



## CMBN – IECB SEMINARS

Supported by ANR FOSET: Foldamer Scaffolds for Electron Transport

**2016**

*June*

27- 28

IECB (bat. B13) auditorium



### **Programme:**

#### **Monday 27<sup>th</sup> of June:**

16h00: **Alberto CREDI**  
*Light on molecular machines and materials*

16h45: **Frédéric COUTROT**  
*Toward multi-interlocked pH-sensitive molecular machines*

#### **Tuesday 28<sup>th</sup> of June:**

14h30: **Gwénaél RAPENNE**  
Technomimetic nanomachines : Molecular wheels, vehicles, rotors and motors

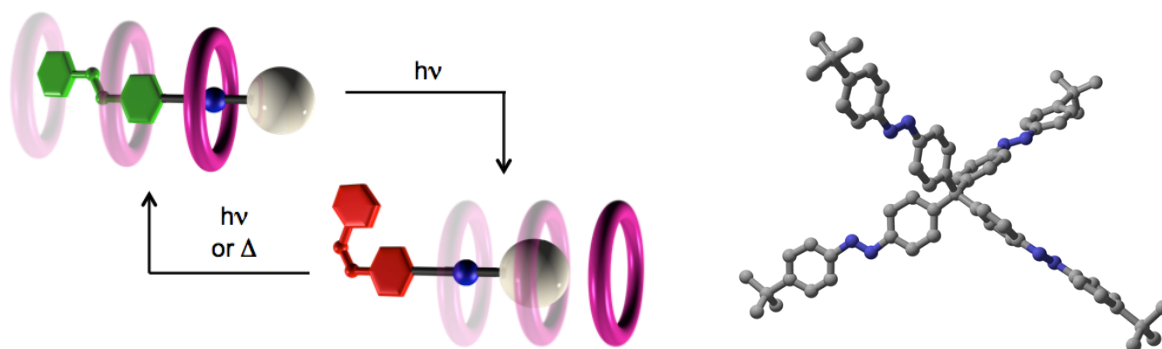
# Light on molecular machines and materials

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The bottom-up design, preparation and characterization of chemical systems that span from molecular scale devices and machines to nanostructured materials is a stimulating challenge of nanoscience [1]. The interest on this kind of systems arises from their ability to perform a (useful) function in response to chemical and/or physical signals. In this context, the use of light stimulation has several advantages, primarily because photons can be used to supply energy to the system (i.e., write) as well as to gain information about its state (i.e., read) [2].

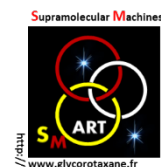
Here we will describe investigations undertaken in our laboratories, aimed at photo-inducing and -controlling large-amplitude molecular motions, both under thermodynamic and kinetic viewpoints, in multicomponent (supramolecular) species that comprise photoreactive elements [3]. Progress towards the construction of light driven molecular pumps (figure, left) [4] and molecular transporters [5] working in solution will be presented. We will also describe the reversible photoisomerization of shape-persistent azobenzene tetramers (figure, right) in the solid state, as an example of how photochromic processes can be utilized to develop molecular materials with valuable light-induced functionalities [6].



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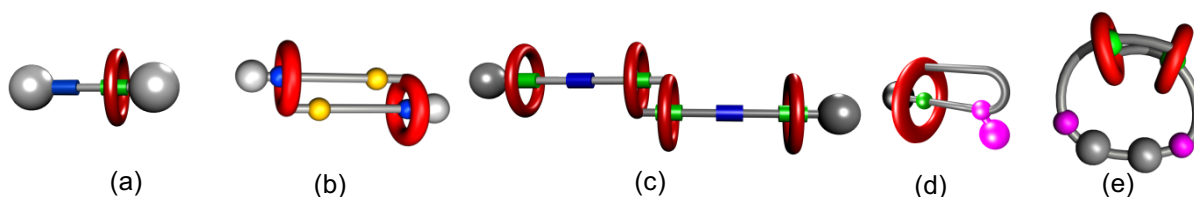
# Toward Multi-interlocked pH-Sensitive Molecular Machines



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Interlocked molecules consist of appealing molecular targets because their physical and chemical properties are closely related to their single topology. In the rotaxane series (*i.e.* a macrocycle encircling a molecular axle), it has already been demonstrated that both the presence and the localization of the macrocycle around a molecular thread allowed tremendous variations of the properties of the surrounded molecule. Hence, synthesizing molecules that are able to adopt various *co*-conformational states in response to an external *stimulus* (*i.e.* *stimulus*-responsive molecular machines) consists of a very attractive domain of research in fields as diverse and wide as material or medicinal chemistry. Different chemical accesses to pH-sensitive interlocked molecular machines will be described here, especially with crown ether macrocycles.<sup>[1]</sup> Among the listed pH-sensitive molecular machines (rotaxanes,<sup>[2]</sup> « molecular muscles »,<sup>[3]</sup> hetero[4]rotaxanes,<sup>[4]</sup> « lassos »<sup>[5,6]</sup> and « molecular jump-ropes »<sup>[6]</sup>), we will describe the conformational variations that can be obtained through the controlled displacement of a macrocycle along a molecular axle that contains ammonium, triazolium and pyridinium amide molecular stations (*i.e.* sites of interactions for the macrocycle).



**Figure 1.** Cartoon representation of (a) a [2]rotaxane, (b) a molecular muscle, (c) a hetero[4]rotaxane, (d) a lasso compound and (e) a double-lasso rotamacrocycle.

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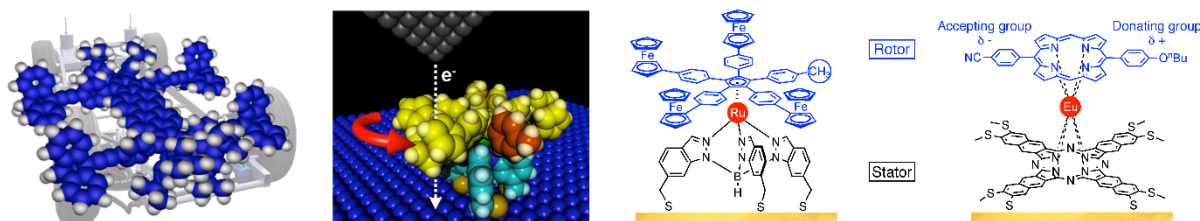
# Technomimetic nanomachines : Molecular wheels, vehicles, rotors and motors

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In the macroscopic world, the movement of rotation is at the source of many examples of machines. Advances in the imaging and manipulation of single molecules has stimulated much interest in the synthesis of molecules exhibiting unique mechanical properties. Technomimetic molecules<sup>[1]</sup> are molecules designed to imitate macroscopic objects at the molecular level, also transposing the motions that these objects are able to undergo.

In this presentation will be presented the preparation and single-molecule study of molecular vehicles capable to transport a cargo and unidirectional molecular motor with a possibility to reverse at will the rotation. The nanovehicles with two<sup>[2]</sup> (wheelbarrow in this case) or four triptycene<sup>[3]</sup> wheels are assemble around a polycyclic aromatic hydrocarbon platform. The molecular motor<sup>[4]</sup> is built around a ruthenium center coordinated to a cyclopentadienyl ligand terminated with ferrocene electroactive groups. The synthesis of the motor will be presented as well as variable temperature NMR experiments, electrochemistry and STM study showing the control of the unidirectional rotation<sup>[5]</sup>. The motor adsorbed on a gold surface can be made to rotate in a clockwise or counterclockwise direction by selective electron tunnelling through different sub-units of the molecule. The directional rotation originates from saw-tooth-like rotational potentials, which are solely determined by the internal molecular structure and are independent of the surface adsorption site. This is the first exemple of a molecular motor working reversibly. During this presentation, I will also show the simultaneous and coordinated rotational switching of europium double-deckers in a network.<sup>[6]</sup>



**Figure:** An exemple of nanovehicle with four triptycene wheels (left), a ruthenium molecular motor on the gold surface with a unidirectional rotation and the europium double-decker (right)

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