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Content

Bachelor Level

Use of orthogonal protecting groups in solid phase peptide synthesis

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Merrifield solid-phase peptide synthesis (SPPS) has become a straightforward approach for chemical synthesis of (poly)peptides. The strategy involves stepwise addition of protected amino acids (apart from the carboxylic group) to a growing peptide chain, which is covalently bound to a solid functionalized resin. The final step consists in removal of the peptide sequence from the solid support [1].

Structural variation of the amino acids and presence of reactive functional groups like NH_2, OH, SH, COOH require use of protecting groups (PG). PG represents a molecular framework that is introduced onto a specific functional group in a polyfunctional molecule to block the reactivity under specific reaction conditions required to make subsequent modifications of the molecule. Moreover, amino acids having two functional groups in their structure (*i.e.* lysine), make use of orthogonal PG, which can be removed selectively by using specific and different conditions.

In this context, we present herein solid phase synthesis of a series of peptides using amino acids protected with various orthogonal PG (fig. 1), in order to study their influence on the resulted peptide. We describe the difficulties encountered during the synthetic approach and characterization of the synthetised peptides.

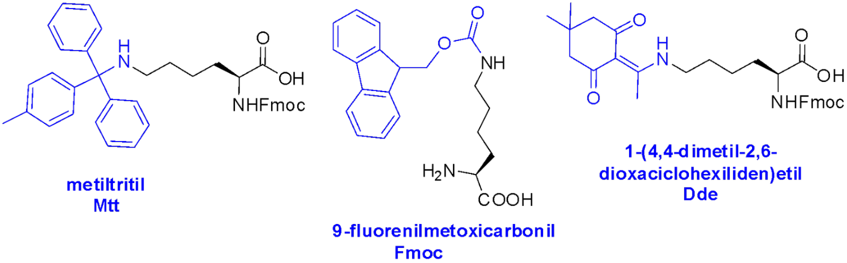

Figure 1. *Chemical structure of Fmoc-Lys(Mtt)-OH, Fmoc-Lys-OH and Fmoc-Lys(Dde)-OH amino acids used for SPPS*

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2-Isopropenyl-2-oxazoline a versatile building block for the synthesis of functional monomers

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Smart organic materials are materials that respond to small changes in their environment with dramatic changes in their physical properties upon exposure to external stimuli such as temperature, light, redox activity, frequency, and pH [1]. Nowadays, there is a high demand for smart materials with integrated functionalities that make them responsive to multiple stimuli, switchable and adaptive. Generally, smart organic materials are obtained via polymerization of functional monomers or post-polymerization modifications. Although the synthesis of such monomers is well established in the literature, the process is tendinous, requiring catalysts and advanced purification techniques. Thus, there is a high need to develop new protocols for synthesizing functional monomers.

2-Isopropenyl-2-oxazoline (iPOx) is a versatile monomer with dual functionality that has recently emerged as a powerful chemical handle because of its simple polymerization conditions and high reactivity towards carboxylic acids without generating by-products or requiring a catalyst [2, 3].

Herein, we report the synthesis of various functional monomers containing specific responsive units such as azobenzene, terpyridine, pyrene, indometacine and so one by chemically modifying iPOx with the corresponding carboxylic acids. Their potential use in the construction of macromolecular and supramolecular architectures for applications such as metallopolymers, polymer conjugates, and luminescent materials is being pursued.

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Rare-earth doped upconversion crystalline phosphors

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Nowadays, there is a high demand for new optical materials. Hence, an increasing attention is paid to rare-earth doped upconversion materials that can convert near-infrared excitation radiation into visible or ultraviolet emission. To achieve a high efficiency of the upconversion process, both the luminescent centers and host matrix are key factors. Concerning the luminescent centers, it is required co-doping activator ions with sensitizer ions that have a matched intermediate-excited state. Upconversion phosphors have a wide range of applications from medicine (tissues bioimaging, biosensing, light-triggered drug delivery etc.) to solar energy harvesting or fluorescent lamps [1,2].

Herein, we report the influence of host matrix ($BaGd_2ZnO_5$ and $LaPO_4$) and the ratio between erbium and ytterbium ions on the luminescence properties of materials. $BaGd_2ZnO_5$:Er, Yb powders with orthorhombic symmetry were obtained by sol-gel method at 900°C, while $LaPO_4$:Er, Yb having monazite structure with monoclinic symmetry were synthesized by precipitation in the 90-120°C temperature range. Then, $BaGd_2ZnO_5$:Er, Yb ceramic pellets were obtained after pressing and sintering at 1200°C for 5h. The samples were characterized by various techniques like Xray diffraction, scanning electron microscopy, dynamic light scattering, FTIR spectroscopy, as well as photoluminescence spectroscopy.

$BaGd_2ZnO_5$:Er,Yb showed better emission than $LaPO_4$:Er, Yb, depending on Er/Yb molar ratio. The emission in red domain increases with Yb content increasing, while the green emission is higher at 1/4 and 1/2 Er/Yb molar ratio for powders and pellets, respectively.

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Kinetic study of catalytic CO_2 valorization by Reverse Water-Gas Shift and Sabatier Methanation reactions as sustainable solutions for energy storage and further transformation to value-added products

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Anthropogenic CO_2 greenhouse gas emissions reached 40 billion tons in 2020 with an alarming increase in the last 20 years [1], with noticeable influence on global warming, climate change and extreme weather phenomena. The concept of circular carbon economy was introduced to mitigate the current status by using CO_2 as a feedstock for large scale hydrogenation to CH_4 (Sabatier Methanation) or CO (Reverse Water-Gas Shift) that can be further transformed to higher hydrocarbons by Fischer-Tropsch synthesis, provided that H_2 can be obtained from water electrolysis using renewable electricity [2].

CO_2 catalytic hydrogenation can be achieved with high yields on common transition metals (Fe, Co, Ni) where the support plays a key role on the catalytic activity and resistance to deactivation (coking): graphene supported Fe/Co catalysts shown unique behaviors and prolonged Time-on-Stream lives [3]. Kinetic studies on oxide-supported Fe, Co or Ni catalysts reported results affected by catalyst deactivation. The aim of the present study is to investigate the kinetics of catalytic reduction of CO_2 to CO on Fe,Co/graphene in absence of noticeable deactivation phenomena.

A matrix of 100 experiments was acquired while varying the H_2:CO_2 mole ratio (7, 4, 2, 1, 0.5:1), P (1, 5, 10, 20 bar) and T (300, 350, 400, 450, 500°C) in a packed bed continuous flow reactor on-line coupled to a gas chromatograph. Reaction rates were determined at low conversion degrees (differential conditions) and mass transfer limitations were ruled out by the value of the Weisz-Prater criterion, calculated with accurate pentacomponent real gas mixture diffusion coefficients. Global activation energies were determined from Arrhenius plots.

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Removal of Orange G dye by homogeneus advanced oxidation processes

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Azo dyes, characterised by the presence of one or more azo groups, represent about 60–70 % of all synthetic dyes produced worldwide and are resistant to biodegradation, under aerobic conditions. Because conventional treatment technologies cannot effectively degrade and mineralize azo dyes, advanced oxidation processes (AOPs) are usually use for degradation of such recalcitrant dyes.

In this study, the degradation of Orange G was achieved either by oxidation with bicarbonate-activated hydrogen peroxide in the presense of cobalt ions (chemical degradation) or by photooxidation in the presence of hydrogen peroxide (H_2O_2) or persulfate ($S_2O_8^{2-}$) by irradiation with a low-pressure mercury lamp (wavelength 254 nm, 40W).

The degradation process is obeying a pseudo-first-order kinetics and is positively influenced by the increase of oxidant species in the tested range. For the same initial conditions, degradation efficiency was higher for UV/ $S_2O_8^{2-}$ system. All methods can be used for degradation of azo dyes, with less overall costs compared with other methods.

The efficiency of RedOx Mediator Systems (SROM) for electrochemical degradation of antibiotics

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Various organic pollutants can be directly degraded by electrochemical oxidation or reduction, indirectly with electrogenerated reagents or by using redox mediated systems (SROM). A SROM is represented by ions of the same metal in two different oxidation states with high oxidation or reduction capacities.

Direct electrochemical degradation of metronidazole on platinum electrodes was performed indirectly by electrogenerated reagents and mediated using SROMs. The direct electrochemical degradation of metronidazole was achieved by electrolysis of a solution of $2x10^{-4}$ M metronidazole, 10^{-1} M Na_2SO_4 on platinum electrodes, under conditions of dynamic stirring of the solution - 300 rpm, for 1 hour. In the case of indirect electrochemical degradation, the supporting electrolyte (Na_2SO_4) was replaced with 0.1 M $Cl^{-1/+1}$ (NaCl), respectively with different SROMs; 10^{-4} M $Ce^{3+/4+}$ ($Ce(SO^4)_2$), 10^{-3} M $Tl^{1+/3+}$ (Tl_2SO_4), 10^{-3} M $Sr^{2+/3+}$ ($SrCl_2$), 10^{-3} M $Pd^{2+/4+}$ ($Pd(ClO_4)_2$). The content of oxidizing organic substances (S.O.O., mg/L $KMnO_4$) and the degree of discoloration were determined both for the standard, non-electrolyzed solution and for the electrolyzed solutions. $Cl^{-1/+1}$ system leads to the deepest degradation, with the lowest content of oxidizing organic substances. $Tl^{+1/+3}$ SROM presents the highest degree of discoloration and a high content of oxidizing organic substances. $Ce^{3+/4+}$ SROM is the most inefficient because it leads to the lowest degree of discoloration and the highest content of oxidizing organic substances. It is followed by $Sr^{1+/3+}$ SROM and $Pd^{2+/4+}$ SROM. The directly degraded sample shows intermediate values both for the degree of discoloration and for the content of oxidizing organic substances.

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Exploring the valorization of sea-bucktorn berries vegetal wastes as cheap adsorbents for wastewater treatment

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Sea-buckthorn (*Hippophaes rhamnoides*) is a plant from oleaster family (*Elaeagnaceae*) which grows in Europe, Caucasus, Asia Minor and Central Asia, Siberia, China and Tibet and it is renowned for its nutritious round berries, usually yellow or orange, which ripen in September. The berries are a rich source of vitamins C, E and P as well as malic acid, citric acid and an oily component made of triglycerides which can be extracted by mechanical cold pressing. This research aims to give an insight on the possibility to valorize the vegetal residue remained after the mechanical cold pressing of the fruits as a cheap adsorbent for transition metals or dye pollutants from wastewater. To this aim Fe and indigo carmine (IC) were selected as model wastewater pollutants. Two different solids were recovered after the juice extraction from fresh sea-buckthorn berries, namely S1 – solid vegetal waste separated after the juice extraction by mechanical cold pressing in a Philips juice extractor and S2 – solid vegetal waste recovered after the centrifugation of the extracted juice at 4000 rpm for 20 min. The solids have been dried at 90^{o}C for 24 h before being used as adsorbents. The adsorption tests were performed using synthetic wastewater samples having the initial concentrations of Fe (0.003 mM) and IC (0.03 mM). The tests have been performed at 25^{o}C in brown tapered bottles under mild stirring (150 rpm) using 20 mL of pollutant solution and a concentration of adsorbent varying in the range 0.1-1.5 g/L. Wastewater samples were analyzed by UV-Vis spectrometry at 1 h time intervals until 6 h and also after 24 h and 48 h. COD and TOC were also determined at the end of the experiments with IC pollutant. The adsorbents were characterized before and after the tests by DRIFTS and DR-UV-Vis. S1 exhibited a higher adsorption capacity (mg pollutant/g of adsorbent) for Fe (7.2) compared to S2 (5.9), while S2 showed the higher adsorption capacity for IC pollutant (7.4 > 5.2).

Synthesis of arylazopyrazole intermediate for novel switching compounds

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Molecules containing C=C, C=N, N=N bonds (*i.e.* alkenes, imines, hydrazones, azobenzene) are able to isomerize under light, usually converting from *trans* isomer (more stable) to *cis* isomer (less stable). Such molecules able to interconvert between two states with different properties have lately found applications as molecular photoswitches.[1]

A heteroaryl azo switch is a molecule which contains an azo group directly linked to a heterocycle and an aryl group. Arylazopyrazoles represents such a class of molecules displaying *E/Z* isomerization by UV or Vis light.[2]

We present herein synthesis of an intermediate belonging to arylazopyrazoles which contains a hydrazide moiety aimed to create a platform for synthesis of a novel library of *N*-acylhydrazones that can also undergo isomerization. Preparation of the target compound (Figure 1) started from *p*-aminobenzoic acid and involved reactions like diazotization, ring-closing condensation or esterification. All products were purified and characterized by physical and spectral analysis (NMR).

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Cellulose and Lignin- Challenges in the Synthesis of Eco-Friendly Fuel Cell Separators

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Due to rising needs for green, cheap and efficient energy generation systems polymer electrolyte membrane fuel cells (PEMFC) were developed. The goal of this study was to analyze previously obtained polymer electrolyte membrane assemblies consisting of Cellulose Acetate (AcCell), acrylic acid and in situ generated conductive polyaniline (PANI) and polypyrrole (PPy) doped with colloidal sillica. The swelling capacity was determined in relation to water, methanol and KOH over 24 hours.
The membranes were characterized using Electropotentiostatic Impedance Spectroscopy (EIS) at room temperature, with a swelling time of 30 minutes. TGA and SEM were used to determine the thermal stability and the surface morphology respectively. The wetting capacity was determined using contact angle evaluation.

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Influence of colchicine on Saccharomyces cerevisiae cells growth on heavy metals medium

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S. cerevisiae is the most widely used eukaryotic microorganism in both the food industry due to its fermentation capacity, and in the biotechnological research, due to the numerous mutans that can be obtained by genes deletion, also due to the fast multiplying and the fact that it is non-pathogenic. One aspect studied in this microorganism is the transport and bioaccumulation of various metal ions. This process can be done with or without energy consumption and is influenced by certain conditions such as pH, temperature, lack or presence of different substances in the environment in which the cells are grown.

Colchicine is a tropolonic alkaloid extracted from *Colchicum autumnale* with the medical application for the treatment of gout attacks, Mediterranean fever and other autoimmune diseases. It is also used as a cytostatic in extreme neoplasms due to its ability to inhibit microtubule polymerization. It has antioxidant properties and prevents lipid peroxidation.

This paper aimed to study the cells growth on solid medium under the influence of heavy metal salts and colchicine, but also to study how cells can accumulate metal cations in liquid medium. The cell lines used were WT, *Δmup1, Δmup3, Δgap1, Δpho84, Δfet4, Δsmf1*. Metal salts of Ag^{+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+} in different concentration were used in the growth experiments on solid medium. In the liquid medium only, the divalent cations were studied for bioaccumulation assays. The growth experiments were followed within 6 days.

The results for the cellular growth in the presence of colchicine, on the solid medium were visibly improved in the case of cells grown on the medium supplemented with Ni^{2+} and Co^{2+}, probably because colchicine had a protective effect.

In the liquid medium, assays of the metal concentration accumulated by the cells showed that a higher concentration of metal accumulated is corelated with a lower toxicity of the metal in the case of wild line. The lack of metal transport proteins, in the case of other mutans cells, defective in genes involved in metal transport, leads to a much lower concentration in the medium supplemented with colchicine.

Cells growth on medium supplemented with colchicine and cadmium present a very low accumulation in the WT strains, showing a synergistic effect. In the case of mutants strains, the bioaccumulation of cadmium in the presence of colchicine was higher than WT, possible due the formation of a less toxic cadmium-colchicine complex in the cells.

Simultaneous spectrometric determination of ellagic acid and gallic acid

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Gallic acid (GA) and ellagic acid (EA) are naturally occuring polyphenolic compounds resulted from hydrolyzable tannins. EA is the dimer of GA and they can be found in fruits like berries and nuts. Both compounds have numerous benefic effects on human health, mostly due to their strong antioxidant activity.

The two analytes absorb visible and UV radiation. Exploiting this property, the aim of this investigation was to compare simple UV-VIS absorption spectrometric methods applied for the simultaneous determination of GA and EA in synthetic mixtures.

In order to establish the optimum working conditions, the influence of the solution pH on GA and EA UV-VIS spectra was investigated. The results emphasized that the best separations between GA and EA absorption bands were achieved in Britton-Robinson buffer (BRB) pH 1.81 and in 1 M NaOH solutions, respectively. Due to the reduced stability of these polyphenols in alkaline media, BRB pH 1.81 was selected for further spectrometric investigations.

For the quantitative simultaneous analysis of GA and EA the absorbance additivity law (λ_{max}: 250 nm, 367 nm for EA and 272 nm for GA) and first order derivative spectrometry (1stDS) (zero crossing: 252 nm and 272 nm for EA and GA, respectively) were applied. Employing the absorbance additivity law, EA was determined with good recoveries in the presence of GA, whereas GA can be satisfactorily quantified only if its concentration is higher than the EA one. In the case of using 1stDS from a mixture of EA and GA, only EA can be determined with good results.

Thus, the investigated spectrometric methods could be applied to the EA quantification in dietary supplements without the interference of GA resulted after eventually EA decomposition after the expiration of the valability period.

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Synthesis and liquid crystalline properties of alkyloxybenzoic acids

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Liquid crystals (LC) have a higher molecular mobility compared to solid crystals. There are many ways in which LC can be classified, one of them being the molecular shape of mesogens: disk-like and rod-like LCs [1]. 4-Alkyloxybenzoic acids are significant examples of LCs that generate molecular interactions of the hydrogen bond type and can, therefore, create linear structures consisting of three aromatic rings and two "alkyloxy" side chains [2]. 4-Alkyloxybenzoic acids can self-assemble into a rod-like shape unit, based on the hydrogen bonding between the carboxylic acid groups.
In this work, two alkyloxybenzoic acids: 4-(dodecyloxy)benzoic acid and 3,5-di(tetradecyloxy)benzoic acid were synthesized and their liquid crystalline properties were studied by using specific techniques: 1H-NMR spectroscopy, IR spectroscopy, polarizing optical microscopy (POM), and differential scanning calorimetry (DSC). Even though these two compounds belong to the same class, only the 4-(dodecyloxy)benzoic acid has characteristics of a LC. This particular behaviour is strongly related to the molecular anisotropy of the two products.

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BCT-BZT based piezoelectric materials

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Piezoelectric materials are an integral part of modern life without which, many electronic devices would simply not exist. Unfortunately, the most commonly used such material is lead zirconate-titanate, also known as PZT, a toxic ceramic by virtue of its lead content which can lead to toxicity for both the consumer and the environment. As such, it is the goal of this project to synthesize and characterize a suitable replacement material, based on barium titanate, for this piezoelectric ceramic, as per new EU regulations.

The first method employed in this endeavor was the solid-state route, which implied mixing all the corresponding oxides/oxide precursors in the proper proportions followed by pressing and sintering. The ceramic discs obtained this way were structurally characterized by XRD and SEM analyses and functionally characterized by dielectric and conductometric measurements.

For the second approach, the sol-gel route was taken in an attempt to obtain a nanostructured ceramic. For this, acetates and alcoxides were dissolved in a mixture of solvents and let to evaporate in an oven, the obtained powder was calcined in order to obtain the proper phases and characterized by XRD.

Finally, an attempt at thin films made of this material was also made. The previously obtained sol was spin coated on HF cleaned, monocrystalline, <100> and <111> oriented Si wafers. The obtained thin films were then characterized by grazing incidence XRD and XRR measurements.

As a result of these experiments, links were established between the curie temperature of the material and its crystal structure or composition.

Synthesis and characterization of molybdenum-based catalysts for hydrogen evolution reaction (HER)

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Hydrogen is envisaged as one of the most promising vectors for green and renewable energy storage and transportation nowadays. In view of the energy and environmental issues, water electrolysis is an efficient and clean technology to generate highly pure hydrogen. As one half of the reaction of water electrolysis, hydrogen evolution reaction (HER), requires highly active and stable catalysts to reduce the overpotential and consequently to increase the efficiency. The extensive search for cost-effective, earth-abundant materials with high HER activity and excellent stability has recently attracted significant interest among the scientists.

Among the preferred electrocatalytic materials, there are molybdenum chalcogenides, especially disulfide molybdenum (MoS_2). There are different types of MoS_2. Nowadays, the most advantageous polytype is 1T grace to its remarkable properties. The purpose of this paper is to obtain supported 1T-MoS_2, with a large proportion of 1T as electrocatalyst for HER. The synthesis methods involve two approaches: (a) the impregnation of potassium ions in various proportions on molybdenum supported on TiO_2, followed by activation of the catalyst by sulfidation; (b) synthesis of TMA (tetramethylammonium)-MoS_2 supported on TiO_2, Al_2O_3 or Vulcan Carbon XC72 by hydrothermal method. The characterization methods are: RAMAN spectroscopy and BET analysis (to determine the percentage of resulted 1T-MoS_2); electrochemical measurements - cyclic voltammetry (for HER).

Mono- and binuclear complexes of 3d and 4f metal ions with polydentate Schiff base ligands derived from

N-(1-naphthyl)ethylenediamine

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Polydentate Schiff base ligands are important tools in designing homo- and heteropolynuclear complexes with 3d and 4f metal ions. Often, the synthesis of such complexes is a stepwise process, in which the 3d ion is introduced firstly, the resulting complex being further used as a ligand towards the 4f ion.

A series of new polydentate Schiff base ligands was obtained from N-(1-naphthyl)ethylenediamine and various phenol aldehydes. These ligands were used solely or in combination with other chelatic ligands in synthesis of mono- and binuclear complexes. The ligands and complexes were structurally characterized by X-ray diffraction on single crystal. The structural investigations revealed the versatility of this family of the Schiff bases, acting as bidentate (Figure 1), tridentate or tetradentate ligands.

The optical properties (IR, UV-Vis, luminescence) of the ligands and complexes were analysed in the solid state.

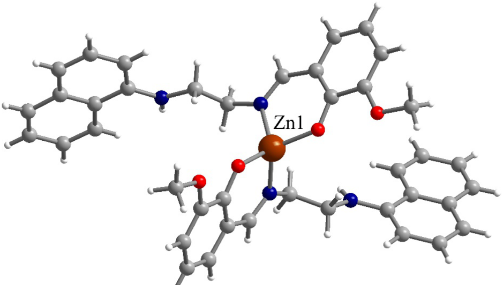

Figure 1. Perspective view of the crystal structure of the complex [Zn(L^3)$_2$], were HL^3 is the Schiff base ligand derived from *o*-vanillin and N-(1-naphthyl)ethylenediamine

Cu(II) and Zn(II) heteroleptic complexes containing the bis(2-pyridylcarbonyl)amine anion

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The bis(2-pyridylcarbonyl)amine (Hbpca) can be easily deprotonated to the bpca$^-$ anion, which is a planar ligand, potentially pentadentate. The coordination of nitrogen atoms of the bpca$^-$ anion to various metal ions generates numerous homoleptic bis-chelated complexes, $[M^{II}(bpca)_2]$ and $[M^{III}(bpca)_2]^+$, which can act as ligands towards a second metal ion through the oxygen atoms. The bpca$^-$ anion behaves as a divergent connector forming oligonuclear complexes and coordination polymers. Therefore, the anionic bpca$^-$ lignad is particularly suitable for assembling 3d−4f systems.

This study aims to combine the bpca$^-$ anion with other chelatic ligands like: 1,10-phenatroline; 2,2'-bipyridine, tris(2-pyridil) triazine, in order the generate heteroleptic mononuclear complexes of Cu(II) and Zn(II) metal ions. These compounds were structurally characterized by X-ray diffraction on single crystal confirming the heteroleptic nature of the complexes (Figure 1).

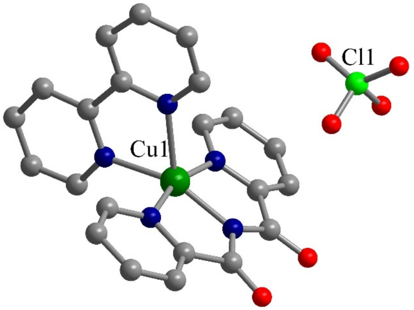

Figure 1. Perspective view of the crystal structure of the complex $[Cu(bpca)(bipy)](ClO_4)$.The hydrogen atoms were omitted for clarity

Also, the optical properties (IR, UV-Vis, luminescence) of the complexes were investigated in the solid state.

Augmentation of the Lewis acidity of organoantimony compounds featuring pendant arms

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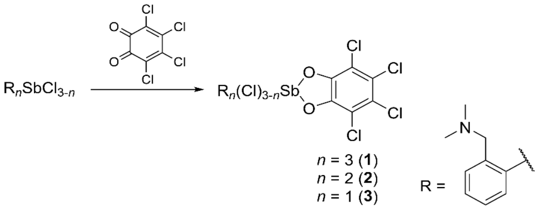
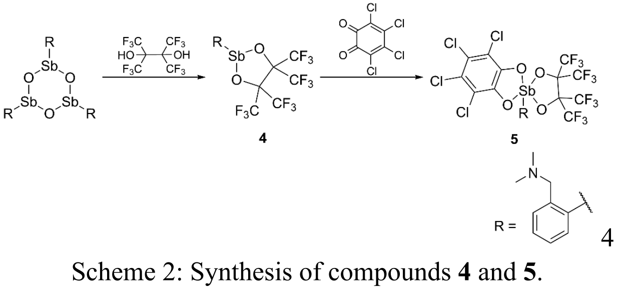
We report here the synthesis and structural characterization of the organoantimony compounds $R_n(Cl)_{3-n}Sb(o\text{-}C_6Cl_4O_2)$ [R = 2-(Me_2NCH_2)C_6H_4; *n* = 3 (**1**), 2 (**2**), 1 (**3**)], RSb(pin_F) (**4**) and RSb(pin_F)(o-$C_6Cl_4O_2$) (**5**) (pin_F = perfluoropinacol). Compounds **1-3** were obtained in a single step by oxidation of R_3Sb, R_2SbCl or $RSbCl_2$, respectively, with *o*-chloranil (Scheme 1). Compound **4** was obtained in the reaction of $(RSbO)_3$ with perfluoropinacol (Scheme 2). Oxidation of **4** with *o*-chloranil afforded **5** in almost quantitative yield.

All compounds were characterized in solution by multinuclear NMR spectroscopy and by mass spectrometry. The molecular structure of compounds **3-5** was determined by single-crystal X-ray diffraction.



Scheme 1: Synthesis of compounds **1-3**.



Scheme 2: Synthesis of compounds **4** and **5**.