Self-assembled supramolecular structures: exploring a new concept for design and function of smart materials

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1. Project objectives

The current proposal is wishing to continue previously collaborations with Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), Université de Cergy-Pontoise, in the design and synthesis of new supramolecular systems for various advanced applications such as in biology, bioelectronics, ionic transport, molecular memories, molecular motion or generation of active layer in organic electronic devices. Moreover, the project offers the possibility for extending the international cooperation of the team involved in the project.

2. Project concept

Macroscopic properties of organic materials result from the combination of molecular structure and macroscopic organization or order. The past decade has witnessed remarkable innovations and progress in polymer science, including the field of supramolecular science as complementary field, which offer great opportunity for new concepts, new materials with unique properties and novel practical applications. The central aim of supramolecular science is to design building blocks with the proper structure that allows them to self-assemble by non-covalent bonding at the molecular level. The incorporation of non-covalent interactions in the construction of polymeric architectures has an impact on the polymer-chain behavior and subsequently generates smart functional polymeric materials. Synergistic combination of the principles of polymer and supramolecular chemistry afford broader and more precise synthetic methods that enable the production of hitherto unknown architectures, microstructures and properties.

The project will be developed in the following major directions and will explore the chemistry, physics and technological applications of innovating supramolecular systems.

Two types of supramolecular structures are considered: a) the primary goals of this project are to apply self-assembly, to form pseudorotaxane structures. Pseudorotaxanes are mechanically interlocked molecular architectures consisting of linear small or polymeric

components (guests) incorporated inside of the macrocyclic cavities (hosts) by non-covalent interactions, Figure 1 left. The work in this first area will be based on the complexation of cyclic species (hosts) with suitable complementary guests.

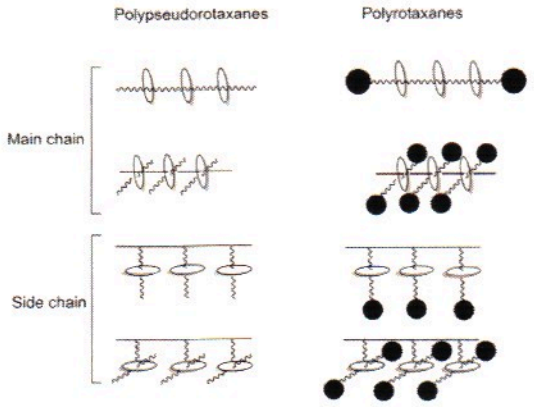

Figure 1: Various types of polypseudorotaxanes/polyrotaxanes

Furthermore, the pseudorotaxanes will be explored by using a large variety of host and guest species. The resultant supramolecular materials will be studied as interpenetrating polymer network (IPN), self-healing (SH) or stimuli responsive materials.

The work in the second are is directed toward to new supramolecular systems by covalently bonding of bulky groups to the ends of the linear guest molecule resulting polyrotaxane structures, Figure 1 right. The increased interest in this field is justified by far, not only for the synthesis of new supramolecular compounds, but more than that to their applications. By controlling the synthesis conditions, a wide variety of polyrotaxanes by association of various polymeric/monomeric backbones with supramolecular host molecules will be constructed as well their reference counterparts.

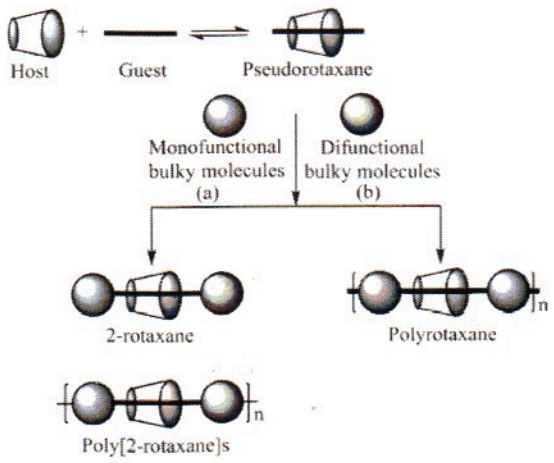

Figure 2. Main routes involved in the synthesis of self-assembled supramolecular structures

Such threading of macrocycles onto the macromolecular chains improves the physical as well as the photophysical and morphological characteristics of the resulting supramolecular assemblies. In addition, these assemblies give rise to the possibility to construct of novel supramolecular compounds soluble in water, which will be studied in interaction with biological systems.

3. Proposal objectives

In this part of the proposal we outline our plan, which are divided into distinct parts as follow:

3.1. Synthesis of new host - guest systems

In general, the employed synthetic strategies of supramolecular structures formation involved as the first step the encapsulation of guest molecules with suitable macrocycles (hosts) by simply threading their backbones through the rings without any covalent bonds between them resulting pseudorotaxanes. By structural modifications either of the host and guest molecules pseudorotaxanes can then be applied for other system formations such as self-healing polymers, stimuli responsive materials, molecular machines, actuators and sensors. The possibility of electrolytic side chains or functionalization of the macrocycles which charge-transporting groups affords also the possibility of to new applications that is still out of our considerations.

3.2. Synthesis of the supramolecular structures

Encouraged by our previously reported results,[1-7] we will develop new supramolecular architectures which should be beneficial for their practical application. The originality of the proposal is not only the synthesis of new supramolecular architectures, but also some of them to be used as neat active layers in bulk heterojunction solar cells (BHJ), because they lend themselves naturally to the fabrication of diffuse heterojunctions between interpenetrating networks of *n*- and p-type semiconductors.

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