

Scientific day ICP/A2U-Chemistry “Supramolecular Chemistry”

Energy HUB, Amiens

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December 5th 2022

9h: Welcome - Coffee

9h30: Presentation of the scientific theme by Florence Pilard, Anne Ponchel & Sophie Fourmentin

10h30-12h30: Conferences – Part 1

- Dominique Armspach (Pr. Université de Strasbourg, Institut de Chimie de Strasbourg, UMR CNRS 7177, Strasbourg)

“Bridged cyclodextrins for catalytic purposes and beyond”

- Patrice Woisel (Pr. Univ. Lille, Centrale Lille, UMR CNRS 8207, UMET, Lille)

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

12h30-13h30: Buffet – Poster session

13h30-16h30: Conferences – Part 2

- Matthieu Sollogoub (Pr. Sorbonne Université/IUF, Institut Parisien de Chimie Moléculaire, UMR CNRS 8232, Paris)

“Control of cyclodextrin self-assembly”

- Nicolas Guiseppone (Pr. Univ. Strasbourg/IUF, Institut Charles Sadron, UPR CNRS 22, Strasbourg)

“Artificial molecular machines that work on all scales”

- Emmanuel Cadot (Pr. UVSQ, Institut Lavoisier de Versailles, UMR CNRS 8180, Versailles)

“Chaotropic effect as an assembly motif in polyoxometalate supramolecular chemistry”

16h30-17h: Closure

Bridged cyclodextrins for catalytic purposes and beyond

Dominique Armspach

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Abstract:

Cyclodextrins are naturally occurring cyclic oligosaccharides that can host a wide range of guest molecules within their well-defined cavity. Bridging cyclodextrins allows the precise positioning of various functionalities in close proximity to the cavity¹ and was found to be critical for applications where rigidity is needed ranging from catalysis to chiroptical and photophysical applications.

Our contribution over the years in this field has mainly concentrated on the use of phosphine-² and NHC-capped³ cyclodextrins in metal catalysis. The first part of this presentation will trace back the evolution of the cavity-shaped phosphorus ligands from monophosphines⁴ and *trans*-chelating diphosphines⁵ to *cis*-chelating P^N⁶ and diphosphine ligands⁷ with a special focus on asymmetric catalysis. Very recent work dealing with the impact of metal confinement on the photophysical properties of luminescent copper complexes⁷ and the use of noncovalent bonds for the effective transfer of chirality from the cyclodextrin torus to a chiroptically responsive biphenyl bridge⁸ will also be presented.

References :

- 1) E. Engeldinger, D. Armspach, D. Matt, *Chem. Rev.* **2003**, *103*, 4147-4174.
- 2) M. Jouffroy, D. Armspach, D. Matt, *Dalton Trans.* **2015**, *44*, 12942-12969.
- 3) Z. Kaya, L. Andna, D. Matt, E. Bentouhami, J.-P. Djukic, D. Armspach, *Chem. Eur. J.* **2018**, *24*, 17921-17926.
- 4) E. Engeldinger, L. Poorters, D. Armspach, D. Matt, L. Toupet, *Chem. Commun.* **2004**, 634-635.
- 5) L. Poorters, D. Armspach, D. Matt, L. Toupet, S. Choua, P. Turek, *Chem. Eur. J.* **2007**, *13*, 9448-9461.
- 6) Y. Li, K. Pelzer, D. Sechet, G. Creste, D. Matt, P. Braunstein, D. Armspach, *Dalton Trans.* **2022**, *51*, 11226-11230.
- 7) T. A. Phan, N. Armaroli, A. S. Moncada, E. Bandini, B. Delavaux-Nicot, J. F. Nierengarten, D. Armspach, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214638.
- 8) G. Preda, S. Jung, G. Pescitelli, L. Cupellini, D. Armspach, D. Pasini, *Chem. Eur. J.* **2023**, *n/a*, e202302376.

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

Patrice Woisel

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Keywords: Thermoresponsive polymers, Host-guest complexation, memory function, synergistic control of host reactivity

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 three 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. The second study will report a supramolecular approach for developing an intelligent thermoresponsive polymeric hydrogel featuring a dual temperature and time memory function based on a kinetic control of the material's (de)complexation and (re) swelling behaviours. The last study will illustrate how a thermo-induced phase separation mechanism can regulate on demand the Diels-alder reactivity of 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, with maleimide in water. Thanks to a supramolecular control over the topology of **CBPQT⁴⁺-Fu** combined with a thermoresponsive supramolecular regulator, we reported a rare example of decreased reactivity upon increasing temperature.

References :

1) V. R. de la Rosa and coll., *Mater. Today*, **2016**, 19, 44-55; 2) N. Herzer and coll. *J. Am. Chem. Soc.* **2012**, 134, 7608–7611; 3) H. Guo and coll. *Polym. Chem.* **2022**,13;25, 3742-3749, 4) P. R. Ashton and coll. *Angew. Chem.*, **1988**, 27, 1550-1553; 5) L. De Smet and coll. *ACS Materials Letters*, **2022**,5;1, 235-242; 6) C. Ribeiro and coll. submitted

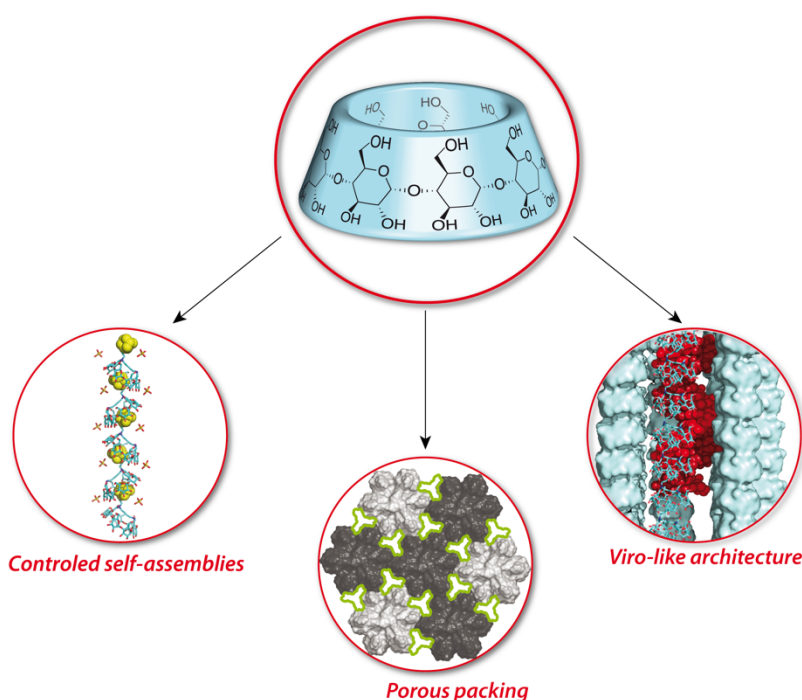
Control of cyclodextrin self-assembly

Matthieu Sollogoub

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Abstract:

Cyclodextrins are cyclic oligosaccharides possessing a cavity able to include a guest. This property is used in our daily life, where cyclodextrins serve as deodorants, excipients or in chiral stationary phases. In these applications, cyclodextrins are unfunctionalized or randomly functionalized. More sophisticated applications require efficient functionalizations which were unavailable for a long time. Over the years, we delineated several strategies to efficiently and selectively access poly-hetero-functionalized cyclodextrins.^[1] The ability to place different functions anywhere on a cyclodextrin allowed us to induce and control their self-assembly.^[2] The addition of a second function on the cyclodextrin further produced well-defined architectures.^[3] Co-assemblies with DNA could also be made to form viro-like constructs.



References :

- 1) M. Sollogoub, et al. *Nature Commun.* **2014**, 5, 5354; *Angew. Chem. Int. Ed.* **2021**, 60, 12090
- 2) M. Sollogoub, et al. *Org. Chem. Front.* **2014**, 1, 703 ; *Angew. Chem. Int. Ed.* **2018**, 57, 7753.
- 3) M. Sollogoub, et al. *Angew. Chem. Int. Ed.* **2014**, 53, 7238; *Chem. Eur. J.* **2023**, e202300150

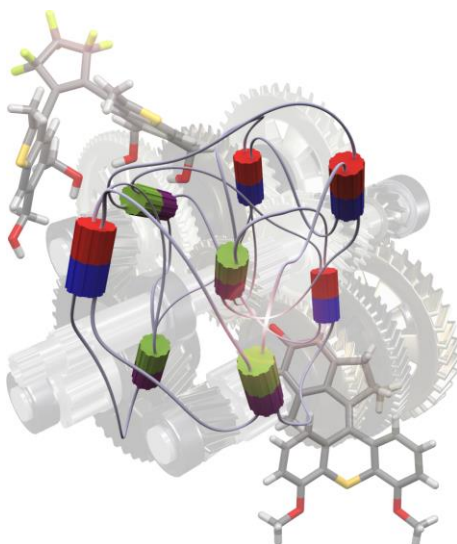
Artificial molecular machines that work on all scales

Nicolas Giuseppone

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Abstract:

Making molecular machines that can be useful in our macroscopic world is a challenging long-term goal of nanoscience. Inspired by the protein machinery found in biological systems, and based on the theoretical understanding of the physics of motion at nanoscale, organic chemists have developed a number of molecules that can produce work when triggered by various external chemical or physical stimuli.¹ In particular, basic molecular switches that commute between (meta)stable states, and more advanced molecular motors that produce unidirectional cyclic motions out-of-equilibrium when fueled with external energy, have been reported. However, the integration of individual molecular motors in a continuous mechanical process that can have measurable effects at various length scales and up to the macroscale remains an important objective. We will discuss advances developed by our group on artificial molecular machines, which involve their mechanical coupling with polymer systems. We will show how it becomes possible to integrate them and to make use of their mechanical work going from individual molecular devices to macroscopic materials.



References :

1) (a) D. Dattler, G. Fuks, J. Heiser, E. Moulin, A. Perrot, Y. Xuyang, N. Giuseppone, *Chem. Rev.* **2020**, 120, 310-443; (b) E. Moulin, L. Faour, C. Carmona-Vargas, N. Giuseppone, *Adv. Mat.* **2020**, 201906036.

Chaotropic effect as an assembly motif in polyoxometalate supramolecular chemistry

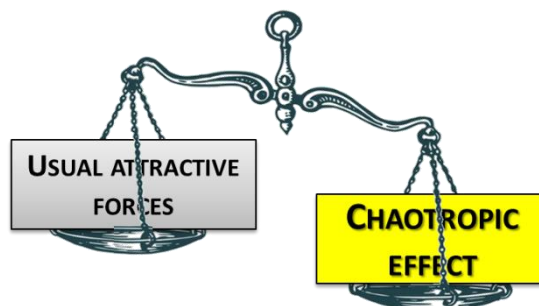
Clément Falaise, Mohamed Haouas, Nathalie Leclerc, and Emmanuel Cadot,

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Abstract:

The ability of biochemical substances such as phospholipids, glycans, or proteins to interact with discrete inorganic species is essential for some biological functions.^[1] Then, designing supramolecular hybrid architectures including dynamics and responsive behavior requires a fine balance between the conglomerate of weak forces such as electrostatic, ion-dipole, dipole-dipole, hydrogen-bonding, dispersion, etc., that drives the aggregation processes.

Recent reports highlight the intriguing properties of certain inorganic polynuclear anions, such as polyoxometalates (POMs) or polynuclear clusters for their extremely high propensity to interact strongly in aqueous solution with non-ionic organic components such as macrocycles or surfactants.^[2,3,4] This striking driving force has been identified as a strong solvent effect arising from chaotropic nature of the polyoxometalates in aqueous solution. In this communication, we will highlight the origin of this effect by proposing a classification of the chaotropic character of a large series of polyoxometalates, ranging from the Keggin type ions to the large nanoscopic ring-shape molybdenum blue. However, we will give some relevant examples showing how the chaotropic effect can be used to monitor supramolecular hybrid assemblies such as molecular core-shell, supramolecular MOFs or POM-containing bilayer type membrane.



References :

- 1) Zhong, W.; Alexeev, D.; Harvey, I.; Guo, M.; Hunter, D. J. B.; Zhu, H.; Campopiano, D. J.; Sadler, P. J.. *Angew. Chem. Int. Ed.* **2004**, *43* (44), 5914–5918.
- 2) Assaf, K. I.; Ural, M. S.; Pan, F.; Georgiev, T.; Simova, S.; Rissanen, K.; Gabel, D.; Nau, W. M. *Angew. Chem. Int. Ed.* **2015**, *54* (23), 6852–6856.
- 3) Moussawi, M. A.; Haouas, M.; Floquet, S.; Shepard, W. E.; Abramov, P. A.; Sokolov, M. N.; Fedin, V. P.; Cordier, S.; Ponchel, A.; Monflier, E.; Marrot, J.; Cadot, E. *J. Am. Chem. Soc.* **2017**, *139* (41), 14376–14379.
- 4) Falaise, C.; Khelifi, S.; Bauduin, P.; Schmid, P.; Shepard, W.; Ivanov, A. A.; Sokolov, M. N.; Shestopalov, M. A.; Abramov, P. A.; Cordier, S.; Marrot, J.; Haouas, M.; Cadot, E. *Angew. Chem. Int. Ed.* **2021**, *60* (25), 14146–14153.