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Artificial Phosphodiesterases in Supramolecular Chemistry - from Nanostructured Enzymes Mimics to Temporally Controlled Catalysts

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Artificial Phosphodiesterases in Supramolecular Chemistry – from Nanostructured Enzymes Mimics to Temporally Controlled Catalysts

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Guanidinium units and metal cations such as Zn^{II} and Cu^{II} frequently occur in nature as key components of many enzymes, owing to their ability to act as electrophilic activators and nucleophile carriers, particularly in phosphodiesterases. In recent years, several supramolecular catalysts have been developed to mimic natural phosphodiesterases [1,2]. Kinetic data and titrations indicate that, in many cases, the active species feature a deprotonated water molecule coordinated to a metal cation (Figure 1a) [2].

The cooperative action of metal cations and guanidinium units can be exploited through a variety of molecular architectures, from conventional scaffolds such as calix[4]arenes to nanostructured supports including gold nanoparticles (AuNPs), polymer brushes grafted onto silica nanoparticles [2], hydrophobic aggregates [3], and carbon-based materials such as nanodiamonds [4]. These systems will be discussed in the seminar from a mechanistic perspective.

The pH sensitivity of these enzyme mimics suggests that their reactivity can be tuned by modulating solvent properties. Activated Carboxylic Acids (ACAs) have been shown to reversibly alter the pH via a rapid drop followed by gradual recovery through decarboxylation and base generation (Figure 1b) [5]. We employed this strategy to design supramolecular artificial phosphodiesterases whose activity can be repeatedly switched off and slowly reactivated. By varying the ACA identity and concentration, buffer strength, and initial pH, we achieved precise temporal control over catalytic activity. This tunable, dissipative behaviour could be extended to a broad range of out-of-equilibrium systems and catalysts, offering insights into the design of functional materials.

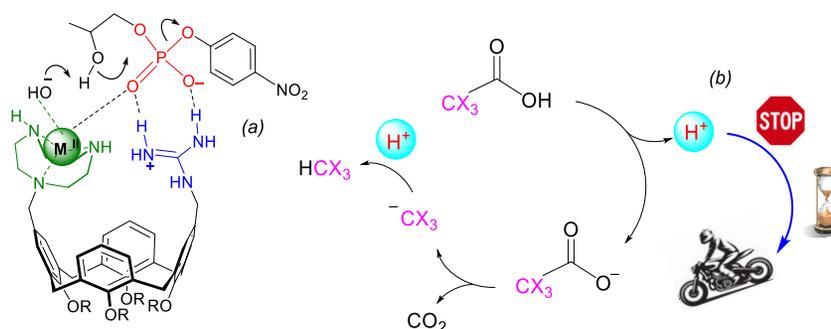


Figure 1: (a) mechanism of action of an artificial phosphodiesterase based on a calix[4]arene scaffold; (b) deprotonation and decarboxylation of an ACA employed in the design of a dissipative catalytic system.

References

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- [2] A. Casnati, R. Salvio, *Coord. Chem. Rev.* **2025**, 531, 216479
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