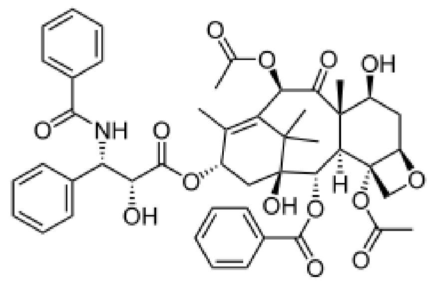
International Master "Molecular Catalysis and Green Chemistry"
University of Rennes 1, France
Programme 2017-2018

UE 2 - Modern molecular synthesis and industrial chemistry (36 h)
ECTS credits 4

1- Advanced organic synthesis, retrosynthesis and multi-step synthesis (S9-UE2-M1 – 24 h)

Teacher: Prof. C. Darcel



- Protecting groups
- Chemoselective methodologies in reductions and oxidations
- Classic and greener methods to make a C=C bond
- Cycloadditions, aldol reactions
- Retrosynthesis analysis
- Multi-step synthesis (prostaglandines, alcaloides, ...)

2- Chemistry and catalysis in industry (S9-UE2-M2 - 12 h)

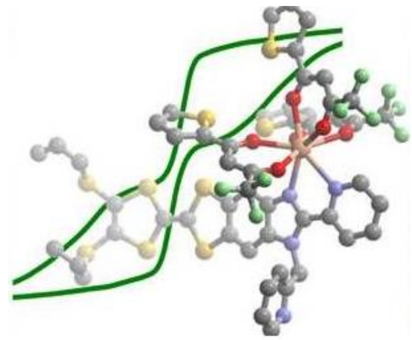
Teacher: Dr. E. Kirillov

- Presentation of industry of bulk and fine chemicals: products and markets
- Green chemistry concepts applied in industry
- Modern ways to produce C-C and C-N bonds in industry
- Enantioselective catalysis in industry, ligands and catalysts syntheses.
- Industrial oxidation processes: homolytic oxidation, catalytic oxidation, molecular oxygen activation, enantioselective oxidation
- Green aspects of industrial processes: hydrosilylation, hydrocyanation, hydroamination, use of CO, hydroformylation, carbonylation, applications of CO_2.
- Main catalytic processes in petrochemistry
- Production and applications of aromatic bulk intermediates (alkenes, etc.)

UE 3 - Advanced organometallic chemistry (36 h)
ECTS credits 4

1- Advanced organometallics Chemistry with transition metals (S9-UE3-M1 et S9-UE3-M2 - 24 h)

Teachers: Prof. C. Darcel (16h); Dr. V. Guerchais (8h)



The description of the organometallic and coordination complexes derived from transition metals will be made using Green formalism and the related number of electrons, valence number, oxidation state and coordination number. The reactivity of the complexes will be rationalized by the 9 fundamental elemental reactions involved in organometallic chemistry (oxidative addition, reductive elimination, non oxidative addition, non reductive elimination, oxidative coupling, reductive decoupling, insertion, extrusion/ β-elimination, X ligand exchange).

Several main families of complexes will be then studied (preparation, main characteristics, main uses in molecular materials, homogeneous catalysis, etc.):

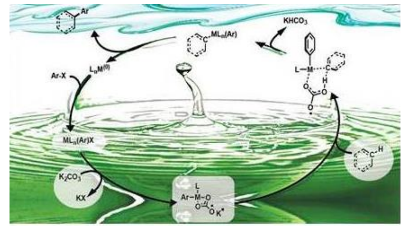
- Metal-olefins, metal-dienes, metal-carbonyl, metal-phosphine, metal-amine and metal-pyridine (application in homogeneous catalysis such as hydroformylation, carbonylation, hydrogenation and molecular materials)
- Metal-arene, metal-cyclopentadienyl (Application to metallo-assisted organic synthesis)
- Metal-hydride, metal-alkyl (application to the activation of C-H, Si-H bonds, etc.)
- Metal-carbene (including N-heterocyclic carbenes, NHC), metal-carbyne and metal-cumulene (application to olefin metathesis, polymerisation)

2- Organometallic chemistry of lanthanides (S9-UE3-M3 – 12 h)

Teacher: Dr. Y. Sarazin (12h)

Basic chemistry of lanthanides (structures, reactivity, synthesis)

UE 4 – Sustainable homogeneous catalysis for fine chemistry (36 h)
ECTS credits 4



As one of the 12 principles of green chemistry, catalysis is nowadays a crucial methodology in synthesis. Thus, this course will deal with transition metal catalysis: molecular catalyst design and important catalytic reactions for fine chemicals production.

1- Asymmetric catalysis (S9-UU4-M1 - 14 h):

Teacher: Prof. J.-F. Carpentier

- Use of chiral inductors in synthesis. Origins of stereoselectivity (thermo-dynamic and kinetic controls)
- Catalyzed formation of C-C bonds (cross-coupling reactions, allylic substitution, aldol reactions…), catalyzed reduction (hydroboration, hydrogenation, hydride transfer) and oxidation (epoxidation, dihydroxylation, hydroxyamination),
- Organocatalysis

2- Cross-coupling reactions and carbonylation (S9-UE4-M2 - 10 h) :

Teacher: Prof. C. Darcel

- Palladium-catalyzed cross-coupling reactions for C-C, C-O and C-N bond formations
- Earth abundant catalyzed cross coupling reactions
- Carbonylation

3- C-H bond activation/functionalization (S9 – UE4-M3 – 6 h)

Teacher: Dr. H. Doucet

- Ruthenium and palladium catalyzed Csp^2-H activation
- Palladium Csp^3-H activation.

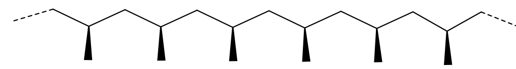
4- Metathesis (S9-UE4-M4 - 6 h)

Teacher: Dr. C. Fischmeister

- Catalyzed cross metathesis
- Lewis acid activation of C-C multiple bonds

UE 5 - Polymers and spectroscopy (36 h)
ECTS credits 4

1- Metal-catalyzed polymerization (S9-UE5-M1 – 12 h)

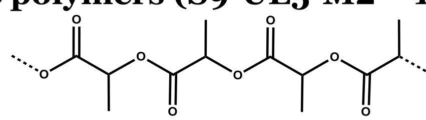


Teacher: Dr. E. Kirillov

- Basic principles of polymerization (polyolefins and related polymers, average molecular weights, polydispersity, polymerization degree; crystallinity and thermo-mechanical properties; analytical methods); Mechanisms of polymerization. Radical polymerization *vs* coordination/insertion
- Industrial olefin polymerization processes: Ziegler-Natta, metallocene and related catalysis
- Single site catalysts for polymerization (metallocenes, hemi-metallocenes, post-metallocenes); Late-transition metal catalysts; p-Block catalysts
- Principles of stereoselective polymerization (isotactic and syndiotactic polypropylene; syndiotactic polystyrene); Mechanisms of stereocontrol
- Synthesis of multiblock polymeric materials (copolymerization, chain-shuttling polymerization, “oscillating” catalysis)
- Metathesis polymerization (ROMP, ADMET); RIM

2- Synthesis of biodegradable & biocompatible polymers (S9-UE5-M2 – 12 h)

Teacher: Dr. S. Guillaume



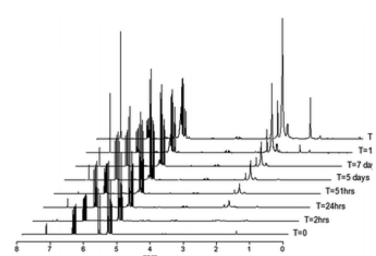
- Socio-economic aspects & concerns
- Current terminology: definitions and good use of terms
- Natural and synthetic biodegradable polymers
- Natural biodegradable polymers (polysaccharides: cellulose, starch, cellulose vs starch, chitin and citosan, alginate; polypeptides of natural origin: poly(α-aminoacid)s, collagen and gelatin; bacterial polyesters (PHAs): PHB, PHV)
- Synthetic biodegradable polymers (polyesters: PLA, PLGA, PCL, PTMC, PMLA, polymers with carbon backbone, polyamides, polyurethanes and polyureas, polypeptides, polyanhydrides, polyorthoesters)
- Degradation of synthetic polymers (non degradable polymers, readily degradable polymers, controlled degradable polymers, degradation processes)
- Applications of degradable polymeric materials (biodegradable polyesters, biodegradable polymers in drug delivery systems)

3- Characterization by spectroscopy (S9-UE5-M3 – 12 h)

Teacher: Dr. L. Norel

The synthesis of polymers requires adequate use of a variety of spectroscopic tools. The objective of this module is to make students able to select the appropriate spectroscopic tool or combination of tools in order to elucidate the structure of organic molecules (monomers), organometallic complexes (catalysts) or materials (polymers).

The skills that students will develop in the analysis of NMR data, infra-red spectroscopy and other complementary techniques are essential in the characterization of polymers and of many other types of molecular materials and will be developed mainly through spectroscopy problems combining 1D and 2D NMR spectra (^1H, ^{13}C), heteronuclear spectroscopy, variable temperature experiments and vibrational spectroscopy.



UE 6 - Smart molecular and supramolecular materials (36 h)
ECTS credits 4

1- Pi-conjugated molecular systems for opto-electronic applications (S9-UE6-M1 – 12 h)

Teacher: Prof. M. Hissler

Over the last twenty years, π-conjugated oligomers and polymers have received increasing interest owing to their versatile functions that are demanded for breakthroughs in many interdisciplinary fields like bio-imaging or plastic electronics (OLEDs, organic field effect transistors and organic photovoltaic cells). The demand for new organic π-conjugated materials with improved electrical and optical properties for plastic electronic applications is still very important and necessitates extensive experimental molecular engineering and theoretical investigations of underlying structure-property relationships. This lecture will begin with an introduction on the properties of π-conjugated systems (p and n doping, modulation and estimation of the HOMO-LUMO gap, estimation of the HOMO and LUMO energies by different techniques). A special focus will be made on the synthesis, properties of molecular and polymeric conjugated materials. Then, an introduction on organic light-emitting diodes, solar cells and field effect transistor will be provided.

2- Conducting Molecular Materials (S9-UE6-M2 – 12 h)

Teacher: Prof. D. Lorcy

This part of the course will focus on the synthesis of conducting molecular materials either multi-component or single-component materials. The selection of the precursors on structural aspects, reactivity and their ability to form radical species will be presented. The synthesis and the characterizations of these organic precursors, π-electron donor and π-electron acceptor, will be discussed. The control of the organization of these precursors in the solid state is an important parameter for the transport properties and different strategies will be detailed as well as the properties of the materials *versus* organization. Potential applications of these materials as non-volatile memories, field effect transistors, sensors… will be presented.

3- Macromolecular materials (S9-UE6-M3 – 12 h)

Teacher: Prof. S. Rigaut

This third part is devoted to “advanced supramolecular chemistry” based on metals (coordination and organometallic chemistry) for molecular (nano)materials with remarkable optical and electronic properties. This will include, synthesis, chelating/template effects, self-assembling of various metal containing nanostructures and coordination polymers that require a true engineering at the molecular and supramolecular levels. Applications in molecular machines, engines, sensors, catalysis, and design of biomimetic complexes will be also presented and complemented by several examples. This course will allow the students to become familiar with the field of nanoscience, particularly with molecular nanomaterials, a topic highlighted by the 2016 Nobel Prize.

UE 7 – Green Chemistry – Concepts and methodologies (36 h)
ECTS credits 4

1- Concepts of green chemistry and sustainable development (S9-UE7-M1 – 12 h)

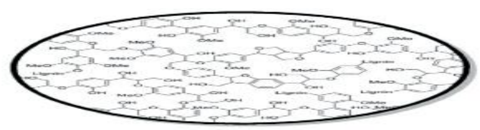
Teacher: Dr. C. Fischmeister

- The fundamentals of green chemistry
- Replacing toxic chemicals, alternative solvents and reaction media
- Selective catalysis, energy and environment: economic and environmental interests
- The environmental factor in chemical research and development management
- Green solvents
- Basics of flow chemistry
- Basics of filtration processes for catalyst recycling

2- The 3 main origins of biomass resources (S9-UE7-M2 – 12 h)

Teacher: Dr. J.-F. Soulé

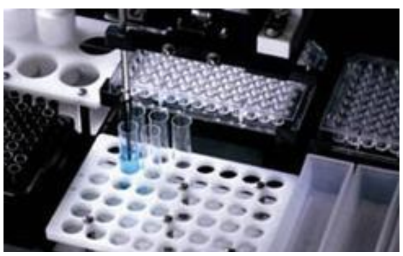
- Polysaccharides and carbohydrates
- Oils
- Lignine, cellulose.



This module will describe the main origins of biomass resources and the related chemical transformations

3- High throughput screening and non conventional technologies for green syntheses (S9-UE7-M3 – 12 h)

Teachers: Prof. J.-P. Bazureau, Dr. F. Geneste



Molecular Diversity

- Introduction to combinatorial chemistry: concepts, strategy, tools
- Library synthesis: mixture of molecules, parallel synthesis (liquid and solid phase, 2D library), split and pool, introduction to dynamic combinatorial chemistry with mixing of monodentate ligands

High Throughput Screening: GC, HPLC, NMR, IR, Mass spectrometry, thermography, visual detection with selected examples in catalysis

Non-conventional reaction media:

- Solvent ionic liquid technology in bulk chemistry, ionic liquid phase in combinatorial chemistry, toxicology and ecotoxicology
- Alternative deep eutectic solvents: From physical and chemical properties to applications in organic synthesis

Microwave in organic synthesis: from microwave/material interactions to pilot scale reactors in bulk heterocyclic chemistry

UE 8 – Tutorial green project in laboratory: revisiting a classical synthesis of a molecule or a process in terms of green chemistry
ECTS credits 4

(S9-UE8 – 12 h)

The main objective of this personal project is to be able to propose an alternative sustainable synthesis of known molecules or to propose alternative eco-compatible process to old one.
Based on a critical analysis of a bibliographic survey, the student will have to analyze in a green and sustainable point of view the synthesis or the process of preparation of a molecule (solvents, reactants, conditions, toxicity, risks, energy expense, etc.) and then to propose and alternative more eco-compatible synthesis.

The student will have (i) to write a concise report on his critical analysis, (ii) to prepare a support for the (iii) oral defense which will be made in front of a jury.

UE 1 - French course
ECTS credits 2

(S9-UE1 – 24 h)

This module is dedicated to students who have no bases in French language. They will learn the basics in order to be able to communicate in daily situations (Shops, railway station, airport, doctor meeting, etc.).

UE 9 - Bibliographic survey and research seminars in English
ECTS credits 10

(S10-UE1 – 12 h)

Teacher: Dr. H. Doucet

The main objective of this bibliographic survey module is to give the student efficient tools in order to prepare and present a bibliographic survey on a selected topic.

The teaching program is:

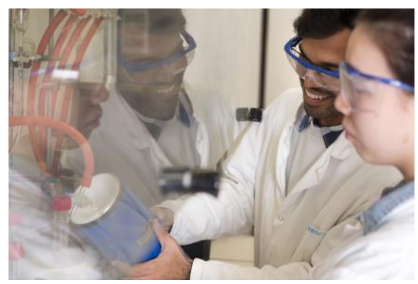
- Use of bibliographic data bases (e.g. Scifinder, Titanesciences, etc.)
- Write a bibliographic survey on the research project developed during the internship particularly with bibliographic references written following the general rules used in peer reviewed journals
- Prepare an oral presentation support

The student will have to write a concise report with a specific part for the notation of the bibliographic references following the general rules used in peer reviewed journals. He will have then to make an oral defense using an iconographic support in front of a jury (30 minutes including the discussion with the jury).

UE 10 Research Stay – Master thesis
ECTS: 20

(S10-UE2)

The student will be inserted in a research group under the guidance of an experimented researcher in the joint University of Rennes 1 – CNRS Unit "Institut des Sciences Chimiques de Rennes" (UMR 6226) in order to acquire a solid experience in research (bibliographic survey, molecular synthesis, characterization (NMR, IR, UV-vis, X-ray analysis, chromatography, Mass spectroscopy, etc.). The Master thesis is aimed at being published in international journals.



The student will have to write a concise scientific report. He will have then to make an oral defense using an iconographic support in front of a jury (30 minutes including the discussion with the jury).

A master student has to earn as followed:

Compulsory scientific courses (7*4 + 10 = 38 credits), French course (2 credits) and Master Thesis (20 credits).