CNRS GDR Groupement de recherche
CHIRAFUN
Chiralité et Multifonctionnalités

Program
GDR Chirafun days (on line)
April 19-20-21 2021

1 Course

- Dr Nicolas Vanthuyne (Chirosciences Institut des Sciences Moléculaires de Marseille)
  “Preparative chiral resolution by enantioselective chromatography at lab scale: materials and methods”

2 Invited Conferences

- Dr Gennaro Pescitelli (Università di Pisa, Dipartimento di Chimica e Chimica Industriale)
  “Stereochemical analysis by circular dichroism spectroscopies”

- Dr Laurent Bouteiller (Institut Parisien De Chimie Moléculaire (IPCM) Sorbonne Université)
  “Supramolecular chirality in hydrogen bonded supramolecular polymers”

17 Young Researchers Oral Communications

Monday 04/19/2021

Zoom	https://u-bordeaux.fr.zoom.us/j/81343350524?pwd=ekJubWxSVjdZVy9SV3luMnVJTUJXdz09 ID de réunion : 813 4335 0524 Code secret : ChiRaFun		
13h40	Welcome	Jeanne Crassous	
14h00-15h00	Course	Dr. Nicolas Vanthuyne	Preparative chiral resolution by enantioselective chromatography at lab scale : materials and methods
15h00-15h20	Oral Comm.	Mayte Martinez-Aguirre	Chirality amplification in supramolecular helical catalysts: dissecting the role of the sergeant
15h20-15h40	Oral Comm.	Hoshang Sahib	Engineering guided circular polarization by linear and chiral birefringence competition in rib/ridge chirowaveguides
15h40-16h00	Oral Comm.	Anne-Doriane Manick	Inherently chiral calixarene combined secondary phosphine oxide: synthesis, resolution, characterizations and catalytic activity
16h00-16h20	Oral Comm.	Antoine Comby	Fast optical determination of enantiomeric excess using photoelectron elliptical dichroism
16h20-16h40	Oral Comm.	Sitthichok Kasemthaveechok	Helically and axially chiral cationic radical bicarbazoles
16h40-17h00	Oral Comm.	Jenifer Dupont	Photoelectron circular dichroism as a probe for conformational isomerism in 1-indanol

Tuesday 04/20/2021

Zoom	https://u-bordeaux-fr.zoom.us/j/89894000562?pwd=QW1NWlZkVG5BUHJxeU0rUU1pM3h0UT09 ID de réunion : 898 9400 0562 Code secret : ChiRaFun		
14h00-15h00	Invited Lecture	Dr. R. Pescitelli	Stereochemical analysis by circular dichroism spectroscopies
15h00-15h20	Oral Comm.	Chunyang Li	Synthesis of chiral hemicryptophane cages: application to enantioselective recognition
15h20-15h40	Oral Comm.	Antonio Carone	Induced plasmonic chiral response on Au@Ag nanoparticles by small thiolated molecule
15h40-16h00	Oral Comm.	Raphaël Pepino	Enantioseparation of chiral biosignatures using multidimensional gas chromatography applied to extraterrestrial samples
16h00-16h20	Oral Comm.	Kais Dhbaibi	Helicene-lanthanide complex for magneto-chiral dichroism and NIR CPL properties
16h20-16h40	Oral Comm.	Peizhao Liu	Optically Active Inorganic Semiconductor Nanocrystals Helical Arranged on Inorganic Silica Nanohelices

Wednesday 04/21/2021

Zoom	https://u-bordeaux-fr.zoom.us/j/86273780846?pwd=dDByWUtKS2diZFBmQkVwRmQzUUNlUT09 ID de réunion : 862 7378 0846 Code secret : ChiRaFun		
14h00-15h00	Invited Lecture	Dr. L. Bouteiller	Supramolecular chirality in hydrogen bonded supramolecular polymers
15h00-15h20	Oral Comm.	Yajie Chou	Atropisomeric palladium-NHC complexes: A new design for chiral catalysts
15h20-15h40	Oral Comm.	Rafael Rodriguez	Switching chiral communication mechanisms in helical polymers
15h40-16h00	Oral Comm.	Dr. Alexandre Abhervé	Molecular conductors based on chiral metal-bis(dithiolene) complexes: structures and transport properties under very high pressure
16h00-16h20	Oral Comm.	Martin Doll	Are the physical properties of Xe@Cryptophane complexes easily predictable? The case of the syn and anti tris-azacryptophanes
16h20-16h40	Oral Comm.	Marine Hoquante	Theory and practice on the continuum between supramolecular chirality and intrinsic chirality
16h40-17h00	Oral Comm.	Justin Lange	A novel proteomics-based strategy for the investigation of peptide sequences in extraterrestrial samples

Molecular conductors based on chiral metal-bis(dithiolene) complexes: structures and transport properties under very high pressure

Alexandre Abhervé [1], Nabil Mroweh [1], HengBo Cui [2], Enric Canadell [3], Narcis Avarvari [1]

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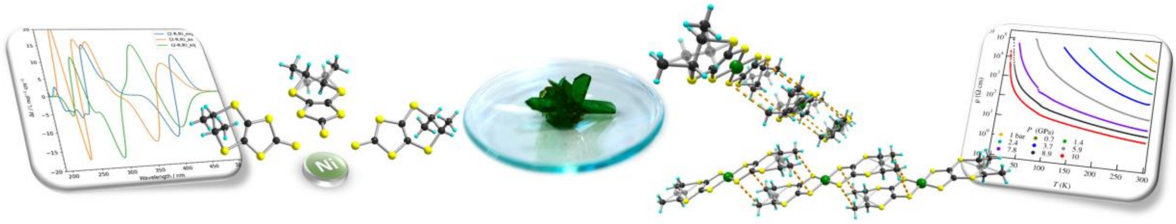
Keywords: Molecular conductors, chirality, nickel-bis(dithiolene)

Résumé : Metal-bis(dithiolene) complexes are an important family of molecular conductors since they usually have a small HOMO-LUMO energy gap and can thus present a metallic band structure under pressure. Recently, we have reported the first examples of chiral single-component molecular conductors of formula [M(dm-dddt)$_2$] (M = Au, Ni; dm-dddt = 5,6-dimethyl-5,6-dihydro-1,4-dithiin-2,3-dithiolate).[1] Transport measurements on single crystals of both (*S*,*S*,*S*,*S*) and (*R*,*R*,*R*,*R*) enantiomers indicated a semiconducting behaviour of the open-shell gold complexes and activation energies strongly influenced by hydrostatic pressure.

In the last years, resistivity measurements under very high pressure could be performed using a diamond anvil cell (DAC). It has shown the appearance of metal-like behaviours in molecular semiconductors and the emergence of the Dirac electron system in the single-component molecular conductor [Pd(dddt)$_2$].[2]

Here we designed a series of nickel-bis(dithiolene) complexes based on the chiral ligands 5-methyl-5,6-dihydro-1,4-dithiin-2,3-dithiolate (me-dddt) and 5,6-dimethyl-5,6-dihydro-1,4-dithiin-2,3-dithiolate (dm-dddt) and performed resistivity measurements under very high pressure. We showed that the use of chiral dithiolene ligands with one or two stereogenic centres, together with variation of the counter-ion in the anionic complexes, represents a powerful strategy to modulate the conducting properties of such molecular materials.[3] Both tetrabutyl-ammonium and tetramethyl-ammonium radical anion salts are Mott insulators with antiferromagnetic ground state, as suggested by spin polarized DFT band structure calculations. However, the TMA salts are one order of magnitude more conducting than the TBA counterparts. The neutral materials are direct band gap semiconductors, as determined by DFT and extended Hückel band structure calculations, with their conductivity drastically increased up to 0.05 – 3.3 S cm^{-1} under the highest applied pressures of 10 – 11 GPa. At equivalent applied pressures the dm-dddt materials are more conducting than the me-dddt ones, in agreement with the lower calculated activation energy and higher bands dispersion for the former. Subtle differences of conductivity are also observed within both series of neutral complexes between the enantiopure and racemic forms.



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INDUCED PLASMONIC CHIRAL RESPONSE ON Au@Ag NANOPARTICLES BY SMALL THIOLATED MOLECULE

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Keywords: gold nanoparticles, seed-mediated growth process, plasmonic, chirality

The chirality is well a known property which represent a key factor to be controlled in every field that involve a synthetic process, from organic chemistry, biochemistry and material science. In this latter field, the community is more and more interested in the synthesis of inorganic chiral nanostructures, and especially in noble plasmonic metal nanostructures[1,2]. This interest derives from the attractive possibility to induce the strong plasmonic resonance to have a chiroptical activity[3]. The application fields for a material with these characteristics are wide, and range from catalysis, (bio)sensing and photonics. However, easily fabricating such nanostructures -ideally with an up-scalable, low cost, reproducible and versatile process- is currently a huge challenge. We want to address this challenge by developing the colloidal synthesis and self-assembly of a class of gold nanoparticles with unusual chiral shape. We will present our recent efforts to synthetize chiral nanoparticles using pentatwinned AuNPs as a starting point in a seed-mediated growth process in presence of amino acids (L-cysteine and L-glutathione). Previously synthetized gold bipyramids by a protocol developed in our group[4] are modified in presence of L-cysteine to create a new core-shell structure of Au@Ag and Au@AgAu with tunable chiroptical activity in the visible spectrum.

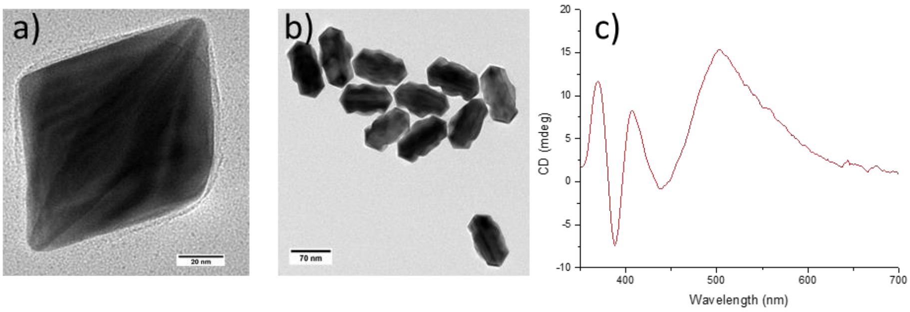

Fig1. a) TEM image ofs Au@Ag nanoparticle, b) TEM image of Au@AuAg nanoparticles, c) CD spectrum of of Au@Ag

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2 Ma W. et al., *Chem. Rev.* **2017**, 117, 8041
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4 Chateau D. et al., *ACS Appl. Mater. Interfaces*, **2019**, 11, 39068

Atropisomeric palladium-NHC complexes: A new design for chiral catalysts

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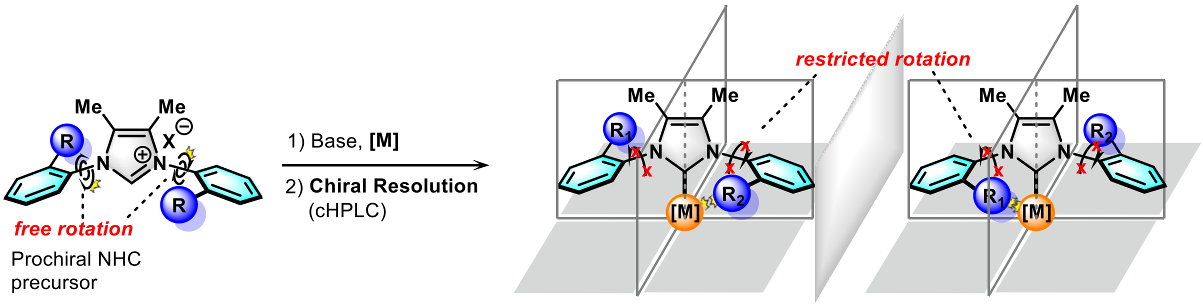
Keywords: Asymmetric catalysis, N-heterocyclic carbenes, palladium, α-arylation reaction

Résumé :

Transition-metal asymmetric catalysis is an efficient methodology giving access to complex molecular architectures in an enantioenriched fashion. Over the past few decades, a huge amount of chiral ligands has been designed, most of them are based on point chirality, but also on axial chirality and planar chirality.

Our group has great interest in the design and the synthesis of chiral catalysts. Recently, we proposed a new design of chiral metal-based complexes bearing a N-heterocyclic carbenes (NHCs) with an axial chirality.[1] Imidazolium salts with dissymmetric N-aryl substituents have designed and synthezised. Albeit these NHCs precursors possess an axis of chirality, they are not conformationnally stable due a free rotation of the aryl substituent along the C-N bond. However, after a metalation step, the resulting complexes exhibit a restricted rotation and enantiomers could be separated by chiral HPLC at preparative scale with excellent optical purities (up to 99.5% ee).

The syntheses of palladium-based complexes, their resolution by chiral HLPC, the study of the configuration stability will be presented as well applications in enantioselective intramolecular α-arylations of carbonyl compounds.[2]



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2. L. Kong, M. Jean, M. Albalat, P. Nava, S. Humbel, N. Vanthuyne, H. Clavier, *manuscript in preparation.*

Fast optical determination of enantiomeric excess using photoelectron elliptical dichroism

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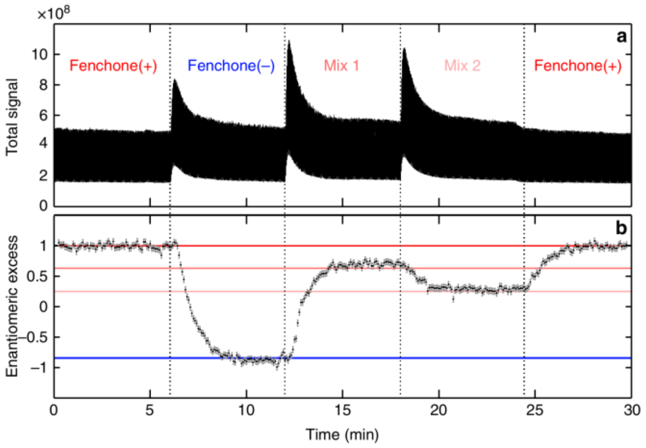
Keywords: Laser, Photoelectron, Dichroism, Enantiomeric Excess

The fast and accurate analysis of chiral chemical mixtures is crucial for many applications but remains challenging. The photoionization of chiral molecules was recently identified as an efficient process for chiral analysis, because it provides very strong signals from gas-phase samples through the photoelectron circular dichroism effect [1-4]. Here we use elliptically-polarized femtosecond laser pulses at high repetition rates to photoionize chiral molecules. The 3D photoelectron angular distribution produced provides molecular fingerprints, showing a strong forward-backward asymmetry along the laser propagation direction, which depends sensitively on the molecular structure and degree of ellipticity. Continuously scanning the laser ellipticity and analyzing the evolution of the rich, multi-dimensional molecular signatures allows us to observe real-time changes in the chemical and chiral content present with unprecedented speed and accuracy. We measure the enantiomeric excess of a gaseous compound with an accuracy of 0.4% in 10 min acquisition time, and follow the evolution of a mixture with an accuracy of 5% with a temporal resolution of 3 s [5]. This method is even able to distinguish isomers, which cannot be easily distinguished by mass spectrometry.



Continuous monitoring of enantiomeric excess. (a) Total photoelectron signal as a function of time, as different samples are successively connected to the chamber. (b) Measured enantiomeric excess. The horizontal lines are the theoretical values of the enantiomeric excesses of the different mixtures

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Helicene-lanthanide complex for magneto-chiral dichroism and NIR CPL properties

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(Single-Molecule Magnet, Circularly Polarized Luminescence, Magneto-Chiral Dichroism, Helicene)

Preparing molecular magnets with additional features such as conductivity, photo-reactivity, and optical properties is an exciting goal for scientists and a key challenge in modern materials science.[1] Combining magnetism and chirality in molecules also furnishes a beautiful demonstration of how powerful is the association of physics and chemistry fields to build-up new multifunctional molecules giving rise to new phenomena like the Magneto-Chiral Dichroism (MChD).[2] Lanthanide ions are able to retain their magnetization in a given direction, thus generating a special class of Single-Molecule Magnet (SMM) thanks to their specific magnetic and optical properties.[3] We reasoned that the combination of chiral organic ligand with a given f element may lead to an attractive and unusual example of SMM molecules merging chiroptical, luminescence, and magnetic properties.[4] Helicenes are polycyclic aromatic compounds with nonplanar screw-shaped skeletons formed by ortho-fused benzene or other aromatic rings, and can be regarded as valuable inherently chiral building blocks for reaching intense chiroptical properties.[5] In this context, a new family of enantiopure helicene-based ligands was prepared and their complexation with various lanthanide ions was performed. Chiral ytterbium complex (Figure 1) allows for the first time the investigation of MChD through NIR light absorption, along with an intense Circularly Polarized Luminescence (CPL) activity in the NIR region.[6]

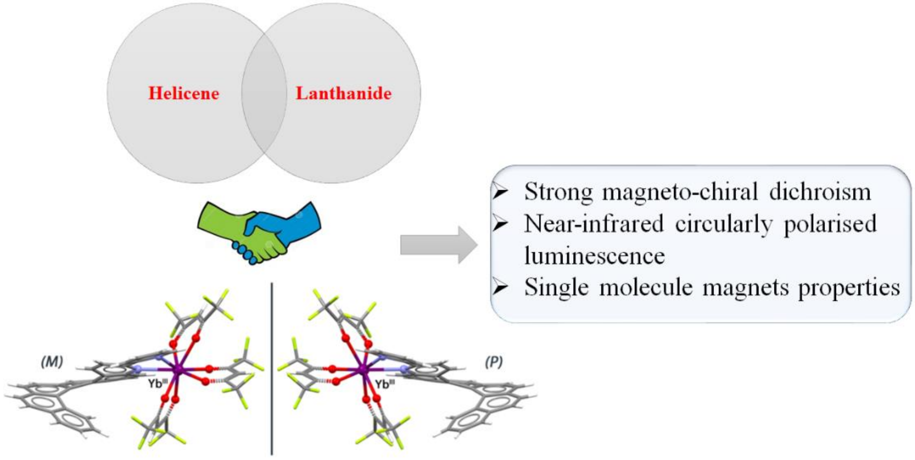

Fig. 1: Co-existence of SMM, MChD, and CPL properties in enantiopure ytterbium complex based helicene ligand.

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Are the physical properties of Xe@Cryptophane complexes easily predictable? The case of the *syn* and *anti* Tris-azacryptophanes

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Keywords: Chiral supramolecular receptors, xenon encapsulation, circular dichroism, hyperpolarized (HP) ^{129}Xe NMR, influence of heteroelements

Abstract: Cryptophanes are a family of synthetic organic macrocycles, designed for molecular recognition, which were conceived in 1981 by André Collet.[1] They are made of two cyclotribenzylene units (CTB) connected by three linkers, giving them often a chiral structure. They possess a hydrophobic cavity, which allows strong and selective binding either of small molecules (CH_4, $CHCl_3$, Xe) or cations (Cs^+, Tl^+).[2],[3] Moreover, cryptophanes chirality allows enantioselective binding of small organic molecules and the use of chiroptical techniques for host guest binding studies.[3],[4] Among the large variety of guests encapsulated by cryptophanes, xenon is of prime interest. Indeed, high binding constant and slow exchange kinetics make cryptophanes by far the most interesting receptors for xenon encapsulation. Recent development targets therefore the formation of molecular functional bioprobes for hyperpolarized (HP) ^{129}Xe MRI.[5]

We recently developed new aniline-analogues called tris-aza-cryptophanes (Figure 1a), in order to study the influence of a heteroelement on xenon binding properties. To this purpose, these molecules can be compared to their oxygenated equivalents (cryptophanes A and B) that have been earlier reported.[1],[6] Aniline groups are also protonated at low pH, inducing drastic decrease of electron density of the cryptophanes. After the development of a synthetic pathway from an aniline-CTB derivative (template method), we were able to isolate simultaneously two tris-azacryptophanes diastereoisomers. Chiroptical studies of these compounds allowed the determination of their relative and absolute configurations. HP ^{129}Xe NMR studies showed unexpected exchange kinetics of xenon in the aza-cryptophanes (Figure 1b), as well as a promising shift in the signal of encapsulated xenon under pH variations.

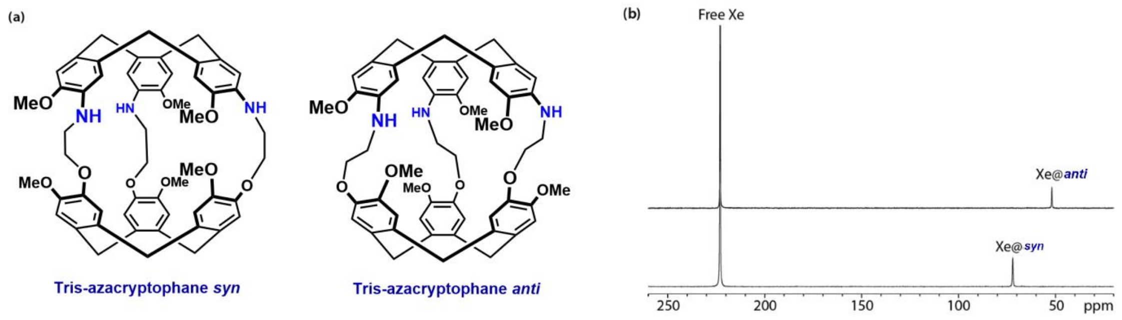

Figure 1: a) Structure of the two-triazacryptophanes. b) HP ^{129}Xe NMR in presence of triazacryptophanes *anti* (top) and *syn* (bottom) showing xenon encapsulation with slow exchange ($C_2D_2Cl_4$, 298 K, 11,7 T).

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Photoelectron circular dichroism as a probe for conformational isomerism in 1-indanol

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Keywords: photoelectron circular dichroism ; chirality ; conformations

Photoelectron circular dichroism (PECD) consists in a forward/backward asymmetry with respect to the light propagation axis in the photoelectron angular distribution after ionization of a chiral molecule by a circularly polarized light. PECD has shown a strong sensitivity to molecular conformations[1]. This is the reason why we applied this technique to a chiral flexible molecule: 1-indanol. Indeed, this molecule exists in one or two conformers in a supersonic beam, depending on the nature of the carrier gas (Figure 1)[2].

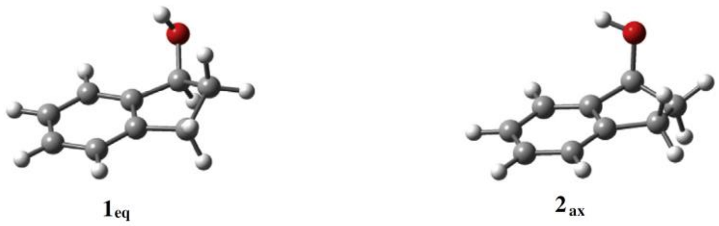

Figure 1: Conformations of the jet-cooled 1-indanol in argon (1_{eq}) and in helium (1_{eq} and 2_{ax})

Photoelectron spectra (PES) and PECD spectra of jet-cooled (S)-1-indanol and (R)-1-indanol were recorded in helium and argon at several photon energies on the DESIRS beamline at the SOLEIL Synchrotron. The PECD spectra exhibit a very good mirroring between the two enantiomers of 1-indanol in both carrier gases and show differences when changing the carrier gas (Figure 2). Quantum calculations were performed to support and understand better the experimental results.

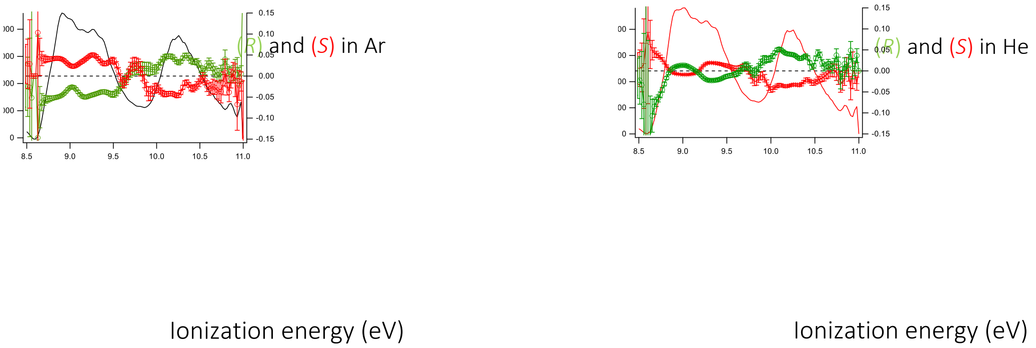

Figure 2: Photoelectron (left axis) and PECD (right axis) for 1-indanol in argon (left graph) and in helium (right graph), recorded at hv = 11.0 eV

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Theory and practice on the continuum between supramolecular chirality and intrinsic chirality

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Prochiral molecules which crystallize in a chiral space group, could lead to predict conglomerate forming systems of closely related chiral molecules [1]. If, in addition to this relationship, they could form mixed crystals (i.e. a complete solid solution), it is possible to have a continuum between supramolecular chirality and intrinsic chirality.

In this work, we show that a chiral sulfoxide is a conglomerate forming system and the corresponding non-chiral sulfone crystallize in the same space group with very similar crystallographic parameters. Consistently, two symmetrical complete solid solutions have been pointed out.

Evidence of deracemization of the sulfone [2] by means of TCID (Temperature Cycle Induced Deracemization) will be given [3] and the control of the chirality by one molecule induces the control of the other [4].

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Axial and Helical Chiral Bicarbazole Systems: A New Family of Persistent Chiral Mono- and Diradical Cations

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Keywords: Chirality, Organic radicals, SOMO-HOMO inversion, spin interaction, carbazoles.

Chiral π-conjugated materials have recently emerged as a promising direction in material science due to their specific interaction with circularly polarized (CP)-light and the potential of the latter in several applications such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic magnets.[1] While extensive researches have been focusing on organic chiral dyes with closed-shell electronic configuration, a few attention has been given to their open-shell counterparts, so-called radicals, due to their low configurational stability and high chemical reactivity especially diradicals. These radicals may bring additional conductive and magnetic properties owing to their accessible high-spin triplet state, offering innovative opportunities for chiral-optoelectronic applications.[2] With the ultimate goal of exploring innovative stable chiral radicals, we develop new molecular chiral bicarbazoles systems where axial configuration dramatically enhances both chemical and configurational stabilities of corresponding mono- and diradical species comparing to the helical ones. The obtained chiral open-shell compounds were investigated by photophysical, chiroptical and, magnetic properties. Formation mechanism of these radicals occurs via an uncommon SOMO-HOMO inversion process in the monoradical state, which enhances the resulting radical stability (**Figure 1**).[3]

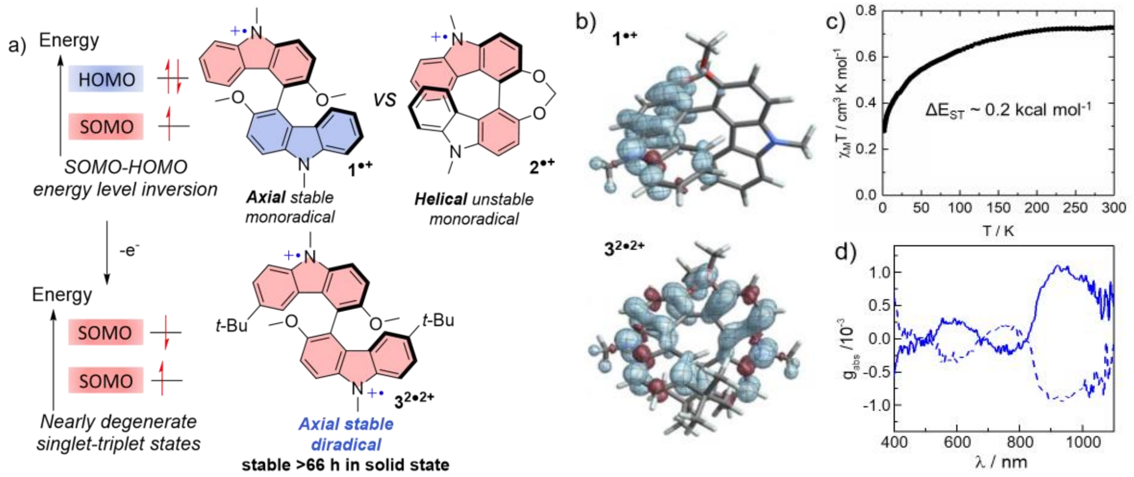

Figure 1. a) Axial and helical chiral bicarbazoles with chirality dependent stability where color shows spin distributions. Counter anions were omitted for clarity reason. b) calculated spin density of $\mathbf{1^{\bullet+}}$ (top) and $\mathbf{3^{2\bullet2+}}$ (bottom). c) plot between product of molar magnetic susceptibility (χ_M) and T vs T of diradical $\mathbf{3^{2\bullet2+}}$ showing curie constant (C) equal to 0.79 cm^3 K mol^{-1}. d) absorption dissymmetry factor (g_{abs}) of $\mathbf{3^{2\bullet2+}}$ from Near infrared electronic circular dichroism.

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A Novel Proteomics-Based Strategy for the Investigation of Peptide Sequences in Extraterrestrial Samples

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Keywords: Meteorites - building blocks – chiral method – APM – peptide

Many organic molecules present in comets or asteroids may have been delivered to Earth during the early phases of the planet's formation in the first hundred million years of the solar system. Molecular identification has become a key challenge in astrobiology in order to understand the molecules' potential roles in the emergence of life. Within this framework, numerous building blocks of living systems, such as amino acids, sugars, and nucleobases, have been highlighted in various extraterrestrial environments. In contrast, the direct or indirect detection of macromolecules such as peptides, that would represent a major advance for understanding the origin of organized molecular systems on the early Earth, remainschallenging.

Until now, gas chromatography coupled to mass spectrometry (GC-MS) has been the technique of choice for analysis of amino acids and other water-soluble compounds in extraterrestrial objects. For the detection of these molecules, samples have to undergo several chemical pretreatments, typically consisting of an acid hydrolysis (usually with hydrochloric acid) followed by a derivatization reaction to enhance the compounds' volatility or detectability. However, such processes impose rather harsh conditions which are likely to degrade organic compounds (fragmentation reactions, oxidation, rearrangements, racemization), hence giving incomplete information on the structure of the molecules present in the native sample. Therefore, the presence of peptide sequences in such extraterrestrial samples cannot be deduced by this analytical procedure. Here, we present a new strategy designed to highlight, without ambiguity, amino acids involved in peptide bonds within extraterrestrial samples. For this purpose, we transferred a proteomics approach based on the use of aminopeptidase M (APM, EC 3.4.11.212,13), which catalyzes stereoselectively the stepwise removal of L-α-amino acids from the N-terminal end of peptides. To get a proof of presence of peptide sequences in meteorite extracts, we developed a chiral UPLC-MRM MS method to enable the enantiomeric separation of amino acids in a very short analysis time. This method used a chiral crown ether-bonded stationary phase as chiral selector.

This experiment clearly demonstrates the ability of this proteomics-based strategy for indicating L- and D-amino acids specifically involved in peptide sequences within a meteorite extract. Thus, it opens a new pathway to explore molecules included in minor bodies, for instance through the investigation of other enzymatic systems.

Synthesis of chiral hemicryptophane cages: application to enantioselective recognition

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Keywords: hemicryptophane-tren, enantioselectivity, binding constants

Abstract: The design of chiral containers is very attractive because they can mimic biological systems such as enzymes, apart from chiral cyclodextrins, calixanes, and cavitands, which present remarkable properties, cryptophanes and hemicryptophanes, which inherent chirality benefit from CTV (Cyclotriveratrylene) are giving increasing promising properties to molecular receptors. In our study, two enantiopure hemicryptopphane-tren cages containing the C_3-symetrical tris(2-aminoethyl)amine ligand and different sizes of cavities have been synthesized, based on the optical resolution of key intermediates, CTVs, their the energy barrier for racemization have been calculated to guarantee there is no racemization exist during the last steps. The assignment of the absolute configurations of hemicryptopphane-tren cages are performed by ECD (electronic circular dichroism), the enantiopurity of cages which is deduced directly from enantiopure CTV is investigated by NMR spectroscopy in the presence of enantiopure norephedrine and ephedrine (as guests), an obvious enantioselectivity towards the C_3-symetrical cages (as hosts) are observed, the binding constants of the hosts towards guests are calculated after modeling of the titration curves. Due to the different sizes of the cavities and flexibility of cages, hemicryptopphane-tren cages show different enantioselectivity on guests, but all the cages are efficient chiral receptors, exhibiting substrate-, diastereo-, and enantioselective recognition.

Optically Active Inorganic Semiconductor Nanocrystals Helical Arranged on Inorganic Silica Nanohelices

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Key words: Optically active, Semiconductor nanocrystals, silica nanohelices, helical organization

Abstract

Optically active semiconductor nanocrystals (NCs) represent emerging types of chiral materials due to their outstanding optical properties and applications.[1,2] In this report, Inorganic silica helices were used as chiral templates to endowing optically active properties to luminescent semiconductor NCs. The prepared NCs grafted on right-(or left-) handed silica helices do not show any optically active properties in suspension as figures (a-f) shown. However, when they are dried on substrates, the NCs-right/left-handed silica nanohelices show strong CD and CPL signals as shown in figure (g) and (h). Cryo-EM of solvated and TEM images of dried NCs grafted silica helices show clear differences between NCs and silica nanohelices (figure (c) and (d)), i.e. in the absence of solvent, these NCs show much closer arrangement around the surface of silica helices. The different optically active properties between solution and drying film state are due to the nanocrystal self-organization during the solvent evaporation process. Besides, the NCs with different sizes, crystal structures, and shapes grafted on the surface of silica nanohelices were studied. Such drying effect shed light on the way to achieve optically active functional materials with inorganic building blocks. Also, this system shows excellent temperature stability which gives a great possibility to future applications.

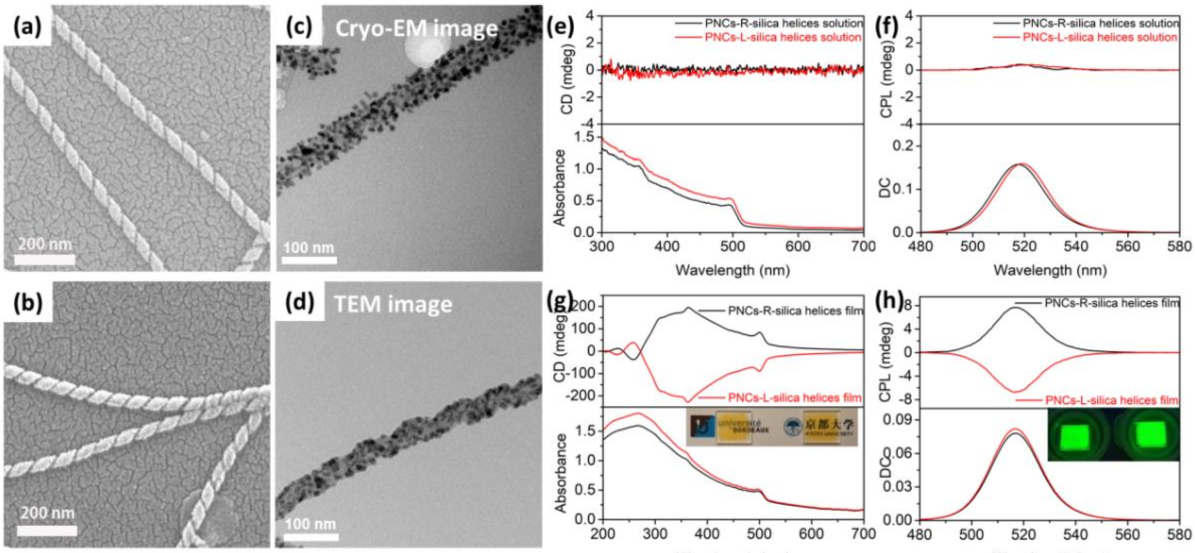

Figure 1. The SEM images of R/L-silica nanohelices (a), (b); The Cryo-EM image (c) and TEM image (d) of PNCs-R-silica nanohelices; The CD and absorption spectra (e) and the CPL and DC spectra (f) of $CsPbBr_3$-R/L-silica nanohelices in toluene suspension; The CD and absorption spectra (g) and the CPL and DC spectra (h) of $CsPbBr_3$-R/L-silica nanohelices film. The inset picture in (g) shows the films under natural light, while the inset picture in (h) shows the films under a UV lamp at 365 nm.

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Inherently chiral calixarene combined secondary phosphine oxide: synthesis, resolution, characterizations, and catalytic activity

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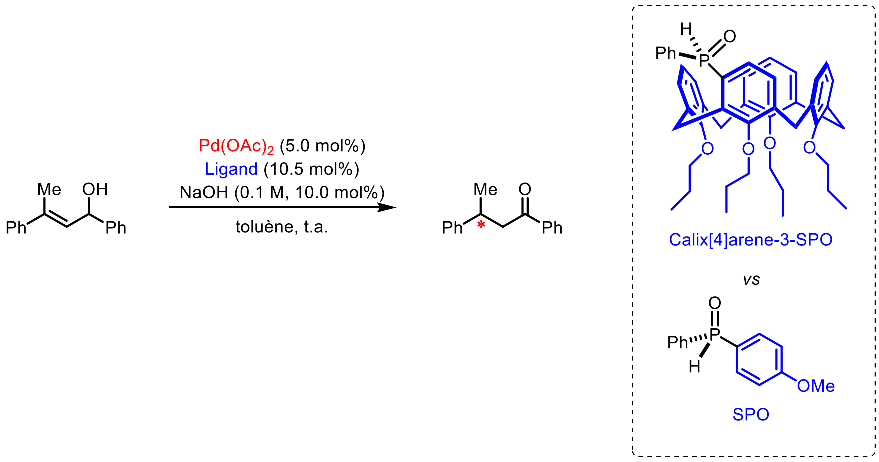
Keywords: chiral calixarene, secondary phosphine oxide, enantioselective catalysis, palladium catalysis

Calixarenes are probably one of the most frequently used macrocyclic compounds in supramolecular chemistry.[1] The simple one step synthesis of their core, the easy modification of the resulting upper and lower rims and their host-guest properties, can account for the interest arouse by this class of compounds. Supramolecular catalysts based on calixarene scaffold have been also developped and displayed remarkable properties : the confinement of the substrate and/or the catalytic site in their cavity can induce strong changes in the rate or selectivity of the reaction.[2] In particular, calixarene have been functionnalized with phosphorus atoms, giving rise to original supramolecular ligand for transition metal. To our knowledge, examples are limited to phosphine, phosphate and phosphite linked to the calixarene core.[3]

In this context, we report on the synthesis of an inherently chiral calixarene bearing a secondary phosphine oxide (SPO) unit. In fact, the SPO ligands are very attractive for metal catalysis because of their air and moisture stability and the configurational stability of chiral phosphorus. The resulting compound has been obtained enantiomerically and diastereomerically pure and then used as chiral ligand in palladium-catalyzed isomerization reacction of allylic alcohol in comparing with the chiral SPO model.



In this communication, we will present the synthesis of this attractive ligand and the effect of the combination of a P -stereogenic ligand and new secondary chirality inductors on the catalytic activity and the enantioselectivity.

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“Chirality amplification in supramolecular helical catalysts: dissecting the role of the sergeant”

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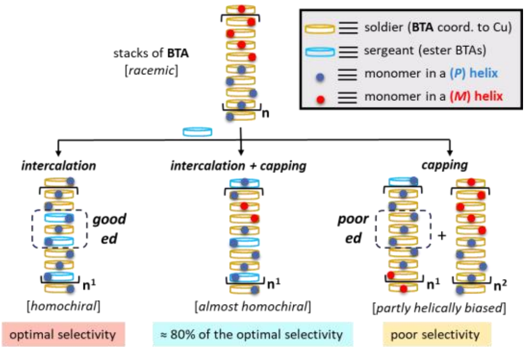
Keywords: supramolecular catalysis, helical catalyst, sergeants and soldiers effect, supramolecular chirality

Amplification of chirality is a unique phenomenon that refers to the ability of small chiral bias to fully control the main chain helicity of polymers and assemblies.[1] Single-handed helices can be obtained not only from homopolymers of enantiopure monomers but also from copolymers consisting of a mixture of enantiopure and achiral monomers. The so-called “sergeants-and-soldiers” (S&S) effect[2], a type of chirality amplification, arises when a minor amount of chiral units (the “sergeants”) are able to control the local conformation of an excess of achiral units (the “soldiers”).

Benzene-1,3,5-tricarboxamides (BTAs) and their derivatives,[3] are unique in regards to their ability to form remarkably stable supramolecular helices by a combination of hydrogen bonding and aromatic interactions. In these helical systems the S&S effect allows to obtain very long one-dimensional helices which are one-handed at the condition that a few percent of sergeants are present in the coassemblies.[4] Previously, our group observed that the extent of enantioselectivity displayed by supramolecular helical catalysts composed of achiral BTA ligands (coordinated to Rh[5a] or Cu)[5b] and enantiopure co-monomers is directly due to a high helical purity and length of the helical co-assemblies.

In order to determine the effect of the sergeant structure on chirality induction and amplification of catalytic supramolecular helicesmixtures composed of a benzene-1,3,5-tricarboxamide (BTA) ligand coordinated to copper and seven enantiopure BTAs derived from various α-amino esters were evaluated in a catalytic reaction of reference and characterized by circular dichroism (CD), UV-Vis absorption, Fourier-Transform Infrared (FT-IR) and Small-Angle Neutron Scattering (SANS) analyses. Our study indicates that, whatever the sergeant, the enantioselectivity of the reaction is directly proportional to the optical purity of the supramolecular helices, as probed by the Kuhn anisotropy factor. However, the factor of proportionality depends on the sergeant structure. Structural studies of the different co-assemblies reveal the following situations : i) the sergeant intercalates (almost) completely into the stacks of the ligand and generates long homochiral helices, ii) the sergeant acts as pure chain capper and thus leads to the formation of partly helically biased and short assemblies and, iii) both intercalation and chain capping occurs. Accordingly, not only the optical purity but also the composition and length of the supramolecular helices are key parameters that affect the selectivity of these intricate sergeants-and-soldiers type assemblies. This work also sheds some light on the possibility to control the structure of the co-assemblies via subtle modifications into the nature of the sergeant, not only by changing the groups directly connected to its stereogenic center but also by varying the bulkiness of its achiral side chain.[6]



Scheme 1: Schematic representation of the role of the sergeant in determining the structure and selectivity of supramolecular helical catalysts composed of a BTA ligand coordinated to copper and different types of sergeants. Depending on the role adopted by the sergeant, the Cu complexes exhibit different levels of enantiodiscrimination (ed) in the course of the asymmetric reaction.

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Enantioseparation of chiral biosignatures using multidimensional gas chromatography applied to extraterrestrial samples

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Keywords: Gas chromatography; Amino acids; Carbohydrates; Derivatization; Chirality

At a molecular scale, life is asymmetric. Proteins and DNA are built of homochiral monomers: L-amino acids and D-deoxyribose, respectively. This phenomenon, known as biological homochirality, could have been triggered by circularly polarized light in the interstellar medium[1]. Indeed, this chiral entity can produce partial enantiomeric imbalance from racemic mixtures[2]. The enantioselective analysis of chiral biosignatures in extraterrestrial matter and interstellar ice analogs seeks to understand the chemical roots of the origins of biomolecular homochirality. Chiral biosignatures such as amino acids and carbohydrates, precursors to contemporary enzymes and the genetic material, have already been detected in various meteorites[3]. However, analyzing such complex samples is challenging in many respects. Steps such as extraction, purification, fractionation and derivatization for subsequent gas chromatographic analyses are required. The latter is critical in order to reliably quantify each individual compound and potential enantiomeric bias. Here we report on the optimization of multidimensional gas chromatography for the enantioselective analyses of amino acids (Fig. 1) and sugar molecules highlighting the importance of sufficiently high signal response of derivatives, repeatability, and baseline resolution.

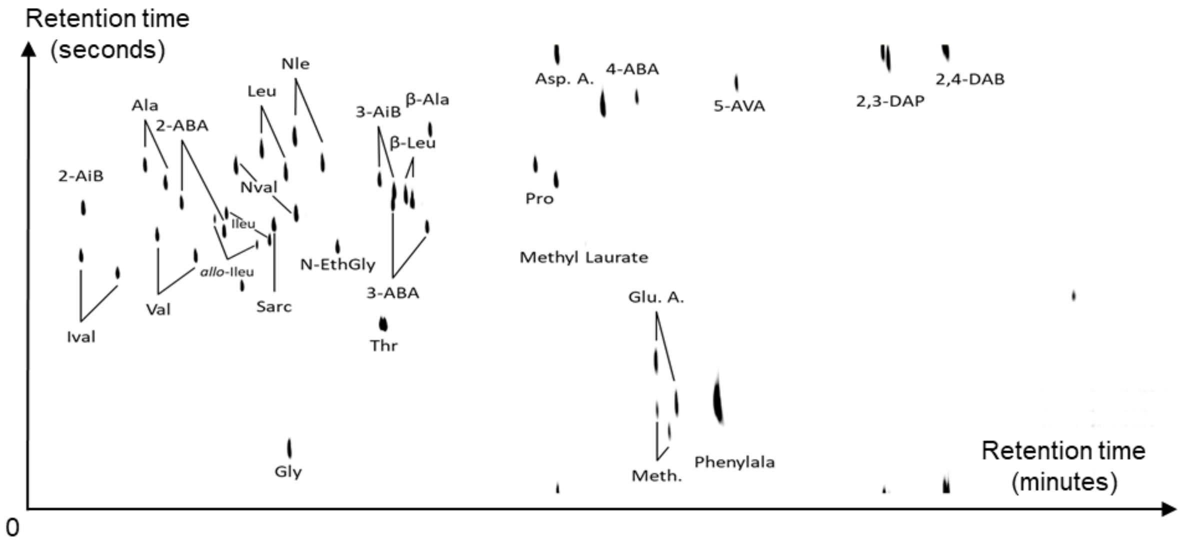

Figure 1: GC×GC-TOF-MS analysis of amino acid derivatives resolved on a Lipodex E column.

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Switching Chiral Communication Mechanisms in Helical Polymers

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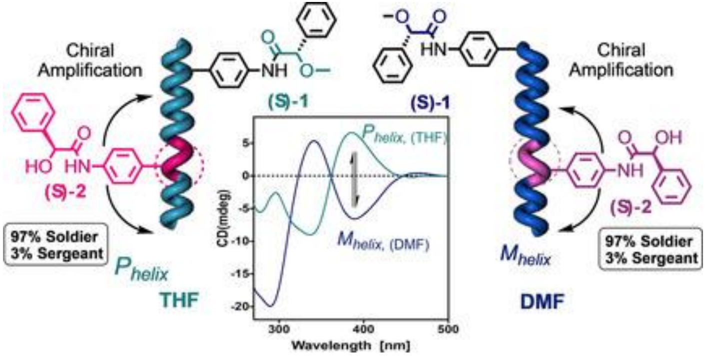
Keywords: Chiral amplification, Sergeants and Soldiers, Helical Polymers,

Résumé: Helical polymers represent a unique example of synthetic polymers whose macromolecular helical structure —handedness and elongation degree— can be manipulated by applying different external stimulus. This property allowed their application in different cutting-edge fields such as chiral stationary phases for HPLC, spin filters, sensors or CPL sources among many others.[1] A intringuing way to induce a specific handedness in a copolymer chain was reported by Green and co-workers by copolymerizing chiral and achiral units, which was denoted as «Sergeants and Soldiers» (SaS) effect. The origin of the chiral amplification phenomena relies in a chiral communication process where the chiral unit commands a specific comformation on the achiral one, promoting at the very end the adoption of a *P* or *M* helix.[2]

Herein we report a new concept based on the SaS effect in copolymers composed by two chiral components (chiral sergeants and chiral soldiers). The chiral monomeric units present different conformational composition, that can interact among them as well as being selectively manipulated by external stimulus. Therefore, playing both with the conformational composition and the absolut configuration of the monomeric units we can selectively switch chiral communication mechanisms like SaS, Chiral Coalition, or Chiral Accord among many others.[3]



Scheme 1. Conceptual representation of the switchable chiral communication process

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CHIRAFUN
Chiralité et Multifonctionnalités

Engineering guided circular polarization by linear and chiral birefringence competition in rib/ridge chirowaveguides

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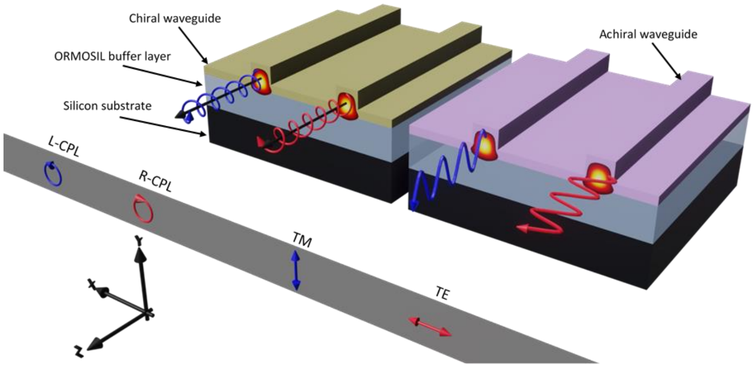
Keywords: Chirowaveguides, linear birefringence, cicular birefringence, PIC.

Résumé: The famous chiral property of light that is used for enantiomers differentiation is not supported by the miniature form of optical setups so-called Photonic integrated circuits (PICs)[1]. These circuits main components (waveguides) are basically made of dielectric materials and behave like linear birefringence devices; they only support two perpendicular linear eigenmodes which are transverse electric (TE) and transverse magnetic (TM)[2]. Chirowaveguides as an alternative are waveguides made of chiral materials. Besides the linear birefringence, these waveguides are also circular birefringent[3]. Therefore, chirowaveguides support elliptical eigenmodes, and ellipticity of the eigenmodes depends on the chirality of the system[4]. Recently, by using our organically modified silica (ORMOSIL) films, we succeeded to prove the concept of chirowaveguides by sandwiching the chirowaveguides in symmetric cladding[5]. However, because of the thick cladding part, these systems can not be used as waveguide based chiral sensors.
Here, we present our work in fabricating asymmetric chirowaveguide structures (rib/ridge waveguides). Taking advantage of the low linear birefringence of the waveguides, we show for the first time channel PIC waveguides with the ability to propagate any polarizations as schematically shown in figure 1. The natural structure of these channel waveguides easily allow interaction with the external medium. Furthermore, we show how these unique channel waveguides are sensible to the surrounding environment.



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