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CONTENTS

REDOX-SWITCHABLE CATALYSTS

Evamarie HEY-HAWKINS, **Peter LÖNNECKE, John POPP, Axel STRAUBE**

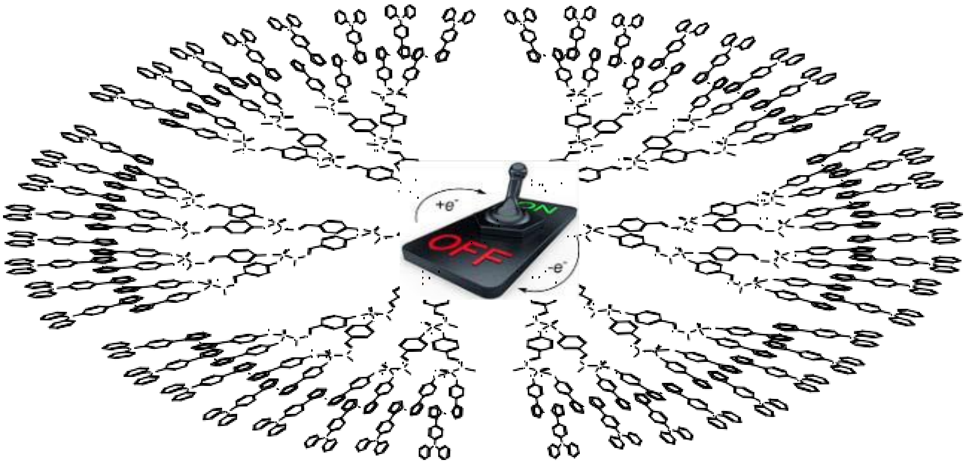
Leipzig University, Faculty of Chemistry and Mineralogy, Institute of Inorganic Chemistry,
Johannisallee 29, D-04103 Leipzig, Germany.
hey@uni-leipzig.de

For many years, research in catalysis has mainly focused on the development of new catalysts and the optimisation of their performance to achieve high conversion and selectivity. Inspired by nature, scientists are now also looking at possibilities to develop catalysts that change their activity and/or selectivity in response to an external stimulus, such as light, changes in pH or redox reactions.

Among the external stimuli, redox-switchable catalysis (RSC) is a field of growing importance in which redox-active functionality is incorporated in a ligand framework to allow the catalytic activity of the coordinated metal centres to be influenced in situ. Oxidation and reduction influence the electron-donating ability of the ligand and thus result in altered activity or selectivity of the catalyst, which may facilitate a new transformation altogether. The ultimate goal is to design a catalyst displaying orthogonal activity for different substrates on changing its electronic nature. Thus, catalysts have been switched to change their solubility (for catalyst recycling) or to modulate the activity of the transition metal (electronic communication between the redox-active group and the catalytic centre).

In our group, we are focusing on ferrocene-based switchable catalysts, including those grafted to the surface of dendrimers [1] or novel *C*3-symmetric tris(ferrocenyl)- arene-based tris-phosphanes [2].

In this presentation, an overview on switchable catalysts will be given with a specific emphasis on RSC.



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LIQUID CRYSTAL PHASE OF COUNTER-TWISTING RIBBONS AND STARS – FIRST EXAMPLES OF ANTIFERRO- AND FERRICHIRALITY

Ya-xin LI[1,2], Yi-nan XUE[1], Yan WANG[1], Goran UNGAR[1,2], Xiao-hong CHENG[3], Rui-bin ZHANG[2], Xiang-bing ZENG[2], Liliana CSEH[4], Hong-fei GAO[3], Feng LIU[1], Kutlwano GABANA[2], Gillian A. GEHRING[2]

[1]*Xi'an Jiao-tong University, Xi'an, China*
[2]*University of Sheffield, Sheffield, UK*
[3]*Key Laboratory of Medicinal Chemistry from Natural Resources, Kunming, China*
[4]*Romanian Academy, Coriolan Dragulescu Institute of Chemistry, Timisoara, Romania*

Helical structures continue to inspire, and there is considerable temptation to attribute helicity to columnar LCs. While short isohelical sequences are undoubtedly present, and longer ones in chiral or chiral-doped compounds, the order is only short-range, equivalent to a paramagnet without or with field, respectively. However, here we report a confirmed example of a true LC phase, not a soft crystal, of achiral compounds, chiral compounds and their racemic mixtures, as well as polymers. They all form the new phase consisting of columns, each being a long-range homochiral helix [1]. Long-range periodicity and isochirality are maintained by intercolumnar interaction. This orthorhombic LC, spacegroup *Fddd*, is discovered in compounds with either bent or straight rod-like pi-conjugated cores (see Fig. 1), and is subsequently found in other systems, including polymers. The structure is equivalent to an antiferromagnet with twist replacing spins. A theory based on interacting quadrupoles confirms this structure as energetically favoured over all tested alternatives. Due to cancellation, the current *Fddd* phase has no overall chirality. However, in non-racemic mixtures and in mixtures of non-equivalent enantiomers the *Fddd* symmetry is broken, creating additional novel chiral LC phases.

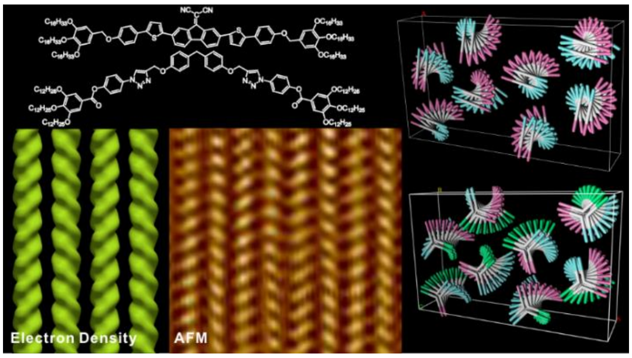

Figure 1. Top left: Some of the compounds displaying the *Fddd* phase. Bottom left: Electron density map (green) and AFM phase contrast image of the (110) plane, showing alternating left- and right- twisted ribbon-like columns. Right: schematic of packing of straight-core (top) and bent-core molecules (bottom) [1].

This work is supported by EPSRC (EP-K034308, EP-P002250), the 111 Project 2.0 of China (BP2018008) and the NSFC (No. 21865038).

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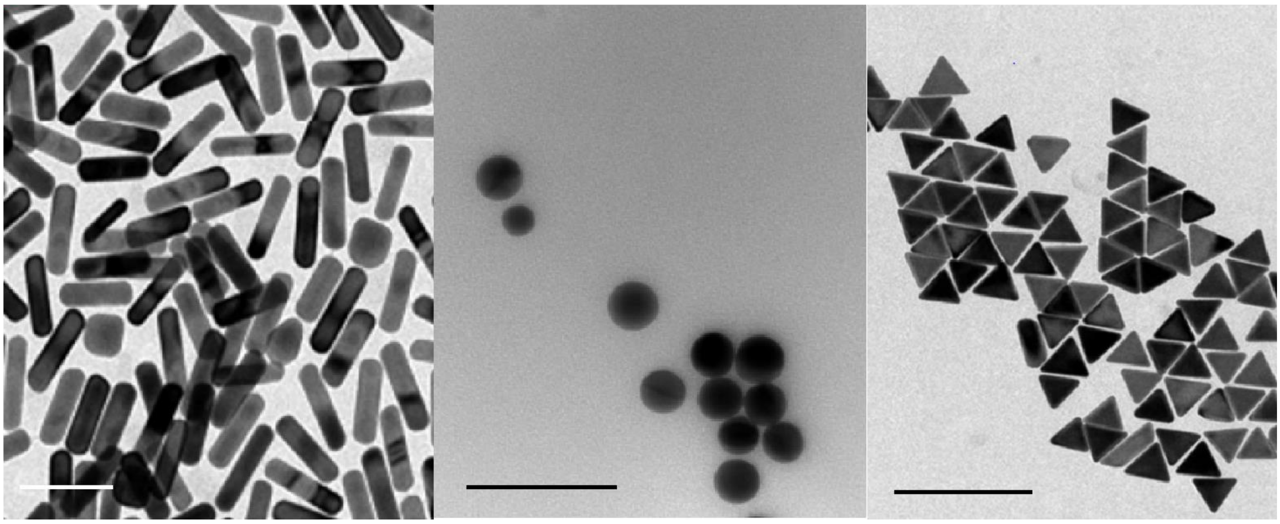
LUMINESCENT SELF-ASSEMBLED MONOLAYER ON GOLD NANOPARTICLES: TUNING OF EMISSION ACCORDING TO THE SURFACE CURVATURE

Angela CANDREVA, Giuseppe DI MAIO, Francesco PARISI, Francesca SCARPELLI, Massimo LA DEDA

University of Calabria, Department of Chemistry and Chemical Technologies, I-87036 Rende (CS) - Italy
massimo.ladeda@unical.it

The ability to form a self-assembled monolayer (SAM) on a surface has been until now investigated according to deposition techniques, which in turn depend on the surface-coater type interaction [1,2]. In this research we pursued two goals: to form a SAM on a gold nanosurface and to correlate its formation to the nanosurface curvature. To achieve these objectives, gold nanoparticles of different shape (spheres, rods and triangles, see Figure) were functionalized with a luminescent thiolated bipyridine (Bpy-SH), and the SAM formation was studied by investigating the photophysics of Bpy-SH. We have shown that emission wavelength and excited state lifetime of Bpy-SH are strongly correlated to the formation of specific aggregates within the SAMs, the nature of these aggregates being in close correlation with the nanoparticles shape.



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ELECTROSPUN Cu DOPED TiO_2 NANOFIBER COMPOSITES WITH HIGH PHOTOCATALYTIC ACTIVITY

Petronela PASCARIU, **Mihaela HOMOCIANU**

"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487, Iasi, Romania
dorneanu.petronela@icmpp.ro or pascariu_petronela@yahoo.com

One of the main problems of our day's research is environmental protection, especially the purification of wastewater and air that has caused globally alarming concern. Many studies have been based on the development of new oxide semiconductor materials with improved photocatalytic activity under UV or sunlight irradiation, for both wastewater treatment and air pollution [1-3]. We report herein, TiO_2 and Cu doped TiO_2 nanocomposite photocatalytic fibrous materials fabricated by electrospinning followed by removal of the organic components by calcination at high temperature. This method leads to materials with remarkable photocatalytic activity on the degradation of Amaranth dye. Typical characterization of the fabricated nanocomposites was performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), FT-IR, Raman spectroscopy, ultraviolet-visible spectroscopy (UV–vis). The maximum color removal efficiency of 99.84% was found for the degradation of Amaranth dye for an initial concentration of 25 mg/L, after 240 minutes of UV-light irradiation. Excellent results were found for the case of Cu (0.05%) doped TiO_2 nanocomposite (calcined at 400 ºC) that yielded a maximum value for the constant rate ($k=2.089 \times 10^{-2}$ min^{-1}). As compared to the undoped material (TiO_2/400 ºC), the Cu (0.05%) doped TiO_2 nanocomposite had an almost double reaction rate (the constant rate increasing from 1.015×10^{-2} to 2.089×10^{-2} min^{-1}). In addition, the Cu (0.05%) doped TiO_2 nanocomposite calcinated at 400 ºC was tested for the degradation of Amaranth dye under visible-light irradiation. Thus, at catalyst dosages of 0.4 to 0.8 g/L, the reaction rate constant attained the order of 10^{-2} min^{-1} under visible irradiation. These results are outstanding when compared with previously reported works.

This work was supported by a grant of the Romanian Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P1-1.1-TE-2019-0594, within PNCDI III.

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HYPERCOORDINATED ORGANOPNICOGEN(III) (Sb, Bi) COMPOUNDS - C-H BOND ACTIVATION AND REACTIVITY

Gabriel DUNEŞ, Alpar PÖLLNITZ, Alexandru SAVA, Cristian SILVESTRU

Supramolecular Organic and Organometallic Chemistry Centre (SOOMCC) at Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 400028 Cluj-Napoca, Romania
cristian.silvestru@ubbcluj.ro

C-H bond activation [1] and *carbon dioxide fixation / activation* [2] using heavy organopnicogen(III) species are both topics of seminal interest in the modern organometallic research. 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 oxides, *cyclo*-$Ar_2Pn_2O_2$ (Pn = Sb, Bi), 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 [3]. The preparation and reactivity of peculiar [2,6-$(RCH_2)_2C_6H_3$]Pn[C_6H_2-^{t}Bu_2-3,5-O-4] (Pn = Sb, Bi) towards CO_2, CS_2 and other compounds with C=N double bonds will be also discussed.

Financial support from National University Research Council (CNCSIS, Romania; Research Project No. PN-III-P4-ID-PCE-2020-2651) is highly acknowledged.

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LUMINESCENT MOFS AND METAL PHOSPHONATE MATERIALS

Gary HIX

School of Sciences, University of Wolverhampton, Wulfruna St., Wolverhampton, WV1 1LY, UK.
g.hix@wlv.ac.uk

As we enter the Anthropocene Epoch a new geological time period triggered by human activities, the impact of those activities is increasingly under scrutiny. Climate change, triggered by greenhouse gas emissions, is continually in the news and the effects on everyday lives is becoming ever more serious. A large part of those emissions arise from the production of power; through burning fossil fuels to run vehicles or generate electricity.

Energy experts predict that the world will need 30 terawatts (TW) of energy by 2050, which must come from renewables [1]. The US Office of Energy Efficiency and Renewable energy has set a target of reducing costs to 3 cents per kW, to make it affordable against initial costs, stating that the three key challenges are: high efficiency, low cost and long life. It is also estimated that 10% of energy usage in the average home, and 20-40% in commercial premises. The EU Renewable Energy Directive in conjunction with the Energy Performance in Buildings Directive has set targets to increase energy efficiency in excess of 32.5% by 2030. As the amount of solar energy received onto the earth in an hour is estimated to be more than the entire annual world energy usage, the utilisation of photovoltaics (PV) for energy production is highly attractive.

Luminescent materials can provide a means to generate electricity from sunlight or to generate light using low power energy sources [2] depending on their composition and electronic structure.

Metal Organic Frameworks (MOFs) and Metal Phosphonates present exciting possibilities in both applications. These materials can be synthesized to contain photo-active metal ions or organic functional groups which readily absorb high energy light and remit light in the visible spectrum [3]. Furthermore the porous nature of these materials means that they can also act as hosts for nanoparticles of (semiconducting) materials [4]. Variation of the chemistry of the frameworks and the guest nanoparticles allows the absorption and emission characteristics materials to tailored to specific applications.

In this paper we report the design, synthesis and characterization of a number of MOF and Metal phosphonate systems, demonstrating their efficiency in the generation of light through photoluminescence. We consider the inclusion and stabilization of halide perovskite nanoparticles in MOF frameworks and the future of power generation using composite materials in photovoltaic devices.

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GLIOBLASTOMA TREATMENT WITH PHOTO-NANOTHERAPEUTICS: THE SYNERGISTIC COMBINATION $[Ir(ppy)_2(en)]OOCCH_3$ COMPLEX/GOLD NANOPARTICLES

Loredana RICCIARDI

CNR NANOTEC - Institute of Nanotechnology, 87036, Rende (CS), Italy
loredana.ricciardi@cnr.it

The hybrid combination transition metal complexes/gold nanostructures represents a synergistic merger of multiple functionalities for combinatorial cancer therapy strategies [1].
Recently, we have reported the design and the development of a photo-triggered hybrid nanosystem obtained by embedding the highly luminescent water soluble Ir(III) complex $[Ir(ppy)_2(en)]OOCCH_3$ - where *ppy* = 2-phenylpyridine and *en* = ethylenediamine [2] - into gold core-silica shell nanoparticles, for in vitro/in vivo cancer tharanostics application [3,4].
In vitro photo-cytotoxicity tests and in vivo studies on xenograft mouse model clearly demonstrated the potential of this nanoplatform in the imaging and treatment of glioblastoma, one of the deadliest and most aggressive cancers, remarkably resilient to current therapeutic approaches [5,6].
In particular, the results emphasized striking synergistic photodynamic and photothermal effects by combining the photophysical properties of the transition metal complex with the thermoplasmonic effects of resonant gold nanospheres, leading to an exclusively light-mediated and then highly localized treatment.

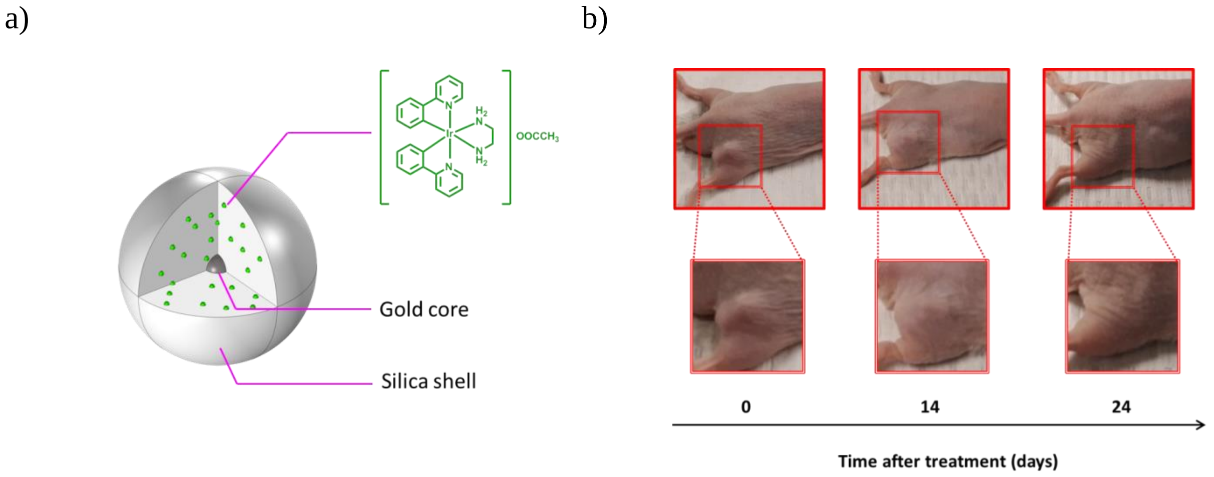

Figure 1. a) Chemical structure of $[Ir(ppy)_2(en)]OOCCH_3$ complex and schematic representation of the developed nanoplatform for in vitro/in vivo glioblastoma treatment. b) Follow-up of a representative glioblastoma xenograft mouse after photo-treatment.

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COORDINATION POLYMERS AS BIOMEDICAL PLATFORMS

Rosario M.P. COLODRERO[1], Aurelio CABEZA[1], Gary HIX[2]

[1]Universidad de Málaga, Dpto Química Inorgánica, Facultad de Ciencias, Campus de Teatinos s/n, 29071, Málaga, Spain
[2]University of Wolverhampton, Faculty of Science & Engineering, Wulfruna Street, Wolverhampton WV1 1LY, UK
colodrero@uma.es

MOFs and metal phosphonates (MPs) are Coordination Polymers (CPs) formed by metal ions or metal clusters connected via organic ligands. MPs specifically contain at least one PO_3^{2-} functional group which bonds strongly to metal ions to form a lattice in which the R groups endow the material with the characteristic properties of the organic moiety. The thermal and chemical stability of M-O-P bonds and the ability of these ligands to coordinate with many metals make phosphonic groups ideal building blocks in the design of new network materials. The synthetic chemistry of phosphonates is well developed, so phosphonic acids can be obtained through simple, well-known reactions, enabling the synthesis of phosphonate derivatives of non-steroidal anti-inflammatory drugs (NSAIDs) to be carried out [1, 2].

We report here, general characteristics of a new serie of isostructural compounds resulting from the combination of the polyfunctional R,S-hydroxyphophonoacetic acid (HPAA) with transition metal ions, AgCoHPAA and AgZnHPPA. All compounds were synthesized under hydrothermal conditions and their crystal structures were solved from single crystal diffraction data. The antibacterial activity of AgZnHPAA and AgCoHPAA was evaluated using three different bacterial strains: *Staphylococcus aureus* (NCIMB 6571), *Escherichia coli K12 W-T* (W1485 Cardiff Collection) and *Pseudomonas aeruginosa (NCIMB 8295)*. Preliminary results regarding their antibacterial properties will be presented and discussed.

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SMALL MOLECULE G-QUADRUPLEX BINDERS: A SUPRAMOLECULAR PROBLEM AND SOLUTION?

Dan G. PANTOȘ, **Dora-M. RĂSĂDEAN**

University of Bath, Department of Chemistry, Bath BA27AY, UK
g.d.pantos@bath.ac.uk

G-quadruplex DNA (G4 DNA) has emerged as a promising target for anti-cancer therapies as it is over-expressed in the promoter regions of a wide number of oncogenes as well as telomeres [1,2]. The G-quadruplexes self-assemble from DNA sequences that are rich in guanine (G). These sequences allow four Gs to form hydrogen bonded interactions in Hogsteen fashion leading to G-tetrads. Typically, three tetrads π-stack to generate the G-quadruplex structure. The directionality of the DNA strands defines the topology as parallel, antiparallel, or hybrid conformation for the G-quadruplex. The entire structure is stabilized by monovalent cations that co-ordinate the O6 atom of each G. The entire structure is driven by supramolecular interactions and in this talk we will discuss ways to stabilize or de-stabilize these supramolecular entities by using small molecules [1-6].

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SILVER NANOPARTICLES PRODUCTS FOR POTENTIAL BIOLOGICAL APPLICATIONS

Cristian MOISA[1], Andreea I. LUPITU[1], Adriana CSAKVARI[2], Dana RADU[1], Dorina CHAMBRE[1], Lucian COPOLOVICI[1], Dana M. COPOLOVICI[1]

[1] "Aurel Vlaicu" University of Arad , Faculty of Food Engineering, Tourism and Environmental Protection and Institute of Technical and Natural Sciences Research-Development-Innovation of "Aurel Vlaicu" University of Arad, Elena Dragoi St, Nr. 2, 310330 Arad, Romania
[2] Biomedical Sciences Doctoral School, University of Oradea, University St., Nr. 1, 410087, Oradea, Romania
dana.copolovici@uav.ro

Green synthesis of nanoparticles (NPs) could be mediated by plant extracts, bacteria, yeast, fungi, and algae. Plant extracts are well studied due to the existence of the wide plant kingdom, diverse plants being used to obtain metal NPs that are evaluated for diverse applications, including bio-medical, industrial, agricultural applications.

In our study we obtained silver nanoparticles (AgNPs) by using aqueous plant extracts from *Cannabis sativa*, *Thymus vulgaris*, *Lavandula angustifolia*, and *Origanum vulgare*.

The chemical composition of the extracts was determined by chromatographic and spectroscopic methods. AgNPs with less than 70 nm were obtained and characterized by UV-VIS, FT-IR spectroscopy, SEM. The antioxidant activity (DPPH and ABTS assays) and the antibacterial properties against Gram-positive and Gram-negative bacteria of some of the samples were evaluated. More studies are needed to obtain AgNPs suitable for products that could be used in health management, especially to overcome the antibiotic resistance problem.

The use of AgNPs as therapeutics is desired in order to launch a standard platform for their application in medicine, including as antimicrobial, and anticancer agents.

This work was supported by the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-PD-2019-0607, within PNCDI III.

PREPARATION AND CHARACTERIZATION OF GOLD NANOCUBES TWO-DIMENSIONAL MONOLAYERS

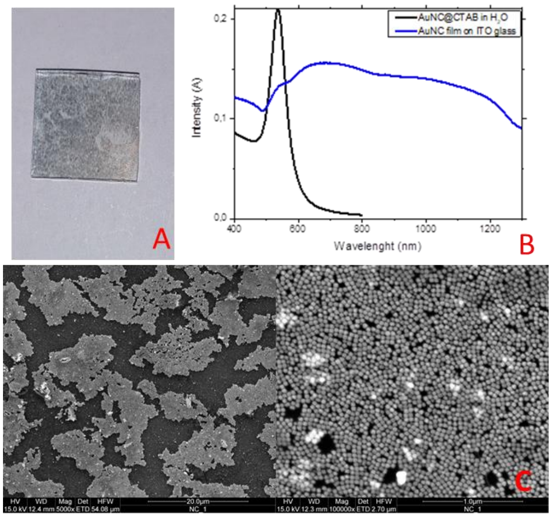
Giuseppe DI MAIO, Angela CANDREVA, Francesco PARISI, Francesca SCARPELLI, Nicolas GODBERT, Iolinda AIELLO and Massimo LA DEDA

University of Calabria, Department of Chemistry and Chemical Technologies, 87036, Rende (CS), Italy
giuseppe.dimaio@unical.it

Gold nanoparticles assembled in dense 2D monolayers have shown interesting optical and electronic properties that leads the way to new applications in optoelectronic and optothermal devices, sensors and so on. The assembly of nanoparticles in large, defect-free superstructures is not a trivial problem and various deposition techniques was proposed in the last decade to reach this goal [1]. Self-assembly of nanoparticles at water-hexane interface represents a simple, quick and low cost strategy to obtain highly ordered closed-packed gold nanoparticles monolayers [2].

Gold nanocubes, with their planar surface morphology and a strongest localized plasmonic field than others gold nanoparticles due to the presence of sharp edges [3] are interesting candidate as building blocks for the preparation of 2D monolayers.

A water dispersion of gold nanocubes coated with CTAB (hexadecyltrimethylammonium bromide) was synthesized using a seed mediated growth approach already reported in literature [4] and then assembled in close-packed 2D array at water-hexane interface using ethanol to destabilize the water dispersion and 1-dodecanethiol in the hexane phase to promote nanoparticles assembly. The obtained gold-shining/dark-blue film was transferred on ITO glass using a drain-to-deposit approach [5] and characterized by Uv-Vis spectroscopy and electronic microscopy (SEM). The extinction spectra and SEM images registered was reported in figure 1.



Analysis of SEM images of the film show large islands of assembled nanocubes with dimension varying from 5 to 20 µm. Inside these islands nanocubes form a dense close-packed 2D array with some voids of the size of few particles due to a slight tendency to overlap.

The extinction spectra of the film show a large multi-peaked plasmonic band in the visible-NIR range of the electromagnetic spectra with maximums centred at 548, 690 and 990 nm. The details of the synthesis and deposition of gold nanocubes and the correlation between the morphology of the monolayer and its plasmonic properties will be discussed.

Figure 1. (A) Optical image of the self-assembled monolayer of gold nanocubes on ITO glass. (B) Extinction spectra of gold nanocubes in water solution (black line) and self-assembled on ITO glass (blue line). (C) SEM images of gold nanocubes monolayer in two distinct magnifications.

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SYNTHESIS AND CHARACTERIZATION OF HYPER BRANCHED NANOPARTICLES WITH MAGNETIC AND PLASMONIC PROPERTIES

Angela CANDREVA[1,2], Francesco PARISI[1], Rosa BARTUCCI[1,3], Rita GUZZI[2,3], Giuseppe DI MAIO[1], Francesca SCARPELLI[1], Iolinda AIELLO[1,2], Nicolas GODBERT[1] and Massimo LA DEDA[1,2]

[1] Department of Chemistry and Chemical Technologies, University of Calabria, 87036 Rende (CS), Italy
[2]CNR-NANOTEC, Istituto di Nanotecnologia U.O.S, Cosenza, 87036 Rende (CS), Italy
[3]Department of Physics, Molecular Biophysics Laboratory, University of Calabria, 87036 Rende (CS), Italy
angela.candreva@unical.it

Hybrid nanoparticles, composed of an iron oxide magnetic core embedded with gold fractal-grown hyper branches (Fig.1), have been synthesized by seed mediated growth approach. Magnetic and plasmonic properties were ascertained and according to the hydroxylamine amount, used as surface-catalysed reducing agent, the number of branches and the intensity of the fractal growth have been both finely tuned. The superparamagnetic core allows their motion control via an external magnetic field. The plasmonic properties of these hyper branched hybrid nanoparticles are similar to the ones display by gold branched nanoparticles (Fig.2), but interestingly, they are characterised by a better photothermal response.

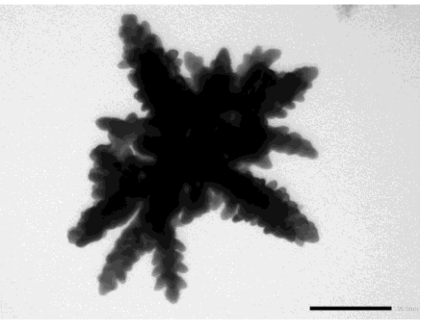

Figure 1. Hybrid nanoparticles, composed of an iron oxide magnetic core embedded with gold fractal-grown hyper branches (TEM image)

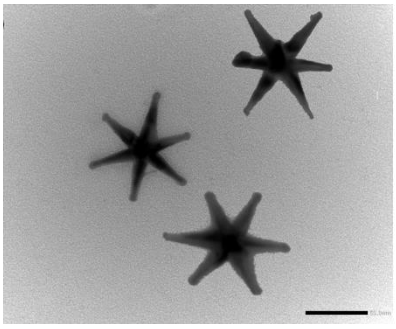

Fig.2 Gold branched nanoparticles (TEM image)

SELECTION OF THE BEST SENSITIVE MATERIAL FOR URIC ACID DETECTION FROM COMPLEXES OF A FUNCTIONALIZED PORPHYRIN AND CuNPs, PtNPs OR Pt@CuNPs

Camelia EPURAN[1], Ion FRATILESCU[1], Diana ANGHEL[1], Mihaela BIRDEANU[2], Eugenia FAGADAR-COSMA[1*]

[1] *Institute of Chemistry "Coriolan Dragulescu", M. Viteazu Ave. 24, 300223-*
Timisoara, Romania, Tel: +40256/491818; Fax: +40256/491824
[2]*National Institute for Research and Development in Electrochemistry and Condensed Matter,*
P.Andronescu 1, 300224- Timisoara, Romania;
efagadar@yahoo.ro

The importance of detecting uric acid, 7,9-dihydro-1H-purine-2,6,8(3H)-trione, arose from the medical necessity of monitoring its levels in human fluids, because an excess of uric acid indicate kidney disease, cardiovascular or renal risk, or hypertension [1,2].

The purpose of this work was to develop potential hybrid nanomaterials based on a porphyrin derivative: 5,10,15,20-tetrakis(4-amino-phenyl)-porphyrin (TAmPP) and simple or mixed metal nanoparticles, such as: CuNPs, PtNPs OR Pt@CuNPs, capable to detect uric acid in the domains with diagnosis relevance.

For enabling the selections, comparative optical testing (UV-vis spectroscopy) was performed using porphyrin alone, its complex nanomaterials with CuNPs, PtNPs and platinum covered copper core nanoparticles (Pt@CuNPs). The influence of interfering species usually present together with UA in human serum and urine, such as: glucose (Glu), ascorbic acid (AA), NaCl, KCl, CH3COONa, MgSO4, KI, lactic acid (LA), sodium salicylate (SS), were assessed in the presence of UA, but using 1000 fold more concentrated solutions than that of UA.

All the synthesized hybrid materials can be applied in the detection of uric acid in human fluids in a combined range between 0.582 × 10-6 - 1.5763 × 10-5 M UA concentrations, the lowest detection being realized by TAmPP alone with a detection limit of 0.18 µM UA. In each case, the complexation of metal nanoparticles like CuNPs, PtNPs or of mixed nanoparticles with Cu core and Pt shell (Pt@CuNPs) with porphyrin-base, enlarged the detection range.

The authors kindly thank for the support of Romanian Academy - Programme 3/2021 from Institute of Chemistry Timisoara.

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ORGANOCHALCOGEN COMPOUNDS WITH RELEVANCE FOR BIOLOGY. STRUCTURE AND REACTIVITY

Anca SILVESTRU

Centre of Supramolecular Organic and Organometallic Chemistry, Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Arany Janos 11, RO-400028, Cluj-Napoca, Romania
anca.silvestru@ubbcluj.ro

A continuously increased attention was paid during last years to organochalcogen compounds bearing organic groups with nitrogen or/and oxygen atoms, due to their potential in biology, organic synthesis or microelectronics [1]. Our recent interest is focused on organochalcogen species with organic groups with pendant arms, *e.g.* 2-$(R_2NCH_2)C_6H_4$ (R = Me, Et, Pr^i) or 2-$[E(CH_2CH_2)_2NCH_2]C_6H_4$ (E = O, NMe) [2] as well as on several dialkylchalcogenides [3].

As a continuation of our studies, we report here several new species of type R^1R^2Se {R^1 = 2-$(Me_2NCH_2)C_6H_4$, 2-$(Et_2NCH_2)C_6H_4$, 2-$[O(CH_2CH_2)_2NCH_2]C_6H_4$; R^2 = CH_2phtz or CH_2CH_2pz (phtz = phenylthiazole, pz = pyrazole)}, R^1 = R^2 = 2-$CH_3C_6H_4CH_2$ or 2-$BrC_6H_4CH_2$}, as well as their metal complexes.

The new compounds are characterized in solution by multinuclear NMR (^{1}H, ^{13}C, ^{77}Se) and mass spectrometry and in solid state by single-crystal X-ray diffraction.

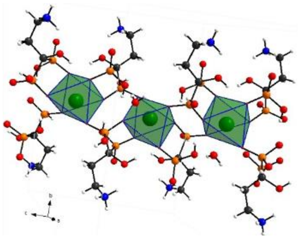
FIGHTING OSTEOPOROSIS: CONTROLLED RELEASE DRUG DELIVERY SYSTEMS BASED ON COORDINATION POLYMERS

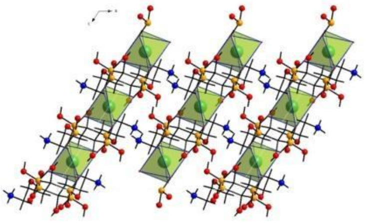
Konstantinos D. DEMADIS

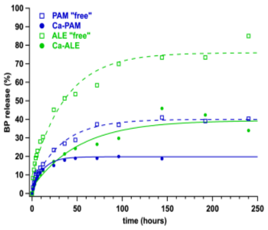
Crystal Engineering Growth and Design Laboratory, Department of Chemistry, University of Crete, Heraklion, Greece
demadis@uoc.gr

Osteoporosis is among the well-known bone diseases (other are osteoarthritis, multiple myeloma, Paget's disease etc.), which burdens millions of people compromising patients' quality of life. The recommended pharmaceutical treatment is the use of bis-phosphonates (BPs, a.k.a. "-dronates"). Their success in mitigating osteoporosis notwithstanding, these "-dronate" drugs present a number of challenges including fast excretion, and numerous side-effects, such as osteonecrosis of the jaw, hypocalcemia, esophageal cancer, ocular inflammation, atrial fibrillation, etc. Nevertheless, the main drawback of BPs is their limited oral bioavailability. It is, therefore, imperative to design and fabricate "smart" systems that allow controlled delivery of the active BP agent, which will depend on the patient's needs and idiosyncrasies.

In this presentation we discuss bis-phosphonate drug delivery systems that are based on Metal-Organic Frameworks (MOFs). MOFs are well defined crystalline materials that possess an "inorganic" part (the inorganic metal ion) and an "organic" part, a molecule that can form coordinating bonds with the metal ion. In these materials we have used biologically acceptable inorganic metal ions (eg. Ca^{2+}) and bisphosphonates as the organic portion. These materials have been reliably synthesized, and structurally characterized.







The above-mentioned materials were studied for the self-sacrificial release (by pH-driven dissolution) of the bisphosphonate active ingredient. Several such materials were prepared with a variety of bisphosphonate drugs. They exhibit variable release rates and final % release, depending on the actual structure of the metal-bisphosphonate material.

Several factors affect the controlled release of bisphosphonate drugs from their parent metal-bisphosphonates, such as the nature of the drug itself (chemical groups present, geometrical features, polarity, etc.), the nature of the metal ion present, the temperature, and the framework dimensionality.

Keywords: Bis-phosphonates, MOFs, coordination polymers, pharmacology, osteoporosis, drug delivery, controlled release

EFFECT OF DIANHYDRIDE SEGMENT STRUCTURE ON THE ELECTROCHROMIC PROPERTIES OF NOVEL TRIPHENYLAMINE-BASED POLYIMIDES

Catalin-P. CONSTANTIN, Andra-E. BEJAN, Mariana-D. DAMACEANU

"Petru Poni" Institute of Macromolecular Chemistry, Electroactive Polymers and Plasmochemistry Department, Aleea Grigore Ghica Voda 41A, Iasi - 700487, ROMANIA
constantin.catalin@icmpp.ro

Chromism phenomenon can be regarded as the color change of a material in response to an outside stimulus. In the particular case of electrochromism, the electroactive compounds can render different colors in form of oxidized or reduced species that can be produced during electrochemical processes. In recent years, a great applicative potential of electrochromic materials has gradually emerged in our lives, being used in smart windows, sunglasses, electrochromic mirrors, and so on. EC materials containing triphenylamine (TPA) units possess remarkable color transitions, being widely investigated in order to understand the underlying methods responsible for the color change. Our group has been working on triarylamine-based derivatives since 2013, and various TPA-based materials have been successfully developed, like polyimides (PIs) [1], polyazomethines [2], or sensitizers for dyes sensitized solar cells [3]. Recently, perylene-based polyimides incorporation TPA units [4] were studied, and interesting color transitions with desirable EC reversibility were achieved. Polyimide materials are known to come close to the ever-demanding requirements of advanced technologies, due to a combination of high-performance features like high thermal and chemical resistance, mechanical strength, thermal, electrical or sound insulation properties, long-term durability, among others. The remarkable performance and versatility of PIs are attested by their successful use in key technological areas: polymeric matrices for advanced composite materials, thin dielectric films for electronic applications, passivation layers and mechanical substrates for flexible, printed circuit boards, structural adhesives and sealants, encapsulants for implantable devices, etc. The polyimides reported here bring into the light an innovative structural approach by incorporating in the same polymer chain of unique structural features. Thereby, TPA units were incorporated in PIs to ensure the electrochromic response, while the triphenylmethane was used as building block to render the necessary solubility for an easier processability into thin films and coatings, as it was previously proved [5]. This study reports on the main physico-chemical characteristics of these polymers, with focus on the effect of polymer structure on both enhanced electrochromic efficiency and stable electrochromic behavior. By spectroelectrochemical measurements, the variation of absorption bands upon potential increase was demonstrated, contingent on radical cations and dicationic species formation. The electrochromic devices realized with these PI rendered color variation between neutral and oxidized forms, with promising response times and stable cyclic switching. The electrochromic response was consistent with the degree of the conjugation provided by the phthalimide skeleton, which rendered variable electron mobility along the polymer chain.

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ACHIEVEMENTS IN POLYURETHANE FOAM DEGRADATION AND RECYCLING, ADDRESSING CURRENT ENVIRONMENTAL CHALLANGES

Gabriel KISS[1,2], Gerlinde RUSU[1], Geza BANDUR[1], Francisc PÉTER[1,3]

[1]University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, C. Telbisz 6, 300001Timişoara, Romania
[2]Momentive Performances Materials, Carl-Duisberg-Str. 101, 51373 Leverkusen, Germany
[3]University Politehnica Timişoara, Research Institute for Renewable Energies, G. Muzicescu 138, 300501 Timişoara, Romania
gabriel.kiss@momentive.com

The flexible polyurethane (PU) foam production reached 5 Million tons in 2020 due to a continuously increasing demand. Due to its unique properties, this polymer became very attractive for various end applications. Foam waste is generated through the production and conversion process of PU foam, as well as through post-consumer waste, becoming an emergent environmental problem.

This study focuses on new trends in both laboratory and industrial depolymerization of the PU foam waste by glycolysis and acidolysis methods, and reuse of the recycled polyol in formulations similar with those industrially employed. For the glycolysis method, the waste was reacted in autoclave with diethylene glycol, in the presence of a catalyst, allowing the conversion of the polyurethane foam waste in a fully recyclable product, able to be added in certain amounts to the raw polyol without any purification step [1]. Another recycled polyol was obtained industrially by an acidolysis process. For comparison, a standard petroleum based polyol was used. The polyols were characterized by dynamic viscosity, hydroxyl number, water content, density, as well as by FT-IR spectroscopy and thermal analysis. The amount of the recycled materials was optimized for successful reuse in the polyurethane foam production, replacing the petroleum-based polyols. As noticed, the utilization of recycled polyol enabled similar polyurethane foam properties as the standard polyol. Comparing the glycolysis and acidolysis methods, it has been observed that acidolysis allowed higher amount of recycled polyol in the polyurethane foam formulation [2]. Based on the foam emission data, the optimized foam formulation using recycled polyol also allowed the reduction of volatile organic compounds emission, leading to improved environmental impact.

The results open the way of further optimization studies of industrial polyurethane foam formulations using improved degradation processes to recover the PU foam waste, and ultimately address the sustainability challenge of this thermoset polymer material. This work was realized with the support of Momentive Performance Materials Inc. (Leverkusen, Germany) and Ikano Industry (Rogoźno, Poland).

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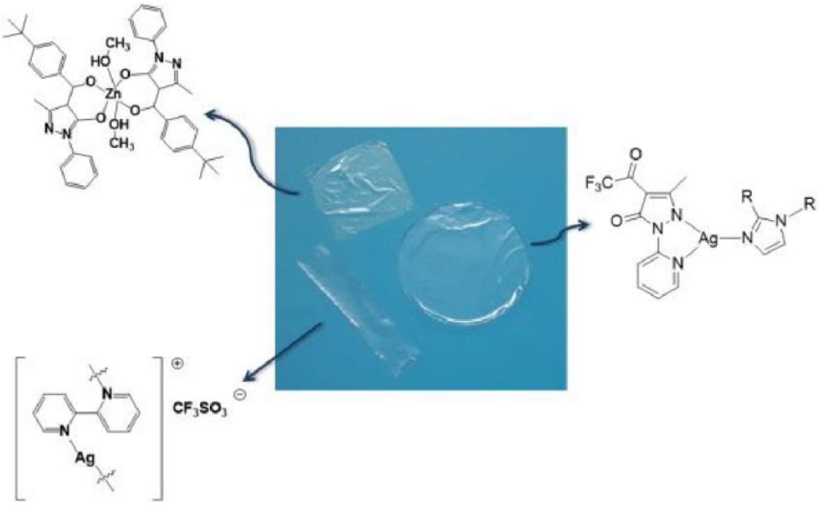
METAL-BASED ACTIVE BIOFILMS: MODULATION OF PROPERTIES BY USING ZINC AND SILVER COORDINATION COMPOUNDS

Alessandra CRISPINI[1], Francesca SCARPELLI[1], Debora POLICASTRO[1], Iolinda AIELLO[1], Massimo LA DEDA[1], Fabio MARCHETTI[2], Corrado DI NICOLA[2], Riccardo PETTINARI[2], Claudio PETTINARI[2]

[1]Department of Chemistry and Chemical Technologies, via P. Bucci, University ofCalabria, Italy.
[2]School of Pharmacy, Chemistry Section, University of Camerino, Via S. Agostino 1, Camerino MC, Italy
crispini@unical.it

Biopolymers derived from renewable resources are believednowadays to be the future generation of coating materials in several field such as biomedical devices and food packaging [1-3]. Biopolymers are excellent raw materials to producedifferent formulations spanningfrom various sized particles to gels, fibers and films. The film-forming properties allow the preparation of films with good mechanical properties, selective gas permeability and good entrapping properties for active compounds, able to improve the biologically properties of the pure polymer matrices. Indeed, a novel method to improve the properties of biopolymerfilms is the use of biologically active additives to be incorporated within the chosen polymer matrix, spanning from organic molecules to essential transition metal ions and metal complexes[4,5].The useof transition metal complexes, as active component for the functionalization of polymeric materials, could represent a novel strategy towards the production of materials specifically tailored for their application taking advantage of the inherent flexibility of transition metal complexes.To this end, several recent examples of the addition of new zinc and silver complexes into variousnatural polymeric matrices, will be given, focusing on the synthesis, chemical physics characterization and antioxidant and antimicrobial properties of the so formed active polymeric films.



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BISMUTH-BASED LAYERED PHOTOCATALYTIC MATERIALS FOR ENVIRONMENTAL REMEDIATION

Mirabbos HOJAMBERDIEV*

Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin, Germany
hmirabbos@gmail.com

Water and air pollution has been one of the most challenging environmental issues in today’s world. Since the Honda-Fujishima effect was first reported in 1972 [1], a semiconductor-based photocatalysis has been regarded as one of the most green and economical processes for potential application in environmental remediation [2]. Bismuth-based semiconductors are regarded as a promising class of advanced photocatalytic materials due to their suitable band gap for visible light response, an increased mobility of photo-generated charge carriers because of well-dispersed Bi 6s orbital, non-toxicity, and easy tailoring of their morphologies. To utilize their full potential in environmental remediation, various studies have been conducted to enhance the photocatalytic performance of bismuth-based semiconductors [3,4]. In this study, we have particularly explored a wide variety of bismuth-based layered photocatalytic materials, namely Bi_2O_3, Bi_2MO_6 (M = Mo, W), $BiVO_4$, BiOX (X = Cl, Br, and I) and $(BiO)_2CO_3$ for environmental remediation. As a narrow band gap semiconductor, Bi_2O_3 has five polymorphs: α-Bi_2O_3 (monoclinic), β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (body-centered cubic), δ-Bi_2O_3 (cubic), and ω-Bi_2O_3 (triclinic). Among them, β-Bi_2O_3 has the strongest absorption in the visible light region with a smaller band gap (E_g = 2.0–2.4 eV) and demonstrated a good photocatalytic performance than other polymorphs under visible light irradiation, and is inexpensive, nontoxic, and stable in acidic conditions. To further enhance its photocatalytic performance, β-Bi_2O_3 was composited with MoS_2 quantum dots and Pd/PdO nanoparticles, and doped with Gd^{3+} ions. Also, the $(BiO)_2CO_3/Fe_3O_4$, $(BiO)_2CO_3/Bi_2O_3$, and $(BiO)_2CO_3$/Ag/AgBr composites were synthesized to enhance the visible light absorption and improve photocatalytic performance for the degradation of various organic pollutants under visible light irradiation. The present work shows that the bismuth-based photocatalytic nanomaterials have potential to be applied in wastewater treatment and air purification systems in the future.

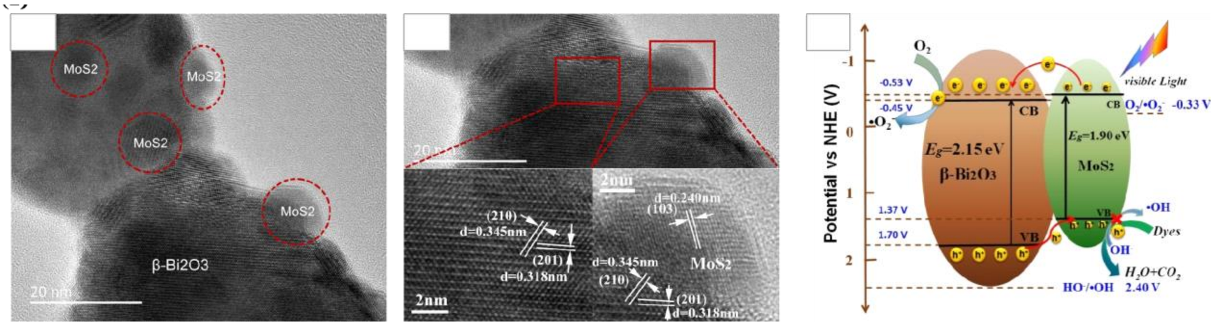

Figure 1. (a,b) TEM images of β-Bi_2O_3 particles loaded with 1.0% MoS_2 and (c) a schematic diagram of the photocatalytic mechanism and the photogenerated charge transfer process in MoS_2/β-Bi_2O_3.

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ARE COMPOSITES THE BEST DIRECTION FOR DEVELOPING NEW APPLICATIONS OF TUNGSTOPHOSPHATES?

Snežana USKOKOVIĆ-MARKOVIĆ

University of Belgrade - Faculty of Pharmacy, Vojvode Stepe 450, 11221 Belgrade, Serbia
snezaum@pharmacy.bg.ac.rs

Tungstophosphate belongs to an attractive group of heteropoly compounds (HPC), designed by condensation of more than two different mononuclear oxoanions, in the form of metal oxide clusters, which can be preserved in the solid state. Among the HPC, the subclass of compounds of the Keggin structure stood out due to their stabilities and ease of synthesis. Either as an acid form, $H_3PW_{12}0_{40}$, or their salts, e.g., $K_3PW_{12}0_{40}$, tungstophosphates with a Keggin structure possess great potential of useful activities. Most often they are applied as acid as well as oxidation catalysts, due to their unique physico-chemical, acid-base and redox properties.

The immobilization of these tungstophosphates onto high surface area supports, generally leads to improvement of active phase dispersion and availability. Various types of supports including silica, alumina, zirconia, active carbon, MCM-41, SBA-15 and clays with large surface area, as well as different zeolite have been successfully applied for this purpose. Such new composite materials, retain good characteristic of both parent components, overbridged inappropriate behavior of tungstophosphates, and even to discover new fields where such composites may take their place. The activity of composites are strongly dependent on various parameters including the type of the support, amount of HPC loading, and conditions of pretreatment and post-synthetic procedures.

To obtain even more applicable materials, our group has synthetized several kinds of tungstophosphate based composites, with zeolites, carbon materials, as well as mesoporous silicas. Our more than a decade long investigations of the tungstophosphate composites were focused on the importance of the synthesis procedures and multi-instrumental characterization of the obtained materials. Finally, the composites were tested for potential applications as catalysts, electrochemical storage materials, pesticide adsorption, and bioactivities, such as antioxidant and antimicrobial activity. These materials possess great potential to find their position in the future application related to biosystems, industry and environmental protection, as well.

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BOTTOM-UP SYNTHESIS OF NOVEL 3- & 4-CONNECTED BORON IMIDAZOLATE FRAMEWORKS

Konstantinos E. PAPATHANASIOU[1,2], Vera I. ISAEVA[3], Pawel ZAJDEL[4], Leonid M. KUSTOV[2,3], Gary B. HIX[1]

[1]University of Wolverhampton, School of Sciences, University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1LY, United Kingdom
[2] International Laboratory of Nanochemistry and Ecology, National University of Science and Technology MISiS, Moscow, Leninsky Prosp. 4, 119991 Moscow, Russia.
[3]Russian Academy of Sciences, N. D. Zelinsky Institute of Organic Chemistry, Russian Federation, Leninsky Prosp. 47, 119991 Moscow, Russia.
[4] Institute of Physics, University of Silesia in Katowice, 75 Pułku Piechoty 1, Chorzów, 41-500, Poland
[5]Faculty of Chemistry, Lomonosov Moscow State University, 119992 Moscow, Russia.
Institute or University, Faculty, Full Postal address, City, Country
k.papathanasiou@wlv.ac.uk

In recent years functional porous materials have attracted tremendous interest based on their properties and promising applications in gas storage, separation, catalysis, and energy storage and conversion [1-2]. To date, Metal-Organic Frameworks (MOFs) and zeolites comprise the most famous porous materials families. Both categories can exhibit advantages such as porosity and/or chemical functionality, but they suffer drawbacks such as sensitivity to aqueous environments, air stability etc. [3]. Last decades Zeolitic Imidazolate Frameworks (ZIFs) arose as a particular class of porous materials, which have the four connected topologies of zeolites and the high surface areas of MOFs [4]. More specifically, a novel sub-family of ZIFs based on Boron imidazolates (BIFs) has been developed by crosslinking boron imidazolate ligands with tetrahedral cations (Li+ and Cu+) [5-7]. One fundamental feature of BIFs is that both three-connected tripodal ligands and four-connected tetrahedral ligands can be readily synthesized before solvothermal synthesis. In these recently reported BIFs with 4-connected zeotype topologies, the coordination mode of each metal centre is always tetrahedral. Furthermore, for the synthetic design of neutral zeolitic BIFs, the selection of tetrahedral metal centres is currently still limited to Li+ and Cu+ ions. It is highly desirable to go beyond Li+ and Cu+ to include a much wider variety of metal ions, which might provide access to a broader range of zeolite topologies. This study reports Boron Imidazolate Frameworks based on a battery of pre-synthesized 4-connected boron imidazolates with Cobalt(2+) cations. Using the unsubstituted imidazole as a reference, we explore the relationship between BIFs' structures and potential properties in the field of catalysis. A systematic substitution (-methyl, -ethyl, -phenyl) of used imidazoles lead us to functionalize the synthesis as well as the properties of final porous products.

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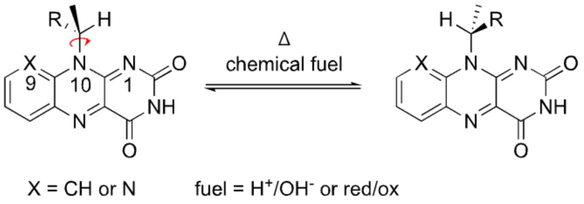
FLAVIN-BASED MOLECULAR ROTORS

Dora-M. RĂSĂDEAN, Dan G. PANTOȘ

University of Bath, Department of Chemistry, Bath, BA2 7AY, U.K.
dmr35@bath.ac.uk

The development of synthetic nanomachines that mimic the macroscopic and biological worlds is in full swing [1,2], and its importance has been supported by the Nobel Prize award in 2016. Numerous molecular machines are reported and controlling their rotation/motion is the key towards successful construction [1-3]. Inspired by the ubiquitous flavoenzymes, we report the first generation of synthetic flavin-based molecular rotors. The stator is an isoalloxazine core in which the benzene ring is replaced by pyridine. The rotor unit is attached on the *N*10 position of isoalloxazine following a protocol we have recently published [4]. The rotors series includes scaffolds with cyclic, alkyl chain and aromatic functionalities and chiral centre in the 〈 position. The driving force behind their motion is the ability of the proton in the 〈 position to forming intramolecular hydrogen bonding with nitrogen atoms in positions 1 (imide station) and 9 (pyridine station) as shown below. We control the rotation and directionality of these molecules through disrupting and reforming the hydrogen bonding by acidbase equilibria and reduction of the isoalloxazine core. TDDFT calculations complement the experimental data.



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PHENOXAZINE-BASED POLYMERS WITH BLUE AND GREEN LIGHT EMISSION IN SOLID STATE FOR LIGHT-EMITTING DIODE APPLICATIONS

Mariana-D. DAMACEANU, Catalin-P. CONSTANTIN

"Petru Poni" Institute of Macromolecular Chemistry, Electroactive Polymers and Plasmochemistry
Laboratory, Aleea Grigore Ghica Voda 41A, Iasi, 700487, Romania
damaceanu@icmpp.ro

Organic light-emitting diodes (OLEDs) can be regarded as the next generation of lightning sources and electroluminescent devices for displays due to some advantageous features, like high light emission efficiency, chemical versatility, mechanical flexibility or straightforward fabrication, among others, being feasible for mass manufacture of small- to medium-sized displays. However, there are still technological and cost challenges to produce large TV displays, the efficiency of OLEDs depending on the materials used for fabrication [1]. The emissive materials can be grouped into small molecules and polymers that can be conjugated or non-conjugated [2]. Polymers containing phenoxazine are potential candidates for use in LEDs since phenoxazine has a strong electron donating capability, being an attractive heterocycle for use as building block in the development of organic molecules designated for optoelectronic applications [3]. Although phenoxazine–based compounds are known as efficient laser dyes and exhibit good luminescence quantum yields, they were only occasionally investigated as electroluminescent materials [4] or charge balance layers in OLEDs [5,6]. The incorporation of phenoxazine with other chromophoric units into organic compounds can lead to conjugated molecules endowed with favorable transport of charge carriers, beside high emission efficiency [7].

In our attempt to develop efficient electroluminescent materials, we have designed and synthesized some phenoxazine-based polymers able to emit blue or green light in solid state contingent on the solvent used for film deposition. In addition to the general characteristics of the polymers, like chemical structure, solubility and morphology, this study concentrates on the photo-physical and electrochemical features of these polymers explored by cyclic voltammetry, UV-Vis absorption and fluorescence spectroscopy. The obtained data recommend their use as emissive or charge transporting layers in light-emitting diode applications.

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project PN-III-P2-2.1- PED-2019-3993, contract no. 485PED/2020, within PNCDI III.

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DEXTRAN-BASED ANTIMICROBIAL POLYMERS

Magdalena Cristina STANCIU, Marieta NICHIFOR

"Petru Poni" Institute of Macromolecular Chemistry, Grigore Ghica Voda Alley, 41A, 700487,
Iasi, Romania
cstanciu@icmpp.ro

New amphiphilic dextran esters (Fig.1) were achieved by polysaccharide derivatization with several substituted 1,2,3-triazoles-4-carboxylic acid via *in situ* activation with N, N'-carbonyldiimidazole. 1,2,3-triazole derivatives were obtained by "click reaction" between organic azides and ethyl propiolate. Elemental analysis, FTIR and ^{13}C-NMR afforded the structural characterization of the compounds. The self-assembling capacity of the esters was studied by using dynamic light scattering and transmission electron microscopy. Fluorescence spectroscopy allowed the determination of the critical aggregation concentration values for dextran polymers which were lower than those of low molecular weight surfactants. The antimicrobial activity of triazoles and their corresponding polymers against Gram positive bacteria (Staphylococcus aureus ATCC 25923), Gram negative bacteria (Escherichia coli ATCC 25922, Pseudomonas aeruginosa ATCC 27853) and pathogenic yeasts (Candida albicans ATCC 90028) was investigated by disc-diffusion method [1,2]. All compounds showed a moderate to good antibacterial activity versus Staphylococcus aureus ATCC 25923 and also, a very good antifungal activity against Candida ATCC 90028. The polymers having the best results concerning antimicrobial activity were tested for the Minimal Inhibitory Concentration and Minimal Bactericidal Concentration/Minimal Fungicidal Concentration by using broth microdilution method [1, 2].

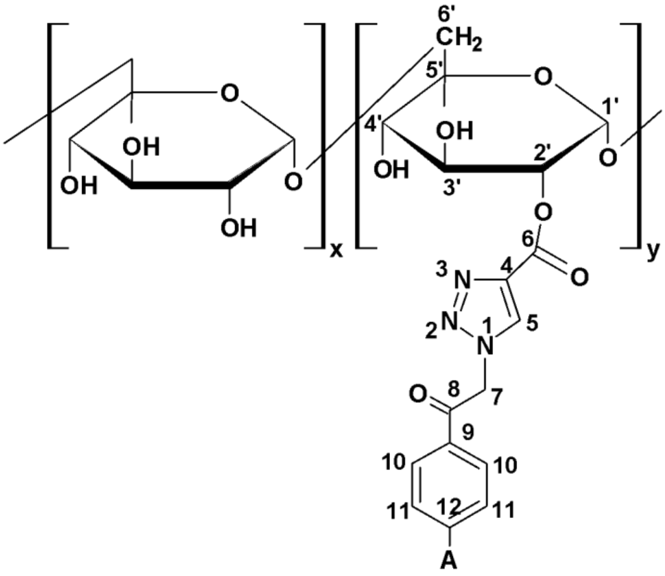

Figure 1. Chemical structure of dextran esters (A = H, F, Cl, Br, CH_3, OCH_3)

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HYBRID SILICA MATERIALS CONTAINING PLATINUM, IMPREGNATED WITH PORPHYRINS AND/OR PLATINUM NANOPARTICLES FOR FUCHSINE B COLOR REMOVAL FROM WASTEWATERS

Ion FRATILESCU[1], Zoltán DUDÁS[2], Mihaela BIRDEANU[3], Camelia EPURAN[1], Diana ANGHEL[1], Ionela FRINGU[1], Anca LASCU[1], Adél LEN[4], Eugenia FAGADAR-COSMA[1*]

[1] “Coriolan Drăgulescu” Institute of Chemistry, M. Viteazul Ave. 24, 300223-Timisoara, Romania;
[2]Neutron Spectroscopy Department, Centre for Energy Research, Konkoly-Thege street 29-33, 1121 Budapest, Hungary;
[3]National Institute for Research and Development in Electrochemistry and Condensed Matter, P. Andronescu Street 1, 300224- Timisoara, Romania;
[4]Civil Engineering Department, University of Pécs, Boszorkány Street 2, 7624 Pécs, Hungary;
efagadar@yahoo.com

Fuchsine B, 4-[(4-Aminophenyl)-(4-imino-1-cyclohexa-2,5-dienylidene)methyl]aniline hydrochloride, is a fluorescent magenta-colored dye widely used in the textile industry. The removal of Fuchsin B from wastewater systems is a demand due to its potential carcinogenicity and poor biodegradation [1].

Hybrid materials that were investigated as adsorbents for fuchsine B dye removal were obtained by *in situ* incorporation into silica matrices of: (i) platinum nanoparticles alone (PtNPs); (ii) Pt(II)-5,10,15,20-tetra-(4-allyloxy-phenyl)-porphyrin (PtTAOPP) [2, 3] and (iii) PtNPs accompanied by the same free-porphyrin, 5,10,15,20-tetra-(4-allyloxy-phenyl)-porphyrin (TAOPP). The hybrid organic-inorganic silica matrices were obtained by two steps acid-base catalyzed sol-gel technique using as precursor tetraethyl orthosilicate (TEOS).

Nitrogen porosimetry, Small Angle Neutron Scattering (SANS), Scanning Electron Microscopy, Atomic Force Microscopy, and UV-vis spectroscopy were used to fully analyze the morphology, textural and optical properties of the hybrid materials.

The adsorption depends on fuchsine B concentrations in wastewaters, the values of the specific surface area of each hybrid material and the dosage concentration of the silica-hybrid adsorbent materials. Kinetic studies reveal that the second order kinetic model is better fitting with the test results, revealing that the adsorption involves both physical and chemical processes. Chemisorption of fuchsine B is favored due to platinum affinity towards the two primary amine groups from fuchsine B and also because these groups are capable to interact with hydrogen at the surface of silica hybrids.

The result to be notified is that the absorption process of fuchsine B, is fast and reach 100% performance in very colored solutions of 10^{-5} M concentration, thus expanding the environmental applicability. Fare yields in the range of 86–98% were obtained by all investigated materials for a higher concentration range of fuchsine B, from 10^{-3} to 5×10^{-4} M. In addition, this simple procedure permits to reuse the materials at least 3 times. [4]

The author kindly thanks for the support of "Coriolan Drăgulescu" Institute of Chemistry - Program 3 and financing from UEFISCDI-FET Project 76 PCCDI/2018, ECOTECH-GMP.

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PHOTOCATALYTIC COMPOSITE MEMBRANES FOR WATER TREATMENT: RESULTS, LIMITATIONS, AND NEW INSIGHTS

Mihaela HOMOCIANU, Petronela PASCARIU

"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487, Iasi, Romania
mlupu@icmpp.ro or michalupu@yahoo.co.uk (Mihaela Homocianu)

The current increase in technologies, population, and environmental pollution causes main water contaminants and requires the development of advanced water treatment strategies. These aspects led to the need to purify water with advanced intelligent materials. In this study, we explore recent advancements in the photocatalytic composite membranes used for water purification. For this purpose, the authors highlighted the following aspects: relevant materials used for developing photocatalytic membranes [1], the latest developments and applications of photocatalytic membranes in water purification [2], limitations of the photocatalytic process or the photocatalytic membranes and new insights [3].

A remarkable combination of properties for photocatalytic composite membranes, such as antimicrobial activity, super hydrophilicity, high photocatalytic oxidation, and separation, allows photocatalytic membranes to eliminate and degradation of organic pollutants, bacteria, and viruses from water. These materials (membranes) are considered a green tool due to: the end products of photocatalysis are eco-friendly, such as H2O, simple salts, and minerals, no other oxidants are required for the process (atmospheric oxygen is enough), the photocatalyst is non-toxic, low cost-effective, chemical, and biologically inert, renewable, and reusable, activation of the photocatalyst occurs by the action of sunlight as well as artificial light.

Recently, photocatalytic membranes have become emerging innovative products with great potential to be used at industrial level water purification. Moreover, superhydrophilic photocatalytic membranes are promising for treating oil-contaminated waters because of their simultaneous efficiency in both degrading and separating organic contaminants from the water.

More extensive studies that allow the transition of the use of photocatalytic membranes from the laboratory stage, a pilot installation on a commercial scale are in the pioneering phase and remain a challenge for researchers in view of large scale application [4].

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SILVER TUNGSTOPHOSPHATE/BETA ZEOLITE – A SOLUTION FOR PESTICIDE INDUCED OXIDATIVE STRESS

Dejana JANIĆIJEVIĆ[1], Anka JEVREMOVIĆ[1], Aleksandra JANOŠEVIĆ LEŽAIĆ[2], Bojana NEDIĆ VASILJEVIĆ[1], Snežana USKOKOVIĆ-MARKOVIĆ[2], Maja MILOJEVIĆ-RAKIĆ[1], Danica BAJUK-BOGDANOVIĆ[1]

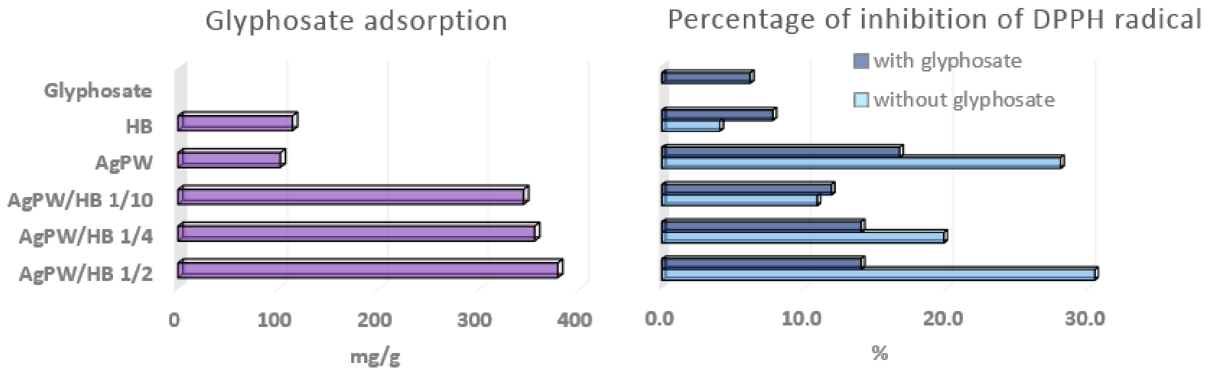
[1]*University of Belgrade-Faculty of Physical Chemistry, Belgrade, Serbia.*
[2]*University of Belgrade-Faculty of Pharmacy, Belgrade, Serbia.*
danabb@ffh.bg.ac.rs

Oxidative stress, in non-targeted species exposed to pesticides, results in increased amount of reactive oxygen species. Since radicals are responsible for the harmful effects on the biochemical functions of living organisms, it is essential to examine the ability of pesticide adsorbents to act as radical-scavengers. Composites of silver tungstophosphate (AgPW) and Beta zeolite (HB) were designed for advanced applications [1]. Materials were prepared with three mass ratios of precursors, AgPW/HB, at 1/2, 1/4 and 1/10, for simultaneous glyphosate and radicals removal. Guided by the question, whether a material used as pesticide adsorbent retains any antioxidant properties after adsorption, we have tested antioxidant activity of the composites with and without glyphosate adsorbed.

Our results revealed that the HB zeolite shows very little scavenging activity, while an increase in antioxidant activity with a higher AgPW fraction, as the radical-scavenging active phase in composites, was expected [2]. Better results for the composite material than for AgPW is a confirmation of even salt distribution on the zeolite surface, which enabled superior availability of proton-donor centres than is the case of bulk salt.

All composites where AgPW is present in amounts over 20% adsorb glyphosate in the highest capacity, and there is a decrease in radical removal, since glyphosate and radical reagent (DPPH) are binding via amino groups at the same AgPW active sites. An AgPW expressed a lower decrease in activity in comparison to composite samples as it was proved to be an inferior adsorbent, and glyphosate did not occupy all active sites, allowing radical reaction with protons surrounding hydrated silver ions. Similar to HB, for composites with high zeolite content, the rise in antioxidant activity is regarded as glyphosate interaction with radical species.

Glyphosate pesticide definitely provokes modulation of high antioxidant activity of AgPW/HB adsorbents, which can still act as both, radical-scavenger and pesticide adsorbents.



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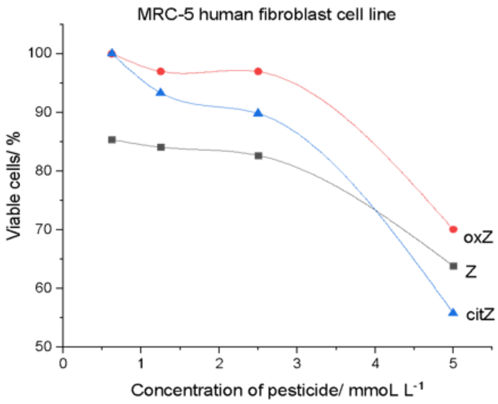
IN VITRO CYTOTOXIC RESPONSE OF THE BEA ZEOLITE/ACETAMIPRID SYNERGISTIC ACTION

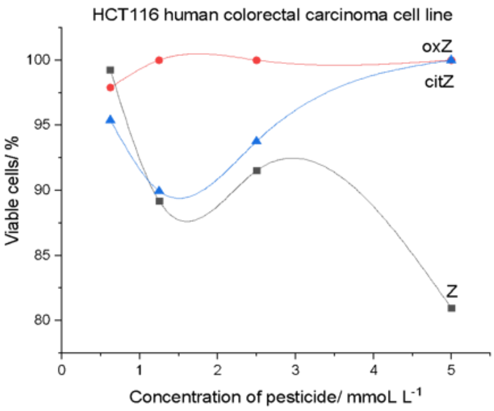
Anka JEVREMOVIĆ[1], **Dragana ARSENIJEVIĆ** [2], **Aleksandar ARSENIJEVIĆ**[2], **Bojana VASILJEVIĆ NEDIĆ**[1], **Danica BAJUK-BOGDANOVIĆ**[1], **Maja MILOJEVIĆ-RAKIĆ**[1]

[1]*University of Belgrade-Faculty of Physical Chemistry, Belgrade, Serbia*
[2]*University of Kragujevac–Faculty of Medical Sciences, Department of Pharmacy and Center for molecular medicine and stem cells research*
anka@ffh.bg.ac.rs

The increasing use of pesticides, due to the accelerated food production, has led to changes in the entire ecosystem. This set them recognizable as serious pollutants for the human health. Recently, insecticides from the group of neonicotinoids, have been in the public spotlight due to their harmfulness to the bees. They are systemic pesticides, which in contrast to contact pesticides, who remain on the surface of the treated leaves, systemically reach the inner parts of the plant [1]. Most of them do not decompose microbiologically, so different methods and materials are being developed to remove them from the environment.

The aim of this study was to examine the cytotoxic and synergetic effects of insecticide acetamipride (P) and BEA zeolite, in pristine (Z) and modified (oxZ and citZ) forms on two types of cell lines, MRC-5 human fibroblast and HCT116 human colorectal carcinoma. BEA zeolite was modified with iron, using dilute solutions of ferric citrate (citZ) and ferrous oxalate (oxZ) through an aqueous ion-exchange method while the cytotoxic measurements were performed using the methylthiazol-tetrazolium (MTT) colourimetric assay.





Results have shown that BEA zeolite in presence of acetamiprid gives no significant cytotoxicity to the MRC-5 human fibroblast cells (graph on the left). Improvement is detected for modified BEA zeolite, oxZ and citZ as almost no cytotoxic effect was recorded, up to acetamiprid concetraction of 5 mmoL/L, thus showing that modified zeolites reduce pesticide toxicity more than BEA zeolite itself. In the graph on the right, the opposite effect was obtained, showing that the cancer cells were more sensitive to the presence of pesticide. Cell viability at the highest used pesticide concentration was lower in the all samples in comparison to MRC-5 human fibroblast cells. In our previous study [2], viability of MRC-5 human fibroblast cells, with acetamiprid and FAU zeolite was found to be ~60 %. It can be concluded that BEA zeolite is more effective in reducing the toxicity of acetamiprid than FAU zeolite, which may be caused due to its higher Si/Al ratio [3].

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SYNTHESIS, CHARACTERIZATION AND CO$_2$ ADSORPTION-DESORPTION OF MCM-48 AND MCM-41 MOLECULAR SIEVES

Silvana BORCĂNESCU[1], Alexandru POPA[1], Paul BARVINSCHI[2], Orsina VERDES[1], Mariana Suba[1]

[1]"Coriolan Drăgulescu" Institute of Chemistry Timisoara, Bl.Mihai Viteazul 24,
300223 Timisoara, Romania
[2]Faculty of Physics, West University of Timisoara, B-dul V. Parvan, Nr. 4,
300223 Timisoara, Romania
silvana.borcanescu@gmail.com

The present work is focused on synthesis, characterization and CO$_2$ adsorption-desorption by thermal programed desorption of functionalized MCM-48 and MCM-41 molecular sieves. Tetraethylorthosilicate was used as pure silica source and 3-aminopropyltrimethoxysilane as modifying agent. MCM-48 was synthesized by the method developed by Ortiz et al. [1] while MCM-41 was prepared after the method developed by Beck et al.[2]. The structural features and physical properties of the prepared composites were investigated by IR spectroscopy, X-ray diffraction spectra, nitrogen adsorption/desorption and thermogravimetry. CO$_2$ adsorption desorption measurements were performed by thermal programed desorption at different temperatures. FT-IR spectra present similar behavior with characteristic vibrational bands of MCM-48 and MCM-41 type materials [3], as can be seen in Figure 1.

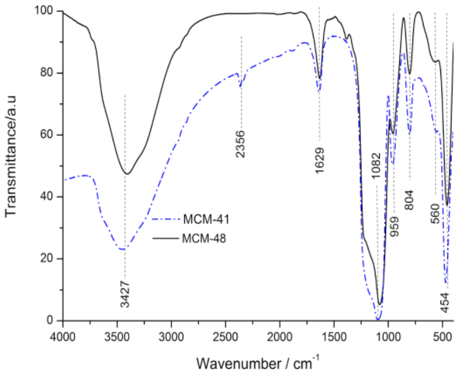

Figure 1. FT-IR spectra of the MCM-48 and MCM-41 molecular sieves

Through N$_2$ adsorption-desorption isotherms, it was observed type IV isotherms, attributed to mesoporous materials and large surface areas: 1466 m^2/g for MCM-48 and 1299.7 m^2/g for MCM-41, respectively. Due to high surface area and large pore size distribution, MCM-48 and MCM-41 functionalized molecular sieves represent promising structures for CO$_2$ adsorbents and catalyst support [4].

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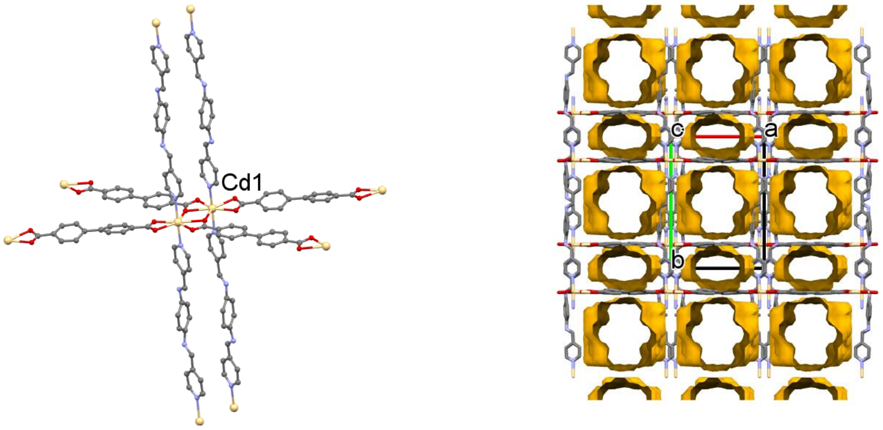
3D Cd(II) COORDINATION POLYMER ASSEMBLED FROM BIPHENYL-4,4'-DICARBOXYLIC ACID AND N,N'-(1,4-PHENYLENE)BIS(1-(PYRIDIN-4-YL)METHANIMINE) LIGANDS

V. N. LOZOVAN[1,2], **Victor Ch. KRAVTSOV**[3], **Marina S. FONARI**[3]

[1]Institute of Chemistry, MD-2028, Chisinau, Republic of Moldova;
[2]Tiraspol State University, MD-2069, Chisinau, Republic of Moldova;
[3]Institute of Applied Physics, MD-2028, Chisinau, Republic of Moldova
lozovanvasile90@gmail.com

Coordination polymers and metal-organic frameworks are currently among the most prolific research areas of inorganic chemistry and crystal engineering. Their properties such as low density, large surface area, pore function regulation and structural flexibility offer them the possibility to be applied in gas storage, catalysis, magnetism, optics, etc. [1]. The selection of spaced dicarboxylic ligands offers the possibility of obtaining structures with large cavities. The blend of biphenyl-4,4'-dicarboxylic acid (*H_2bpda*) with the azomethine N,N'-type ligand N,N'-(1,4-phenylene)bis(1-(pyridin-4-yl)methanimine) (*bda4bPy*) led to the 3D coordination polymer [Cd(bpda)(bda4bPy)]$_n$, whose crystal structure was confirmed by single-crystal X-ray diffraction analysis (Figure 1).



(a) (b)

Figure 1. Structure of compound [Cd(bpda)(bda4bPy)]$_n$. (a) View of binuclear Cd(II) building node; (b) fragment of crystal packing with indication of solvent accessible voids.

Compound crystallizes in the monoclinic P2/c space group. Each Cd(II) atom takes the N_2O_5 pentagonal bipyramidal geometry. One carboxylic group coordinates in a chelate mode, the other – in a chelate-bridging mode (Fig. 1a). Dicarboxylate ligands provide the metal-carboxylate 2D coordination network. The *bda4bPy* double pillars withstand perpendicular to this plane and provide the Cd···Cd separations along the crystallographic *b* axis of 20.063(2) Å. The big rhombohedral cavities in the metal-carboxylate layer provide possibilities for interpenetration, and the crystal packing revealed the two-fold parallel interpenetration of 3D networks. Voids constitute 39.7% or 1723.6 Å^3 of the unit cell volume and were registered as an alternation of rows of wide and narrow channels (Fig. 1b).

V.Ch.K. & M.S.F. are indebted to the project ANCD **20.80009.5007.15** for support. **V.N.L.** is indebted to the project ANCD **20.80009.5007.28** for support.

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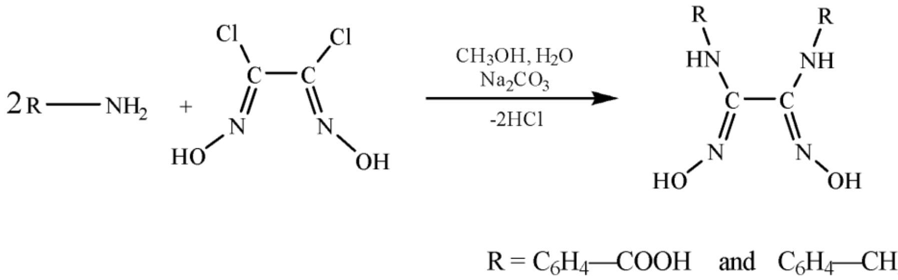
NOVEL *vic*-DIOXIME LIGANDS AND ITS ANTIMICROBIAL ACTIVITY

Dumitru URECHE

Institute of Chemistry, 3, Academiei str., MD-2028, Chisinau, Republic of Moldova
dumitru.ureche@ichem.md

The vic-dioximes are compounds with various industrial uses and scientific applications [1–3]. Many coordination compounds have been synthesized based on vic-dioximes. This study presents the synthesis and full characterization of two vic-dioximes based on dichloroglyoxime, p-aminobenzoic acid and p-aminotoluene. The reaction proceeded according to the scheme:



Their structures were proved by IR, ${}^{1}H$, ${}^{13}C$ and ${}^{15}N$ NMR spectral analysis and single crystal X-ray diffraction. After diffraction, the new *vic*-dioxime bis(*p*-aminobenzoic acid) glyoxime hydrate ($H_4L^1 \cdot H_2O$, **1**) and bis(di-*p*-aminotoluene glyoxime) mono-*p*-aminotoluene trihydrate ($(H_2L^2)_2 \cdot pat \cdot 3H_2O$, **2**), were obtained. Antimicrobial activity was tested for both ligands. One of the reported vic-dioximes, bis(di-p-aminotoluene)glyoxime mono-p-aminotoluene trihydrate showed good to moderate antimicrobial activity against both non-pathogenic Gram-positive and Gram-negative bacteria (*Bacillus subtilis* and *Pseudomonas fluorescens*), phytopathogenic (*Xanthomonas campestris, Erwinia amylovora, E. carotovora*) and the fungi (*Candida utilis* and *Saccharomyces cerevisiae*) at MIC – 70-150 µg/mL (Table).

Table 1. In vitro antifungal and antibacterial activities of compound **1** and **2**.

	MBC and MFC, µg/mL						
Compd	*Bacillus subtilis*	*Pseudomonas fluorescens*	*Erwinia amylovora*	*Erwinia carotovora*	*Xanthomonas campestris*	*Candida Utilis*	*Saccharomuces cerevisiae*
1	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2	70	150	70	150	150	70	150

MBC – *minimal bactericidal concentration*;
MFC - *minimal fungicidal concentration;*
N/A – non active

Looking to the data presented in Table it is well seen that compound **2** exhibits variable biological activity depending on the bacterial or fungicidal species. A possible cause of this variation could be the impermeability of the cells of the microorganism or the difference between the ribosomes of the microbial cells [4].

This work was supported by State Programs of National Agency for Research and Development R. Moldova 20.80009.5007.28.

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THE CYCLIC ADSORPTION-DESORPTION OF CO_2 ON KIT-6 AND NI/KIT-6 STUDIED BY TEMPERATURE-PROGRAMMED DESORPTION

Mariana SUBA[1], **Alexandru POPA**[1], **Orsina VERDEȘ**[1], **Silvana BORCĂNESCU**[1], **Paul BARVINSCHI**[2]

[1]"Coriolan Drăgulescu" Institute of Chemistry, Bl. Mihai Viteazul, No.24, 300223, Timisoara, Romania
[2]Faculty of Physics, West University of Timisoara, Vasile Parvan, No. 4, 300223, Timisoara, Romania
marianasuba@gmail.com

Carbon dioxide is the primary greenhouse gas, responsible for about three-quarters of emissions. It can linger in the atmosphere for thousands of years. Thus, the research directions were directed towards obtaining materials with CO_2 adsorption-desorption properties [1-4].

This study investigates the cyclic adsorption-desorption of CO_2 on KIT-6 sil and Ni/KIT-6 sil by Temperature-Programmed Desorption. Modified silicas denoted as KIT-6 Sil and Ni/KIT-6 sil were prepared by grafted of 3-aminopropyl triethoxysilane in solution at 110°C. These composites were characterized by FT-IR spectroscopy, X-ray diffraction at low angles, nitrogen physisorption at 77 K, and evaluated by the adsorption of CO_2 and its temperature-programmed desorption TPD. Thermal stability was investigated by TGA and DTA methods.

The CO_2 adsorption/desorption of KIT-6 Sil showed that both the adsorption capacity (mmoleCO_2/g adsorbent) and the efficiency of amino groups (moleCO_2/mole NH_2) depend on the temperatures. The best results were obtained for KIT-6-Sil at 40 °C.

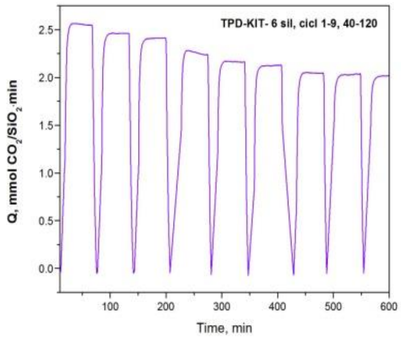

Figure 1. The cyclic adsorption-desorption of CO_2 on KIT-6 sil by TPD

In order to investigate the regenerability and cyclic stability of KIT-6 sil and Ni/KIT-6 sil, multistage CO_2 adsorption–desorption cycles were performed by DTA/TG at 40-120°C. The good cyclic adsorption/regeneration behavior of the adsorbents is critical for long-term operation. Fig. 1 presents the values of (Q mmol CO_2/SiO_2) for KIT-6 sil over nine adsorption/regeneration cycles.

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EXPLORATION OF MAO-B INHIBITORS AS A POTENTIAL ANTI-DIABETIC DRUG

Daniela ISTRATE, Luminita CRISAN, Alina BORA

"Coriolan Drăgulescu" Institute of Chemistry, 24 Mihai Viteazu Avenue, 300223, Timişoara, Romania
istrate.dana@acad-icht.tm.edu.ro

In recent years, an alarming increase in people with diabetes mellitus type 2 (T2DM), has been monitored. This disease affects also children and teens. Diabetes worsens over time, so there is a stringent need to develop new efficient therapy, adequate preventive measures and a new medicine with an improved profile and fewer side-effects to control the illness. The commercial drug, pioglitazone, a specific inhibitor of human monoamine oxidase B (MAO-B), was used as a reference molecule to search a compiled set of 280 experimentally tested MAO-B inhibitors and select compounds with potential anti-diabetic effects. To reach the goal, 3D similarity search, toxicity related risks profiles, and ADME parameters were applied. According to ROCS similarity coefficients, toxicity and ADME profiles, ten MAO-B inhibitors were prioritized and further analyzed by molecular docking in the active site (PDB ID: 2OAG) of dipeptidyl peptidase 4 enzyme, which is related to the pathophysiology of T2DM. The 3D-similarity and docking results in conjunction with pharmaceutical profiles revealed the potential use of MAO-B inhibitors as anti-diabetic candidates.

This study was financially supported by the Project No. 1.2/2021 of the "Coriolan Dragulescu" Institute of Chemistry. The authors are indebted to OpenEye Ltd for providing us academic license (dr. Simona Funar-Timofei laboratory).

A WEB TOOL TO COMPUTE THE DIFFRACTION PRECISION INDEX OF PROTEIN STRUCTURES

Cristian NEANU, Sorin AVRAM

Department of Computational Chemistry, "Coriolan Drăgulescu" Institute of Chemistry Timisoara,
24 Mihai Viteazul Av., 300223 Timisoara, Romania
cristi@acad-icht.tm.edu.ro

The Protein Data Bank (PDB) [1] is one of the main open access digital data resource in biology and medicine. Data collected in the PDB archive on biological macromolecules contain general information about the structures stored in the archive, as well as information specific to the types of methods of determining the structure (X-rays or NMR) [2].

The diffraction-component precision index (DPI) estimates the average accuracy of atomic coordinates obtained by the structural refinement of protein diffraction data, with application in crystallography and computational chemistry.

The heterogeneous nature of PDB structure files makes automated DPI computation difficult, limiting its use.

We developed a free DPI-online server to compute DPIs in real-time for the prioritization of high-quality PDB structures and quality-assessment of docking results.

The proposed computational tool compute DPI using Cruickshank, Blow and Goto DPI equations [3], [4], [5], [6] and will be available online on (https://www.chembioinf.ro).

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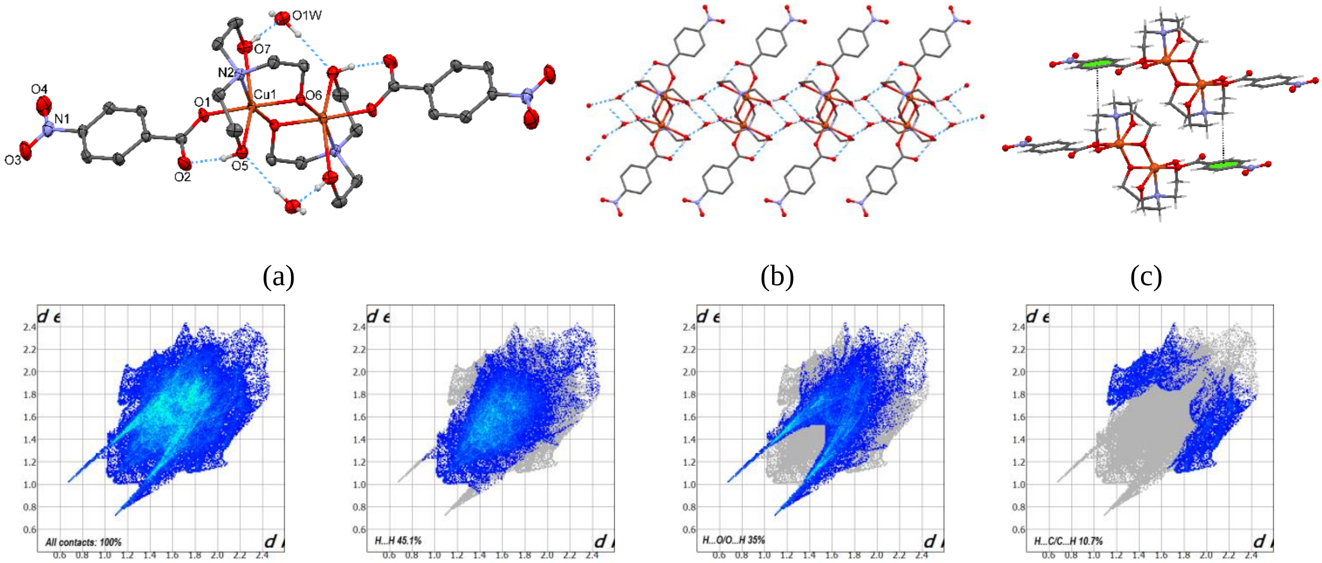
INSIGHTS INTO CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF Cu(II) TRIETHANOLAMINE 4-NITROBENZOATE

Anastasia GOROBET[1], Manuela E. CRISAN[2], Paulina N. BOUROSH[1], Lilia CROITOR[1]

[1]Institute of Applied Physics, Academy str., 5 MD2028, Chisinau, Republic of Moldova;
[2]"Coriolan Drăgulescu" Institute of Chemistry, 24 Mihai Viteazu Blvd., 300223, Timisoara, Romania
nasteagorobet@gmail.com

Over the time, dinuclear Cu(II) amino alcohol complexes have received particular attention, as building blocks in metallo supramolecular chemistry, as model of copper enzymes and precursors of molecular magnetic and catalytic materials. Recently, there have been reports of Cu(II) triethanolamine (TEA) carboxylate complexes used as a selective catalyst for alkanes oxidation and ferro-/antiferromagnetic behaviour. This study investigates the role of triethanolammonium 4-nitrobenzoate salt (HTEA)(4NB) in the structure formation of new metal complexes, focusing on dialkoxo bridged Cu(II) complex $[Cu_2(TEA)_2(4NB)_2]\cdot 2H_2O$ (**1**) with potential biological activity. The compound consists of centrosymmetric dinuclear units, in which two Cu(II) ions are bridged by two $\mu:\eta_1$ oxo bridges of two TEA anions, adopting a NO_5 distorsional tetragonal bipyramidal geometry. Dinuclear complexes are hydrogen-bonded with outer-sphere water molecules by intermolecular O–H···O hydrogen bond interactions in a 1D supramolecular chain and further interlinked by C–H···π stacking interactions.



(a) (b) (c)

(d)

Figure 1. The molecular structure of **1** (a). Fragment of hydrogen-bonded supramolecular chain (b). Representation of C–H···π stacking interactions between the resulted chains (c). 2D fingerprint plots calculated from the Hirshfeld analysis of different interactions (for all contacts, H···H, H···O/O···H, and H···C/C···H)

The structural investigation indicates that non-covalent intermolecular interactions, such as O–H···O and C–H···π, contribute to the packaging of the components in the crystal, while the Hirshfeld surface and 2D fingerprint graphs quantify these interactions and show their priority.

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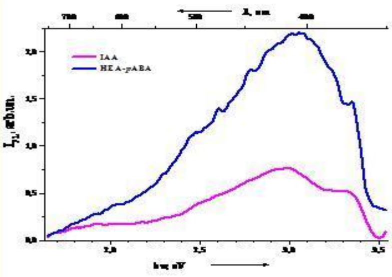
PROSPECTIVE FLUORESCENT PLANT GROWTH REGULATORS AND THEIR RESPONSE IN PLANTS

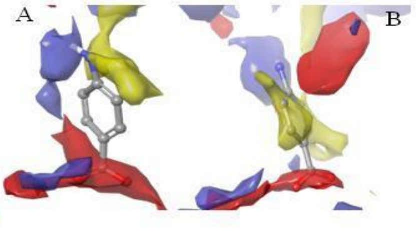
<u>Manuela CRISAN</u>[1], Liliana HALIP[1], Radu SUMALAN[2], Lilia CROITOR[3], Anatolii SIMINEL[3], Paulina BOUROSH[3], Yurii CHUMAKOV[3], Massimo MAFFEI[4]

[1]"Coriolan Drăgulescu" Institute of Chemistry, 24 M. Viteazul Blvd., 300223 Timisoara, Romania
[2]Faculty of Horticulture and Forestry, Banat' s University of Agriculture Science and Veterinary Medicine "King Michael Ist of Romania" from Timisoara, Calea Aradului nr 119, 300645 Timisoara, Romania
[3]Institute of Applied Physics, Academy str. 5, MD2028, Chisinau, Republic of Moldova
[4]Department of Life Sciences and Systems Biology, University of Turin, via Quarello 15/a, 10135 Torino, Italy
mdorosencu@yahoo.com

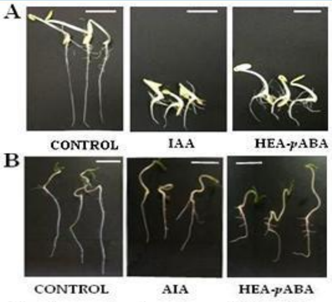
The development of environmentally friendly plant growth regulators (PGRs) has become a necessity for sustainable agriculture. Our research provides the synthesis, structural and physico-chemical characterization, as well as biological assessment of new fluorescent compounds based on non-toxic components or natural metabolites as alternatives to classical PGRs [1-3]. Crystallographic studies reveal the versatility of alkanolamine-substituted benzoic acid systems, which generate various supramolecular assemblies guided by one or more non-covalent interactions [4, 5]. The results show that ethanolammonium *p*-aminobenzoate (HEA-*p*ABA) has higher fluorescence intensity than classical auxin indole-3-acetic acid (IAA) and auxin-like behavior on the model plant Arabidopsis (*Arabidopsis thaliana*), as well as two main commercial vegetables cultivated in Europe, cucumber (*Cucumis sativus*) and tomato (*Solanum lycopersicum*). The binding modes and affinity of HEA-*p*ABA in relation to IAA into TIR1 auxin receptors (*C. sativus* - CsTIR1, *S. lycopersicum* – SlTIR1) were investigated by computational approaches such as homology modeling and molecular docking. Both experimental and theoretical results highlight HEA-*p*ABA as a fluorescent compound with auxin-like activity in studied plants. Therefore, alkanolammonium benzoates can be considered promising PGRs with great potential to be efficiently used in sustainable vegetable crops.



Emission spectra of HEA-*p*ABA and IAA



Binding model of HEA-*p*ABA in the auxin-binding site of CsTIR1 (A) and SlTIR1 (B)



Root growth phenotype of *C. sativus* (A) and *S. lycopersicum* (B)

The authors thank for the support of the "Coriolan Dragulescu" Institute of Chemistry - Program 2, Project 2.1 and of the Institute of Applied Physics - project ANCD 20.80009.5007.15.

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DISCRETE AND POLYMERIC Mn(II) COORDINATION COMPOUNDS WITH DIHYDRAZONE SCHIFF BASES

Olga DANILESCU[1], **Lilia CROITOR**[2], **Maria COCU**[1], **Paulina N. BOUROSH**[2], **Ion BULHAC**[1], **Victor Ch. KRAVTSOV**[2], **Oleg PETUHOV**[1]

[1]*Institute of Chemistry, Academiei str., 3 MD2028, Chisinau, R. Moldova*
[2]*Institute of Applied Physics, Academiei str., 5 MD2028, Chisinau, R. Moldova*
olgadanilescu@mail.ru

Hydrazones ($R_1R_2C{=}NNR_2R_4$) represent a class of organic ligands capable to coordinate with diverse metal centers generating varied molecular architectures. The Schiff base with the hydrazone fragment provide a good platform for generating a verity of new ligands their metal complexes with promising chemical, physical, biological properties useful for their practical applications. The interest in Mn(II)-based coordination compounds arise not only from its biomimetic roles or as a cofactor for some enzymes, but also because they are good precursors for magnetic materials, as well as for its intricate structures.

The crystals of discrete coordination compounds $[Mn(H_2L^1)_2(H_2O)_2](NO_3)_2$ (**1**) and $[Mn_3(H_2L^1)_2(NCS)_2Cl_4(H_2O)_2]$ (**2**) were obtained by template assembly of components, while 2D coordination polymers $\{[Mn_3(L^1)_3(H_2O)_2]\cdot 1.5C_2H_5OH\}_n$ (**3**) and $\{[MnL^2]\cdot dmf\}_n$ (**4**) by the direct reaction between pre-synthesized 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (H_2L^1) and 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H_2L^2) ligands and manganese sulfate salt (Figure1).

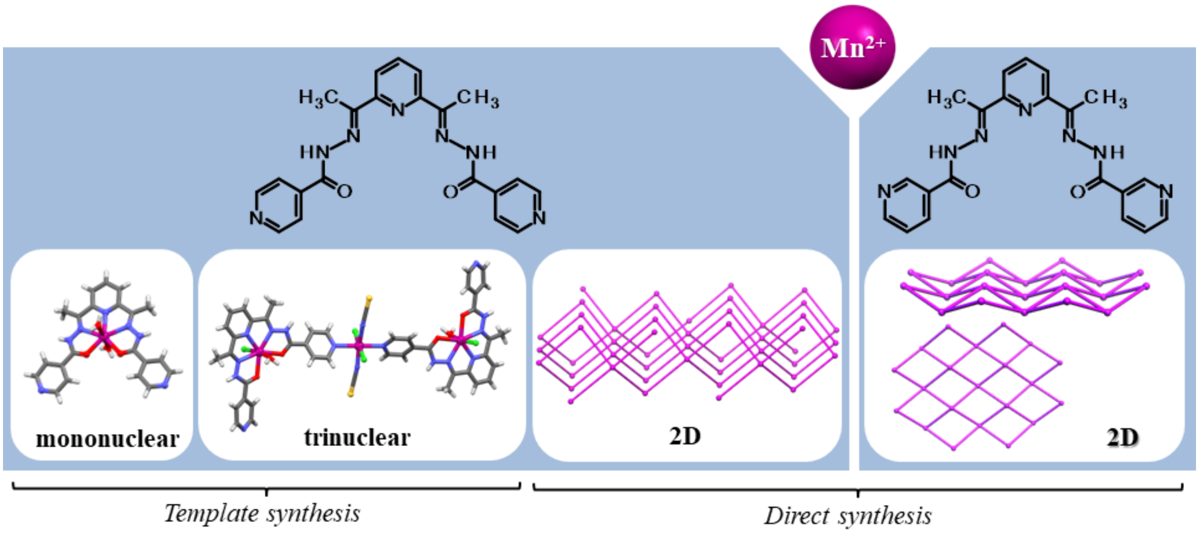


Figure1. Schematic representation of Mn(II) coordination compounds preparation.

Single-crystal X-ray diffraction analysis shows that Schiff bases behave as neutral (**1** and **2**) and bideprotonated (**3** and **4**) ligands and coordinate to the Mn(II) ion through azomethine and central pyridyl nitrogen atoms, as well as through carbohydrazide oxygen atoms, while isonicotinic/nicotinic pyridine rings extend the structure dimensionality up to 2D in **2-4**. The thermal analysis has been established the influence of the inorganic anion on the stability of synthesized compounds, thus, compound **1** which contains the nitrate anion begins to decompose at a lower temperature than the H_2L^1 ligand due to the nitrate ion oxidizing effect. The chloride ion, on the other hand, increases the thermal stability of the coordinating compound. In the absence of the inorganic anions, it was noticed that compounds begin to decompose at a temperature close or slightly higher to the ligand.

The authors are grateful to projects 20.80009.5007.28 and 20.80009.5007.15 financed by NARD of Republic of Moldova.

HOMO- AND HETEROMETALLIC Zn(II) AND Cd(II) COORDINATION POLYMERS CAPABLE OF RETAINING GUEST MOLECULES

Olga DANILESCU[1], Paulina N. BOUROSH[2], Oleg PETUHOV[1], Olga V. KULIKOVA[2], Yurii M. CHUMAKOV[2], Ion BULHAC[1], Lilia CROITOR[2]

[1]*Institute of Chemistry, Academiei str., 3 MD2028 Chisinau, R. Moldova*
[2]*Institute of Applied Physics, Academiei str., 5 MD2028, Chisinau, R. Moldova*
olgadanilescu@mail.ru

Coordination polymers (CPs) are an attractive area of research in coordination chemistry and crystal engineering due to their intriguing topological architectures and various applications. Schiff bases derived from 2,6-diacetylpyridine are suitable candidates for the development of magnetic homo- and/or heterometallic CPs.

Herein, we present our method for the synthesis of Zn(II) and Cd(II) CPs based on the 2,6-diacetylpyridine bis(nicotinoylhydrazone) Schiff base ligand (H_2L), which led to the obtention of two homo- $\{[ZnL]\cdot0.5dmf\cdot1.5H_2O\}_n$ (**1**) and $\{[CdL]\cdot0.5dmf\cdot H_2O\}_n$ (**2**) and as well as one heterometallic $\{[Zn_{0.75}Cd_{1.25}L_2]\cdot dmf\cdot0.5H_2O\}_n$ (**3**) 2D isostructural and isomorphous coordination layers, where dmf = N,N-dimethylformamide.

The Monte Carlo generator of Special Quasirandom Structures code was used to generate the Special Quasirandom Structure (SQS) to find the sequence of metals in the CP **3** in a ratio of 0.75:1.25. All obtaining CPs accommodate solvent guest (water and dmf) molecules in their cage-shaped interlayer spaces, which are released when the samples are heated. Thus, the association of thermal and IR methods was used to degas the accommodated guest samples at different temperatures (140 and 240/250°C) and their photoluminescent (PL) and adsorption-desorption properties were recorded in order to validate this assumption. The degassing crystals reveal a significant increase of volume pores and specific surface area, as well as PL emission with respect to synthesized ones (Figure 1). These findings make the layered compounds excellent small solvent sensor materials, expanding the family of CPs with interesting properties.

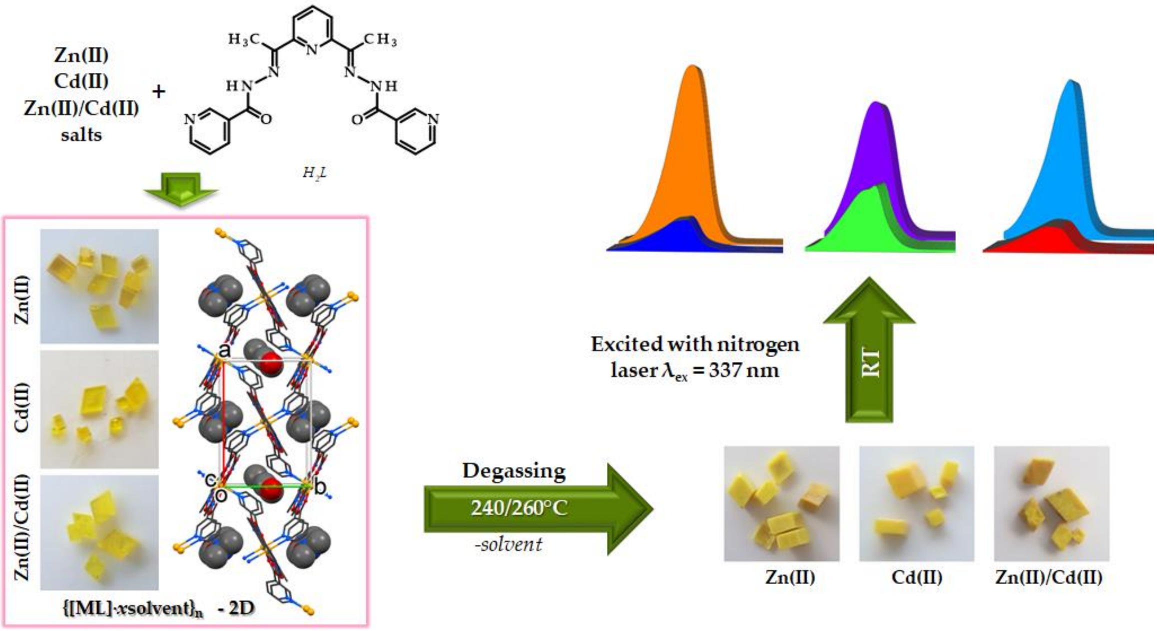


Figure 1. Schematic representation of the synthesis of coordination compounds **1**–**3**, photos of synthesized and degassed crystals and comparable solid-state emission plots (λ_{ex} = 337 nm) for compounds **1**–**3** and degassed samples.

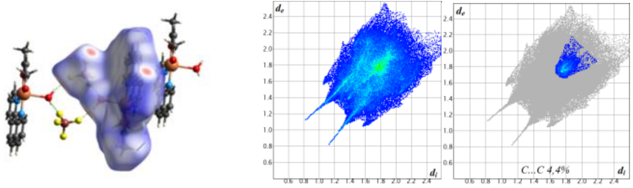
The authors are grateful to projects 20.80009.5007.28 and 20.80009.5007.15 financed by NARD of Republic of Moldova.

HIRSHFELD SURFACE ANALYSIS OF π-π STACKING INTERACTIONS IN THE CRYSTALS OF Cu(II) COMPLEXES WITH AROMATIC LIGANDS

Elena MELNIC, **Yurii M. CHUMAKOV**, **Victor Ch. KRAVTSOV**

Institute of Applied Physics, Academiei str. 5, MD-2028, Chisinau, Republic of Moldova
elena.melnic@ifa.md

Intermolecular interactions are responsible for most biochemical processes and often play crucial role in formation of structure and physical properties of molecular solids. Among them the π···π stacking interactions between metallacycles formed by aromatic ligands play an essential role for rational design of metal-organic materials with desired architecture. The contribution of these interactions in overall crystal packing is important for crystal engineering development.



all interactions *C...C*, 4,4%

a **b**

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

This work presents the results of the analysis of stacking interactions and their influence on the architecture of seven crystal structures of mono- and binuclear copper(II) complexes with composition [Cu(acac)(phen)(dmf)]BF_4 (**1**), [Cu(acac)(phen)H_2O]BF_4 (**2**), Cu(acac)(phen)Cl]MeOH (**3**), [$Cu_2(acac)_2(phen)_2$(4,4´-bpy)]$(BF_4)_2$ (**4**), [$Cu_2(acac)_2$(2,2´-bpy)$_2$(4,4´-bpy)]$(BF_4)_2$ (**5**), [$Cu_2(acac)_2$(2,2´-bpy)$_2$(bpe)]$(BF_4)_2(H_2O)_2$ (**6**) and [Cu(acac)(2,2'-bpy)(H_2O)][Cu(acac)(2,2'-bpy)]$(BF_4)_2$ (**7**) [1], (acac=acetylacetonate, phen=phenanthroline, bpy= bipyridine, and bpe=1,2-bis(4-pyridyl)ethane). Hirshfeld surfaces (HS) analysis [2] and the calculation of energies interactions based on the program CrystalExplorer 17.5 [3] have been performed to study the contributions of different intermolecular interactions in crystalline packing of (**1-7**). The Hirshfeld surfaces were plotted in the range 0.4-2.4 Å for each of and d_i and d_e. The analysis of 2D fingerprint plots show that a major HS contribution of 13.6- 21.8% and 36,4-48.6% comes from two types of contacts, namely C···H and H···H, respectively. The contribution of C···C interactions largely correspond to π-π stacking interactions, which contribute to 1.9 - 6.2% of the Hirshfeld surfaces and appear on the fingerprint plots as a single triangle at about $d_e = d_i \approx 1{,}7$ Å (Figure1). These interactions dominate in the packing of the structure of mentioned compounds.

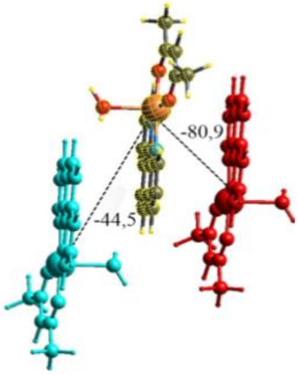


Figure 2. Interaction energy between neighboring molecules in the fragment of crystal packing in **2**

The intermolecular energy analysis calculated according to the energy model CE-B3LYP with 6-311G (d,p) basis set has revealed that the energy of π-π stacking interactions between the fragments involving metal chelate and the ligands fall in the range -41.1 – -80.9 kJ / mol and confirmed a significance of such interaction to the stabilization of supramolecular architecture.

Authors thank the projects **ANCD 20.80009.5007.15** (Republic of Moldova) for financial support.

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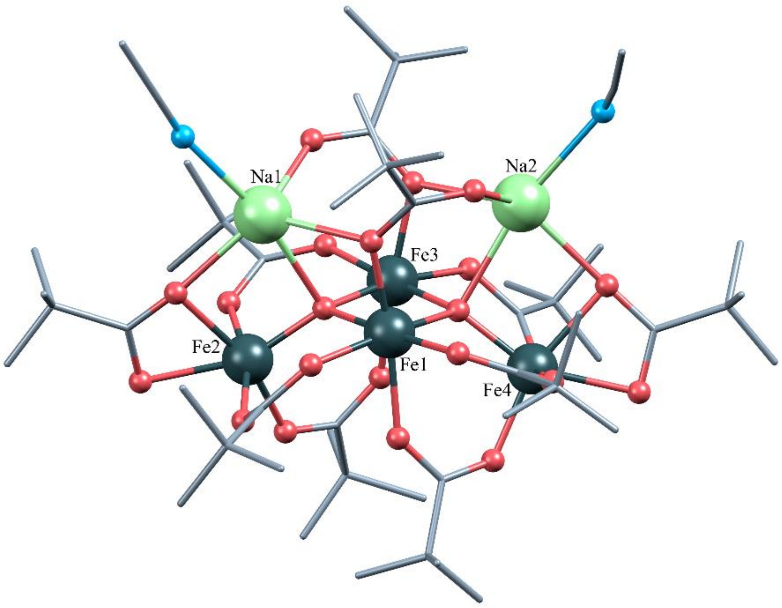
HETEROMETALLIC {$Fe^{III}_4Na_2$} PIVALATE CLUSTER – SYNTHESIS AND STRUCTURE CHARACTERISATION

Daniel PODGORNII[1,2], Svetlana G. BACA,[1] Victor Ch. Kravtsov[1]

[1]*Institute of Applied Physics, MD-2028, Chisinau, Republic of Moldova*
[2]*State University of Moldova*
daniel.podgornii@ifa.md

Coordination compounds with biological active ions and molecules are of great interest in biotechnology and biomedicine. Coordination compounds such as iron containing enzymes, siderophores, and others are known for their essential role in life processes as oxygen carriers [1]. The importance of alkali metals in biological systems is well-known. Coordination chemistry of lithium, sodium and potassium has colossal value due to their remarkable role in different biological mechanisms, especially for cell biology and natural fluids biochemistry. For example, Na^+ and K^+ are responsible for maintenance of the ionic equilibrium in living bodies and for electrochemical gradients across cell membranes which affect transmission of nerve impulse and regulation of cell functions [2].



Herein, we report a new coordination cluster with composition $[Fe_4Na_2O_2(piv)_{10}(MeCN)_2]$ (**1**) synthetized by refluxing the mixture of hexanuclear iron (III) pivalate, $[Fe_6O_2(OH)_2(piv)_{12}]$ (Hpiv = pivalic acid) and sodium azide NaN_3 in MeCN. X-ray structural analysis revealed that compound **1** crystalizes in monoclinic *Cc* space group with following unit cell parameters: a = 19.3924(9), b = 19.1240(15), c = 20.0436(12) Å, β = 91.136(4)º. The cluster core {Fe_4Na_2} contains two Fe-Fe edge sharing distorted Fe_3Na tetrahedra with μ_4-O_2 bridges inside each tetrahedron. Coordination spheres of Na^+ ions consist of four O atoms from three pivalate ligands, one μ_4-O^{2} moiety and one N atom from capped acetonitrile molecule, resulting in NO_4 distorted trigonal-bipyramidal surrounding. Peripheral ligation of Fe and Na atoms is provided by six bridging in η^1:η^1:μ_2 mode and four bridging in η^1:η^2:μ_3 pivalate ligands. The bond distances Na O are in the range 2.255(14) – 2.486(10) Å, Na N equal 2.415 (16) and 2.549(16) Å, Fe O bond distances fit the interval of 1.847(8) – 2.196(9) Å. All iron atoms are hexacoordinated, displaying O_6 distorted octahedra. The BVS calculations and charge balance prove the Fe(III) oxidation state of all iron atoms in the cluster.

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

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BIMETALLIC LIQUID CRYSTALLINE FUNCTIONAL MATERIALS

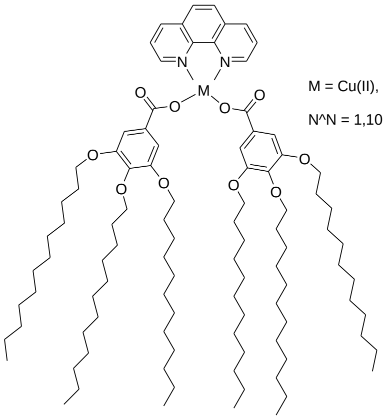
Evelyn POPA, Bianca N. BADESCU, Alexandru VISAN, Sorin MARINESCU, Ildiko BUTA, Carmen CRETU, Elisabeta I. SZERB

“Coriolan Drăgulescu” Institute of Chemistry, 24 Mihai Viteazu Bvd., Timişoara – 300223, ROMANIA
evspopa@gmail.com

The continued extension of liquid crystal science to additional technologies requires new types of mesomorphic materials that integrate novel structural elements and physical properties [1] due to their applications in sensing, used as backlighting in displays, security inks and so on [2].

1,10-phenantroline has been extensively used as a metal chelating ligand due to its robust redox stability and ease of coordination with *d*-block metals while lipophilic benzoate was showed to be an excellent monodentate ligand able to induce liquid crystallinity into metal complexes, avoiding several steps required to functionalize the main ligands [2].

On this background, herein we present the synthesis of new heteroleptic liquid crystalline coordination complexes of Cu(II) and Zn(II). The complexes were characterized structurally by spectroscopic methods as nuclear magnetic resonance (NMR), infrared spectroscopy (FT-IR) and atomic absorption spectrometry (AAS), while their liquid crystallinity was investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC).



M = Cu(II), Zn(II)

N^N = 1,10-phenanthroline

Figure 1. Proposed chemical structure of the new heteroleptic Cu(II) and Zn(II) coordination complexes

Moreover, willing to obtain bimetallic functional liquid crystalline materials, and taking into advantage the similar molecular structure and mesophase type of the two complexes, mixtures of both of the complexes in different proportions were obtained and their mesomorphic properties studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC).

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.

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LINEAR TRINUCLEAR COBALT(II) ISOBUTYRATE WITH 1,10-PHENANTHROLINE

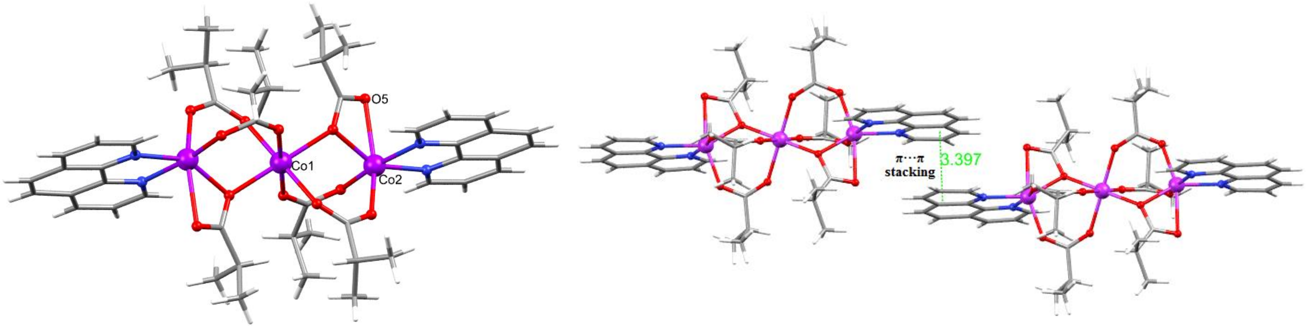
Ecaterina NIRCA, **Victor Ch. KRAVTSOV**, **Svetlana G. BACA**

Institute of Applied Physics, Academiei 5, MD-2028 Chisinau, R. Moldova
ecaterina.nirca@ifa.md

The polynuclear cobalt complexes are of great current interest due to its wide potential applications such as: catalysts, electron transfer mediators in dye-sensitized solar cells, antiviral agents and nanomagnet molecules. A new Co(II)-containing compound, $[Co_3(is)_6(phen)_2]$ (**1**) was obtained from the reaction of $Co(is)_2$ (His = isobutyric acid) with 1,10'-phenanthroline (phen) in acetone/dmso (1:1) mixture under ultrasonic treatment. The compound has been characterized by elemental analysis, IR spectroscopy, ESI MS spectrometry, and single-crystal X-ray diffraction studies.

The IR spectrum of **1** displays the asymmetric and symmetric C–H stretching vibrations of $–CH_3$ and –CH groups of isobutyrates and phen in the range of 2963–2869 cm^{-1}. These are accompanied by peaks at 1513 and 1469 cm^{-1} and a doublet at 1368 and 1354 cm^{-1} arising from asymmetric and symmetric bending vibrations of these groups, respectively. The characteristic strong peaks observed at 1584 and 1415 cm^{-1} corespond to the asymmetric and symmetric stretching vibrations of the coordinated isobutyrate groups, respectively.

Compound **1** crystallizes in the orthorhombic *Pbca* space group with a = 15.2497(4), b = 16.6307(4), c = 18.9246(5) Å, V = 4799.53 $Å^3$. In the structure, trinuclear complex reside on special position and has a C_i molecular symmetry with central Co1 atom of the trimers located on a crystallographic inversion center and is coordinated octahedrally by six oxygen atoms of six isobutyric carboxylate ligands. Four of these carboxylates form bridges to the peripheral Co2 atoms in the bidentate mode, while the other two in a bidentate chelate-bridging mode in which a single oxygen atom, bridges two Co centers (Fig. 1). The Co–O bond distances are in the narrow range 2.012–2.126 Å except elongated Co2 O5 bonds of 2.367 Å. The peripheral Co2 atoms additionally are chelated by phen ligands with the Co–N bond distances equal 2.099 and 2.173 Å to form a distorted octahedral environment around Co2. The Co1…Co2 separation is 3.458 Å. In the crystal structure trinuclear clusters form supramolecular chain along the b crystallographic axis due to $\pi\cdots\pi$ stacking interactions between phen ligands. The interplanar separations are 3.397 Å.



a ***b***

Fig. 1. Molecular structure (**a**) and a supramolecular chain formed due to $\pi\cdots\pi$ stacking interactions in $[Co_3(is)_6(phen)_2]$ (**b**).

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

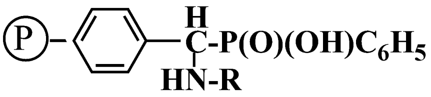
REMOVAL OF ACETYLSALICYLIC ACID FROM AQUEOUS SOLUTIONS USING POLYMERS CONTAINING AMINOPHOSPHINIC GROUPS

Radu ARDELEAN[1], Aurelia VISA[2], Adriana POPA[1]*, Manuela MIHETIU[1], Corneliu-Mircea DAVIDESCU[1]*

[1]*Politehnica University Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Blv, 300223, Timisoara, Romania*
**corneliu.davidescu@upt.ro*
[2]*"Coriolan Dragulescu" Institute of Chemistry, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania *apopa@acad-icht.tm.edu.ro; apopa_ro@yahoo.com*

Water pollution is currently a serious threat to human health and ecosystems. It also addresses the issue of depletion of clean water resources. One of the sources that cause water pollution, even at low concentrations, are pharmaceutical products [1]. They can remain undegraded in the human body even in about 30-90% of the given dose and are largely excreted as active compounds [2]. An effective method that has attracted attention is the adsorption of pollutants from wastewater. It is a promising procedure due to its effectiveness and possibility of regeneration and reuse of the adsorbents [1, 2].

In the presented study, polymers containing aminophosphinic acid groups (see Figure 1) have been used for removal acetylsalicylic acid from aqueous solution.



$$Ⓟ-C_6H_4-\underset{HN-R}{\overset{H}{C}}-P(O)(OH)C_6H_5$$

Figure 1. Styrene-6.7%DVB copolymers containing aminophosphinic acid groups.

Where: AAP1:R=-C_3H_7; AAP2:R=-CH_2-C_6H_5; AAP3:R=-C_4H_9.

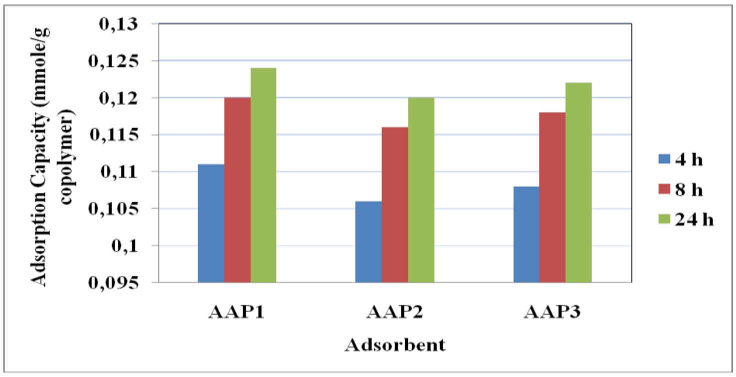


Figure 2. Comparative representation of the amount of acetylsalicylic acid adsorbed after 4, 8 and 24 hours respectively, at 298 K.

The adsorption rate is high at the beginning, in each case, after 4 hours about 90% of the total amount of acetylsalicylic acid was absorbed. In the case of adsorption of acetylsalicylic acid from aqueous solutions on solid adsorbents, the process is usually a molecular adsorption.

The efficiency of the 3 adsorbents tested, in terms of acetylsalicylic acid adsorption varies in the following sequence: AAP1 > AAP3 > AAP2. The efficiency of the adsorption process could be correlated with the structure and configuration of the adsorption active centers. The most effective for the adsorption of acetylsalicylic acid from aqueous solution were the adsorbents AAP1 and AAP3 having in structure alkyl radicals while the adsorbent AAP2 in which the functionalization was performed using benzylamine, had a little lower adsorption capacity.

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POLYMERS OF VINYLPHOSPHONIC ACID WITH DIALKYLVINYL PHOSPHONATES AND THEIR ANTICORROSION PROPERTY

Lavinia MACARIE, Nicoleta PLESU, Gheorghe ILIA, Milica TARA-LUNGA-MIHALI, Adriana POPA

"Coriolan Dragulescu" Institute of Chemistry, 24 Mihai Viteazul Bv., 300223-Timisoara, Romania, lavi_mac@yahoo.com

Functional synthetic copolymers based on vinylphosphonic acid (VPA) with different monomers have gained great importance in polymer chemistry due to their special properties given by the presence of phosphonic group. Vinylphosphonic acid homopolymer (PVPA) and its copolymers have found applications in diverse domains: in water treatment processes, control steel corrosion, adhesives for metallic surfaces, polymer electrolytes membranes for fuel cells, ion exchange membranes, in the composition of products for bone reconstruction and tissue engineering in medical field and in dental cement.

The aim of this paper is to study the properties in aqueous solution of copolymers of vinylphosphonic acid with dimethylvinylphosphonate and to investigate the possibility to apply these copolymers in surface protection against corrosion.

Homopolymer of vinylphosphonic acid (PVPA) and copolymers of vinylphosphonic acid (VPA) with dimethylvinylphosphonate (DMVP) at different molar ratio from 1:1 to 4:1, respectively, were obtained by radical polymerization using UV light and photoinitiator.

The polymers were tested as corrosion inhibitors for iron and their presence in aqueous solution decreased the corrosion current density by the formation of protective film on iron surface. The presence of phosphonate groups from dimethylvinylphosphonate in copolymers was beneficial and at a molar ratio VPA:DMVP 4:1 and 3:1 enhanced the anticorrosion property in comparison with homopolymer of vinylphosphonic acid.

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ORDERED MESOPOROUS SILICA FUNCTIONALIZED WITH AMINOPROPYL GROUPS BY CO-CONDENSATION AND POST GRAFTING

Ana-Maria PUTZ[1], Oleksandr I. IVANKOV[2], Cătălin IANĂŞI[1], Marija MILANOVIĆ[3], Ivan STIJEPOVIĆ[3], László ALMÁSY[4]

[1] "Coriolan Drăgulescu" Institute of Chemistry, Bv. Mihai Viteazul, No.24, 300223 Timisoara, Romania
[2]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Joliot-Curie 6, 141980 Dubna, Russia
[3]Department of Materials Engineering, Faculty of Technology, University of Novi Sad, Bulevar Cara Lazara 1, 21102 Novi Sad, Serbia
[4]Institute for Energy Security and Environmental Safety, Centre for Energy Research, Konkoly-Thege ut 29-33, 1121 Budapest, Hungary
putzanamaria@acad-icht.tm.edu.ro

The morphology and the structural properties of mesoporous silica functionalized with aminopropyl groups by the co-condensation and the post grafting methods were evaluated. Nitrogen sorption, small angle neutron and X-ray scattering methods (SANS and SAXS) demonstrated high surface area and well-ordered hexagonal pore structure suitable for applications as adsorbents of metals from waste waters. SANS and SAXS data show that the increase of the amount of organic silica precursor in the co-condensation process leads to the decrease of the long-range order of the parallel channels and that an uneven distribution of the functional groups, by the post grafting method has been obtained. Zeta potential measurements revealed that by functionalization, the particles are stable and positively charged in a wide range of pH. The colloidal stability of the particles increases with higher amount of APTES and increases as well by using post grafting method comparatively with the co-condensation method [1, 2].

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CRYSTALLINE MULTI-COMPONENT COMPOUNDS INVOLVING HEXAAMMINE COBALT(III) CATIONS AND THEIR EFFECTS AGAINST PLANT PATOGENIC BACTERIA

Mariana DARII[1], Ecaterina NIRCA[1], Victor Ch. KRAVTSOV[1], Paulina BOUROSH[1], Jürg HAUSER[2], Silvio DECURTINS[2], Shi-Xia LIU[2], Olga SULTANOVA[3], Svetlana G. BACA[1]

[1]Institute of Applied Physics, Academiei 5, MD-2028 Chisinau, R. Moldova
[2]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012-Bern, Switzerland
[3]Practical Scientific Institute of Horticulture and Food Technology, Vierul 59, MD-2070 Chisinau, R. Moldova
svetlana.baca@ifa.md

A new series of multi-component compounds containing the cation $[Co(NH_3)_6]^{3+}$ and various N-, N,O-, and O-donor ligands has been synthesized and crystallized. The series involves $[Co(NH_3)_6]Cl_3 \cdot 2(phen) \cdot 3H_2O$ (**1**), $[Co(NH_3)_6](Hbdc)(bdc) \cdot 3H_2O$ (**2**), $[Co(NH_3)_6]Cl_2(Hpht) \cdot 4H_2O$ (**3**), $[Co(NH_3)_6]Cl(Hpht)_2 \cdot 3H_2O$ (**4**) $[Co(NH_3)_6]Cl(2,3\text{-}pdc) \cdot H_2O$ (**5**), $[Co(NH_3)_6]_{11}[Co(2,5\text{-}pdc)_3]_8Cl \cdot 84H_2O$ (**6**), $[Co(NH_3)_6][Co(3,5\text{-}pdc)_2(H_2O)_4]Cl \cdot 3H_2O$ (**7**) $[Co(NH_3)_6]Cl(sb) \cdot 4H_2O$ (**8**), and $[Co(NH_3)_6]_2(sb)_3 \cdot EtOH \cdot 3H_2O$ (**9**) (where phen = 1,10-phenanthroline, H_2bdc = diphenyl-4,4′-dicarboxylic acid, H_2pht = *o*-phthalic acid, H_2pdc = 2,3-/ 2,5-/ 3,5-pyridinedicarboxylic acid, H_2sb = 4-sulfobenzoic acid). The complexes have been characterized by elemental analysis, IR-spectroscopy, and single crystal X-ray diffraction studies.

In these compounds, the $[Co(NH_3)_6]^{3+}$ cation serves as a building block for the incorporation of various anions/molecules containing O, N or Cl atoms as donor for hydrogen bonds and promotes the formation of multi-component compounds. Note, in addition to the $[Co(NH_3)_6]^{3+}$ cations, compounds **1–9** comprise Cl^-, deprotonated phthalate, diphenyldicarboxylate, pyridinedicarboxylate and sulfonate anions or complex $[Co(2,5\text{-}pdc)_3]^{4-}$ and $[Co(3,5\text{-}pdc)_2(H_2O)_4]^{2-}$ anions as well as neutral 1,10-phenanthroline, and solvent ethanol and water molecules as constituents of crystallization. The role of hydrogen bonds in the formation of the second coordination sphere of Co^{III} and in the crystal packing is investigated. The structures **1**–**9** reveal multiple charge-assisted H-bond interactions between cations and anions and others such as H-bonds between charged···neutral and neutral···neutral components, and π-π stacking interactions (Fig. 1).

The compounds **1-9** have been tested *in vitro* against *Rhizobium* (Agrobacterium) *vitis*, an oncogenic bacteria that causes the formation of tumors in plants. Compound **1**, comprising hexaammine cobalt(III) chloride and 1,10-phenanthroline, shows the highest inhibitory potential and is thus qualified for an application against bacterial cancer in plants.

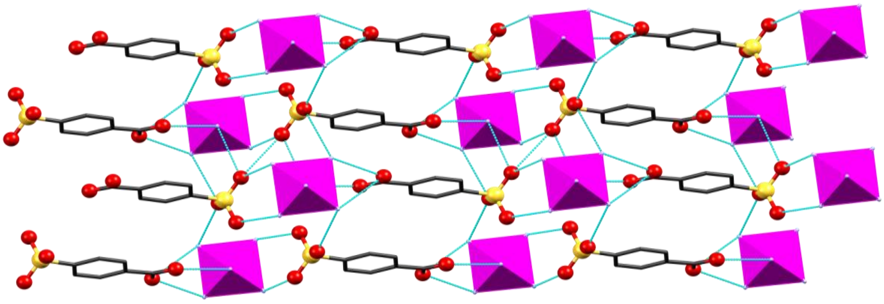


Figure 1. Hydrogen-bonded layer formed between $[Co(NH_3)_6]^{3+}$ cations (shown as pink octahedra) and sb^{2-} anions in $[Co(NH_3)_6]Cl(sb) \cdot 4H_2O$ (**8**).

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

APPLICATION OF FULL FACTORIAL DESIGN FOR ADSORPTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION

Maria Andreea NISTOR, **Simona Gabriela MUNTEAN**, **Liliana HALIP***

"Coriolan Dragulescu" Institute of Chemistry, 24 Mihai Viteazul Bvd., 300223, Timisoara, Romania
sgmuntean@acad-icht.tm.edu.ro , lili.ostopovici@gmail.com

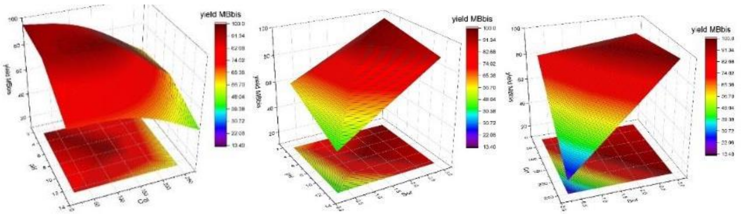
The problems of treatment and elimination of colored pollutants (dyes) from the effluents obtained as a result of textile, food, printing or dyeing industries require a lot of attention.

Synthetic dyes, characterized by a complex aromatic molecular structure, are not biodegradable and have a high stability to light and heat, which makes them difficult to remove [1]. The application of adsorption process as a wastewater treatment method has proven to be an efficient process and generated the development of new material used as adsorbents.

In this study, a full factorial design experiment was carried out to model and optimize the removal of Methylene Blue (MB) dye by adsorption on a new magnetic nanocomposite (NMC). The NMC was synthesized through a single-step combustion reaction technique, and it was characterized by X-Ray Diffraction, Fourier transform infrared spectroscopy, magnetic properties, N_2 adsorption-desorption isotherm, Thermal analysis and Scanning Electron Microscopy [2]. The experiment was designed using the responses surface methodology based on four independent variables: the initial pH of the dye solution, the initial dye concentration, the quantity of adsorbent, and the temperature [3].

The results were statistically analyzed to define the significance of the independent variables as well as their interactions using the analysis of variance (ANOVA). A regression model with very good predictive power, low estimated standard error, and low values of the p-test was proposed.

Using contour maps and 3D representations for each pair of factors present in the model (Figure 1), it was established that a good removal efficiency of MB is obtained for a pH value between 7.0 and 8.0, an initial dye concentration of 125 mg/L, an amount of 1.6-1.7 g/L NMC and 25°C.



a) b) c)

Figure 1. The contour plot and combined effect of a) pH and initial dye concentration b) pH and NMC dose c) initial dye concentration and NMC dose on removal of Methylene Blue dye

The equilibrium studies were performed under optimal conditions determined from factorial design studies, and the maximum adsorption capacity obtained for MB was 157.58 mg/g. The adsorption thermodynamic parameters, namely ΔG°, ΔH° and ΔS°, were determined, indicating that the adsorption process of MB dye is endothermic and spontaneous.

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LACCASSES STABILIZATION BY COVALENT IMMOBILIZATION ONTO FUNCTIONALIZED MAGNETIC AND SEPABEADS SUPORTS

Ioan BÎTCAN[1], **Andreea PETROVICI**[1], **Andrei ȘTEFAN**[1], **Anamaria TODEA**[1],
Iulia PĂUȘESCU[1], **Francisc PÉTER**[1,2]

[1]*University Politehnica Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Bvd, 300223, Timisoara, Romania*
[2]*Research Institute for Renewable Energy, Gavril Musicescu 138, 300501 Timisoara, Romania*
anamaria.todea@upt.ro

Lacases (benzendiol: oxygen reductases) belong to the group of copper protein enzymes, which catalyze the oxidation of substrates, generally phenolic, with the simultaneous reduction of molecular oxygen to water [1]. Laccases present advantages in food, pharmaceuticals textile and paper fields, in biodegradation of environmental pollution [2] but their use at an industrial level has been restricted due to: low stability, reusability issues, high sensitivity to denaturing agents, and high production costs [3]. Although the immobilization of laccases has been previously reported the development of efficient supports that can retain a higher enzymatic activity during immobilization remains an interesting goal [4].

In this work, two native commercially available laccases from *Aspergillus* sp. and *Trametes versicolor* were covalently immobilized onto six functionalized solid supports: three magnetically and three methacrylic polymers matrices (ReliZyme™). Compared to the well-known Fe_3O_4 magnetic particles, in this work, Ni-Zn or Ni-Zn-Co based magnetic particles spinel ferrites (MFe_2O_4) with different metallic cations (M: Zn, Mn, Co, Cr, Ni) were used. These particles have attracted interest due to their magnetic properties like superparamagnetism, spin glass behavior, with a range of applications in different fields such as magnetic recording, high frequency electronic cores, biomedical applications [5]. Prior immobilization, the magnetic supports were functionalized using two amino silane precursors and the attachment of the enzymes was performed using glutaraldehyde as cross-linking agent. The epoxy functionalized Sepabeads were used without any pre-activation step, meanwhile for the amino terminated Sepabeads the glutaraldehyde was used as linker. The activity of the resulted 24 enzymatic preparations was evaluated in the oxidation reaction of 2,6-dimethoxyphenol. The most active biocatalysts, containing the laccase from *Tramestes versicolor*, were selected and have been characterized in detail in terms of stability and reusability, demonstrating enhanced storage, pH and thermal stability compared to the native enzymes. The biocatalysts were successfully used in five reaction cycles.

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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ENZYMATIC APPROACH FOR THE SYNTHESIS OF ε-CAPROLACTAM AND HYDROXY ACIDS POLYESTERAMIDES

Ioana-Cristina BENEA[1], Diana Maria DREAVĂ[1], Anamaria TODEA[1], Lajos NAGY[2], Sándor KÉKI[2], Francisc PÉTER[1,3]

[1]*University Politehnica Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Bvd, 300223, Timisoara, Romania*
[2]*Department of Applied Chemistry, Faculty of Science and Technology, University of Debrecen, H-4032 Egyetem tér 1, 4032 Debrecen, Hungary*
[3]*Research Institute for Renewable Energy, Gavril Musicescu 138, 300501 Timisoara, Romania*
francisc.peter@upt.ro, nagy.lajos@science.unideb.hu

Recently, the trends in polymer synthesis are being characterized by a dynamic development of the enzymatic synthesis pathway, emphasizing in this manner the production of biodegradable, biocompatible, and functional polymeric materials. The growing interest in the use of enzymes as biocatalysts for biopolymer synthesis can be substantiated by the fact that enzymes are benign for the environment [1]. Along with the continuous development of green processes, there is an increasing interest in polymers synthesis using *in vitro* biocatalysis. The new biobased polymeric products are exhibiting a remarkable diversity, meeting the criteria of sustainability, biocompatibility, and eco-friendliness [2].

Polyesteramides are a group of polymers with several possible applications in the biomedical and pharmaceutical fields [3]. These compounds can be degraded at a sufficiently high rate under mild conditions and have better mechanical and thermal properties compared to polyesters due to hydrogen bonds formed between amide groups [4].

Currently, the enzymatic synthesis of new polyesteramides is increasingly being studied to obtain biocompatible and biodegradable materials with specific properties. Consequently, polymers with new functions can be synthesized, which can be further used in various applications. Controlled release drug delivery systems are an important application for polyesteramides and one of the topical issues in the medical field. Due to these reasons, great efforts are made to design various processes for obtaining polyesteramides starting from different monomers and using variable ratios of raw materials [5]. A wide range of raw materials from biomass can be converted to ε-caprolactam. In recent years, there has been an expansion of ε-caprolactam synthesis from renewable resources. As a result, ε-caprolactam is regarded as one of the most important biobased *co*-substrates for novel polyesteramides synthesis [6].

In this work, the enzymatic synthesis of novel copolymers of ε-caprolactam with two hydroxy-acids was investigated. The reactions were carried out in solvent-free systems and organic solvents, at temperatures up to 80°C, using Novozyme 435 and GF-CalB-IM biocatalysts. Cyclic and linear products have been synthesized, and their chemical structures were confirmed by FT-IR, MALDI-TOF and NMR analysis. The thermal properties of the new polyesteramides were determined by TG and DSC.

This work was supported by a grant of the Romanian Ministry of Education and Research, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2019-2638, withinPNCDI III, contract number 272PED.

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POLYMERIC SORBENT FOR DYE RETAINING

Milica TARA-LUNGA-MIHALI, Nicoleta PLESU

“Coriolan Dragulescu” Institute of Chemistry Timisora, Mihai Viteazul Bul. 24,
300223-Timisoara, Romania
mihali_mili@yahoo.com

The conductive polymer has already been known for their remarkable physico-chemical and electrical properties. The polymers resulting from the polymerization of aniline, polyaniline (PANI) and 3-aminophenyl boronic, poly-3- aminophenylboronic (PABA), are highly studied conductive polymers. Their unique is give by the electrical properties reversibly controlled, by both charge transfer doping, as well as by protonation. PABA also has a relatively high surface area and porosity and aminoboronic functional groups, which it recommends for many applications. PABA-based composites add new physical and chemical properties [1,2]. The paper presents the results obtained when retaining dyes on polymethylmethacryl microspheres (PMMA), on which a layer of PABA was chemically deposited (Figure1).

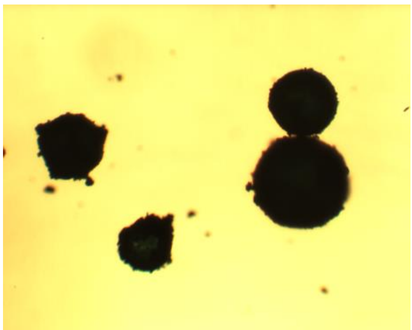

Figure 1. PMMA-PABA composite, magnitudes 5×

The use of PABA / PMMA salt as sorbents for the retention of dyes in wastewater was evaluated spectrophotometrically as a function of various experimental parameters, such as initial dye concentration, temperature and pH of the solution.

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MODULATED SYNTHESIS OF Zr(IV) METAL-ORGANIC FRAMEWORK BASED ON A DICARBOXYLIC ACID (H_2BDC)

Elena-Mirela PICIORUS, Alexandru POPA, Catalin IANĂȘI, Elisabeta I. SZERB, Carmen CRETU*

"Coriolan Dragulescu" Institute of Chemistry, Romanian Academy, 300223, Timisoara, Romania
carmencretu78@gmail.com

Metal-organic frameworks (MOFs) are an emerging class of crystalline porous materials constructed from metal nodes or clusters coordinated by organic linkers into extended periodic network structures with interest in various applications [1, 2, 3]. In this paper it is presented a fast modulated synthesis of micro/meso-sized ZrMOF, porous materials known as UIO-66, containing terephthalic acid (H_2BDC) as organic linker and an excess of $ZrOCl_2{\cdot}8H_2O$ salt precursor. Different amount of acetic acid were added in order to control the crystallite and particle sizes of the product [4]. An improvement of the surface area and a modification of diameter pore structure were observed by increasing of the modulator concentration.

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NATURAL PRODUCTS AS ANTI-HIV AGENTS: AN *IN SILICO* INSIGHT

Luminita CRISAN, Alina BORA*

"Coriolan Dragulescu" Institute of Chemistry, 24 M. Viteazu Ave, 300223 Timisoara, Romania
alina.bora@gmail.com

In the present work, *in silico* approaches were applied to find natural products (NPs) with similar bioactivity to non-nucleoside reverse transcriptase inhibitors (NNRTIs) but with different chemotypes, as promising candidates to treat human immunodeficiency virus type 1 (HIV-1) infection. The FDA-approved drug, etravirine, was used as reference molecules in a virtual screening experiment. The ZINC15 database of 224205 NPs was screened and filtered using 3D-similarity search, ADMET, and molecular docking simulations. Three NPs having higher docked scores and superior ADMET profile than etravirine were selected for further investigations. For these NPs, hydrogen bonds and hydrophobic interactions with key binding site residues (Lys101, Tyr181, Tyr188, Trp229, and Tyr318), along with free binding energies, argue that ligands can bind to HIV-1 reverse transcriptase. In conclusion, these three compounds were proposed as potential anti-HIV inhibitors. Moreover, our proposed workflow might be helpful to design novel potential NNRTIs from natural sources.

The authors would like to thank Ramona Curpan ("Coriolan Dragulescu" Institute of Chemistry Timisoara) for providing access to Schrödinger software (Schrödinger, Inc.: New York, NY, USA, 2018, https://www.schrodinger.com); to OpenEye Ltd. (OpenEye Scientific Software Inc. Santa Fe NM, USA https://www.eyesopen.com), BIOVIA software Inc. (BIOVIA Discovery Studio Visualizer, v. 19.1.0, www.3dsbiovia.com), and ChemAxon (Marvin Sketch and Instant JChem software) for the free academic licenses.

MONO- AND OLIGONUCLEAR COMPLEXES BASED ON A *O*-VANILLIN DERIVED SCHIFF-BASE LIGAND

Ildiko BUTA[1], Sergiu SHOVA[2], Sorina ILIES[1], Florica MANEA[3], Marius ANDRUH[4], Otilia COSTISOR[1]

[1]Romanian Academy "Coriolan Dragulescu" Institute of Chemistry, 24 Mihai Viteazu Bvd. 300223-Timisoara, Romania
[2]"Petru Poni" Institute of Macromolecular Chemistry, Gr. Ghica Voda Ave., 41A, Iasi 700487, Romania
[3]University Politehnica Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Bvd. 300223-Timisoara, Romania
[4]"C. D. Nenitzescu" Institute of Organic Chemistry of the Romanian Academy, Splaiul Independentei 202B, Bucharest, Romania
ildiko_buta@yahoo.com

The chemistry of coordination compounds undergoes an important development once polynuclear compounds with special properties are obtained and recommended as materials with potential technological applications [1-5].

Here, we report four new complexes, $[CoL](ClO_4)$ (**1**), $[Zn_2L(CH_3COO)_2]\cdot 2H_2O$ (**2**), $[Cu_3L_2(NO_3)_2]$ (**3**) and $[LaCu_6L_4(H_2O)_2(NO_3)_2](NO_3)_5\cdot 15H_2O$ (**4**), where H_2L stands for the Schiff base N,N'-bis[(3-methoxysalicylideneamino)-propyl]-piperazine. X-ray crystal analysis shows that the H_2L and complexes **1 - 4** crystallize in a monoclinic system, $P2_1/c$ (H_2L and **1 - 3**) and $C2/c$ (**4**) space groups. The pro-ligand, H_2L, exhibits a stable *chair* conformation of the piperazine ring, while its coordination mode, in the dianionic form, changes according to the nature of the metal ion, allowing the formation of mono- (**1**) and oligonuclear (**2 - 4**) complexes (figure 1).

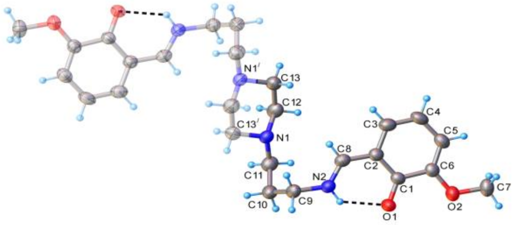

Figure 1. Molecular structure and atom labeling scheme of H_2L. Symmetry generated fragments are shown with faded colours [symmetry code: $i = -x, 1-y, 1-z$].

Compound **1** consists of a mononuclear complex cation, where the double-deprotonated ligand (L^{2-}) encapsulates the trivalent cobalt ion. In compound **2**, L^{2-} acts as a binucleatig ligand through two N_2O sets of donor atoms disposed on each side of the piperazine ring. Compounds **3** and **4** contain trinuclear units where two ligands are coordinated towards three Cu^{II} ions, with the N_3O donor set wrapped around the peripheral $Cu^{II.}$ The remaining NO sets are bound to central Cu^{2+} ion. There are two of this trinuclear moieties coordinate to the La^{3+} ion in crystal structure of compound **4**. Electrochemical behavior of compounds **1** and **3** and luminescent properties of compound **2** are discussed.

We are thankful to the Romanian Academy, "Coriolan Dragulescu" Institute of Chemistry (Project 4.1.3) for financial support.

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SYNTHESIS AND CHARACTERISATION OF 2-HYDROXYBENZYLIDENE DERIVATIVES

Livia DEVESELEANU-CORÎCI[1], Ana Maria PANĂ[2], Anca BELEAN[1], Sergiu SHOVA[3], Valentin BADEA[2], Liliana CSEH[1]

[1] "Coriolan Drăgulescu" Institute of Chemistry, 24 Mihai Viteazu Bvd, 300223, Timişoara, Romania
[2]University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 V. Pârvan Bvd, 300223, Timişoara, Romania
[3]Petru Poni Institute of Macromolecular Chemistry, Inorganic Chemistry, 41A Aleea Gr. Ghica Vodă, 700487, Iaşi, Romania
lcorici@acad-icht.tm.edu.ro

The development of novel photochromic systems capable of existing in more than two forms when subjected to different external stimuli has gained an increased interest in the last decades due to their industrial applications in optical memory devices, sensors, switches, intelligent windows and displays [1-4].

As a continuous work of our research group in the frame of multistate/multifunctional systems we report herein the synthesis, X-ray structure, spectral properties of 2-(2-hydroxybenzylidene)-5-methylcyclohexanone and 1-(2-hydroxybenzylidene) butanone and their behavior as a function of pH. Additionally kinetic information was achieved by carrying out direct and reverse pH jumps.

We are thankful to the Romanian Academy, "Coriolan Dragulescu" Institute of Chemistry (Project 4.1.1) for financial support.

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CHEMICAL SPACE ANALYSIS OF PROTEIN KINASE CYSTEINOME

Luminita CRISAN, Liliana PACUREANU*

"Coriolan Dragulescu" Institute of Chemistry Timisoara, 24 Mihai Viteazu Av., 300223 Timisoara, Romania
pacureanu@acad-icht.tm.edu.ro

In the last 20 years the success of the application of covalent inhibitors in various therapeutic areas inspired the search for novel covalent drug candidates which are now under development. Apart from drug discovery, covalent inhibitors are advantageous tool compounds in chemical biology to detect ligands in proteome-wide screens. In consequence, the interest in covalent drugs and probes is expected to increase in the future, but on the other hand the libraries of covalent inhibitors are insufficient. Hence we carried out the identification and characterization of chemical space of covalent inhibitors from CHEMBL database version 25 for 166 cysteine kinases including compounds whose biological activities were expressed as IC_{50}, K_i, EC_{50} for organism Homo sapiens. After pan assay interference compounds (PAINS) filtering 39,909 compounds remained, whereas 25,715 compounds comply with rule of five (RO5). For compounds with multiple activity values the geometric mean was calculated. Filtering using KNIME for reactive functional groups including novel covalent warheads that can be applied to the development of potential covalent inhibitors, resulting in 6,517 compounds. A number of electrophile warheads including acrylamide, chloroacetic acid, nitrile, acrylic acid ester, sulfuryl fluoride, α,β-unsaturated sulfonamide, acyloxymethyl ketones, vinyl sulfones, 1-methylcyclopropanecarboxylic acid, epoxide, etc. linked to various scaffolds which bear multiple functional groups were detected. A detailed scaffold and reactive functionalities analysis was performed along with potency and selectivity investigation.

EXPLORING THE MOLECULAR BINDING MECHANISMS OF CLINICALLY-RELEVANT SELECTIVE ESTROGEN RECEPTOR MODULATORS THROUGH MOLECULAR DYNAMICS SIMULATIONS

Ramona CURPĂN[1], Liliana HALIP[1], Ana BOROTA[1], Philipp MAXIMOV[2], Craig V. JORDAN[2]

[1]*Department of Computational Chemistry, "Coriolan Drăgulescu" Institute of Chemistry, No. 24, Mihai Viteazul Av., 300223 Timişoara, Romania*
rcurpan@acad-icht.tm.edu.ro
[2]*MD Anderson Cancer Center, Department of Breast Medical Oncology, Houston, TX, USA*

Estrogen receptor alpha (ERα), the representative of the nuclear hormone receptors class, plays different roles in the physiological development and function of numerous organs, including the reproductive, central nervous, skeletal and cardiovascular systems. ERα is essential in the: maturation of female and male reproductive phenotype, maintenance of bone integrity, various aspects of central nervous system development, and cell proliferation in breast tissue-being the key player in the development and evolution of breast cancer (BC), the leading cause of mortality among female population worldwide [1]. Efficient treatment strategies against BC are known, e.g. long-term estrogen deprivation (LTED) with tamoxifen (TAM) or aromatase inhibitors (AIs), but in some cases these therapies lead to drug resistance. Studies have shown that selective estrogen mimicking ligands therapy is effective in treating some patients with advanced BC resistant to TAM and AIs [2,3].

Here, we investigate the molecular mechanism of action for several selective estrogen mimicking modulators, in different stages of clinical development: BMI-135, TTC-352, BPTPE, through molecular docking [4] and molecular dynamics (MD) simulations [5]. The data show BMI-135 and TTC-352 binding to slightly distinct agonist conformations of ERα when compared with estradiol, explaining the partial agonist profile of this compounds [6,7].

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FINGERPRINTING G-PROTEIN COUPLED RECEPTORS SUPERFAMILY

Liliana HALIP, Ramona CURPĂN, Ana BOROTA, Alina BORA, Sorin AVRAM

"Coriolan Drăgulescu" Institute of Chemistry, Mihai Viteazu Bvd., 24, RO -300223, Timişoara, Romania
lili.ostopovici@gmail.com

G-protein coupled receptors (GPCR) represent a family of proteins with significant pharmacological importance, they being involved in the completion of most physiological processes in the human body. Although it is one of the most studied families of proteins - about a third of the drugs on the market target a member of this receptor family - there are still understudied GPCR receptors for which no active or selective ligands have been identified. The present work aims to explore the relationship degrees among GPCR members and to classify all human GPCR receptors based on new approach that allow associations of known GPCR with unstudied members. Thus, innovative binary fingerprints were generated using the 3D protein structures, active ligands and activation/coupling information of GPCR family. Next, GPCR superfamily were topographical mapped in Kohonen networks and results were analyzed. A set of 29 understudied GPCR have been found of interest. The results suggest the applicability and potential of this approach to classify understudied GPCRs.

MANUKA HONEY AND ITS FLAVONOID COMPONENTS - AN AFFORDABLE THERAPEUTIC OPTION TO FIGHT SARS-COV-2 INFECTIONS: *IN SILICO* EVALUATION

Alina BORA, Liliana HALIP, Sorin AVRAM, Luminita CRISAN

"Coriolan Dragulescu" Institute of Chemistry, 24 M. Viteazu Ave, 300223 Timisoara, Romania
alina.bora@gmail.com

Coronaviruses (COVs) are a group of RNA viruses, involving SARS, MERS, and COVID-19, which provoke mild to severe respiratory illness. Coronavirus disease 2019 (COVID-19), a severe acute respiratory syndrome induced by coronavirus 2 exposure (SARS-CoV-2), has spread rapidly and caused a global pandemic, resulting in a large number of confirmed cases and deaths (e.g. global situation at 24 September 2021, 230418451 confirmed cases and 4,724,876 deaths, https://covid19.who.int/). To date, remdesivir is the only FDA-approved drug to manage COVID-19 infection. In this context, there is a continuing need to develop new effective vaccines, new drugs and saviors' protocols that use approved anti-inflammatory and antiviral drugs and/or natural resources as complementary therapy. Honey, a natural resource used primarily as a dietary supplement, has also been shown to have therapeutic potential against a wide range of pathogens such as herpes simplex virus (HSV), rubella virus, hepatitis virus and multidrug-resistant bacterial strains and respiratory tract infections. Due to its demonstrated antiviral efficacy, Manuka Honey and its components can be safely evaluated as alternative option for patients with COVID-19. The present study aims to report the potential of eight natural flavonoids components of Manuka Honey as anti-SARS-CoV-2 through their binding on 3C-like protease ($3CL^{pro}$), main protease (M^{pro}) and viral target angiotensin-converting enzyme 2 (ACE2). Molecular docking study was selected as an appropriate tool to evaluate the interaction of natural flavonoids, quercetin, luteolin, galangin, kaempferol, isorhamnetin, pinocembrin, pinobanksin and chrysin, with the SARS-CoV-2 proteases and ACE2 and to rank the conformations through a scoring function to predict their binding affinity. Additionally, drug-likeness and toxicity related parameters were evaluated. Overall, our preliminary results indicate the potential use of the titled natural flavonoids as safe preventive chemotherapeutic agents as well as a viable solution to reduce the side-effects of conventional medicines.

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SYNTHESIS AND CHARACTERIZATION OF NEW RACEMIC SECONDARY ALCOHOL WITH 5-BENZYL-4-(4-METHYLPHENYL)-3-SULFANYL-1,2,4-TRIAZOLE STRUCTURE

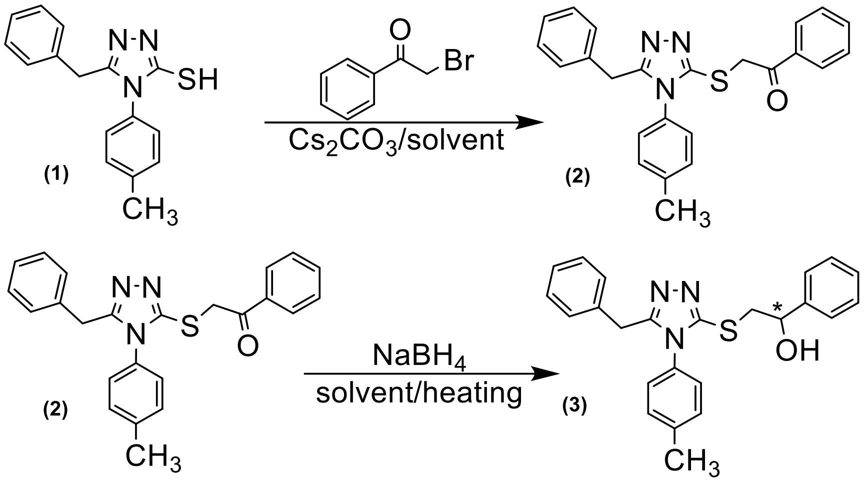
Ion BURCĂ, **Vladislav-Silvestru VALICSEK, Valentin BADEA, Vasile-Nicolae BERCEAN**

University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering,
Carol Telbisz 6, Timişoara, Romania
valentin.badea@upt.ro

The triazole heterocycle can be found in a wide variety of compounds many of which have biological activities e. g. anti-inflammatory [1], anti-bacterial, antifungal [2], anti-HIV [3] and anticonvulsant [4]. Thus, the triazole ring plays an important role in the design and synthesis of novel bioactive compounds.

The 5-benzyl-4-(4-methylphenyl)-4*H*-1,2,4-triazole-3-thiol **(1)** was synthesized using modified procedures from literature [1-4]. Then the compound **(1)** was alkylated with 2-bromo-1-phenylethan-1-one in the presence of cesium carbonate, thus resulting the 2-((5-benzyl-4-(4-phenyl)-4*H*-1,2,4-triazol-3-yl)thio)-1-phenylethan-1-one **(2)**. The ketone was reduced non-selectively, using sodium borohydride, to the corresponding secondary racemic alcohol **(3)**.

All the synthesized compounds were characterized by m. p., IR, 1D and 2D NMR spectroscopy.



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BATCH AND CONTINUOUS FLOW AROMA ESTER SYNTHESIS BY SOL-GEL ENTRAPPED *CANDIDA ANTARCTICA* LIPASE B

Ivana MILOȘ, Mădălina GHEORGHE, Corina VASILESCU,
Francisc PETER, Cristina PAUL

Politehnica University Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, Department of Applied Chemistry and Engineering of Organic and Natural Compounds, Carol Telbisz 6, Timișoara, Romania
corina.vasilescu89@gmail.com

Immobilized lipases are excellent biocatalysts for the enzymatic synthesis of short- and medium-chain fatty esters used as food flavour compounds [1]. Lipase from *Candida antarctica* B (GenoFocus, South Korea) was immobilized by entrapment in sol-gel hybrid matrices obtained with epoxy functionalized silane precursors. The catalytic efficiency of the immobilized lipase was investigated in the synthesis of the flavour ester pentyl hexanoate (apple, pineapple aroma) in organic solvent/solvent free media, by esterification of pentyl alcohol and hexanoic acid. The esterification reaction was performed at 36°C and equimolar ratio of substrates for 16 hours. High reaction yields (>90%) were obtained, the immobilized lipase retaining an activity yield of 96% compared to the free enzyme. The immobilized lipase maintained constant activity for more than 15 reaction cycles. Continuous production of the flavour ester pentyl hexanoate in a packed-bed reactor was developed using the immobilized lipase as a catalyst in a hexane solvent system. Continuous esterification at fixed temperature and substrate ratio was performed and the effect of flow rate on the molar conversion of alcohol was evaluated. Product formation was determined by GC-FID analysis of samples collected within a set time frame, following the stabilization of the system. The results showed that flow rate has a significant effect on the conversion of substrates, higher rates leading to improved productivity and shorter retention times. This study demonstrates the applicability of sol-gel entrapped lipases in a packed-bed reactor for continuous aroma ester synthesis.

This work was partially supported by the Romanian Ministry of Education and Research, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2019-2638, within PNCDI III, contract number 272PED, and project number PN-III-P1-1.1-TE-2019-1179, within PNCDI III, contract number TE94.

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A NEW LANDSCAPE FOR DRUG REPUROSING

Sorin AVRAM, Ramona CURPĂN, Liliana HALIP, Alina BORA

"Coriolan Drăgulescu" Institute of Chemistry, 24th Mihai Viteazu Blvd, 300223 Timisoara, Romania
5orin.4vram@gmail.com

Drug repurposing (DRP) aims to find new indications for old drugs. To facilitate this process, we have developed a classification scheme to catalog chemical structures according to market-availability and protection rights: off-patent (OFP; on-market drugs with expired patent and/or exclusivity), on-patent (ONP; on-market drugs with ongoing patent and/or exclusivity) and off-market (OFM; discontinued drugs). Further, we mapped these groups into a self-organizing map (SOM) model generated based on chemical properties, bioactivity, and clinical profiles of 959 drugs. The resulted map validates known drug classes and offers unexpected drug groups with potentially new indications.

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AUTHOR INDEX