Minisymposium

Jeudi 6 février 2025 de 9h30-11h30
Amphithéâtre Henri Benoît

Prof. Patrice Woisel
UMET Lille

Thermoresponsive polymers and host-guest chemistry: a win-win combination

Dr. Olivier Colombani
IMMM Le Mans

Supramolecular polymeric nanocylinders via cooperative hydrogen bonding in solution: from homogeneous 1D structures to stimuli-responsive and Janus particles

Minisymposium organisé dans le cadre de la soutenance de thèse d'Axel Pinabiaux à 14h le même jour.

Les personnes souhaitant rencontrer les orateurs sont invitées de prendre contact avec Emilie Moulin.

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Thermoresponsive polymers and host-guest chemistry: a win-win combination

P. Woisel and Coll.

This lecture will be given in tribute to Sir Pr. J.F. Stoddart

Abstract:
The combination of heat-sensitive polymers and supramolecular chemistry has recently led to the development of fascinating adaptive materials. In this context, most studies have focused on exploiting host-guest interactions to control the physicochemical properties of polymeric materials.(1) This approach has notably enabled the creation of materials with programmable thermosensitivity and sensor properties.(2)
In contrast, the exploitation of polymer thermoresponsiveness to control the recognition properties of host-guest systems at the molecular level is much less developed, and a perfect understanding of the mechanisms triggering thermo-induced decomplexation or complexation is still elusive.
In this communication, we will illustrate through different studies how the host-guest chemistry and the thermo-induced phase separation mechanisms can “talk together” to synergistically tune the coil↔globule transition and the complexation state of polymeric systems. The first example3 will concern a comparative analysis of the behaviour of complexes formed from different naphthalene end-functionalized LCST or UCST polymers and the electron-deficient cyclobis(paraquat-p-phenylene) tetrachloride (CBPQT4+, 4Cl-) (3) host when subjected to heat treatment. This study provided an understanding of the mechanisms triggering the thermo-induced (de)complexation of such complexes. Furthermore, this knowledge has enabled us to generalize the use of LCST phase transitions to dissociate other Pillararene-based complexes efficiently and on demand.(4) The third study will report a supramolecular approach for developing smart thermoresponsive polymeric hydrogels featuring a dual temperature and time memory function based on a kinetic control of the material's (de)complexation and (re) swelling behaviours(5). The last study will report a rare example of decreased chemical reactivity upon increasing temperature thanks to exploiting a thermo-induced phase separation mechanism.(6) This will be illustrated from a synthetic self-complexing host-guest molecular switch CBPQT4+-Fu, consisting of an electron-rich furan unit covalently attached to the electron-deficient CBPQT4+ host. Thanks to the LCST-mediated control topology of the functionalized host, the Diels-alder of CBPQT4+-Fu with maleimide in water can be switched on at lower temperatures (below the Tcp) while it is switched off at elevated temperatures (above Tcp), representing a rare example of lower reactivity at raised temperature. This work provides thus essential insight into synergistically controlling chemical reactivity through supramolecular topological chemistry, combined with different regulators (molecular and thermal), providing an important step towards synthetic molecular reaction networks.

References :
1) V. R. de la Rosa and coll., Mater. Today, 2016, 19, 44-55
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4) X. Guan and Coll. Macromolecules, 2025, accepted
5) L. De Smet and Coll. ACS Materials Letters, 2022,5;1, 235-242
6) C. Ribeiro and Coll. Chem.Eur. J., 2024,30, e2023023

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Dr. Olivier Colombani, IMMM Le Mans

Polymer bottle-brushes consist of a long linear polymer backbone so densely grafted with polymer side-chains, typically on every monomer unit, that the backbone becomes rigid and extended, affording a cylindrical (1D) morphology. Such particles have already found applications in various fields in anti-fouling, nanolithography, templates for the design of inorganic nanocylinders, design of supersoft thermoplastic elastomers or medicine (drug delivery, sensing, signaling, detection). Nature also uses polymer bottlebrushes for joints lubrication, cell protection and lung clearance. Being able to control the dimensions of these nanocylindrical particles or to endow them with stimuli-responsiveness or with different functionalities impacts their properties and therefore their applicative relevance. An attractive strategy to this respect is to prepare polymer bottle-brushes through supramolecular association via cooperative hydrogen bonding in solution. In this presentation, it will be shown that this strategy allows a fine control over the characteristics of the nanocylinders via multiple parameters: length and chemical composition of the polymer arms, strength of the hydrogen bonding units, solvent, process, temperature. Moreover, it affords the possibility to trigger the dissociation of the nanostructures using external stimuli such as light or redox systems, sometimes in a reversible way. Finally, breaking the symmetry of the hydrogen bonding stickers may lead to the formation of Janus particles, consisting of two faces with different chemistries. This versatility makes supramolercular bottle-brushes potential candidates for new applications in the field of material science, some of which are currently being investigated.

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