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INFLUENCE OF THE MICROWAVES ON THE SOL-GEL CHEMISTRY

Acad. Maria ZAHARESCU

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MULTIFACETED CHEMISTRY WITH PHOSPHORUS-FUNCTIONALISED FERROCENE DERIVATIVES

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Cyclopentadienes with a P-functionalised alkyl or aryl side chain are useful precursors for mono- and dianionic bifunctional ligands in main group and transition metal chemistry. We have developed two synthetic approaches for several (chiral) phosphanylalkyl or -aryl cyclopentadienyl complexes: a) employing lithium phosphanylalkyl- and -arylcyclopenta-dienides, such as $Li[(C_5H_4)\text{-}X\text{-}PR^1R^2]$ [R^1 = H, alkyl, aryl; R^2 = alkyl, aryl; X = alkylene, arylene] [1], as transfer reagents for the organic ligand, and b) by modification of the metal-bound cyclopentadienyl ring in ferrocenes.

Primary (Fig. 1) and secondary ferrocenyl phosphines were obtained by method b). These phosphines display interesting reactivity and can be used as starting materials for further functionalisation of the phosphanyl group [2] or for ferrocenyl-substituted P-B-based polymers (Fig. 2) [3].

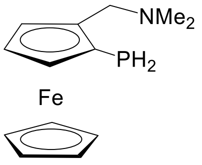


Fig. 1

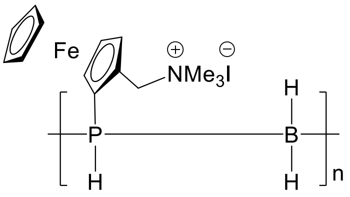
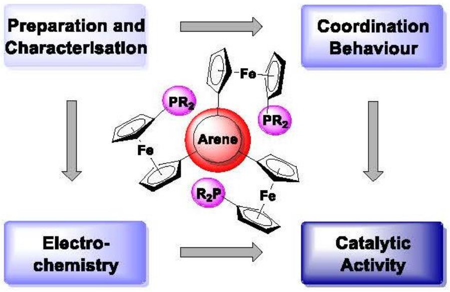


Fig. 2



Tertiary ferrocenyl phosphines have applications in catalytic reactions. The corresponding 1,1'-substituted ferrocenes can be used for immobilisation, for example on dendrimers [4] or other cores [5].

Synthetic routes to these ferrocenyl phosphines, their properties and applications will be discussed.

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ORGANOPNICOGEN(III) COMPOUNDS CONTAINING Pn−CHALCOGEN (Pn = Sb, Bi) - STRUCTURE AND REACTIVITY

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Recent results in the synthesis, characterization and reactivity of organopnicogen(III) (Sb, Bi) aryloxides and related thio derivatives, $ArPn(EAr')_2$ (E = O, S), as well as related chalcogenides, *cyclo*-$[ArPnE]_n$ (Pn = Sb, Bi; E = O, S, Se), will be presented. The organic Ar groups attached to the metal atom are aromatic ligands with one or two pendant arms of the type of 2-$(Me_2NCH_2)C_6H_4$ and 2,6-$(R_2NCH_2)_2C_6H_3$ (R = Me, ^{i}Pr) or 2,6-$\{E'(CH_2CH_2)_2NCH_2\}_2C_6H_3$ (E′ = NMe, O), with potential for intermolecular coordination.[1, 2] Significant differences, depending on the nature of the pnictogen, were revealed in solid state. The reactivity of particular $ArPn(EAr')_2$ (E = O, S) towards chalcogens (oxygen, sulfur or selenium) and iodine will be also discussed. Topics of seminal interest as *C-H bond activation* [3] and *carbon dioxide fixation / activation* [2b, 2c, 4] using heavy organopnicogen(III) species will be also briefly emphasized.

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This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2020-2651, within PNCDI III.

COMPUTATIONAL EVALUATION OF THE HUMAN HEALTH EFFECTS OF THE DEGRADATION PRODUCTS OF BIOPOLYMERS

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According to their availability, different biopolymers and their derivatives are used in the medicine and pharmaceutical field as implants, wound healing, regenerative medicines, cellular proliferation, controlled drug delivery, etc. The wide range of applications the biopolymers of are due to their versatile nature, they can be prepared as nanocomposites, scaffolds and/or hydrogels [1]. Among these biopolymers, chitosan, polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) are widely used as drug delivery systems, in tissue engineering and/or biomedical devices. These biopolymers are degraded in the human organism under the action of some enzymes and the pharmacokinetics profiles of their degradation products should be assessed. Within the present study the absorption, distribution, metabolism, excretion and toxicity (ADMET) profiles and the toxicological endpoints of the short oligomers of chitosan, PLA and PHAs have been predicted using a computational approach. The short oligomers of these biopolymers revealed favorable pharmacological profiles and limited toxicological effects on humans. Chitosan oligomers were considered to produce phospholipidosis and to reveal a weak potential of cardiotoxicity and endocrine disruption and their effects were strongly influenced by their chemical properties [2-4]. The oligomers of PHAs could produce skin irritation and emphasized a low antagonistic effect on the androgen receptor [5]. Short oligomers of PLA revealed minor probability to affect the androgen and glucocorticoid receptors and to produce a weak potential of hepatotoxicity [6]. The oligomers of all investigated biopolymers were considered as inhibitors of the organic anion transporter peptides [2-6]. These outcomes may be used to guide experimental toxicity tests such as to enhance the properties of the degradation products of biopolymers.

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HIGH-TECH AND BIO-ORIENTED POLYMER COMPOSITES

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Nowadays, polymers obtained from regenerable resources are reconsidered as sustained substitutes of the vanishing fossil materials. In this context, the presentation deals with polysaccharide nanocomposites designed for application as polyelectrolyte membranes for fuel cells (Fig. 1) or as biocompatible matrices for drug delivery systems (Fig. 2). Details on the proposed preparation methods and on the structure-property relationships will be given.

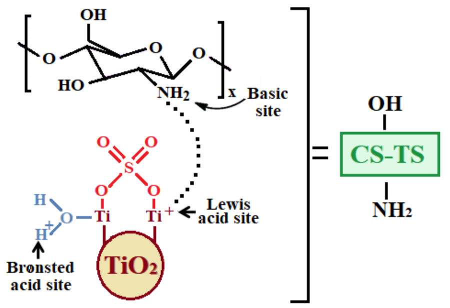

Fig. 1. Chitosan-sulfated titania polyelectrolyte membranes

Fig. 2. Chitosan-based drug delivery systems

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BIS(TRICHLOROMETHYL)CARBONATE (BTC, TRIPHOSGENE): A SAFER ALTERNATIVE TO PHOSGENE?

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Bis(trichloromethyl)carbonate (BTC, triphosgene) is a versatile compound that enables highly efficient syntheses. In addition, because of its solid state, it is a very convenient compound for small-scale phosgenations. Consequently, this compound is favored as a phosgene substitute in research and development and in small-scale production.

Although BTC is highly toxic, safe handling is possible as long as the properties and chemical reactivity of this compound are understood and considered. However, branding as “safe phosgene” or “safer phosgene” is misleading. The solid state of BTC leads to the misconception that there is no significant exposure. However, the vapor pressure is sufficiently high to easily result in toxic concentrations. In addition, proper monitoring is not yet possible. Proper use of BTC could be more complex than the handling of phosgene itself. However, handling of BTC is normally always associated with phosgene and has its own toxicity. Therefore, the use of BTC will become more regulated in the future, which will directly increase responsibility in route selection during process development. A stringent safety concept for phosgenations using BTC is necessary. Because of the interconnection with phosgene, the safety concept for BTC will likely be an extended version of the safety concept for phosgene.

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MAGNETICALLY CONTROLLABLE FLUIDS-SYNTHESIS, MANIFOLD CHARACTERIZATION AND SOME APPLICATIONS

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Ferrofluids are ultrastable colloidal suspensions of magnetic nanoparticles, which manifest simultaneously fluid and magnetic properties. Their magnetically controllable and tunable feature proved to be an extremely fertile ground for a wide range of engineering applications. More recently, biocompatible ferrofluids produced a considerable increase of the applicative potential in nanomedicine, biotechnology and environmental protection. This talk offers a brief overview on the synthesis and advanced characterization of ferrofluids, bio-ferrofluids and ferrofluid based magnetorheological fluids. There will be summarized results of electron microscopy, vibrating sample magnetometry, Mössbauer spectroscopy, dynamic light scattering, small-angle X-ray and neutron scattering, and magneto-rheometry investigations revealing the similarities and differences between the three types of magnetically controllable fluids. The applications will be exemplified by leakage-free rotating seals operating in nuclear power units, MR flow controller devices in hydraulic machines, hybrid semi-active MR dampers for earthquake protection systems and by ferrofluid droplet splitting for antibody extraction processes.

A NEW HIGH THROUGHPUT ASSAY FOR CIS PROTEOLYTIC ACTIVITY IDENTIFIES NEW CHEMICAL SCAFFOLDS WITH INHIBITORY ACTIVITY AGAINST HEPATITIS C VIRUS NS2 CYSTEINE PROTEASE

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Viral proteases are important drug targets for infectious diseases therapy. Protease inhibitors are used in the standard of care or they are in the development phase against various viral infections with RNA viruses like Hepatitis C Virus, Human Immunodeficiency Virus or SARS CoV-2. RNA viruses are synthesized as polyproteins which are sequentially processed by endogenous and viral proteases. Both "*in trans*" and "*in cis*" proteolytic activities are required for the viral polypeptide processing. Most of the protease inhibitors screening campaigns rely on biochemical assays and quenched probes to identify small molecule inhibitors against the "*in trans*" protease activity. Thus, there is a need for "*in cis*" protease activity assays which may be miniaturized and used in HTS campaigns. Herein, we developed an original cell based assay for HCV NS2 cysteine autoprotease which is an exclusive "*in cis*" acting protease. The assay was miniaturized in 384 well plates and used to perform a primary screening. The targeted screening library was selected using "in silico" molecular docking. Then, a secondary screen was used using the HCV subgenomic replicon system. The most active chemical scaffolds were further validated as inhibitors of HCV replication using the full length HCV cell culture system. The most active chemical scaffolds were in low micromolar range IC_{50}. A bicistronic recombinant virus which replicates independently of NS2 protease activity became resistant to inhibition. Free energy landscape estimation and structure activity relationship studies revealed a possible mode of action of the inhibitor in the context of the precleavage structure of the NS2-3 protease. The assay design may be extrapolated to other viral cis acting proteases and it may help to identify new chemical scaffolds with anti-viral activity.

THE STUDY OF CHITOSAN, CHITOOLIGOSACCHARIDES AND DERIVATIVES REGARDING THEIR EFFECTS ON AQUATIC ORGANISMS

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Taking into account their production and use in numerous fields of application, the contamination of the aquatic environment with chitosan, chitooligosaccharides and derivatives is possible, potentially producing toxic effects on aquatic organisms. In the present study, the effects of chitosan, chitooligosaccharides and derivatives with different properties were evaluated by both an experimental approach and a computational approach. The target aquatic organisms were *Lemna minor,* for the experimental approach, and *Tetrahymena pyriformis*, *Daphnia magna* and fathead minnow, for the computational approach. The *Lemna minor* EC_{50} values highlighted the higher toxicity of D-glucosamine, a "slightly toxic" chitooligosaccharide, in comparison with the other tested samples which were "practically nontoxic". The results obtained in the experimental approach were in agreement with the results obtained in the computational approach. The predictions obtained using admetSAR2.0 emphasized that the analyzed chitooligosaccharides and derivatives were not toxic towards the three target organisms. The predictions obtained using ADMETLab2.0 showed that the lowest values obtained for the three target organisms were observed for totally acetylated chitooligosaccharides. The effects of the tested chitosan, chitooligosaccharides and derivatives were dependent on parameters such as molecular weight, deacetylation degree, acetylation pattern and solubility.

ANTIMICROBIAL CELL-PENETRATING PEPTIDES

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Antimicrobial peptides (AMPs) can be useful in eliminating bacteria, fungi, viruses, and parasites, and have been reported to present immunomodulatory and anticancer properties. [1, 2, 3] Most AMPs have net positive charges and amphiphilic structures. Cationic AMPs (CAMPs) are able to kill bacteria through selective membrane destruction, while cationic cell-penetrating peptides (CPPs) can enter bacterial cells without destroying the cell membrane and afterthat attack intracellular targets, confirming their antimicrobial activity. We present development of cell-penetrating AMPs with dual effects, alone or as part of combination therapy (e.g. with antibiotics), that represent an alternative platform of therapeutic agents for treating intracellular infections. [1, 2, 3, 4]

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This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS - UEFISCDI, project number PN-III-P4-PCE-2021-0639, within PNCDI III.

ANCHORING CHITOSAN-BASED BIOCONJUGATES HYDROGEL LAYER ONTO POLY(LACTIC ACID) SUBSTRATE

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The interaction between the materials and biological media occurs through the interface therefore their performance is highly dependent on the surface characteristics [1]. Hence, the designing of surfaces has been used extensively to improve the bioactive properties. Hydrogels, which are three-dimensional networks of polymeric chains, present a great potential for modification of the surfaces of various substrates. They are known as soft materials with features that mimics the native extracellular matrix (ECM), with a great ability to uptake large volumes of water and usually with good biocompatibility. Engineering of the surface of polymeric materials by anchoring thin hydrogel layers of functional polymers represents a promising strategy to develop biomaterials with improved interaction with the biological surroundings [2]. The aim of this research was to create a biomaterial with tailored surface able to control cells adhesion. This was achieved by developing a hybrid combination of hydrogel and solid non-porous material, containing biocompatible chitosan (CH)-proteins conjugates and plasma functionalized poly(lactic acid) (PLA) film. Hydrogel coatings were obtained by immersion of PLA films (previously functionalized by plasma treatment) into precursor solutions of bioconjugates, followed by crosslinking under UV irradiation. Crosslinking allows formation of microporous layers with good mechanical stability – Figure 1. The functionalized PLA supports maintain adhesion, multiplication and proliferation of fibroblast cells, without affecting cell morphology, which indicates the biocompatibility of material.

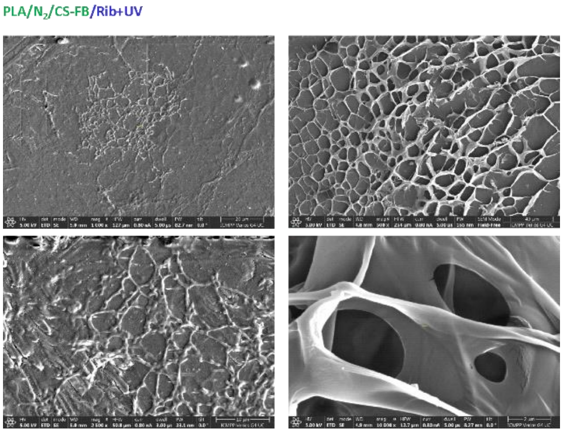

Figure 1. SEM micrographs of PLA films functionalized at the surface with UV cross-linked chitosan bioconjugate hydrogel.

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The project “KSP-S- Bio-farming for bioactive compounds”, funded by Research Council of Norway, Contract number 320740/09.12.2020 is greatly acknowledged.

ROBOSAMPLE: A MOLECULAR SIMULATION PROGRAM THAT COMBINES ENHANCED SAMPLING WITH HIGH-SPEED ROBOTICS ALGORITHMS

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Structure-based in silico drug screening is an important step in a drug design pipeline, prior to in vitro high-throughput screening. While rigid receptor docking is rather successful for ligands pose prediction, flexible receptor or induced fit models yield rather poor results. Improvement on latter usually employs simulation-based methods which are also used for free energy calculation.

Simulations, however, are computationally demanding in biological cases due to the size of the receptor. To this end, we introduce Robosample, a program that combines the advantages of fast constrained simulations using rigid bodies with Gibbs sampling to maintain ergodicity. Robosample uses Hamiltonian Monte Carlo coupled with Gibbs sampling, where random variables are divided among molecular degrees of freedom. In this way, parts of the molecule can be regarded as rigid and sub-sampled if their motion amplitude is low. For the fast motion of the rigid bodies we use established robot mechanics algorithms, and ergodicity is achieved by augmenting the simulation with fully flexible Cartesian dynamics. We show Robosample effectiveness on HCV NS2 protein where it reveals high irregularity of the binding site shape, up to exposing new pockets.

LIQUID CRYSTALS, ELECTROCHEMISTRY AND SENSORS

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Metallomesogens (**MMs**) are functional supramolecular materials with order in at least one direction and/or orientation of molecules, properties that, in cooperation with the ones derived from the presence of a metal center promote them as active materials in several application fields like electrooptics, chemosensors, information storage devices and so on [1,2]. Electrochemical sensors based on metal nanostructures as new instruments for detection of critical physiological parameters are lately receiving increased attention. On the other hand, metal oxides (**MO_x**: ZnO[3], CuO[4]), have been widely studied as catalysts for non-enzymatic sensing. They show excellent properties like low detection limits (down to the nM range), high sensitivity and selectivity and wide linear response range. The integration of **MO_x** nanomaterials within inorganic nanoplatformes like nanostructured carbon-based supports[5] exhibit excellent electroanalytic performance due to the synergy between nano-***MO_x*** properties and those of supports (relative inertness, high conductivity, wide potential range, stability, fast heterogeneous electron transfer). Herein we present **MMs** based on bioavailable metals (copper and zinc)[6-8] with well-determined supramolecular organisations in the mesophase used to modify carbon-based supports to generate randomized or organized **MO_x** nanoelectrode arrays (**MONA**)[9] by electrochemical treatment for the fabrication of electrochemical high performance hybrid sensors for non-invasive real time biomedical applications. The project aims an integrative approach for in-depth understanding of surface and interface chemistry and charge transport.

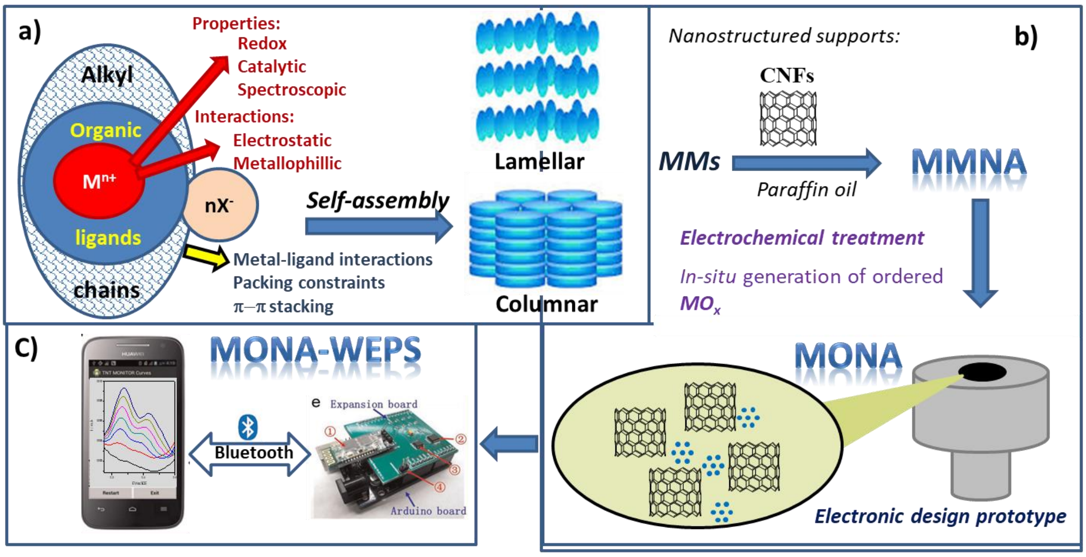

Figure 1. a) the design of ***MMs*** and the role of different molecular parts for the self-assembling into liquid crystalline phases; b) the obtaining of **MONA**: as example carbon nanofibres (CNFs) functionalised with carbon nanodots are represented; c) tdevelopment of a Wireless Electronics-integrated Portable ultrasensitive Sensors (**WEPS**) based on **MONA**.

The presentation cover the designing and prototyping steps needed to obtain a functional sensor (Wireless Electronics-integrated Portable ultrasensitive Sensors - **WEPS**), which uses the above materials as working electrode. Also, the consideration in the electronic system are briefly described, the electronic circuit act as a potentiostat with wireless communication, in our particular case Bluetooth. We will be able to present the real system, sensor plus electronic circuit. The advantage of using latest technologies in semiconductors together with a new perspective of using the raw data of electrochemical measurement will be also covered.

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„This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1958, within PNCDI III".

SPHERICAL CONFINEMENT OF CHIRAL CHROMONICS

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The spontaneous arising of chirality in natural system is an intriguing issue. In recent years, a lot of attention has been focused on native and/or induced chirality in lyotropic chromonic liquid crystals (LCLCs). These water-based systems show a spontaneous chirality when confined in curved geometries. This natural chirality may be enhanced by doping LCLCs with L and D peptides.

Confinement of chiral-induced chromonics is not trivial since they are three component systems whose time stability is a delicate thermodynamic balance. Here we report on the possibility to obtain, in microspheres of a chiral induced chromonic embedded in a poly(dimethylsiloxane) matrix, well-defined periodic Frank–Pryce textures indistinguishable from the ones obtained in chiral thermotropic liquid crystals [1] as well as other peculiar textures [2]. The periodicity of the Frank-Pryce texture can be tuned using different chiral moieties and can be stabilized in the perspective of applications in sensing and anti-counterfeiting devices [3].

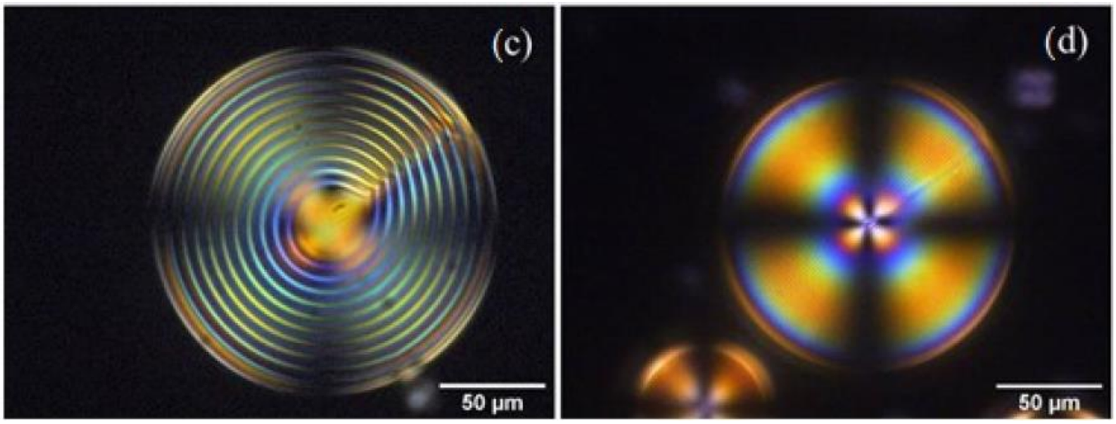

Figure: Chiral LCLCs microspheres

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BIOACTIVE MATERIALS BY IMMOBILIZATION OF NATURAL COMPOUNDS INTO POLYMERIC MATRICES

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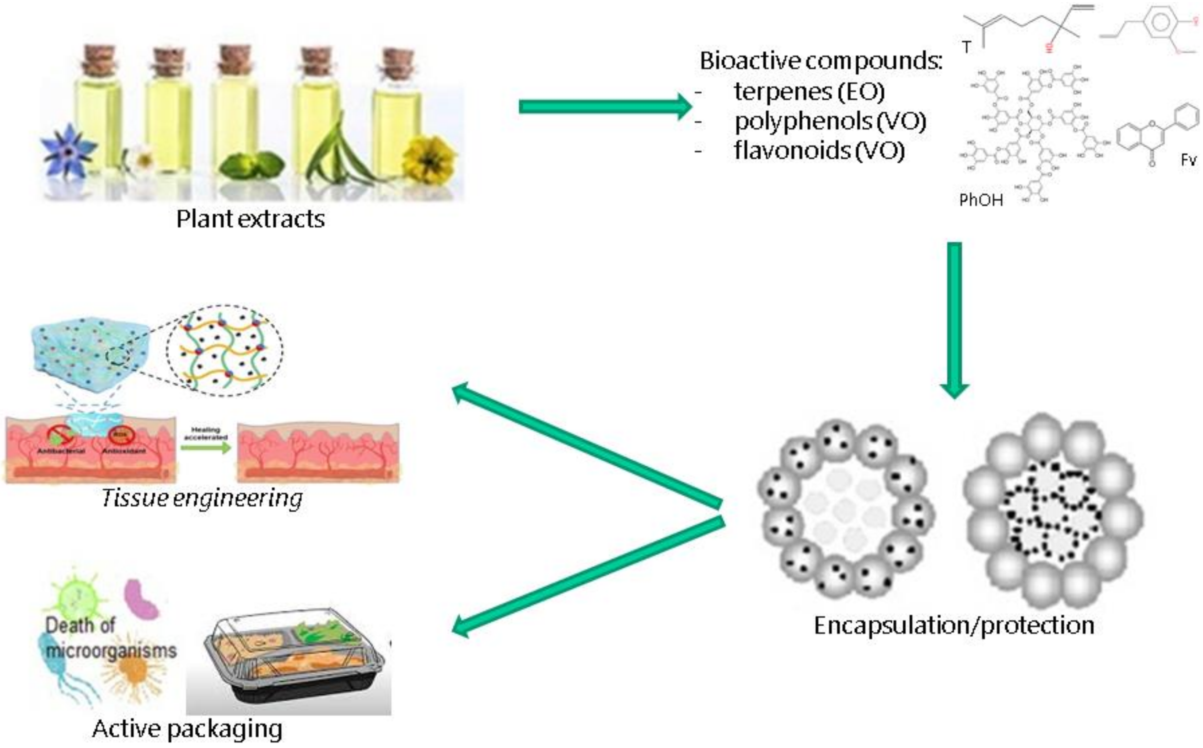
Bioactive materials are gaining a lot of interest since they provide supplementary functionalities in applications where interactions with living organisms are especially envisaged. For example, negative effects on development and proliferation of undesired microorganisms such as pathogenic bacteria and fungi are required in prevention or treatment of diseases [1] as well as in food safety [2]. On the other hand, positive interactions are intended in materials designed as support for cellular growth and tissue regeneration [3]. Natural products, especially those derived from plants, offer numerous advantages compared with synthetic antibiotics or food preservatives to which microbial resistance is largely observed. Proper methods for immobilization of natural compounds into polymeric matrices can lead to advantageous combination of beneficial properties of components in the system. Several procedures such as bulk embedding or surface coating and the properties of obtained bioactive materials will be presented.



Schematic representation of immobilization of natural products into polymeric matrices.

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The project "KSP-S- Bio-farming for bioactive compounds", funded by Research Council of Norway, Contract number 320740/09.12.2020 is greatly acknowledged.

INFRA SUPRACHEM LAB - CENTER FOR ADVANCED RESEARCH IN SUPRAMOLECULAR CHEMISTRY

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1. General information

- *Beneficiary*: Petru Poni Institute of Macromolecular Chemistry Iasi (Institutul de Chimie Macromoleculara Petru Poni, ICMPP)
- Project co-financed by European Regional Development Fund under the Competitiveness Operational Program 2014-2020
- *Priority Axis 1* – Research, Technological Development and Innovation to Support Economic Competitiveness and Business Development
- *Investment priority 1a* – Improving research and innovation infrastructures and capacities to develop excellence in RDI and promoting centers of expertise, especially those of European interest
- *Action 1.1.3* Creating synergies with the RDI actions of the European Union's HORIZON 2020 framework program and other international RDI programs
- *Period*: 25.02.2021 – 24.06.2023.
- *MySMIS*. 108983

2. General objective

The overall objective of the Infra SupraChem Lab project is to create an advanced infrastructure that deserves the supramolecular chemistry working group SupraChem Lab, a group created within the Horizon 2020 Project WIDESPREAD 2-2014: ERA Chairs (667387) - SupraChem Lab Laboratory of Supramolecular Chemistry for Adaptive Delivery Systems ERA Chair initiative.

3. Specific objectives / Expected results

O1. Realization of the design component for the Infra SupraChem Lab project - objective already in implementation
O2. Realization of the infrastructure of the SupraChem Lab center
O3. Equipping and launching the SupraChem Lab center
O4. Dissemination and publicity
O5. Project management

The implementation of the **Infra SupraChem Lab project** represents the creation of an adequate structure for the activity of the **SupraChem Lab group**, a group formed through a Horizon 2020 ERA CHAIR project (Horizon 2020 WIDESPREAD 2-2014: ERA Chairs Project no 667387). The SupraChem Lab project started in 2015 and with the support of EC investment of 2.5 MEuro, the foundation of a young team of researchers was laid, focused on the principles of supramolecular chemistry knowledge. The team's research areas range from the creation of dynamic systems for targeted biomedical applications to the dynamic molecular modeling of the interaction of complex supramolecular systems. The group human resource represents a secure core for the training of new generations of specialists, able to continue and develop new fields with great applicative impact.

Over the last ten years, ICMPP's research directions have clearly evolved into interdisciplinary fields and have been adapted to global research trends, while also presenting their own original directions, based on knowledge and experience gained over time. The implementation of the Infra SupraChem Lab project would contribute to the improvement of the existing research within ICMPP and SupraChem Lab team and to the development besides the fundamental research directions and of some applied research directions for new top products. An important part in the development of new directions is based on a modern infrastructure, aimed at interdisciplinary research. An infrastructure based on the synthesis and complete characterization of new materials represents a real support for the development of application fields. The Infra SupraChem Lab infrastructure is a step forward to create the premises for application of the results of fundamental research obtained by the newly created group.

Infra SupraChem Lab will be set up in spaces owned by the ICMPP - in buildings currently unused, under conservation. The new center will also benefit from the arrangement of auxiliary spaces, for the storage of chemicals, glassware and laboratory materials as well as the related access ways to facilitate the access to the research infrastructure.

The structure of Infra SupraChem Lab will include the following departments:

A. **Operating department** consisting of:

A1. Chemical and biochemical synthesis laboratory
A2. Laboratory for the study of special properties and possible applications
A3. Physical and chemical characterization laboratory

The laboratories are be provided with chemical ventilation niche and specific laboratory equipment for chemical syntheses (eg: magnetic stirrers, inert gas purification installations, vacuum pumps, electric ovens, etc.), study of properties and material characterization (e.g. X-ray diffractometer for wide angles, Photo-DSC, Automatic confocal imaging system for scanning, characterization and data analysis in cell biology, Semi-automatic inverted fluorescence microscope, Diffractometer with dual X-ray source for single crystals, Motorized stereomicroscope with fluorescence with the possibility of in-depth analysis, and many others).

B. **Data processing department**

Within this department, the data will be processed and structural optimization studies will be performed.

C. **Department of projects and technology transfer**

All departments are provided with computers connected to the Internet and implicitly to the internal network of the center.

The project has as **direct beneficiaries** the SupraChem Lab team, the project being addressed also to other interest groups as follows:

- graduates of the universities of Iasi and not only who could join the SupraChem Lab team or could benefit from training within the newly created Center
- teachers from universities in Iasi and not only, who will be able to carry out educational activities within the center
- researchers from ICMPP or other collaborating research institutions, who will be able to perform tests or determinations on the equipment within the center
- different SMEs that will be able to benefit from technology transfer facilities of the patented results that will be obtained within the center

PETRU PONI
INSTITUTE OF
MACROMOLECULAR
CHEMISTRY

Infra SupraChem Lab
Center for Advanced Research in Supramolecular Chemistry

UNIUNEA EUROPEANĂ

Instrumente Structurale
2014-2020

ICT - INTERDISCIPLINARY CENTER FOR SMART SPECIALIZATION IN CHEMICAL BIOLOGY, RO-OPENSCREEN

Manuela CRIŞAN, Alina BORA, Liliana PĂCUREANU, Liliana CSEH

"Coriolan Drăgulescu" Institute of Chemistry, 24 M. Viteazu Av., 300223, Timisoara, Romania
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General information

- *Beneficiary*: "Coriolan Dragulescu" Institute of Chemistry - ICT, Timișoara
- Project co-financed by European Regional Development Fund under the Competitiveness Operational Program 2014-2020
- *Priority Axis 1* – Research, Technological Development and Innovation to Support Economic Competitiveness and Business Development
- *Investment priority 1a* – Improving research and innovation infrastructures and capacities to develop excellence in RDI and promoting centers of expertise, especially those of European interest
- *Action 1.1.1.* Large research and development infrastructures
- *Period*: 20.07.2020 – 31.12.2023
- *MySMIS Code*: 127952
- *Investment Value*: 42,587,899.61 RON

General objective

The aim of the **RO-OPENSCREEN** project implemented by "Coriolan Dragulescu" Institute of Chemistry is to create an *Interdisciplinary Center for Smart Specialization in Chemical Biology*, *RO-OPENSCREEN* with high-level academic research, addressed to the Romanian and European scientific community. The Center will carry out integrative research by applying advanced technologies of automated management of compound libraries, chemical synthesis, structural analysis, determination of biological activities and chemoinformatics.

Description of the investment

The implementation of the project consists of two main components:

I. Modernization/consolidation of two of our own buildings under conservation, namely C20-Materials warehouse and C21- Laboratory. These two buildings considered for development of the new ICT interdisciplinary research center are located in Timișoara, 22 Cornelia Salceanu Street. The modernization/consolidation works include: design and technical assistance, obtaining approvals and authorizations and the actual works: site organization and modernization/consolidation works of the two buildings.

II. The provision of research tools and equipment for three laboratories with specific interdisciplinary biological chemistry, united in the new ICT research center, will ensure the functionality of the following laboratories: (*i*) - Chemoinformatics laboratory; (*ii*) - Chemical bookstore laboratory; (*iii*) - Chemical synthesis, characterization and analysis laboratories. The thermal power plant, reagent transfer station, IT and communication systems are located in the C20-Materials warehouse.

The laboratoratories will be set up with high-performance equipment including automated imagining and multimode microplate reader, automated liquid handling and acoustic transfer of nanovolumes platforms, SAXS/WAXS diffractometer with GISAXS module, polarized and fluorescence optical microscope with hot stage, benchtop NMR spectrometer, ultra-performance liquid chromatography–high-resolution mass spectrometry, thermogravimetric analysis/ FTIR-Raman, circular dichroism coupled with chiral liquid chromatography, high-performance computing and communication system, etc., will place the Center within a rich national and European scientific networks.

The new Center will offer an integrated research infrastructure, unique in Romania, that allows extensive physico-chemical investigations and complete analytical services on the structure of chemical compounds following approved European procedures. Moreover, the center's interdisciplinary research infrastructure developed by combining chemical screening and *in vitro* bioassays will accelerate the process of discovering new compounds with biological activity. These compounds will form the *National Library of Biological Activity Compounds (LNCB).*

Description and valorization of the results

The research infrastructure provided by the project will facilitate the collection and quality management of LNCB's chemical compounds. This library will be connected with the EU-OPENSCREEN's compounds collection through the RoChemBioNet national network. High-capacity, systematic and automatic biological screening workflow of chemical compounds in LNCB, will be implemented. The LNCB will enable the scientific community to explore chemical space with the goal of developing new molecular structures transferable to the clinic and the drug industry.

The complex and high-performance equipment, mandatory to organize an integrated system of research laboratories dedicated to synthesis, structural characterization and primary biological evaluation, will facilitate the increase of ICT competitiveness and attractiveness for new cooperation initiatives at national, regional and European levels. Moreover, the infrastructure will afford to continue the current topic research to a superior level and allow new research directions by developing complex drug discovery projects, agricultural agents, cosmetics, etc.

The training programs through the project implementation will provide a framework to develop strengths, encourage innovation and will boost adherence to high research standards of human resource.

Overall, it is RO-OPENSCREEN's focus on a high-quality compound library and modern research infrastructure that strengthens our attractiveness as a location that facilitates the research scientific community with knowledge exchanges, access to perform tests, determinations and analysis on state-of-the-art equipment and exploring the chemical space through a unique compound collection.

ICT - Interdisciplinary Center for Smart Specialization in the Field of Chemical Biology, RO-OPENSCREEN

(MULTI)FUNCTIONAL IONIC POLYMERS. SYNTHESIS, MATERIALS DESIGN, APPLICATION

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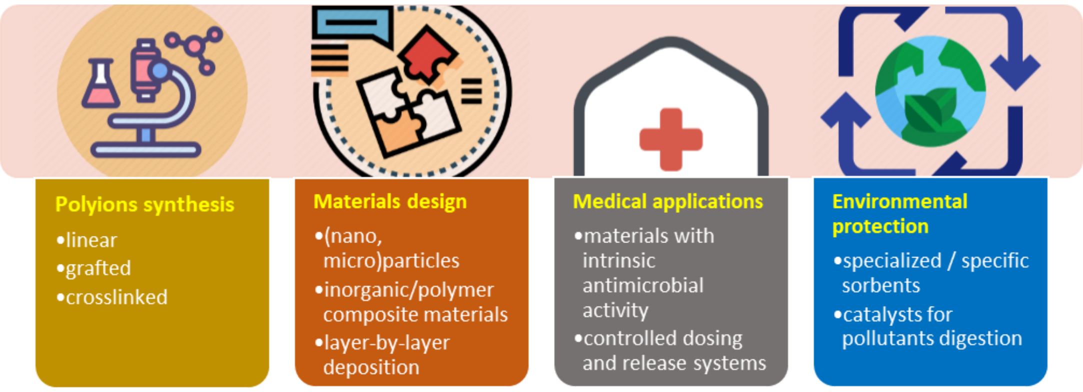
The multifunctional materials, obtained through the synthesis and use of a wide range of synthetic and natural ionic polymers, with preestablished functions and architectures represent an interesting and dynamic research field, both from basic research and application perspective. The use of polyelectrolytes in multicomponent systems is based on their ability to interact, through electrostatic interactions, with species of opposite charges, which can be micro- or macromolecular compounds in solution or with charged surfaces. Thus, polyelectrolytes with opposite charges interact with each other resulting polyelectrolyte complexes, materials with properties that are fundamentally different from the starting compounds. The complexation property of polyelectrolytes leads also to the formation of polyelectrolyte multilayers.



Our studies followed (above scheme): (1) synthesis of (multi)functional ionic polymers: linear, grafted and crosslinked [1]; (2) development of complex nanostructured materials as (micro)particles and beads [2], "hard-soft" composite polymeric materials based on inorganic compounds and polyions [3] or layer-by-layer polycation/polyanion deposition [4]; (3) use of complex (composite) materials in medicine (materials with intrinsic antimicrobial activity, controlled dosing and release systems) and in environmental protection (specialized / specific sorbents for removal of priority organic and inorganic pollutants from simulated and real water). The studies aim to elucidate the role of the initial components and the influence of various synthesis parameters on the structure and morphology of new materials, developing of new materials with ionic/ionizable functionalities and with targeted applications in water cleaning and in medicine.

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BIOMEDICAL APPLICATIONS OF METAL PHOSPHONATES AND OTHER COMPLEXES

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Compounds containing metal anions are well known in the treatment of a number of diseases and medical conditions. The use of *cis*-Platin, $[Pt(NH_3)_2Cl_2]$ as a cancer treatment is one of the most famous such compounds. Furthermore silver has been used for many years as an antibacterial agent. and is regularly included in clothing and wound dressings.

We have demonstrated the synthesis of silver phosphonates whose structure plays an important role on the rate of silver released [1, 2] and on the anti-bactericidal properties exhibited by the materials formed [3, 4]. However Silver is not the only metal capable of acting as an antibacterial agent. silver, it can be mixed with other metals such as Zn and Co which themselves have antibacterial properties.

In this paper we report the activity of a number of new compounds, including metal phosphonates and complexes of some novel ligands based on NSAIDS (non-steroidal anti-inflammatory drugs) in biomedical applications. Specifically this talk will focus on applications as anti-bacterial and in the treatment of colorectal cancer, which is responsible for around 39,000 deaths in the UK alone.

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ELECTROCATALYTIC PROPERTIES OF COBALT PHOSPHIDES AND PYROPHOSPHATES DERIVED FROM PHOSPHONATE-BASED-MOFs

Rosario M.P. COLODRERO, **Aurelio CABEZA, Álvaro VÍLCHEZ-CÓZAR, Montse BAZAGA-GARCÍA, Fernando CAÑAMERO, Pascual OLIVERA-PASTOR**

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As a class of coordination polymers (CPs), metal phosphonates (MPs) are constructed by coordination bonds connecting metal sites and phosphonate (RPO_3^{2-}) ligands, where the metal sites are dispersed uniformly at the atomic level. This feature facilitates the construction of metal-phosphorous-based/nano-carbon composites by one-step pyrolysis, making them very attractive precursors of Non-Precious Metal Electrocatalysts (NPMCs) [1, 2].
In this work, we report the synthesis, characterization and electrochemical properties of three cobalt(II) coordination polymers derived from the N,N-bis(phosphonomethyl)glycine (BPMGLY), $Co(C_4H_9O_8NP_2 \cdot nH_2O$ (n=2-4). These MPs, with different frameworks according to the crystallographic data, are used as precursors of new NPMCs by pyrolytic treatment under 5%-H_2/Ar at different temperatures. The electrochemical behavior of the resulting compounds, mainly crystalline cobalt pyrophosphates and/or phosphides, is fully investigated regarding to the Oxygen Evolution and Reduction Reactions (OER and ORR, respectively) as well as Hydrogen Evolution Reaction (HER). In general, cobalt phosphides (CoP) derived from compound Co-BPMGLY-I (n=4), displayed better performances for the HER with an overpotential of 156 mV.

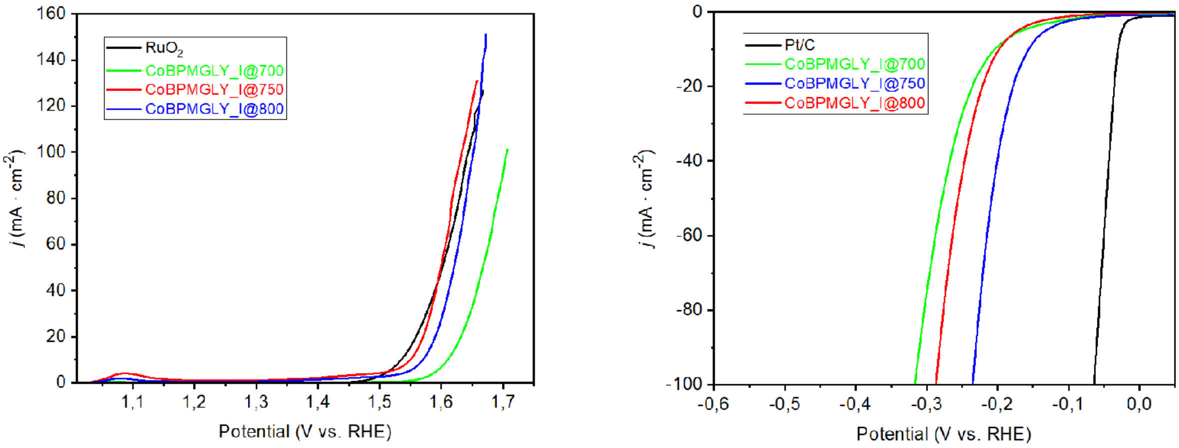

Fig. 1 LSV curves of selected materials for OER in 1.0 M KOH (left) and for HER in 0.5 M H_2SO_4 (right).

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This work was funded by PID2019-110249RB-I00 (MICIU/AEI, Spain) and PY20-00416 (Junta de Andalucía, Spain/FEDER) research projects. A.V.C. thanks MICIU for PRE2020-094459 student grant; M.B.G. thanks PAIDI2020-DOC_00272 research grant (Junta de Andalucia, Spain) and R.M.P.C. thanks University of Malaga under Plan Propio de Investigación for financial support.

NEARLY-FREESTANDING SUPRAMOLECULAR ASSEMBLY WITH TUNABLE STRUCTURAL PROPERTIES

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We report on a novel approach to prepare highly crystalline molecular assemblies with tunable structural properties. We make use of the high-reactivity of the carboxylic acid functional moiety and of the predictable structural features of non-polar alkane chains to synthesize 2D supramolecular assemblies of 4-(decyloxy)benzoic acid (4DBA; $C17H26O3$) on a Au(111) surface. By means of scanning tunneling microscopy, density functional theory calculations and photoemission spectroscopy, we demonstrate that these molecules form a self-limited highly ordered and defect-free two-dimensional single-layer film of micrometer-size, which exhibits a nearly-freestanding character. We prove that by changing the length of the alkoxy chain it is possible to modify in a controlled way the molecular density of the "floating" overlayer without affecting the molecular assembly. This system is especially suitable for engineering molecular assemblies because it represents one of the few 2D molecular arrays with specific functionality where the structural properties can be tuned in a controlled way, while preserving the molecular pattern.

DEVELOPMENT OF ACTIVATED CARBONS FROM AMORPHOUS CELLULOSE AND PRELIMINARY TESTS ON FUNCTIONALIZED SILICA FOR HYDROGEN STORAGE APPLICATION

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Activated Carbons (ACs) are a type of materials showing a microporous structures, which means pores width < 2 nm [1], that together with their structural stability, regenerability and high cyclability make them able to obtain excellent hydrogen (H_2) adsorption capacity. A further advantage comes from the ease of production and the use of recyclable and biocompatible materials. With this in mind, ACs samples have been produced starting from amorphous cellulose (raw material) by different procedures and synthesis processes, such as pyrolysis with physical activation in carbon dioxide. Changing activation temperature values and exposure intervals to oxidizing gas, optimization of the production process of ACs can be obtained leading to high specific surface area (SSA), pore volume and high fraction of micropores. Therefore, the synthesized ACs samples have been investigated in terms of porosity features together with their affinity to H_2 adsorption.

As a result, we have obtained structures with a very high degree of microporosity and an average value of pore width between 5 and 6 Å (analyzed with NLDFT) [2]. This ultra-microporous samples show high SSA values, evaluated by the BET method [3], reaching about 1500 m^2/g as a maximum value. The reported morphology strongly influences the H_2 adsorption properties, where the adsorbed molecules quantities at 1 bar and 77 K reach values very close to the ideal monolayer coverage [4, 5].

Moreover, another class of material belonging to the silica family has been analyzed. In particular, various functionalized mesoporous silica has been synthetized, in order to explore the influence of new functional groups upon the H_2 storage capacity. The materials synthesis was performed in alkaline conditions and with alkyl (16 carbon atoms) chain cationic surfactant, hexadecyltrimethyl ammonium bromide (CTAB). In this step, we have analyzed the influence of CTAB on the porosity features and possible interaction with the H_2 molecules. This study represents an important preliminary test to acquire starting data and carry out a comparison with the next samples synthetized without CTAB in order to improve the H_2 adsorption and understand better the adsorption mechanism at the solid-gas interface for this kind of materials.

For both type of materials (ACs and Silica), textural and adsorption properties have been investigated by means a commercial volumetric apparatus (ASAP 2460, Micromeritics) at 77 K of temperature and pressure range 0-1 bar, through the acquisition of N_2 and H_2 isotherms.

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CIGARETTE BUTT-DERIVED CARBONS AS POSSIBLE SOLUTION TO H_2 AND CH_4 STORAGE

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Discarded cigarette butts are a major waste disposal and environmental pollution hazard due to mainly containing cellulose acetate which is non-biodegradable. Unless causing litter, they contain contaminants such as toxic heavy metals, which can leach into waterways, potentially causing harm to both humans and wildlife [1].

The present experimental work, in an effort to turn dangerous waste into high value products, explores the possibility of valorize discarded smoked cigarette butts to obtain carbon nanostructures with high specific surface area. All porous carbons derived from cigarette butts, via pyrolysis and activation treatment by tuning synthesis parameters, own specific surface area up to circa 1600 m^2/g, a total pore volume of 0.82 cm^3/g and a percentage of microporosity (<2nm) up to 71%. Material's textural properties were evaluated by nitrogen adsorption measurement by using an ASAP 2460 (Micromeritics inc.) in a well-detailed and precise way since the ability of these material to store gas molecules strictly depends on them.

Hydrogen (H_2) and methane (CH_4) adsorption properties were evaluated with a homemade, optimized Sievert-type (volumetric) apparatus named f-PcT [2] for accurate and reliable gas adsorption measurements. Experiments were carried out at liquid nitrogen (77 K) and room (298 K) temperature in a pressure range (0-80) bar for H_2, while only room temperature and pressure up to 35 bar was evaluated in the case of CH_4. Each sample, before adsorption tests, were subjected to Helium (He) picnometry analysis in order to get information on skeletal density value [3].

The reported synthesis procedure aim to increase surface area and optimize pore diameter to improve adsorbent-adsorbate interaction. The obtained cigarette-butt-derived carbons exhibit interesting hydrogen and methane storage capacity compared to similar carbon based porous materials.

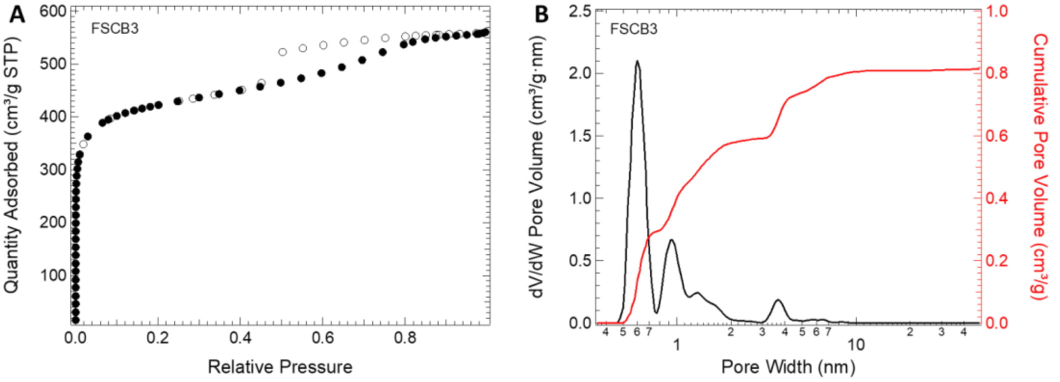

Figure: N_2 adsorption–desorption isotherms at 77K (A), Pore size distribution and cumulative pore volume (B) of the analysed samples.

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DESIGN, PROPERTIES, AND APPLICATIONS OF METAL-CONTAINING SOFT MATERIALS: A BRIEFSURVEY IN THE REIGN OF LIQUID CRYSTALS.

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Metal coordination of organic ligands provides an everlasting approach for the synthesis of “non-conventional” systems, with chemical and physical properties modulated by the contribution of different and tunable molecular building blocks: the metal–ligand central unit, the different type of ligands and the flexible substituents, variable in size and number.[1] In this context, significant progress has been made in the field of liquid crystals based on metal complexes (metallomesogens), modulating factors such as nano-segregation, molecular motifs functional to specific intermolecular interactions and molecular shapes. Indeed, transition metal complexes can organize themselves generating mesophases strictly related to the shape of the single molecules and to the supramolecular organization governed by many different types of intermolecular interactions (hydrophilic/hydrophobic/metallophilic interactions, π-π stackings, hydrogen-bonds….).[2] in the reign of metallomesogens, unconventionally shaped complexes with ordered supramolecular organization in mesophases are not so uncommon, perhaps requiring an update of the standard definitions used to classify both thermotropic and lyotropic systems. In this communication, a library of thermotropic and lyotropic, conventional and un-conventional shaped, metallomesogens, as well as ordered metallogels as soft materials, very close in the supramolecular organization to lyotropic metallomesogens, will be illustrated, showing that the design and the modulation of the molecular shape (by changing the metal ions and the organic ligands) and non-covalent interactions (by changing substituents on the molecular organic fragments) are the key for the generation of remarkable properties.

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MIXING TWO LIQUID AMPHIPHILES: A SIMPLE WAY TO INDUCE THE GENERATION OF EMERGING PROPERTIES, UP TO IONIC LIQUID FORMATION

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Binary mixtures of pure liquid surfactants are usually characterized by enhanced nano-segregation as a consequence of the amphiphilic nature of their constituent molecules. Therefore, such mixtures can exhibit interesting transport properties and complex macroscopic behavior [1].

Chosing surfactants characterized by strongly interacting (polar) head groups, we were able to generate mixtures with enhanced conductivity properties [2], anomalous proton diffusion [3], enhanced solubilizing properties towards inorganic salts [4], and “anti-Arrhenian” behavior of proton conductivity [5]. Even smart materials fully responsive to an external magnetic field have been prepared using this recipe [6].

If acidic surfactants are mixed with basic ones, then a proton transfer takes place, with the consequent formation of protonated and deprotonated species in the liquid state [7]. This means that ionic liquids are formed.

This is an unprecedented, easy, versatile and cheap way to prepare ionic liquids. Structural and dynamic information of some representative samples are given to show this strategy.

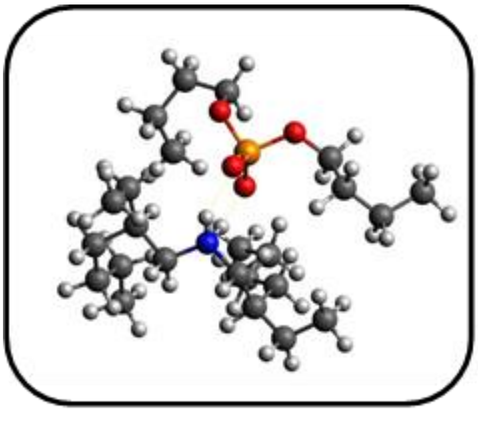

Fig.1: DFT optimized structure of a dibutyl phosphate - bis(2-ethylhexyl)amine complex. The proton transfer from dibutyl phosphate to bis(2-ethylhexyl)amine is evident and takes place with zero activation energy

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SYNTHESIS, ENZYMATIC KINETIC RESOLUTION AND ASSIGNING THE ABSOLUTE CONFIGURATION BY NMR OF NOVEL RACEMIC SECONDARY (*R*,*S*)-2-[(4,5-DIARYL-4*H*-1,2,4-TRIAZOL-3-YL)SULFANYL]-1-ARYL ETHANOLS

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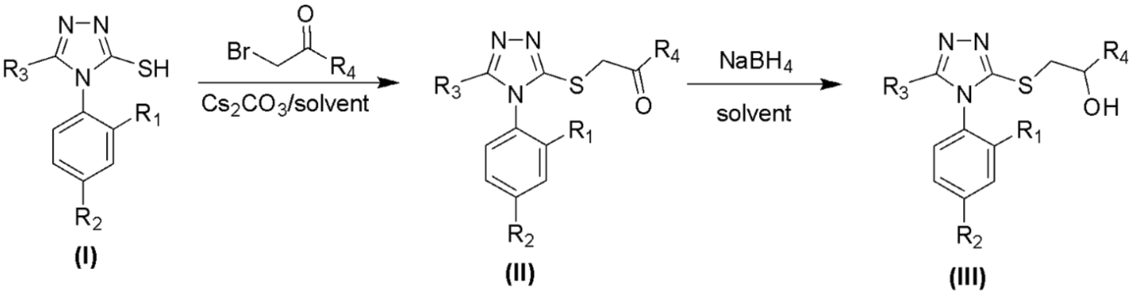
Heteroaromatic building blocks that contain secondary alcohol moieties present great importance due to their perspective applications, particularly in the pharmaceutical field [1]. Some of the biological activities of *S*-alkylated 1,2,4-triazoles include: antimicrobial [2], anti-inflammatory [3], antifungal [4], antidiabetic [5].

In the present work, the new racemic secondary racemic alcohols **(III)** were obtained in a two-step process, in which the corresponding 3-sulfanyl-1,2,4-triazoles **(I)** were *S*-alkylated in basic medium, using α-haloketones after which the corresponding obtained ketones **(II)**, were non-enantioselective reduced at the carbonyl functional group:



(I) $R_1 = H$, $R_2 = OCH_2CH_3$; $R_1 = OCH_3$, $R_2 = OCH_2CH_3$; R_3 = 4-OCH_3-Ph;

(II,III) $R_1 = H$, $R_2 = OCH_2CH_3$; $R_1 = OCH_3$, $R_2 = OCH_2CH_3$; R_3 = 4-OCH_3-Ph;
$R_4 = CH_3$, Ph, 4-Br-Ph, 4-OCH_3-Ph

Synthesis of heteroaromatic secondary alcohol is followed by resolutions of the obtained racemate (*R*,*S*) by HPLC chromatography using a column containing a chiral stationary phase. The reason of obtaining enantiomerically pure secondary heteroaromatic alcohols is most often the different biological activity between the *R*,*S* enantiomers.

To assign the absolute configuration of secondary alcohols (*R* or *S*) numerous reagents have been developed and used. The most common of these are aryl carboxylic acids and the most well-known are (*R*) and (*S*)-α-methoxy-α-trifluoromethyl-phenylacetyl chlorides (MTPA-Cl, Mosher's reagent) [6, 7].

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This work was supported by a grant of the Ministry of Research, Innovation and Digitization,CNCS/CCCDI—UEFISCDI, project number PN-III-P2-2.1-PED-2019-3414, within PNCDI III.

ADSORPTION OF CO_2, CH_4 AND H_2 IN POROUS SORBENTS: ELUCIDATING GAS DISTRIBUTION AND THEIR MOLECULAR DYNAMICS BY NMR METHODS

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Porous solid materials such as zeolites, MOFs, activated carbons and silica-based mesoporous materials have been receiving increasing attention for their use in gas purification and capture technologies with negligible environmental impact [1]. Since the discovery of this new family of sorbents research effort primarily focused on the synthesis and performance analysis of these compounds [2]. Contrarily, the systematic study of adsorption mechanisms and gas distribution in micro- meso-porous sorbents was, to date, very limited [3]. However, it is well established that internal arrangement as well as the diffusion of gas molecules on the porous sorbents have great influence on the adsorption process, which thus deserve much more attention. To our knowledge, only theoretical studies have been proposed so far from MD simulations of CO_2, CH_4 and H_2 gas on porous sorbents [4].

NMR technique is a powerful tool for reveling structural details and adsorption mechanism at molecular level [5]. Consequently, it can potentially clarify the sites of adsorption, microscopic distribution of adsorbed molecules in porous materials and, finally, determine the self-diffusion coefficient of the trapped gas. Despite this, very few experimental studies are currently reported on gas adsorption and diffusion behavior on porous molecular sieves.

In the presentation, a wide overview of the NMR method to study the microscale distribution and molecular dynamics in porous systems is provided. In details, peak fitting analysis and T_1-relaxometry can be used to clarify internal arrangement of CO_2, CH_4 and H_2 molecules in the material micro- and mes-pores whereas pulsed field gradient (PFG) NMR is used to elucidate gasses mobility trough through direct measurement of the self-diffusion coefficients. The aim is to provide a general description of the gas management inside the porous systems. The proposed approach is crucial to properly address the future design and preparation of mesoporous sorbents with improved capture performances.

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LIPASE CATALYZED PRODUCTION OF SUGAR FATTY ACID ESTERS IN REACTIVE NATURAL DEEP EUTECTIC SOLVENTS

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Introduction

Biosurfactants are receiving increased attention due to their industrial applications including foods, cosmetics, pharmaceuticals, toiletries, cleaners, paints, and biotechnology. Sugar fatty acid esters (SFAEs), a particular class of glycosilated lipids, are odorless, flavorless, nontoxic, possess antimicrobial activity, excellent emulsifying properties and foaming ability, and exhibit high biodegradability and biocompatibility [1]. Biocatalytic routes for carbohydrate esterification show the important advantage of carrying out the reactions in a single step, without protection/deprotection of the hydroxyl groups, but also face some challenges, one of the most important being the selection of the appropriate solvent, as the solubilization of sugars, the stability and regioselectivity of lipases in the reaction medium as well as the environmental issues must be solved [2, 3]. Biocatalytic esterification of carbohydrates in natural deep eutectic solvents (NADES) is a promising solution for most of the problems related to the reaction media in biocatalytic transformations, as they are nontoxic, biodegradable and biocompatible [4].

Objectives

Exploiting the intrinsic properties of NADES, in this study we explored the new concept for the enzymatic synthesis of fatty acid esters of carbohydrates and carbohydrate polyols, using reactive NADES where the sugar is simultaneously the co-substrate and part of the NADES solvent.

Results and discussions

Binary and ternary hydrophilic NADES based on choline chloride (ChCl) as hydrogen bond acceptor (HBA) and different hydrogen bond donors (HBD) such as urea (U), monomethyl urea

(MU), sugar alcohols (sorbitol, xylitol, arabitol), monosaccharides (glucose), disaccharides (sucrose, maltose), and oligosaccharides (inulin, maltodextrin) where prepared and characterized.

Between 40 - 80ºC, the optimal temperature range of enzymatic reaction, all NADES tested were stable and fluid. The lowest viscosities were exhibited by ChCh:glucose:water, Urea:ChCl:sugar and ChCl:polyol NADES systems. Lipases from *Candida antarctica B (CalB)*, *Candida antarctica A (CalA)*, *Pseudomonas stutzeri (Ps. stutzeri)*, and *Aspergillus oryzae* and immobilized CalB (N435), showed significant esterification activity in all 18 different binary and ternary ChCl-based NADES prepared. Moreover, the selected enzymes showed relatively high thermal stability in NADES at 70°C. The immobilized CalB (N435) showed not only high activity in the selected NADES, but also exceptionally high thermal stability, maintaining 92% of activity upon incubation at 70°C for 72 h. Synthesis with good conversion of mono-lauryl and di-lauryl esters of carbohydrates (e.g. glucose, sucrose, maltose) and polyols (e.g. arabitol, xylitol, sorbitol) catalyzed by immobilized *C. antarctica* lipase B (N435) in the corresponding ChCl/sugar or ChCl/polyol reactive NADES was demonstrated by HPLC, MALDI-TOF-MS and 1D and 2D NMR.

Conclusions

A large spectrum of choline chloride based reactive NADES with physical and fluid properties suited for biocatalysis were successfully obtained with various sugars and polyols as hydrogen bond donors. Native and immobilized lipases maintain catalytic activity and thermal stability in NADES, which proved to be suitable reaction medium for the enzymatic synthesis of a high variety of esters of lauric acid with alcohols, polyols and carbohydrates. Biocatalytic conversion in reactive NADES enable the selective esterification of carbohydrate polyols and mono-, di- and oligosaccharides, at high substrate load and high yields. This work opens the way to further optimization of the biocatalytic synthesis of SFAEs in reactive NADES, to process development and scale up.

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This work was supported by a grant of the Romanian Ministry of Education and Research, CCCDI-UEFISCDI, project number PN-III-P4-ID-PCE-2020-2177, within PNCDI III, contract number PCE 157/2021.

WASTES-DERIVED POROUS CARBONS WITH RELEVANCE IN ENVIRONMENTAL PROTECTION

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The main method for creating nanocarbon is still pyrolysis of carbon-rich raw materials, which is recognized for inducing the chemical breakdown of organic molecules by heat. Modern trash from people, animals, and plants contains significant organic matter. Thus, waste cellulose and polymers can be securely disposed of by pyrolysis, as opposed to direct burning or combustion, which is bad for the environment. The solid carbon residues left over after the pyrolysis of waste materials, the procedure being researched the most in both industry and academia, also have a wide range of applications. Additionally, because it is inexpensive, renewable, cheap, simple to obtain, and produced in vast quantities as carbon-rich raw materials, pyrolysis of waste foam-like materials, including various organic molecules, could produce considerable carbonaceous materials batches.

Therefore, to generate lightweight carbonaceous materials with a large specific surface area, a wide range of foam-like materials can be found all around us, including sunflower and corn stalk pith, corn starch peanuts, as well as polyethylene foam, last both used for packing, were taken into consideration in the current investigation (Fig.1).

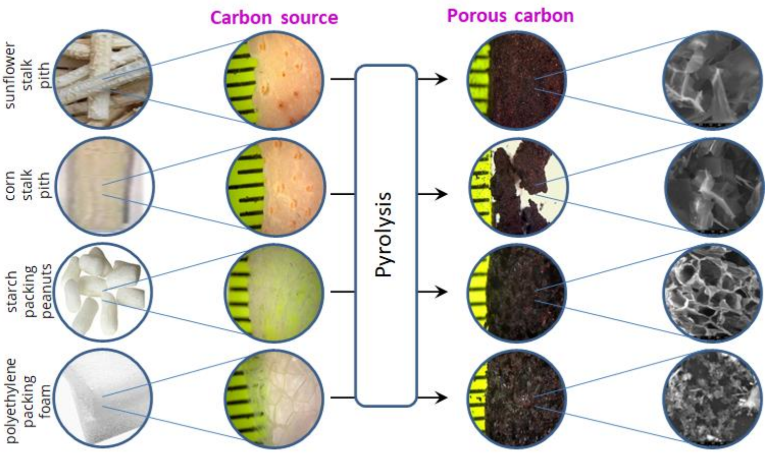

Fig.1. Schematic preparation of porous carbons by the pyrolytic process at high temperatures.

The produced monolithic carbon foams show a potential use for the adsorption and separation of oil or organics from water due to their inherent hydrophobic features and high sorptive capacities. Accordingly, a number of run experiments on oil and solvent spill cleanup solutions are presented for their use.

The financial support of the European Fund for Regional Development, Competitiveness Operational Programme 2014-2020; POC/163/1/3 – Project 4WASTEUPGRADE (Contract no. 386/390062/4.10.2021, cod MySMIS: 120696) is gratefully acknowledged.

COMPUTATIONAL ASSESSMENT OF THE TOXICOLOGICAL EFFECTS OF THE MYCLOBUTANIL ON THE HUMAN HEALTH

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Myclobutanil is a chemical entity used as a fungicide. This fungicide persists in the soil and it is known that some traces accumulated in fruits, vegetables and drinking water, consequently may present a risk the human health. Within this study, a computational approach has been used to evaluate the toxicological effects of the myclobutanil on the human health. It integrates predictions of absorption, distribution, metabolism, excretion and toxicity (ADMET) profiles. Several toxicological effects have been identified: inhibition of cytochromes, possible eye corrosion and irritation, neurotoxicity, mutagenicity and the potential to produce effects on the respiratory system. Myclobutanil also has a good oral bioavailability and a high probability of binding to plasma proteins, this underlines the fact that it can be distributed in the human body where it can exert the previously listed effects.

This work was supported by the grant PN-III-P1-1.1-PD-2019-025 ”Assessment of the environmental effects of triazole fungicides that are approved for use in European Union for the protection of cereals”.

DETECTION OF HEAVY METALS IN THE *SIDERITIS RAESERI* (Çaj mali) PROVIDED AT ALBANIAN PHARMACIES

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The use of heavy metals in industry, agriculture, medicine, and technology has increased their presence in the environment, causing damage to plant, animal, and human health. Due to their chemical composition, so-called heavy metals are also often called “systemic toxicants”. They are also known human carcinogens and can cause damage even at lower exposure levels. Of particular importance is determining heavy metals in medicinal and herbal plants for curative purposes.

This work focuses mainly on the qualitative and quantitative analyzes of five metals (Pb, Cd, Hg, Sn, and As) detected in tea (herbal tea) found in the Albanian pharmacies as mountain tea. After a preliminary treatment of the sample with microwave digestion and extraction using Clevenger, an analytical technique such as ICP-MS was used, and also the AOAC 2015, 6-19: 2019 method was applied. The determination of heavy metals was found in the leaf and the essential oil.

From the measurements, it was observed that the concentration of these metals was within the defined standards and that the highest percentage was tin (Sn) with 75 % in the herbal leaves and 40% in the extracted oil. When comparing the levels of heavy metals in the leaves and the extracted oil, it can be noticed that arsenic levels have decreased significantly from 0.125 mg/kg to < 0.001 mg/kg and tin levels have decreased significantly from 0.557 mg/kg to 0.004 mg/ kg. A decrease in the number of other metals was also noticed.

In conclusion, we can say that greater attention should be paid to the presence of heavy metals to protect the environment, plants, and human health, and their presence, even in small quantities, can cause irreparable damage.

Keywords: heavy metals, ICP-MS method, HDC (hydro distillation), essential oil.

DETECTION OF DIFFERENT QUINONE DERIVATIVES USING Pt(II)-METALLOPORPHYRIN-AuNPs HYBRID NANOMATERIALS

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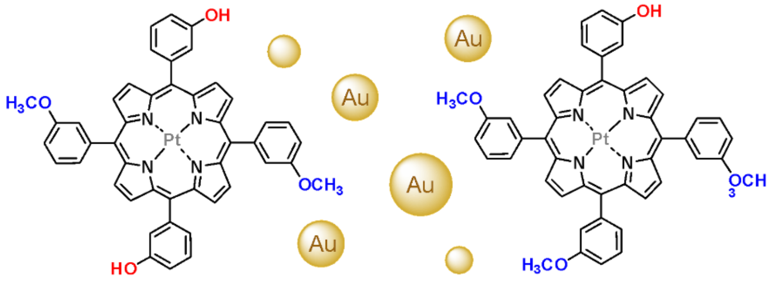
Two asymmetrically A_2B_2 and respectively A_3B porphyrin structures, mixed substituted with hydroxyl and methoxy- groups on phenyl *meta*-position, were synthesized using the multicomponent Adler-Longo method. These porphyrins were further metallated with platinum (Figure 1) and then used to obtain plasmonic hybrid materials with gold nanoparticles (AuNPs). These nanomaterials were tested as sensitive materials in the optical detection of hydroquinone and potassium anthraquinone-1-sulfonate [1, 2], both compounds having clinical relevance.



(a) (b)

Figure 1. Chemical structure of A_2B_2 type Pt(II)-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)-porphyrin (a), and A_3B type Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin (b)

The porphyrinic structures were fully characterized by physico-chemical methods and the morphostructural differences and aggregation properties were highlighted by AFM and SEM methods.

The detection mechanisms studies evidenced that in the case of potassium anthraquinone-1-sulfonate are based on strong hydrogen bonds between the peripheral *trans* –OH groups in A^2B^2 porphyrin and the C=O substituents of the analyte, amplified by the high affinity of the sulfur atom for gold nanoparticles. These multiple influences ultimately generate a basket-like structure based on host-guest interaction. In the case of hydroquinone, semiquinone radicals and 1,4-benzoquinone that are generated from hydroquinone, could establish OH···O=C weak bonds, or $C–O^{−}···OH$ interactions between the OH-group of the A^3B platinum porphyrin and the semiquinone specie [3].

The sensitive material formed between gold nanoparticles and the A^3B Pt-metalloporphyrin is able to detect with high accuracy and precision hydroquinone in the concentration range from 0.04 µM to 6.71 µM. The A^2B^2 Pt-porphyrin-AuNPs plasmonic material proved to be highly selective in the optical detection of the potassium anthraquinone-1-sulfonate in the concentration range: 0.024 − 0.25 µM [1, 2].

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The author kindly thanks for the support to Romanian Academy - Programme 3/2022 from ICT and to UEFISCDI for financed Project PED 528/2020 CERAPOR-CORR.

PRIORITIZATION OF KINASE CRYSTAL STRUCTURES FOR DOCKING, USING B-FACTOR INDEX FOR THE BINDING SITE

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Protein kinases have become widely studied as effective drug targets due to their importance in pathological cellular processes. During the last two decades, a large number of kinase crystal structures, have been made publicly available, which makes docking a particularly suited tool for cheminformatics to study kinase-ligand interactions. If multiple structures are available, reliable parameters should be used to select the most accurate complex. In this matter, our group proposed a new metric, i.e., B-factor index for the binding site (BFI^{bs}) and demonstrated unparalleled correlation with molecular docking outcomes on large scale. In this study, we explore in detail the relationship between BFIs and key properties of kinase-ligand complexes. We performed docking on 2432 crystal structures and examined the results, relative to the binding site conformations, ligand properties and binding site interactions. The results indicate that BFI^{bs} values < 1 can significantly increase the chances of finding the crystal structures with accurate re-docking results (RMSD, root-mean-square-deviation values < 2 Ǻ). Moreover, kinases in inactive state conformations, with ligands interacting with the gate and back pockets (but not front cleft), are prioritized by the BFI^{bs} with accurate docking results. Further, we found a statistically significant inverse correlation ($p < 0.05$) between BFI^{bs} values and the number of interactions in the binding site. In conclusion, we demonstrated that BFI^{bs} values can enhance drug discovery of kinase inhibitors based on docking.

CYTOPATHOLOGICAL CHANGES AND DNA DAMAGE IN HUMAN TUMOR CELLS AFTER TREATMENT WITH ZN(II)/AU(I) AND ZN(II)/AG(I) COMPLEXES WITH SCHIFF BASES

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Cancer is one of the leading causes of death in the world. The most common treatment options are chemotherapy, radiation, and surgery. Chemotherapy is a systemic treatment that presents a number of drawbacks and unwanted side effects, with the potential for normal tissue toxicity and multidrug resistance. One of the modern strategies to counter these drawbacks is to come up with new safe compounds that have high specificity, selectivity, and the ability to kill malignant cells with minimal side effects.

In this context, researchers turned to the study of metal-based compounds, which were among the most famous means of treatment for many diseases since ancient times, and this conviction centered on the great therapeutic success of the use of cisplatin, carboplatin, and oxaliplatin.

In view of all the above, it was the main reason we chose to study the bioactivities, such as anti-tumor and anti-viral properties, of 9 newly synthesized complexes of Zn(II)/Ag(I) and Zn(II)/Au(I) with Schiff bases derived from 2,6-diformyl cresol (diald) - Aepy, Ampy and Dmen.

Our previous studies showed that these complexes have promising antiproliferative/cytotoxic activity on several types of cancer cell lines, by using different cytotoxicity assays with different mechanisms of action and targets in cells such as MTT test, neutral red uptake, and crystal violet staining. The cytotoxic effect of Zn(II)/Au(I) complexes was comparable or even better in comparison to conventionally used in clinical practice anticancer agents.

These results prompted us to continue studying the ability of these compounds to cause cytopathological changes and DNA damage in human cancer cell lines.

As an experimental models were used various human tumor cell lines: SAOS-2 (osteosarcoma), A549 (non-small cell lung cancer), HeLa (carcinoma of the uterine cervix), MCF-7 (luminal type A breast cancer, ER+, PR+, HER2-) and MDA-MB-231 (triple negative breast cancer, ER-, PR- and HER2-). The study was performed by following methods: hematoxylin and eosin staining (HE), double staining with acridine orange, and propidium iodide (AO/PI), AnnexinV/FITC and Comet assay.

The results obtained revealed that the compounds investigated applied at a concentration range of 0.1–100 µg/ ml induce cytopathological changes, cause double-strand breaks in the DNA molecules and apoptosis in the treated cells. A complete agreement with the previously obtained facts that ZnDmenAu and ZnAmpyAu expresses the highest cytotoxic activity and metal complexes are more pronounced cytotoxic agents as compared to ligands was found.

This study was supported by a bilateral project between Romanian Academy and Bulgarian Academy of Sciences; Grant № КП-06-M41/1 from 27.11.2020, National Science Fund, Bulgarian Ministry of Education and Science.

EVALUATION OF BIOLOGICAL ACTIVITY (CYTOTOXIC, ANTIVIRAL) OF 1,8-NAPHTHALIMIDE DERIVATIVES

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The aim of our study was to evaluate the cytotoxic / antitumour and antiviral activities of first generation polypropylene imine dendrimer modified with 1,8-naphthalimide and chitosan modified with 4-amino-1,8-naphthalimide.

The following cell lines were used as model systems: LSR-SF-SR (sarcoma in rat induced by Rous sarcoma virus strain Schmidt-Ruppin), HeLa (human cervical carcinoma), MDA-MB-231 (human triple negative breast cancer), MCF-7 (human luminal type A breast cancer), Lep-3 (non-tumor human embryonic cells) and MDBK (bovine kidney). The investigations were carried out by: i) short-term experiments (treatment period is 24-72h, performed with monolayer – 2D cell cultures) performed using MTT test, neutral red uptake cytotoxicity assay, crystal violet staining and double staining with acridine orange and propidium iodide; ii) long term experiments – the influence of 1,8-naphthalimide derivatives on viability and 3D growth of cancer cells was assessed during 2-3 weeks by 3D colony-forming technique. The effect of the compounds on the replication of Herpes simplex virus type 1 (HSV-1, strain F) and hype 2 (HSV-2, Strain BA) was examined in MDBK cells by the method of Reed and Muench.

The results obtained revealed that modified chitosan has more pronounced cytotoxic activity than the first generation polypropylene imine dendrimer modified with 1,8-naphthalimide and non-modified chitosan. Non-tumor Lep-3 human cells are less sensitive to the cytotoxic effect of the compounds examined as compared to MDA-MB-231 and MCF-7 breast cancer cells. The 1,8-naphthalimide derivatives do not affect significantly the replication of HSV-1 (strain F) and HSV-2 (strain BA).

This study was supported by Grant №КП-06-КОСТ/16 from 16.12.2020, National Science Fund, Bulgarian Ministry of Education and Science; COST Action CA18132.

β-PHOSPHONATED GLYCINE PENDANT GROUPS GRAFTED ON POLYMER: SYNTHESIS AND APPLICATION AS HETEROGENEOUS PHOTOCATALYST

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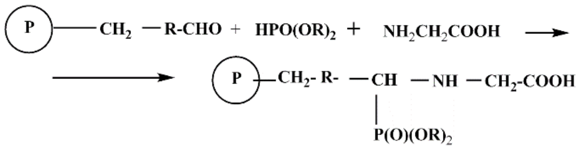
Environmental pollution resulting from organic pollutants caused by textile dyes is a real situation danger. Wastewater from the textile industry has high organic loads due to both the dyes used and the chemical compounds added to the their preparation. Among the azo dyes, the bright red dye Congo red (CR) is extensively used as a model dye in the studies concerning treatment of wastewater resulted in textile dyeing [1, 2]. The degradation of textile dyes from wastewater by heterogeneous photocatalysis has attracted more and more attention in recent decades. Heterogeneous photocatalysis consists in the UV light irradiation of different types of dyes in wastewater in the presence of a solid catalyst and is considered one of the important techniques for the purification and reuse of aqueous effluents [3, 4]. In the present study, two new compounds of type β-phosphonated glycine pendant groups grafted on S-DVB copolymer were used for the decontamination of water polluted with Congo red dye. They were prepared using amino acid (glycine), diethylphosphite/dibenzylphosphite and aldehyde copolymers as matrices (see Scheme 1).



$$\textcircled{P}-CH_2-R-CHO + HPO(OR)_2 + NH_2CH_2COOH \longrightarrow$$
$$\longrightarrow \textcircled{P}-CH_2-R-\underset{\substack{|\\ P(O)(OR)_2}}{CH}-NH-CH_2\text{-}COOH$$

Scheme 1. Synthesis of [(diethyl)/(dibenzyl)(phosphono)methylene]glycine pendant groups grafted on styrene-6.7%divinylbenzene copolymer; where: R= -O-C_6H_4-; R= Et:-ethyl, Bz:-benzyl; (*Code: EthylAmAcid / BenzylAmAcid*)

They were characterized by Fourier transform infrared, scanning electron microscope, EDX spectroscopy, thermogravimetric analysis. The band of the carboxyl group (γC=O at 1697 cm^{-1}) decreases in intensity, indicating the consumption of the –CHO groups. The phosphorus content is 1.51%, respectively 1.11% for functionalized copolymers with pendant groups having radicals: ethyl and respectively benzyl. TG/DTG analysis in nitrogen for EthylAmAcid sample was studied. After 900 °C, the decomposition of EthylAmAcid sample gives 19.3 % residue.The synthesized materials were utilized as catalysts in the photo-oxidation process of Congo red. It was studied the influence of initial concentration of dye and solid:liquid ratio on the process of photocatalytic oxidation. The lower the initial concentration of the dye, give the higher the efficiency of the heterogeneous photocatalytic process. Increasing the solid:liquid ratio from 0.5 g/L to 1 g/L improve the efficiency of the process, but an increase from 1 g/L to 2 g/L does not bring improvements to the efficiency. By utilizing 25 mg/L initial concentration of Congo red dye, a solid:liquid ratio of 1 g/L and after 240 minutes of irradiation, the efficiencies of the photocatalysis were 98.6% in case of EthylAmAcid and 92.7% in case of BenzylAmAcid, respectively. The results suggest that obtained materials could be effectively used as photocatalysts in the degradation process of Congo red dye-containing waters under UV-VIS light irradiation.

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ACETAMIDE DETECTION WITH RELEVANCE IN LIVER FIBROSIS CONTROL USING A DIMER COMPOUND BASED ON PORPHYRINS

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Two porphyrins, the first being symmetrically grafted with sulfonic groups and the other with only one carboxylic functional group, were complexed in acidulated DMSO/water of pH =2 to form a dimer compound. The process was monitored by UV-Vis spectroscopy.

Thioacetamide (TAA) is known to be widely used for producing of useful fungicides, pesticides, pharmaceuticals and rubber chemicals, in spite of its potential for inducing liver, kidney and bone damage [1], including fibrosis even if in low concentrations of 0.025 mM [2]. That is the reason why monitoring TAA levels is required in many industries.

The detection of TAA using the dimeric porphyrin is represented in Figure 1 by using UV-Vis spectroscopy. By increasing the concentration of thioacetamide, the spectra change as follows: a continuous decrease in the intensity of all UV-Vis absorption peaks of the dimer accompanied by a continuous increase of a new band located at 320.5 nm can be noticed, along with the appearance of an isosbestic point located at 365 nm.

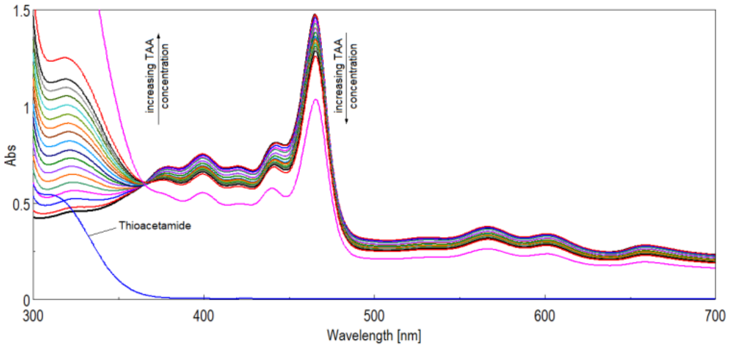

Figure 1. The overlapped absorption spectra of dimeric compound when adding increased amounts of TAA, in water/DMSO

The dependence between the intensity of the dimer intensity read at 465.5 nm and the TAA concentration is linear in the range $0.78\times10^{-4} \div 12.8\times10^{-4}$ M, which is a relevant field for the control of liver fibrosis. The correlation coefficient of 99.71% represents a very promising result.

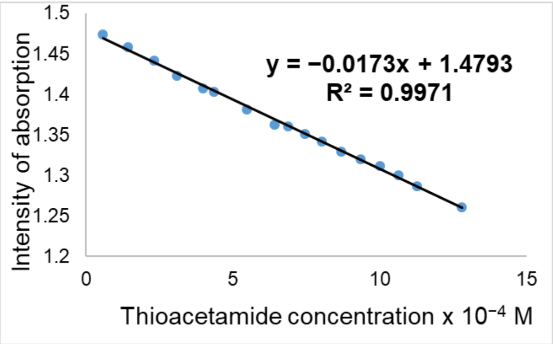

Figure 2. Linear dependence between the absorption intensity of the dimer read at 465.5 nm and the concentration of thioacetamide

In conclusion, we obtained a simple and fast UV-Vis spectrophotometric method for the detection of thioacetamide by using the porphyrin-dimeric compound as sensitive material. The method is viable and presents good accuracy in the range of thioacetamide concentrations from $0.78 \times 10^{-4} \div 12.8\times10^{-4}$ M.

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The authors kindly thank for the support of Romanian Academy - Programme 3/2022 from Institute of Chemistry Timisoara.

SYNTHESIS AND CHARACTERIZATION OF A HETERO-PORPHYRIN TRIMER

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Taking into consideration that phosphorus porphyrins possess strong fluorescent properties [1] and that platinum porphyrins are sensitive compounds for the detection of oxygen and organic dyes [2-4], a supramolecular complex porphyrin structure comprising one Pt(II)-5,10,15,20-tetrakis-(4-allyloxyphenyl)-porphyrin molecule (Pt(II)-TAPP) and two (5,10,15,20-tetraphenylporphinato)dichloro-phosphorus(V) chloride molecules (P(V)-porphyrin) (Figure 1) was obtained, with the purpose to design a novel fluorescent sensor.

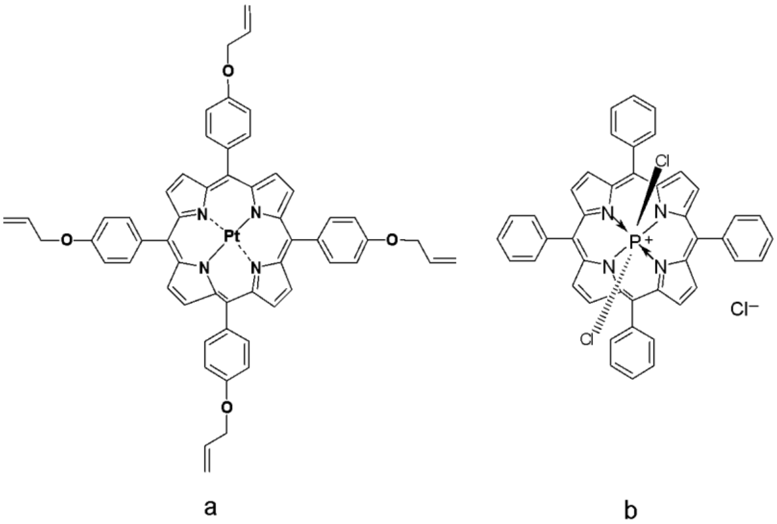

Figure 1. Chemical structures of Pt(II)-TAPP (a) and P(V)-porphyrin (b)

The complex was formed by successive adding of portions of P(V)-porphyrin solution in water (c = 2.91 x 10^{-5}M) to 5 mL Pt(II)-TAPP solution (c = 9.9 x 10^{-6}M) in DMSO. Monitoring the formation of the complex was performed by registering the UV-Vis spectra after each adding and overlapping them (Figure 2).

The two P(V)-porphyrin molecules are bound through the central phosphorus atoms to two oxygen atoms from the allyloxy-phenyl substituents *trans* positioned in Pt(II)-TAPP molecule. The afinity of phosphorus to oxygen atoms is highly recognized, so that the design of this trimer was based on this knowledge. This complex structure was confirmed by calculation of the molar ratio of the starting porphyrins and by the analysis of the ATR spectra, that evidenced the newly formed the P-O bonds.

The structure of the supramolecular complex was optimized by PyMOLMolecular Graphics System, Version 1.7.4 Schrödinger, (LLC New York, NY, USA, 2015) (Figure 3).

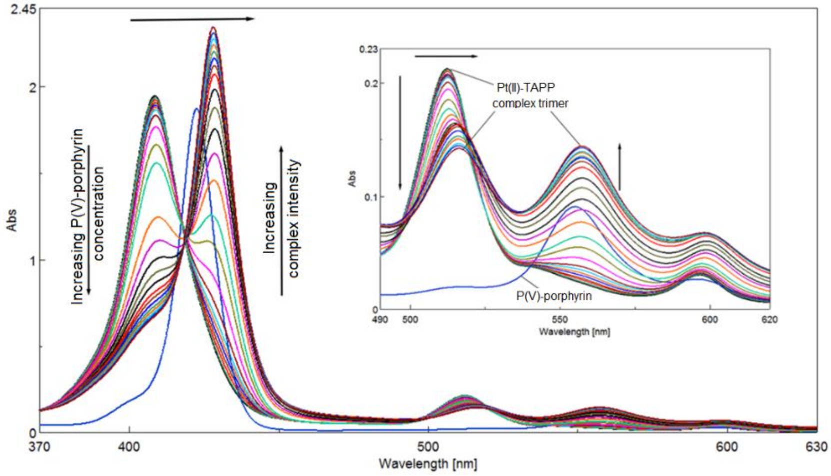

Figure 2. Superposed UV-Vis spectra when adding P(V)-porphyrin solution over Pt(II)-TAPP solution. The detail presents the Q bands.

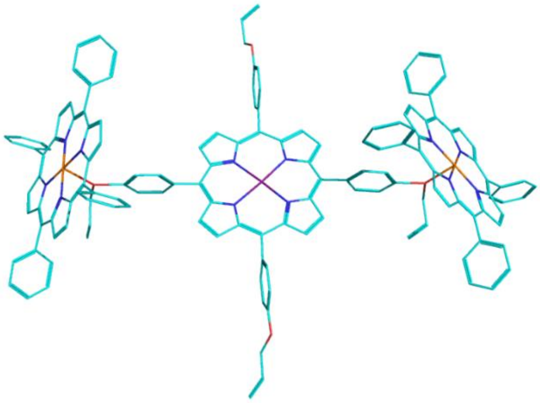

Figure 3. Optimized representation of the complex formed between two P(V)-porphyrin molecules and one Pt(II)-TAPP molecule

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The authors kindly thank for the support of Romanian Academy - Programme 3/2022 from Institute of Chemistry Timisoara.

SYNTHESIS, CRYSTAL STRUCTURES AND MODELING OF CO_2 BINDING SITES IN Zn(II) AND Cd(II) MOFS BASED ON 4,4'-BIPHENYLDICARBOXYLATE AND AZINE LIGANDS

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The metal-organic frameworks (MOF) as multifunctional porous materials are currently in high demand and as adsorption supplies represent a real alternative for industrial scale implementation. The sorption of carbon dioxide is a major environmental issue today and in this regard, the azine-moieties of bis-pyridine type ligands as functional groups on the pore surfaces of MOFs can act as Lewis bases and facilitate the CO_2 physisorption [1]. Four MOFs $\{[Zn(bpdc)(3\text{-}bmphz)]\cdot 1.5(dmf)\}_n$ (**1**), $\{[Zn(bpdc)(3\text{-}bmphz))]\cdot dmf\cdot 0.5Py\}_n$ (**2**); $\{[Zn(bpdc)(4\text{-}bmphz)](MeOH)\cdot 0.5(H_2O)\}_n$ (**3**); $\{[Cd(bpdc)(bda4bPy)]\cdot 2.5(dmf)\}_n$ (**4**) were obtained in soft synthetic conditions using the blends of 4,4'-biphenyldicarboxylic acid (H_2bpdc) with three different N-bases, 1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine (3-bpmhz), 1,2-bis(1-(pyridin-4-yl)ethylidene) hydrazine (4-bpmhz), and

N^1,N^4-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine (bda4bPy); dmf=dimethylformamide, Py=pyridine. The synthesized crystalline solids represent 3D networks with **dia** (**1**) and **pcu** (**2-4**) topologies, while **1** and **2** are the supramolecular isomers. Despite the three-fold (**1**, **3**) or two-fold (**2**, **4**) interpenetration the crystals expose porous structure (Fig. 1a, b). The activated forms of **1** and **4** with the solvent accessible volumes of 30.1% and 43.7% reveal efficient capture of nitrobenzene registered by IR spectroscopy.

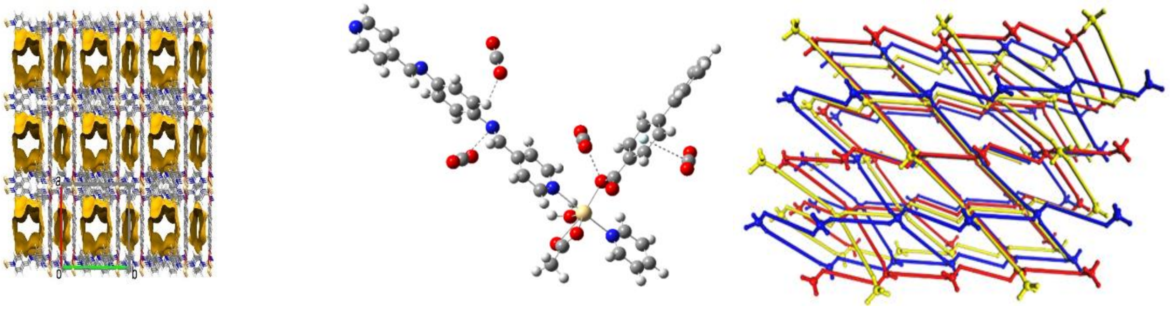
(a) **(b)** **(c)**

Figure 1. Three-fold interpenetration of **dia** topology in **1** (**a**)**;** porous structure of two-fold interpenetrated network with **pcu** topology in **4** (**b**); preferable simulated CO^2 binding sites in **4** (**c**).

The symmetry adapted perturbation theory analysis was used to clarify the binding sites for the efficient capture of CO^2 molecules on the walls of studied MOFs (Fig. 1c). The high porosity of **4** and formation of pnictogen bonds may lead to promising application of this compound for CO^2 capture. The Boltzmann transport equation and the density functional theory also revealed the significant thermoelectric properties for **4**.

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The authors thank the project ANCD 20.80009.5007.15. V.L. thanks the project ANCD 20.80009.5007.28.

SYNTHESIS, CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF IONIC ADDUCT OF 2,4-DIAMINO-6-PHENYL-1,3,5-TRIAZINE WITH MALONIC ACID

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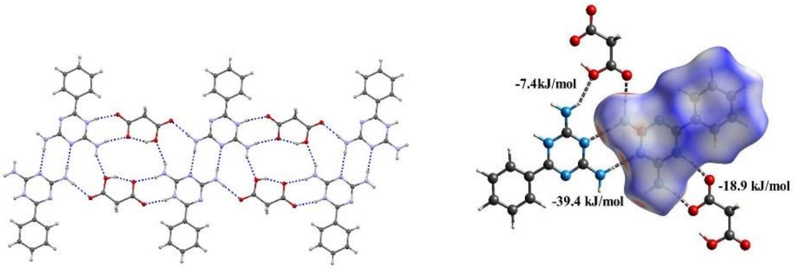
2,4-Diamino-6-phenyl-1,3,5-triazine (dpt) is a popular molecule widely used both in coordination and supramolecular chemistry due to the availability of nitrogen-rich organic triazine core acting as a good donor and acceptor in supramolecular synthesis to design materials with desired physicochemical properties. Co-crystallization of dpt with various organic and inorganic acids resulted in multidimensional supramolecular architectures [1, 2]

In this paper, we report synthesis, and single crystal X-ray structure of dpt adduct with malonic acid (H_2mal) prepared by mixing of reactants in 1:2 molar ratio in solvent mixture CH_3OH/CH_3CN. Hirshfeld surface analysis and two-dimensional fingerprint plots were used to quantify the percentage contributions of the intermolecular interactions present in the crystal. The binary salt-like adduct with the composition [Hdpt]·[Hmal] belongs to the monoclinic crystal system with $P2_1/c$ space group. The asymmetric unit comprises 2,4-diamino-6-phenyl-1,3,5-triazin-1-ium cation and hydrogen malonate anion. Two cations are self-assembled through N-H···N hydrogen bonds (N···N distance is 3.034(5) Å) to form a supramolecular homosynthon $R_2^2(8)$, while hydrogen malonate anions are paired with $[Hdpt]^+$ by N-H···O hydrogen bonds through two supramolecular heterosynthons, $R_2^2(8)$ and $R_3^3(10)$, N···O distances being in the range of 2.786(4)–2.871(4) Å. These interactions govern the H-bonded supramolecular chain formation and play a dominant role in stabilizing the crystal structure. Hirshfeld surface analysis revealed that the H···H (34.5%), O···H (18.4%) and N···H (13.1%) interactions make the highest contributions to the Hirshfeld surface. The intermolecular energy evaluation calculated according to the energy model CE-B3LYP with 6-311G (d,p) basis set revealed that the N-H···N hydrogen bonds from homosynthon are more effective, having a higher energy value (-39.4 kJ/mol) compared to the N-H···O hydrogen bonds in heterosynthons (-18.9 kJ/mol and -7.4 kJ/mol), thus confirming significance of such interactions for stabilization of supramolecular architecture.



a b

Fig.1. a) Supramolecular chain and b) Hirshfeld surface with highlighting supramolecular synthons of the title compound

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Authors thank the project ANCD 20.80009.5007.15 (R. Moldova) for support.

ASSESSMENT OF TRIAZOLE FUNGICED REGARDING THEIR AQUATIC TOXICITY

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Triazole fungicides, used for the treatment of fungal diseases of various crops, can reach the aquatic environment and have ecotoxic effects on the present aquatic organisms. In this study, the potential ecotoxicological effects of some triazole fungicides on some aquatic organisms were analyzed by combining a computational study with an experimental one. The target aquatic organisms were *Lemna minor* (the common duckweed), in the experimental approach, and fish, crustaceans, aquatic invertebrates and algae, in the computational approach. The experimental data were obtained by exposing *Lemna minor* to six triazole fungicides (flutriafol, metconazole, myclobutanil, tebuconazole, tetraconazole and triticonazole), through a growth inhibition assays. Based on the plotted dose-response curves and the calculated EC_{50} values, metconazole was highly toxic, while tebuconazole and tetraconazole were moderately toxic. The other three fungicides were slightly toxic against duckweed. The computational data were obtained by the analysis of an extended set of triazole fungicides (difenoconazole, epoxiconazole, flutriafol, metconazole, myclobutanil, paclobutrazol, tebuconazole, tetraconazole, triadimenol, triticonazole) on several aquatic organisms. The highest toxicity was observed for epoxiconazole and difenoconazole. Mitigation of the effects of triazole fungicides on organisms in the aquatic environment is possible through an adequate management of these fungicides in agricultural practices, contributing to a sustainable development of agriculture.

DFT CALCULATIONS OF MAGNETIC INTERACTIONS IN {Mn_2Ln_2, Ln = Gd, Tb, Dy} COORDINATION CLUSTERS

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The field of molecular magnetism attracts significant interest owing to the rising need to miniaturize magnets. Advances in this field require a deep understanding of the electronic structure of magnets, and computational approaches play a key role in understanding of the magnetic properties. To study the magnetic properties of materials from first principles, it is often required to map the full electronic interactions to effective Heisenberg spin Hamiltonian, which will help to understand the origin of the magnetic interaction and enables large-scale magnetic property simulation, e.g. with spin dynamics or Monte Carlo. One of the most successful method for doing this is the approach which takes the local rigid spin rotation as a perturbation and use the Green’s function method to compute the magnetic interaction parameters.

The exchange constants and spin dynamics of heterometallic tetranuclear $[Mn_2Ln_2O_2(piv)_8(Hpiv)_2(EtOH)_2]$ (Ln = Gd, Tb, Dy; HPiv = pivalic acid) coordination clusters have been calculated with the help of TB2J python package [1] which implements aforementioned method, and can use of the SIESTA [2] output. The isotropic exchange (*J*), anisotropic exchange tensor, and the Dzyaloshinskii-Moriya interactions have been calculated for the studied compounds. The antiferromagnetic coupling was found practically between all nearest neighbor magnetic centers with exception of Mn-Gd and Dy-Dy where the *J* values are equal to 2.11 and 0.04 *meV*, respectively.

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This work has been supported by the State Program of R. Moldova (project ANCD 20.80009.5007.15).

CHITOSAN-NISIN MEMBRANES WITH ENHANCED ANTIMICROBIAL PROPERTIES: PREPARATION AND PHYSICO-CHEMICAL CHARACTERIZATION

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Pristine chitosan possesses an antibacterial effect, but its antibacterial properties are dependent on several physico-chemical characteristics, mainly molecular weight (MW) and degree of acetylation (DA%), but also on the pH and chitosan formulation and derivatives [1]. The use of chitosan in combination with antimicrobial peptides (AMPs) has become a common practice, in order to replace the use of conventional antibiotics to overcome the increase of antibiotic resistance [2]. Nisin, is a polycyclic cationic peptide classified as a Type A (I) lantibiotic molecule, with a GRAS status, mainly used as food preservative [3], but recent studies revealed activity even against drug-resistant bacteria, therefore it`s application can be extended to biomedical fields as well [4,5]. Several types of chitosan, of different MW and DA, were used to prepare membranes (Figure 1i), via the solvent casting method [6]. To obtain chitosan-based material with enhanced antibacterial properties, nisin, an antimicrobial peptide was incorporated into the chitosan membrane-forming solution. The physico-chemical properties of chitosan-nisin membranes were observed and the results showed a good swelling capacity and water vapor transmission rate of the membranes. The *in vitro* biodegradability assay demonstrated good stability of the films under enzymatic degradation and the optical characterization data showed that chitosan-based membranes could provide UV-light protection [7]. The antibacterial effect of chitosan-based biomaterials was monitored against *Staphylococcus aureus* MRSA (Gram-positive bacteria) and *Pseudomonas aeruginosa* (Gram-negative bacteria), and the results showed that the addition of nisin improved significantly the antibacterial effect of the membranes, while the nisin-chitosan membrane-forming solutions had a bactericidal effect against both Gram-positive and Gram-negative bacteria (Figure 1ii) [7]. Given the fact that nisin is considered a non-toxic compound as an approved bacteriocin for food preservation, chitosan-nisin membranes not only could be used for bioactive food packaging but also could be considered as a starting material for wound dressing applications.

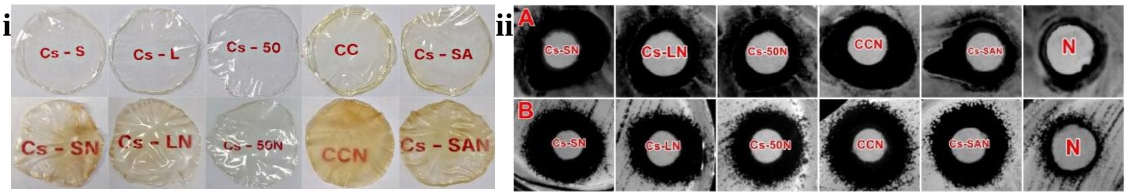

Figure 1. (**i**) Digital images of the chitosan and chitosan-nisin membranes; (**ii**) Disk diffusion method: Inhibition zone of Cs-N solutions against A) *P. aeruginosa* (G-), B) *S. aureus* MRSA (G+)

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COMPUTATIONAL EVALUATION OF THE STRUCTURAL STABILITY AND FLEXIBILITY OF THE ENZYMES BELONGING TO FAMILY 1 OF SULFOTRANSFERASES (SULT1)

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Sulfotransferases (SULTs) are phase II drug-metabolizing enzymes that catalyze the sulfation of a wide diversity of endogenous and exogenous chemical compounds. In humans, SULTs are classified into five families SULT1, SULT2, SULT3, SULT4 and SULT6 that can be found in various tissues [1]. The SULT1 family includes: SULT1A1, SULT1A2, SULT1A3, SULT1B1, SULT1C1, SULT1C3a, SULT1C3d, SULT1C4, SULT1E1. Our computational study considered for all the human SULT1 enzymes the sequence alignment, the global physicochemical properties, the distribution of the hydrophobicity and average flexibility along the enzymes chains and analysis of structural stability and flexibility of these enzymes and of the several of their frequent allelic variants [2]. The enzymes belonging to SULT1 family share at least 48% identity (SULT1C2 and SULT1E1), the most similar sequences being revealed by SULT1A1 and SULT1A3 (93%). Despite the low sequence identity, the structural similarity of the SULT1 enzymes is high. Also, the flexible regions are usually conserved, but there also are some differences in the flexibility of several regions of these enzymes, one of them being correlated with the ligands biding [3]. There usually are alterations of the flexibility of the enzymes produced by the amino acid replacements corresponding to the allelic variants and it may be responsible of the affected metabolism of numerous drugs.

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ELEVATED CARBON DIOXIDE INFLUENCES ON PLANTS POLYPHENOLS

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In the last years, carbon dioxide concentrations have increased more than ever. The actual carbon dioxide concentration achieved 420 ppmv in July 2022 for the first time. For plants, more carbon dioxide could be benefical as the rate of photosynthetic carbon fixation is increasing, resulting in increased biomass output. In contrast, high carbon dioxide could influence plants' primary and secondary metabolic pathways.

We used plant species from the *Brassicaceae* family (*Brassica oleracea* variety *capitate, Brassica oleracea,* variety *botrytis, Sinapis alba, Raphanus sativus, Brassica oleracea* variety *italica*) grown at high carbon dioxide (800 and 1200 ppm) to test the influence of elevated carbon dioxide on plants polyphenols.

It has been shown that the polyphenols (as syringic or cumaric acid) concentration decrease for plants grown at high carbon dioxide concentrations while ascorbic acid concentration increase.

This work was supported by a grant from the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-III-P4-ID-PCE-2020-0410

SYNTHESIS AND CHARACTERIZATION OF A MULTI-IONIC POLYMERIC COMPOUND INVOLVING HEXAAMMINECOBALT(III), POTASSIUM, 4-SULFOBENZOIC, AND CHLORIDE IONS

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Cobalt complexes are playing an increasing role due their therapeutic use as excellent anticancer, antiviral and antibacterial agents. Microorganisms develop resistance to existing drugs very rapidly, thus there is a need to look for new classes of drugs, especially those that show broad-spectrum properties. Hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$, shows antiviral properties against Sindbis virus, adenovirus, and also exibits activities against human immunonodeficiency virus (HIV) and the Zaire Ebola (ZEBOV) strain [1]. Recently, we reported that compounds comprising $[Co(NH_3)_6]^{3+}$ cations and various N-, N,O- and O-donor moieties showed inhibitory potential against bacterial cancer in plants [2,3].

A new $\{K_2[Co(NH_3)_6]Cl(sb)_2\}_n$ (**1**) compound (Fig. 1) has been prepared from the reaction of $[Co(NH_3)_6]Cl_3$ with the potassium salt of 4-sulfobenzoic acid in H_2O/EtOH mixture. The compound has been characterized by elemental analysis, thermogravimetry, IR spectroscopy and single-crystal X-ray diffraction studies. X-ray structural analysis reveals that **1** crystalizes in tetragonal *I*4/*m* space group, with unit cell parameters: $a = b = 14.3265(5)$, $c = 24.7933(16)$ Å, $V = 5088.8(5)$ Å^3. The compound comprises a potassium and $[Co^{III}(NH_3)_6]^{3+}$ cations whose charge is compensated by 2 sulfobezoic dianions and a chloride anion. The components in **1** are aditionally associated by hydrogen bonds of the type: N−H···N, N−H···O, S-O···H, C−O···H, N–H···Cl. Hirshfeld surfaces (HS) analysis and the two-dimensional (2D) fingerprint plots have been performed to study the contributions of different intermolecular interactions in crystalline packing for **1** (Fig. 2).

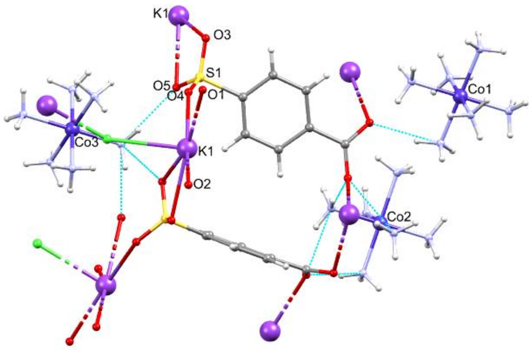
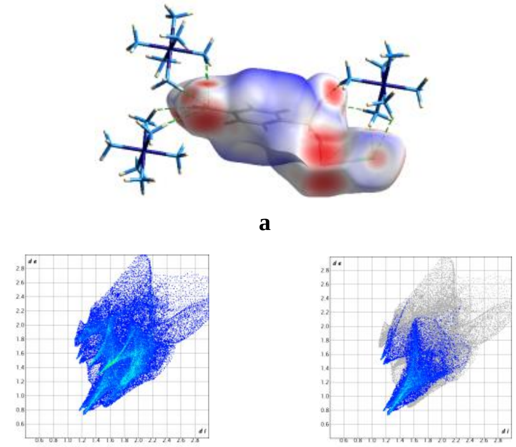


Fig. 1. The structure of **1**



a

b

All interactions

O…H/H…O: 28,9%

Fig. 2. The HS over d_{norm} (a) and 2D fingerprint plots (b) in **1**

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This work has been supported by the State Program of R. Moldova (project ANCD 20.80009.5007.15).

ASSESSMENT OF THE EFFECTS OF THE FUNGICIDE MYCLOBUTANIL ON THE SOIL ENVIRONMENT

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Myclobutanil is a widely used triazole fungicide that is moderately persistent in soil and it may also be persistent in aquatic systems under certain conditions. Within this study we have used both an experimental and a computational approach to assess the effects of the myclobutanil on soil microorganisms and soil enzymes. Following the experimental study, regardless the dose of the myclobutanil, the activity of the dehydrogenase was decreased during the 28 days, and those of the phosphatase and urease during the 21 days, but the decrease was always higher for the double dose of the fungicide. Under the given experimental conditions, the obtained results indicated that myclobutanil did not have major toxic effects on the microbial communities, the bacterial population was not affected by the presence of fungicide in the soil samples. Regarding the fungal population, there is a slight decrease in the number of colonies observed. The molecular docking study illustrated that the myclobutanil was able to bind to the active sites of dehydrogenase, phosphatase and protease, the non-covalent interactions being mainly hydrophobic and hydrogen bonds. The highest binding affinities of myclobutanil are illustrated for the *Clostridium beijerinckii* dehydrogenase which indicates that this enzyme could be the most sensitive to the action of this triazole fungicide. These results should be taken into account when using myclobutanil in agricultural management.

This work was supported by the grant PN-III-P1-1.1-PD-2019-0255 ”Assessment of the environmental effects of triazole fungicides that are approved for use in European Union for the protection of cereals”.

GLYCOSYLATED RECOMBINANT CHITINASE A, A SUITABLE ENZYME FOR BIOTECHNOLOGICAL PROCESSES OF CHITIN CONVERSION

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The tons of chitin waste produced annually on the planet by marine crustacean fauna are a challenge both for people living in cities near the oceans and for scientists looking for ways to turn it into products with properties superior to natural polymer. Global regulations require environmentally friendly solutions to convert these waste. In this respect, chitinases, the enzymes that break down chitin polysaccharide into higher compounds (chitooligosaccharides), are being intensively studied and analysed biochemically. There is a need to identify chitinases with properties that serve the purpose of rapidly and efficiently converting chitin to chitooligosaccharides. Characteristics of chitinases such as enzymatic activity and resistance to high temperatures, activity in wide pH ranges, presence of glycans on their surface, make them suitable for biotechnological processes of chitin conversion. In order to identify and describe some biochemical properties (enzyme activity for glycosylated and deglycosylated enzyme, thermostability) of chitinase A (ChiA) from Bacillus licheniformis, heterologously expressed in Pichia pastoris, deglycosylations with Endo Hf, PNGase F enzymes were performed in the present study. The enzyme activity of the glycosylated and deglycosylated forms was measured using each deglycosylase, and the temperature resistance of chitinase A was determined at several temperatures (40, 60, 80, 100oC) for 2 h of incubation. The results show that at 40 and 60oC, after 1 h and 30 min of incubation, glycosylated chitinase A activity is above 60%, indicating that the enzyme is stable at these temperatures. At 80 and 100oC the enzyme retained between 60-80% of activity after 10 min of temperature exposure, with chitinase activity decreasing significantly to disappearance after 1 h and 30 min of incubation.

Deglycosylation, in the case of both deglycosylation enzymes, had a negative effect on chitinase activity. After 1 h of deglycosylation, the relative enzyme activity decreased to about 60% compared to the activity of the glycosylated variants, such that after 4 h of deglycosylation, ChiA retained only 30-40% of its activity. The results obtained in the thermal stability experiments at 100oC for the deglycosylated variants compared to the glycosylated ChiA variant show, after the first 10 min of incubation, that there is a similarity between the glycosylated variant and the deglycosylated variant with PNGase F in terms of enzyme activity (both retained around 60% of activity). We therefore conclude that recombinant glycosylated ChiA is an enzyme that can be used in industrial processes to convert chitin to chitooligosaccharides.

INDUSTRIAL WASTES RECLAIMING AS LAYERED DOUBLE HYDROXIDES – BIOMASS COMPOSITES

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The recovery of useful substances from industrial waste has become a necessity with the increase of the society's needs for reducing wastes production and environmental protection.

In the present study, two residual solutions (from the hot-dip galvanizing process and from the printing of electronic circuit boards, respectively) were chosen as sources of metals, as well as wood sawdust from furniture manufacturing, as a source of biomass.

In general, the hot-dip galvanizing process consists of four stages: surface preparation, treatment with fondant, electroplating and finishing. The preparation stages consist of cleaning and pickling operations that free the surface from dirt, grease, rust, and crusts. The fondant treatment step serves to dissolve oxides that can form on the surface of iron or steel after pickling and prevents the subsequent formation of rust. Galvanization of clean parts is carried out by immersion in molten zinc. Finishing operations include cooling, elimination of excess zinc and inspection [1]. At all stages of the hot-dip galvanizing process, waste is generated, both in solid state (slag and zinc ash, sludges, metals and metal oxides) and in liquid (wastewater from washing and pickling) or gaseous (dusts containing heavy metals, acid aerosols, waste gases). The residual solution from the pickling process is discontinuously discharged and contains significant amounts of iron (Fe^{2+} and Fe^{3+}), zinc and chlorides and has an acidic pH (pH = 2) and was utilized as a source of Fe on the layered double hydroxide-biomass composite synthesis.

The process of printing electronic circuit boards includes the following steps: designing the boards, engraving (printing) with layers of metal copper chemically deposited, removing excess copper, finishing and quality control. The process of removing excess copper involves several methods: oxidation of metallic copper with hydrogen peroxide and its dissolution in hydrochloric acid or dissolution in basic solutions [2]. The residual solution from the oxidative pickling of copper from the printing process of electronic circuit boards contains 172 g/L Cu, has pH = 1.75 and was used as a source of Cu in our synthesis. All the waste used in this study comes from companies in the city.

The residual solutions, as well as sawdust were used together for the synthesis of layered double hydroxides MgCuFe-biomass type, both by the ultrasonication method and by the co-synthesis method. In parallel, the same types of materials were synthesized using chemical reagents and sawdust.

The identification of the crystalline phases in the structure of the synthesized materials was made by X-ray diffraction analysis. The presence and quantity of metals (Mg, Cu, Fe) in the synthesized materials were evidenced by quantitative analysis by atomic absorption spectrometry.

Four composite materials (layered double hydroxides – biomass) were synthesized by ultrasonication process, starting from MgCuFe-type layered double hydroxides obtained from chemical reagents and industrial waste, as well as from wood sawdust. The ultrasonication process of synthesis has led to the obtaining of composite materials that have a structure similar to that of the layered double hydroxides from which they come but are less crystalline. The mass ratio between sawdust and layered double hydroxides of 1 : 2 has been preserved in all synthesized samples.

Two composite materials (layered double hydroxides – biomass) were synthesized by co-precipitation: one starting from chemical reagents (nitrates of the metals components of layered double hydroxides) and chemically activated sawdust and one starting from residual solution from the pickling of parts subjected to galvanization (Fe source), residual solution from the pickling of electronic circuit boards and chemically activated sawdust. The material obtained from industrial waste has, in addition to the layered double hydroxide of MgCuFe-type, a secondary phase of copper(I) oxide, and the material obtained from chemical reagents has a single crystalline phase, the layered double hydroxide.

The synthesized materials were used in the process of retaining from water of two dyes, Congo Red and Methylene Blue. It was found that the efficiency of the process is higher in the case of composite materials than in the case of layered double hydroxides, and the presence of sawdust increases the efficiency of the adsorption process.

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A SMALL STRUCTURAL REARRANGEMENT IN {$Co^{III}_2Dy^{III}_4$} SMMs AFFECTS MAGNETIZATION QUANTUM TUNNELING

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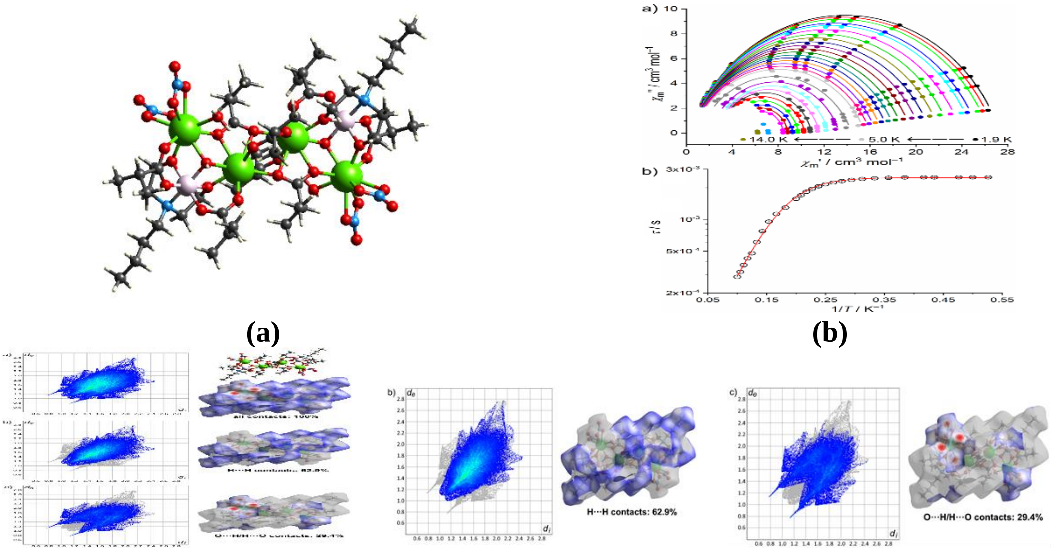
The pursuit of molecular magnetic materials with single-molecule magnet (SMM) properties, especially pronounced hysteresis of the magnetization, and the understanding of associated magnetization relaxation pathways, continues to be an important topic in molecular magnetism. Transition metal- and lanthanide-based systems are extensively investigated in this context, with efforts focusing on increasing the effective energy barriers (U_{eff}) and blocking temperatures (T_{B}).
The coordination cluster compound $[Co^{III}_2Dy^{III}_4(OH)_2(ib)_8(bdea)_2(NO_3)_4(H_2O)_2]\cdot 2MeCN$ (**1**) (Fig. 1a) self-assembles in a high-yield reaction of cobalt(II) isobutyrate (ib) with $Dy(NO_3)_3\cdot 6H_2O$ and *N*-butyldiethanolamine (H_2bdea) in MeCN. The C_i-symmetric {$Co^{III}_2Dy^{III}_4$} core fragment features two {$CoDy_2(\mu_3\text{-}OH)$} triangles, joined by one of their Dy sites via μ-O and μ-carboxylate bridges.

This results in a flat zig-zag metal skeleton, in contrast to previously reported hexanuclear {Co_2Ln_4} clusters exhibiting a more condensed combination of two {$CoLn_2(\mu_3\text{-}OH)$} triangles. According to ac susceptibility measurements, this rearrangement in **1** reduces quantum tunneling of the magnetization and hence pushes up the onset of pronounced out-of-phase signals at zero bias field (1 kHz) to 14K (Fig. 1b), a significant change vs. more condensed {Co_2Dy_4} structures. As supramolecular interactions between coordination clusters in the solid state are well known to also influence SMM features, we present comparative Hirshfeld surface analyses (Fig. 1c).



(a) **(b)**

(c)

Fig. 1. (a) Structure of the {Co_2Dy_4} cluster in **1**, (b) Cole-Cole plot of out-of-phase (χ_m'') vs. in-phase (χ_m') molar magnetic susceptibility of **1** at zero static magnetic bias field in the temperature range 1.9–14.0 K, (c) Hirshfeld surface analysis.

This work has been supported by the State Program of R. Moldova (project ANCD 20.80009.5007.15).

RECOVERY OF PALLADIUM IONS FROM AQUEOUS SOLUTIONS ON EFFICIENT ADSORBENTS MATERIALS Mg^{3}Al LDH FUNCTIONALIZED WITH METHYL TRIALKYL AMMONIUM CHLORIDE

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Pd, which belongs to the noble metals group, has a wide range of industrial applications and is considered indispensable in state-of-the-art technology. Due to the continuous increase in the demand for precious metals, in recent years the recovery of palladium from secondary resources is considered a potential solution, an important scientific, technological, economic and environmental points of view [1]. Thus, particular attention has been paid to the recovery of Pd from secondary sources, especially from wastewater. One of the most efficient methods for recovering Pd from aqueous solutions is the use of adsorption processes due to its well-known advantages [2]. The challenge in the adsorption process is represented by the development of new efficient adsorbent materials. The attention was focussed on the use of double layered hydroxides and ionic liquids in the functionalization process of solid support. Therefore, in this work, Mg_3Al-LDH will be functionalized with ionic liquid, methyl trialkyl ammonium chloride and will be used as adsorbent material for the recovery of Pd ions from aqueous solutions. Palladium adsorption studies onto the studied materials were conducted in batch mode, performing both equilibrium and kinetic studies. Due to the presence of the ionic liquid onto the obtained LDH materials, a significant increase in the maximum adsorption capacity could be observed (qMg_3Al = 142.9 mg/g, qMg_3Al IL-US = 227.3 mg/g, and qMg_3Al IL-COS = 277,8 mg/g). It has been shown that both raw materials (hydrotalcite and ionic liquid) used to obtain the adsorbent material contribute to the process of removing palladium from aqueous solutions, due to their synergistic effect.

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This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-1555, within PNCDI III.

HETEROMETALLIC HEXANUCLEAR {Fe_4Ln_2, Ln = Dy, Gd} PIVALATE CLUSTERS

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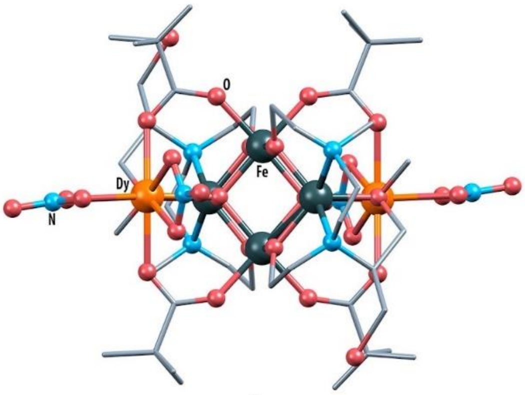
Mixed-metal materials remain attractive over the years due to their interesting structures and magnetic properties. Single molecule magnets and single chain magnets behavior of polynuclear 3d/4f complexes determines their potential application in high-density data storage and Quantum computing. Several synthetic strategies have been employed by molecular chemists in the search for new 3d/4f coordination compounds and interesting magnetic properties. One of these strategies is the utilization of carboxylates due to their variety coordination modes and the diversity of R groups – features that can tune and support some specific properties or behavior. Multifunctional flexible alkanolamines, also has been proven as good candidates to connect metals in clusters owing to presence of oxygen and nitrogen atoms with good affinity to metal atoms, and possibility to generate diverse structural motifs.

Herein, we present synthesis, structural characterization and magnetic properties of two new heterometallic $[Fe_4Dy_2O_2(piv)_4(Hteed)_2(NO_3)_4]$ (**1**) and $[Fe_4Gd_2O_2(piv)_4(Hteed)_2(H_2O)_2(NO_3)_4]$ (**2**) pivalate clusters. Compounds **1** and **2** were obtained by US treatment of MeCN mixture of $[Fe_3O(piv)_6(H_2O)_3](piv)\cdot Hpiv$ (Hpiv = pivalic acid), H_4teed (N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine), $Ln(NO_3)_3\cdot 6H_2O$ (Ln= Dy (**1**), Gd (**2**)), and NaN_3 (**1**) or piperazine (**2**). X-ray structural analysis revealed that **1** crystalizes in triclinic *P*-1 space group with unit cell parameters: a = 10.872(2), b = 12.834(3), c = 13.712(3) Å; α = 66.13(3), β = 70.64(3), γ = 87,01(3)° and compound **2** crystalizes in monoclinic *C*2/*c* space group with unit cell parameters: a = 15.146(3), b = 29.174(6), c = 36.074(7) Å; β = 90.00(3)°. All Fe atoms in **1** and **2** are hexa-coordinated displaying O_6 and N_2O_4 distorted octahedral surrounding, all Dy atoms reveal O_8 while all Gd O_9 coordination geometry. Magnetic properties were studied to understand structural effects on the magnetic interactions and will be discussed.



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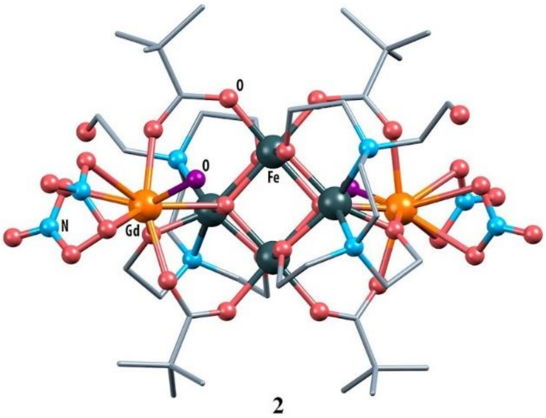

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This work has been supported by the State Program of R. Moldova (project ANCD 20.80009.5007.15).

CONGO RED DYE ADSORPTION FROM AQUEOUS SOLUTION BY MAGNETIC NANOCOMPOSITE: PROCESS OPTIMIZATION STUDY

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Toxicity of dyes on ecosystems has led to intensified research on their removal from wastewater [1,2]. The paper presents the efficient application of a carbon magnetic nanocomposite as adsorbent for elimination of an anionic dye (Congo Red) from aqueous solutions. The nanocomposite material was synthesized using an innovative combustion technique, using carbon, iron nitrate, citric acid, and silver nitrate [3]. A Box-Behnken factorial design combined with the response surface methodology (RSM) [4] was conducted to investigate the effect and interactions of the three process variables: solution pH, initial dye concentration, and adsorbent dose, on the Congo Red adsorption process.

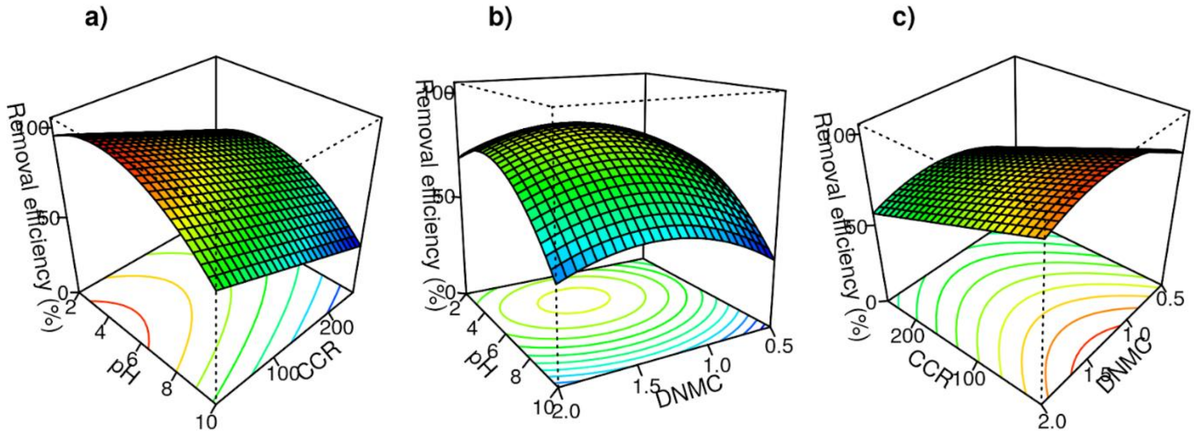

Fig. 1. Response surface plot for Congo Red (a-c) adsorption at stationary point slice

Highly significant ($p<0.001$) second-order polynomial models were developed and the correlation coefficient was of 0.9804 for Congo Red adsorption. The obtained experimental data were in agreement and close with the theoretical results, which supports the applicability of the method. The maximum removal efficiency for Congo Red was obtain to be 98.67% under the optimal conditions of pH 3, 30 mg/L concentration of dye solution and 1g/L of sorbent. The kinetic study indicated that a combination of kinetic models: pseudo-second order and intraparticle diffusion, were applied appropriately, for Congo Red adsorption on carbon magnetic nanocomposite. The maximum adsorption capacity determined from the Sips isotherm model was obtained to be 201.66 mg/g. The high adsorption capacity obtained in a short time, the easy separation of carbon magnetic nanocomposite from aqueous solutions, as well as the good regeneration of adsorbent, support the good applicability of investigated material for colored wastewater treatment.

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This work was supported by Program 2 of the “Coriolan Drăgulescu” Institute of Chemistry, Research Projects 2.3.

EFFICIENT REMOVAL OF ANIONIC AND CATIONIC DYES BY ADSORPTION USING A NEW MAGNETITE/CARBON NANOCOMPOSITE

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The efficient removal of dyes from colored wastewater is becoming a worldwide priority for increasing the quality of life [1, 2].

In this work, a new magnetite/carbon nanocomposite (PM) was synthesized by the combustion method [3, 4], and characterized by the most indicated and modern methods: X-Ray Diffraction, FT-IR, N_2 adsorption-desorption isotherm, thermal analysis and Scanning Electron Microscopy. The synthesized material has a specific surface of 930 m^2/g, and magnetic properties determined by the presence of magnetite in the composition, the saturation magnetization being 4.04 emu/g.

The nanocomposite was tested as adsorbent for the removal of an anionic dye (AO7) and a cationic (MB) from single and binary component aqueous solutions.

The effect of the working conditions: solution pH (2÷12), the amount of adsorbent (0.25÷3 g/L), initial dye concentration (10÷250 mg/L), and temperature (25°C, 40°C, 55°C), on the dyes removal efficiency was investigated. Working under normal conditions: natural solution pH, and room temperature (25°C), very good removal yields were obtained, greater than 92% for both dyes. In order to evaluate the adsorption performance of the synthesized magnetic nanocomposite, the study was extended to the simultaneous adsorption of dyes from two-component systems. In the binary systems, no significant competitive adsorption was observed, very good removal yields of over 90% for AO7, and 95% for MB respectively, were obtained.

Kinetic studies indicated that the adsorption process was best described by the pseudo-second order model for investigated dyes. The data obtained at equilibrium were described by the Sips isotherm, and the maximum adsorption capacities were determined as: 136.36 mg/g for AO7, and 132.52 mg/g for MB. The determined values of thermodynamic parameters (Gibbs free energy, enthalpy, and entropy) indicate that the adsorption process is spontaneous and endothermic in nature. The regeneration capacity of the synthesized nanocomposite was studied in adsorption-desorption cycles, yields of over 75% being recorded even after the 6th cycle for the investigated dyes.

The experimental results indicate that the synthesized magnetite/carbon nanocomposite exhibits a very good adsorption capacity, which recommends it as a versatile and promising material for industrial wastewater treatment.

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This work was supported by Program 2 of the “Coriolan Drăgulescu” Institute of Chemistry, Research Projects 2.3.

IDENTIFICATION OF NOVEL DPP-4 INHIBITORS FOR TYPE 2 DIABETES: A PRELIMINARY COMPUTATIONAL INVESTIGATION

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The present work reports a virtual screening experiment involving pharmacophore generation, drug-likeness evaluation, and molecular docking simulations to identify potential Dipeptidyl Peptidase 4 (DPP-4) inhibitors with improved physicochemical profile. The virtual screening of 3 (CHEMBL, MCULE-ULTIMATE, and ZINC) large compound databases using pharmacophores, molecular shape and energy minimization criteria identified forty-seven compounds similar to query alogliptin. Moreover, the drug-likeness analysis delivered 8 out of 47 compounds for docking simulation step. Of these, two compounds named ZINC31808581 and ZINC72404849 with CG4 docking scores superior to alogliptin, were prioritized as potential DDP-4 inhibitors.

POLYSULFONE-BASED COMPOSITE FIBROUS MEMBRANES: INFLUENCE OF THE SOLUTION PARAMETERS ON THE ELECTROSPINNING PROCESS

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The manufacture and design of the electrospun fibrous membranes has recently gained increased attention due to their favorable properties, low cost and easy processability, as well as ability to be tailored in accordance with the intended purpose. In this context, the main scope of the work is to develop new polysulfone-based composite fibrous membranes which will be used as separations medium in advanced device of medical treatment. Therefore, by combining the properties of the

quaternized polysulfone (PSFQ), cellulose acetate phthalate (CAP) and polyvinylidene fluoride (PVDF), and controlling their weight ratio (e.g., 70/25/5, 70/22/8, 60/30/10, 40/50/10, 30/65/15), through electrospinning process, the induction of a surface model with improved characteristics for the desired application was followed. Thus, the aim of the present study is to analyze the rheological behavior of PSFQ/CAP/PVDF system and to acquire information about the effects of the polymers from blend, and also of the used solvent in electrospinning process. To understand the PVDF influence on the fibers formation process and to establish the optimal electrospinning conditions, the dynamic viscosity of solutions was determined (Figure 1).

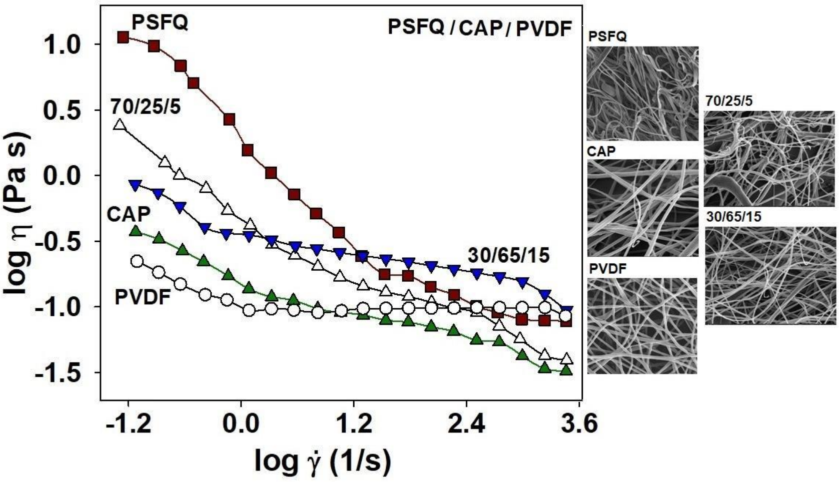

Figure 1. Dynamic viscosity *versus* shear rate for PSFQ/CAP/PVDF system at different compositions and 25°C, and corresponding SEM images recorded at 5 μm scan area and magnification of 10,000×.

By evaluating the dynamic viscosity, it was possible to establish and control the optimal compositions of the studied blends in order to obtain continuous cylindrical and defect-free fibers. Thus, the optimum ratios to obtain the fibers with improved morphological characteristics were found to be the ones containing more than 10 wt.% PVDF. This finding reflects that for compositions as 40/50/10 and 30/65/15 PSFQ/CAP/PVDF, the blends viscosities generate a good overlapping and entanglement of the polymer chains. Therefore, the solution parameters associated with the blend polymers and solvent properties, were the key factors in electrospinning process, directly affecting the morphology of the electrospun fibrous membranes.

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2021-2700, within PNCDI III.

SONOCHEMICAL SYNTHESIS OF AgNPs USING SOLUBLE STARCH AND MIE THEORY SIZE ESTIMATION

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Silver nanoparticles, AgNPs have long attracted the attention of scientists, due to their excellent optical, microbiological, chemical, and physical properties [1, 2]. The authors made the synthesis of colloidal silver nanoparticles (Ag-NPs by ultrasonic disruption), using soluble starch as a reducing agent and further as a stabilizing agent for produced Ag-NPs [3]. The aim of this paper is to present a simple and easy way to synthesize silver nanospheres using starch as a stabilizing and reducing agent and to theoretically investigate and determine the obtained nanoparticle size using the theory developed by Gustav Mie [4]. The obtained sample was characterized using UV-VIS spectrophotometry, scanning electron microscopy and transmission electron microscopy to further investigate the morphology of the final obtained sample. The obtained results show that a close correlation between the theoretically obtained size and the experimental one, which resulted from scanning electron microscopy and transmission electron microscopy analyses.

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This paper was financially supported by the Project “Network of excellence in applied research and innovation for doctoral and postdoctoral programs” / InoHubDoc, project co-funded by the European Social Fund financing agreement no. POCU/993/6/13/153437

NEW 3d-4f HETEROPOLYNUCLEAR SYSTEMS OBTAINED USING SCHIFF-BASE LIGANDS

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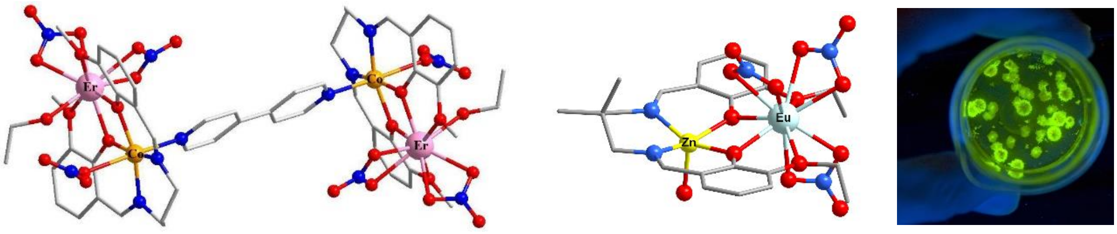
Even if the study of various 3*d*-4*f* systems started more than two decades ago, these are still of high interest nowadays, due to their potential applications as *state-of-the-art* materials in magnetism, fluorescent lamps, electroluminescent devices, or catalysis. Such systems yield interesting in-depth case studies that can generate novel scientific models and theories. The main advantage of heterometallic systems arises from synergistic properties emerging from having 4*f* and 3*d* metal ions in close proximity to each other; this may generate new multifunctional materials with properties which could not be obtained in homometallic systems. Lanthanide ions, by themselves, are ideal candidates for a wide range of applications due to their large and, in some cases, high anisotropic magnetic moments, as well as their narrow emission bands, large Stokes’ shift, and relatively long luminescence lifetimes.

We herein describe new heteropolynuclear complexes obtained starting from 3*d*-4*f* heterodinuclear *nodes* [where M(3*d*) = Co^{II}, Ni^{II}, Zn^{II}; M(4*f*) = various Ln^{III} ions] containing Schiff-base ligands obtained from 3-Ethoxysalicylaldehyde (Hesal) or 3-Methoxysalicylaldehyde (Hval) and various aliphatic diamines such as 1,3-diaminopropane (pn), 2,2-dimethyl-1,3-diaminopropane (dmpn), 1,2-diaminopropane (men). Using the "*node* and *spacer*" approach we attempted to connect these *nodes* using various exobidentate ligands (4,4'-bipyridine = bipy, 1,2-bis(4-pyridyl)ethane = bpa, 4,4'-azopyridine = azbpy, polycarboxylic acids).

Structures ranging from 0-*D*/discrete ones (Figure 1) to 1-*D*, and 2-*D* coordination polymers have been obtained for the new complexes. All reactions were performed at room temperature and single-crystals suitable for X-Ray diffraction have been collected after several days in all cases. X-Ray powder diffraction, UV-VIS and IR spectroscopy have also been used to characterize the new compounds in solid state.



(a) (b) (c)

Figure 1. (a) Crystal structure of tetranuclear $[Co^{II}(valpn)(ONO_2)Er(O_2NO)_2(OEt)]_2(bipy)$ complex; (b) Crystal structure of dinuclear $[Zn(H_2O)(esaldmpn)Eu(O_2NO)_3]\cdot CH_3CN\cdot H_2O$ *node*; (c) Luminescent emission of $[Zn(H_2O)(esaldmpn)Tb(O_2NO)_3]\cdot CH_3CN\cdot H_2O$ complex

Keywords: heteropolynuclear complexes; luminescent complexes; coordination polymers; 3*d*-4*f* nodes; *node* and *spacer* approach

Financial support from PN-III-P1-1.1-TE-2019-1534 research grant is gratefully acknowledged.

DRUG REPOSITIONING OPPORTUNITIES IN POST-MARKETING ADVERSE EVENTS DATA

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Despite scientific achievements and increased funding for drug discovery process, some drugs are withdrawn from the market, most often due to serious adverse events. Drugs interact with several biological targets outside the outside the mechanism-of-action, which often results in light side effects. Such off-target effects represent one of the biggest challenges in drug development, allowing at the same time an alternative design for next generation, more effective, but less toxic, therapeutic agents.

In the present work, the side effects of approximately 1000 approved drugs were analyzed from the perspective of the chemical structures. For this purpose, we used the data from the Food and Drug Administration – FDA's - Adverse Events Reporting System (FAERS) platform where drug events of marketed drugs monitored. Drugs were first classified based on their chemical structure, using extended connectivity method and then analyzed by their reported adverse events. The fingerprint descriptors were used to group drugs hierarchically, with the purpose of finding candidate drugs for repositioning within cluster events.

SYNTHESIS, CHARACTERIZATION AND TEMPERATURE PROGRAM DESORPTION INVESTIGATIONS OF SOME MESOPOROUS MOLECULAR SIEVES

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In this paper was investigated the adsorption-desorption of CO_2 and the influence of temperature for CO_2 adsorption on amino-functionalized mesoporous molecular sieves by using temperature programmed desorption – TPD method. Amino functionalized SBA-15, MCM-41 and MCM-48 were synthesized by grafting technique, using 3-aminopropyl triethoxy silane (APTES) as functionalization agent. These samples were denoted as SBA-15-APTES, MCM-41-APTES and MCM-48-APTES respectively. SBA-15 was synthesized following the procedure published by Zhao et al. [1], MCM-41 was prepared after the method developed by Beck et al. [2] while MCM-48 was synthesized by the method developed by Ortiz et al. [3]. The prepared amino-functionalized

mesoporous materials were further characterized by different investigation methods: FT-IR spectrometry, X-ray diffraction analysis, nitrogen physisorption analysis at 77 K. After the use of the functionalization agent (APTES) for all three mesoporous molecular sieves, BET specific surface areas decreases from 726 m2/g for SBA-15 to 288m2/g for SBA-15-APTES, from 1299 m2/g for MCM-41 to 655.8 m2/g MCM-41-APTES and from 1466.06 m2/g MCM-48 to 314.57 m2/g for MCM-48-APTES as presented in Table 1.

Table 1. Textural properties of investigated mesoporous molecular sieves.

No.	Sample	Specific surface area (m^2/g)	Pore volume BJH_{Des}(cc/g)	Avarage pore diameter BJH_{Des}(nm)
1.	SBA-15	725.0	1.19	6.64
2	SBA-15-APTES	288.8	0.664	6.63
3.	MCM-41	1299.7	0.695	3.30
4.	MCM-41-APTES	655.8	0.611	3.25
5.	MCM-48	1466.06	0.802	3.48
6.	MCM-48-APTES	314.57	0.230	3.11

The mass loss of amino-functionalized molecular sieve above 250 °C was due to the oxidation and decomposition of amino propyl functional groups. This means that the composites could be used for adsorption of CO_2 at temperatures below 250 °C. The CO_2 adsorption/desorption experiments showed that carbon dioxide sorption capacities depend on the textural characteristics and the temperature used for the adsorption process. Good CO_2 adsorption capacities were obtained for all prepared samples, the optimal temperature for CO_2 adsorption–desorption by TPD is 60 °C. Some of the studied functionalized mesoporous molecular sieves were further tested for stability and recyclability during prolonged period operation time to justify their consistency for practical applications.

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This research was funded by Romanian Academy Project No. 4.3.

ENZYMATIC SYNTHESIS OF FURAN-BASED OLIGOESTERS BY USING MICROBIAL LIPASES

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The enzymatic synthesis of biopolymers currently represents an alternative method for chemical polymerization due to the biodegradability and natural origin of enzymes, efficient catalytic activity in mild reaction conditions and low impact on the environment. The most efficient enzymes used for polyester synthesis are lipases mainly the lipase B from *Candida antarctica*. The polyesters obtained through enzymatic polymerization are important for their applicability in food industry, medical and pharmaceutical fields [1].

5-Hydroxymethylfurfural is a platform chemical from which many valuable compounds such as 5-hydroxymethyl-2-furoic acid (5OH2FA) can be obtained and used subsequently as monomers for the production of bio-based polyesters. To improve the properties of furan-based polyesters, in particular their biodegradability, monomers with furan units are mixed with biodegradable co-monomers [2].

One biodegradable compound that can be used as monomer for furan-based polyester synthesis is ricinoleic acid which due to its structure (double bond, hydroxyl and ester groups) is an important resource for obtaining functional polymers [3].

In this work the optimization of the oligoesters based on 5-hydroxymethyl-2-furoic acid (5OH2FA) and ricinoleic acid (RCA) was performed by Design of Experiments (DoE). Three parameters were selected (temperature, biocatalyst concentration reported to the amount of monomers, molar ratio between monomers) and their influence on the average molecular weights and relative content of the reaction products was studied. The temperature varied between 60 and 80°C, the proportion of the biocatalyst in relation to the monomers between 10 and 30%, and the molar ratio RCA: 5OH2FA from 1:1 to 5:1 were investigated. Based on the MALDI-TOF MS spectra and GPC analysis of each sample, the average molecular weights (Mn, Mw), and the relative composition of the reaction product (homopolymers and copolymers) were calculated and used as response variables. The optimal reaction conditions were determined based on DOE results and statistical analysis. The structure of the copolymer was demonstrated by NMR analysis. Although the polymerization degree is modest and the obtained products could be useful in pharmaceutical, food, or medical applications.

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-1573, within PNCDI III, contract number TE 101.

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THE ADSORPTION-DESORPTION OF CO_2 ON AMINO-FUNCTIONALIZED KIT-6 AND Ce/KIT-6

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Carbon dioxide concentration are rising mostly because of the fossil fuels that people are burning for energy. Because we put more carbon dioxide into the atmosphere than natural processes can remove, the amount of carbon dioxide in the atmosphere increases every year. Carbon capture and storage technologies have been developed in recent years as a way to mitigate the release and proliferation of CO_2 in the atmosphere [1-4].

In the present study, KIT-6 composites containing cerium were prepared by impregnating the hydrothermally prepared mesoporous KIT-6 support with 30 wt% metal oxide content, followed by functionalization with aminopropyl trietoxisilane (APTES) and the influence of metals on the performance of CO_2 adsorption on functionalized mesoporous silica was investigated. These composites were characterized by FT-IR spectroscopy, X-ray diffraction, nitrogen physisorption at 77 K, and evaluated by the adsorption of CO_2 and its temperature-programmed desorption TPD at different temperature. Thermal stability was investigated by TGA and DTA methods. The CO_2 adsorption/desorption on amino-functionalized KIT-6 Sil and Ce/KIT-6 Sil showed that both the adsorption capacity (mmoleCO_2/g adsorbent) and the efficiency of amino groups (mole CO_2/mole NH_2) depend on the temperature. An important increase of both the adsorption capacity and the efficiency of amino groups was evidenced for functionalized Ce/KIT-6 in comparation with parent KIT-6 Sil.

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This research was funded by Romanian Academy Project No. 4.3.

SYNTHESIS AND LIQUID CRYSTALLINE PROPERTIES OF BENZOTHIENO-THIOPHENE AND FLUORENONE BASED MOLECULES

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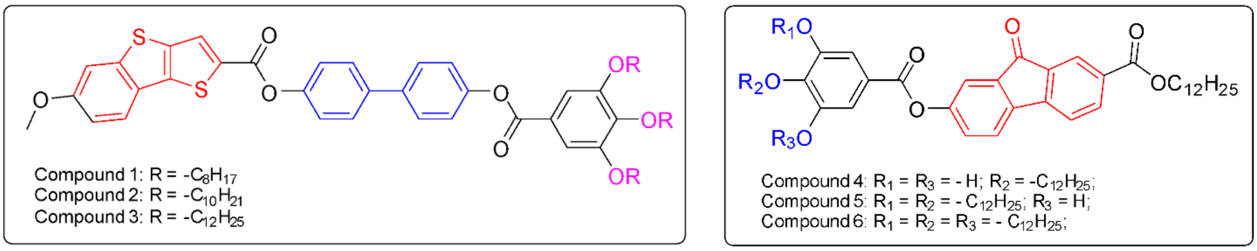
Liquid crystals (LCs) have attracted much interest in the last decade due to their unique properties and uses. They represent a fascinating state of matter which combines order and mobility at a molecular and supermolecular level with important applications in modern technology. Their mesomorphic properties depend on the molecular shape, rigidity and polarity of the molecular fragments [1-3]. Introduction of lateral dipole moments by grafting polar groups to the rigid core gives tilted phases, for example, smectic C (SmC), which are of great practical importance for switching devices [4]. A successful and widely reported rigid building block promoting the formation of SmC phase is fluorenone which has a planar and slightly bent aromatic structure [5-7].

Another interesting rigid building block for organic liquid crystals is thiophene where the polarizability of the mesogenic group is changed due to the presence of sulphur atom which changes the polarity of the local bonds.

Here we present the design, synthesis and characterization of six novel potential mesogens carrying biphenyl-benzothieno-thiophene or fluorenone rigid cores with two or more peripheral flexible alkoxy side chains of different lengths (Scheme 1). The purity and structural characterization of the intermediates and target compounds were carried out using 1D and 2D-NMR spectroscopy and elemental analysis, while the mesomorphic properties were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray scattering (XRD). The synthetized compounds carrying biphenyl-benzothieno-thiophene rigid core were shown to support cubic phase formation depending on the length of the flexible side chains, while fluorenone-based compounds displayed smectic phase depending on the number of side chains.



Scheme 1. Chemical structures of biphenyl-benzothieno-thiophene and fluorenone-based molecules

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This work was supported by Program 4 of the “Coriolan Drăgulescu” Institute of Chemistry, Research Projects 4.1.

MATERIAL BASED ON BISMUTH AND CARBON ENRICHED WITH IRON OXIDES USED FOR THE RECOVERY OF GOLD FROM AQUEOUS SOLUTIONS

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Gold is from the group of natural precious metals with high economic value. Chemically, it tends to be less reactive than other elements. The recovery of this metal due to high use in electronics is a demand in this period of time [1,2].

Using bismuth carbonate and carbonaceous as starting precursor, two materials were obtained. Iron oxide material was used in the second sample to enhance the adsorption proprieties of materials for gold recovery [3]. The materials were characterized by XRD, SEM, EDX, BET and AFM. The results on the morphology of the samples indicate that when iron is introduced into the material, it clearly shows a decrease in the size of the particles even if their specific surface is similar of ~40 m^2/g. The adsorptive properties of the materials were highlighted in order to recover Au(III). For this, static adsorption studies were carried out. The parameters that influence the adsorption process were studied, namely: the pH, the contact time, the temperature and the initial concentration of the metal ions in the used solution. In order to establish the mechanism of the adsorption process, kinetic, thermodynamic and equilibrium studies were carried out indicating a total adsorption capacity of 13.1 mg Au(III)/g material [4].

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This paper was financially supported by the Project “Network of excellence in applied research and innovation for doctoral and postdoctoral programs” / InoHubDoc, project co-funded by the European Social Fund financing agreement no. POCU/993/6/13/153437 .

We are thankful to the Romanian Academy (Project 4.1.) for the financial support.

GALLATE LIGANDS FUNCTIONALIZED WITH FERROCENE CONTAINING ALKYL CHAINS AS PRECURSORS FOR BIMETALLIC LIQUID CRYSTALS

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Over the last decades metallomesogens (MMs - metal containg liquid crystals) have received growing attention, due to versatile physico-chemical properties imparted by the metal ions employed, such as luminescence, magnetism, redox properties, etc [1].

Although a wide variety of homonuclear MMs with novel mesomorphic properties were reported, examples of bimetallic heteronuclear mesogens are still quite rare [2a]. The combination of dissimilar metals in one molecule may give rise to improved physicochemical properties [2b]. Recently, highly luminescent Zn(II) coordination complexes based on differently functionalized tridentate terpyridinic ligands were reported [3]. The introduction of room temperature liquid crystalline properties was realized through monodentate gallate units functionalized with several long alkyl chains. A versatile synthesis permits the obtainment of lipophilic gallates decorated with different chains.

On this background, herein we report the synthetic strategy of obtaining a series of gallates differently substituted with two types of chains: *n*-alkoxy chains and alkyl chains containing a ferrrocenic unit. The ligands were used to obtain bimetallic mesogens based on Zn(II) and Cu(II) ions. The purity and structural characterization of the gallate precursors and the final compounds were carried out using AAS, FT-IR, ^{1}H-NMR spectroscopies. The mesomorphic properties were preliminary investigated by Polarized Opical Microscopy (POM) and Differential Scanning Calorimetry (DSC). Thermal stability was determined by TGA analysis.

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This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1958, within PNCDI III.

BIMETALLIC LIQUID CRYSTALLINE MATERIALS BASED ON Zn(II) AND Cu(II) COORDINATION COMPLEXES

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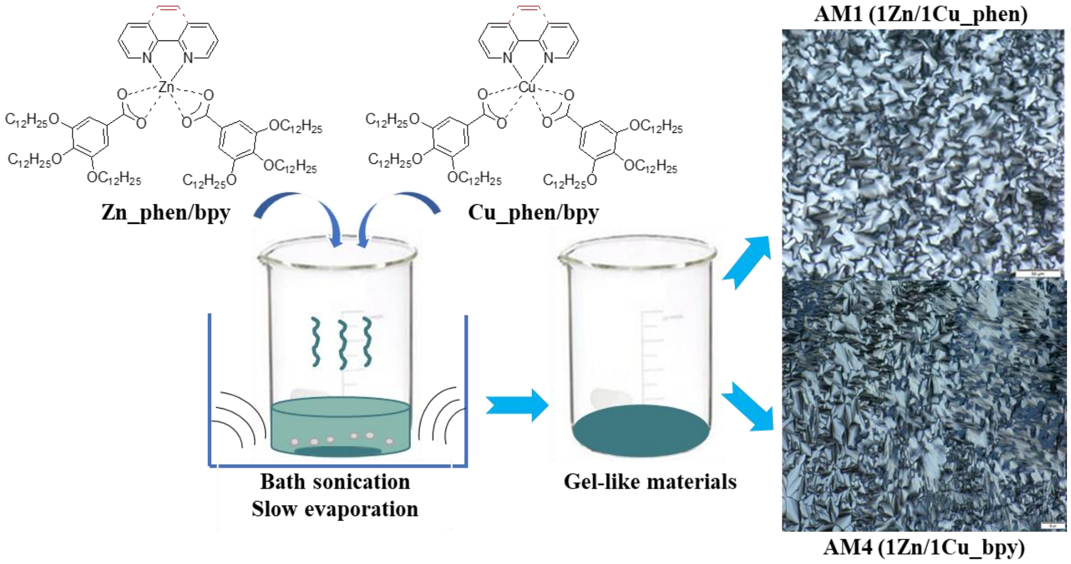
“Soft” metal-based materials are known to have applicability in nanotechnology, electrooptics, bio- and chemosensors, etc. [1,2]. The importance of the metal centers in inducing useful properties in functional metallomesogens for practical applications was well described over the time [3]. However bimetallic systems where less explored. The development of bimetallic systems with liquid crystalline properties constitutes a further step in the field of functional advanced materials since they may exhibit not only the properties deriving from the metal center but new and synergistic properties should be expected. In this regard, herein we present a series of new Cu(II) and Zn(II) mononuclear metallomesogens in which the liquid crystalline properties were induced through two bulky trialkyl bidentate benzoates, the coordination around the octahedral metal center being fulfilled by a chelating N^N ligand. Bimetallic liquid crystalline systems with optical and thermal behaviors different from those of the precursors were obtained by simply mixing the mononuclear metallomesogens in different molar ratios. The purity and structural characterization of the metallomesogenic precursors were carried out using AAS, FT-IR, ^{1}H-NMR spectroscopies. Mesomorphic properties of the precursors and the bimetallic systems were investigated with Polarized optical microscopy (POM), Differential Scanning Calorimetry (DSC) and small- and wide-angle Xray scattering (SWAXS).



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This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1958, within PNCDI III.

HONEY NATURAL PRODUCTS AS AN ADJUNCTIVE TREATMENT FOR CHALLENGING DISEASES

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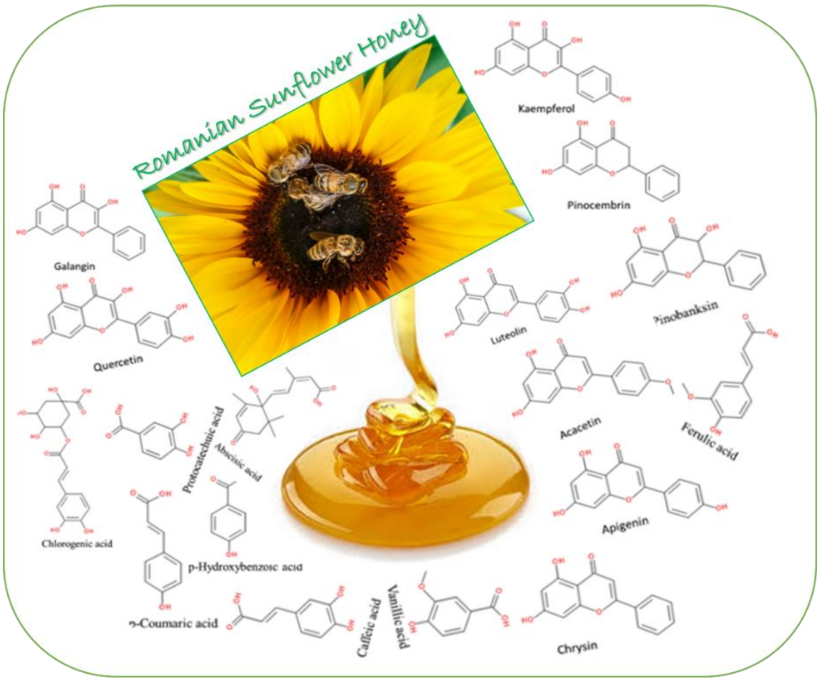
Since ancestor times, honey and its components are well-known for their antiviral, antimicrobial, antidiabetic, anticancer, antifungal and antiinflamatory enhancing immune system capabilities. Moreover, honey is considered a viable therapeutic choice to mitigate the unavoidable side effects and recently as an alternative treatment with promising results for the coronavirus. [1, 2]
The present study aims to explore the Romanian sunflower honey, Figure 1, as an adjunctive treatment for the biggest global health threats such as human immunodeficiency virus type (HIV-1), severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) and diabetes, emphasizing its bioactive composition and biological activities. In-silico scenario involving molecular docking, ADMET and antiviral activity prediction, and comorbidities activity spectra showed that several components of sunflower honey could interact with target proteins including cyclooxygenase-2 enzyme (i.e., pinobaskin, galangin, pinocembrin), non-nucleoside reverse transcriptase (i.e., pinobaskin, galangin, kaempferol, chlorogenic acid) and peroxisome proliferator-activated receptor gamma (i.e., luteolin, quercetin chlorogenic acid). ADMET analysis indicated a high safety profile and orally bioavailability in terms of drug behavior, enhancing the chances of success in clinical

trials. Strengthening this potential adjuvant behavior may allow HIV-1, diabetes and SARS-CoV-2 infected individuals to gain better control over their disease.

Fig.1. Romanian sunflower honey components



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This work was supported by Project 1.2, from the "Coriolan Dragulescu" Institute of Chemistry, Timisoara, Romania.

THE THERMAL BEHAVIOUR OF ALKYLVINYLPHOSPHONATES-ACRYLATES COPOLYMERS

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The presence of phosphorus as phosphonic or phosphonate groups in the acrylic-based polymer structure enhanced thermal resistance and flame retardancy. The copolymerization of diacrylate and monomer containing phosphonic or phosphonate functional group is more practical and efficient way to obtain polymers with enhanced thermal resistance. The copolymers of dialkylvinylphosphonates with diacrylates could be designed to have several special properties such as flame-retarding effects, adhesion to metal oxides, anticorrosion properties, selective polymer sorbents and biomedical applications [1-3]

Homopolymer of tri(propylene glycol) diacrylate and its copolymers with different molar ratios of comonomers dimethylvinylphosphonate from 1:1 to 5:1 molar, respectively, were obtained by exposure to UV light in the presence of photoinitiator (3% weight versus monomers) and characterized. The influence of phosphonate groups on thermal degradation and flammability has been investigated by thermal analysis (TGA) and limited oxygen index (LOI).

All polymers containing phosphonate groups are thermally stable up to high temperatures under both nitrogen and air atmosphere. It is worth to note that the polymers in the ester form undergone major weight loss above 320°C, while homopolymer of tri(propylene glycol) diacrylate lost weight under 290°C. The copolymer dimethylvinylphosphonate: tri(propylene glycol) diacrylate 3:1 is the most stable material in this series. The measurements of limited oxygen index showed that the presence of phosphonated groups decreased the flammability of polymer with at least 10%.

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STRUCTURAL AND OPTICAL PROPERTIES OF 3d METAL COORDINATION COMPLEXES WITH N- AND O- DONOR LIGANDS

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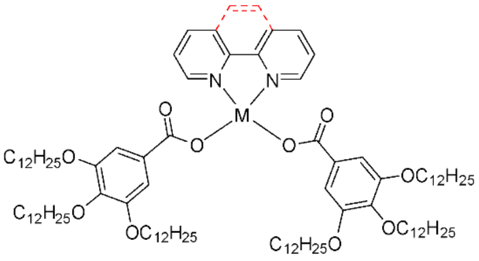
Liquid crystalline compounds based on metal complexes have been extensively studied due to their specific properties related to metal ions employed, like luminescence, magnetism, and redox properties [1, 2].

Here, we present the synthesis of two isostructural Ni^{II} and Zn^{II} coordination complexes based on N^N-chelating ligands (2,2’-bipyridine and 1,10-phenanthroline) and an O-donor ligand (3,4,5-tridodecyloxybenzoate) and their structural characterization by spectroscopic and analytic methods.



M = Zn^{II} and Ni^{II}

Figure 1. Proposed structures of Ni^{II} and Zn^{II} complexes

The complexes self-assemble into liquid crystalline supramolecular architectures, their mesomorphic properties being analysed by a combination of Polarized Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC) techniques. The metallomesogens show typical columnar textures and are liquid crystalline over a wide range of temperatures. Preliminary results regarding the emission properties of the complexes are presented.

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We thank the Romanian Academy, Institute of Chemistry “Coriolan Dragulescu” (Project 4.1.3) for financial support. This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2020-1958, within PNCDI III.

DESIGN, SYNTHESIS AND EVALUATION OF NOVEL PHENOTHIAZINIUM DYES FOR TUMORAL CELLS VISUALIZATION

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Organic dyes containing phenothiazinium chromophore are well known for their medicinal applications derived from its metachromatic staining, antimicrobial and photosensitizer properties [1, 2].

Novel methylene blue (MB) analogues were designed aiming the red-shift of UV-vis absorption maxima compared to the parent MB and furthermore the cancer cell staining ability was investigated. The synthetic route involves a nucleophilic substitution of the phenazathionium tetraiodide with primary and secondary amines using different synthetic protocols as ultrasound irradiation or mechanochemical procedures. The structures of the new phenothiazinium dyes were assigned using HRMS and ^{1}H-,^{13}C-NMR spectroscopic data.

The novel phenothiazinium dyes staining ability was investigated on human normal BJ fibroblast cells and two ovarian cancer cell lines, A2780 and OVCAR-3, and was evidenced by conventional epi-fluorescence images, confocal one-photon excited Fluorescence Lifetime Imaging Microscopy (FLIM) and Two-photon excited FLIM (TPE-FLIM) assays.

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Financial support from CNCSIS-UEFISCDI, Projects PN-III-P4-PCCF-2016-0142

PHENOTHIAZINYL-VINYL-PYRIDINIUM DYES WITH POTENTIAL APPLICATIONS AS SELECTIVE CELLULAR STAINING AGENTS

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In the last years, the methine dyes gained special attention in bioimaging due to their high molar extinction coefficients, high fluorescence quantum yields, large range of absorption and emission wavelengths reaching NIR domain and a good ability to penetrate through the cell membranes [1-3].

The synthesis and structural characterization of cationic methine dyes based on phenothiazinyl-vinyl-pyridinium (PVP) scaffold, together with optical (absorption/emission) properties and potential applicability of PVP dyes as NIR fluorescent labels, were investigated. The in vitro cytotoxicity of the new PVP dyes on B16-F10 melanoma cells was evaluated by WST-1 assay while their intracellular localization was assessed by fluorescence microscopy imaging and two-photon excited fluorescence lifetime imaging microscopy (TPE-FLIM).

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Financial support from CNCSIS-UEFISCDI, Projects PN-III-P4-PCCF-2016-0142

CHARACTERIZATION OF BIOMASS RESIDUES FOR THERMOCHEMICAL APPLICATIONS

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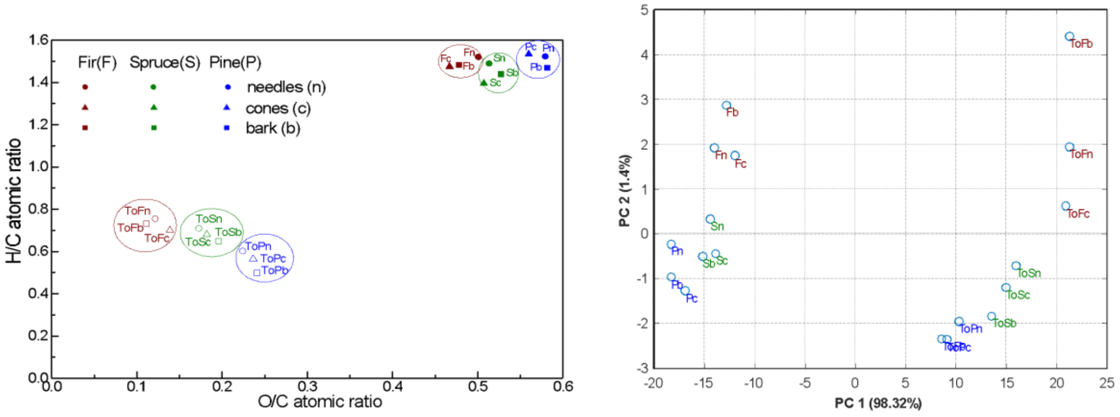
Energy derived from biomass is considered a versatile renewable alternative to fossil fuels. Efficient thermal conversion of biomass into valuable bioproducts or bioenergy requires careful adjustment of process parameters with the properties of biomass feedstock and the intended use of the final products. This study involves thoroughly characterization of several types of biomass residues to determine their potential use as source of valuable compounds. Proximate/ultimate and morphological analysis as well as thermal behavior showed that the studied materials are promising candidates for biomass valorization by torrefaction. The elemental analysis of biomass residues was performed and the calculated O/C and H/C atomic ratios showed that torrefaction placed the solid materials in the region of coals, close to the origin of the Van Krevelen diagram. In addition, it was revealed that fir samples contain significant amounts of phenolic and flavonoid compounds. The exploratory data analysis offered the possibility to combine multiple information obtained from detailed characterization of samples into a global view of the system. The PCA and hierarchical clustering revealed differences between biomass samples of various origins.



Example of differentiation between various biomasses before and after torrefaction, according to the Van Krevelen diagram and the PCA analysis.

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Support by the Ministry of Research, Innovation and Digitization, CNCS/CCCDI-UEFISCDI, through the project PN-III-P4-PCE-2021-1141, within PNCDI III is gratefully acknowledged.

NEW ONLINE TOOL FOR KINASE CRYSTAL STRUCTURES PRIORITIZATION IN DOCKING ANALYSIS

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In cheminformatics, protein-ligand docking is a powerful tool applied for virtual screening, pose prediction, and binding affinity estimation. However, docking results depend on the quality of the crystal protein structures.

The B-factor index of the binding site (BFIbs), is a recently proposed parameter that relates the atomic fluctuations in the binding site to the entire protein [1]. In a large-scale docking exercise comprising 26,019 protein-ligand complexes, BFIbs proved to significanlty correlate with docking power (ligand pose prediction).

Herein, we describe a new digital tool -BFI in kinases- publicly available at www.chembioinf.ro, which provides researchers with computed BFIbs values and a series of crystallographic data, ligand descriptors, and insights into protein-ligand binding for 2433 crystal structures capturing kinases.

This new resource can support the selection of crystal structure complexes towards improved docking results and ultimately facilitate a more efficient search for new kinase inhibitors.

10. Halip, L., Avram, S., Neanu, C. The B-factor index for the binding site (BFIbs) to prioritize crystal protein structures for docking. Struct Chem 32 (2021) 1693–1699.