



COST Action CA17120
CHEMOBRIONICS
Program & Abstracts

January 29 – 31, 2020
University of Chemistry and Technology Prague
Czech Republic



Wednesday, January 29

8:00	Respirium	Registration
8:50 – 9:00	hall B1	Opening
9:00 – 9:40	hall B1	IS Laurie Barge <i>Chemobrionics and the Search For Life Elsewhere</i>
9:40 – 10:05	hall B1	LP Sean McMahon <i>Chemical gardens and the fossil record</i>
10:05 – 10:20	hall B1	SP Ignacio Sainz-Diaz <i>Formation and characterization of tubular chemical gardens in flow conditions</i>
10:20 – 10:35	hall B1	SP PawanKumar <i>Bio-inspired flow-driven gardens</i>
10:35 – 10:50	hall B1	SP Steen Rasmussen <i>Thermodynamic enhancement of primitive molecular replication dynamics</i>
10:50 – 11:20	Respirium	Coffee
11:20 – 12:20	room B06	WG1 meeting
12:20 – 13:20	room B06	WG4 meeting
13:00 – 15:00	Blox	Lunch
15:00 – 15:40	hall B1	IS Shigeru Deguchi <i>Supramolecular Processes under Conditions Mimicking Deep-Sea Hydrothermal Vents</i>
15:40 – 16:05	hall B1	LP Piotr Szymczak <i>Evolving network model of dissolution and precipitation in porous media</i>
16:05 – 16:20	hall B1	SP Antonio Ranieri <i>Speciation of self-assembled copper structures, a new material able to accumulate fundamental molecules for life and industrial applications</i>
16:20 – 16:35	hall B1	SP Julyan Cartwright <i>Chemobrionics: the state of the art in 2020</i>
16:35 – 17:00	Respirium	Coffee
17:00 – 18:30	hall B1	Management committee meeting

IS = invited speaker (40 minutes)

LP = long presentation (25 minutes)

SP = short presentation (15 minutes)

SSP = student short presentation (15 minutes)

Thursday, January 30

9:00 – 13:00	Respirium	Poster session, discussion session
9:00 – 9:15	Uhelna	SSP Stefano Cadeddu <i>Synthesis and self-assembly studies of a new family of amphiphilic molecules based on glyco-peptoids</i>
9:15 – 9:30	Uhelna	SSP Michael Emmanuel <i>Flow-driven crystallization and precipitation kinetics in the lithium-phosphate system</i>
9:30 – 9:45	Uhelna	SSP Carlos Gutiérrez Ariza <i>Seedless Image Velocimetry as a new approach to study chemical garden's hydrodynamics</i>
9:45 – 10:00	Uhelna	SSP Miruna Chipara <i>Chemobionic structures serving as cellular scaffolds for bone tissue substitutes</i>
10:00 – 10:15	Uhelna	SSP Pamela Knoll <i>Flow-Induced Precipitation in Thin Capillaries Creates Helices, Lamellae, and Tubes</i>
10:15 – 10:30	Uhelna	SSP Richard Loeffler <i>A camphor–camphene alloy for studies on self-propelled motion of objects with varied shapes</i>
10:30 – 10:45	Uhelna	SSP Lorenzo Sebastianelli <i>Effect of the presence of sulfide anion on iron (III)/(II) and copper (II) Chemical Garden</i>
10:45 – 11:00	Uhelna	SSP Dimitra Spanoudaki <i>Oscillatory budding dynamics of a chemical garden within a co-flow of the two reactants</i>
11:00 – 11:30	Respirium	Coffee
11:30 – 12:15	Uhelna	WG3 meeting
12:15 – 13:00	Uhelna	WG2 meeting
13:00 – 14:30	Blox	Lunch
14:30 – 15:10	hall BI	IS Carlos Gershenson <i>Guiding the Self-organization of Cyber-Physical Systems</i>
15:10 – 15:35	hall BI	LP Gaetano Angelici <i>Conformational properties of (S)-indoline-2-carboxylic acid oligomers: an experimental and theoretical study</i>
15:35 – 16:00	hall BI	LP Omer Markovitch <i>Autocatalysis through self-assembly</i>
16:00 - 16:30	Respirium	Coffee
16:30 – 16:45	hall BI	SP Gorecki Jerzy <i>Inversion of self-propelled rotors under periodic stop and release operations</i>
16:45 – 17:00	hall BI	SP Geoff Cooper <i>Automated Evolution of Soft Materials in a Chemorobotic Platform with Machine Learning</i>
17:00- 17:15	hall BI	SP Silvia Holler <i>Interfacing artificial life with natural life: liquid droplets as transporters for living cells</i>
17:15 – 17:30	hall BI	SP Janno Torop <i>Electroactive ionogel composites for actuator/sensor applications in soft robotics</i>
18:00 – 20:00	Blox	Dinner

Friday, January 31

9:00 – 9:40	hall BI	IS Oliver Steinbock <i>Explaining Biomorph Growth</i>
9:40 – 10:05	hall BI	LP Nikolai Denkov <i>Could oil drops be the first protobionts?</i>
10:05 – 10:30	hall BI	LP Pasquale Stano <i>Is Research on "Synthetic Cells" Moving to the Next Level?</i>
10:30 – 10:45	hall BI	SP Nathaniel Virgo <i>Self-organisation in messy chemistry</i>
10:45 – 11:00	hall BI	SP Shin-ichiro Nomura <i>Cell-sized molecular robots made by motorized vesicles</i>
11:00 – 11:30	Respirium	Coffee
11:30 – 11:55	hall BI	LP Erik Hughes <i>Engineering Chemobronic Biomaterials for Tissue Regeneration Applications</i>
11:55 – 12:10	hall BI	SP Nanasaheb Thorat <i>Magnetically active breast cancer chemotherapeutics using superparamagnetic hybrid nanoconjugates</i>
12:10 – 12:25	hall BI	SP Ágota Tóth <i>Magnetic-Field-Manipulated Growth of Flow-Driven Precipitate Membrane Tubes</i>
12:25 – 12:40	hall BI	SP Dezso Horvath <i>Modeling of precipitate formation in a microfluidic reactor</i>
12:40 – 12:55	hall BI	SP Gábor Schuszter <i>Flow-driven precipitation patterns in confined geometry: The coupling of crystallisation characteristics and hydrodynamics</i>
13:00 – 14:30	Blox	Lunch
14:30 – 14:55	hall BI	LP Simone Giannerini <i>Circular codes, universal properties of codon bias, and translation efficiency</i>
14:55 – 15:20	hall BI	LP Majdi Hochlaf <i>In silico multiscale modelling of CO₂ capture by nanoporous materials</i>
15:20 – 15:35	hall BI	SP Marcello Budroni <i>Emergent behaviours driven by chemohydrodynamic interplay in A+B\rightarrowC systems</i>
15:35 – 15:50	hall BI	SP Srecko I. Kirin <i>Transmission of chirality in artificial metallated oligoamides</i>
15:50 – 16:05	hall BI	SP Cláudia Lopes <i>Adsorption of Technology Critical Elements from aqueous solutions</i>
16:05 – 16:20	hall BI	SP Tan-Phat Huynh <i>(Metal sulfide)-polymer composites grown from the gel/liquid interface</i>
16:20 – 16:40	hall BI	Closing, Best student presentation award ceremony
16:40 – 17:30	Respirium	Farewell coffee

POSTERS

Nevin Aytemiz

Classical and Nonclassical Behavior of Ethylene Oxide within the Clathrate Hydrates: Experiment and theory

F. Mine Balci

Solvation of N₂O in cold nanodroplets of small organic molecules

Fabrizio Bernini

Iron (III) Chemical Garden interacting with sucrose

Ana Borrego-Sánchez

Formation and characterization of tubular carbonates in flow conditions

Elizabeth Escamilla-Roa

Abiotic production of oxygen precursors from the interaction of calcium perchlorate with olivine surface: Implications to formation of Martian's regolith

Sonja Grubisic

Force Field Refinement and Molecular Dynamics Simulations of Imidazolium-Based Ionic Liquids

Alfonso Hernández-Laguna

DFT Study of the Hydrolysis reaction on Cluster Models simulating (001) and (010) surfaces of Phyllosilicates

Marjatta Louhi-Kultanen

Recovery of critical metals by crystallization from aqueous electrolyte solutions

Lara Mikač

Gamma-irradiation synthesis of silver nanoparticles in the presence of aminodextran

František Muzika

Comparison of discrete Turing patterns of glycolytic oscillatory reaction in cyclic arrays of chemical computing systems

Emmanuele Parisi

New non-molecular hybrid organic-inorganic systems for application in electronic and photonics

Pedro A. Sánchez

Theoretical modeling of active magnetic colloids and nanoparticles

Igor Schreiber

Reaction networks, motifs for oscillatory dynamics, and parameter estimation in complex biochemical mechanisms

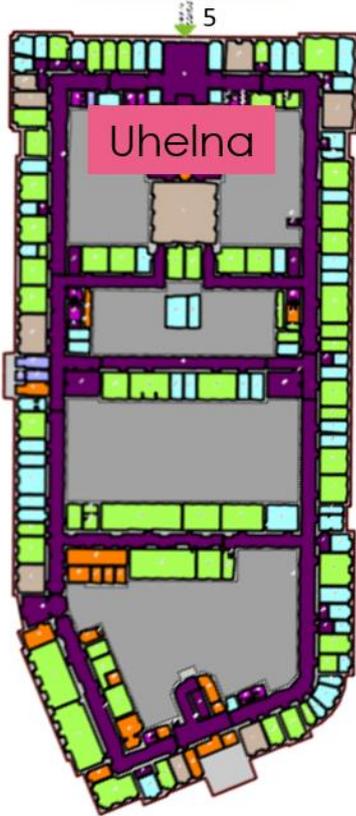
Fabienne Trolard

Acquiring thermodynamic data on mineral and organic systems and linking them with mobilities of elements in natural environments: an ongoing challenge

Eniko Volceanov

Silicate-garden system formation during hardening of stamped mortar with wood ash admixtures

Building A



Technická

Building B



UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

BLOX RESTAURANT

Wednesday, January 29

13:00 – 15:00 Lunch

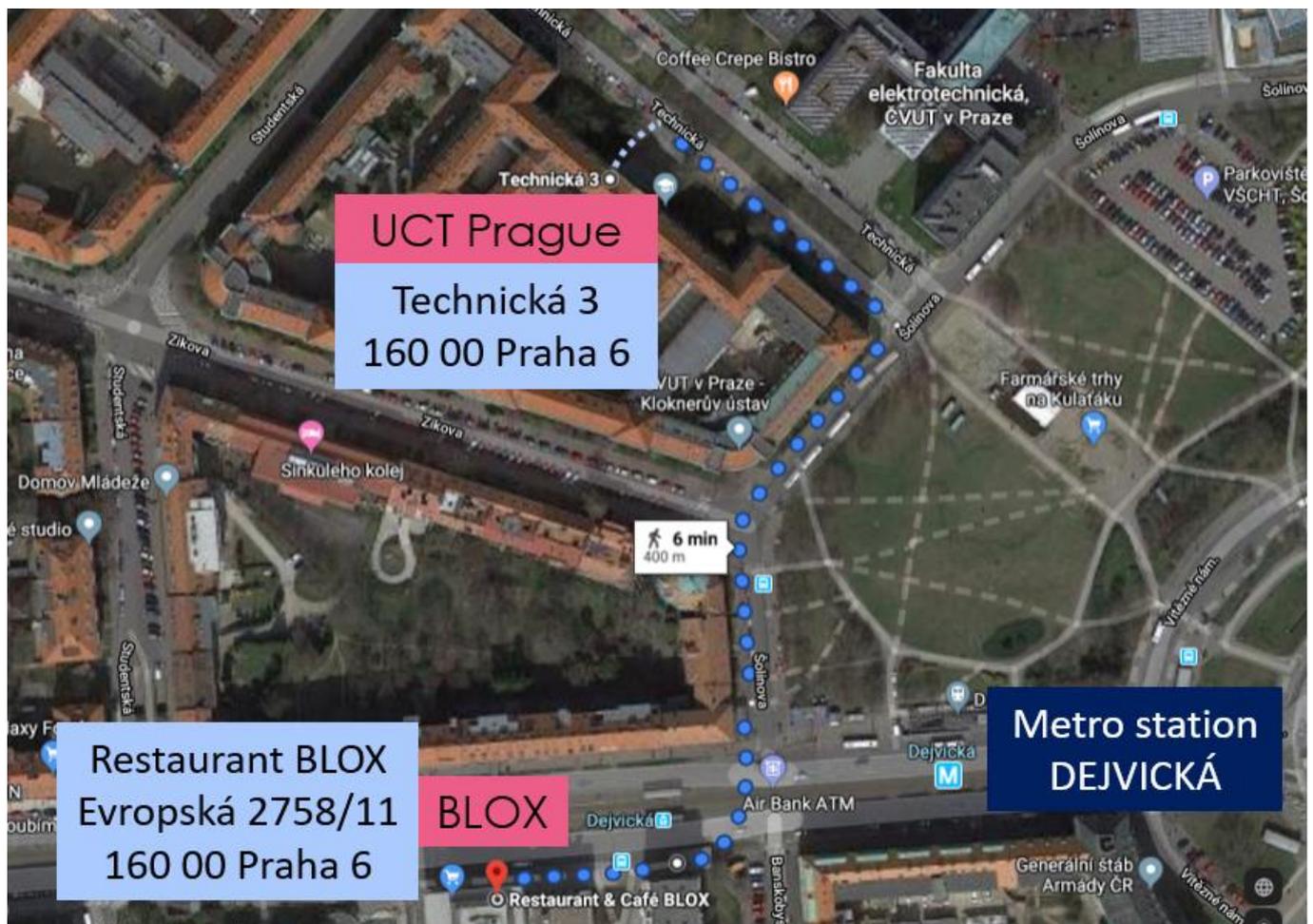
Thursday, January 30

13:00 – 14:30 Lunch

18:00 – 20:00 Dinner

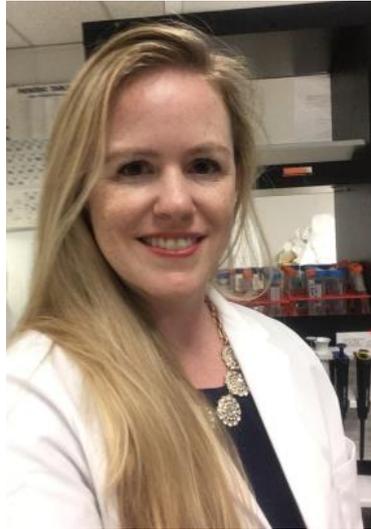
Friday, January 31

13:00 – 14:30 Lunch



ABSTRACTS

Alphabetical order by the name of a presenting author



Chemobrionics and the Search For Life Elsewhere

Laurie Barge

Jet Propulsion Laboratory, NASA, USA

In order to develop strategies to search for life elsewhere, it is important to understand the transition between life and non-life, and how self-organization and complexity can emerge in completely non-biological systems. Chemobrionic systems provide an example of how dynamic chemical systems can give rise to self-assembling structures, maintenance of disequilibrium, and can even drive organic-inorganic interactions. I will discuss laboratory approaches that are useful for simulating different aspects of these systems, and how such experiments can be used to investigate the origin of life and habitability on other worlds.



Supramolecular Processes under Conditions Mimicking Deep-Sea Hydrothermal Vents

Shigeru Deguchi

Research Center for Bioscience and Nanoscience, Japan Agency for Marine-Earth Science and Technology, Japan

Deep-sea hydrothermal vents are hot springs occurring in the deep oceans at tectonically active areas. Hot and compressed water gushes out from the vents and is rapidly cooled to near-freezing temperature by surrounding cold water. The vent water sometimes exceeds the critical condition of water ($T_c = 374\text{ }^\circ\text{C}$, $P_c = 22.1\text{ MPa}$). Under such extreme conditions, water exhibits properties that are remarkably different from those of ambient water. For example, supercritical water freely mixes with various hydrocarbons. In this talk, supramolecular processes under conditions mimicking the hydrothermal vents will be presented. Possible implication of such processes for the chemical origin of life will be discussed.



Guiding the Self-organization of Cyber-Physical Systems

Carlos Gershenson

Departamento de Ciencias de la Computación, Instituto de Investigaciones en Matemáticas Aplicadas y en, Sistemas Universidad Nacional Autónoma de México

Self-organization is present in several physical, chemical, and biological systems. Also, it offers a promising approach for designing and engineering adaptive systems. Given the inherent complexity of most cyber-physical systems, adaptivity is desired, as predictability is limited. I will mention different concepts and approaches that can facilitate self-organization in cyber-physical systems, and thus be exploited for design. Then I mention real-world examples of systems where self-organization has managed to provide solutions that outperform classical approaches, in particular related to urban mobility. Finally, I identify when a centralized, distributed, or self-organizing control is more appropriate.



Explaining Biomorph Growth

Oliver Steinbock

Florida State University, United States

Biomorphs are polycrystalline aggregates that self-assemble during inorganic precipitation reactions. The shape repertoire of these microstructures include sheets, helices, funnels, and coral-like structures. I will present a short introduction to this fascinating system and discuss a possible explanation of these life-like shapes in terms of nonlinear reaction-diffusion processes.

Conformational properties of (S)-indoline-2-carboxylic acid oligomers: an experimental and theoretical study

Gaetano Angelici, Matteo Pollastrini, Luca Pasquinelli, Gennaro Pescitelli, Marcin Górecki, Filippo Lipparini, Federica Balzano, Gloria Uccello Barretta

Università di Pisa - Dipartimento di Chimica e Chimica Industriale

Conformational diversity is one of the most important way of nature to disclose fundamental properties, like biological function, structural support or biochemical transport. The comprehension of conformational equilibrium of foldamers, small pseudopeptides or amphiphilic molecules helps to understand not only their activity in solution, but also some important aggregation phenomena. Therefore, following a bottom-up approach, it could be possible to envision the synthesis of supramolecular materials with properties on-demand. In particular, the synthesis and conformational studies of oligomers based on indolin-2-carboxylic acid will be presented. The cis/trans amide equilibrium of this proline/phenylalanine mimetic is dependent on the polarity of the solvent, bringing to the formation of polyproline I-like structure in polar solvents in solution and in its crystal structure. Deep spectroscopic investigations, using ECD, VCD, NMR techniques and ab-initio calculations helped to rationalize the conformational preferences of these oligomers.

Classical and Nonclassical Behavior of Ethylene Oxide within the Clathrate Hydrates: Experiment and theory

Zafer Maşlakçı, J. Paul Devlin and Nevin Aytemiz

Bandırma Onyedi Eylül University, Turkey

Clathrate hydrates are (CHs) crystalline nonstoichiometric solids that host guest gas molecules. Two most common classic structural types are structure I (sI) and structure II (sII). The stability of the clathrate hydrates is due to the van der Waals interactions occurred between the guest and host water network. However, there are some certain molecules that enable H-bonding with the water of the host cages, for example, small ethers, i.e., dimethyl ether (DME), trimethylene oxide (TMO), tetrahydrofuran (THF), and methanol, acetone as well as NH₃. [1-4] These molecules are generally large cage guest molecules and it has been reported that some certain small cage guest molecules and temperature can change the “classical” structure of the large cage molecules to the “nonclassical” structures. [2] In this communication, the nonclassical behavior of ethylene oxide (EO) molecule within the sI CH will be discussed in terms of FTIR spectroscopy and ab initio molecular dynamics.

1.V. Buch, J. P. Devlin, I. A. Monreal, B. Jagoda-Cwiklik, N. Uras-Aytemiz, and L. Cwiklik, “Clathrate hydrates with hydrogen bonding guests,” *Phys. Chem. Chem. Phys.* 11, 10245 (2009).

2.I. A. Monreal and J. P. Devlin, Z. Maşlakçı, M. B. Çiçek, and N. Uras-Aytemiz, “Controlling nonclassical content of clathrate hydrates through the choice of molecular guests and temperature,” *J. Phys. Chem. A* 115, 5822 (2011).

3.J. P. Devlin, “Catalytic activity of methanol in all-vapor subsecond clathrate hydrate formation,” *J. Chem. Phys.* 140, 164505 (2014).

4.Maşlakçı, Z., Devlin, J. P., Uras-Aytemiz, N. 2017. “NH₃ as unique non-classical content-former within clathrate hydrates”, *J. Chem. Phys.* 146, 234508.

Acknowledgments

Support of this research by the National Science Foundation (NSF) through Grant Nos. CHE–1213732 and CHE–1566600 is gratefully acknowledged. N. U.–A. is appreciative of partial support for this project by Karabük University–Turkey, through Grant No. KBU- BAP-13/2-DR-001. The numerical calculations reported in this paper were fully performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources). N. U.–A. would like to acknowledge the contribution of the COST Action CA17120.

SOLVATION OF N₂O IN COLD NANODROPLETS OF SMALL ORGANIC MOLECULES

F. Mine Balci and Nevin Uras-Aytemiz

Süleyman Demirel University, Faculty of Arts and Sciences Department of Chemistry, Isparta, Turkey

N₂O is one of the important molecules that play an important role in atmospheric chemistry. It is to be in the source of NO_x radicals that causes the formation of ozone depletion in the stratosphere [1]. Besides, N₂O causes a global warming, like as CO₂ and both of are known as greenhouse gas molecules in the troposphere [2]. Moreover, N₂O is extensively used molecule especially in weak interaction studies because of its properties. This study is focused on the nature of the intermolecular interaction of N₂O molecule with small organic molecules such as, methanol (CH₃OH), dimethyl ether (DME), trimethylene oxide (TMO), acetone (ACE) and acetonitrile (ACN) molecules at low temperatures. For this purpose, computational and FTIR spectroscopic studies were conducted to understand gas phase solvation of N₂O in cold nanodroplets of these organic molecules. The results will be discussed in terms of structure, energetic, spectroscopic and topologic perspectives.

[1] A. R. Ravishankara, J. S. Daniel, and R. W. Portmann, *Science* 326, 123 (2009).

[2] S. A. Montzka, E. J. Dlugokencky, and J. H. Butler, *Nature (London)* 476, 43 (2011).

Acknowledgments

N. U.–A. is appreciative of Prof. J. Paul Devlin for the experimental part of this study. N. U.–A. and F. M. B. would like to acknowledge the contribution of the COST Action CA17120.

Iron (III) Chemical Garden interacting with sucrose

Fabrizio Bernini, Antonio Ranieri, Elena Castellini, Lorenzo Sebastianelli, Claro Ignacio Sainz-Diaz, Daniele Malferrari, Adele Mucci and Marco Borsari

University of Modena and Reggio Emilia, Italy

It has been shown that it is possible to stabilize polynuclear nanoparticles of $[\text{Fe}(\text{OH})_3]$ or $[\text{FeO}(\text{OH})]$ by exploiting surface interactions with organic molecules (proteins in living organisms) or carbohydrates. The carbohydrate sucrose forms an outer-sphere complex on the surface of these nano-particles forming a compound of high molecular weight known as sucroferric oxyhydroxide (the corresponding medical product is known as Velphoro). This compound is used in pharmacology as a drug against sideremia. To find new ways of synthesizing these complexes of pharmacological interest, it was decided to study the interaction of growing chemical gardens from Fe(III) and Cu(II) with saccharose and glucose. These systems have been characterized by several experimental techniques: elemental analysis, electronic spectroscopy (DR-UV-Vis-NIR), vibrational spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), X-ray powder diffraction (XRPD). In addition to pharmacological applications, the importance of these systems is linked to the possibility of preparing surface suitable for the growth of bacteria, in particular, those that require the presence of iron.

Formation and characterization of tubular carbonates in flow conditions

Ana Borrego-Sánchez, Carlos Gutiérrez-Ariza, C. Ignacio Sainz-Díaz and Julyan H. E. Cartwright

Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Spain

Nanoscale precipitation of carbonates and other metal oxides grown in the surfaces of tubular materials generated in flow conditions out of equilibrium have been obtained following the phenomenon of chemical gardens. Carbonate formation can be interesting for the CO₂ cycle being related with the alteration of its formation in natural systems in the climate change risks. Besides, the surfaces of these minerals can be also a scenario for the first prebiotic chemistry related with the origin of the life [1]. Experimentally, soluble metal salts are added into aqueous solution containing sodium carbonate. Later, biomimetic structures are formed due to the spontaneous formation of a semipermeable membrane which form a concentration gradient and form precipitates. Therefore, chemical gardens of carbonates have been prepared at laboratory. Different nano-morphology and crystallographic transformations have been studied by the formation of these complex self-organizing structures in nonequilibrium process. The formed materials were characterized by X-Ray Powder Diffraction (XRD) and Environmental Scanning Electron Microscope (ESEM). The results showed nanocrystals with different morphology and chemistry depending on the growth conditions.

[1] Barge, L. M.; Cardoso, S. S. S.; Cartwright, J. H. E.; Cooper, G. J. T.; Cronin, L.; De Wit, A.; Doloboff, I. J.; Escribano, B.; Goldstein, R. E.; Haudin, F. et al. From Chemical Gardens to Chemobrionics. *Chem. Rev.* 2015, 115, 8652–8703.

Emergent behaviours driven by chemohydrodynamic interplay in $A+B \rightarrow C$ systems

Marcello Budroni, Virat Upadhyay and Laurence Rongy

Department of Chemistry and Pharmacy, University of Sassari, Italy

Chemical processes as simple as bimolecular reactions can self-sustain chemical oscillations and waves in batch conditions, in the absence of any nonlinear chemical feedback or external trigger. We show this phenomenon in a typical $A+B \rightarrow C$ system where two reactants A and B, initially separated in space, react upon diffusive contact. The product can activate the medium by inducing in-situ convective Marangoni flows. These flows combine, in turn, with the reaction-diffusion dynamics, inducing damped spatio-temporal oscillations of the chemical concentrations and the flow field. Different scenarios can be found depending whether the reaction locally increases or decreases the surface tension. By means of numerical simulations, we single out the mechanisms and minimal conditions for the onset of these emergent behaviors. We show how the antagonistic coupling with buoyancy convection, due to concurrent chemically-induced density gradients, can control the oscillation properties, further sustaining or suppressing this phenomenon depending on the relative strength of buoyancy- and surface-tension-driven forces. The oscillatory instability is characterized in the relevant parametric space spanned by the reactor height (Lz), the Marangoni (Ma) and the Rayleigh (Ra) numbers of the chemical species, the latter ruling the surface tension and buoyancy contributions to convection, respectively.

Synthesis and self-assembly studies of a new family of amphiphilic molecules based on glyco-peptoids

Stefano Cadeddu, Sebastiano Di Pietro, Valeria Di Bussolo and Gaetano Angelici

Università di Pisa - Dipartimento di Chimica e Chimica Industriale, Italy

Peptoids are peptidomimetic oligomers composed of N-substituted glycine units. For their intrinsically modular nature and easy synthesis, they represent an extremely promising choice for a systematic study of glyco-conjugates. The advantage with respect to peptides, is that, peptoids do not have extensive hydrogen bonding interactions on the backbone as a result of the N-substituents; diminishing therefore, the energetic penalty for desolvating tertiary amides. Moreover, it is now possible to control the cis/trans isomerism of the backbone tertiary amide of peptoids, which otherwise might have shown conformational lability. Conjugated with different sugars they might give access to a new library of amphiphilic molecules, amphiphilic peptoids (APOs), with self-assembly properties in aqueous media. It is possible to modify the length of hydrophobic chains, the nature of polar groups, the nature of capping groups and sequential position of the residues to “tune” the physical properties of new self-assembled materials, like micelles, vesicles, membranes etc. Many applications can be envisioned for the use of APOs, like drug delivery, artificial membranes and stabilization and crystallization of membrane proteins.

Chemobrionics: the state of the art in 2020

Julyan Cartwright

Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Granada, Spain

I will sum up where we are now, in 2020, with the field of chemobrionics. We are something over a year into the COST action, we have a growing number of researchers – in chemistry, physics, geosciences, engineering and beyond – working on a series of related questions involving self-organization and self-assembly, fluid mechanics, chemical precipitation, and osmotic forces, and we aim to make a difference with this meeting and this action by linking together these related questions, which range from the origin of life on Earth and beyond, to the formation of artificial life, to the creation of new materials with interesting and useful properties (as well as a better understanding of old problems in materials), to applications to biomedicine and the understanding of environmental processes.

Chemobrionic structures serving as cellular scaffolds for bone tissue substitutes

Miruna Chipara, Erik A. B. Hughes, Thomas J. Hall 1, Richard L. Williams and Liam M. Grover

School of Chemical Engineering, University of Birmingham, UK

Development of synthetic bone graft replacements is essential to address the issues associated with the currently used grafts including autologous and allograft which employ the transplantation of natural bone. Bone, however, has a complex hierarchical architecture starting from nano- to macroscopic structures which is difficult to mimic. Among others, porosity and specific microstructures like Haversian canals are important for allowing the vascular system to expand across the bone structure in order to transport cells, nutrients, oxygen, hormones, and remove metabolic waste. Vascularization plays an important role in fracture healing and bone development, representing a necessary aspect in artificial bone design. Chemobrionic principles could resolve some of the issues related to the high level of difficulty associated with bone tissue. Chemobrionic applications not only allow for the generation of structures to the level of nano- and microscale but also structures with materials biologically analogous to that of bone. Using these principles, microscopic calcium phosphate tubules were generated using a calcium loaded hydrogel – phosphate solution system. The scaffolds were characterised both as prepared and following a thermal treatment in air at 650 °C, revealing a composition of calcium deficient hydroxyapatite (CDHA, $\text{Ca}_9(\text{PO}_4)_5\text{HPO}_4\text{OH}$) and beta tricalcium phosphate (β -TCP, $\beta\text{-Ca}_3(\text{PO}_4)_2$), respectively. Calcium phosphate-based ceramics constitute a potential avenue for bone tissue engineering for more than 20 years. It was demonstrated in previous studies that bone-derived cells adhere and are cytocompatible with calcium phosphates such as HA and β -TCP. In this study, bone marrow derived mesenchymal stem cells (BMSCs) cultured on the chemobrionic-derived scaffolds showed high cytocompatibility, as well as attachment and elongation, proving their potential for tissue engineering applications as bone substitutes.

Automated Evolution of Soft Materials in a Chemorobotic Platform with Machine Learning

Geoff Cooper

University of Glasgow, United Kingdom

Evolution, once the preserve of biology, has been widely emulated in software, while physically embodied systems that can evolve in populations of physically interacting chemical entities are very rare. Recently, we presented a liquid-handling robot built with the aim of investigating the properties of oil droplets as a function of composition via an automated evolutionary process. The robot made the droplets by mixing four different compounds in different ratios and placing them in a Petri dish, after which they were recorded using a camera and the behaviour of the droplets was analysed using image recognition software to give a fitness value. A fitness function discriminated based on movement, division and vibration over 21 cycles, and gave successive fitness increases. Analysis and theoretical modelling of the data yielded fitness landscapes analogous to the genotype–phenotype correlations found in biological evolution. Inorganic chemical cells (iCHELLs) are compartment structures consisting of polyoxometalates (POMs) and cations, offering structured and confined reaction spaces bounded by membranes. These precipitation structures are part of a wider class of materials covered by the field of chemobrionics. Having successfully built robotic systems to investigate oil droplet systems, we are now moving towards automated chemobrionic experiments.

Could oil drops be the first protobionts?

Nikolai Denkov, Diana Cholakova and Slavka Tcholakova

Sofia University, Bulgaria

The mechanisms of the transition from simple organic molecules to the first living cells remain one of the greatest mysteries in science. This transition is believed to involve several stages, including (1) the formation of functional polymers, (2) the compartmentalization of the chemical reactions on the surface and/or in the interior of some protocellular entities called “protobionts”, (3) the development of stable information-coding and replication mechanisms, and (4) the development of protocell division mechanisms which allow the transfer of the genetic information into the next generations able to adapt to environmental changes, thus creating the basis for the well-known bio-evolution via natural selection [1-3]. Many of these stages and the processes involved in them depend crucially on the nature and the structure of the first protobionts. The leading hypotheses proposed in the literature are that these could be vesicular structures from amphiphilic molecules (closed lipid shells composed of one-chain or double-chain lipid molecules) [4], gel-like molecular aggregates (coacervates) [5] or oily drops [2]. Recently we discovered [6-9] that surface phase transitions in micrometer-sized oil droplets can lead to a variety of dynamic phenomena which resemble closely several phenomena seen in living cells (though driven by different molecular mechanisms). These observations will be reviewed in the context of the possible first protobionts and with link to the hot area of active micro-particles.

References:

- [1] P. L. Luisi, *Origin life evol. biosphere* 28 (1998) 613-622.
- [2] A. Sharov, *BioSystems* 166 (2016) 8.
- [3] S. A. Kauffman, *A world beyond physics: the emergence and evolution of life*. Oxford University Press, 2019.
- [4] P. Luisi et al., *Curr. Opin. Colloid Interface Sci.* 4 (1999), 33.
- [5] A. I. Oparin, *The origin of life on Earth*, 3rd ed. Academic Press, New York 1957.
- [6] N. Denkov et al., *Nature* 528 (2015) 392–395.
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- [8] R. Gordon et al., in “Habitability of the Universe Before Earth”, R. Gordon & A. Sharov eds., Academic Press, 2018, pp. 427-490.
- [9] D. Cholakova, N. Denkov, *Adv. Colloid Interface Sci.* 269 (2019) 7.

FLOW-DRIVEN CRYSTALLIZATION AND PRECIPITATION KINETICS IN THE LITHIUM-PHOSPHATE SYSTEM

Michael Emmanuel, Ágota Tóth and Horváth Dezső

University of Szeged, Hungary

Fine tuning of the structural form during precipitation is possible through self-organization in flow-driven systems. The precipitation reaction between lithium chloride and sodium phosphate was investigated in a microfluidic system. The reacting precursors were pumped simultaneously from the reservoirs into the microchannel where the precipitate was formed along the concentration gradient of the reactants. The growth kinetics was studied by analyzing the images obtained over time and the particle growth along and transverse to the flow was determined. Parallel to the microfluidic study, kinetic measurements in well-stirred system were also carried out where the dependence of the induction time on the chemical composition was found to be in good agreement with the results obtained from Classical Nucleation Theory.

Abiotic production of oxygen precursors from the interaction of calcium perchlorate with olivine surface: Implications to formation of Martian's regolith

Elizabeth Escamilla-Roa, Maria-Paz Zorzano, Javier Martin-Torres, Alfonso Hernández-Laguna and C. Ignacio Sainz-Díaz

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Perchlorates have been found widespread on the surface of Mars, however their origin and degradation pathways are not understood to date yet. We investigate here, from a theoretical point of view, the potential redox processes that take place in the interaction of minerals surfaces, such as olivine, with anhydrous and hydrated perchlorates by means of quantum mechanical methods based on Density Functional Theory. For this theoretical study, we take the (100) surface of forsterite as mineral substrate, and a calcium perchlorate salt in conditions related with a Martian scenario. Our results suggest a reduction pathway to chlorate and chlorite. When the perchlorate has more than 4 water molecules, this mechanism, which does not require high-temperature or high energy sources, results in parallel with the oxidation of the mineral surface, forming magnesium peroxide, MgO_2 and ozone. Because of the high UV irradiance that reaches the surface of Mars, this may be a source of O_2 on Mars. This process may be a natural removal pathway for perchlorates from the Martian regolith, which in the presence of atmospheric water for salt hydration, could furthermore lead to the production of oxygen. This mechanism of surface-atmosphere interaction may thus have implications on the present and future habitability of the Martian and may be provide a source of O_2 to the atmosphere in this and other planets, and the early Earth.

Circular codes, universal properties of codon bias, and translation efficiency

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Circular codes represent a form of coding allowing detection/correction of frame-shift errors. Still, the biological functions associated with circular code properties are basically unexplored. These properties may arise as a fossilized memory of comma-free (self-synchronizable) coding in primeval forms of life, or be tentatively associated with reading frame maintenance during protein synthesis. Building on recent theoretical advances on circular codes, we provide evidence that protein coding sequences exhibit taxon-independent universal properties with a strong hierarchical organization. Independently from codon usage, universal in-frame circular code marks are present in coding sequences and are absent in introns. These properties strongly correlate with translation speed, codon influence and protein expression levels. The results provide promising universal tools for sequence indicators and sequence optimization for bioinformatics and biotechnological applications, and can shed light on the molecular evolution of the genetic code.

Inversion of self-propelled rotors under periodic stop and release operations

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We propose a simple mathematical model that describes the time evolution of a self-propelled object on a liquid surface using such variables as the object location, the surface concentration of active molecules and the hydrodynamic surface flow. The model is applied to simulate the time evolution of a rotor composed of a polygonal plate with camphor pills at its corners. We have qualitatively reproduced results of experiments, in which the inversion of rotational direction under periodic stop- and release- operations was investigated. The model correctly describes the probability of the inversion as a function of the duration of the phase when the rotor is stopped. Moreover, the model allows to introduce the rotor asymmetry unavoidable in real experiments and study its influence of the studied phenomenon. Our numerical simulations have revealed that the probability of the inversion of rotational direction is determined by the competition among the transport of the camphor molecules by the flow, the intrinsic asymmetry of the rotor, and the noise amplitude.

Force Field Refinement and Molecular Dynamics Simulations of Imidazolium-Based Ionic Liquids

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Room temperature ionic liquids (RTILs) are salts of organic cations and, typically, inorganic anions. Their low melting temperature, together with their low vapor pressure, high thermal stability, and electrical conductivity make them unique as solvents, electrolytes, etc. The high functionality of RTILs is due to the tunable interplay of intermolecular interactions from weak short-range Van der Waals to strong long-ranged Coulombic. To properly reproduce their structural and dynamical properties in simulations it is necessary to use proper force field parameters, and recently we have optimized the non-bonded parameters to study the structural and dynamical properties of the DMIMCl ionic liquid (1-Decyl-3-methylimidazolium chloride) both in the neat IL and in mixtures with water, validating the parameters by comparing the results with the experimental densities measured at several temperatures, and with diffusion data reported in literature. A very good agreement with reference data (ab initio and experimental) has been obtained for all of the investigated structural and dynamical properties. These new parameters are required for improving the sampling of dynamics of this RTIL and to predict with QMMM the NMR parameters used to study the mesomorphic behaviour of this and similar ILs.

Seedless Image Velocimetry as a new approach to study chemical garden's hydrodynamics

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Chemical gardens are biomimetic forms where chemical and physical phenomena join together. They are an example of self-organizing systems formed in out-of-equilibrium conditions whose formation is related to Chemobrionics. When soluble metal salts are added to aqueous solution containing anions complex biomimetic structures are formed. These structures, despite their chemical diversity, have one common feature: the spontaneous formation of a semipermeable membrane. This membrane shows a selective transport of ions and molecules producing a concentration gradient providing energy for possible prebiotic reactions as well as a confined space for them to happen. Similar systems can be found in nature, such as the hydrothermal vents on the ocean floor that can be very interesting due to their possible role in the origin of life. These structures, although larger, and more complex than in the laboratory chemical gardens, exhibit similar mechanisms of formation. A lot of work has been done studying the fluid dynamics behind chemical garden formation but it's yet far from being completely understood. In this work we search for a systematic way of studying the hydrodynamics involved in chemical garden's growth via Schlieren technique, an optical method proven especially useful to study non-homogeneous media in a non-intrusive way, and image correlation velocimetry algorithms which can become handy when there are no actual particles to track as it happens in PIV (Particle Image Velocimetry). Some interesting and unexpected behaviour is observed before and after the precipitation and formation of the tube in 2-D and 3-D dimensions. Two different flow directions were detected indicating the formation of more than one membrane and adding complexity on how these structures were thought to be formed. Several examples of flow dynamics will be presented along with result discussions.

DFT Study of the Hydrolysis reaction on Cluster Models simulating (001) and (010) surfaces of Phyllosilicates

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Phyllosilicates are important minerals usually found in the Earth's crust, they are included in rocks and soils; besides, they form part of the hydrothermal vents on sea-beds. The confined nanospace provided by the interlayer space of phyllosilicates and the abiotic membrane behavior of these minerals indicate that they provide a good scenario for the first prebiotic chemistry. Water interacts with these minerals, being firstly adsorbed on the surface of these mineral and afterwards reacting with the different chemical groups. Acid pH increases the rate of reaction. The computational chemistry allows us to understand these interactions at atomic level. This methodology has been previously used on small cluster models of the tetrahedral (T) sheet of the (001) surface of phyllosilicates. In this work, these models have been increased: i) the T sheet of phyllosilicates is modeled by an hexagonal crown of SiO₄ units, closing the dangling bonds with hydrogen atoms; ii) one T and one octahedral (O) sheet model (T-O); these two first models try to simulated the (001) surface; and iii) two T sheets sandwiching one O sheet (T-O-T) for simulating the (010) surface. Critical points (CP) of the potential energy surface (PES) of the hydrolysis reaction on neutral and protonated models are calculated at quantum mechanical level.

Three mechanisms are found, one at neutral pH, where CP of PES agree with the previous small models, and the water molecule attacks to one O-Si-O group and a transition state is found, where one H of the water molecule is transferred to siloxane O and one OH to the Si, hydrolysing the Si-O bond. For the acid model, a different mechanism is found, where the interaction of water molecule increases the H+O-Si bond, decreasing the activation energy. However, in the T-O model these reactions do not progress, because the T sheet bonded to the O sheet loses its flexibility and the possibility of reaching the reactive configurations. Working on the T-O-T model, including two protons on two oxygens of the O sheet and two water molecules in the surrounding, and minimizing the energy and forces, a third mechanism is found: the protonated Al³⁺-O bonds are broken down. This last reaction indicates the favorable acid dissolution of the phyllosilicates at the (010) surface.

In silico multiscale modelling of CO₂ capture by nanoporous materials

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Using first principles approaches, we characterized the bi- and trimolecular interactions between Zn - nitrogen rich heterocycles (imidazole, triazole, ...) and /or CO₂ and / or H₂O. For this purpose, the minimum energy geometries corresponding to these systems have been searched and optimized using various ab initio and DFT methods. Our calculations show that long-range interactions between these medium-sized molecules and gases are strongly dependent on the electronic correlation. Accurate energetics are derived using the newly tested explicitly correlated coupled cluster approaches. We also established the good performance of M05-2X (+D3) and PBE0 (+D3) DFTs for the accurate description of these systems and therefore that of the larger macromolecular structures. Moreover, we found that the complexes formation follows energetically favored multi-channel. Afterwards, we designed a new nitrogen-rich triazole-type metal-organic framework (MOF) helped by rational design and theoretical molecular simulations. Indeed the structure of this model MOF is a modified MAF-66, where we replaced the amine-organic linker by a triazole. We also used grand-canonical Monte Carlo (GCMC) simulations based on generic classical force fields to predict correctly the adsorption isotherms of CO₂. We show that this new nanoporous material exhibits exceptional high CO₂ uptake capacity at high pressures, even better than MAF-66. In addition, we investigated the influence of water on CO₂ adsorption on this model MOF. The GCMC simulation results reveal that the CO₂ adsorption is enhanced when water molecules are present in the nanopores. This work represents an in silico material search and design with good adsorbents for CO₂ capture and hence for low carbon future. For illustration, diverse examples will be presented [1-11].

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Interfacing artificial life with natural life: liquid droplets as transporters for living cells

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Soft matter systems can be driven out of equilibrium and can respond to externally imposed stimuli. The transition from equilibrium to non-equilibrium can be driven through for example chemical potential, external fluid flow or static external fields. An example of soft matter systems that show response to these kinds of transitions are liquid droplets. Liquid droplets can be created mixing two immiscible fluids (oil and water) and can exhibit behaviors such as fission, fusion and movement. Movement is normally shown by living cells and organisms and can be defined as a 'life-like' behavior. We were able to create systems of oil-in-water droplets that self-organize and move in response to external stimuli. Decanol droplets move for example in response to pH or salt gradients. We exploited droplets to transport objects such as cells. Specifically, we developed chemotactic droplets able to move light cargos such as hydrogel alginate capsules embedded with living cells. Using this system, we demonstrate efficient and sterile transport of a few types of bacteria and yeast, and even human cell lines. We recently discovered that some eukaryotic cell lines, only when placed in capsules, secrete compounds that act as surfactants, thereby reinforcing the interface between the artificial and living systems. This is an example of not only how the interface between artificial life and biological life could be designed but how the one system can augment the other.

Modeling of precipitate formation in a microfluidic reactor

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Precipitate formation in the presence of flow is addressed by studying the behavior of small solid particles in a flow field. In our model the Navier-Stokes equation is coupled to a chemical reaction that produces solid product, the motion of which is monitored by Lagrangian particle tracking. We consider both the nucleation and the growth of particles as two reactants are flown into a microfluidic reactor.

Engineering Chemobronic Biomaterials for Tissue Regeneration Applications

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A diverse range of complex patterns and mineralised hierarchical microstructures can be derived from chemobronic systems, with formation driven by complex reaction–diffusion mechanisms far from thermodynamic equilibrium. In these experiments, self-assembling calcium phosphate tubes are generated using hydrogels made with 1 M calcium solutions layered with solutions of dibasic sodium phosphate over a range of concentrations between 0.2–1 M. Self-assembling structures prepared using 0.8 M dibasic sodium phosphate solutions were selected to assess cell–material interactions. Candidate chemobronic scaffolds were characterised by micro-X-Ray fluorescence (μ -XRF) spectroscopy, Raman spectroscopy, powder X-ray diffraction (XRD), helium pycnometry and scanning electron microscopy (SEM). As prepared tubes were formed from non-stoichiometric hydroxyapatite (HA, $\text{Ca}_{10-x}(\text{PO}_4)_6-x(\text{HPO}_4)_x(\text{OH})_{2-x}$ ($0 \leq x \leq 1$)), which was confirmed as calcium deficient hydroxyapatite (CDHA, $\text{Ca}_9(\text{PO}_4)_5\text{HPO}_4\text{OH}$). Thermal treatment of tubes in air at 650 °C for 4 h converted the structures to beta tricalcium phosphate (β -TCP, $\beta\text{-Ca}_3(\text{PO}_4)_2$). The potential of these scaffolds to support the attachment of bone marrow derived mesenchymal stem cells (BMSCs) was investigated for the first time, and we demonstrate cell attachment and elongation on the fabricated tubular structures.

(Metal sulfide)-polymer composites grown from the gel/liquid interface

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Carrageenan, sulfated polysaccharides extracted from seaweed, has strong affinity to complex heavy metal ions in form of hydrogels. Inspired from “Chemobrionics”, new functional materials are grown at the interface of the metal-complexed hydrogels and liquid sulfide through precipitation process. The structure of the precipitates is controlled by concentration of solutes, time, gel viscosity, and pH. The resulting precipitates, herein (metal sulfide)-carrageenan composites, exhibit many interesting properties to be used as photocatalysts and sensing materials.

Transmission of chirality in artificial metallated oligoamides

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Biological homochirality is often discussed as signature of living systems.[1] The origin of biological homochirality is still an open question in contemporary research. In addition to the initial symmetry breaking, particular attention of recent studies is focused on the transmission of chirality at the molecular level, as well as its translation on a larger scale in order to facilitate a number of applications.[2] In our laboratory, we investigate self-assembled hydrogen-bonded motifs of artificial metallated oligoamides.[3] Interestingly, out of the large variety of possible structures, only very few are actually found those systems. In particular, the chirality of the distant building blocks is transmitted to the initially prochiral metal center. Herein, several new examples will be discussed, including organometallic iron(II) metallocene and ruthenium(II) piano-stool complexes.

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Flow-Induced Precipitation in Thin Capillaries Creates Helices, Lamellae, and Tubes

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Precipitation reactions under flow in confined media are relevant to the control of pathological biomineralization, processes affecting aquifers, and challenges in the petroleum industry. Here we show that for a simple geometry, such conditions create macroscopic structures including helices, tubes, lamellae, slugs, and disordered patterns. All structures emerge when salt solution is slowly injected into thin capillaries filled with hydroxide solution. For the helices, the pitch is proportional to the pump rate revealing a constant period of 0.63 s. Different morphologies of the insoluble metal hydroxide can co-exist causing random transitions along the capillary. On average, 15 % of the final system contains residual hydroxide solution. While mechanically stable for flow speeds above 25 mm min⁻¹, structures collapse and sediment for slower injection speeds. Some of the observed features share similarities with precipitate tubes in chemical gardens and the dynamics of liquid–liquid pipe flow.

Bio-inspired flow-driven gardens

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New type of chemical gardens based on chitosan sol-gel materials studied by injecting the chitosan acidic solution into the basic hydroxide solution. We observed various structures of the hydrogels like tubes, branches, complex shapes, and wavy patterns. Tubular structure grows in the vertical direction through the fracturing process. Wavy patterns were formed on the surface of the hydrogel, wherein gel makes contact with the cuvette surface. Our findings can attribute a new path to the field of chemobrionics for the understandings of their mechanisms.

A camphor–camphene alloy for studies on self-propelled motion of objects with varied shapes

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We report on a new material that modifies the self-propelling properties and the malleability of camphor by addition of camphene. The speed of the self-propelled objects and the trajectory depend on the shape and camphor–camphene weight ratio. Furthermore, the new material has wax-like mechanical properties at room temperature and can be formed into any required shapes by simple manipulation. This provides a simple method to study the effect of shape on the trajectory of an object as well as swarming behavior of different shapes.

Adsorption of Technology Critical Elements from aqueous solutions

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At the beginning of the 2019, the European Chemical Society (EuChemS) launched the EuChemS Periodic Table, a new version of the Mendeleev Table of Elements, which depicts the element scarcity. Element scarcity is intrinsically linked with several issues including Circular Economy, more efficient recycling practices, consumer behavior and innovative alternatives. For instance, we know now that our phones are made up of more than 30 elements – over half of which may give cause for concern in the years to come because of increasing scarcity. More, is estimated that every month around 10 million smartphones are discarded or replaced, only in the European Union[1], and unless solutions are provided in the next years, we risk seeing many of the natural elements that make up the world around us run out or become unusable, due to facts such as limited supplies, location in conflict areas, or our incapacity to fully recycle them[1]. This fact alerts us that serious actions are needed to tackle these challenges ahead. In this context, a new line of research has emerged in recent years that seeks to find new sources for the elements considered in risk (Technological Critical Elements - TCE). In our research group we particularly interested in the development of efficient processes for the recovery and recycling of TCE elements from electronic waste. We have been preparing and applying some nano magnetic adsorbents in the recovery and recycling of some of these critical elements. One of these examples is a magnetic composite prepared with magnetite nanoparticles and exfoliated graphite, which can remove lanthanides (La, Eu and Tb) from aqueous solutions at low concentrations. More recently, are also looking to new possibilities such as tubular structures produced through 'silica garden' route. These structures, which span at least 8 orders of magnitude in size from nanometers to meters, can be form from different chemical systems and materials[2], including less explored cations such as terbium (Tb³⁺) and europium (Eu³⁺), which create beautiful luminescent structures. Although known from the alchemists age, chemical gardens, can hide new possibilities for technological applications, including selective adsorption-desorption processes of interest, for example, the removal of toxic metals from water or the recovery of critical elements. It is known that these micro- or nanotubes can have internal reactive surfaces with chemical and adsorptive properties to be used as interesting nanoadsorbents. It is our goal to explore these possibilities for application in the concentration of TCE from aqueous solutions.

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Recovery of critical metals by crystallization from aqueous electrolyte solutions

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Due to increased urbanization and diminishing natural resources, there is globally a great need to develop separation and purification technologies for sustainable carbon-neutral circular economy applications. The demand for battery chemicals, for instance, will increase significantly since the production capacities of electric vehicles are expected to increase greatly in future. The present work shows the results obtained by the batch cooling crystallization of nickel sulphate, semi-batch precipitation of lithium carbonate and precipitation of double sulphate salt to recover a rare earth element, i.e. lanthanum, from the aqueous leaching solution of battery wastes. Realtime process monitoring based on the Focused Beam Reflectance Measurement (FBRM) was used to collect crystallization kinetics data during the batch and semi-batch crystallization systems. FBRM gives the count rates of different size fractions based on chord length distribution measurement. The role of various impurities on crystalline product properties and the influence of crystallization temperature on crystallization kinetics are discussed.

Autocatalysis through self-assembly

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A system comprised of a peptide-functionalized dithiol building block has been previously shown to spontaneously give rise to complex dynamics and eventually self-replication. The building blocks are rapidly oxidized and dynamically form a combinatorial library of small to large macrocycles, which can dynamically interconvert via reversible exchange reactions. A particular size macrocycle, hexamer, was found to grow exponentially and form fibers in a supramolecular polymerization fashion. Seeding a fresh library with pre-formed hexamers immediately leads to exponential growth of the hexamer and its fibers, providing firm evidence for the self-replication ability. Here, we address the dynamics of the different species in the system by mass-action chemical modelling in order to underpin the reactions occurring in this system and their rate-constants.

A total conversion of the system's mass into hexamers is achieved only when fibers are allowed to serve as catalysts for reactions between cyclic and non-cyclic species, in a tri-molecular reaction. The interaction between cyclic and non-cyclic species in the vicinity of fibers is supported by a high-speed-atomic-force-microscopy study showing that cyclic species tend to amass on existing fibers as part of fiber elongation.

Using parameters estimation via data-fitting between the model and experiments, experimentally-verified apparent rate-constants are assigned to all of the reactions.

In summary, we report an unprecedented detailed and experimentally verified model of self-assembly driven self-replication. Current efforts focus on the formulation of stochastic simulations in order to explore the long-term evolution of such a complex chemical system.

Chemical gardens and the fossil record

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It was suggested nearly a century ago that naturally occurring chemical gardens might be found in ancient rocks and that they might look misleadingly like fossil microorganisms. Nevertheless, this idea has been widely neglected by palaeontologists (except for the important special case of silica-carbonate biomorphs) until recently.

Assemblages of microscopic filaments and hollow tubes composed of nano- or microcrystalline iron (oxyhydr)oxides and iron (alumino)silicates (and less commonly of similar magnesium or manganese minerals) have now been found in diverse rocks of all ages, including submarine hydrothermal deposits and mineral-filled fractures and pores in limestones and basaltic lavas; they are particularly common in agates. Because of their life-like morphology, these tiny structures are widely interpreted as fossil bacteria or fungi, and currently include Earth's oldest purported fossils and Earth's oldest purported fungi. Such "fossils" have often been proposed as exemplars of "biosignatures" that forthcoming missions should seek on Mars.

I have argued that both the composition and the morphology of these structures are at least equally consistent with abiotic origins through chemical garden-like processes. After reviewing this argument, I will discuss which precursor minerals and geochemical conditions might give rise to chemical gardens in these varied geological settings. I will highlight the need for further experimental work to test these hypotheses and to develop a better understanding of chemical garden morphogenesis in nature, particularly inside porous rocks. This need presents an important opportunity for collaboration between inorganic chemists/chemobrionics specialists, and geologists/palaeontologists/astrobiologists.

Comparison of discrete Turing patterns of glycolytic oscillatory reaction in cyclic arrays of chemical computing systems

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Our work is focused on designing a model of a cyclic array of coupled cells with glycolytic oscillatory reaction to be compared with experimental results of system of coupled cuvettes with glycolytic oscillatory reaction with peristaltic reciprocal pumping. The experimental system utilize yeast extract as a source of glycolytic enzymes and D-glucose as a substrate for enzymatic reaction. The main autocatalytic reaction in top part of glycolysis occurs on phosphofructokinase, where ATP is consumed and ADP is produced. ADP back-double activates phosphofructokinase providing positive feedback loop. ADP is recycled into ATP in lower part of glycolysis providing negative feedback loop. The model for this system was proposed by Moran and Goldbeter [1]. Based on kinetic parameters, which can be controlled by temperature or by pH, glycolytic system is able to provide stationary state, oscillations, birhythmicity, soft excitation and hard excitation. By addition of diffusion element via peristaltic reciprocal pumping between two stirred cuvettes, a discrete reaction diffusion system is created. Discrete spatiotemporal patterns can occur in such system, if condition of inhibitor transport rate coefficient higher than activator transport rate coefficient is met[2]. After modifications of kinetic parameters, discrete spatiotemporal patterns can occur in a system with equal transport rate coefficients for both activator and inhibitor[3,4]. Condition of equal transport rate coefficients is experimentally met by using peristaltic reciprocal pumping via capillaries.

Both cuvettes are heated and metabolites in them are measured at 340nm (NADH metabolically connected to ATP/ADP) using UV-VIS spectrophotometer Agilent 8453 and 8454. The coupling capillaries are solved in our models as: a) a membrane, b) plug flow reactors without axial dispersion treated as a cascade of 9(each capillary) continuous stirred tank reactors with the same volume as cuvettes, c) plug flow reactors without axial dispersion treated as a cascade of 9(each capillary) continuous stirred tank reactors with volume of 1/9 of 1.089ml compared to cuvette with volume 2.6ml.

The reaction-diffusion models are compared in a plane of inhibition rate coefficient and stationary concentration of ADP in the first cell and in a plane of inhibition rate coefficient and transport rate coefficient.

The system is capable of chemical computing by switching between discrete nonuniform stationary states and uniform oscillations by carefully targeted perturbations. If parameters are set correctly, all systems show NOR function and OR function. On the other hand, system of 20 coupled cells is also able to provide tautology.

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Cell-sized molecular robots made by motorized vesicles

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Synthesizing live cells from scratch is one of the ultimate goals of engineers. Before facing that stage, there is a practical theme of building a programmable complex consisting of functional molecular devices. We shall call such an integrated artificial chemical system as molecular robots. By creating a molecular robot to work in a tiny, wet and random world, it is expected to understand how to connect the hierarchy between cells and molecules, and to acquire new design principles of artifacts. We have constructed an artificial cell-like 'robots' using lipid membrane vesicles in a bottom-up manner. The latest model, amoeba robot consists of a body (cell-sized vesicle), an actuator (kinesin/microtubule), and a designed control device (molecular clutch: made of artificial DNA). The molecular clutch couples the motors with the body by the single-stranded DNA having a specific sequence, and this "robot" started a continuous shape change from a stationary state. Also, when the clutch is disconnected by another DNA signal, the shape change behavior stopped. These results show that the constituent elements of various molecules are integrated as a system and lead the potential to control the behavior by DNA computing. These prototypes are designed to be able to install and evaluate unique molecular devices developed by researchers, and we are convinced that it will provide a useful platform for artificial-cell /molecular robot engineering. In addition, I will introduce recent research results aiming at implementing a more powerful, programmable and multicellular system to the molecular robots.

New non-molecular hybrid organic-inorganic systems for application in electronic and photonics

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Intermolecular interactions between coordinated ligands can be used to tailor the structure and properties of a metal-organic framework. An interesting application of this study is given by the synthesis and chemico-physical characterization of new hybrid organic-inorganic non molecular systems in which the coordinated ligands have complementary functions with respect to a given intermolecular interaction. Fused-ring aromatic heterocycles, 1,2,5-benzoselenadiazole and 1,2,5-benzothiadiazole, are used as organic ligands while Copper (II) chloride/bromide is used as the inorganic components. The aim is to employ molecular design and structural modifications of these heteroaromatic ligands, endowing specific opto-electronic properties, in order to tune the photophysical properties of the hybrid systems. Moreover, the coordination geometry of the metal in these systems can be also influenced by the strength of chalcogen bonding between the inorganic and organic ligands.

Speciation of self-assembled copper structures, a new material able to accumulate fundamental molecules for life and industrial applications

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Self-assembled structures as chemical garden (CG) can be achieved and characterized with multiple approaches and techniques. In this work we have focused our attention on copper-based CG and used a plethora of experimental techniques to characterize it. The presence of metal cations capable of interacting with complexing molecules makes the CGs good candidates for the capture of small molecular species. In this way the affinity of the CG obtained from CuSO₄ for ammonia was evaluated in particular. The material under NH₃ exposure undergoes extremely rapid and marked changes denoting strong capabilities to capture ammonia. This chemical garden, both on whole “tree” structure or ground form, was characterized morphologically and through FTIR and DR UV-Vis spectroscopies, XRD, NMR, and XAS measurements, and revealed ability to immobilize large amounts of ammonia very quickly (up to 10% in 4 hours) forming a tetra amino copper(II) complex. These results shed light on fabrication of new materials for applications in industrial and environment context and, moreover, can be assumed similar to that revealed for “hydrothermal vents” which were considered as primary organized structures able to accumulate fundamental molecules useful for life.

Thermodynamic enhancement of primitive molecular replication dynamics

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Anchoring a primitive metabolic system and a primitive information system on the exterior of a vesicle may create a minimal self-replicating physicochemical system: a protocell [1]. We have previously shown that 8-oxo-guanine from the informational system may act as an electron donor for a ruthenium based photo-driven metabolism [2]. This metabolism can both generate decanoic acid for the vesicle container growth [3] and ligate short nucleotide strings [4] for the informational replication system. The main challenge for realizing a fully functional protocellular system has been the well-known product inhibition phenomenon for non-enzymatic nucleotide replication processes [5]. However, using a lesion induced DNA amplification (LIDA) scheme [6] together with kinetic data from our photo-driven ligation process [4] we can show in simulation how product inhibition can be avoided and how non-enzymatic exponential DNA amplification is possible for a wide range of conditions.

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Formation and characterization of tubular chemical gardens in flow conditions

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The formation of tubular materials at room temperature has great interest in material science and prebiotic sciences. Surfaces of these materials can create also confined spaces and favourable conditions for the first prebiotic chemistry related with the origin of the Life [1]. These chemobronic materials have been generated in flow conditions out of equilibrium as chemical gardens. Metal salts are added into aqueous solution containing anions, such as, silicate and carbonate, and then, biomimetic structures are formed due to the formation of a semipermeable membrane with osmotic properties. When this osmosis pressure is higher than the resistance of the membrane, this one breaks and fluid flows occur producing precipitation of solids forming the tubular materials. These materials can be found also in nature in macroscopic submarine vents and in microscopic minerals with tubular morphology. However, the formation mechanisms are not well understood and we propose a mechanism similar to the chemical gardens can participate in their formation.

Theoretical modeling of active magnetic colloids and nanoparticles

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"Active matter" is a generic name for systems out of equilibrium in which one or more entities transform energy obtained from the environment into directed motion. The concept is extremely broad, as it applies to systems of any characteristic length scale. Importantly, such "active" behavior is one of the main characteristics of life: a paradigmatic example of active entities are animals, from large mammals to bacteria, but also other biological entities such as that polymers forming the cytoskeleton of all living cells. Artificial active materials, created for either specific applications or the fundamental study of active mechanisms and their emergent properties, are one of the most important modern topics in research of novel materials and complex systems. Among them, microscopic systems based on colloids and nanoparticles are attracting a large attention in recent years. Here, recent theoretical investigations based on computer simulations of active magnetic micro- and nanoparticles that combine different anisotropies are presented. This includes the study of the self-assembly and active behavior of Janus magnetic microparticles, as well as the magnetic control of the active motion of hybrid nanoparticles formed by a combination a chemical nanomotors and magnetic nanocubes.

Reaction networks, motifs for oscillatory dynamics, and parameter estimation in complex biochemical mechanisms

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Reaction network theories are tools for stability analysis of open reacting systems provided that stoichiometric (chemical) equations are given for each reaction step together with power law rate expressions. Based on stoichiometry alone, elementary subnetworks (known also as elementary modes or extreme currents) are identified and their capacity for displaying dynamical instabilities, such as bistability and oscillations, is evaluated by examining associated Jacobian matrix. This analysis is qualitative in the sense that only reaction orders are needed as input information. This information is sufficient for determining the core part of the mechanism providing for oscillations, often referred to as an oscillatory motif. However, the network theory can be extended by formulating a set of constraint equations aimed at parameter estimation of the unknown/unspecified rate coefficients by applying convex optimization, which takes into account data obtained from experiments at the onset of oscillations or a bistable switch. As an example of this approach, we i) present major oscillatory motifs for enzyme reactions and ii) show how the experimentally observed oscillations in the catalase-glucose oxidase system are used to determine unknown kinetic parameters in an assumed model that simulates well the experiments.

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Flow-driven precipitation patterns in confined geometry: The coupling of crystallisation characteristics and hydrodynamics

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Thanks to the coupling between chemical precipitation reactions and hydrodynamics, new dynamic phenomena may be obtained and new types of materials can be synthesized. Here we experimentally investigate how the characteristic microscopic crystal properties affect the macroscopic pattern obtained. To shed light on such interactions, different reactant solutions (A) are radially injected into various host solutions (B) at different volumetric flow rates in a confined geometry. Depending on the reactants used and the flow conditions, deformed precipitate membranes have been observed due to reaction-driven viscous fingering. In such cases we show that upon injection a large number of small particles is produced in situ by reaction at the miscible interface between the two reactant solutions. Therefore, a colloidal gel composed of those tiny particles is pushed forward by the injected aqueous solution giving rise to viscosity gradient-driven hydrodynamic instability.

Effect of the presence of sulfide anion on iron (III)/(II) and copper (II) Chemical Garden

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Sulfide compounds constitute one of the most important ore minerals. From a geochemical point of view, characterizing the chemical behaviour of sulfides is essential to know their mechanism of formation and, hence, to understand the geochemistry by which their ore deposits have formed. In particular, iron and copper sulfides are largely widespread in the nature and involved in several industrial processes of relevant interest. Furthermore, some prebiotic theories suggest sulfides as starter material for the earliest electron transport centers. In our work we have evaluated the effect of sulfide on iron and copper silica chemical garden in three different scenarios: sodium sulfide directly dissolved in the growth solution; sodium sulfide mixed inside the pellet of the metal salt (iron (III) sulfate, iron (II) sulfate or copper (II) sulfate); exposure of dried chemical garden in closed environment saturated by hydrogen sulfide vapours. A collection of techniques has been exploited to provide a general overview on the products: electronic spectroscopy (DR-UV-Vis-NIR) and vibrational spectroscopy (ATR-FTIR) to compare exposed and non-exposed materials, scanning electron microscopy (SEM) to evaluate the micromorphology of the chemical garden's tubules, X-ray powder diffraction (XRPD) for the determination of the phases and X-ray absorption spectroscopy (XAS) to understand the chemical speciation of the chemical anions. The exposure to sulfide causes a rapid and sharp change in color of the materials and it is possible to see formation of branches on each tubule. The presence of sulfide affects both micromorphology and spectroscopic characteristics. A general disorganization of the material was visible by SEM images on every product. In particular, in the case of copper chemical garden, partial amorphization occurs as highlighted by X-ray diffraction. Characteristic phenomena involving iron chemical gardens grown in silicate-sulfide solution include migration of the sulfide anion inside the tubules, reaction with iron(III) to give iron(II), formation of iron(II)-sulfide followed by its partial dissolution in the growth solution. XAS measurements indicate that both iron(III) and copper(II) chemical garden undergo reduction caused by oxidation of sulfide. Copper chemical garden shows high affinity for hydrogen sulfide vapours, the adsorption process proceeds through a catalytic cycle at the surface of the material and causes the fixation of hydrogen sulfide molecules probably as sulfur.

Oscillatory budding dynamics of a chemical garden within a co-flow of the two reactants

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The oscillatory growth of chemical gardens is studied experimentally in the budding regime using a co-flow of two reactant solutions within a microfluidic reactor. The confined environment of the reactor tames the erratic budding growth and the oscillations leave their imprint with the formation of orderly spaced membranes on the precipitate surface. The average wavelength of the spaced membranes, the growth velocities of the chemical garden and the oscillations period are measured as a function of the flow velocity of the two reactants. By means of materials characterization techniques, the micro-morphology and the chemical composition of the precipitate is explored. Scanning Electron Microscopy images reveal self-similar micro-membranes at the surface of the macro-membranes.

Is Research on “Synthetic Cells” Moving to the Next Level?

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Synthesizing proteins inside liposomes and other microcompartments is a well-established practice. However, the origin of this research is not from the distant past, dating back to 1999–2004, when the first successful attempts were published. Protein synthesis and other reactions inside artificial compartments are approaches that lead to the construction of “synthetic cells” [1,2,3], a hot topic in bottom-up synthetic biology (Figure 1). The entire field ultimately relies on the convergence between chemistry, biochemistry and the chemistry and physics of artificial micro-compartments in the “colloidal domain”. Being biomimetic structures, synthetic cells can contribute to a deeper understanding of the biological organization and moreover they can be designed for very innovative uses in biotechnology. Here we summarize some technical and theoretical aspects of synthetic cell research, mainly based on gene expression and other enzymatic reactions inside liposomes, and in particular we will comment on the most recent trends. Such a tour will be an occasion for asking whether times are ripe for a sort of qualitative jump toward novel SC prototypes: is research on “synthetic cells” moving to a next level?

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Evolving network model of dissolution and precipitation in porous media

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Dissolution and precipitation in a porous medium is a complex process, involving the interplay between flow, transport, reaction and geometry evolution. The nonlinear couplings between these processes may lead to the formation of intricate patterns, the characteristics of which depend strongly on the fluid flow and mineral dissolution rates. In particular, in a broad range of physical conditions the flow spontaneously focuses in channel-like structures. To study this process, we model the porous medium as a system of interconnected pipes with the diameter of each segment increasing in proportion to the local reactant consumption. Moreover, the topology of the network is allowed to change dynamically during the simulation: as the diameters of the eroding pores become comparable with the interpore distances, the pores are joined together thus changing the interconnections within the network. With this model, we investigate different growth regimes in an evolving porous medium, allowing for both erosion and precipitation of the dissolved material. We relate the results to the experimental observations and the features of natural systems.

Magnetically active breast cancer chemotherapeutics using superparamagnetic hybrid nanoconjugates

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New generation nanoscale systems that utilize remotely active as well as controlled drug release was established in order to enhance the cancer therapeutics. Although many existing nanodrug carriers have shown numerous advantages, their efficacy is largely constrained by their lack of the ability to achieve on efficient demand drug release. In light of the growing interest in the search for next generation effective solutions for cancer treatment, we designed novel magneto-thermally active nanocarrier in which the drug release can be activated on demand upon exposure to a magnetic field. Magnetically active graphene oxide/iron oxide nanocomposite that can be triggered using magnetic hyperthermia initiated from an external alternating magnetic (AC) magnetic field. The unique remotely-triggered functional nanocomposite with well-defined size and uniform distribution were designed. The synergetic effect of both the drug and magnetic hyperthermia is observed in the killing of the cancerous cells. The overall simplicity of action, durability and biocompatible nature of nanocomposite demonstrated herein are key for successful tumor cells targeted therapeutic systems for the kinds of cancer therapy being sought for modern personalized and precision medicine.

Electroactive ionogel composites for actuator/sensor applications in soft robotics

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The rapid development in soft micromanipulation techniques for human friendly electronics has raised the demand for the devices able to carry out a mechanical work on the micro- and macroscale. The natural cellulose-based ionogels (CEL-iGEL) show a great potential for application as soft artificial muscles due to flexibility, low driving voltage and biocompatibility. The described CEL-iGEL composites undergo to reversible bending displacement already at ± 500 mV step-voltage values. In actuator applications the electrodes are a composites of the polymer and a conductive fillers which are intentionally synthesized through a precipitation process. The role of the conductive fillers are not only to conduct electron and increase charge injection but also to enhance Young's modulus, and porosity of the electrode material, leading to larger strain, output force, and speed of the actuator.

Magnetic-Field-Manipulated Growth of Flow-Driven Precipitate Membrane Tubes

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A noninvasive external magnetic field was applied to gain control over the directionality of membrane structures obtained by injecting one reactant solution into the other in a three-dimensional domain. The geometry of the resulted patterns was quantitatively characterized as a function of the injection rate and the magnitude of magnetic induction. The magnetic field was proven to influence the microstructure of precipitate tubes by diminishing spatial defects.

Acquiring thermodynamic data on mineral and organic systems and linking them with mobilities of elements in natural environments: an ongoing challenge

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Throughout the 20th century, chemists and mineralogists acquired basic data experimentally to characterize the enthalpies of formation of many inorganic and organic constituents identified on Earth. These works gave birth to thermodynamic databases, which are an essential link between thermodynamic chemical modeling and mobilities of elements in solutions in different pH and redox conditions. If, as a first approximation, we can be satisfied with the values accumulated in the literature, quickly, when we study a particular system, we notice inconsistencies, contradictory results or even the propagation of errors over time. To illustrate our point of view, two examples of such anomalies concerning major elements of Earth crust: Al, Fe, Si and H₂O, will be developed. The first example concerns the Al₂O₃ - SiO₂ - H₂O system with the Halloysite - Kaolinite - Gibbsite parageneses. By this example, we show that in the literature, there is only one experimental value for the enthalpy of halloysite formation. However, by over-interpretation of the system and in particular in the definition of the degree of hydration of halloysite, other values have been proposed for this mineral. Based on these values, there are inconsistencies, which do not explain certain parageneses observed in nature. Aluminum condensation in solution and its polymerization explains its solubility is more than 100 times the classical value based upon the monomeric model. The Gibbsite – Kaolinite – Quartz system was thus reevaluated. The second example concerns the Fe(OH)₂ - H₂O system under alkaline conditions. In the literature, three solubility curves of Fe(OH)₂ are proposed. By acquiring new data in the laboratory, it was possible to demonstrate that the three curves were valid. The explanation was obtained from the analysis of the speciation of Fe in solution, which leads to different condensation pathways of the solution to the hydroxide. In this case too, in reducing and alkaline conditions, Fe(II) solubility is 100 times larger when polymerization occurs than predicted on the basis of the monomeric model. A better knowledge of speciation in solution is thus required to link thermodynamic properties of minerals and mobilities of elements in natural environments differing by P, T, pH and redox conditions.

Self-organisation in messy chemistry

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Biochemistry as we know it occupies only a tiny corner of the space of possible organic molecules. Out of all the possible molecules that could be built from the chemistry of a cell, only a small number of building blocks are built, and these are assembled into sequences that occupy only a tiny fraction of the space of possible sequences. This is in contrast to typical abiotic chemistry, which can be broadly classified on a continuum from "clean" systems (in which only a few products can be formed) to "messy" ones, in which not only are there a combinatorially huge number of possible products, but all of these products are, to some degree, actually produced. Life differs from both of these in that it is self-selecting: the set of reactions that occur is a complex function of the system they make up.

No non-biological example of such complex, self-selecting behaviour is known, but I argue that it is more likely to be found when starting from a messy initial state than from a clean one. I present modelling work suggesting that a form of self-selection can occur in messy autocatalytic systems, as long as the contrast between reaction rates is high enough. This occurs through a process that has something in common with natural selection, despite the lack of RNA-like informational replicators. I suggest that transitions of this kind may have occurred at the earliest stages of the origin of life, and may it be possible to exhibit them experimentally.

SILICATE-GARDEN SYSTEM FORMATION DURING HARDENING OF STAMPED MORTAR WITH WOOD ASH ADMIXTURES

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Self-assembled fluid-flow-templated tubes are found in the so-called chemical gardens, and also in geophysical cases as volcanoes, soda straws in caves, and brinicles under sea ice. Chemical gardens of carbonates have been prepared at laboratory forming different nano-morphology and crystallographic transformations by nanoscale precipitation of carbonates and other metal oxides grown in the surfaces of tubular materials generated in flow conditions out of equilibrium. The formed materials were characterized observing nanocrystals with different morphology and chemistry depending on the growth conditions. The purpose of the present paper is to investigate the influence of ash coming from the complete burning of poplar wood and willow wood, respectively. For this purpose, plaster mortar with ash with 2 and 5% admixtures to a commercial reference mortar was prepared. The major elements in the investigated wood ash are calcium, magnesium, potassium and carbon. Sulfur, phosphorus and manganese are present at around 1%. Silicon, sodium, iron, aluminum, copper, zinc, and boron are present in relatively smaller amounts. Strong peaks corresponding to $\text{Ca}(\text{CO}_3)_2$ were identified in both ash. The willow ash contains relatively higher amounts of potassium compared to poplar ash and show strong peaks corresponding to $\text{K}_2\text{Ca}(\text{CO}_3)_2$. Willow ash being richer in sulphur and potassium has $\text{K}_2\text{Ca}(\text{SO}_4)$. Similarly, poplar, being richer in sodium, displays very weak peaks corresponding probably to $\text{Na}_2\text{Ca}(\text{SiO}_2)_3$ compound. The addition of ash, regardless of its nature (poplar or willow) or its amount did not contribute to the increase of the resistance of the commercial reference mortar after 3 days, 7 days or 28 days of hardening. Their role was mainly of filler together with pre-existing silica aggregates from the commercial mortar. The filamentar structures we have found in our samples in some ways resemble tubular structures grown in laboratory chemical garden experiments. The chemistry involved in the formation of Portland cement may be seen as a type of silicate-garden system. The hardening of the cement consists of the formation of a mesh of these filaments. The compression strengths determined experimentally in our works after 28 days of hardening place these mortars with ash admixtures below the values accepted by the starting reference mortar class. However, the use of poplar or willow ash generated after calcination at 650°C as admixtures for binder materials in mortar seems to be effective for their recycling in plastering mortars. These results open interesting applications of these materials for environmental applications.