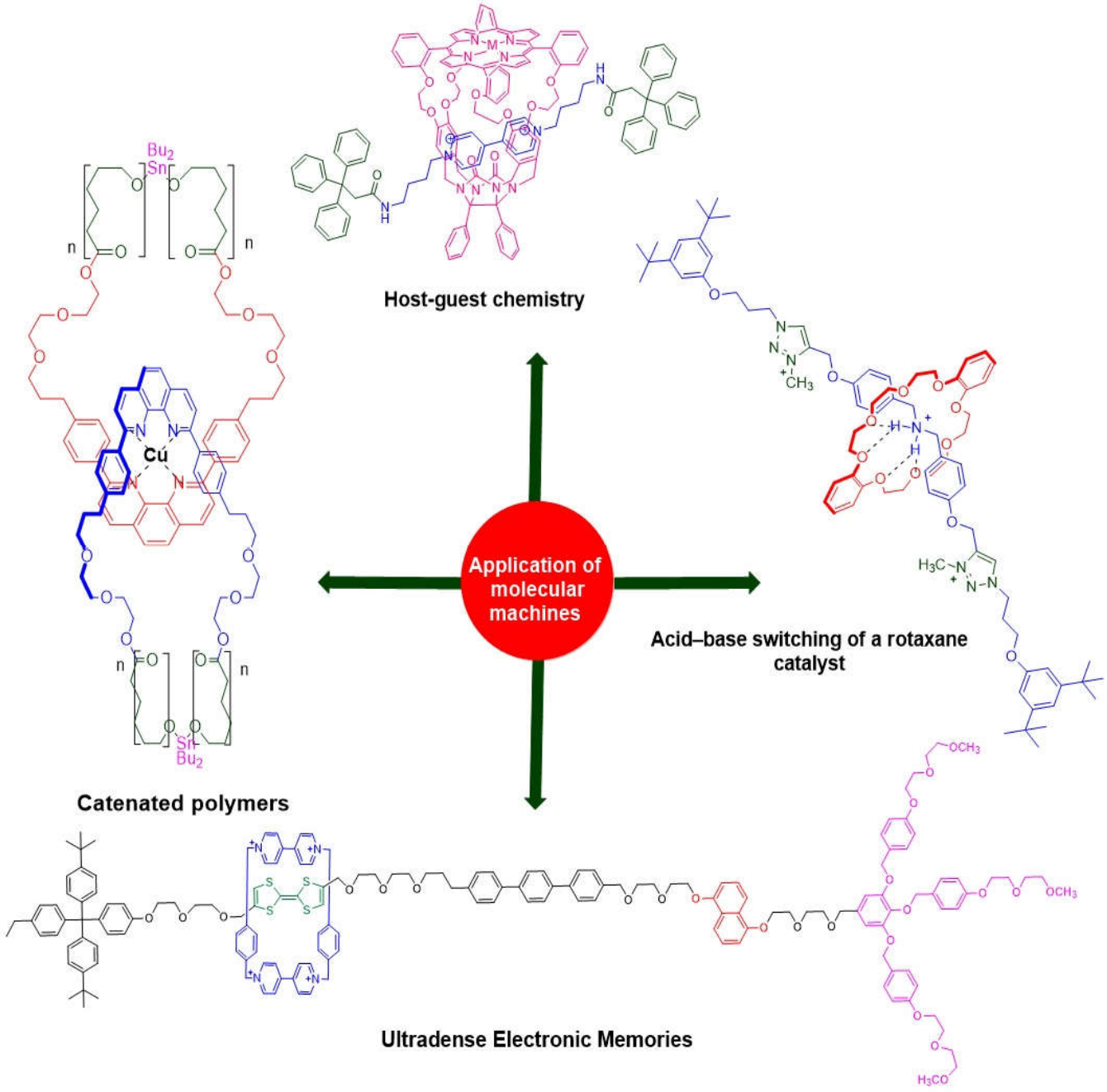


Fig. 1. Catenane and rotaxane in molecular machines

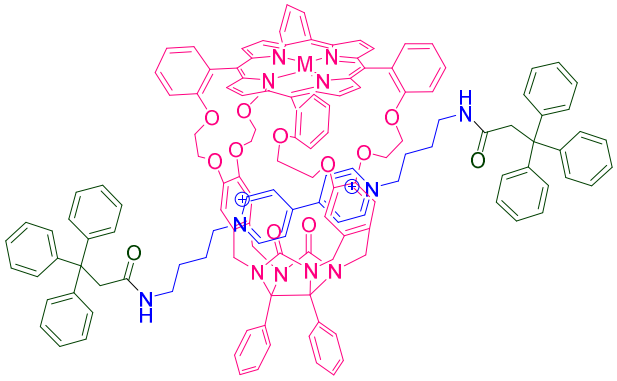
One of the most important applications of molecular machines, is their catalytic applications in synthetic chemical processes. Catalysts are essential in progress of modern manufactures due to interconvert different types of energy to each other [6]. Molecular machines with dynamic properties and particular topological structures have catalytic potential [6]. The chemistry of molecular machines comprehensively has been reviewed [7-11]. In this spotlight, the catalytic performance of molecular machines in synthetic reactions was highlighted.



Scheme 1. Several applications of molecular machines.

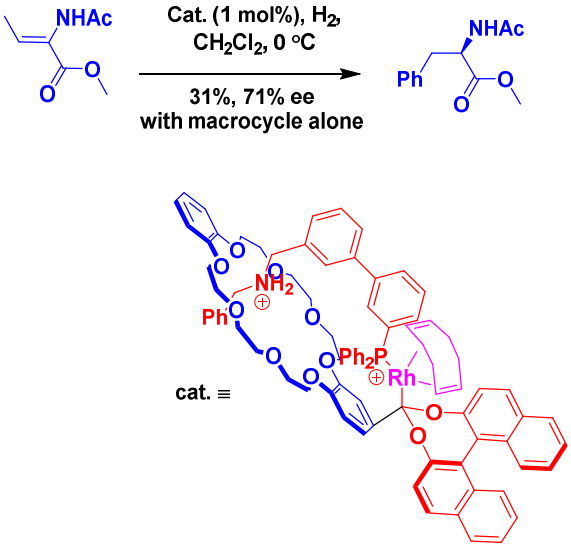
Abstracts

(A) In 2004, Takata and co-workers have been reported the catalytically active rotaxane for the first time. They have been synthesized thiazolium containing rotaxane that have a chiral binaphthyl unit in its structure. This chiral group allowing to the thiazolium unit to performs benzoin condensation with high enantioselectivity [12].

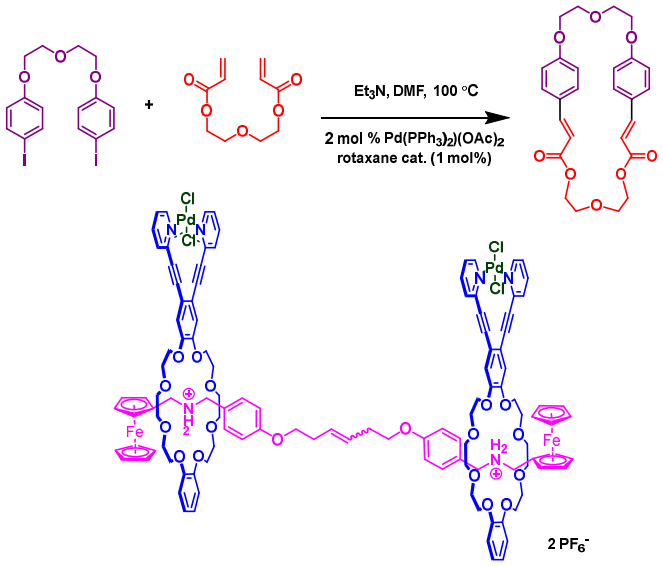


Host-guest chemistry

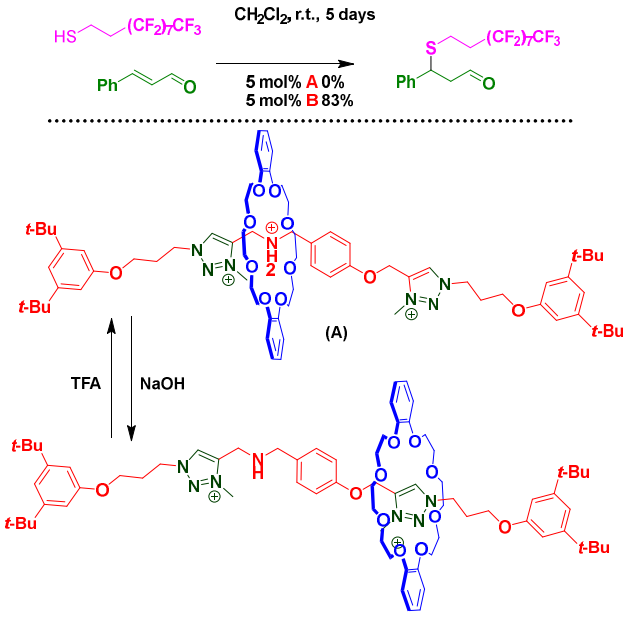
(B) Another catalytic application of molecular machines is enantioselective hydrogenation which has been reported by Nishibayashi and Fan in 2007 and 2008, respectively. They have been applied chiral pseudorotaxane rhodium complexes as catalyst. Nishibayashi and co-workers, had synthesized pseudorotaxane as an efficient and enantioselective catalyst for the hydrogenation of enamides. These systems have been approved a good potential of threaded constructions in transition metal catalysis [13, 14].



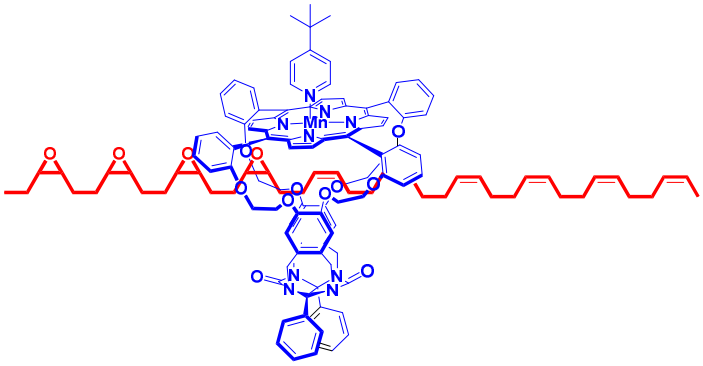
(C) Osakada and co-workers had reported a di-nuclear Pd catalyst based on a rotaxane which mediates the Mizoroki–Heck reaction. The mentioned rotaxane have a flexible framework and when a bifunctional alkene and organohalide was employed, the position of the two palladium centers have create a suitable distance to better macrocyclization. Accordingly, the yields of produced macrocycles by using di-nuclear Pd rotaxane as a catalyst is enhanced relative to using a simple mono-nuclear Pd catalyst [15].



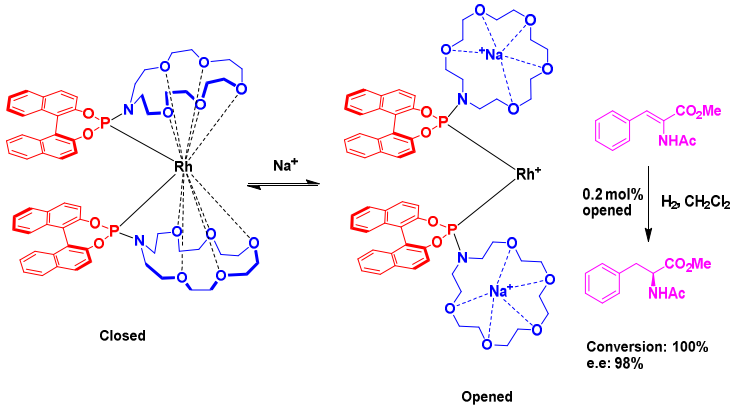
(D) A rotaxane catalyst by mimics of a basic functions of an enzyme has been reported by Leigh and co-workers. They have been synthesized steric hindrance macrocycle that can operate by opening and closing channels. This system is based on the application of non-degenerate crown ether as an organocatalyst for the conjugate addition of a thiol to cinnamaldehyde. When the central amine unit is protonated, the catalytic performance did not observe over 5 days at room temperature. In contrast, when the ammonium unit was deprotonated by shaking a solution of (A) with NaOH, the macrocycle is occupying the triazolium stations and the rotaxane catalysis the conjugate addition reaction efficiently, with 83% conversion over 5 days at room temperature [16].



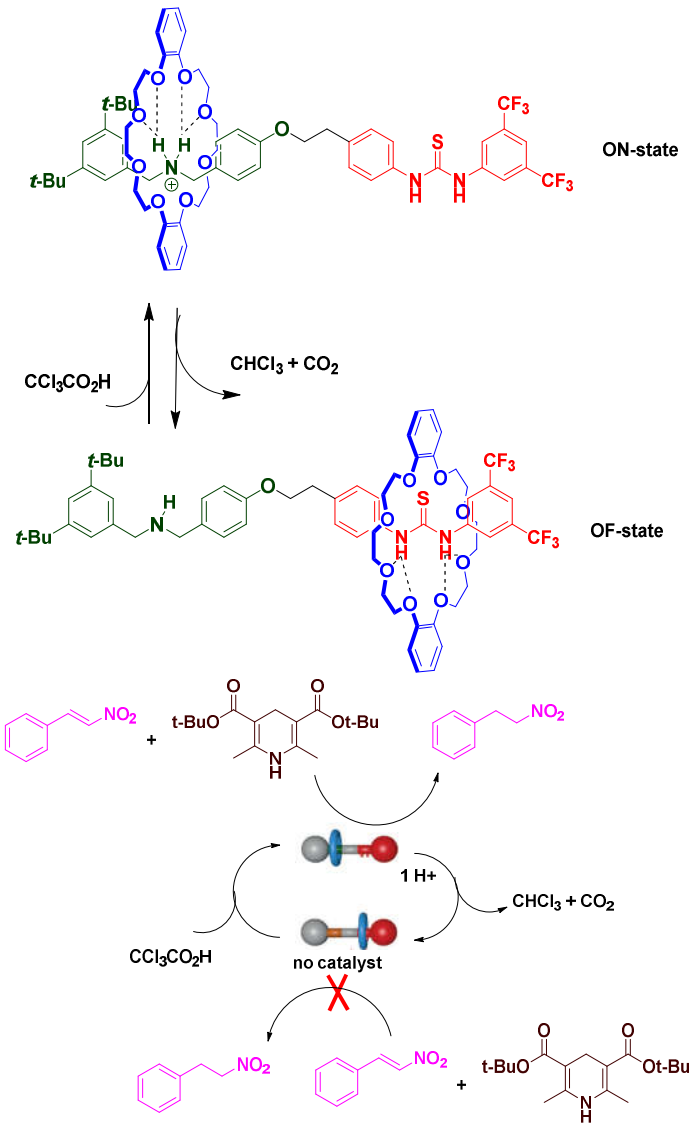
(E) In 2003, Rowan and Nolte have been reported an example of artificial processive molecular machine with epoxidation of a polybutadiene unit through glycoluril based macrocycle that have a manganese porphyrin with a catalytic application. The butadiene rapidly has been converted to the corresponding epoxides by addition of *t*-BuOOH to the reaction mixture in the presence of described molecular machine. By this molecular machine the stereochemistry arrangement of epoxide is in favor of cis (80 : 20 cis–trans), While by a non-interlocked Mn–porphyrin catalyst the stereochemistry arrangement of product is in favor of trans (20 : 80 cis–trans) [17].



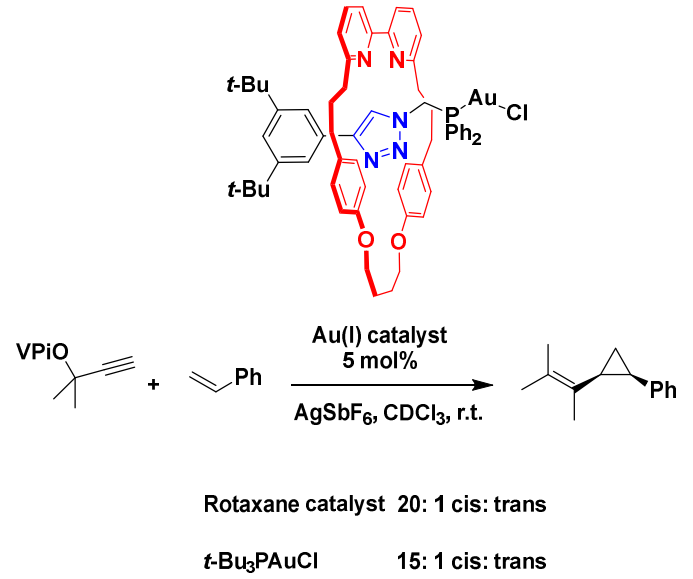
(F) Another kind of molecular machines are the allosteric molecular machines that generally have been observed in biology. Artificial allosteric supramolecular catalysts too have alike performance with biological allosteric molecular machines. Allosteric systems can be change conformational aggregate upon binding of an effector. Fan have been developed an allosteric molecular tweezer based on a rhodium complex and aza-crown-ether that has been modified by phosphoramidite ligands. In the closed state, the aza-crown ethers bind to cationic rhodium, causing the catalyst to be switched off. By addition of Na^+ and interacting with crown ether moieties, rhodium moiety will have activated. This system can be performed catalytic asymmetric hydrogenation of dehydroamino acid [18].



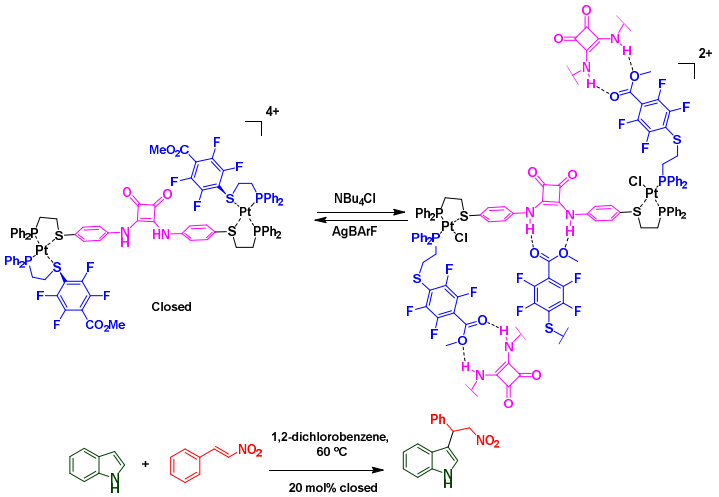
(G) In 2019, Biagini and co-workers have been reported a catalyst by a chemical fuel-induced for charging of molecular machine. A rotaxane that have secondary ammonium/amine and thiourea in its structure, has been converted between catalytically inactive and active states by pulses of a chemical fuel (trichloroacetic acid). The ON-state of the rotaxane catalyzes the reduction of a nitrostyrene by transfer of hydrogen. This molecular level machine is charged by each of pulses and can be perform succession in several times. However, in the absence of the mentioned rotaxane, no reaction progress has been observed [19].



(H) In 2015, switchable rotaxane catalyst based on phosphine complex has been reported by Goldup groups. This catalyst has been applied in cyclopropanation between propargylic alcohol and styrene. In this reaction, when the rotaxane is used as catalyst, the high diastereoselectivity was observed. It should be noted that the non-interlocked phosphines are unstable by oxidizer agents, while the rotaxane stabilizes the phosphine [20].



(I) Mirkin had produced a squaramide-based triple-layer hydrogen bond-donor organocatalyst and applied in Michael addition of indole to nitrostyrene. Catalyst is active in closed state. The amount of product in oligomers form in the semi‑open state by hydrogen bonding between the squaramide and the external spacers is negligible after 24 h, while in the closed state, oligomer formation is prohibited and the catalytic sites of squaramide are disengaged and its performance is better than open-state [21].



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