

EFFET DE L'HYPERCONJUGAISON SUR LA RÉACTIVITÉ DU FRAGMENT DE DIÈNE DANS LES DÉRIVÉS D'AMIDE ET DE THIOAMIDE DU 1-MÉTHYLTÉTRAZOLO[5,1-A]ISOINDOLE

HYPERCONJUGATION EFFECT ON DIENE REACTIVITY IN 1-METHYLTETRAZOLO[5,1-A]ISOINDOLE-DERIVED AMIDES AND THIOAMIDES

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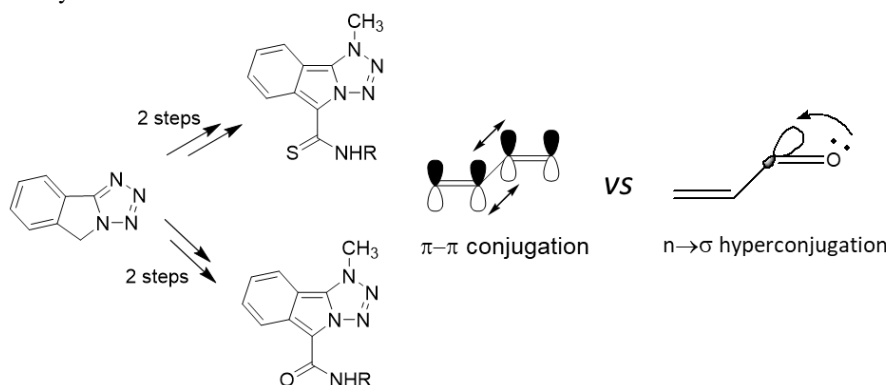
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Hyperconjugation effects are considered as weak compared to conjugation, although as early as in 1941, Mulliken and co-workers demonstrated their influence on bond lengths, spectral properties and relative conformer stability in organic compounds.¹ In the hyperconjugational interactions, either single bonds or lone pairs can be electron density donors,² whereas σ or π antibonding orbitals can act as acceptors. Hyperconjugation has been considered commonly only for systems with a single bond between the donor and the acceptor sites.² It was stated *a priori* that since hyperconjugative interactions are weaker than those with participation of π -orbitals, they cannot affect geometry of the molecular fragment, where the double bond is central.²

Earlier we have shown for the first time that hyperconjugation is possible between an oxygen atom lone pair and a σ -antibonding orbital of the single bond in the molecule of acrolein $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$, despite the central bond for this interaction is double.³ It was found that geometry of the acrolein molecule is affected by both double bond conjugation and the above-mentioned hyperconjugative interactions. Conjugation is one of the fundamental characteristics of diene systems, which strongly influences their reactivity. Classical theoretical organic chemistry concepts suggest that replacement of the terminal carbon atom of the diene by more electronegative oxygen should increase the conjugation degree and result in shortening of the central single bond. However, a number of experimental spectral methods show that this is not true. Our study showed that this is a result of two opposite effects which are similar by their energy: conjugation and $n \rightarrow \sigma^*$ hyperconjugation.³ These results led us to further search for experimental evidences that analogous systems where the central bond between the donor and the acceptor of the hyperconjugative interactions is (partially) double could exist. It was revealed that isoindole derivatives are such systems.

In this work, we have addressed the following question: do amides and thioamides of 1-methyltetrazolo[5,1-*a*]isoindole series demonstrate diene reactivity?



Optimized synthesis of 1-methyltetrazolo[5,1-*a*]isoindole-derived amides and thioamides was elaborated. Based on ¹³C NMR spectroscopy and X-Ray diffraction studies data, it was proposed that zwitterionic resonance structures contributed significantly to the structure of these compounds. Geometry optimization was performed in *vacuo* using m06-2x/cc-pvtz method taking into account polarizing effect of environment (PCM model) and specific intermolecular interactions. Electronic density distribution in these molecules was analyzed using NBO method. Using $\Delta(\text{HOMO}_{\text{diene}}-\text{LUMO}_{\text{dienophile}})$ for amides and thioamides in *vacuo* and in a protic solvent, possibility of Diels–Alder reaction was evaluated. Energies of π - π conjugation and $n \rightarrow \sigma^*$ hyperconjugation for the amide derivative were estimated in *vacuo*, aprotic and protic solvents.⁴

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COMPLEXES DE COBALT ET DE FER POLYVALENTS POUR LA POLYMÉRISATION RADICALAIRE ET PAR OUVERTURE DE CYCLE

VERSATILE COBALT AND IRON COMPLEXES FOR BOTH RADICAL AND RING-OPENING POLYMERIZATION CATALYSIS

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Nowadays, synthetic polymers are found in almost every material of our daily life and have replaced conventional materials such as wood, steel or glass in many areas. The need of well-defined (co)polymers for high-tech applications has triggered both academics and manufacturers to work on the development or improvement of polymerization methods. In this context, reversible deactivation radical polymerization (RDRP) techniques (*e.g.* ATRP, RAFT, ITP...) have made a number of breakthroughs.¹ To date, a wide range of vinyl monomers are precisely (co)polymerized using these techniques, however a limitation remains for the so-called less-activated monomers (LAMs).²

Concurrently, the ring-opening polymerization (ROP) of bio-based cyclic esters (*e.g.* lactide, ϵ -caprolactone) or cyclic carbonates for the formation of well-defined biodegradable polyesters/polycarbonates has attracted much attention.³ Such polymeric materials also have potential applications in various fields and are sustainable alternatives to petrochemical-based plastics. We are interested in the development of new air-stable initiators/moderators, which could operate under both CRP and ROP conditions. We will present here the synthesis, characterization and reactivity of several cobalt and iron complexes and their performances in polymerization catalysis.^{4,5}

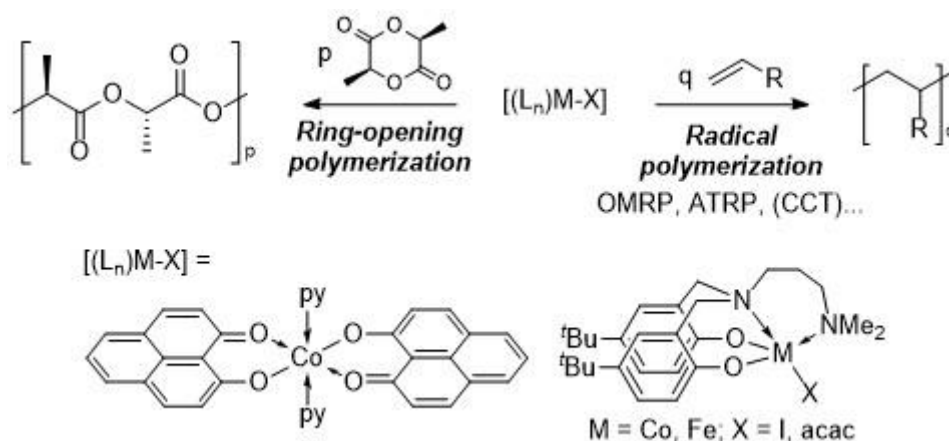


Figure 1. Complexes of interest and applications in ring-opening and/or radical polymerization catalysis.

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² S. Banerjee, V. Ladmiral, A. Debuigne, C. Detrembleur, R. Poli, B. Améduri, *Angew. Chem. Int. Ed.*, **2018**, 57, 2934.

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ETUDE DE LA TERMINAISON RADICALAIRE CATALYTIQUE DU SYSTEME CU/ME₆TREN

INVESTIGATION OF CU/ME₆TREN-CATALYZED RADICAL TERMINATION

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Over the last 20 years the polymer community has shown tremendous interest in Reversible Deactivation Radical Polymerization (RDRP).¹ This has led to the development of several techniques (ATRP, NMP, RAFT, OMRP), all based on the same principle of trapping the propagating species in a reversible manner. Therefore, an equilibrium is formed between a dormant species and the active radical which leads to controlled chain growth. In our investigation we focused on “Atom Transfer Radical Polymerization” (ATRP) and on “Organometallic-Mediated Radical Polymerization” (OMRP). These two techniques were shown to interplay in different systems. In this study we aimed at a better understanding of this interplay and of its impact on the termination reaction in ATRP. Indeed, during ATRP, the organometallic dormant species could induce a Catalyzed Radical Termination (CRT). Over the two last years there has been a discord on the mechanism of CRT and on the product formed.^{2,3}

To gain a better understanding of this phenomenon, we investigated the decomposition of a radical initiators (AIBN) in the presence of different copper complexes. The effect on the termination products was investigated both experimentally and computationally. OMRP dormant species stability was also investigated by performing polymerization with different ratio of Cu/Me₆TREN. The results obtained during these investigations, which enlighten the intimate CRT mechanism, will be presented.

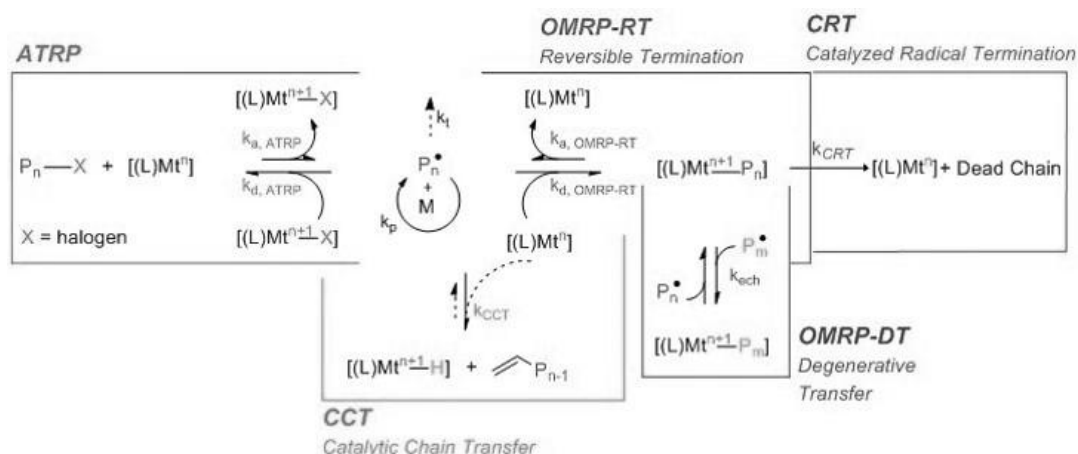


Figure 1 Interplay between ATRP and OMRP

¹ A. Debuigne; R. Poli., C. Jérôme, R. Jérôme et C. Detrembleur, *Prog. Polym. Sci.*, **2009**, 34, 211-239

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Sondes lumineuses Eu, Tb stables et hydrosolubles basées sur la plateforme pyridinophane

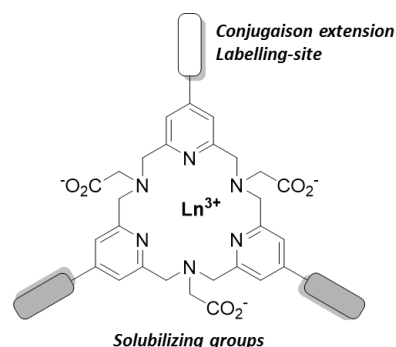
Stable and water-soluble luminescent Eu, Tb probes based on the pyridinophane platform

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Luminescent and stable Ln^{III} complexes remain attractive as luminescent probes and sensors in biological systems because of their long luminescence lifetimes and their large Stokes shifts in contrast to the typical organic fluorophores. For the preparation of suitable luminescent Ln^{III} complexes, we recently demonstrated that the pyridinophane framework acts as an effective hosting unit for the Ln^{III} cations with the corresponding Ln^{III} complexes exhibiting the advantages of a high thermodynamic stability and kinetic stability¹. This platform contains three pyridine rings and three secondary amino groups substituted with aminocarboxylic pendant arms in a highly C3-symmetrical 18-membered macrocyclic structure.

We will show in this work how this scaffold can be functionalized on the pyridine ring with variable substituents to ensure an improvement of these luminescent properties in aqueous media with the extension of the conjugation on the pyridine chromophore (brightness / light excitation), the addition of two solubilizing groups and one labelling-site suitable for bioconjugation². The synthesis and the photophysical properties of the lanthanide complexes will be thus described.



¹N. Leygue, A. Perez e Iñiguez De Heredia, C. Galaup, E. Benoist, L. Lamarque, C. Picard, *Tetrahedron*, 74, 4272-4287, 2018. ²L. Lamarque, C. Picard, C. Galaup, N. Leygue, J. Zwier, E. Bourrier, *PCT Int. Appl.*, WO 2017098180 A1 20170615, 2017.

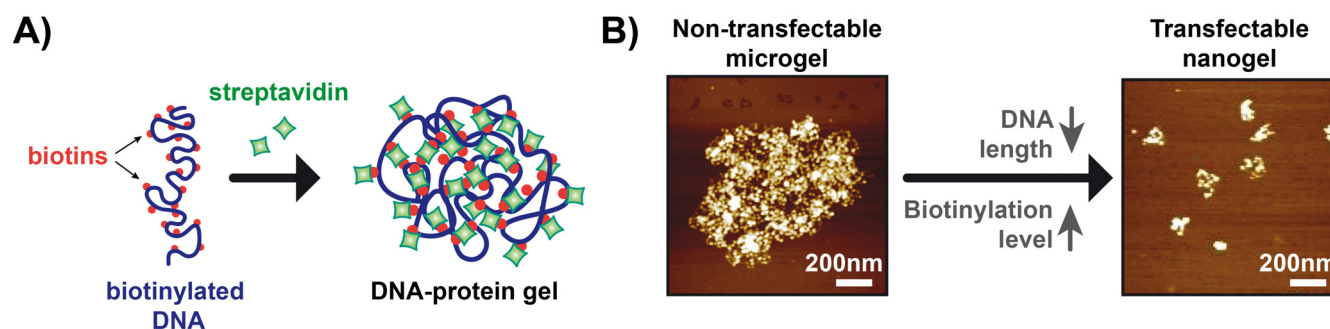
NANOGELES ADN-PROTEINE : VERS DES REACTEURS ENZYMATIQUES TRANSFECTABLES EN CELLULES

DNA-PROTEIN NANOGELES AS CELL-TRANSFECTABLE ENZYMATIC NANOREACTORS

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DNA nanogels are nanometer-sized bio-polymeric materials possessing many useful characteristics such as biocompatibility and programmability, making them promising candidates for molecules vectorization and drug delivery. Traditionally, DNA nanogels are obtained either by base-pairing between complementary DNA sequences¹ or by chemical covalent crosslinking strategy.² Recently, in our team a new approach for obtaining submicrometer-size DNA-protein gels have been developed by mixing multibiotinylated giant DNA with streptavidin in order to establish stable non-covalent intramolecular crosslinks within the DNA backbone (*Figure A*).³ In addition, streptavidin can be easily conjugated with other molecules, thus allowing easy functionalization of the DNA gels, as it has been demonstrated using streptavidin-enzyme conjugates. The main purpose of my PhD thesis is to investigate the possibility and the mechanism of transfection of functionalized DNA nanogels into the living cells. However, previously obtained gels were too soft and big (~850 nm), and were thus not compatible with cell transfection. That is why my first objective was to obtain nano-scale gels with controllable size and density for biomedical and biotechnological applications compatible with DNA transfection technology. For this purpose we developed a strategy to form more dense DNA-protein gel having size of the order of 100 nm by using shorter DNA scaffold with higher biotinylation level. We demonstrated that photochemical binding of psoralene-biotin conjugate to DNA cannot give high density of biotinylation, however the ratio of 1 biotin per 10 base pairs has been achieved via an enzymatic approach involving PCR in presence of biotinylated dCTP (*Figure B*). During this research, we also compared different approaches for purification of biotinylated DNA and nanogels (e.g. fast protein liquid chromatography (FPLC)), as well as adapted a method for precise detection of DNA biotinylation efficiency. The developed technology will be then applied for transfection into living cells of the nanogels that could be functionalized with enzymes, important for their catalytic activity, antibodies for targeting, and magnetic nanoparticles for spatio-temporal control of their intracellular distribution.



¹H. Xue et al., *Chem. Commun.*, **2019**, DOI: 10.1039/c9cc00175a.

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6-OXYINDAN-1-ONES AVEC DES FRAGMENTS D'ACIDE AMINÉ ET DE PEPTIDE

6-OXYINDAN-1-ONES WITH AMINO ACID AND PEPTIDE FRAGMENTS

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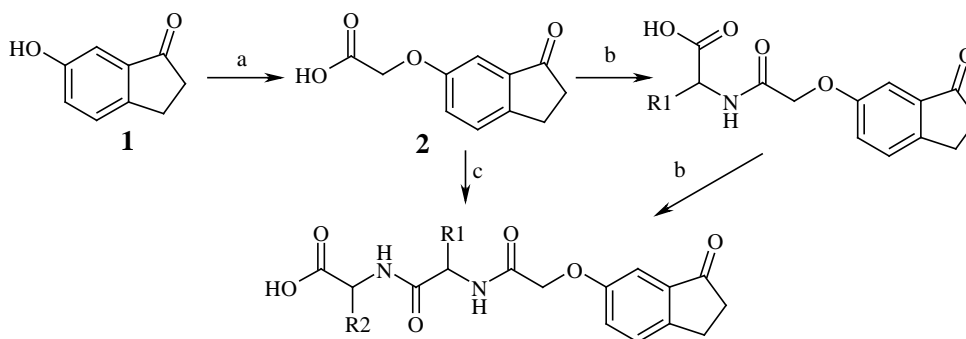
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Compounds containing an indane fragment are objectively widely represented in nature and have interested researchers for their bioactivity [1, 2]. It has been interesting and beneficial for medicinal chemistry to combine the indane cycle with the peptide fragment. As a base object for modification we chose 6-hydroxyindan-1-one **1**. Firstly, its molecule contains a phenolic OH group, convenient for connection of the amino acid residue *via* an amide bond with a hydroxylacetic linker; furthermore, exactly the indan-1-one system is observed in natural high-bioactive pterosins. Known at first only as a synthetic compound, 6-Oxyindan-1-one was recently found in live nature: this compound was isolated from the plant *Scrophularia ningpoensis*, known in traditional Chinese medicine due to cardioprotective properties [3].

Previously, we obtained a number of amino acid derivatives of compound **2** [4]. Continuing the work, we received a number of peptide derivatives of 6-oxyindan-1-on. Two approaches were used to introduce the dipeptide fragment: affiliation the officinal dipeptide or gradually increasing the peptide chain.



R¹, R² – H, CH₃, CH(CH₃)₂, CH₂CH(CH₃)₂, CH₂CH₂SCH₃, CH₂-Indole

1. BrCH₂COOCH₃, K₂CO₃, acetone; 2. K₂CO₃, Δ, MeOH/H₂O;
1. N-hydroxysuccinimide, *N,N'*-dicyclohexylcarbodiimide, dioxane; 2. Amino acid, K₂CO₃, dioxane/H₂O;
1. N-hydroxysuccinimide, *N,N'*-dicyclohexylcarbodiimide, dioxane; 2. Dipeptide, K₂CO₃, dioxane/H₂O;

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CONDUCTIVITE IONIQUE DE MEMBRANES D'ELECTROLYTE SOLIDES A BASE DE COPOLYMERES EN BLOC, CONSTITUES DE SEQUENCES HYDROPHILES

IONIC CONDUCTIVITY OF SOLID ELECTROLYTE MEMBRANES BASED ON DOUBLE HYDROPHILIC BLOCK COPOLYMERS

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Solid polymer electrolytes (SPEs) are an essential component being used in most energy storage/conversion devices, particularly Li-ion batteries (LBs), dye-sensitized solar cells (DSSCs), organic solar cells, etc. For these devices a non-corrosive, high conductive, electrochemically and chemically stable, low cost electrolyte is very important. The solid solvent-free polymer electrolyte based on amorphous polymer materials could be the best for these purposes.

Nowadays, the mainstream polymer matrix of the SPEs remains poly(ethylene oxide) (PEO) and its derivatives due to good chain flexibility, superior electrochemical stability to lithium metal, low glass transition temperature (T_g), and excellent solubility to conductive lithium salts and good interface stability against Li anode.

However, the high crystallinity of PEO leads to low ion conductivity and inferior Li^+ transference numbers (0.2–0.3) at room temperature, which affects the high rate capability of LBs.

In the present work, we investigated PEO-containing triblock copolymers PAAm-*b*-PEO-*b*-PAAm with interacting polyether and polyacrylamide blocks as perspective ion-conducting membranes for LB and DSSC. Two triblock copolymer samples with variable PEO block length ($M_{n\text{PEO}}=1.4\cdot 10^4$ and $3.5\cdot 10^4$ kDa) were synthesized and used for this purpose. We determined their molecular parameters using ^1H NMR spectroscopy. The bulk structure and ionic conductivity of solid membranes formed by initial triblock copolymers and their compositions with Li-salt and the couple KI/I_2 were studied by the methods of differential scanning calorimetry (DSC), wide-angle and small-angle X-ray scattering (WAXS and SAXS), and impedance spectroscopy.

The evidence of fully homogeneous amorphous mass-fractal-organized structure of triblock copolymer membranes was obtained due to structural investigations and was attributed to existence of the developed system of hydrogen bonds between chemically complementary PEO and PAAm blocks. Due to both the long amorphous PAAm chains and the hydrogen-bond system, triblock copolymer structure preserved an amorphous character even at high length of the crystallizable PEO block. This fact as well as the mass-fractal organization of the copolymer structure was dominant for a production of solid electrolytes for LBs and DSSCs, which were based on pure triblock copolymer membranes and those doped by corresponding ionic components such as LiPF_6 and the couple KI/I_2 .

The pure and doped triblock copolymer membranes showed the high level of ionic conductivity, in particular, $2\cdot 10^{-6}\div 4\cdot 10^{-4}$ $\text{S}\cdot\text{cm}^{-1}$ for pure copolymer membranes, $7.52\cdot 10^{-6}\div 1.53\cdot 10^{-4}$ $\text{S}\cdot\text{cm}^{-1}$ for the copolymer membranes filled with LiPF_6 salt, and $\sim 3\cdot 10^{-6}\div 9.4\cdot 10^{-3}$ $\text{S}\cdot\text{cm}^{-1}$ for the copolymer membranes doped with KJ/J_2 couple. Analysis of these data indicated the main factors determining a high ionic conductivity of copolymer membranes: i) the formation of hydrogen bonds between PEO and PAAm blocks, ii) the homogeneous distribution of bound segments in the membranes, and iii) the porous mass-fractal organization of membrane structure.

The obtained results allowed us to consider PEO/PAAm triblock copolymers with interacting blocks as perspective matrices for producing solid electrolyte membranes and their application in Li-batteries and solar cells.

Détection de micropolluants de l'eau via un dosage par compétition sur molécules uniques

A Single-Molecule Competitive Assay for the Detection of Water Micropollutants

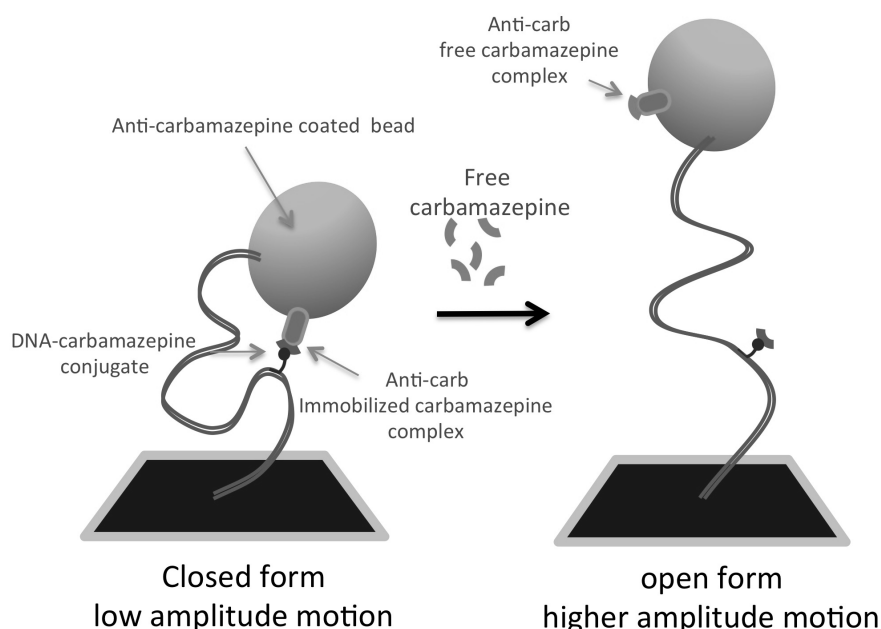
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Abstract: Micropollutants, among them pharmaceuticals, represent an alarming concern for water quality due to their toxicity, persistence, and low removal rate by conventional water treatments. The EU parliament pointed to the need for innovative solutions for treatment but also control of those emerging pollutants for which high quality monitoring data are particularly lacking. Here, we propose to develop an original sensing method for the specific, rapid and sensitive detection of molecules in water. Our solution, based on our single-DNA tethered particle mobility sensor in combination with recognition elements, involves cutting edge techniques and know-how in bionanotechnology, chemistry and immunodetection. Focused on the anticonvulsant carbamazepine, a particularly relevant substance, our work aims at developing a generic solution for the detection of a large panel of molecules and will pave the way towards a versatile platform for the cost-effective monitoring of surface waters.



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- Plénat T., Salomé L., Tardin C., et al Biopuces pour l'analyse de la dynamique de molécules d'acide nucléique. Patent n° FR 1057031 filed Sept 3rd, 2010, extension PCT/EP 2 611 940 B1, on Apr 8, 2015

LIMITES DE LA PRECISION DE L'EMPLACEMENT DES MONOMERES EN POLYMERISATIONS RADICALAIRES CONTROLEES

LIMITS OF PRECISION MONOMER PLACEMENT IN CONTROLLED RADICAL POLYMERIZATIONS

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Precise control over the location of monomers in a polymer chain has been described as the ‘Holy Grail’ of polymer synthesis. Controlled chain growth polymerization techniques have brought this goal closer, allowing the preparation of multiblock^{1,2} and multisite³ copolymers with ordered sequences of functional monomers. But the statistical nature of reversible deactivation radical polymerization places strong limits on the structural control that can be obtained (Figure 1).⁴ At the same time, we have a strong tendency to overestimate the degree of precision that is achieved.⁵ This poster discusses both best-case and more realistic scenarios for structural distributions in precision polymers prepared by chain-growth polymerizations, and shares some ideas^{5,6} for representing such distributions in a more intuitive way.

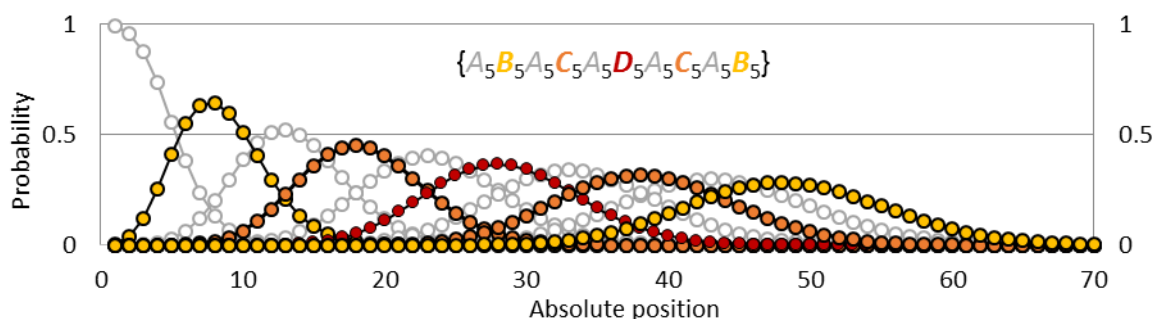


Figure 1 – Probability of finding monomers from each block of an ideal $A_5B_5A_5C_5A_5D_5A_5C_5A_5B_5$ decablock copolymer as a function of position in the chain.

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COMPLEXES DE RHENIUM TRICARBONYLES A BRAS BENZOSULFONAMIDE COMME NOUVEAUX INHIBITEURS DE L'ANHYDRASE CARBONIQUE IX

BENZENESULFONAMIDE-BASED TRICARBONYL RHENIUM COMPLEXES AS NEW CARBONIC ANHYDRASE IX INHIBITORS

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In this work, the synthesis, structural and spectroscopical characterizations (IR, NMR, MS, UV-Vis, elemental analysis, X-ray diffraction...) of two bidentate ligands (**L_x**, **x** = **1** or **2**) containing a 4-substituted benzenesulfonamide pharmacophore prepared by classical click chemistry procedures as well as their corresponding rhenium complexes of general formula [ReCl(CO)₃(**L_x**)] were presented and the inhibitory activity of each prepared compound against cytosolic human carbonic anhydrase isoforms discussed.

In short, two new bidentate 2-pyridyl-1,2,3-triazole ligands with a pendent 4-substituted benzenesulfonamide arm and their corresponding Re(CO)₃-complexes were successfully synthesized following a three- or four-step procedure. All the prepared compounds were fully characterized by classical spectroscopic methods and X-ray, as well as theoretical studies for both complexes. While in the solid state, rhenium complexes showed classical distorted octahedral geometry, ligand **L₁** adopted an uncommon *cis*-configuration arising from a network of intermolecular hydrogen-bonding interactions.

Preliminary investigation on the inhibitory activity of these compounds against the cytosolic human carbonic anhydrase I, II and the membrane associated isoforms IX (hCAs I, II and IX) revealed an activity in the nanomolar range for hCA IX isozyme. In particular, this preliminary study showed that ligand **L₁** exhibited a strong affinity *K_i* of 2.8 nM for hCA IX. Additionally, complex [ReCl(CO)₃(**L₂**)] exhibited a pronounced selectivity against hCA IX over the off-targets isoforms hCA I and hCA II which makes this compound a promising potential anticancer drug candidate.

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Nouveaux Bioconjugués dérivés de la plateforme macrocyclique PCTA[12]

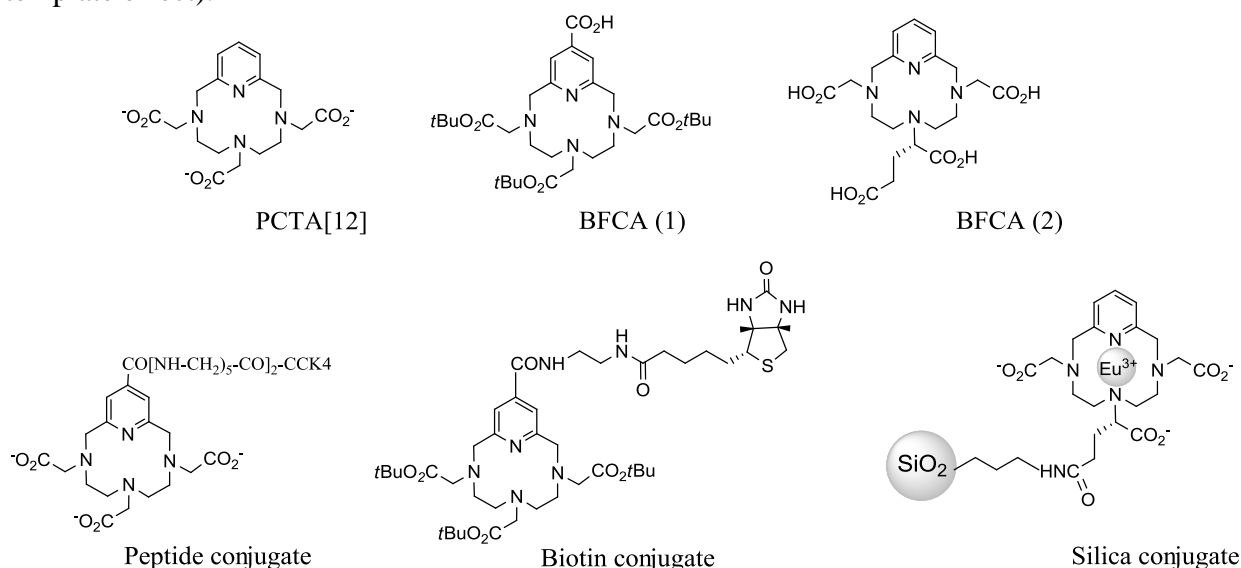
New Bioconjugates derived from the PCTA[12] macrocyclic platform

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PCTA[12] is a 12-membered tetraaza-macrocyclic ligand that incorporates a pyridine unit within the macrocyclic ring and three acetate pendant arms. Unlike DOTA and NOTA chelators, PCTA is a recent entry to the field of macrocyclic polyaminocarboxylate ligands available to complex a variety of M^{2+}/M^{3+} ions for biomedical applications such as diagnostic and radiotherapeutic.¹ Despite its promising properties, only few papers on bifunctional chelators agents (BFCAs) based on the PCTA structure have been published so far.²

In this work, we report the efficient synthesis of two BFCAs displaying a carboxylic acid function either on the 4-position of the pyridine ring (BFCA (1)), either on the central side arm (BFCA (2)). For the preparation of these compounds we have used our recently reported synthetic methodology for building the skeletal backbone of PCTA with high efficiency in the crucial macrocyclization step (metal-ion template effect).³



These BFCAs-PCTA were used for conjugation with a tetrapeptide (cholecystokinin analogue), a bioactive molecule (biotin), or a solid support (silica gel). As demonstrated in this work, conjugation of these BFCAs to vectors can be performed with protected chelators, followed by deprotection and complexation with a selected ion; or alternatively by using a preformed metallic complex.

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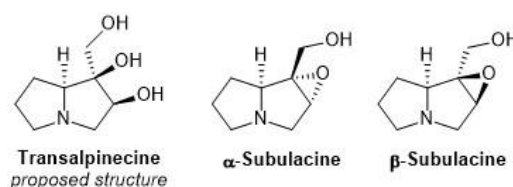
TRANSALPINECINE ET ANALOGUES : PREMIERE SYNTHÈSE TOTALE, REVISION STEREOCHIMIQUE ET EVALUATION BIOLOGIQUE

TRANSALPINECINE AND ANALOGUES: FIRST TOTAL SYNTHESIS, STEREOCHEMICAL REVISION AND BIOLOGICAL EVALUATION

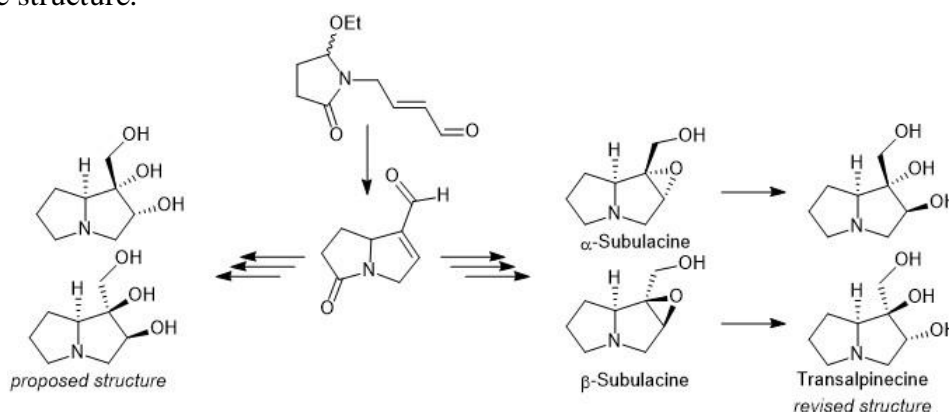
Stéphanie Ballereau, Tessa Castellan, Morgane Enel, Christiane André-Barrès, Yves Génisson and Cécile Dehoux

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Pyrrolizidine alkaloids (PAs) are of particular interest for synthetic chemists because of the panel of biological activities associated to their relatively simple structure.^{1,2} Among these PAs, the transalpinecine was extracted from *Heliotropium transalpinum* and described in 2009,³ in addition to known alkaloids subulacines and .



The concise synthetic route developed towards these unusual iminosugar like natural compounds relies on an intramolecular Morita-Baylis-Hillman reaction. The four diastereoisomers of transalpinecine, as well as the two diastereoisomers of the parent epoxide subulacine, were prepared. ¹H NMR based stereochemical assignment of these different diastereoisomers was substantiated by quantum calculations of NMR shifts and coupling constants, allowing revision of the initially reported transalpinecine structure.



Tested for its capacity to rescue the defective function of cystic fibrosis transmembrane conductance regulator (CFTR) responsible for cystic fibrosis, the α -subulacine proved to significantly enhance the correction of F508delCFTR function by VX-809.⁴

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THERMOCHIMIE DE TERNAIRE Ge-Mn-Gd MELTS

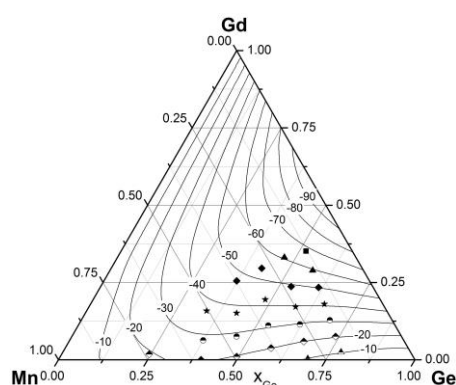
THERMOCHEMISTRY OF TERNARY Ge-Mn-Gd MELTS

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Numerous intermetallic compounds in RE–Mn–Ge ternary systems (where RE is rare-earth metal) attract much attention due to their interesting electronic and magnetic properties. In particular, Gd-containing intermetallics in Gd–Mn–Ge system exhibit antiferromagnetic character of ordering and are able to transform into ferrimagnetic, paramagnetic and even to ferromagnetic state under the influence of temperature and/or magnetic field. Magnetic properties of amorphous ternary phases in this system are also the subject of interest. Thermodynamic properties of liquid phase can be valuable source of information that allows to estimate glass forming tendency of corresponding alloy. In present investigation we have used previously obtained calorimetric data on enthalpies of mixing in the Gd–Mn–

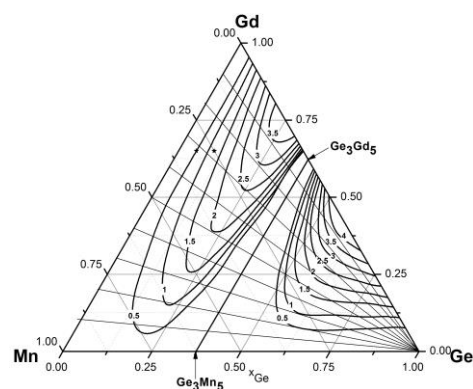


Ge system [1] and have applied thermodynamic approach [2] to assess the glass forming tendency of various alloys of this system. The data of the high-temperature calorimetric experiment of liquid Ge–Mn–Gd alloys at 1830 K [1], as well as the $\Delta_m H$ concentration dependences for the boundary binary systems of the ternary system, were processed using the Redlich-Kister-Muggianu method. Experimental data on the integral enthalpy of mixing were treated by the multi-regression analysis and the term of a specific ternary interaction was obtained. The obtained projections of the isolines of the integral enthalpy of mixing of the ternary Ge–Mn–Gd melts at

1830 K onto the concentration triangle are shown in Fig. 1 (kJ mol^{-1}). The described approach to the treatment of experimental data and the resulting determination of the ‘ternary’ term allow to model enthalpies of mixing throughout the whole concentration triangle providing reasonable extrapolation of properties onto a concentration region yet unexplored experimentally. Thus, it is possible to determine the properties at any point of the ternary system, that greatly expands the possibility to perform a great variety of calculations. So, we have calculated the value of GFT (glass forming tendency), which allows to determine how the alloy of this composition is inclined to easy amorphization compared to the pure components. This method was firstly proposed in [2]. Fig. 2 demonstrates certain projections of the GFT isolines onto the concentration triangle for the quasi-binary system Ge– Ge_3X_5 (where X = Gd, Mn). Ge_3X_5 is cluster that exist in liquid phase and can contribute to an easy amorphization of liquid alloys. The undercooling temperature necessary for the estimation of GFT was assumed to be 730 K. Analysis of Fig. 2 allows to

conclude that within the concentration range from pure germanium up to 0.6 molar fraction fraction of germanium and from pure gadolinium up to 0.4 molar Ge_3X_5 , the glass formation for the ternary Ge–Mn–Gd alloys is much easier than for the pure germanium and gadolinium. As the content of manganese in ternary alloys increases, the GFT is reduced sharply.

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COMPOSES HOMO- ET HETERO-MULTIVALENTS POUR LE TRAITEMENT DE LA MALADIE DE GAUCHER

HOMO- AND HETERO-MULTIVALENT COMPOUNDS FOR THE TREATMENT OF GAUCHER DISEASE

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Gaucher disease is caused by deficient lysosomal glucocerebrosidase (GCase) activity. Mutations in GCase result in the accumulation of glucosylceramide in the lysosomes leading to severe symptoms with sometimes central nervous system involvement.¹ Two chemotherapeutic strategies are developed to struggle this disease.² The substrate reduction therapy is based on the use of glucosylceramide synthase inhibitors in order to limit the pathological lysosomal storage of glucosylceramide. Enzymatic enhancement therapy is the most innovative approach involving the use of a pharmacological chaperone to increase the activity of the misfolded Gcase.

This study aims to develop a new therapeutic approach combining substrate reduction and enzyme enhancement therapies. In order to associate these two strategies, we plan to link a glucosylceramide synthase inhibitor pharmacophore and a pharmacological chaperone pharmacophore on a multivalent dendrimeric scaffold by click chemistry. In addition to the potential multivalent effect, the synergistic action of both pharmacophores in decreasing glucosylceramide synthesis and increasing its lysosomal degradation is expected to efficiently limit the pathological lysosomal storage and hence reduce the symptoms of Gaucher disease.

Herein we will report the synthesis of the clickable analogues of a glucosylceramide synthase inhibitor and a pharmacological chaperone of GCase. Preliminary results concerning the preparation of homo-multivalent and hetero-multivalent compounds will also be described.

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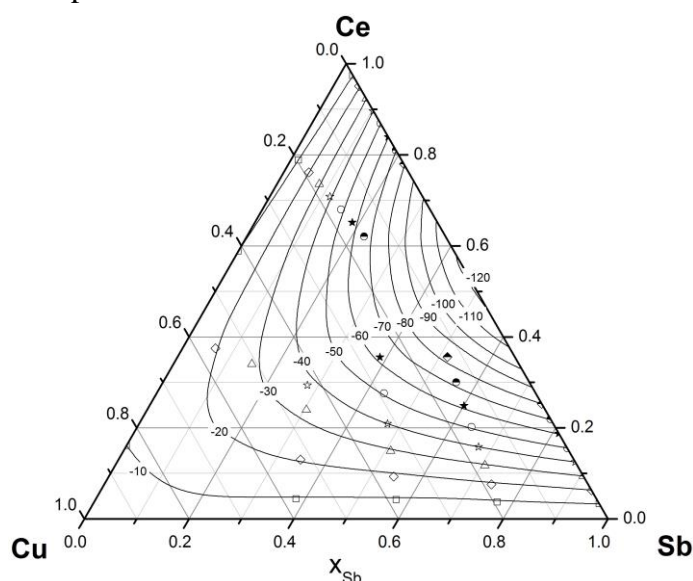
ENTHALPIES DE MELANGE D'ALLIAGES LIQUIDES TERNAIRES Ce–Cu–Sb

ENTHALPIES OF MIXING OF TERNARY Ce–Cu–Sb LIQUID ALLOYS

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Multicomponent Sb containing alloys with 3d transition metals attract much attention due to their wide applications as semiconductors, thermoelectric materials, and some other practically important applications. A great number of alloys of ternary Ce–3dMe–Sb systems are widely investigated during last two decades due to their interesting electrophysical and magnetic properties as well as specific features of their electronic structure. Recently we have modeled the enthalpies of mixing ($\Delta_m H$) for ternary alloys of the Ce–Cu–Sb system using so called ‘geometrical’ solution models and compared the obtained results with the experimental data obtained along the section ($x_{Cu} / x_{Sb} = 0.2/0.8$) of this system via isoperibolic calorimetry at 1300 K [1]. At present moment a complete calorimetric study of the liquid alloys of this system has been carried out, the enthalpies of mixing along the five sections has been determined at 1380 K, three sections with x_{Cu} / x_{Sb} constant ratio up to $x_{Ce} = 0.35$ and two – for x_{Cu} / x_{Ce} constant ratio up to $x_{Sb} = 0.25$. The enthalpies of mixing in the ternary system were found to be rather exothermic and steadily increasing in absolute values from the binary boundary systems Ce–Cu and Cu–Sb towards the Ce–Sb boundary, reaching the minimum value of approximately (-120) kJ·mol⁻¹ in the vicinity of the phase CeSb.

As a result of the coherent processing of these data by the multi-regression analysis we have determined the term of a specific ternary interaction and have calculated the enthalpies of mixing for the whole concentration triangle using the Redlich-Kister-Muggianu formula, the $\Delta_m H$ surface for the liquid alloys of this system was built. The topology of the isoenthalpy lines of the enthalpies of mixing calculated for the Ce–Cu–Sb melts at 1380 K (solid lines) is presented at the figure in comparison with experimentally obtained values of enthalpies (various geometric markers). It is clear that due to determination of the term of ternary interaction, a very good agreement between the results of the Redlich-Kister-Muggianu modeling and the experimental ones is observed. So we can reasonably extrapolate the experimentally obtained concentration dependencies of the enthalpies of mixing to the composition region yet unexplored.



The gradual increasing of exothermic ΔH values from the alloys with low Ce and Sb contents to those with higher ones is observed, demonstrating that pairwise interactions between Ce and Sb affect to a great extent the resulting enthalpy of alloy formation. This influence mainly originates from the large difference of the electronegativities of Ce and Sb, approaching to 0.74 eV (according to the Allred–Rochow scale). The present study indicates that the addition of Cu as the third component to the Ce–Sb melts leads to an evident weakening of component interaction in the ternary system.

MODELISATION THERMODYNAMIQUE DES INTERVALLES DE CONCENTRATION DE L'AMORPHISATION D'ALLIAGES LIQUIDES Gd–Al(In)–Mn

THERMODYNAMIC MODELING OF CONCENTRATION RANGES OF AMORPHIZATION OF Gd–Al(In)–Mn MELTS

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In the present work, the enthalpies of mixing of liquid alloys of the ternary Gd–Al–Mn systems have been calculated using the regular solution model by the Redlich–Kister–Muggianu formula. Also a comparison was made of calculated values of enthalpies of mixing in this system with the experimentally determined thermochemical properties of liquid alloys of the Gd–In–Mn ternary system obtained previously [1]. In general, we estimate that the values of the enthalpies of mixing in the Gd–Al–Mn ternary system should be more exothermic than in the Gd–In–Mn one. This fact can be explained taking into consideration the main features of the component interaction in the boundary binary systems, namely, such important characteristics as electronegativity of the components, their electron work functions and a large difference in size of atoms. It can be concluded that it is the binary Al–Mn system that makes a significant contribution to the formation energy of ternary alloys. An imaginary line drawn through the points of maximum curvature of the isoenthalpic lines is considerably shifted towards the binary Al–Mn boundary, thus expanding significantly the region of rather exothermic enthalpies of mixing in the corresponding ternary system. For the two indicated ternary systems the size mismatch entropy (S_σ) has been calculated within the framework of hard spheres model and the S_σ / k_B (where k_B is the Boltzmann constant) parameter has been determined (Figure). On the base of the comprehensive analysis carried out, the criteria for the probability of occurrence of regions of easy amorphization in these ternary systems are proposed (red dash lines on Figure).

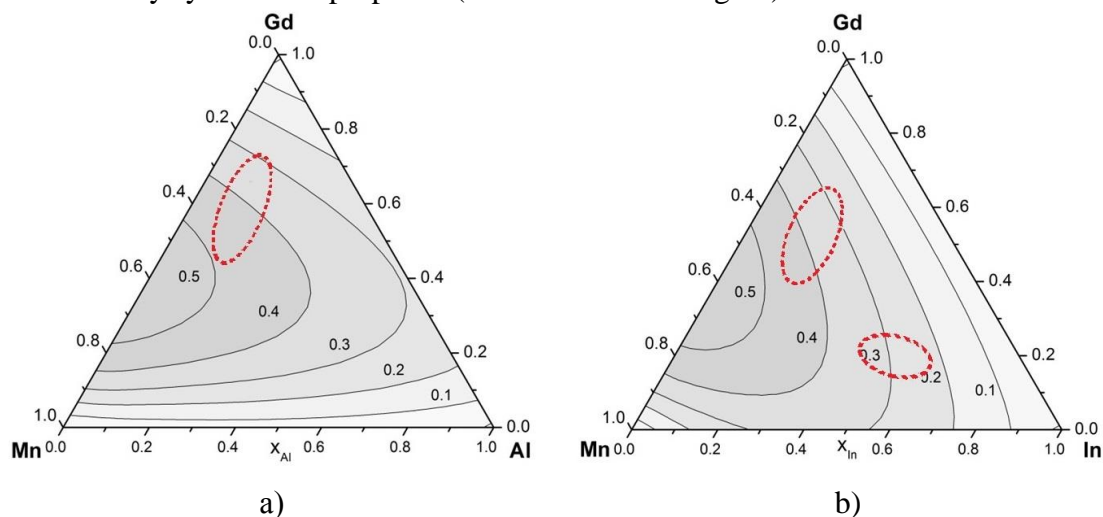


Figure. The isolines of the S_σ / k_B values for ternary Gd–Al–Mn (a) and Gd–In–Mn (b) systems applied to the Gibbs concentration triangle (solid lines)

The determination of the topology of the mixing enthalpy surface and the S_σ / k_B parameter for the melts of studied ternary systems together with the data on binary and ternary compounds existing in these systems allowed to reasonably assume the concentration regions where the investigated ternary alloys have tendency for easy amorphization while rapid cooling of the melt. The simultaneous realization of the following three conditions was taken as a criterion for the possible existence of a region of easy amorphization: the absolute value of the enthalpies of mixing is at least $6 \text{ kJ} \cdot \text{mol}^{-1}$, the S_σ / k_B parameter is not less than 0.3–0.4 and a certain distance from the concentration region corresponding to the exact composition of binary or ternary compounds.

NOUVEAUX DIARYLES HEPTANOÏDES MACROCYCLIQUES CONTRE L'ATHEROSCLEROSE

NEW LINEAR AND MACROCYCLIC DIARYL HEPTANOIDS AGAINST ATHEROSCLEROSIS

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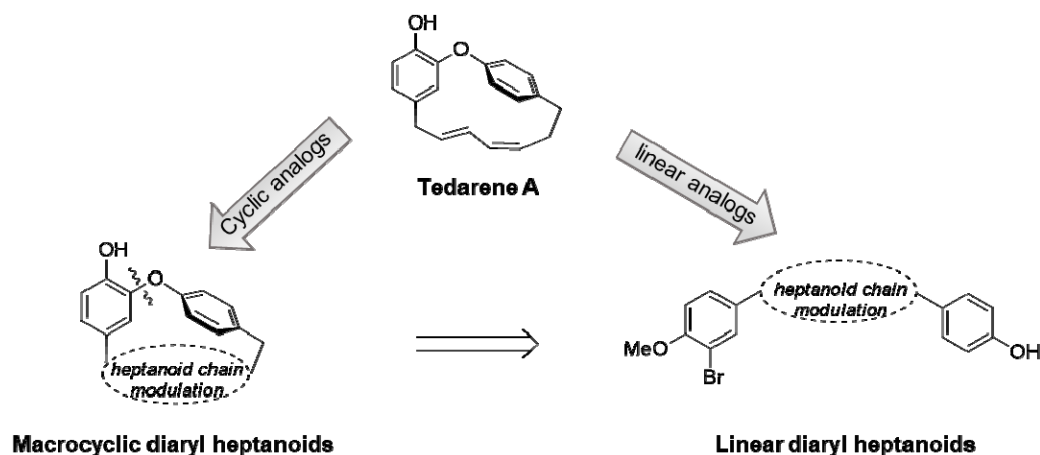
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In our industrialized countries, atherosclerosis is the first cause of mortality. It is at the origin of different problems such as cerebrovascular accident, heart attack. Atherosclerosis is a chronic inflammatory disease that involves oxidized LDL (Low Density Lipoproteins), monocytes and the cellular material of the arterial wall. Oxidative stress due to the presence of reactive oxygen species and a self-sustainable inflammatory process constitute the two important events in the atherogenesis process.¹ So, our aim is to develop new agents with an antioxidant and an anti-inflammatory activities.

Natural and synthetic diaryl heptanoids have attracted our attention for their interesting pharmacological properties such as antioxidant, anti-inflammatory, antiviral and anticancer activities.² Tedarene A,³ a macrocyclic diarylether heptanoid, extracted from the fire sponge and recently synthesized in the laboratory,⁴ significantly inhibits the production of NO, an important signaling agent of inflammation. Inspired from the Tedarene A framework, different linear and macrocyclic analogs were designed and synthesized by introducing chemical modifications onto the heptanoid chain moiety in order to modulate their biological properties. The different agents were evaluated for their antioxidant and anti-inflammatory activities.⁵



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MATÉRIAUX Fe@FeO_x NANOSTRUCTURÉS, CATALYSEURS POTENTIELS POUR LA DECOMPOSITION DE L'EAU

NANOSTRUCTURED Fe@FeO_x MATERIALS, POTENTIAL CATALYSTS FOR WATER SPLITTING

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Solar water splitting is a promising technology for the mass production of hydrogen which can be transported and used as a clean fuel. Solar water splitting can be done by using a photoelectrochemical cell in which both oxygen and hydrogen are generated in the photoanode and photocathode, respectively. Due to thermodynamically uphill and slow kinetics of the electrochemical water oxidation reaction, advanced catalysts are required to reduce the overpotential and consequently increase the efficiency of this electrochemical process. Over the last decade, efforts have been dedicated to the development of catalysts for this purpose¹. A promising strategy envisages the use of photosensitizers (PS) incorporated with nanoparticles (NPs) from abundant first row metals and has attracted extensive research².

Herein, we present the organometallic synthesis of Fe NPs³ and Fe@FeO_x core-shell NPs with a good control of morphology, surface state and crystallinity (figure 1). Later on, amino phosphonic acid⁴ and Ru complexes-based PS have been grafted on the surface of these NPs as a strategy for advanced water oxidation photocatalysts. The obtained nanomaterials have been characterized by different techniques (TEM, HR-TEM, WAXS, FT-IR, ICP-MS, EA, *etc.*) in order to have in depth understanding of the structure-properties-activity relationship.

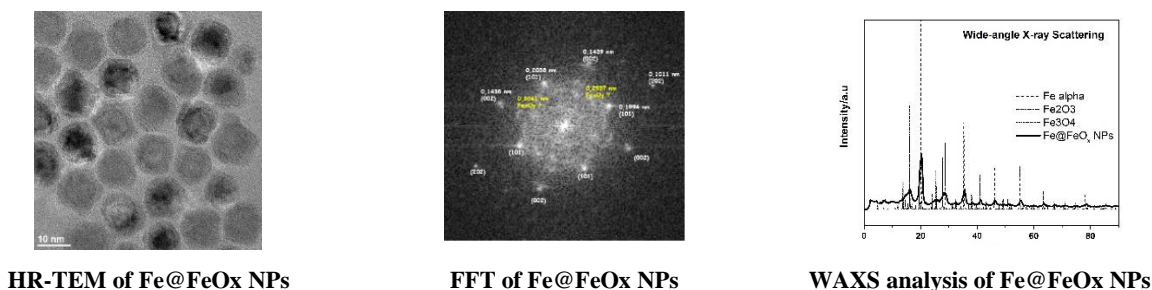


Figure 1. Characterization of Fe@FeO_x core-shell nanoparticles

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APPROCHES SYNTHÉTIQUES DE TETRAALKOXYTHIACALIX[4]ARENES DANS LE CONFORMATION *CONIQUE*

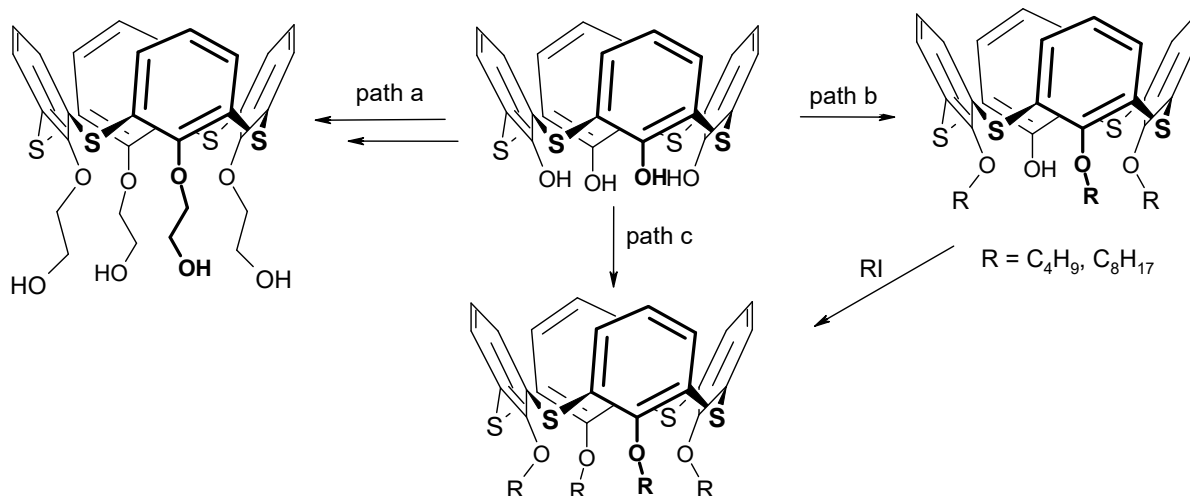
SYNTHETIC APPROACHES TO TETRAALKOXYTHIACALIX[4]ARENES IN *CONE* CONFORMATION

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Thiacalix[4]arene is a widely used macrocyclic platform for design of bioactive compounds, extractants for separation of actinides and lanthanides from radioactive wastes, sensor systems and other¹.

Chemical modifications of thiacalix[4]arene platform exploited only lower or upper rim of macrocycle, not both. It is caused by the fact that alkylation of thiacalixarenes leads to conformation *1,3-alternate*¹ (in contrast to calix[4]arenes), which highly limits potential applications of such compounds. The goal of this work is to develop a simple and efficient synthetic route to tetraalkoxythiacalixarenes in the *cone* conformation. We used the known Williamson method of alkylation by α -bromoacetic esters (path a on scheme) and further conversion to alcohol, which can be easily acylated. Also we developed synthesis of tri- and tetraalkoxythiacalixarenes in *cone* conformation by the Mitsunobu reaction (paths b and c on scheme).



According to X-Ray data trialkoxythiacalixarenes exist in the *flattened cone* conformation. Further alkylation using NaH and alkyl iodide leads to tetraalkoxythiacalixarenes with ratio *cone* : *paco* 79 to 21 and yield 85%. One-stage path c gives tetraalkoxythiacalixarenes with ratio *cone* : *paco* 45 to 52 and yield 90%. These conformers were succeeded to separate by column chromatography. Interestingly, among all conformers the *cone* demonstrates slow-motion dynamic in NMR spectra, its structure was decisively confirmed by high-temperature NMR.

These results are remarkable because *p-tert-butyl*thiacalix[4]arene gives predominantly *1,3-alternate* in the conditions of excessive alkylation by the Mitsunobu reaction².

¹ R. Kumar, Y. Ok Lee, V. Bhalla, M. Kumar, J. S. Kim *Chem. Soc. Rev.* **2014**, 4824-4870

² V. Csokai, A. Grun, B. Balazs, A. Simon, G. Toth, I. Bitter, *Tetrahedron* **2006**, 62, 10215-10222

**SYNTHÈSE, CONFIGURATION ABSOLUE
ET PROPRIÉTÉS DE RECOGNITION
DES ACIDES CALIXARENES ACETIQUE CHIRAUX INHERENTES**

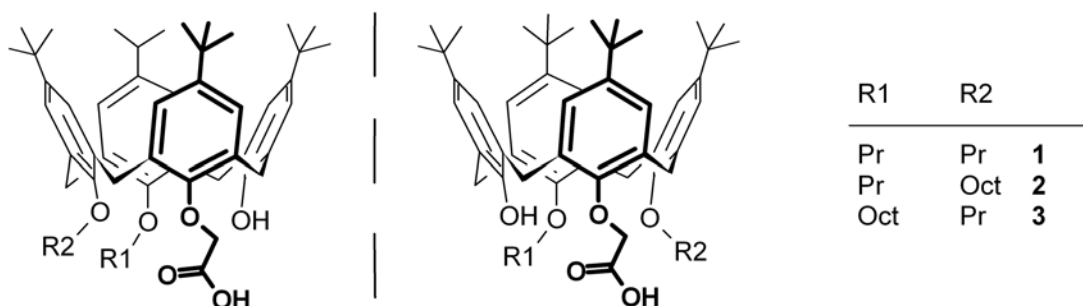
**SYNTHESIS, ABSOLUTE CONFIGURATION AND
RECOGNITION PROPERTIES OF ENANTIOPURE INHERENTLY CHIRAL
CALIXARENE ACETIC ACIDS**

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Chiral calixarenes can be used to create chiral catalysts, shifting agents in NMR spectroscopy, chiral stationary phases for chromatography and enantioselective sensors.¹

Previously, we synthesized enantiomerically pure forms of inherently chiral dipropoxy-calix[4]arene acetic acid **1**² (type AABH) and it was shown that they enantioselectively bind L- or D-forms of amino acids³. In this paper, optically pure forms of calixarene acetic acids **2** and **3** (type ABCH) with propyl and octyl substituents at the proximal positions of the lower rim of the macrocycle were synthesized and absolute configuration of their stereoisomeric forms was established.



By the NMR spectroscopy method it was shown that in CDCl₃ solution acids **1-3** recognize the L- and D-forms of α -aminopropanol, 1-phenylethylamine and lactic acid. The NMR titration showed that calixarene acetic acids **1-3** form 1:1 complexes with α -aminopropanol. The stability constants and binding energy of the complexes are calculated. It has been shown that the binding selectivity (from 1.5 to 2.2) allows use of the calixarene acetic acids to create chiral chemosensors and chromatographic columns.

¹ Boiko V.I., Kalchenko V.I., Yesipenko A.A. *Chiral Calixarenes*. Saarbrücken.: LAMBERT Academic Publishing, **2014**. - 230 p.

² Karpus A.O., Yesipenko O.A., Andronov L.P., Boyko V.I., Garasevich S.G., Voitenko Z.V., Chernega A.N., Kalchenko V.I. *Tetrahedron: Asymmetry*. **2012**, 1243-1250.

³ Andreyko E.A., Stoikov I.I., Antipin I.S., Karpus A.O., Sikorsky A.M., Yesipenko O.A., Rozhenko A.B., Boyko V.I., Kalchenko V.I. *Macroheterocycles*. **2013**, 227-233.

Ti(NMe₂)₄ AND TERT-BUTYLAMINE: REACTIFS SIMPLES, ... MAIS GRANDE COMPLEXITE ET DIVERSITES DES PRODUITS FORMES.

Ti(NMe₂)₄ AND TERT-BUTYLAMINE: SIMPLE REAGENTS, ... BUT GREAT COMPLEXITY AND DIVERSITY IN THE PRODUCTS FORMED

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In the last few decades, imido complexes of transition metals (TM) have attracted growing interest due to their implication in many stoichiometric or catalytic processes, as well as for their potential use as precursors to inorganic materials (metal nitrides). Imido complexes are now accessible through a variety of synthetic protocols, depending on the metal studied and the imido function needed. Despite the fact that many imido complexes of TM have been prepared (and in particular for early and mid-TM), there is still a need to discover new imido functions with particular properties or reactivity, and new imido precursors for enhanced catalytic activity or new applications.

Some years ago, we initiated a research program to investigate the general synthesis of early TM terminal or bridging imido complexes from commercially available M(NMe₂)₄ (M = Ti, V) and primary amines RNH₂. [1] We reported that, in the presence of trimethylchlorosilane, the important synthons M(=NR)Cl₂(NHMe₂)₂ are available in a very convenient one-pot reaction, and with the possibility to generate a great diversity of terminal imido complexes. Other “base-free” imido precursors of the type “{M(NR)Cl₂}_n” could also be obtained by changing the experimental protocol. [2]

More recently, while preparing the tert-butyl-imido analogue of such V-phosphine adducts, V(=N^tBu)Cl₂(PR₃)₂ that were used as catalyst for olefin polymerization, [3] we noticed that the isolation of a well-defined corresponding intermediate (hypothetical oligomeric or ionic intermediate precursor such as {V(=N^tBu)Cl₂}_n) was not as straightforward as for the aryl-imido Ti- or V-congeners. This observation incited us to study in more detail the reactions leading potentially to the formation of such elusive ^tBu-imido species. Herein we provide our observations on the reaction of V(NMe₂)₄ with ^tBuNH₂ followed by treatment with Me₃SiCl, as well as chemical insight into the same reaction conducted with Ti(NMe₂)₄ leading to mixture of diverse terminal or bridging imido multinuclear species.

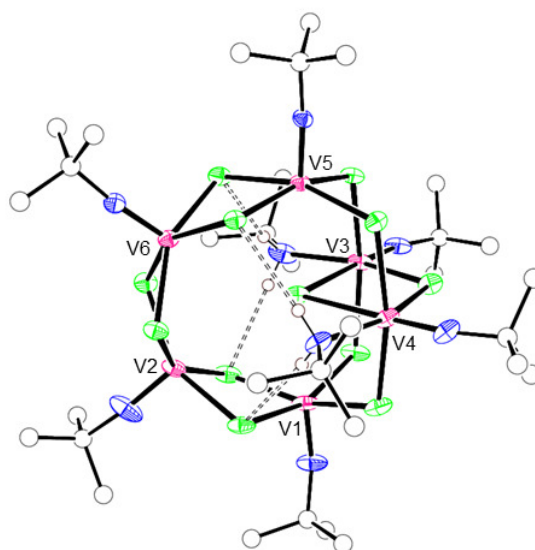


Figure: One example of a complex that was obtained

[1] C. Lorber, R. Choukroun, B. Donnadieu, *Inorg. Chem.*, **2002**, *41*, 4217-4226. C. Lorber, R. Choukroun, L. Vendier, *Eur. J. Inorg. Chem.* **2006**, 4503-4518.

[2] C. Lorber, L. Vendier, *Inorg. Chem.*, **2013**, *52*, 4756-4758.

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ACIDES PHOSPHONIQUE DES CALIXARENES POUR LA DETECTION D'ACIDES AMINES

CALIXARENE PHOSPHONIC ACIDS AS AMINOACIDS SENSORS

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Oleg Silenko¹, Svetlana Marchenko², Sergiy Dzyadevych^{2,3}, Vitaly Kalchenko¹

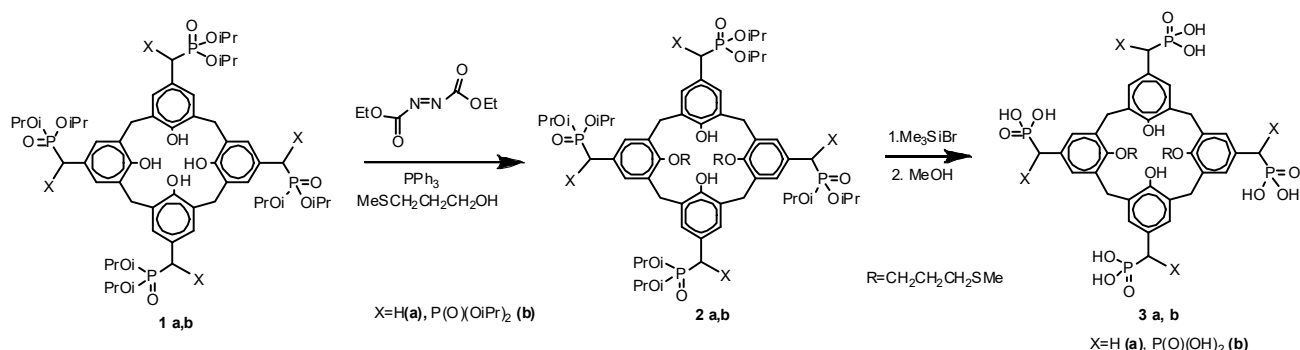
¹Institute of Organic Chemistry NAS of Ukraine, Kyiv, 02660, oik@ioch.kiev.ua

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Methods for synthesis of calix[4]arenes possessing phosphonic acid groups at the upper rim of macrocycle, capable of forming supramolecular complexes with amino acids,¹ and anchoring alkylsulfido groups at the lower rim of macrocycle capable of chemical bonding with the gold surface of the microchips of the conductometric sensors were developed.

By the Mitsunobu reaction of isopropyl esters of tetrahydroxycalixarene phosphonic acids **1a,b** with 3-methylsulfidopropanol the bis-alkylsulfido derivatives **2a,b** were obtained. The desirable 3-methylsulfidopropoxy-calixarene phosphonic acids **3a,b** were synthesized by dealkylation of esters **2a,b** by the consecutive reaction with trimethylbromosilane and methanol.



The stability constants ($K_A = 1000-41000 \text{ M}^{-1}$ in H₂O) of the inclusion complexes of acid **3b** with 16 amino acids were determined by the HPLC method. Conductometric sensor for the aminoacids analysis on the base of the calixarene **3b** was elaborated.²

¹ R. Rodik, S.Cherenok, O. Kalchenko, O.Yesypenko, J. Lipkowski, V. Kalchenko. *Current Organic Chemistry*. **2018**. 22. 2196-2218.

² O.O. Soldatkin, S.V. Marchenko, O.V. Soldatkina, S.O. Cherenok, O.I. Kalchenko, O.S. Prynova, O.M. Sylenko, V.I. Kalchenko, S.V. Dzyadevych. *Chemical Papers*. **2018**. 72. 2687-2697.

CE QUI SE CACHE DERRIÈRE LE MÉCANOFLUOROCHROMISME D'UN DÉRIVÉ DE 2-PHÉNYLBENZOXAZOLE AUX PROPRIÉTÉS AIEE

LOOKING BEHIND THE MECHANOFUOROCHROMIC PROPERTIES OF AN AIEE-ACTIVE 2-PHENYLBENZOXAZOLE DERIVATIVE

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Stimuli-responsive organic materials that exhibit fluorescence emission changes upon mechanical stress in the absence of any chemical reaction, i.e. mechanofluorochromic (MFC) materials, have recently gained increasing attention both in the fundamental research field of solid photophysics and in the applied field of polymer stress sensors, security inks, data storage and memory devices.¹⁻³ We looked for this property in the 2-phenylbenzoxazole (PBO) series, many derivatives of which are known for their excellent chemical, thermal and photochemical stability, and unique emission properties in the solid state.⁴ It appeared that the presence of a dicyanovinyl group on the robust 2-PBO framework led to the emergence of aggregation-induced emission enhancement (AIEE) characteristics. A mechanofluorochromic (MFC) behaviour was also observed. The pristine microcrystals emitted yellow-green light, which became golden yellow upon grinding, and *vice versa* by heating or solvent fuming. This phenomenon was accompanied by a reversible evolution of the photoluminescence quantum yields and lifetimes. These variations were conventionally attributed to the formation of different types of emissive species in the crystalline phases and in the ground material, which is a mixture of very small microcrystals and amorphous matter. Remarkably, evidence was also given for other spectroscopic effects, which depend on the size, compactness and heterogeneity of the solid samples. These effects are presumably linked to the generation of regions rich in low-energy exciton traps in polycrystalline and pressed samples, and to light reabsorption. They are enhanced by the fact that the pristine platelets exhibit self-waveguided edge emission, and they are all the more significant as the MFC effect is rather weak. Confusion between these effects and the genuine MFC effect could explain the apparent lack of repeatability and reproducibility that may be encountered in this delicate field of research.⁵

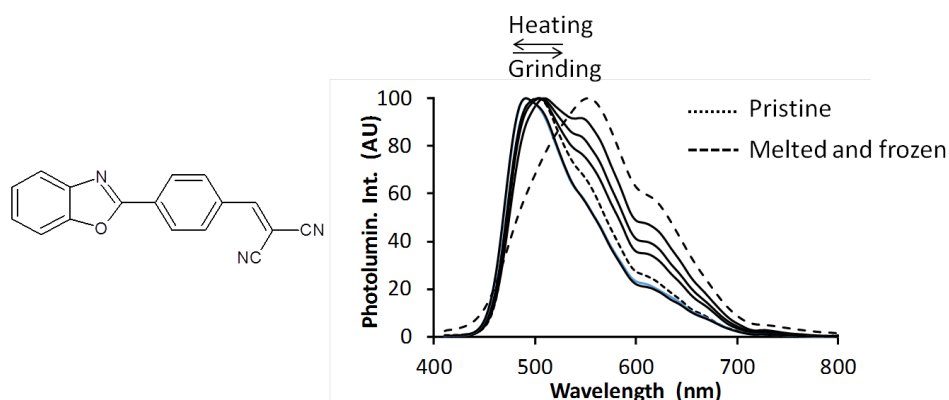


Figure 1. Chemical structure of 2-(4'-(1,1-dicyanovinyl)phenyl)benzoxazole and photoluminescence spectra of the various solid samples (pristine microcrystalline powder; powder after heating and grinding; polycrystalline melted and frozen sample) ($\lambda_{ex} = 380$ nm).

¹ R. Tan, S. Wang, H. Lan, S. Xiao S. *Curr. Org. Chem.* **2017**, 21, 236–248.

² D. R. T. Roberts, S. J. Holder. *J. Mater. Chem.* **2011**, 21, 8256–8268.

³ C. Wang, Z. Li. *Mater. Chem. Front.* **2017**, 1, 2174–2194.

⁴ C. Carayon, S. Fery-Forgues, *Photochem. Photobiol. Sci.*, **2017**, 16, 1020–1035.

⁵ C. Carayon, A. Ghodbane, N. Leygue, J. Wang, N. Saffon-Merceron, R. Brown, S. Fery-Forgues, *ChemPhotoChem*, **2019**. DOI:10.1002/cptc.201800261

**SYNTHÈSE ET STRUCTURE
DES CALIXARENES CHIRAUX INHERENTES
FONCTIONNALISÉES SUR LA JANTE SUPÉRIEURE**

**SYNTHESIS AND STRUCTURE
OF THE INHERENTLY CHIRAL CALIXARENES
FUNCTIONALIZED AT THE WIDE RIM**

Oleksandr Trybrat^a, Oleksandr Yesypenko^a, Svitlana Shishkina^b, Eduard Rusanov^a, Zoya Voitenko^c, Vitaly Kalchenko^a

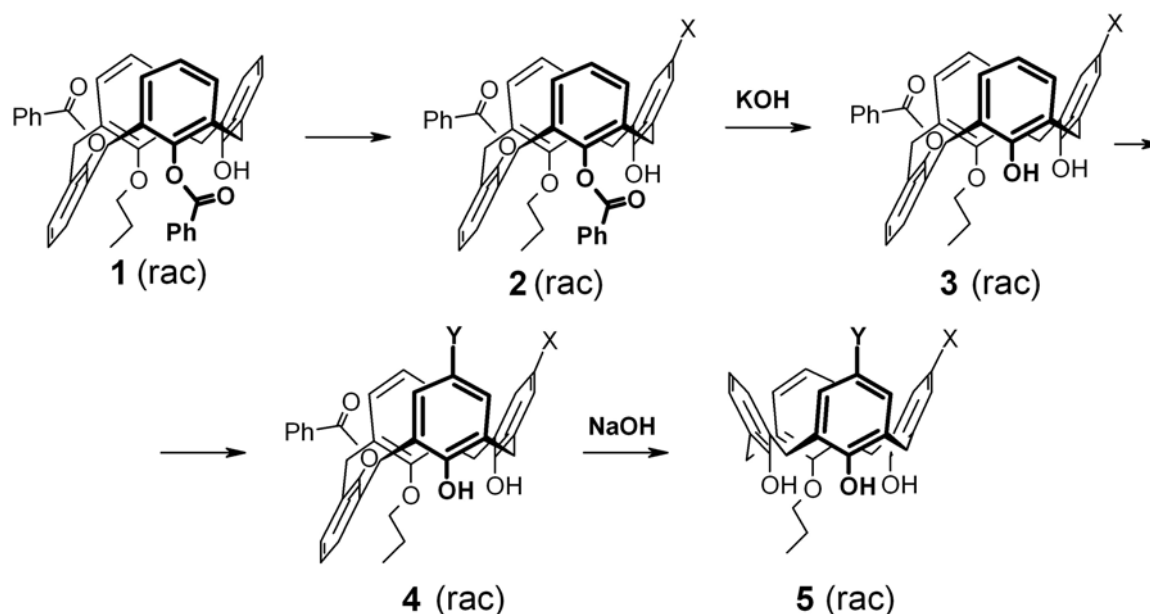
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Chiral calixarenes, bearing functional groups at the lower or the upper rim of the macrocycle are used as ligands of metallocomplexing catalysts of organocatalysts of asymmetric synthesis, enantioselective sensors or sorbents, chiral shift reagents for NMR studies, etc.¹

In this study methods synthesis of the inherently calix[4]arenes functionalized at the upper rim with functional groups of different nature and existing in the *cone* or *partial cone* conformation were developed². Spatial structure of the compounds was examined by X-ray methods.



X = -Br, -NO₂, -CH=O, -CH₂OMe, -C(O)OH, -CH₂NH₂

Y = -Br, -NO₂, -CH=O

Racemic mixtures of the chiral calixarenes formed in some cases were divided into optical antipodes.

¹ Boiko V.I., Kalchenko V.I., Yesipenko A.A. *Chiral Calixarenes*. Saarbrücken.: LAMBERT Academic Publishing, **2014**. - 230 p.

² O.A.Yesypenko, M.A.Klyachina, M.V.Dekhtyarenko, V.V.Pirozhenko, S.V.Shishkina, V.I.Boyko, Z.V.Voitenko, V.I.Kalchenko *Supramolecular Chemistry*, **2017**, 49-58.

SYNTHÈSE, CARACTÉRISATION ET EVALUATION ANTIVIRALE ET ANTICANCÉREUSE *IN VITRO* D'UNE SÉRIE DE NOUVELLES 2-(DICHLOROMÉTHYLE)PYRAZOLO[1,5-*a*][1,3,5]TRIAZINES

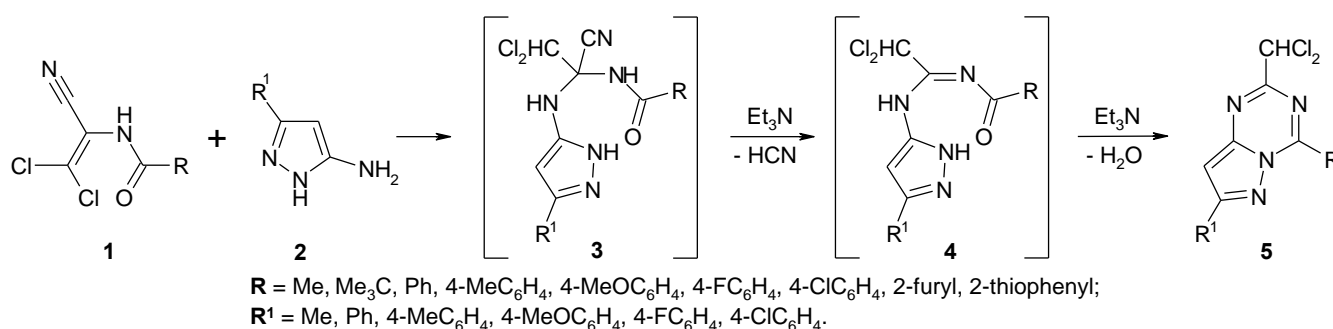
SYNTHESIS, CHARACTERIZATION, AND *IN VITRO* ANTIVIRAL AND ANTICANCER EVALUATION OF A SERIES OF NEW 2-(DICHLOROMETHYL)PYRAZOLO[1,5-*a*][1,3,5]TRIAZINES

Yevheniia Velihina^{a,b}, Maryna Kachaeva^a, Stepan Pil'o^a, Vladimir Zyabrev^a, Yevgen Karpichev^b, Volodymyr Brovarets^a

^a V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry NAS of Ukraine, Murmanskaya str. 1, Kyiv, 02094, Ukraine

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The *N*-(2,2-dichloro-1-cyanoethenyl)carboxamides¹ **1** were found to react with 1*H*-pyrazol-5-amines **2** in the presence of triethylamine to give 2-(dichloromethyl)pyrazolo[1,5-*a*][1,3,5]triazines **5**. Apparently, this cyclocondensation consists of the following steps: (i) activated C=C bond is attacked by the NH₂ group to form amide intermediate **3**, (ii) elimination of HCN promoted by triethylamine to give the second amide intermediate **4**, and (iii) intramolecular cyclisation into the final product **5** with H₂O elimination.



A series of 53 novel 2-(dichloromethyl)pyrazolo[1,5-*a*][1,3,5]triazines **5** have been characterized by means of IR, ¹H and ¹³C NMR, elemental analysis, and LCMS.

Five 2-(dichloromethyl)pyrazolo[1,5-*a*][1,3,5]triazines were tested against: (i) Dengue virus 2 (strain New Guinea C, cell line Huh7); (ii) Tacaribe virus (strain TRVL 11573, cell line Vero); (iii) Zika virus (strain MR766, cell line Vero 76); (iv) human cytomegalovirus (strain AD169, cell line HFF); (v) herpes simplex virus 1 (strain E-377, cell line HFF); (vi) Varicella-Zoster virus (strain Ellen, cell line HFF). All compounds showed rather low activity except the 2-(dichloromethyl)-4,7-diphenylpyrazolo[1,5-*a*][1,3,5]triazine, which however had comparably high toxicity.

Eight type **5** compounds have been screened on 60 cancer cell lines in the National Cancer Institute for the five-dose assay according to its own protocol. All evaluated compounds displayed high anticancer activity at submicromolar, micromolar or decimicromolar concentrations.

This work could be useful for the further search of biologically active compounds among pyrazolo[1,5-*a*][1,3,5]triazines.

This resyarch is partially supported by Dora Plus programme 2014 - 2020.4.01.16-0025, Activity 2.2., funded by European Regional Development Fund.

¹ B.S. Drach, E.P. Sviridov, T.Y. Lavrenyk, *J. Org. Chem. USSR (Engl. Transl.)*, **1974**, 1278–1280.

CAPILLARY ELECTROPHORESIS SEPARATION OF TRYPTOPHAN IN MOUSE PLASMA

SEPARATION DU TRYPTOPHANE DANS LE PLASMA DE SOURIS PAR ELECTROPHERE CAPILLAIRE

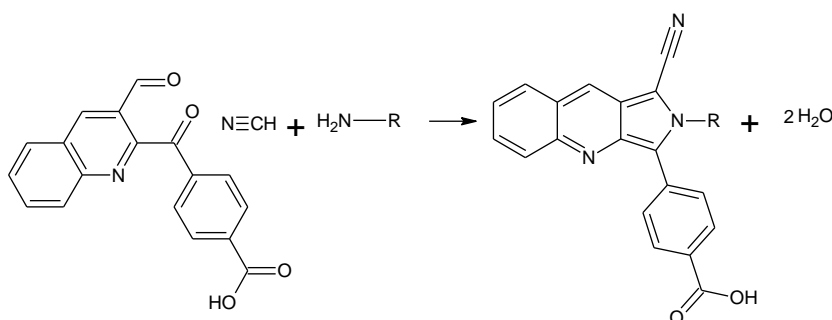
Lucie Perquis, Hai Yen Ta Hai, Varravaddheay Ong-Meang, Véréna Poinso, Cédric Sarazin, Bruno Guiard, Fabrice Collin, François Couderc

IMRCP Laboratory, Paul-Sabatier University, 118 route de Narbonne, 31062 Toulouse, France
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The purpose of our study is to detect, in the serum of diabetic mice, the amino acids (AA) (Isoleucine (Ile), Leucine (Leu), Tryptophan (Trp), Valine (Val)) involved in antidepressant resistance.

AA labeled with 3-(4-carboxybenzoyl)quinoline-2-carboxaldehyde (CBQCA, Invitrogen by Thermo Fisher Scientific, Lui et al, 1991) are studied in CE-LEDIF (480nm, Picometrics-Adelis). It is very difficult to identify Trp labeled with CBQCA. A quenching phenomenon can complicate the detection of this AA by CE-LEDIF.

In mass spectrometry, we have verified that Trp is well labeled by the CBQCA and in spectrofluorometry, we have shown that the compound obtained is 100 times less fluorescent than the Leu-CBQCA. Thus in order to detect this AA in the plasma we have developed a pre-concentration step by LVSS (Large Volume Stacking Sample). Yet we realize that Trp-CBQCA in plasma is always difficult to identify correctly. In order to have another method of analysis, CE-C⁴D (conductimetric detection, Wynsep) can be used which makes it possible to observe and to measure all the AA in the mouse plasma.



APPROCHE DE TYPE "SCAFFOLD HOPPING" POUR LE DÉVELOPPEMENT DE NOUVELLES 7-PIPÉRAZINE- AND 7-(1,4-DIAZÉPANE)-[1,3]OXAZOLO[5,4-d]PYRIMIDINES SUBSTITUÉES COMME AGENTS ANTICANCÉREUX PROMETTEURS

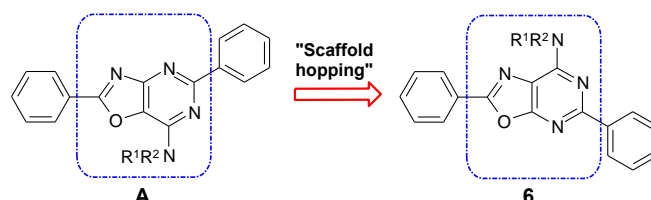
SCAFFOLD HOPPING APPROACH FOR DESIGNING NEW 7-PIPERAZIN- AND 7-(1,4-DIAZEPAN)-SUBSTITUTED [1,3]OXAZOLO[5,4-d]PYRIMIDINES AS PROSPECTIVE ANTICANCER AGENTS

Yevheniia Velihina^{a,b}, Denys Bondar^b, Maryna Kachaeva^a, Stepan Pil'o^a, Yevgen Karpichev^b, Volodymyr Brovarets^a

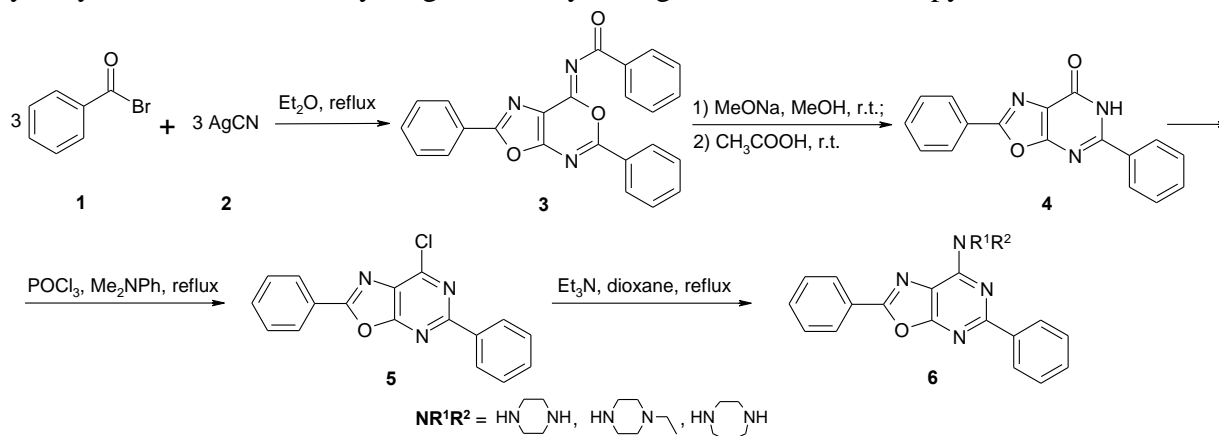
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Previously, we have synthesized the promising anticancer agents 7-piperazin- and 7-(1,4-diazepan)-substituted [1,3]oxazolo[4,5-d]pyrimidines **A**^{1,2}. To develop this approach, the 7-piperazin- and 7-(1,4-diazepan)-substituted [1,3]oxazolo[5,4-d]pyrimidines **6** have been prepared and investigated.



The new [1,3]oxazolo[5,4-d]pyrimidines **6** were designed via a scaffold hopping strategy and obtained by the sequence of reactions starting from available benzoyl bromide **1**. Treating of **1** with silver cyanide **2** in diethyl ether afforded the cyclocondensation product N-(2,5-diphenyl-oxazolo[5,4-d][1,3]oxazin-7-ylidene)-benzamide **3**. In the reaction of compound **3** with sodium methoxide followed by hydrolysis in acetic acid, recycling occurred yielding [1,3]oxazolo[5,4-d]pyrimidine³ **4**.



The reaction of compound **4** with trichlorophosphate in the presence N,N-dimethylaniline proceeded 2,5-diaryl-7-chloro[1,3]oxazolo[5,4-d]pyrimidines **5**. Compound **5** were converted into **6** by reaction with the corresponding piperazines and homopiperazine.

This research work is partially supported by Dora Plus programme 2014 -2020.4.01.16-0025, Activity 2.1 and 2.2., funded by European Regional Development Fund.

¹ Ye.S. Velihina, M.V. Kachaeva, S.G. Pilyo, V.V. Zhirnov, V.S. Brovarets, *Der Pharma Chem.*, **2018**, 1-10.

² Ye.S. Velihina, M.V. Kachaeva, S.G. Pilyo, O.P. Mitiukhin, V.V. Zhirnov, V.S. Brovarets, *Chem. R. J.*, **2018**, 81-93.

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SYNTHESE EFFICACE DE DERIVES ALLYLIQUES FERROCENIQUES

EFFICIENT SYNTHESIS OF FERROCENYL ALLYLIC DERIVATIVES

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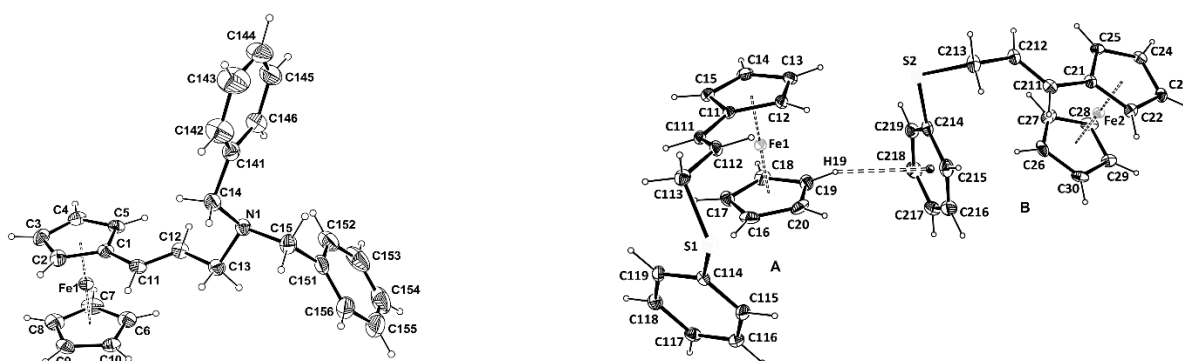
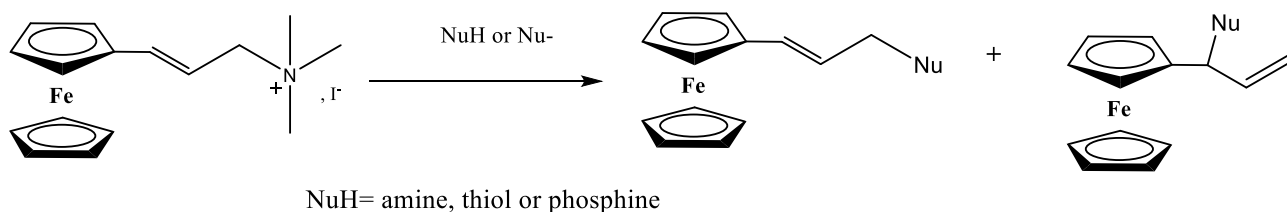
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Ferrocene chemistry has developed into one of the most fruitful fields in organometallic chemistry and new uses are still being explored for the remarkable metallocene moiety. Over the recent years, one of the most exciting developments in this area is the coordination chemistry of ferrocene derivatives, especially those containing hetero-atoms with good electron donating abilities (i.e. nitrogen, sulfur, phosphorus, etc.)¹ for various potential applications, as drugs,² materials³ or in catalysis.⁴ In this contribution, we will present the reactivity of a new ferrocenyl allylammonium salt to prepare novel *hetero-functionalized ferrocenyl allyl derivatives*.

(3-(N,N,N-trimethylammonium)-(1-propenyl))ferrocene iodide (1) was successfully synthesized, in good yields, by a novel synthetic route. Its reactivity with different nitrogen,⁵ sulfur⁶ or phosphorus⁷ nucleophiles led to the formation of various compounds as regioisomeric mixtures. Control of the reaction conditions has allowed us to efficiently tune the reactivity in favor of one selected regioisomer. A mechanistic proposal to rationalize the experimental observations will be presented.



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³ P. D. Beer, C. Blackburn, J. F. McAleer, H. Sikanyika, *Inorg. Chem.*, **1990**, *29*, 378-381.

⁴ C. Zuniga, S. A. Moya, P. Aguirre, *Catal. Lett.*, **2009**, *130*, 373-379.

⁵ R. Bouchene, J.-C., Daran, S. Bouacida, E. Manoury *Eur. J. Inorg. Chem.*, **2017**, 340-350.

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Nanoréacteurs polymériques hydrosolubles contenant des complexes NHC du rhodium(I) pour la catalyse biphasique.

Hydrosoluble Polymeric Nanoreactors Containing Rh(I)-NHC Complexes for Biphasic Catalysis

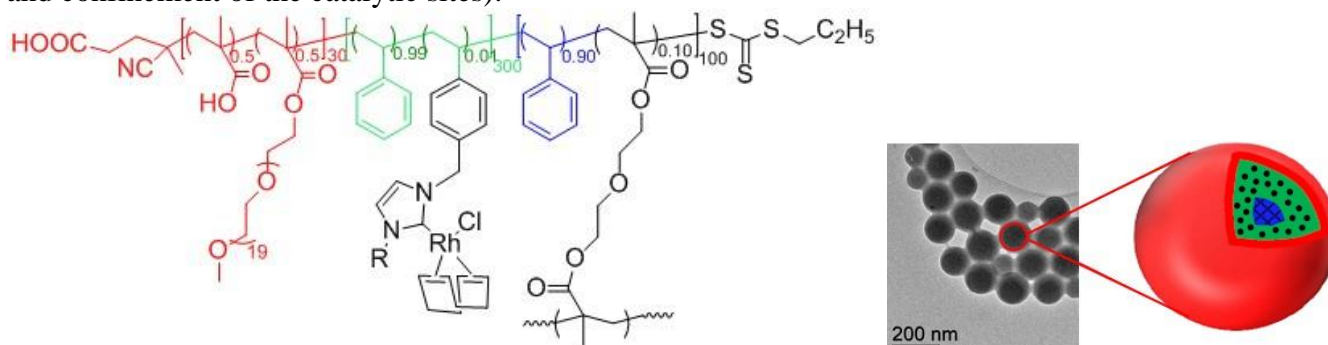
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The recovery and recycling of catalysts have become essential prerequisites, for industrial applications, to improve energetic efficiency, limit the environmental footprint and lower the cost, especially when rare metals are involved.

The use of polymeric structures with controlled architecture as catalytic supports is an emerging area. Our group has been interested for some time in the synthesis of unimolecular nanoreactors, obtained by cross-linking linear amphiphilic polymers at the core after their self-assembly as micelles [1]. The main advantages of these objects compared to classical micelles are the faster decantation of emulsions and the absence of amphiphilic noncrosslinked arms with consequent reduced leaching. They also offer a very well organized structure that gives specific properties in catalysis (affinity for reagents, selectivity and confinement of the catalytic sites).



We have developed core-shell nanoreactors (core-cross-linked micelles, CCMs) incorporating rhodium(I) complexes bearing monodentate N-heterocyclic carbene ligands [2]. The complexes have been covalently bound to the polymeric chains by incorporation of a polymerizable unit on the NHC ligand. The substituents on the NHC have been changed in order to study its influence on the CCM properties and their catalytic activity. The CCMs have been characterized by Dynamic Light Scattering and Transition Electron Microscopy, and have been evaluated as nanocatalysts for the hydrogenation of alkenes under biphasic conditions.

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PHOTOSENSIBILITÉ DE CONTENANT LE TITANE HYBRIDE INTERPÉNÉTRANT DES RÉSEAUX DE POLYMÈRE BASÉS SUR LE POLYURÉTHANE ET POLY (HYDROXYETHYL METHACRYLATE)

PHOTOSENSITIVITY OF HYBRID TITANIUM-CONTAINING INTERPENETRATING POLYMER NETWORKS BASED ON POLYURETHANE AND POLY(HYDROXYETHYL METHACRYLATE)

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In last decade materials based on titanium dioxide and poly(titanium oxide) have attracted great attention of researchers, due to possibilities of their practical application as catalyst, photo catalyst and membrane, as well as in solar and fuel cells, biomedicine and in other areas, where their unique optical properties can be used and also this material may become interesting for nonlinear optical applications.

Titanium-containing interpenetrating polymer networks (Ti-IPNs) based on the cross-linked polyurethane (PU), poly (hydroxyethyl methacrylate) (PHEMA) and poly (titanium oxide) ($(-\text{TiO}_2-)_n$), previously synthesized by sol-gel method in the presence of 2-hydroxyethyl methacrylate (HEMA) were obtained. The formation of $(-\text{TiO}_2-)_n$ occurred by hydrolysis-condensation reactions of $\text{Ti}(\text{OPr})_4$, in the presence of 0.1 N HCl as the catalyst. The molar ratio of HEMA/ $\text{Ti}(\text{OPr})_4$ was 8/1 and the molar ratio of $\text{Ti}(\text{OPr})_4/\text{H}_2\text{O}$ were 1/1 (sample Ti-IPN-1) and 1/2 (sample Ti-IPN-2). The ratio of PU/PHEMA components in the IPN and Ti-IPNs was 30/70 wt %.

The results obtained by method of optical spectrophotometry have shown that the light transmission coefficients (T, %) of Ti-IPNs samples before UV-irradiation evaluated at $\lambda=650$ nm was (90.7-91.0)%. The optical transparency for Ti-IPNs samples after UV-irradiation within 240 minutes decreased to 61.0% (Ti-IPN-1) and 48.0% (Ti-IPN-2), respectively. The Ti-IPN samples UV-irradiated area became black. The differences observed are apparently due to the different morphology of poly(titanium oxide) in Ti-IPN-1 and Ti-IPN-2 hybrids, which affects the efficiency of the formation of Ti^{3+} centers.

According to EPR data UV irradiation on air at room temperature of samples of Ti-IPNs is accompanied by the appearance of signal of paramagnetic centers with broad isotropic signal at $g_1=2.010$ and also noticeably split signals at $g_2=1.966$ and $g_3=1.940$. First of them can be ascribed to oxygen contained "hole scavenger" were as the second one to anisotropic signal of Ti^{3+} paramagnetic ions. Such a signal is not present in the initial sample spectrum. The low rate of the electron-hole pair recombination in Ti-IPN matrix at 25°C demonstrates efficient separation of the charged particles in a hybrid material and can be approximated by the inverse function $y=1/(a+b/t)$. Using nitroxyl spin probe it was revealed essential compaction of the polymer matrix (three times Ti-IPN-1 and twofold Ti-IPN-2) due to irradiation-recombination processes.

According to the wide-angle X-ray scattering data initial Ti-IPN-2 sample have an amorphous structure. Its X-ray diffractogram is an amorphous halo with several maxima at angular positions ($2\theta_m$) of 13,7°, 19,0° and 31,2°. Comparison of the sample X-ray diffractogram before and after UV-irradiation it was found that position of diffraction maximum at 31,2° moves toward less angle ($2\theta_m=28,8^\circ$). Thus, UV-irradiation novel titanium-containing IPNs cause the substantial change of his structure.

STABILISATION AMÉLIORÉE DE L'INTERFACE EAU-SCCO₂ PAR DES COPOLYMÈRES À GRADIENT SPONTANÉ DE TYPE BLOC

ENHANCED STABILIZATION OF WATER-SCCO₂ INTERFACE BY BLOCK-LIKE SPONTANEOUS GRADIENT COPOLYMERS

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Abstract: There is an increasing interest in the specific physicochemical properties of gradient copolymers at interfaces. In this work, the phase behavior and interfacial properties of amphiphilic gradient copolymers at the water-CO₂ interface are explored and compared to that of diblock copolymer counterparts. It is observed that spontaneous amphiphilic block-like gradient copolymers made of N, N-dimethylacrylamide, vinyl pivalate and vinyl acetate exhibit slightly lower cloud point pressures in supercritical carbon dioxide (scCO₂) than the corresponding diblock copolymers. Much more pronounced differences are established at the water/scCO₂ interface, with larger critical aggregation concentration (CAC), much faster adsorption kinetics and equilibration, and lower surface tension for gradient copolymers. RAFT/MADIX polymerization allows the control of molar mass, composition and microstructure of the copolymers of the study. These findings shed light on how microstructural control in amphiphilic copolymers can give access to a new range of macromolecular emulsifiers for CO₂ media with improved properties.

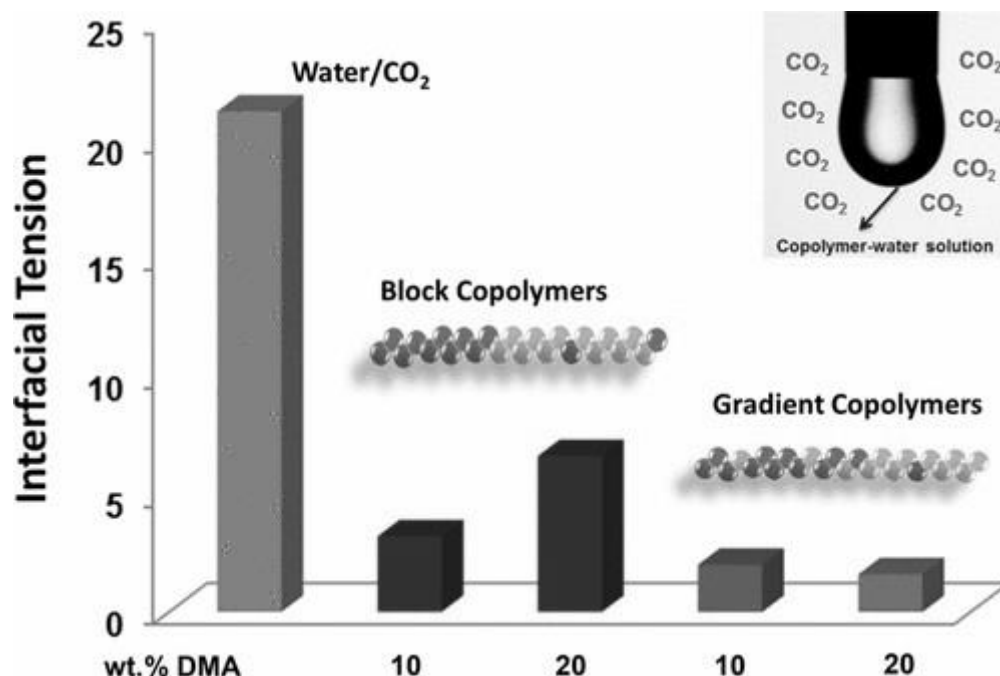


Figure 1: Fluorine-free gradient copolymers cause rapid and significant reductions in the interfacial tension of CO₂/water interfaces

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FORMATION DE LA COMPÉTENCE PROFESSIONNELLE CHEZ LES ÉTUDIANTS—CHIMISTES LORS DE L'ÉTUDE DE LA LANGUE FRANCAISE

FORMATION OF THE PROFESSIONAL COMPETENCE OF CHEMISTRES STUDENTS IN THE STUDY OF FRENCH

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Foreign language becomes a universal means of professional, industrial life, so when teaching a foreign language at non-specialized faculties, the problem of development and formation of professional competence of students becomes more and more urgent.

A professionally-oriented approach to teaching a foreign language at non-linguistic faculties of universities, in particular when teaching French at the chemical faculty of our University, is of particular relevance. Professionally-oriented approach to training provides for the formation of students' professional competence, which allows them to communicate in specific professional, business, scientific fields and situations, taking into account the peculiarities of professional thinking, in the organization of research activities.

Vocational education is understood as education based on the needs of students in the study of a foreign language, dictated by the characteristics of the future profession or specialty. It involves a combination of mastering a professionally-oriented foreign language with the development of personal qualities of students, knowledge of the culture of the country of the studied language and the acquisition of special skills based on professional and linguistic knowledge [1].

Professionally-oriented communication can take place in formal and informal settings, in the form of conversations with foreign colleagues, speeches at meetings, conferences, collective discussions, writing business letters and e-mail. Therefore, the content of foreign language teaching should be professionally and communicatively oriented. It is necessary to clearly define the goals of teaching a foreign language to non-linguist students. Students' interest in the subject increases when they clearly represent the prospects of using the knowledge gained, when this knowledge and skills in the future will increase their chances of success in any activity. The formation of professional competence contributes to the expansion of educational horizons of students, socialization of future professionals, preparing them for life in a multi-ethnic and multicultural world.

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INVESTIGATION OF REGIOSELECTIVITY OF ELECTROPHILIC HETEROCYCLIZATION OF ALKENYL DERIVATIVES OF THIENOPYRIMIDINONE BY ARYLTELLURIUM TRICHLORIDES

Onysko M.Yu., Kut M.M., Lendel V.G.

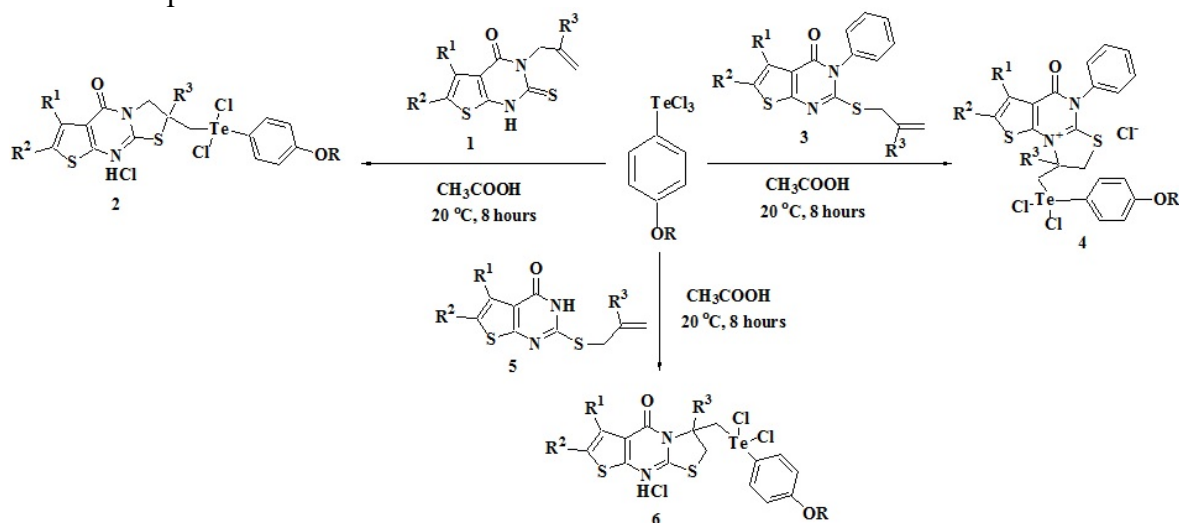
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Annulation of heterocyclic nuclei to a condensed pyrimidine cycle by electrophilic intramolecular cyclization reveals new perspectives and opportunities for the formation of new functional derivatives of pyrimidine. The purpose of this work is to study the regiochemistry of the process of electrophilic intramolecular cyclization of N(S)-alkenyl derivatives of thienopyrimidinone with *p*-alkoxyphenyltellurium trichloride. It was found that 3-N-alkenyl derivatives of thieno[2,3-*d*]pyrimidine **1** are cyclized regio-selectively by the action of *p*-alkoxyphenyltelluriumtrichlorides in acetic acid with the participation of an exocyclic Sulfur atom with the formation of polycyclic systems **2** of linear structure.

Regio-direction of the cyclization of 2-S-alkenyl derivatives of thieno[2,3-*d*]pyrimidine by the action of *p*-alkoxyphenyltellurium trichlorides depends on the presence of the substituent in the **3** position of the pyrimidine ring. Thus, the halides of thiazolothienopyrimidinium **4** of the angular structure with an exocyclic aryltellurium fragment were obtained at the tellurocyclization of 3-N-phenyl-2-S-alkenyl derivatives of thienopyrimidinone **3**. Instead, 2-S-alkenyl 3-N-unsubstituted thienopyrimidinones **5** contain two alternative nucleophilic centers that may participate in the process of electrophilic intramolecular cyclization under the action of aryltellurium trichlorides to form condensed systems of linear or angular structure. We have found that the electrophilic intramolecular cyclization of 2-S-alkenyl-3-N-unsubstituted thienopyrimidinones with *p*-alkoxyphenyltelluriumtrichlorides takes place regio-selectively with the participation of the 3-N atom of the pyrimidine ring to form linear tetracyclic systems **6**. The formation of products of linear structure in this case is presumably caused by the intramolecular coordination of the carbonyl oxygen of the Oxygen atom of carbonyl group on the Tellurium atom in electrophilic reagent.

The structure of cyclization products is proved by NMR spectra, including correlation, and infrared spectra.



CONCEPTION D'ACIDES ARYLHYDROXAMIQUES N-SUBSTITUÉS COMME RÉACTIVATEURS CATALYTIQUES D'ACÉTYLCHOLINESTÉRISE

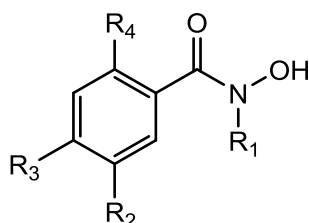
DESIGNING N-SUBSTITUTED ARYLHYDROXAMIC ACIDS AS CATALYTIC ACETYLCHOLINESTERASE REACTIVATORS

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Hydroxamic acids are a major class of organic compounds. They have a wide variety of pharmacological actions presumably by means of forming tight complexes with transition metal ions, particularly zinc and thus act as metalloproteases inhibitors¹. Being α -nucleophiles, the anions of hydroxamic acids provide fast and irreversible cleavage of toxic organophosphates under mild conditions². Among the criteria set in designing efficient systems for the chemical decontamination and potent antidotes towards acetylcholinesterase (AcChE) inhibited by OP, the catalytic action of a nucleophile remains being a challenging one. Hydroxamic acids are well known to undergo Lossen rearrangement that involves the conversion of an *O*-activated (phosphorylated, in essence) hydroxamic acid into the corresponding isocyanate intermediate³, which does not afford catalytic action of the hydroxamate ions. Introducing a substituent at the nitrogen -atom prevents involvement of the proton and, therefore, expected providing regeneration of the hydroxamate species rather than undergoing Lossen rearrangement.

Synthesis of a series of arylhydroxamic acid have been optimized to prepare N-methyl, and butyl, and N-phenyl derivatives of benzhydroxamic (1), 3-methoxy- (2) and 4-methoxy (3) benzhydroxamic acids, as well as corresponding salicylhydroxamates (4).



1a-d: R₂=R₃=R₄=H; R₁=H (**1a**), Me (**1b**), Bu (**1c**), Ph (**1d**)

2a-d: R₂=OMe; R₃=R₄=H; R₁= H (**2a**), Me (**2b**), Bu (**2c**), Ph(**2d**)

3a-d: R₃=OMe; R₂=R₄=H; R₁= H (**3a**), Me (**3b**), Bu (**3c**), Ph (**3d**)

4a-d: R₄=OH; R₂=R₃=H; R₁= H (**4a**), Me (**4b**), Bu (**4c**), Ph (**4d**)

In continuation to our previous comprehensive study on designing oxime-functionalized ILs⁴, the compounds **1** – **4** are being investigated towards their catalytic action in the reaction with paraoxon (used as CWA simulant) along with evaluating reactivation potency towards AcChE inhibited by miscellaneous OP and toxicity screening against the mammalian cells. The found regularities are to use in the further improvement of the structures of perspective antidotes.

This research is partially supported by NATO SPS MYP G5565 Project and Dora Plus programme 2014 -2020.4.01.16-0025, Activities 2.1 and 2.2., funded by European Regional Development Fund.

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NANOCOMPOSITES Co-Fe DÉPOSÉS SUR Al₂O₃ DANS LA RÉACTION DE L'HYDROGÉNATION DE CO₂

Co-Fe NANOCOMPOSITES DEPOSITED ON Al₂O₃ IN THE REACTION OF CO₂ HYDROGENATION

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Carbon dioxide is a gaseous pollutant broadly presented in the atmosphere. Among various scaled-up methods to be used for the reduction of air pollution, catalytic hydrogenation of CO₂ to CH₄ has a great challenge. From the economic and environmental reasons, the development of a metal catalyst that has advanced activity and selectivity to CH₄ is important. For high CH₄ yields, today the CO₂ hydrogenation has been studied over numerous supported metal catalysts.

One of the most effective methods for increasing the activity of a catalyst is its application to an inert carrier. In this way, it is possible to improve the selectivity of the process by the given product, to achieve a higher yield of products or to lower the temperature of their maximum output.

In this study, different type of alumina oxide was used as carrier for the catalyst: α -Al₂O₃ with specific surface $S_{sp} = 190 \text{ m}^2/\text{g}$ (A1), α -Al₂O₃ with $S_{sp} = 68 \text{ m}^2/\text{g}$ (A2) and γ -Al₂O₃ with $S_{sp} = 310 \text{ m}^2/\text{g}$ (A3). The composition of the applied active mass was Co 93 wt%-Fe 7 wt%. The samples of alumina supported metal catalysts were tested in the reaction of CO₂ hydrogenation. Applying of actives on the carrier's surface was provided by impregnation with a metal nitrate solution, further thermal degradation and reduction of metal oxide precursors by hydrogen. The amount of the active phase of 5, 10 and 20% was controlled by weight after treatment.

The catalytic activity of the samples was studied in a fixed bed reactor in flow of 2 % CO₂ + 55 % H₂ mixture (balanced with He), at GSV=100 cm³/min and sample mass of 1g. The exiting gaseous mixture was analyzed by gas chromatograph with a thermal conductivity detector (Shimadzu GC-2014, 1 m-length packed column, molecular sieves 5A). The results of catalytic test are presented in the Table:

Catalyst	Reaction temperature (°C)			
	300	350	400	450
Yield, Y_{CH_4} / Y_{CO} (%)				
5% Co ₉₃ Fe ₀₇ /A1	5/0	26/0	54/3	73/6
5% Co ₉₃ Fe ₀₇ /A2	6/0	45/0	79/0	98/0
5% Co ₉₃ Fe ₀₇ /A3	0/0	1 /4	1/5	1/12
10% Co ₉₃ Fe ₀₇ /A1	58/0	88/0	98/0	100/0
20% Co ₉₃ Fe ₀₇ /A1	56/0	85/0	100/0	100/0
20% Co ₉₃ Fe ₀₇ /A2	87/0	97/0	100/0	100/0

The morphology of samples catalyst's surface was observed by scanning electron microscopy (SEM). The formation of a large number of agglomerates of the active component up to 500 nm contributes to the catalytic activity of catalysts.

FLEURS MOLECULAIRES ET CHIMIE DE COORDINATION

MOLECULAR FLOWERS AND COORDINATION CHEMISTRY

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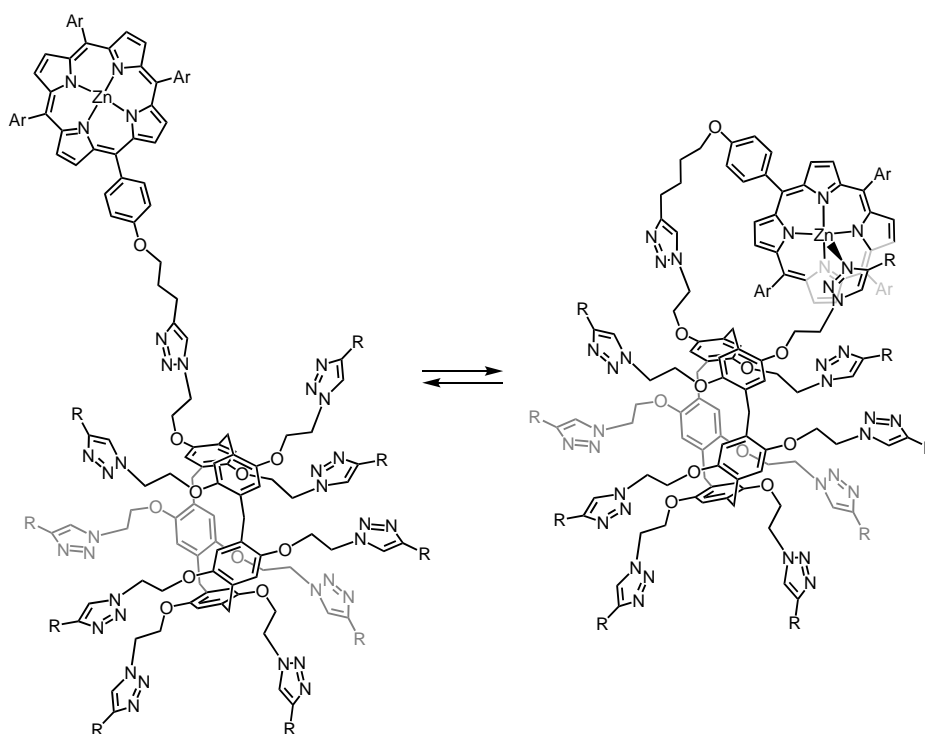
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The flowers presented here are sophisticated pillar[5]arene molecules and their rotaxane derivatives incorporating a macrocyclic core and ten peripheral zinc-porphyrin units.^{1,2} In particular, we will show how NMR and electrochemistry can be useful not only for the characterization of these molecular assemblies but also for the understanding of their controlled blooming.

These original results pave the way for the elaboration of more complex 3D macromolecular systems whose properties or functions can be stimuli-controlled. Indeed, the thermal, electrochemical or chemical stimuli used in this study allow precise molecular conformational changes responsible for the evolution of the properties of these molecular systems.



Schematic representation of the dynamic conformational changes resulting from the intramolecular coordination of a 1,2,3-triazole moiety to a Zn(II)-porphyrin subunit in a pillar[5]arene molecule; only one of the ten R units is represented.

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SYNTHESE DE CONJUGUES CONTENANT DE L'ACIDE BETULONIQUE ET DES FRAGMENTS DE SPIROOXINDOLE / ISOXAZOLE VIA LA «CLICK» CHIMIE

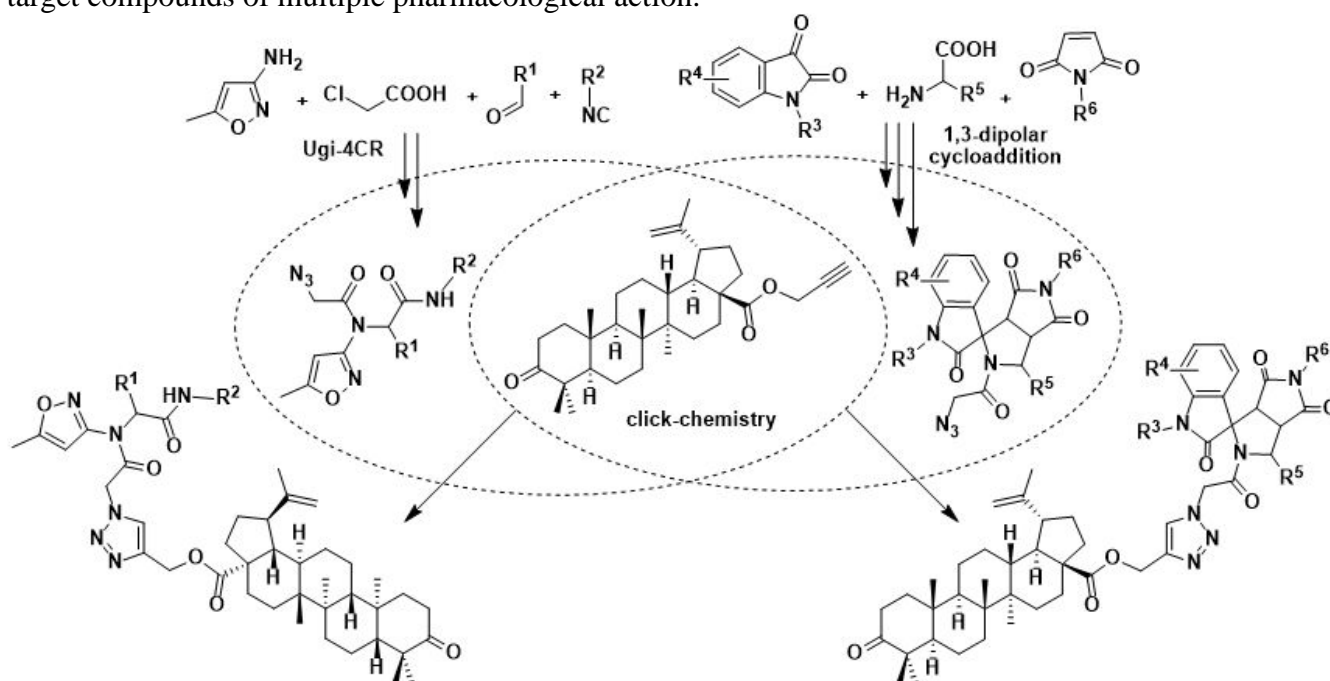
SYNTHESIS OF CONJUGATES CONTAINING BETULONIC ACID AND SPIROOXINDOLE/ISOXAZOLE FRAGMENTS VIA “CLICK” CHEMISTRY

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Plant-derived group of pentacyclic lupane triterpenoids (betulin, betulinic and betulonic acids) is one of the most important classes of natural compounds and is used as structural core for the discovery of new biologically active substances [1]. These secondary metabolites possess a wide range of biological activities, such as anti-inflammatory and antiviral (anti-HIV) effects. Betulonic acid was also found to be an antitumor agent [2]. The development of hybrid molecules that possess both lupane core and pharmacophore fragments is a task of our current interest. Among various biologically active molecules 3,2'-spiropyrrolidineoxindoles and isoxazole derivatives attracted our attention as they are prevalent in a number of lead-compounds and drug candidates of wide spectrum of action, such as anticancer, antimicrobial, anti-inflammatory agents [3,4]. We have prepared series of novel triazoles in “click”-reaction between the propargyl ester of betulonic acid and new complex organic azides. First group of azides contained spirooxindole fragment synthesized in the 1,3-dipolar cycloaddition of isatins, acyclic α -amino acids and maleimide derivatives [5] followed by subsequent formation of azides. Second group was prepared from the Ugi four component reaction products based on 3-amino-5-methylisoxazole, aromatic aldehydes, amines, chloroacetic acid and isocyanides. The obtained conjugates combine analogues of different classes of biologically active compounds, which makes them target compounds of multiple pharmacological action.



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COMPLEXES D'OR(I) NHC POUR APPLICATION ANTI-LEISHMANIAL

GOLD(I) NHC COMPLEXES FOR ANTI-LEISHMANIAL APPLICATION

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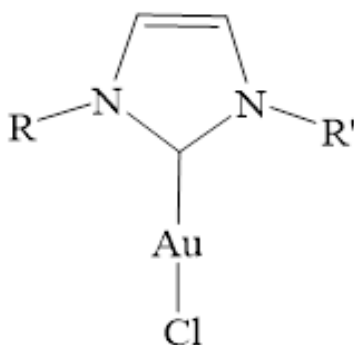
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Abstract :

Leishmaniasis is a parasitic disease, caused by *Leishmania spp.*, spread by the bite of *Phlebotomus* sandflies. *Leishmania* currently affect 12 million people and around 2 million new cases occur each year. Resistance to current antileishmanial drugs is spreading worldwide and requires an active search for new active molecules.

Gold organometallic complexes have been studied for several biomedical applications including their anti-leishmanial activity.^{1,2}

A series of mononuclear neutral gold complexes containing *N*-heterocyclic carbene (NHC) ligands for anti-leishmanial activity have been synthesized, purified and characterized.



R = *i*-Pr, benzyl, quinoline

R' = sulfur and/or fluorine containing groups

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BROMINATION DE SURFACE DE MATÉRIAUX Á BASE DE CARBONE OXYDEE: ETUDE DFT

SURFACE BROMINATION OF OXIDIZED CARBON MATERIALS: A DFT STUDY

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Carbon adsorbents are characterized by a developed porous structure suitable for environmental purification and catalytic processes. Activated carbon (AC) is the most used carbon material having a high thermal, chemical/radiation resistance, good mechanical properties. AC does not swell in aqueous and organic media. The effectiveness of AC depends on the chemical nature of the surface. The surface of AC is covered with oxygen-containing functional groups. Their concentration and ratio depend on the method of preparation or pre-treatment. One should take into account O-containing surface centers when using the pre-bromination to introduce S-, N-, and P-containing groups into the surface layer. To develop *in silico* technology, one should expand the field of application of the density functional theory (DFT) methods. Theoretical evaluations of various reactions in the surface layer are used for predicting reliable physical and chemical properties of substances. We devoted our work within DFT paradigm to examine the reactivity of the active sites of oxidized AC in the bromination reaction.

Figure 1 presents the initial geometry of the model molecule corresponds to the graphite cluster of 54 carbon atoms and having radial symmetry. All dangling bonds were filled by adding of hydrogen atoms. The ORCA code DFT calculations were performed with a generalized gradient approximation for the gradient-corrected Becke exchange and Perdew-Wang correlation potentials with TZV basis sets and *p* polarization function were also implemented. We used the geometry convergence criterion and set the energy convergence tolerance was 5×10^{-6} Hartree, the maximum gradient was 3×10^{-4} Hartree/Bohr; the convergence tolerance in SCF cycles was 1×10^{-8} .

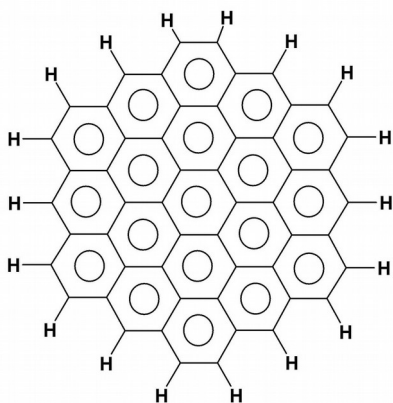


Fig. 1. Honeycomb network of the $C_{54}H_{18}$ cluster.

Based on the presented DFT calculations, it was found that the central cycle is aromatic having high delocalization energy of the π -orbitals and C=C bonds of edge cycles being on an intermediate level between aromatic and localized C=C bonds. Factually, the boundary C=C bonds are active sites in electrophilic addition reactions. They take part in the oxidation reactions on the surface of AC. These bonds are more chemically active compared to other active sites, including C-H bonds in aromatic cycles. It was shown that the oxidation of the surface with the formation of OH groups does not affect the possibility of bromination of the remaining C=C bonds, but only decreases their number. Here, the bromination and oxidation reactions are competing processes. There is a correlation between them established experimentally. When $-COOH$ or $-C=O$ groups forming on the carbon surface, the bromination reaction becomes

much less reliable, which is explained by the acceptor effect of these groups. In comparison with $-OH$ groups, these groups inhibits the bromination reaction, which is associated with the decontamination of active sites—surface C=C bonds. Thus, the ability to brominate the active sites of the oxidized carbon surface is investigated, which helps to understand the carbon reactivity taking into account the reactions at active sites on the carbon surface.

ELABORATION DE MATERIAUX A PARTIR D'UN BIOPOLYMER, ETUDE DE LEURS PROPRIETES PHYSICO-CIMIQUES

DEVELOPMENT OF MATERIALS FROM A BIOPOLYMER, STUDY OF THEIR PHYSICO-CHEMICAL PROPERTIES

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Abstract

Colloids are now essential in many industrial sectors (Painting, food processing, chemistry, textile, pharmacy ...) ^{1,2}. Colloids extracted from seaweed account for 40% of the world market for colloids and they constitute the main way of valorisation of algae.

There are three families of phycocolloids: agars, carrageenans and alginates. It is the rheological properties of alginates that are of industrial interest ³. Indeed, they are mainly used as thickening agent, texturizing, bonding agent for soldering electrodes, flocculant in water treatment, gelling agent, stabilizer for paints and varnishes, or film-forming agent.

Currently, the industry still uses the extraction protocol that was proposed in the 1970s. Our work focuses on the chemical modification of alginic acid using a simple and efficient synthesis process to enhance this biopolymer and transform it into a new material endowed with new physicochemical properties. The results we have obtained concerning the potential applications of the synthesized products are very promising.

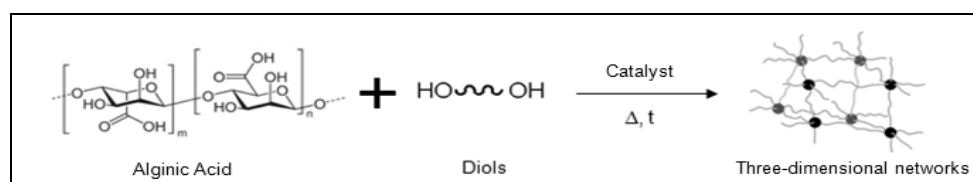


Fig.1: Chemical modification of a biopolymer.

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EFFET DE LA STRUCTURE DE COPOLYMÈRES GREFT SUR LA SYNTHÈSE IN SITU DE NANOPARTICULES D'ARGENT

THE EFFECT OF GRAFT COPOLYMER STRUCTURE ON *IN SITU* SYNTHESIS OF SILVER NANOPARTICLES

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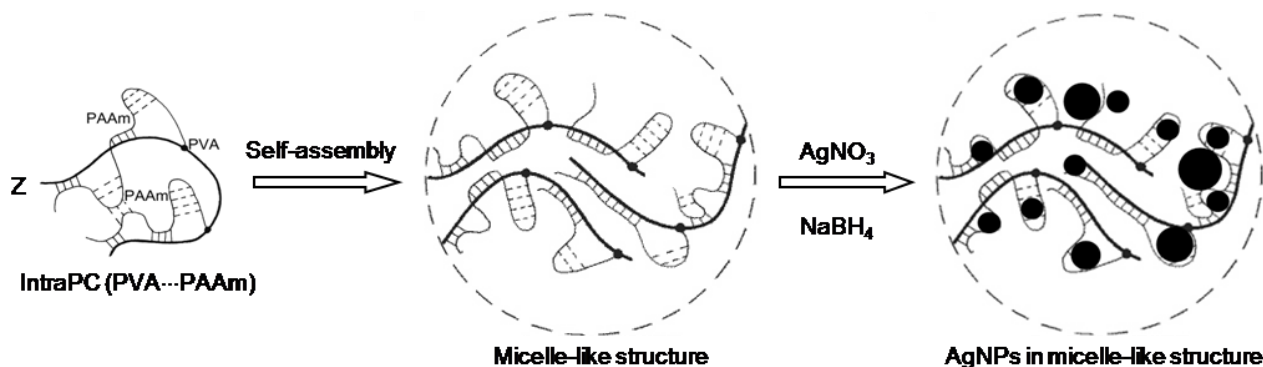
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A series of grafted PVA-*g*-PAAm (GCs) copolymers containing chemically complementary poly(vinyl alcohol) and polyacrylamide with a variable number and length of grafted chains, was synthesized in an aqueous medium using the radical template “grafting from” polymerization technique. A constant concentration of the matrix (PVA with $M_w=90$ kDa) and different concentrations of the redox initiator and monomer were used, which determined the quantity and length of the grafts. The changes in the number N of grafted chains from 10 to 40 per one copolymer macromolecule were found. Due to the interaction between the chains of PAAm and PVA through hydrogen bonds, the GC macromolecules formed intramolecular polycomplexes in aqueous medium, self-assembly of which led to the appearance of micelle-like structures (Figure).

High activity of GCs as templates was revealed in the processes of *in situ* synthesis and stabilization of silver nanoparticles (AgNPs) in water. The kinetic regularities of the formation of AgNPs and the yield of nanoparticle were established using the position and integrated intensities of the surface plasmon resonance band (SPRB) of nanoparticles in UV-Vis spectra. The graft copolymers with micelle-like structure in aqueous solutions (Figure) provided a high rate of formation, a large yield of AgNPs as well as their long-term stabilization in time. An interesting effect of a sharp decrease in the maximum position of SPRB at 16-19 nm in a narrow time interval (~ 3 min) was observed with the accumulation of a large quantity of AgNPs in the reaction mixture. Due to this phenomenon, the process of regularization (crystallization) of primary AgNPs can be fixed in time. The increase in the number of grafts in the copolymer macromolecules from 10 to 40 led to an increase in the yield of nanoparticles, especially at low concentrations of the polymer template. The mechanism of AgNP formation has been separately studied.



The obtained AgNPs/GC compositions were studied using transmission electron microscopy and wide-angle and small-angle X-ray scattering. It was shown that the AgNPs synthesized had a crystalline structure, spherical shape, small size (<10 nm), and low polydispersity. The compositions AgNPs/GCs in a bulk state demonstrated the two-level fractal organization of their structure. Silver nanoparticles with a small size and a smooth surface constituted the 1-st lower level of the fractal structure of the composition, and the mass-fractal clusters of the graft copolymer matrix formed the 2-nd higher level of this structure.

ADSORPTION EFFICACE DE LA RHODAMINE B SUR UN NANO-TALC DE SYNTHÈSE : VERS LA COMPRÉHENSION D'UN PROCESSUS INATTENDU

EFFICIENT ADSORPTION OF RHODAMINE B ONTO A SYNTHETIC NANO-TALC: TOWARDS THE UNDERSTANDING OF AN UNEXPECTED PROCESS

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Synthetic clay minerals of nanometric dimension are layered solids that offer unique control over the chemical structure and physical aspect. Their combination with organic dye molecules leads to organo-mineral hybrids that can be tailored to promote specific optical properties.¹ Since 2006, our team has elaborated a new synthetic talc (ST) under hydrothermal conditions.² This mineral shares some similarities with natural talc, in particular the lamellar tetrahedral-octahedral-tetrahedral (TOT) structure. It also has several distinctive features such as its submicronic size (Fig.1a), hydrophilic behaviour and chemical purity. Moreover ST shows strong and unprecedented adsorption potential towards charged organic dye molecules.^{3,4} This behaviour is particularly intriguing because non-swelling clays like talcs do not contain exchangeable cations, and are therefore known to interact very weakly with organic molecules.

In this work, very stable organo-mineral hybrids were prepared from ST and Rhodamine B (RhB) (Fig.1b). The interactions involved were thoroughly analyzed using complementary analytical techniques (XRD, NMR, IR, electron microscopy, UV-visible absorption and fluorescence spectroscopies). In particular, equilibrium data acquired at various temperatures were fitted to access the thermodynamic parameters.

The elaboration of such nanocomposites is easy, cost-effective and versatile. This study opens a new route towards optical brighteners, cosmetics and fluorescent polymers.⁴ Applications could also be found in the fields of paper milling, inks and depollution.

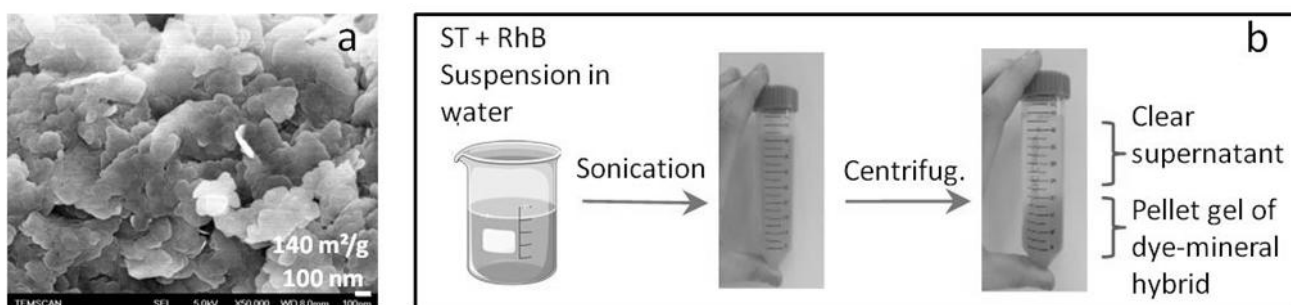


Figure 1. a) Scanning electron microscopy image of ST. b) Schematic preparation of synthetic talc rhodamine B hybrid.

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NANOLITHOGRAPHIE CATALYTIQUE A SONDE LOCALE:
FONCTIONNALISATION DES MONOCOUCHEES
AUTO-ASSEMBLEES ET DU GRAPHENE

CATALYTIC SCANNING PROBE NANOLITHOGRAPHY:
TOWARDS SELF-ASSEMBLED MONOLAYERS
AND GRAPHENE FUNCTIONALIZATION

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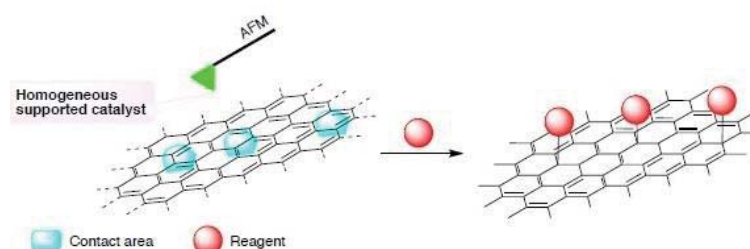
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Nowadays, graphene takes pride of place among two-dimensional materials owing to its unique properties: it is the strongest, thinnest and stiffest material with high electrical and thermal conductance, which enables its potential applications in electronics, biotechnology and energy.¹ Nevertheless, a zero band gap of graphene and its low chemical reactivity raise difficulties for its different applications. It is possible to overcome this obstacle by the functionalization of graphene layers, which allows tuning both chemical and electronic properties. During the last years, many approaches to graphene covalent and non-covalent functionalization were reported,^{2,3} but only a small part of them provides a spatial control.⁴⁻⁶ Scanning probe nanolithography (SPL) is an appropriate method to achieve this goal, but until present time rarely used for graphene.

Previously, our group has successfully implemented catalytic SPL technique to carry out the epoxidation of an alkene-terminated self-assembled monolayer immobilized on SiO₂ at the nanoscale (a spatial resolution of 30 nm) by means of an organometallic catalyst grafted on the apex of the atomic force microscope (AFM) probe.^{7,8}



In the frame of the present work, this approach was extended to the graphene functionalization. In order to confirm our concept, a graphene monolayer grown by chemical vapor deposition was oxidized by a manganese (II) complex grafted onto the AFM tip in the presence of hydrogen peroxide solution in acetonitrile. To develop this method and to demonstrate its versatility, the application of other catalytic systems is envisaged.

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GREFFAGE CHIMIQUE DE SULFO-OXYGENE GROUPE SUR DES FIBRES DE CARBONE

CHEMICAL SULFOGROUPS GRAFTING ON CARBON FIBRES

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For adsorption and catalytic processes, carbon fibers (CFs) should have high thermal and mechanical resistance and developed porosity. To be convenient for the modern chemical industry, CFs adsorbents and catalysts are manufactured in the form of woven and nonwoven textiles. One can achieve significant surface acidity of CFs by chemical grafting. This approach introduces the functional groups of different chemical nature into the surface layer. Resulted carbon solid acids are prospective low-temperature heterogeneous catalysts having hydrolytically resistive sites of high acidity.

Treatment of CFs with oleum or sulfuric acid is the main method for obtaining CFs with grafted sulfogroups. The highest concentration of sulfogroup can be also obtained by sulfurization of carbon materials carbonizable in part. However, the obtained in such way acid catalysts have unsatisfactory mechanical characteristics and insufficient chemical resistance. These complicate the use of acid catalysts in liquid phase processes when heated. The use of catalysts obtained by impregnation methods is limited to gas-solid interface processes because of the leaching of the active component into the reacting solutions.

Covalent bonding of sulfogroups requires new synthetic methods that maintaining the textural parameters of CFs based on polyacrylonitrile. For preparing precursors to sulfonated CFs, here we consider the bromination of double bonds. We reported on the reactive for the bromination separate and conjugated C=C sites.

Bromination of CFs both with liquid bromine and an aqueous solution of Br₂·KBr complex provides up to 0.5 mmol/g of grafted bromine. This grafted bromine is stable and does not hydrolyze being kept in an air or in water for a long time. Short-term boiling in distilled water does not hydrolyze the brominated surface, but hydrolysis occurs under treatment with alkali, at heating.

Sulfidation of the brominated CFs was carried out with sodium sulfide and sodium mercaptoacetate, and the following hydrolytic oxidation has resulted in the sulfonated CFs. They were examined by nitrogen adsorption, TG/DTG, TPD MS, FTIR, Boehm titration and tested as catalysts in the propanol-2 dehydration to propylene.

In fact, the sulfonated CFs that prepared by using sodium sulfide showed the highest catalytic activity, the lowest activity is observed for the CFs that sulfonated by the direct method and having the lowest SO₃H coverage. The total conversion over the most active catalysts takes place at 195–220 °C. For catalysts prepared from non-brominated CFs, this temperature is by 40–65 °C higher.

The low catalytic activity of the pristine CFs, of about 20% propylene yield, can be explained by the action of various oxygen-containing groups. These groups, e.g. carboxyl groups, support the highest acidity when involved in the dehydration reaction. Since their acidity is much less than that of sulfo groups, the total conversion of alcohol could not be reached. When bromine-containing CFs were contacted with sulfating reagents, solid acids with high catalytic activity in the dehydration reaction of isopropanol were obtained. Using bromine-containing precursors resulted in the grafting of a larger number of acidic groups into the surface layer than in the case of the pristine fiber. This leads to an increase of the catalytic activity, especially in the case of modification with sodium sulfide giving advanced surface acidity.

The methodology presented here can be easily scaled up to industrially relevant quantities. This work opens the door to environment saving strategies which can be applied if using sulfonated CFs as solid acid catalysts, to substitute strong acids.

NOUVEL ACIDE AMINÉ FLUORESCENT ALPHA-SUBSTITUE CONÇU COMME UNE ETIQUETTE POUR LES ETUDES PEPTIDIQUES

A NOVEL ALPHA-SUBSTITUTED FLUORESCENT AMINO ACID DESIGNED AS A LABEL FOR PEPTIDE STUDIES

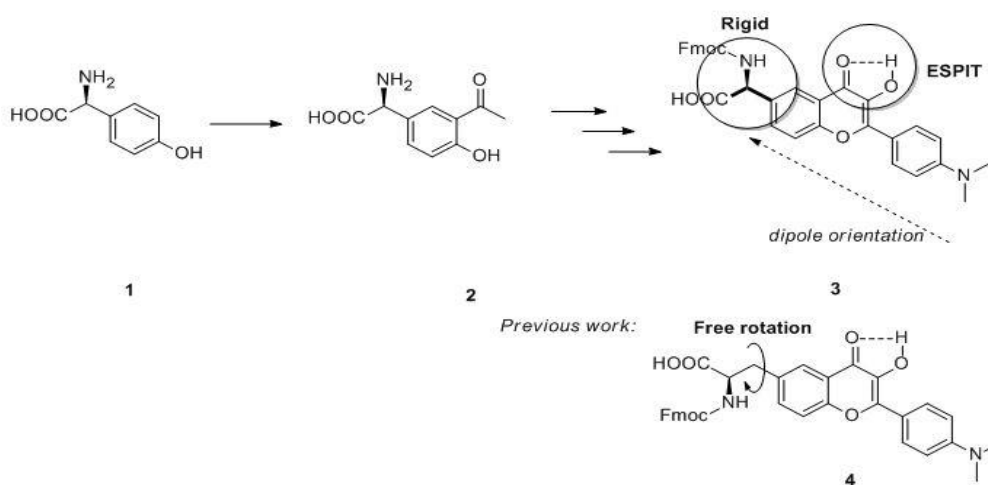
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Fluorescence spectroscopy and imaging are powerful tools for probing complex biological processes involving different types of biomacromolecules. The ubiquity of proteins and peptides in these processes has made them important targets for fluorescence labeling. It can be achieved by two main methods: terminal labelling (at C- or N-terminus) by fluorescent dye or fluorescent amino acid incorporation into backbone of the target macromolecule. This approach allows read out various information about local microenvironment at the labelling site, concerning location, interactions with other biomolecules, and macromolecular dynamics. The nature of chromophore plays key role in the readout process, multichannel probes based on 3-hydroxychromone allow us to determine many local parameters, due to intramolecular proton photo transfer process (ESPIT), including local hydration, pH and spatial orientation of chromophore.

In our previous work, we described synthesis of phenylalanine analog **4**, based on 3-hydroxychromone, and its incorporation into membrane-active peptide melittin and study of its orientation in the membrane media by fluorescence anisotropy [1]. The main drawback of label **4** was non-rigid chromophore attachment to peptide chain, which leads to less definition of spatial orientation of peptide read by fluorescence anisotropy imaging. Our goal was to synthesize a novel fluorescent amino acid, which would be rigidly attached to the backbones when incorporated into peptide molecules. In present study, we developed simple 6-step synthesis of α -substituted fluorescent amino acid **3**



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SPIN CROSSOVER MOLECULAR LAYER ON SUBSTRATE: STUDY OF ITS FORMATION AND ITS USE FOR AN OPTICAL APPLICATION.

FILM MOLECULAIRE D'UN COMPLEXE A TRANSITION DE SPIN SUR SURFACE: ETUDE DE SA FORMATION ET SON UTILISATION DANS LE DOMAINE DE L'OPTIQUE.

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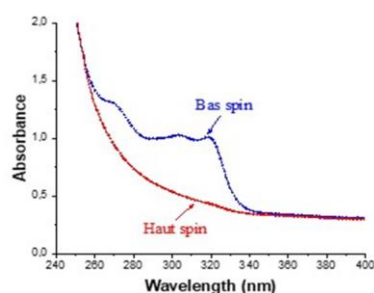
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We have recently been extensively investigating the molecular spin crossover compound $[\text{Fe}^{\text{II}}(\text{HB}(\text{tz})_3)_2]$ ($\text{tz} = 1,2,4\text{-triazol-1-yl}$) (**1**).^{1,2,3,4} It is characterized by an isostructural and abrupt first-order spin transition between its LS and HS configurations, near room temperature (*ca.* 333 K), with a narrow thermal hysteresis loop (*ca.* 2 K width). Moreover, this compound is one rare example of sublimable spin cross-over complexes (globally neutral with low molecular weight), therefore SCO materials of complex **1** can be prepared by evaporation on a substrate. These films can potentially be used for optical applications since molecular layers of **1** are homogeneous, crystalline and with a very high purity and tight thickness control.⁵ The complex in the low spin (LS) state has significantly different chemical and physical properties from the complex in the high spin (HS) state. If we focus on the optical properties, the complex in LS state absorbs much more in UV than the complex in HS state. We should stress that a well crystalline film has a much larger Δ_{Abs} than an amorphous one. The presentation deals with the study of the formation of molecular film of SCO on glass substrate as well as the use of the large Δ_{Abs} in an optical application.



Complex **1**



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SYNTHESE, CHARACTERISATION, PROPRIETES SPECTRALES DE MILIEUX HOLOGRAPHIQUES POLYMERES A BASE DE ROUGE CONGO

SYNTHESIS, CHARACTERIZATION, SPECTRAL PROPERTIES OF CONGO RED BASED POLYMERIC HOLOGRAPHIC MEDIA

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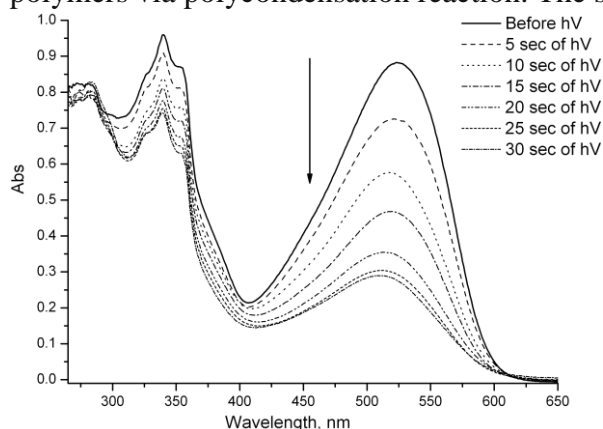
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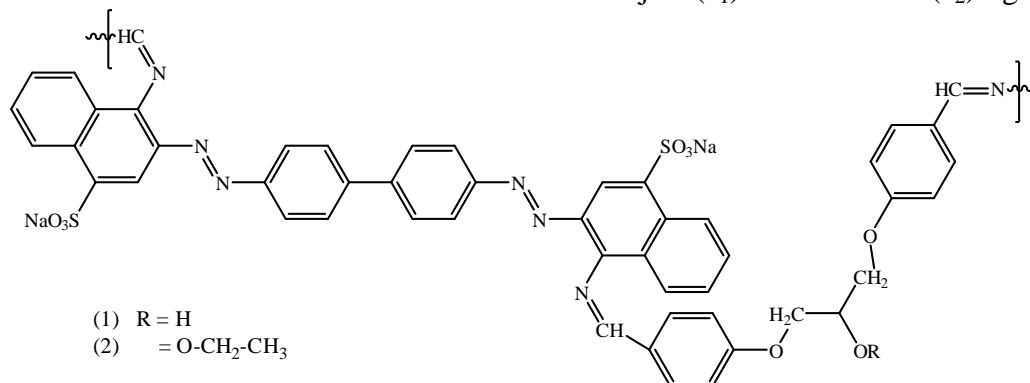
Films of polymers and polymeric composites containing azomethine and/or azobenzene dyes as main and side chain groups are of interest due to possibility of their usage as optically active media, in particular as light controlling elements and polarization sensitive media for optical holographic recording. Linearly polarized light is absorbed by the azo-/azomethine groups resulting in changes of isomeric structure. Photoinduced anisotropy of the polarization appears in the films due to changes of concentration of *trans*- and *cis*-isomers of the azobenzene groups.

In the present work, a poly-Schiff base was obtained from reaction of Congo Red with 1,3-Bis(4-formylphenoxy)propan-2-ol (1) and 1,3-bis(4-formylphenoxy)propan-2-yl propionate (2) to give polymers via polycondensation reaction. The synthesized polymeric Schiff bases were characterized by



¹H NMR, FT-IR, UV and DSC techniques. The thin films (~2 μm) of synthesized polymers have been prepared. To study the effect of the substitution of the free hydroxyl group (1) to the propionic group (2) on both the kinetic parameters of isomerization upon irradiation with light from a wavelength of 254 nm were measured. and the stability of the solutions upon irradiation, changes in the absorption spectra of the polymers upon irradiation with light from a wavelength of 254 nm were measured

Experimental study of the holographic recording and relaxation kinetics of a plane wave front in recording media based on azomethine-azobenzene based polymers have been carried out. The holograms were recorded using a semiconductor laser (532 nm) for parallel ($e_1 \parallel e_2$) and perpendicular ($e_1 \perp e_2$) orientations of the electric vectors of the incident object (e_1) and reference (e_2) light waves.



The dependences of the diffraction efficiency for both cases $\eta_{\parallel}(t)$ and $\eta_{\perp}(t)$ on time t after start and completion of the hologram exposure were measured. After the exposure completion, the relaxation kinetics $\eta_{\parallel}(t)$ and $\eta_{\perp}(t)$ were measured using a object beam with a different direction of polarization with respect to the polarization of the reference beam.

SYNTHESE ET PROPRIETES MECANQUES DE COMPOSITES A BASE D'ALGINATE ET PHOSPHATES DE CALCIUM MODIFIES

SYNTHESIS AND MECHANICAL PROPERTIES OF COMPOSITES ON THE BASE OF ALGINATE AND MODIFIED CALCIUM PHOSPHATES

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Hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and its derivations belong to unique class of compounds which has a considerable industrial, technological and biotechnological interest. It is widely used in the repair, reconstruction, and replacement of diseased or damaged parts of bones or teeth owing to its high biocompatibility and bioactivity, as catalyst of organic reactions, adsorbent for separation of proteins, carrier for antimicrobial effect or drug carrier etc. Much interest was focused on the chemistry of zinc and copper substituted HAP. These materials have the high antibacterial activity, low toxicity, and chemical stability. The antibacterial nature of such metal ions is utilized in the synthesis of biomaterials used for bone tissue.

The main disadvantage of materials based on calcium phosphates is their brittleness, so design of composites based on phosphate and natural polymers allow to solve this problem and obtain the functional materials with improved mechanical characteristics for orthopedic.

This report is devoted to synthesis and investigation of hybrid phosphate-alginate composites on the base of apatite-related Cu^{2+} or Zn^{2+} -containing calcium phosphates. On the first stage, apatite-related Na^+ , CO_3^{2-} -containing calcium phosphate were synthesized by wet precipitation. Cu^{2+} , Zn^{2+} and $\text{Cu}^{2+}/\text{Zn}^{2+}$ ions were incorporated in phosphate matrix using sorption process from aqueous solutions of copper and zinc nitrates ($C(\text{M}^{2+}) = 0.002, 0.02$ and 0.1 mol L^{-1}). Then composites consisting of Na^+ , (Cu^{2+} or Zn^{2+}), CO_3^{2-} -containing calcium phosphate and alginate were fabricated in the form of microspheres (Fig. 1).

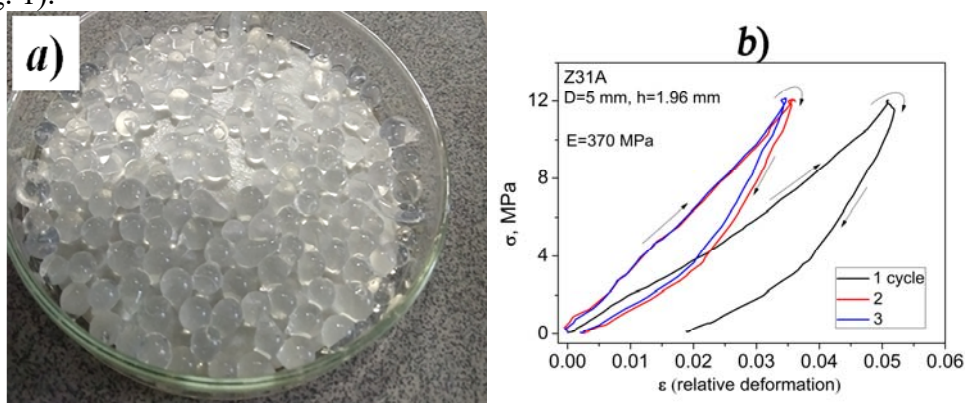


Fig.1. Photo of obtained microspheres Na^+ , Zn^{2+} , CO_3^{2-} -containing calcium phosphate-Alg composite (a) and its “loading-unloading” diagram measured at uniaxial compression during 3 loading cycles (b).

All fabricated samples have a high Young's modulus (370-747 MPa), and their compressive strength is in the range 233-255 MPa, that is within the value for the cortical bone. At the same time, samples containing Alg are characterized by a large plastic deformation with compressing (Fig. 2).

The obtained results can be used at creation of effective biomaterials containing dopant with antibacterial activity.

CHAMP DE FORCE POLARISABLE POUR DES SIMULATIONS DE DYNAMIQUE MOLÉCULAIRE DE LIQUIDES IONIQUES

POLARISABLE FORCEFIELD FOR MOLECULAR DYNAMICS SIMULATIONS OF IONIC LIQUIDS

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Molecular dynamics simulation is a technique of choice to study the interactions and properties of systems of molecular level. The force field plays one of the most important roles in atomistic modelling, describing both intra and intermolecular terms. Traditional force fields keep the charges on the atoms fixed, with polarisation included implicitly and represented by an effective Lennard-Jones (LJ) or similar potential. Despite a good description of the structural and thermodynamic properties, fixed-charge models predict too slow dynamics when compared to experiment. This problem can be solved if polarisation is added explicitly by introducing induced point dipoles,¹ fluctuating charges² or induced Drude dipoles.³ In order to avoid double counting of the polarization (induction) interactions, the parameters of the underlying fixed-charge model should be rescaled, so that the Lennard-Jones potential only accounts for repulsive and dispersive interactions.

Proper scaling of LJ parameters can be derived from an evaluation of the induction and dispersion terms using Symmetry-Adapted Perturbation Theory (SAPT),⁴ as shown in our previous study.⁵ It resulted in an improved prediction of viscosities and diffusion coefficients, whereas structural properties did not undergo significant changes for several representative ionic liquids.

In the present work we propose an efficient, fragment-based method to adapt existing fixed-charge force fields upon introduction of explicit polarization. It requires simple molecular properties, such as electrostatic charges, dipole moment and atomic polarizabilities,⁶ to be calculated, avoiding expensive SAPT calculations to evaluate the induction and dispersion components. The approach suggested was successfully used for imidazolium, pyrrolidinium, pyridinium and quaternary ammonium ionic liquids and their mixtures with molecular solvents (acetonitrile and dimethyl sulfoxide).

In order to test the force field, we performed molecular dynamics simulations of pure ionic liquids and of mixtures with molecular compounds. It was shown that density, viscosity and self-diffusion coefficients were predicted with reasonable, consistent levels of uncertainty, much improved from those of fixed-charge models.

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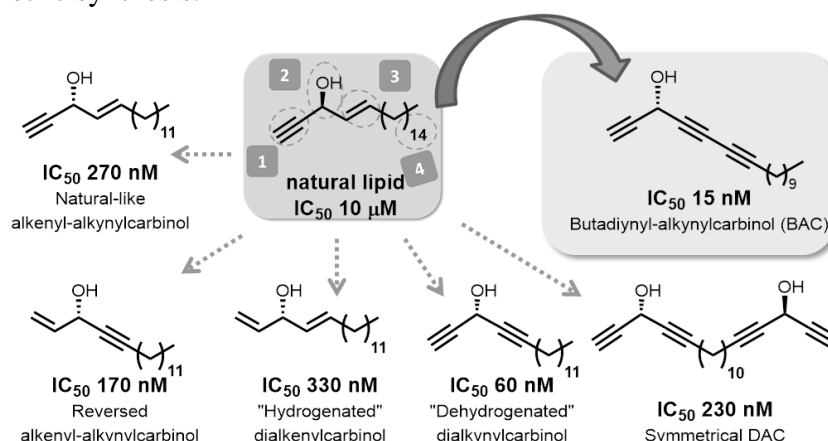
DÉVELOPPEMENT DE LIPIDES ACÉTYLÉNIQUES ANTITUMORAUX BIO-INSPIRÉS À PHARMACOPHORES ALCYNYLCARBINOLS

BIO-INSPIRED ANTITUMOR ACETYLENIC LIPIDS BEARING ALKYNILCARBINOL PHARMACOPHORES

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More than 40% of antitumoral drugs are originally inspired by natural compounds.¹ Identification of potent bioactive species, as well as deep understanding of their mechanism of action is thus of great importance. Over the past decades, natural acetylenic lipids have been isolated from a wide variety of aquatic organisms. Those acetylenes are of particular interest since many of them display important biological activities including immunosuppressive, antitumor and antibacterial properties.² Isolated from marine sponges, an intriguing subclass of these marine acetylenic lipids are characterized by the presence of a chiral alkynylcarbinol moiety along a linear carbon skeleton. This terminal motif is a key pharmacophore for the most cytotoxic derivatives, which display anti-tumoral activities with IC₅₀ in the nanomolar range.³ This work aims at exploring the pharmacological potential of bio-inspired functional acetylenic lipids, while delineating structure-activity relationship and unraveling their mode of action. A systematic study of the chiral alkynylcarbinol pharmacophore is realized on the basis of structural variation of the natural product embedding a typical alkenyl alkynylcarbinol fragment. A truncated synthetic analogue with an original dialkynylcarbinol pharmacophore turned out to be 170 times more potent than the natural compound of reference in HCT116 cells.⁴ Other bio-inspired⁵ sophisticated analogues of C2-symmetry,⁶ as well as fluorescent probes,⁷ and ethnylogues⁸ were prepared by asymmetric synthesis.



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THE MATHEMATICAL MODEL OF FORMATION OF POLYACRYLAMIDE HYDROGELS REINFORCED BY POLYPROPYLENE NETS

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The polyacrylamide hydrogel reinforced by polypropylene nets combines the properties of polymers of different nature. The hydrogel structure provides biocompatibility with the tissues of a living organism, the ability to absorb and release drugs, elasticity, and atraumaticity. The material of the reinforcing polymer provides the necessary mechanical strength when applied. That's why the application of hydrogels requires their covalent fixing on the polymer surface. Such hydrogel structures have been repeatedly described in literary sources [1-3]. In these works, it is described the process of formation of these compositions occurs due to the initiation of radical copolymerization of acrylic monomers. In particular acrylamide (AA), N,N'-methylene-bis(acrylamide) (BAA), potassium acrylate at the same time from the peroxidized surface and initiator in the volume of the reaction mixture.

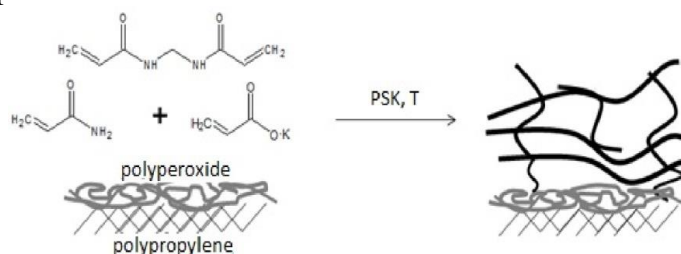


Figure 1. The formation of polyacrylamide hydrogel reinforced by polypropylene nets

The effectiveness of such a fixation of a gelled polymer on the surface to a large extent depends on the concordance of processes. In this paper based on the theory of branching processes, have been made the attempts to construct mathematical models of this process, which would satisfactorily describe the existing experimental material and allow to identify the main factors that influence the concordance of the process and allow its optimal control. In particular, based on the statistical methods of the theory of branching processes is obtained an equation of the dependence of the gelation conversion X_g . It describes the experimental dependence of this parameter according to the synthesis conditions:

$$X_g = 2^{\frac{3}{4}} \frac{\sqrt{k_{11}} \sqrt[4]{k_d k_i} \sqrt[4]{[PSK]_0}}{k_{13} \sqrt{[BAA]_0}}$$

k_{11} , k_{13} - the constant of the chain continuation accordingly to the homopolymerization of AA and copolymerization of AA with BAA;

k_d - the constant of chain termination by disproportionation; k_i - constant of initiation;

PSK - potassium persulfate; BAA - N,N'-methylene-bis(acrylamide).

Based on the equations of the model is shown the dynamics of the ratio of the sol-gel fraction of the structured polymer from the beginning of gelation to the deep stages of the process are detected the stages of the fixing process of the gelation polymer to the peroxidized surface.

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MICROHYDROGELS BASED ON POLYSACCHARIDES AND TWO-BASE α -AMINO ACIDS SYNTHESIZED BY THE STEGLICH REACTION

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Last decades polysaccharides become more and more interesting substance as a base for various biomedical applications, due to their non-toxicity, widespread in nature, low cost, and toleration to the human body. The combination of such properties of polysaccharides with the idea of forming microhydrogels for biomedical purposes can give a significant success.

To achieve set goals, in this theses we present investigation of the interaction between dextran, dextrin, as representatives of polysaccharides, and N-derivates of glutamic acid, as structuring agent, by Steglich esterification (the scheme of interaction is shown on fig.1).

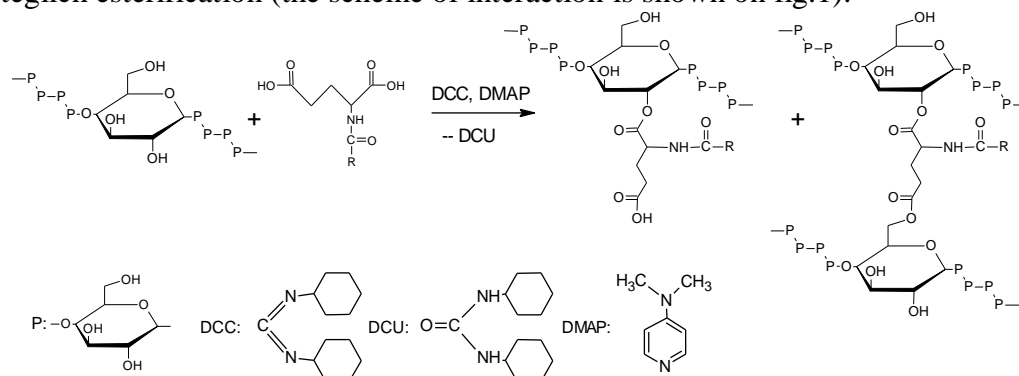


Fig. 1. Scheme of interaction between polysaccharides and N-derivates of glutamic acid

During study was found that as a result of the interaction, on a high conversion level, two different products have been obtained – polysaccharide with branched structure and polysaccharide with structured structure (volumetric structured grid). Using alcohol sedimentation, we managed to divide these products with next characterization of their structure and colloid-chemical properties.

Depending on the ratio of incoming reagents, the effectiveness of grafting and cross-linking of structured agent could be changed. This conclusion was made from mathematical processing of results from ¹H NMR spectroscopy of obtained products. That is why, relying on the different amount of structural agent, can be explained different swelling ability, because in all range of correlation of input reagents we obtained hydrophobic, with the limited swelling ability and infinitely swollen products of modified polysaccharides with volumetric structured structure.

The characteristic of self-stabilization of aqueous dispersions is a structural and mechanical barrier, which in turn is characterized by the ability of solvation, or binding of water molecules. We investigated this ability of both products and showed that branched structure can bind the amount of water that binds the unmodified polysaccharide, that means the possibility of access of water molecules to the whole chain of modified polysaccharide. The structured structure product displays such properties only at a certain ratio of the input components.

Investigation of the particle size showed that the particle size of the product with a branched structure depends on the concentration. To the break on the curve of surface tension isotherms, we received particles with sizes close to 200 nm, at higher concentrations, after the break, these dimensions were in the region of 500-800 nm. The particles of the product of the volumetric structured grid are much larger and are in the region of 4000 nm.

An important characteristic of hydrogels for the biomedical purpose is the ability to bind water-soluble proteins. Therefore the sorption of albumin was studied. On the gel electrophoregram, it has been shown that the product of volumetric structured grid binds albumin in three times better than the product with branched structure.

Within this study was establish the toxicology of obtained products and was showed that, in some cases, the percentage of cell survival from the control group was higher.

SPECTRAL PROPERTIES OF EXPANDED π -SYSTEMS: LIGHT ABSORPTION AND EMISSION OF A TETRAPHENYL CARBO-BENZENE

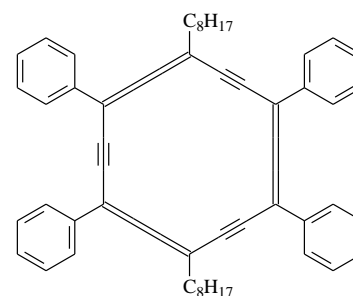
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Carbo-benzenes constitute a relatively new class of organic dyes with a quite unique π -electronic system. While many reports have been devoted to the synthesis of such molecules,^[1] the relative peculiarities of their ground and excited states, their full spectral behaviour, and more generally their one-photon optical properties, have been only partly investigated at the experimental level.^[2]

Results of systematic investigations of the spectral properties of *para*-di-*n*-octyltetraphenyl-*carbo*-benzene (CB) are presented.^[3] The absorption, fluorescence emission and excitation spectra of CB in different solvents and in a wide range of concentrations have been studied. Theoretical predictions of the electronic spectrum of *carbo*-benzenes and confrontation with experimental data showed that all the absorption bands in the range 400–600 nm are due to electronic transitions involving orbitals localized on the *carbo*-benzene core, and can be interpreted by the four-orbital Gouterman model (originally devised for porphyrins).^[2a] Local phenyl transitions and charge transfer transitions between the phenyl and *carbo*-benzene cores were not found.



Investigations of the absorption band positions in solvents of different polarity and nucleophilicity demonstrated the absence of solvatochromism, in agreement with the vanishing dipole moment of the quadrupolar CB molecule in the ground and Franck-Condon excited states, and also with the absence of possible specific interactions between nucleophilic solvent molecules and the CB π -system.

CB exhibits a weak fluorescence, whose intensity decreases with increasing solvent polarity. Measurements of the emission spectra at 70 K showed the absence of phosphorescence: the predominant way of CB fluorescence quenching is thus most likely due to internal conversion $S_1 \rightarrow S_0$.

Fluorescence spectra of CB display three emission bands centered at 550–560, 590–600 and 605–620 nm. The ratio of short-wavelength and long-wavelength bands intensities depends on the CB concentration. The intensity of long-wavelength emission band increases in concentrated CB solutions. Taking into account similarity of the excitation spectra measured for fluorescence at 550 and 610 nm, it is possible to suppose that the long-wavelength emission band is due to an excimer form, and, perhaps, to aggregation-induced emission (AIE).

No solvatofluorochromic effects were detected. This fact, together with very low values of Stokes fluorescence shifts evidence negligible structural and solvent relaxations of CB upon the excitation.

The aim of present work was to study the relationship between CB spectral properties and its electronic structure. The obtained results can be useful for the design of new *carbo*-benzene targets with more or less predetermined spectral characteristics.

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SYNTHESE DE SULFAMIDES A BASE DE 2-PYRROLIDONE

SYNTHESIS OF SULFAMIDES ON THE BASIS OF 2-PYRROLIDONE

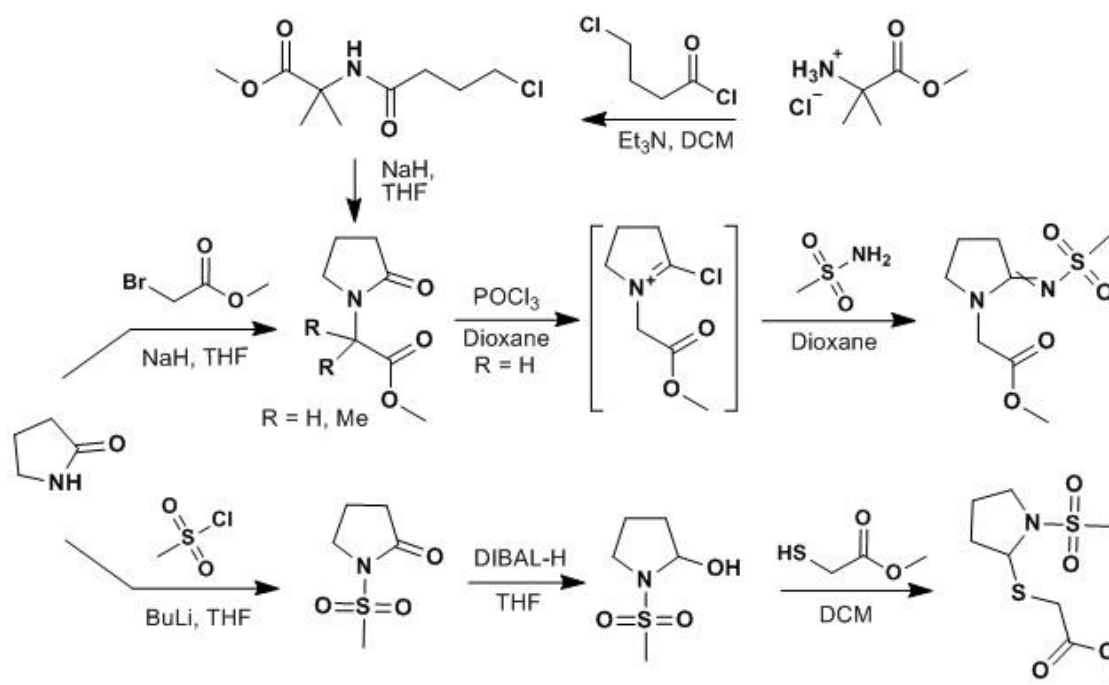
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To date, the fight against cancer has taken a leading place among scientists engaged in medical chemistry. The development of ways to synthesize new drugs that potentially have anti-cancer properties is the first step towards overcoming this disease.

A large number of scientific works are devoted to such a class of compounds as sulfamides. It has been proven that they really have antitumor activity; many of them are also antimicrobial and antidiabetic drugs. And their cyclic analogues (sultames) have an even more powerful action.

In our study, we decided to combine sulfamides with another base of pharmaceutical blocks - pyrrolidine. 2-Pyrrolidone derivatives, for example, take part in the preparation of the racetam group.



In our opinion, the ways of synthesizing modified sulfamides based on 2-pyrrolidone have a great scientific interest. So, we have synthesized several precursors, which in our future developments will be transformed into sultames.

NANOPARTICULES EUMELANIN: STRUCTURE CHIMIQUE, PROPRIETES PHENOSENSIBLES ET MORPHOLOGIE EN MILIEU AQUEUX

EUMELANIN NANOPARTICLES: CHEMICAL STRUCTURE, PH-SENSITIVE PROPERTIES AND MORPHOLOGY IN AQUEOUS MEDIUM

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Melanins of different nature belong to polyphenolic compounds. An important role in their formation is played by the amino acid tyrosine and tyrosinase enzyme, which "launches" the first stages of biosynthesis of melanins. Eumelanins (EM) are formed by oxidation of tyrosine (and / or phenylalanine) with tyrosinase to o-dihydroxyphenylalanine and its quinone derivative, which is subsequently cyclized to 5,6-dihydroxyindole (DHI) or 5,6-dihydroxyindole-2-carboxylic acid (DHCA) (Figure 1).

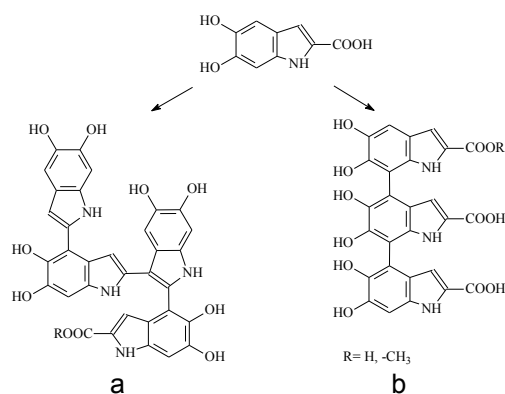


Figure 1. Chemical structure of linear (b) and branched (a) eumelanin molecules based on DHICA

Thus, the black to brown eumelanin is now generally accepted to be a highly heterogeneous macromolecule based on DHI and DHICA units and their oxidized states coupled in oligo- and polymeric structures.

The current work presents a detailed study of chemical structure, solubility, electrochemical and absorption properties of EM sample, which is the vital activity product of black yeast "*Nadsoniella nigra* sp. X-1". The existence in the melanin molecules of indol aromatic rings, phenol hydroxyl groups and some ester groups (-OCOCH₃) formed instead carboxylic ones was established by ¹H NMR spectroscopy. It is revealed the zwitter-ionic character of eumelanin macromolecules due to a presence the charged >NH₂⁺ and -COO⁻ groups in a solid EM sample by FTIR spectroscopy. Acidic properties of both types of the groups were characterized using potentiometric titration. The existence of the region of the buffer capacity minimum at pH=7.94 allowed to calculate the amount of -COO⁻ and >NH₂⁺ groups in 1 gram of EM sample (2.96 and 10.84 mmol·g⁻¹, respectively). Thus, in the examined EM sample was found a significant surplus (3.66 times) of the amine groups in relation to the acid groups. The values of pK₀ were equaled to 4.84 and 9.94 for carboxylic and amine groups consequently. A strong compactization of EM macromolecules in the pH>6 region, which is accompanied by a phase separation of the system, was established. Thus, it was shown that the state and solubility of melanin in aqueous medium is determined by a complex balance of electrostatic interactions and hydrogen bonds. The real state of EM macromolecules in aqueous medium at pH=6 was shown by the TEM images.

PLATEFORME INTEREGREE DE CRIBLAGE DE TOULOUSE (PICT) : UN OUTIL D'ACCELERATION DE LA DECOUVERTE MOLECULAIRE

THE INTEGRATED SCREENING PLATFORM OF TOULOUSE (PICT): A TOOL FOR ACCELERATED MOLECULAR DISCOVERY

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PICT (Integrated Screening Platform of Toulouse) is a multisite research and service platform that provides a complete package of technological solutions allowing: (i) the identification, rational design, preparation (synthesis, analysis and purification) and optimization of ligands of any target and the characterization (structure, dynamics and thermodynamics) of their interactions, (ii) the structural characterization of biological macromolecules, (iii) the discovery of original enzymes, and (iv) the rational and/or combinatorial optimization of enzymes.

Achievements of PICT regarding ligand discovery will be highlighted through several major research programs. Thanks to a combined structure-based virtual ligand screening/NMR based screening/chemical synthesis approach, a precursory chemotype was generated as a potential anticancer treatment sensitizing agent interfering with the XRCC4/DNA ligase IV interface, a protein-protein interaction essential for repairing of DNA double-strand breaks by non-homologous end-joining in humans.¹ In the field of interorganel lipid transfer protein, a unique homogenous time-resolved FRET-based binding assay for the ceramide transfer protein CERT allowed the discovery of the most potent ligand known to date, an alkylated analog of the archetypical CERT antagonist HPA-12 displaying an EC₅₀ three orders of magnitude lower than reference compound.²

The synergistic combination of chemical synthesis, chromatographic analysis and purification operating within the PICT proved also determinant for the study of several enantiomerically enriched chiral cytotoxic compound series. A large family of bio-inspired acetylenic lipids embedding a key alkynylcarbinol pharmacophore was developed.³ Analytical supercritical fluid chromatography was key to readily assess the stereochemical composition of all synthetic samples and demonstrate the determining impact of absolute configuration on cytotoxicity throughout a series of more than 90 derivatives. Synthetic chemistry-driven optimization led to analogs displaying antitumor activity three orders of magnitude higher than that of (*S,E*)-icos-4-en-1-yn-3-ol, the natural compound of reference.⁴ Finally, a straightforward synthetic route to both enantiomers of synthetic analogs of the natural anhydrosphingosine jaspine B was implemented thanks to preparative supercritical fluid chromatography-based enantiomeric resolution of racemic intermediates.⁵ The first example of clickable jaspine B derivative bearing an acetylenic tag at the terminal position of the lipid skeleton was thus developed.⁶ This study led to the first jaspine B analog more cytotoxic than the natural compound and delivered a unique tool for *in cellulo* click chemistry-based imaging, allowing correlation of the strong gap in cytotoxicity between both jaspine B enantiomers with their distinct intracellular localization profile.

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UN NOUVEL AGENT A BASE DE MANGANESE, EFFICACE POUR LA POLYMERISATION RAFT

A NEW EFFICIENT MANGANESE-CONTAINING AGENT FOR RAFT POLYMERIZATION

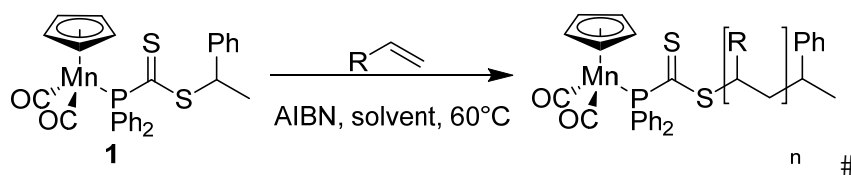
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Phosphorus-containing dithioesters are still rather scarce but their interest has grown in the last years because of their use as potential control agent in RAFT polymerization.^[1] In this contribution, we present a new manganese RAFT agent (**1**)^[2] of formula Cp(CO)₂MnP(Ph)₂C(=S)SCH(CH₃)Ph which was synthesized in a good overall yield by a three-step reaction from cymantrene and diphenylphosphine as the main starting materials.



Polymerization mediated by RAFT agent **1** (R = Ph, CO₂Bu, CONMe₂).

The complex (**1**) proved to be efficient for the control of RAFT polymerization of styrene (\overline{D} =1.10-1.38), *n*-butyl acrylate (\overline{D} =1.10-1.34) and *N,N*-dimethyl acrylamide (\overline{D} =1.26-1.28). The reaction course could be conveniently monitored by ³¹P NMR spectroscopy. The controlled character of these polymerizations and the integrity of the polymer chain ends were demonstrated by the synthesis of diblock copolymers of St and *n*-BA. In the case of long polymerization times (i.e. for PSt), photoinduced polymer chain coupling reactions were detected. Importantly, removal of the Mn-RAFT- ω -chain end by visible light irradiation led to the formation of a monomodal SH-terminated PSt. These phenomena were evidenced by IR spectroscopy, SEC with RI and UV detection modes and by ESI mass spectrometry.

#

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AGENTS RAFT ORGANOSTANNYLES: UNE CLASSE A PART

ORGANOTIN RAFT AGENTS: A RANGE APART

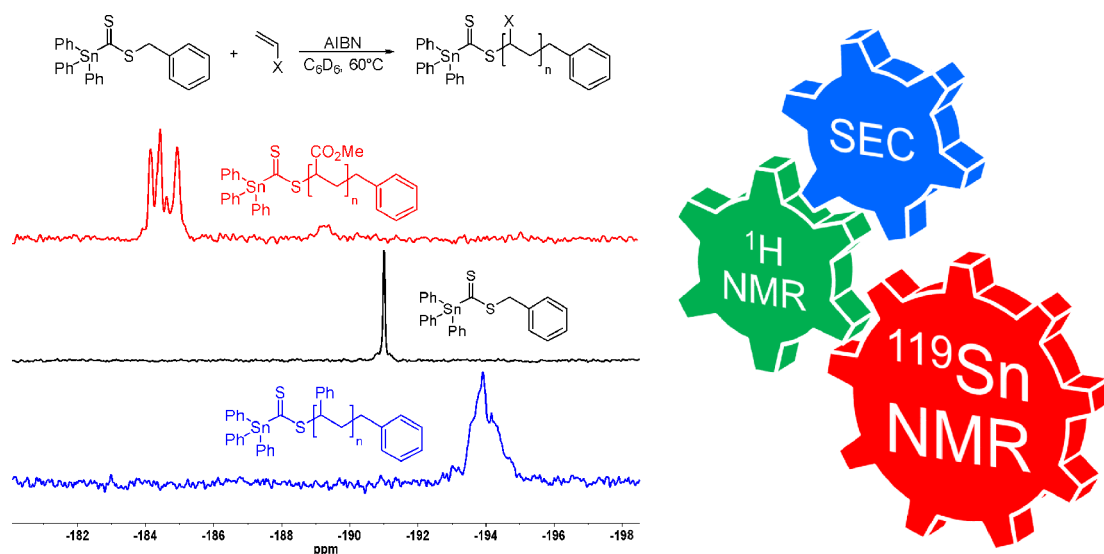
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A range of triaryltin-based reversible addition-fragmentation chain-transfer (RAFT) agents^{1,2} is described and evaluated for the polymerization of acrylamides, acrylates and styrene. These organometallic compounds are highly reactive reversible transfer agents which allow an efficient control of the polymerization of substituted acrylamide monomers, whereas RAFT control for methyl acrylate and styrene polymerization is contaminated by side reactions. The Sn-RAFT chain end appears to be thermally unstable, and degrades over prolonged reaction times. The kinetics and mechanism of degradation is studied with model reactions by simply heating the starting Sn-RAFT agents at different T between 60°C and 110°C. ¹¹⁹Sn NMR is showed to be an informative instrument for the monitoring of Sn-RAFT-mediated model reactions and polymerizations. Sn-RAFT polymerization is one of the few examples of a reversible-deactivation radical polymerization process where heteronuclear NMR allows observation of an initialization step, determination of chain transfer constants and the revelation and identification of RAFT agent decomposition products.



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INVESTIGATION OF REGIOSELECTIVITY OF ELECTROPHILIC HETEROCYCLIZATION OF ALKENYL DERIVATIVES OF THIENOPYRIMIDINONE BY ARYLTELLURIUM TRICHLORIDES

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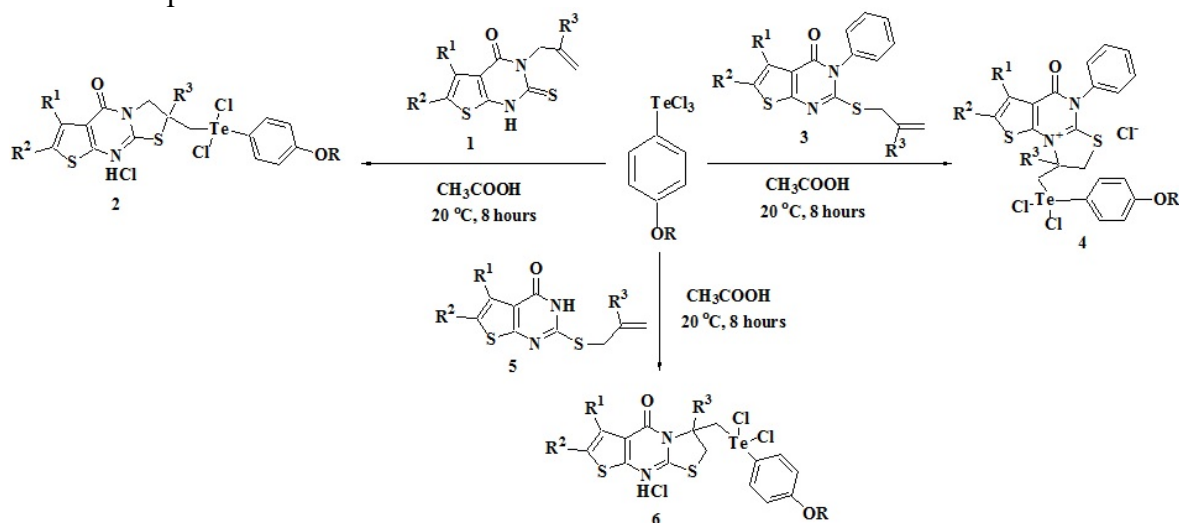
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Annulation of heterocyclic nuclei to a condensed pyrimidine cycle by electrophilic intramolecular cyclization reveals new perspectives and opportunities for the formation of new functional derivatives of pyrimidine. The purpose of this work is to study the regiochemistry of the process of electrophilic intramolecular cyclization of N(S)-alkenyl derivatives of thienopyrimidinone with *p*-alkoxyphenyltellurium trichloride. It was found that 3-N-alkenyl derivatives of thieno[2,3-*d*]pyrimidine **1** are cyclized regio-selectively by the action of *p*-alkoxyphenyltelluriumtrichlorides in acetic acid with the participation of an exocyclic Sulfur atom with the formation of polycyclic systems **2** of linear structure.

Regio-direction of the cyclization of 2-S-alkenyl derivatives of thieno[2,3-*d*]pyrimidine by the action of *p*-alkoxyphenyltellurium trichlorides depends on the presence of the substituent in the **3** position of the pyrimidine ring. Thus, the halides of thiazolothienopyrimidinium **4** of the angular structure with an exocyclic aryltellurium fragment were obtained at the tellurocyclization of 3-N-phenyl-2-S-alkenyl derivatives of thienopyrimidinone **3**. Instead, 2-S-alkenyl 3-N-unsubstituted thienopyrimidinones **5** contain two alternative nucleophilic centers that may participate in the process of electrophilic intramolecular cyclization under the action of aryltellurium trichlorides to form condensed systems of linear or angular structure. We have found that the electrophilic intramolecular cyclization of 2-S-alkenyl-3-N-unsubstituted thienopyrimidinones with *p*-alkoxyphenyltelluriumtrichlorides takes place regio-selectively with the participation of the 3-N atom of the pyrimidine ring to form linear tetracyclic systems **6**. The formation of products of linear structure in this case is presumably caused by the intramolecular coordination of the carbonyl oxygen of the Oxygen atom of carbonyl group on the Tellurium atom in electrophilic reagent.

The structure of cyclization products is proved by NMR spectra, including correlation, and infrared spectra.



POLYURETHANES FONCTIONNALISES PAR DES THIOLACTONES: SYNTHESE, CARACTERISATION ET POSTMODIFICATION CHIMIQUE

POLYURETHANES BEARING THIOLACTONE MOIETIES – SYNTHESIS, CHARACTERISATION AND CHAIN POSTMODIFICATIONS

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Polyurethanes (PU), due to their excellent performance properties, are very commonly used polymers in diverse applications, e.g. medicine, construction, packaging etc.¹ The commercial availability of different polyisocyanates and polyols allows the production of PU with a wide range of properties. Nevertheless, industry needs for high-tech PU applications require newer and newer properties such as adhesion, biological activity or conductivity. These needs can be fulfilled by incorporation of reactive groups into the polymeric chains, which can further react in a postmodification step.²⁻⁴

In this presentation, the application of thiolactones with diol function⁵ in the synthesis of polyurethanes will be presented (Figure 1).

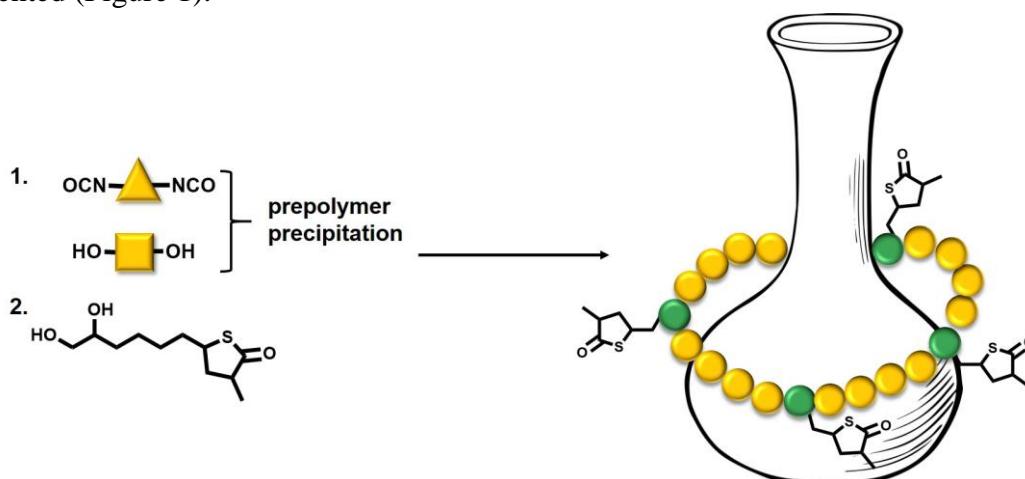


Figure 1 : Two step synthesis polyurethanes with thiolactone functions.

The incorporation of thiolactones in the polymeric chains allows further modification. Thiolactones can be easily opened by primary amines resulting in thiol production which can be further be modified e.g. with unsaturated compounds (in thiol-ene reaction).^{6,7} Examples of modifications of synthesized PU by different amines will also be presented.

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From heptanuclear Fe(II), Ni(II) complexes to single-chain magnets

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In pentagonal bipyramidal geometry 3d metal complexes exhibit magnetic anisotropyⁱ that is a key factor in magnetic materials. For instance, it is at the origin of the slow relaxation of magnetization in SMMs (Single Molecular Magnets)ⁱⁱ. We have considered a series of seven coordinate Fe and Ni complexes constructed with a neutral pentadentate cyclic ligand. (Figure 1). Five Nitrogen atoms located in equatorial positions maintain coordination geometry upon axial ligand substitution, which enables systematic modification of the coordination environment without compromising the geometry. These Fe(II) and Ni(II) complexes possess easy-axis of magnetization characterized by a negative D parameter depending on axial substituents.

We will show that association with other paramagnetic units can lead to the formation of different heteronuclear species. Trinuclear complex and 1-D coordination polymer were obtained in reaction of $[\text{NiL}^{\text{N}5}]^{2+}$ with $[\text{Cr}(\text{L}^{\text{N}3\text{O}2\text{Ph}})(\text{CN})_2]^{-}$ ⁱⁱⁱ (Figure 1). The second one shows SCM behavior characterized by an energy gap for magnetization reversal ($\Delta_{\text{eff}}/k_{\text{B}}$) about 50 K.

The series of $\text{FeL}^{\text{N}5}\text{X}_2$ and $\text{NiL}^{\text{N}5}\text{X}_2$, (X= Cl, Br, I, N₃, NCS, MeOH) complexes, as well as polynuclear compounds and their magnetic properties, will be presented.

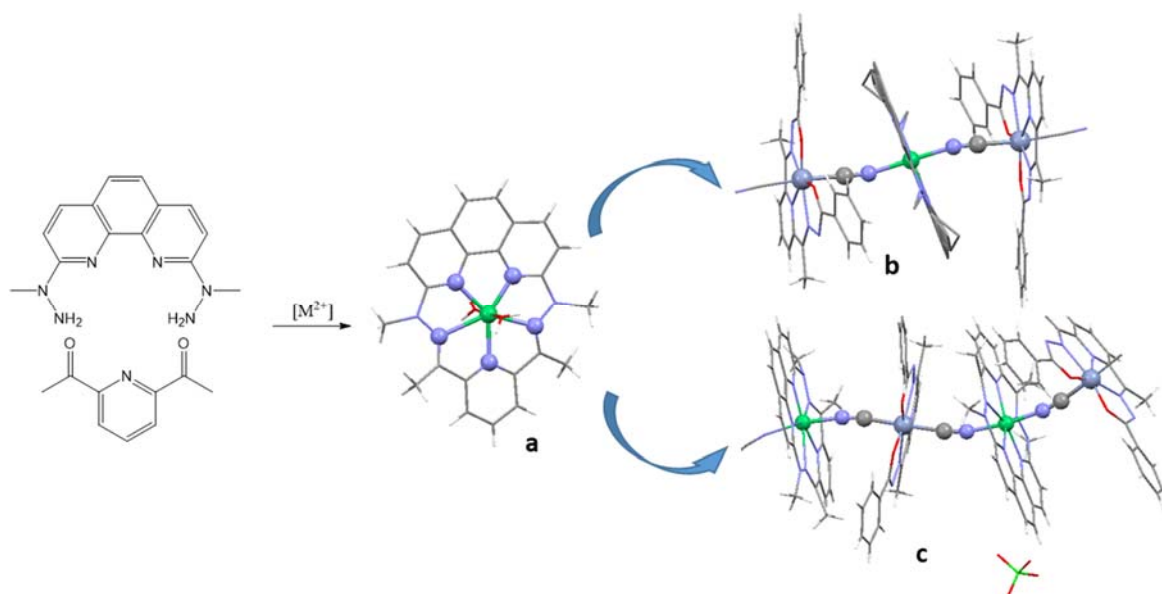


Figure 1.(a) $[\text{NiL}^{\text{N}5}(\text{H}_2\text{O})_2]^{2+}$ complex, (b) Cr_2Ni complex (c) Ni(II)-Cr(III) chain

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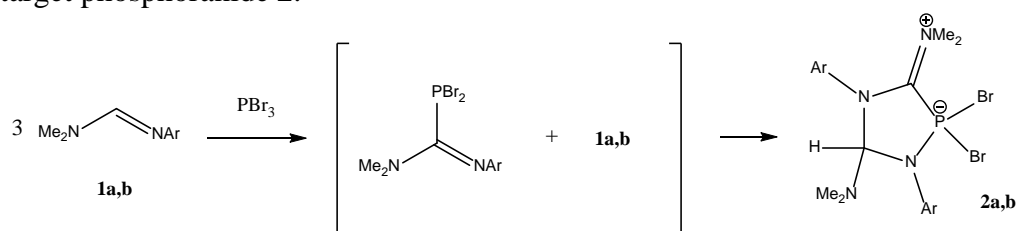
PHOSPHORANIDES AS INTERMEDIATES IN THE REACTION OF PHOSPHORUS HALIDES WITH *N,N*-DIMETHYL-*N'*-ARYLFORMAMIDINES

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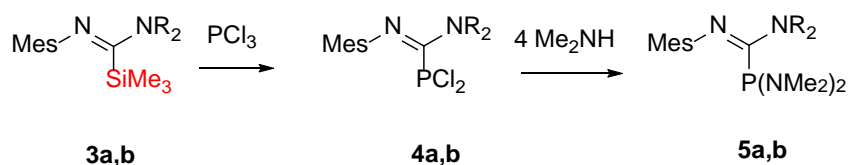
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Phosphoranides are hypervalent anionic phosphorus (III) compounds formally with the 10 electron valence shell and distorted pseudotrigonal bipyramidal arrangement at phosphorus. The more electronegative are ligands forming a phosphoranide, the higher is its stability.

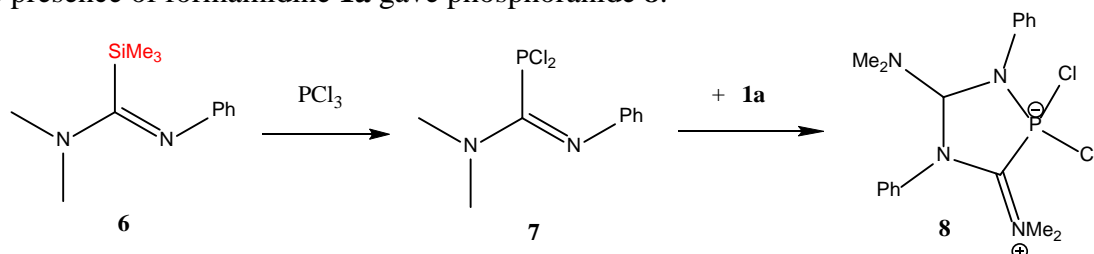
We have found that the reaction of phosphorus tribromide with *N,N*-dimethyl-*N'*-arylformamidines afforded phosphoranides **2** [1]. Mechanism of its formation was proposed based on Density functional theory (DFT) calculations. At the first stage the reaction of phosphorus tribromide and *N,N*-dimethyl-*N'*-arylformamide afforded C-phosphorylated formamide that further reacted with other molecule of *N,N*-dimethyl-*N'*-arylformamide to give the target phosphoranide **2**.



In the course of our further investigations we have prepared *C*-trimethylsilyl-*N,N*-dialkyl-*N'*-arylformamidines and have shown that they react with phosphorus halides giving *C*-phosphorylated *N,N*-dialkyl-*N'*-arylformamidines [2]. In case of sterically hindered formamidines we were able to separate and characterize *C*-dichlorophosphino substituted formamidines **4**.



It gave us an opportunity to check the proposed mechanism for the formation of phosphoranides **2a,b**. Indeed, the reaction of silylated formamide **6** with phosphorus trichloride in the presence of formamide **1a** gave phosphoranide **8**.



The mechanism of formation of phosphoranides **2**, **8** will be discussed as well as some their chemical reactions.

This work was supported, in part, by the EU-project H2020-MSCA-RISE-2016 n° 734759 (VAHVISTUS).

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SYNTHÈSE DE POLYOXOMÉTALATES À PARTIR DE SOLUTIONS $A^+ - Y^{3+} - WO_4^{2-} - H^+ - H_2O$ ($A^+ = NH_4^+, K^+$) ET $M^{2+} - Y^{3+} - WO_4^{2-} - H^+ - H_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}$)

SYNTHESIS OF POLYOXOMETALATES FROM THE SYSTEMS $A^+ - Y^{3+} - WO_4^{2-} - H^+ - H_2O$ ($A^+ = NH_4^+, K^+$), AND $M^{2+} - Y^{3+} - WO_4^{2-} - H^+ - H_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}$)

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The new procedure for the synthesis of sodium heteropoly decatungstoyttriate (III) $Na_9[Y(W_5O_{18})_2] \cdot 35H_2O$ from the aqueous solution $Y^{3+} - WO_4^{2-} - H^+ - H_2O$ acidified to $Z = v(H^+)/v(WO_4^{2-}) = 0.80$ with a ratio $v(Y):v(W) = 1:10$ and with acetone admixture were elaborated. Using ATR-FTIR and FT-Raman spectroscopy it was shown that heteropoly anion contained in the isolated salt has a Peacock–Weakley structure. Using Scanning Electron Microscopy, the surface micromorphology of heteropoly compound was studied, and it was found out that the grain size is within the range of 200–450 nm. Single-phase condition of the synthesized salt was confirmed by the surface uniform contrast in backscattered electron mode.

The conditions for the synthesis of $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2] \cdot 12H_2O$, $K_{10}[W_{12}O_{40}(OH)_2] \cdot 13H_2O$, and $M_5[W_{12}O_{40}(OH)_2] \cdot nH_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}$) in acidified to $Z = 0.80$ solutions of systems $A^+ - Y^{3+} - WO_4^{2-} - H^+ - H_2O$ ($A = NH_4^+, K^+$), and $M^{2+} - Y^{3+} - WO_4^{2-} - H^+ - H_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}$) were determined. All the salts synthesized were characterized by elemental analysis and ATR-FTIR spectroscopy.

Using single crystal X-ray analysis, the structures of $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2] \cdot 12H_2O$ (S-1) ($M_r = 3286.72$, orthorhombic, $Pbca$, $a = 14.063(3)$, $b = 15.671(3)$, $c = 22.915(3)$ Å, $V = 5050.1(4)$ Å³ at $T = 200(2)$ K, $Z = 4$, $d_{calc} = 4.323$ g/cm³), and $K_{10}[W_{12}O_{40}(OH)_2] \cdot 13H_2O$ (S-2) (monoclinic, $P2_1/c$, $a = 11.505(3)$ Å, $b = 14.301(3)$ Å, $c = 15.457(3)$ Å, $\beta = 105.889(7)^\circ$, $V = 2445.9(2)$ Å³, $Z = 2$, $d_x = 4.738$ g/cm³) were solved (see Fig. 1).

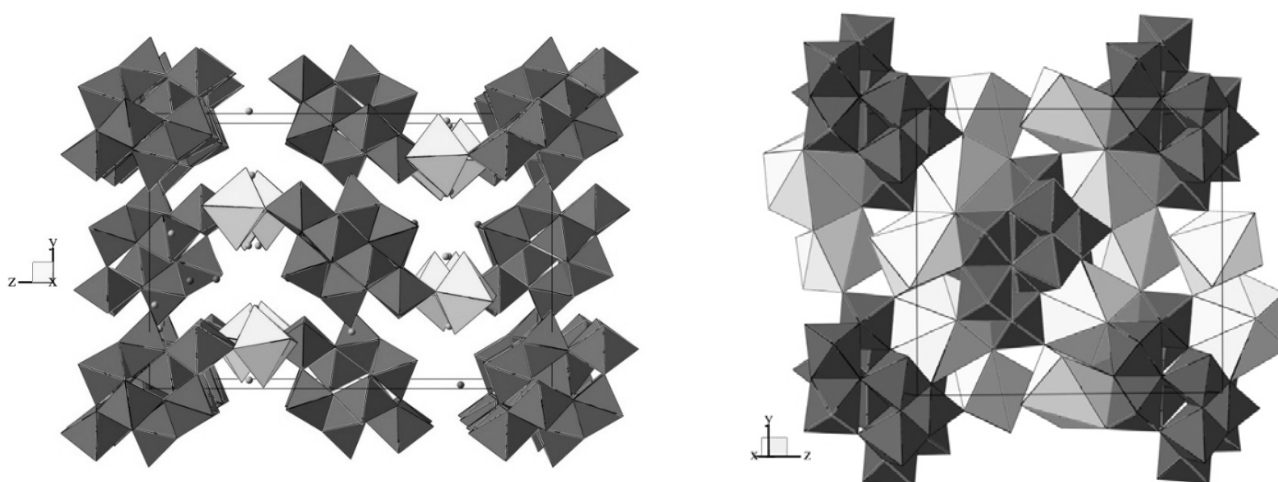


Fig. 1. Left – Polyhedral representation of S-1 along x axis. Color codes: $\{WO_6\}$, dark grey octahedra; $\{NaO_6\}$, light grey octahedra; O (from uncoordinated H_2O molecules), and N (NH_4^+), balls. Right – Polyhedral representation of the layer in S-2. Color codes: $\{WO_6\}$, dark grey octahedra; $\{KO_n\}$, light grey polyhedra.

The study was carried out within the Fundamental Research Programme funded by the Ministry of Education and Science of Ukraine (Project No. 0116U002521, 0119U100025), and with support of Erasmus+ Université Toulouse III Paul Sabatier.

STABLE CARBENES AS STRUCTURAL COMPONENTS OF SULFUR CONTAINING HETEROCYCLES: X-RAY AND QUANTUM CHEMICAL STUDIES.

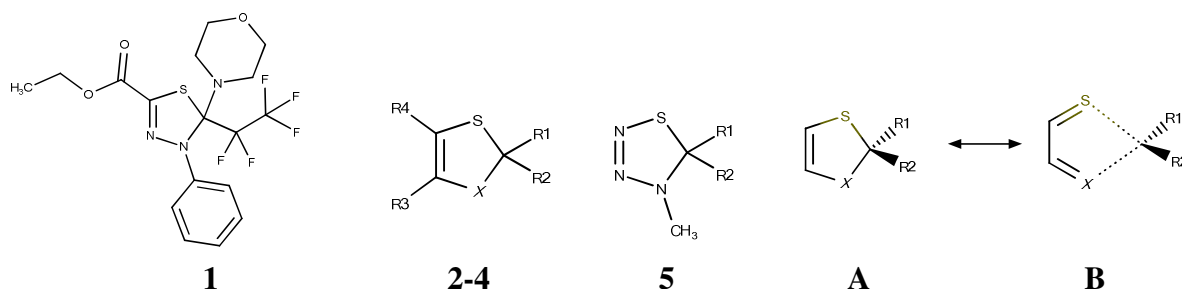
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Recently^[1] we have reported on a crystal structure of compound **1**, which has demonstrated a significantly lengthened Csp^3-S bond (1.885 Å compared to the standard length of 1.82 Å for Csp^3-S in the solid state). In order to figure out the nature of the experimentally found effect, quantum chemical *ab initio* (SCS-MP2/cc-pVTZ) calculations were carried out for the broad series of model heterocyclic structures **2-5**.



2a-g R3,R4=H; **a:** R1,R2=Me; **b:** R1=Me, R2=NMe₂; **c:** R1,R2=NMe₂; **d:** R1=CF₃, R2=NMe₂; **e:** R1,R2=H; **f:** R1,R2=F; **g:** R1,R2=Cl. **2h-m:** R1,R2=NMe₂; **h:** R3,R4=NMe₂; **i:** R3,R4=NO₂; **j:** R3,R4=F; **k:** R3=H, R4=NH₂; **l:** R3=H, R4=NO₂; **m:** R3=H, R4=F.
3 R3,R4=H; **a:** X=NH, R1,R2=NMe₂; **b:** X=NMe, R1,R2=NMe₂.
4a: R3,R4=H, X=O, R1,R2=NMe₂; **4b:** R3=Me,R4=H X=O, R1,R2=NMe₂.
5 a: R1,R2=Me; **b:** R1=Me, R2=NMe₂; **c:** R1,R2=NMe₂.

Calculated C–S bond lengths strongly depend on the nature of the substituents. The most pronounced effect is observed for the cases where R1 and R2 are electronegative π -donor groups. R3 and R4 substituents only slightly influence geometry of the molecules. The observed effect can be explained as an equilibrium between a pure covalent bonding in the structure **A** and a donor-acceptor complex **B**, where a thionic moiety interacts as a donor with the vacant p-type orbital of the carbene R1-C(:)-R2. The contribution of the latter adduct strongly depends on the stability of the corresponding carbene: the more stable the carbene, the longer is the C–S bond. The total range of carbon-sulfur bond variation in the studied series of compounds is almost 0.13 Å. Significantly elongated C–S bonds are predicted for derivatives including the most stable diaminocarbene. Thus, the shortest C–S bond is found for the parent structure **2e** (X= S, R1-R4=H) (1.790 Å), whereas the large C–S distance (1.907 Å) is predicted for bis(dimethylamino)-substituted 2H-1,3-oxathiole (**4a**, X= O, R1,R2=NMe₂, R3,R4=H). On the other hand, the effect in **2-4** can be additionally reinforced by the introduction of electron-withdrawing groups as R3 and R4, reducing the donor properties of the thionic moiety and resulting in the longest in the series C–S distance (1.919 Å) for compound **2i**, where X= S, R1,R2=NMe₂ and R3,R4=NO₂.

A substitution of the carbon atoms in **2** by nitrogens going to **5** probably destabilizes the thionic ligand and shortens the bonds of interest.

This work was supported, in part, by the EU-project H2020-MSCA-RISE-2016 n° 734759 (VAHVISTUS).

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SYNTHESE DE DENDRIMERES FLUORESCENTS SOLUBLES DANS L'EAU

SYNTHESIS OF FLUORESCENT DENDRIMERS SOLUBLE IN WATER

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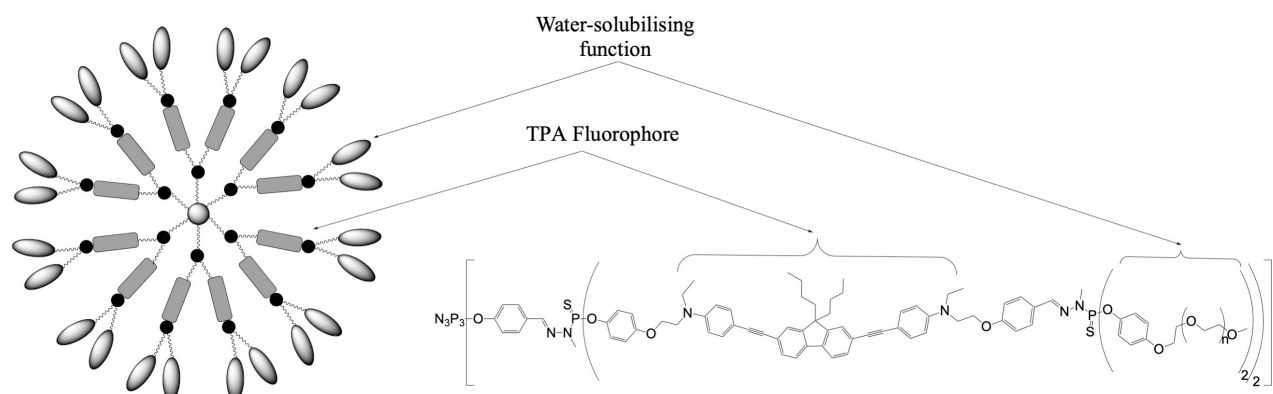
Dendrimers are molecules with an arborescent structure. Despite the fact that dendrimers, like polymers, consist of tens, hundreds and even thousands of units, they have a strictly defined structure thanks to their step by step synthesis. The dendrimers are thus composed of a core on which branches with points of divergence and surface functions are attached. Due to accessible modifiability and well-defined structure, dendrimers have found application in various fields of science.

Fluorescent water-soluble dendrimers are interesting from at least two points of view. On one side, it is known that many fluorophores are quenched by water¹; the association with the dendritic structure might have a shielding effect revealed by photo-physical studies. On the other side, there is always a need for new water-soluble fluorescent labels in biology, to understand biological events at the molecular level; thus, fluorescent water-soluble dendrimers might afford new tools in this field.

The solubility in water can be obtained by using fluorophores (if they are end groups) with ionic functions or by adding cationic (ammoniums), anionic (carboxylates or phosphonates) or neutral groups (PEG) to the dendrimer molecule.

Different locations can be used to include fluorophores inside the structure of dendrimers: on the surface, at the core, or in the branches. In the latter case, it is possible to vary the number of fluorescent fragments in the dendrimer molecule as well as to prevent fluorescence quenching in water. Fluorophores to be incorporated in the branches of dendrimers necessitate two different functions, one for the grafting to the dendrimer, and another one for continuing the growing of the dendrimer.

In recent years, some works have been devoted to the use of dendrimers with Two-Photon adsorbing (TPA) fluorophores for biological studies^{2,3}. Indeed, a highly spatially confined excitation and inherent three-dimensional resolution³, an increased penetration depth in tissues with reduced photo-damage thanks to excitation in the near-infrared region, render two-photon fluorescence excitation extremely attractive for biological imaging, in particular for living animals. Water-soluble fluorescent dendrimers with TPA fluorophores have been synthesized and investigated and their use for biology holds great promises for the future.



¹ A. Hameau, S. Fuchs, R. Laurent, J.-P. Majoral, and A.-M. Caminade. Synthesis of dye/fluorescent functionalized dendrons based on cyclotriphosphazene, *Beilstein J. Org. Chem.*, **2011**, 7, 1577–1583.

² T. R. Krishna, M. Parent, M. H.V. Werts, L. Moreaux, S. Gmouh, S. Charpak, A.-M. Caminade, J.-P. Majoral, M. Blanchard-Desce, Water-Soluble Dendrimeric Two-Photon Tracers for In Vivo Imaging, *Angew. Chem. Int. Ed.*, **2006**, 45, 4645–4648.

³ A. Sourdou, M. Gary-Bobo, M. Maynadier, M. Garcia, J.-P. Majoral, A.-M. Caminade, O. Mongin, M. Blanchard-Desce. Dendrimeric Nanoparticles for Two-Photon Photodynamic Therapy and Imaging: Synthesis, Photophysical Properties, Innocuousness in Daylight and Cytotoxicity under Two-Photon Irradiation in the NIR, *Chem. Eur. J.* **2019**, 25, 3637–3649.

⁴ W. Denk, J. H. Strickler, W. W. Webb, *Science*, **1990**, 73–76.