The general objective of the project is to develop methodology for the fabrication of high surface area electrode materials with the use of a reversibly deposited mediator metal as a new way to improve the performance of the metal film electrodes and their application for the stripping analysis of trace concentrations of metal ions.

During the project realization, the best plating regime for the fabrication of the bismuth film electrode with the use of the mediator metal have been suggested. The bismuth film electrodes prepared with and without use of mediator were applied to the determination of Sn(IV) (chosen as model analyte) in acetate buffer solution [1]. It was found that the use of mediator metal (Zn) in the step of electrode preparation increased the analytical signal of Sn(IV) (Figure 1).

A linear response for the accumulation time of 60 s with a good correlation coefficient ($r^2 = 0.9989$) was obtained for Sn(IV) up to $5 \times 10^{-6}$ mol L$^{-1}$ and obeyed the equation $y = 0.470x + 0.004$, where $y$ and $x$ are the peak current ($\mu$A) and Sn(IV) concentration ($\mu$mol L$^{-1}$), respectively. The detection limit defined as three times standard deviations of the blank (3σ) for the accumulation time of 60 s was estimated at $4.8 \times 10^{-8}$ mol L$^{-1}$. On the basis on the obtained results it can be stated that the proposed procedure of Sn(IV) at the bismuth film electrode prepared with the use of mediator, under the optimal conditions, offers a 3 times lower detection limit to that obtained at an in situ plated bismuth film electrode prepared without use of mediator [1].
Fig. 1. Comparison of the square-wave anodic stripping voltammograms obtained at the BiFE prepared with (lines a and b) and without use (line c) of the mediator zinc in the solution containing 0.1 mol L$^{-1}$ acetate buffer (pH 4.5), 0.4 mmol L$^{-1}$ Bi(III), 0 (line c) or 0.04 mmol L$^{-1}$ (lines a and b) Zn(II), 1.73 mmol L$^{-1}$ caffeic acid and 0 (line a) or $5 \times 10^{-6}$ mol L$^{-1}$ (lines b and c) Sn(IV). The bismuth, zinc and tin were deposited simultaneously for 90 s at -1.2 V and then at -0.85 V for the time of 45 s zinc was stripped from the surface and Bi as well as Sn were further deposited. Square-wave voltammetric scans were performed with frequently of 15 Hz, amplitude of 40 mV and step potential of 5 mV.

References:

*(Grant of the National Science Centre No. 2013/08/M/ST4/00286)*
ELECTRODES MODIFIED WITH METAL FILM PLATED WITH
THE USE OF FUNCTIONALIZED POLISILOXANES IN TRACE
ANALYSIS OF HEAVY METALS BY STRIPPING VOLTAMMETRY

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The introduction of organic group compounds into the silica materials leads
to silica-based organic-inorganic hybrid materials combining in a single solid both
the mechanical stability of a rigid inorganic framework with the chemical reactivity
of the organic components. Such attractive features have been advantageously ex-
ploited for the selective preconcentration of target analytes prior to their detection by
a suitable voltammetric method [1-5].

The general objective of the project is the application of functionalized silica
film and metal particles in the step of the electrode preparation in order to improve
the electrochemical performances of traditionally used metal film electrodes.
The mixture of two silica monomers tetraethoxysilane (TEOS) and mercaptopropyltrimethoxysilane (MPMS)
in the presence of cetyltrimethylammonium bromide (CTAB) have been used to prepare sols by
co-condensation. The thiolated organosilica films were deposited by spin-coating
of sols on the freshly polished and electrochemically activated surface of a glassy
carbon electrode. After template extraction, the thiol-functionalized polysiloxane film
electrode was electrochemically modified with lead particles (in situ electroplating)
and applied to the determination of Hg(II) (chosen as model analyte) in acidic med-
ium. As it can be seen in Figure 1, the sensitivity of thiol-functionalized polysiloxane
film electrodes was remarkably improved by using a lead modifier.

The calibration graph of Hg(II) for the accumulation time of 120 s was linear
from $1 \times 10^{-9}$ to $1 \times 10^{-6}$ mol L$^{-1}$ and obeyed the equation $y = 0.0166 \times - 0.0106$,
where $y$ and $x$ are the peak current (µA) and Hg(II) concentration (nmol L$^{-1}$), respec-
tively. The correlation coefficient ($r^2$) was 0.9995 The detection limit estimated from
3 times the standard deviation for the lowest determined concentration of Hg(II) was
about $3.51 \times 10^{-10}$ mol L$^{-1}$. It has to be noted, that the detection limit can easily be
improved by the prolongation of the accumulation time up to 60 min.
Fig. 1. Square wave anodic stripping voltammograms obtained in the course of the determination of Hg(II) at concentration of $1 \times 10^{-6}$ mol L$^{-1}$ at: a) the thiol-functionalized polysiloxane film electrode, b) the lead-modified thiol-functionalized polysiloxane film electrode. Experimental conditions: preconcentration solution: 0.1 mol L$^{-1}$ HNO$_3$; deposition solution: 3 mol L$^{-1}$ HCl and $1 \times 10^{-6}$ mol L$^{-1}$ Pb(NO$_3$)$_2$; accumulation time: 60 s; amount of MPTMS in the starting sol: 10%; SWASV: lead deposition potential and time: -1.45 V and 60 s; Hg deposition potential: -0.7 V vs. ref., Hg deposition time: 60 s, frequency: 25 Hz, step height: 4 mV, and amplitude: 50 mV.

References:

(Grant of the Ministry of Science and Higher Education No. IP2012 061472)
INVESTIGATION OF IMPLANTS IN ASPECT OF THEIR ADHESION TO BIOLOGICAL MATERIALS

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Due to prolongation of the life span preparation of long lasting implants is required. Moreover, number of young people affected by sports injuries increases. As a consequence implants have become important in regaining health and improving quality of life. In living human body the natural border of the cells are their membranes which are the natural contact area between cells. In the case of implants the cells are in contact with artificial materials. Hence, an attention of scientists is focuses on development of biocompatible implant surfaces by applying various coatings [1-3]. Thus obtained surface modification leads to a better contact between cells and implants. The role of surface characteristic, i.e. the composition, topography, roughness and surface free energy, is of great importance in determining the biological response to the implanted materials. That is, determination which proteins and cells adhere strongly to the implant surface, followed by formation and calcification of the bone. Determination of the above characteristic of the cell’s surface and the implant material may help to develop new implant materials that can be successfully incorporated into the surrounding tissue. However, in living organisms the implanted materials are in contact with a variety of tissues. Hence it is also important to understand the implant surface characteristics optimal for given, specific tissue type. Development of well characterized surface may result in prolongation of the lifespan of implants, as well faster and more solid integration of the device into the host tissue, which allows patients to have a shorter the recovery time.

The major components of biological membranes are phospholipids (like phosphatidylethanolamine (PE) and phosphatidylcholine (PC)), which in natural cell membranes form bilayers. Hence, using lipids as surface modifiers to cover the implant materials could be promising tool to improve implants properties. A variety of lipids can be found in the cell membranes [1].

There are two major classes of phospholipids: the neutral phospholipids (e.g. phosphatidylglycerol (PG), phosphatidylethanolamine (PE), sphingomyelin (SM), and phosphatidylcholine (PC)), and the acidic phospholipids (phosphatidic acid (PA), phosphatidylserine (PS), phosphatidylinositol (PI), and cardiolipin (CDL))[4]. Proteolipids and complexed acidic phospholipids can cause hydroxyapatite mineral deposition in a physiological environment [5].

In the first step of our investigations we plan to optimize lipid layer composition and methods of its deposition onto the implant surface. Then, the physicochemical properties and stability of thus obtained lipid films on different implant surface will be studied via contact angle measurements and surface characterization techniques,
e.g. scanning electron microscopy, atomic force microscopy, optical profilometer, etc.

References:

(Project of European Commission, Initial Training Networks FP7-PEPLE-2013-ITN, grant no. 607861, Complex Wetting Phenomena)
EFFECTS OF POLYSACCHARIDES EXTRACTED FROM BACTERIAL STRAINS RHODOCOCCUS OPACUS ON THE PROPERTIES OF PRECIPITATED CALCIUM CARBONATE

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Biomineralization is a process by which organisms precipitate inorganic minerals. Biominerals are organized hierarchically and are ordered at many length scales that reflect remarkable physical characteristics. Complex mineralized composite systems in nature provide a rich background for insight into mechanisms of biomineralization and novel materials designs. Some of the more common sources of inspiration include sea shells, insect exoskeletons, extracellular matrices involved in bone and other hard tissue and marine silica skeletons. Calcium carbonate (CaCO$_3$) is one of the most abundant biomaterials in nature. It is found as different polymorphs, consisting, in the order of increasing solubility, of calcite, aragonite, vaterite, calcium carbonate monohydrate, calcium carbonate hexahydrate, and amorphous calcium carbonate. In the biological systems, calcite, aragonite, vaterite, and amorphous calcium carbonate can nucleate and grow in a stable way, and their lattice can maintain stability in the presence of bioorganic macromolecules. As a result, calcium carbonate is one of the most suitable and highly focused materials for the research of biomineralization and simulation of mineralization [1].

Currently, a large number of proteins and polysaccharide involved in the control of biomineralization, have been described. There is no single type of polysaccharide associated with biominerals, but such polysaccharides are mainly hydroxylated, carboxylated, or sulfated or contain a mixture of the functional moieties, which can bind Ca$^{2+}$ ions and could control crystal nucleation and growth by lowering the interfacial energy between the crystal and the macromolecular substrate [2].

In this study the ability of polysaccharide layers to act as templates for mineralization of calcium carbonate was examined. Firstly, possible interactions between the polysaccharides and calcium ions were determined by the conductivity and zeta potential measurements. Then calcium carbonate was precipitated in the presence and absence of obtained polysaccharide by mixing up solutions containing calcium and carbonate ions. Raman spectroscopy and scanning electronic microscopy (SEM) were used to characterize the obtained mineral crystals.

It was found that the extracellular biopolymer produced by the bacterial strain Rhodococcus opacus modifies the nucleation and growth of calcium carbonate but does not change the crystal forms (Fig. 1). It is due to adsorption of calcium ions on the biopolymer.
Fig. 1. SEM images of calcium carbonate obtained: A) at 25°C without biopolymer, B) at 25°C with 80 mg/L of biopolymer and C) at 37°C with 80 mg/L of biopolymer.

The obtained results will be published in the next paper.

References:

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STRUCTURE FORMATION IN METAL-ORGANIC OVERLAYERS COMPRISING CROSS-SHAPE FUNCTIONAL MOLECULES

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Surface confined self-assembly of functional star-shaped organic molecules is a promising method to create nanoporous networks with tailorable structure and functions. The Monte Carlo simulation method was used to demonstrate how the morphology of these supramolecular assemblies can be tuned by manipulating intrinsic parameters of the building blocks and modified by the presence of co-adsorbed metal atoms. To that purpose we study the 2D self-assembly of planar cruciform molecules modeled as collections of interconnected segments, some of which were activated to represent discrete interaction centers [1-3]. We consider a few exemplary adsorbed systems in which the molecules with different size, aspect ratio and intramolecular distribution of active centers form superstructures stabilized by short-range metal-segment interactions. The simulated results show that proper encoding of intramolecular interactions into the cruciform building bricks allows for directing the self-assembly towards largely diversified structures ranging from nanoclusters to porous grids. The obtained findings can facilitate designing and optimization of molecular networks comprising cross-shaped units including functionalized porphyrins and phthalocyanines and they can be helpful in preliminary selection of these building blocks.

Fig.1. Metal-organic structures formed by the cross-shaped molecules differing in the distribution of active sites (red) in the backbone.

As we have shown using the simple MC modeling, activation of two or more terminal segments of these tectons leads to the formation of nanostructures ranging from isolated rectangular clusters to ladders, strings and nanoporous grids (also chiral) with 2D void spaces of different size and shape. The systematic comparison of the one-component overlayers and the corresponding metal-organic systems performed in this study enabled the identification of the main structural differences in
the assemblies stabilized by the molecule-molecule and molecule-metal interactions. These findings can be helpful in designing supramolecular architectures on solid surfaces, especially in situations when, for a building block of a given geometry one has to decide which self-assembly method, one-component or metal-organic, is a better choice to achieve the target structure. The simple and general theoretical methodology proposed in this study can be also used for preliminary screening of libraries of available molecular building blocks, with respect to size, shape and interaction pattern, to select the optimal molecule able to create 2D assemblies of presumed properties. Moreover, this approach can also reduce the number of test experiments needed to obtain new cross-shaped functional units with the most appropriate geometry and functions.

References:

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SORPTION OF L-HISTYDINE BY MESOPOROUS SILICA MATERIALS

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Nowadays, the adsorption of pharmaceuticals and biocompounds, such as drugs, enzymes or proteins, from solutions onto solid surfaces is frequently studied [1]. Although above-mentioned biocompounds have a positive effects on living organisms, they can however (in higher concentrations) cause damage in some organs or tissues. Thus, it becomes necessary to control and remove of those biocompounds and other pharmaceuticals in the surrounding environment. Adsorption is one of the most commonly used techniques for removal of many different species, including biomolecules. This is due to the fact that efficient adsorption techniques have huge commercial importance and find applications in different fields, such as biotechnology, biocatalysis, medicine, and controlled drug delivery systems [1].

Nanoporous Silica-based Materials (NSM) are attractive as adsorbents due to their simplicity of synthesis, facility of surface functionalization and biocompatibility. Adsorption of amino acids on mesoporous materials (mainly carbons) have been also tested [2,3] as the understanding of theirs sorption behaviour is important in the field of biotechnology, material extraction, drug delivery and pollutant removal. In the present work, we report the adsorption of L-histidine, onto both, pristine and functionalized SBA-15 silicas. The materials were properly functionalized to introduce amino, and thiol functional groups by co-condensation of tetraethoxysilane with aminopropyltriethoxysilane, and mercaptoprolytrimethoxysilane, respectively.

The effect of pH values on effectiveness of L-histidine adsorption onto silica samples was first examined - the maximum L-histidine uptake was observed in the range of pH between 4 and 5. For the pH values lower and higher that the optimal pH, the adsorption decreases rapidly. It can be explained by the fact that LH in the range of pH≈4-5 exist in zwitterion form, thus the electrostatic interactions between LH and charged silica surface are present [4].

It has been establish that the adsorption process of L-histidine is very fast and adsorption equilibrium is achieved as quickly as several minutes. Such rapid binding of L-histidine to the silica surface is mainly a result of the presence of the developed mesoporous structure facilitating diffusion of amino acid molecules into the mesopores, where majority of the functional groups are located [4].

Adsorption isotherms are presented in Fig. 1. As it can be seen two well defined regions on each isotherm can be distinguished. There is almost linear rise at lower equilibrium concentrations of L-histidine. This feature suggest a remarkable affinity between L-histidine and the silica surface caused by the presence of functional surface groups. However, in the case of the pristine silica sample the surface silanol
groups can serve as the binding sites for L-histidine. Thus, it must be assumed that in the case of amino- and thiol-functionalized samples adsorption of L-histidine occurs due to the presence of both: (i) functional groups introduced by co-condensation, and (ii) surface silanol groups which are always present at the silica surface.

At higher equilibrium concentrations of L-histidine, the adsorption reaches a plateau (i.e. static sorption capacity – SSC). As it can be seen the SSC values remarkably increase for both functionalized samples when compared to the pristine sample (27 mg/g). Adsorbed amounts for amino and thiol-functionalized samples increase by 75% (47 mg/g and 48 mg/g, respectively). Thus, a customized functionalization of the surface of SBA-15 silica can significantly enhance the adsorption behavior of silica-based sorbents with regards to L-histidine (and other amino acids).

**Acknowledgement**
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References:

*(NCN Grant no. 2012/05/D/ST5/03488)*
Ordered mesoporous carbons exhibit many advantages over traditional microporous activated carbons mainly due to their ordered structure, narrow mesopore size distributions (centered at about 3.5-4 nm), high specific surface areas (as high as 1500 m²/g) and large total pore volumes [1,2]. Thus, there is currently an appreciable interest in the synthesis, and characterization of OMCs, as well as in their assessment for applications ranging from electronic devices to adsorbents and catalyst supports, electronics, medicine, catalysis, etc. [3-6].

It is also possible to create additional functionalities on the surface, what is extremely useful in designing new adsorbents that will selectively remove contaminants such as heavy metals ions, phenols or pharmaceuticals. Here, ordered mesoporous carbons have been obtained by nanocasting strategy [1]. They were subsequently modified to investigate the changes in porous structure and surface chemistry upon oxidation and amine-functionalization. In a model synthesis the CMK-3 carbon was prepared by using the SBA-15 silica as a hard template and sucrose as the carbon source (PRC). Further, the pristine CMK-3 carbon was oxidized with ammonium persulfate (OXC) and modified by grafting N-(3-trimethoxysilylpropyl)diethylenetriamine (AMC). The details of the majority of syntheses’ protocols can be found elsewhere [7,8]. The porosity and ordering diminished significantly after oxidation and amino-functionalization; however, the surface chemistry of OXC sample was enriched in oxygen surface functionalities as indicated by the X-ray photoelectron spectroscopy. Pristine, oxidized and amino-functionalized carbons were used as sorbents of different bivalent heavy metal ions (Pb, Zn, Cd, Cu) from aqueous solutions.

The batch mode was used to examine the adsorption/desorption of Cu, Zn, Pb, and Cd ions. After the adsorption equilibrium had been achieved, the solution was separated from the sorbent by filtration. The equilibrium adsorption uptakes were calculated according to the following formula: \( a = (c_i - c) \cdot V \cdot m^{-1} \), where \( c_i \) is the initial metal concentration (mg L⁻¹), \( c \) is the equilibrium metal concentration (mg L⁻¹), \( V \) is the volume of the solution (L) and \( m \) is the mass of the adsorbent (g). Measurements were carried out using the atomic absorption spectrometer AAS-3 (Carl Zeiss) equipped with the Pb, Zn, Cd, and Cu hollow cathode lamps working at a wavelength of 217.0, 213.9, 228.8, and 324.8 nm, respectively.

On the basis of the obtained data we concluded that the increase of adsorption uptake at higher pH (above 6) probably would be due to the surface precipitation, i.e. formation of a multilayer solid phase on the sorbent surface. Thus, it was decided to run all adsorption experiments at pH=5, which provided that the process of heavy metals adsorption will be only adsorption-driven without appreciable surface/bulk precipitation. The observed sorption processes were extremely fast and only a few
minutes were usually needed to adsorb more than 90%-95% of the equilibrium amount. In the case of some sorbents (not described here) even 100% of the equilibrium amount was adsorbed in first two minutes and no appreciable increase in adsorption was observed beyond this time [8].

The values of static sorption capacities are ranging from 29mg/g for Zn(II) to 177 mg /g for Pb(II) depending on both: the type of heavy metal and the type of sorbent. The Pb(II) ions are adsorbed most efficiently on the OXC and AMC samples (177 mg/g) when compared with the PRC sample (119 mg/g). The oxidation resulted in the increase of the static sorption capacity by about 50%. Further amino-functionalization does not induce the further increase when compared with the OXC sample. In the case of Cu(II) and Cd(II) the oxidation treatment causes even the significant decrease in the adsorbed amounts: from 38 to 32 mg/g and from 68 to 48 mg/g, respectively.

After the amino-functionalization treatment the similar increases are observed: from 32 to 42 mg/g and from 48 to 68 mg/g, respectively for Cu(II) and Cd(II). The most significant changes are observed in the case of adsorption of Zn(II) ions: after oxidation the static sorption capacity increased doubly (from 27 to 59 mg/g). However, after amino-functionalization decreases to 44 mg/g. Thus it can be concluded that there is no significant influence of amino-functionalization onto adsorption uptake – pristine or oxidized samples can adsorb higher or comparable amounts of heavy metal ions studied. In two cases (i.e. for Pb and Zn) the oxidation of the PRC sorbent enhanced significantly the adsorption which resulted in higher static sorption capacity.

Acknowledgement
The authors would like to mention that the investigations described in this report have been obtained thanks to the financial support provided by the Polish Ministry of Science and Higher Education in the frame of Grant no. N N204 272639

References:

(MNiSW Grant no. N N204 272639)
The starting point for the IRMFC project was the catalyst for the SRM developed previously in the IRAFC project. It enabled us to achieve very high hydrogen and carbon dioxide and low carbon monoxide (lower than 2 %) selectivity at 200-220°C. The activity and selectivity of that catalyst was fairly stable; only very small deactivation during initial period of its work in the SRM was observed. It was resistant to shutdowns with exposes to air at the room temperature and at 180°C, as well as to the storage in air. The complete methanol conversion could be achieved by adjusting the contact time of the catalyst with the methanol-water reaction mixture. The advantage of that catalyst was also its easy activation at low temperatures, also in the SRM conditions, without any pre-reduction with hydrogen.

In this project, taking into account the cost of the final system, the special attention has been given to lowering of the active phase loading in the catalyst, without decreasing its good properties. In this respect the catalyst synthesis method and catalyst composition were optimized with regard to the activity, stability, reducibility and pyrophoricity behaviour.

A large number of new catalysts was synthesized, characterized and tested in the steam reforming of methanol. The new synthesis method and the catalyst composition have been proposed, which enable better distribution of smaller loading of the active phase (see Fig. 1) and higher homogeneity of all components.

![Fig. 1. Distribution of the active phase in the old IRAFC and in the new SRM catalyst](image_url)
Aiming to diversify gas supplies to Poland resulted in a decision to build a liquefied natural gas (LNG) terminal in Świnoujście, which is the basis for the gas terminal. The creation of the LNG terminal will allow to deliver by sea the liquefied natural gas from any direction, which will help to increase the energy security of the country. About 25% of imported high methane content natural gas is directed to the national ammonia plants.

Fertilizer Research Institute (INS) has performed consequences analysis of the use of the LNG regasification product (with relatively large amounts of higher hydrocarbons) as a raw material for ammonia production.

This became the basis of the project submitted to the National Centre of Research and Development (adaptation of the national ammonia plants for LNG processing with any composition utilizing pre-reforming) [1].

A part of the project conducted in the Department of Chemical Technology since October 2013 concerns the evaluation of thermal stability of modified nickel catalysts and their resistance to coking. Nickel catalysts samples were prepared in the Institute of Fertilizers (Puławy). Catalysts series modified with various amounts of La (1-2 wt. %) were held at temperature 600 and 700°C, respectively.

Currently, there are conducted studies on the influence of the catalysts heating on the size of total and active areas as well as the resistance to coking by the gravimetric method in the steam reforming reaction.

Within the project there was elaborated publication entitled: “Liquefied natural gas (LNG). Properties and use by fertilizer industry”, which was published already in Przemysł Chemiczny [2].

References:
[1] Project „LNG-Fert” conducted by a consortium INS (Fertilizer Research Institute)-Rzeszów Technical University-UMCS Lublin, Puławy 2012.

(The Programe of Applied Research NCBiR No PBS1/A1/6/2012)
STUDY OF ANIONIC POLYACRYLAMIDE ADSORPTION MECHANISM AND ITS IMPACT ON THE CHROMIUM (III) OXIDE SUSPENSION STABILITY

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In the present study particular emphasis was placed on the effects of the type and number of functional groups of anionic polyacrylamide (PAM), its molecular weight and solution pH on the conformation of polymer macromolecules in the adsorption layer formed on the dispersed chromium (III) oxide surface. Determination of PAM adsorption mechanism enabled clarification and understanding of Cr$_2$O$_3$ suspension stability in the polymer presence.

PAM is a primary ingredient in many flocculants used in various fields of human activity. It is applied in the oil regeneration process and for reduction of plough land erosion to improve its stability. PAM is also largely used for minimization of inorganic salt concentrations in drinking water.

The presence of chromium (III) oxide in water is particularly undesirable because of its properties. This oxide is of low-toxicity. However, it has intense green colour, which gives water an unsightly appearance and disrupts life processes.

The spectrophotometry, potentiometric titration, microelectrophoresis, viscosimetry and turbidimetry were applied. They enabled determination of polymer adsorbed amount, surface and diffusion charges of solid particles with and without PAM, thickness of polymer adsorption layer, macromolecule dimensions in the solution and stability of the Cr$_2$O$_3$ - polymer systems, respectively. The anionic PAM samples characteristic is shown in Table 1.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Molecular weight [Da]</th>
<th>Anionic groups content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM 11 000 000_5%</td>
<td>11 000 000</td>
<td>5</td>
</tr>
<tr>
<td>PAM 14 000 000_20%</td>
<td>14 000 000</td>
<td>20</td>
</tr>
<tr>
<td>PAM 14 000 000_30%</td>
<td>14 000 000</td>
<td>30</td>
</tr>
<tr>
<td>PAM 15 500 000_50%</td>
<td>15 500 000</td>
<td>50</td>
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</table>

It was found that adsorption of anionic PAM decreases and thickness of polymeric adsorption layer increases with the increasing pH (Figs 1 and 2). Slightly higher adsorption and thicker polymeric layer formed on the solid surface were obtained for the PAM samples containing a greater number of carboxyl groups. Apart from electrostatic interactions, the hydrogen bridge type interactions play an important role.
in the polymer binding with the solid surface. They are formed mainly between the neutral surface groups –CrOH and carboxyl groups of the polymer, which are preferentially adsorbed in comparison to amide ones.

Fig.1. Adsorbed amount (Γ) of PAM on Cr₂O₃ surface and thickness of polymeric layer (δ) for samples containing different content of anionic groups (pH 3, initial PAM concentration 100ppm).

A slight decrease in Cr₂O₃ suspension stability in the PAM presence at pH 3 is obtained. Under these conditions, the highest adsorption of the polymer, which forms the thinnest adsorption layer, is achieved. A small dissociation degree of carboxyl groups in the PAM macromolecules makes that they adsorb in a more coiled form. Such structure of surface layer favours partial neutralization of positive charges of the solid particles by the adsorbed polymer coils having a number of negatively charged groups.

The decrease of polyacrylamide adsorption at pH 6 leads to the marked improvement of stability properties in relation to the unstable suspension without polymer. This is due to the conformational changes of the adsorbed macromolecules, whose functional groups at pH 6 are almost completely ionized, and the formed adsorption layer has larger thickness than at pH 3. Thus, repulsive interactions appear under these conditions. They are derived not only from the steric layer of the adsorbed polymer, but also on the negative charges distributed along the PAM chains. This type of interactions is defined as electrosteric ones.

At pH 9 there is slight deterioration in the stability of the suspension containing the polymer. Significant development of the adsorbed polyacrylamide chains at pH 9 due to the adsorbent-adsorbate electrostatic repulsion is the reason for bridging interactions appearing in the system. Formation of individual polymer bridges was favoured, on one hand, by the developed conformation of macromolecules on the surface of colloidal particles and on the other hand, by the leaky coverage of solid surface with the polymer layer (the lowest PAM adsorption). This allows connecting two or more colloidal particles by adsorption of one extended chain on their surfaces. As a result bridging flocculation occurs.

Polyacrylamide with the molecular weight 15 500 000 and the carboxyl groups content 50% proved to be the most effective flocculent of chromium (III) oxide suspension.

(Grant of Polish National Center of Science, grant No. 2012/07/B/ST4/00534)
Space-division multiplexing (SDM) is recognized as the most efficient way to meet the challenge of an increasing need for telecommunication network capacity [1], as it allows jumping over the barrier of existing systems based on single-core single-mode fibers (SMF) with the recently reported optical SDM link record capacity of 1 Pb/s [2]. In addition, SDM allows reducing power consumption and system foot-print compared to the transmission over multiple fibers which is of high importance in applications such as, for instance, satellite communication [3]. Two ways of SDM utilization are possible. First, the idea of mode-division multiplexing (MDM) [4,5] in which each mode represents one transmission channel and which can be realized by means of a single core few-mode fiber (FMF) or a multi-core fiber (MCF) with coupled cores. Second, the idea of uncoupled propagation in multiple cores of an MCF. The key feature of such uncoupled propagation is the core isolation which eliminates core-to-core crosstalk (XT), hence allows treating each core as a separate transmission channel. Since the methodology of addressing individual modes in an FMF is technologically complex and the transmission characteristics (e.g., attenuation, chromatic dispersion-CD, etc.) of each mode vary, the use of MCFs with isolated single mode cores seems to be more convenient and commercially applicable. The goal of isolating the cores in an MCF can be realized in various ways. The most intuitive and straightforward method is simply increasing the core spacing which, however, entails larger fiber diameters when more cores are involved. When willing to increase the number of cores while remaining the standard 125 µm fiber diameter, more sophisticated fiber structures such as microstructured trench-assisted, or hole-assisted. MCFs must be applied. An alternative (or complementary) method of increasing the core isolation is differentiating size and refractive index of particular cores. Although this approach is generally correct, the integration of such heterogeneous fibers with standard devices and optical fibers, currently used in optical fiber networks, is troublesome (as each core is characterized by different CD and the mismatch between its size and doping level will introduce additional loss when coupling with existing, SMF based, network components). To overcome this integration issue, while retaining high core density, we have designed and developed a hole-assisted seven-core MCF, in which the transmission parameters for each core (i.e., CD, attenuation, bending loss, etc.) are in accordance with the obligatory standards for telecommunication single core fibers (i.e., ITU-T G.652 and G.657). Moreover, fiber diameter as well as diameter and refractive index of each core are SMF compliant, which enable an immediate employment of our fiber in the existing telecommunication networks.
The proposed MCF structure is created by means of basic cells (Fig. 1a) in which the 8.2 µm diameter and 3.5 mol.% GeO₂ doped core is surrounded by twelve air-holes. In such a basic cell, the refractive index contrast between the core and cladding is the same as in an SMF. The basic cells may be easily combined in a hexagonal grid forming 7-core (Fig. 1b).

In order to experimentally prove our theoretical assumptions and numerical simulation results, we have fabricated a 7-core fiber according to our design with the stack-and-draw technique (Fig. 2). The fiber dimensions measured from a scanning electron microscope picture are: \(d_{\text{core}} = 7.4 \, \mu\text{m}, \lambda = 7.1 \, \mu\text{m}\), and \(d_{\text{hole}} = 5.9 \, \mu\text{m}\).

Dispersion characteristics were measured in a free space Michelson interferometer configuration. The experimentally measured dispersion curve (Fig. 3) is characterized by zero dispersion wavelength (ZDW) of 1313.9 nm, zero dispersion slope coefficient \(S = 0.097 \, \text{ps/(nm}^2 \, \text{km)}\), and a dispersion of 18.42 ps/(nm km) at 1550 nm wavelength which prove high telecommunication potential of the presented design.

Fig. 1. (a) MCFs’ basic cell; (b) 7 core MCF design;

Fig. 2. SEM image of the fabricated fibers cross section and results of chromatic dispersion measurement referenced to the specification of standard SMF-28 (respectively)

References:

*(Projekt realizowany w ramach Programu Badań Stosowanych PBS1/B3/12/2012 „Pasywne i aktywne światłowody wielordzeniowe w telekomunikacyjnych sieciach dostępowych”)*
Decisive influences on the mechanical and optical properties of the fiber have the protective coatings. The coating is a protective outer layer of the fiber, which protect it from external aggressions. Proper selection of the material should provide proper adhesion between the coating and the optical fiber, which greatly affects its durability. In addition, the material must act as a trap for mods as well as protection against microbending losses.

Currently for fibers used in telecommunication, acrylic UV curable coatings are used [1]. Among these the most important are derivatives of esters of acrylic or methacrylic acid which are characterized by very good processing properties, and the corresponding physical and chemical parameters such as the possibility for its modification by using other substrate such as epoxy resins, urethane or silicone. References [1] describe also other polymer materials used in the fabrication of optical fiber protective coatings. The fibers are coated with two layers of different paints with selected properties that serve as a buffer against mechanical influences from outside. These include silicone oils, acrylic paints and the acetate-cellulose and butyl-cellulose, teflon, polybutadiene rubbers, polyamides, polyimides, polyurethanes, polymers of perfluorinated organosols R-Si-O- and others.

Optical fiber technology requires that the coatings were imposed on them online, directly after they have been pulled out Protective coatings are usually UV curable polymers.

So far, little attention has been paid to optimizing the conditions of curing coatings [2-4]. In this work, the comparison of a thermoanalytical and spectroscopic analysis coatings that were cured in an oven in which the power of the UV lamps was changed will be shown.

Thermal analysis (Fig 1) was carried out on a STA 449 Jupiter F1, Netzsch (Selb, Germany) under the following operational conditions: heating rate 10°C min⁻¹, a dynamic atmosphere of helium (40mL min⁻¹) in the temperature range of 40°C – 600°C, sample weight of about 10 mg, sensor thermocouple type S TG-DSC. As a reference empty Al₂O₃ crucible was used.

Based on the obtained results it can be seen that studied coatings are thermally unstable in relatively low temperatures. Therefore, it seems important to control the temperature in which the protective coatings are cured.
Fig. 1. Measurement of soft and tough (respectively) DeSolie® Coating using coupling thermal-spectroscopic methods (heating rate of 10 K/min).

Fig. 2. Histogram for fibers, which coatings were cured in the oven before and after (respectively) modernization.

This is why, in the Laboratory of Optical Fibers Technology, decided to make structural changes of UV oven. From the diagrams listed below you can see the resulting histograms (Fig. 2 and Fig. 3), where the fiber coatings were obtained by using the oven before and after modernization.

It can be seen that fibers which protective coatings were obtained in oven after modernization, have much better mechanical properties.

References:

(Projekt realizowany w ramach Programu Operacyjnego Innowacyjna Gospodarka, nr POIG.01.03.01-06-085/12 „Zaawansowane struktury światłowodów fotonickich dla innowacyjnych sieci telekomunikacyjnych)
POLYMER OPTICAL MICROSTRUCTURED FIBER WITH BIREFRINGENCE INDUCED BY STRESS APPLYING ELEMENTS

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Birefringence in microstructured fibers has typically a geometrical origin. In silica microstructured fibers with hexagonal symmetry, birefringence can be induced by enlarging two cladding holes adjacent to the core [1], diminishing the diameter of the cladding holes in one row [2], making the cladding holes elliptical [3] or placing a small hole of an elliptical shape in the center of the core [4]. There are only a few reports on the fabrication of birefringent polymer microstructured fibers with modal birefringence exceeding $10^{-5}$ in the visible spectral range. So far, the polymer fibers with elliptical cladding holes [5], with smaller [6] or larger [7,8] holes adjacent to the core and the squeezed hexagonal lattice [9] have been described in literature.

In this paper we present, a birefringent microstructured fiber with stress applying elements located in the solid part of the cladding. A primary material used for the fabrication of the reported fiber is poly(methyl methacrylate) (PMMA) of a technical grade. The fiber core is surrounded by three rings of air holes arranged in a hexagonal lattice, which form a microstructured cladding. The air holes were fabricated by mechanical drilling of the PMMA rod. Outside the microstructured cladding, there are two stress applying elements located symmetrically with respect to the fiber core. These elements are made of polystyrene (PS), which has a thermal expansion coefficient different from PMMA, $\alpha_{PS}=9.6\times10^{-5}$ 1/K and $\alpha_{PMMA}=7\times10^{-5}$ 1/K [10]. Therefore, when the fiber is cooled down below the lower glass transition temperature of the two materials ($T_g=105$ °C for PMMA and $T_g=95$ °C for PS) during the drawing process, the polystyrene inclusions give rise to a stress field inducing material birefringence in the microstructured region. The stress applying elements were manufactured by drilling the holes of a proper diameter in the fiber preform and filling them with a liquid mixture of monomer (styrene), initiator (benzyl peroxide) and moderator (thioglicolic acid). Finally, thermal polymerization was conducted to obtain solid inclusions. Polystyrene has a greater refractive index than PMMA [11] ($n_{PS}=1.5862$ and $n_{PMMA}=1.4890$ at $\lambda=656$ nm), therefore to prevent light propagation inside the inclusions, a small (0.01% w/w) amount of carbon micro powder was added to the liquid mixture to increase light absorption. At the initial stage of the polymerization process, when the mixture is still in a liquid phase, the diffusion of styrene monomers into solid PMMA takes place. As the result, the transition layer containing a mixture of PS and PMMA polymers is formed on the boundaries of the PS inclusions. These transition layers provide a good mechanical bounding between the PS stress applying inclusions and the pure PMMA cladding. The distance between the center of the PS inclusions and the fiber core is about $r_1=64$ μm, the diameter of the pure PS inclusion is $d_1=62$ μm, while the diameter of the PS/PMMA transition layers is $d_2=95.5$ μm.
The pitch distance of the microstructured cladding is about $\Lambda = 3.27 \, \mu m$, while the holes diameter varied from $d = 1.3 \, \mu m$ in the first ring to $d = 1.57 \, \mu m$ in the second ring of holes (average value $d = 1.43 \, \mu m$). The fiber external diameter was $D = 235 \, \mu m$.

To study the fiber birefringence, we first measured the beat length using the lateral force method and calculated the spectral dependence of the phase modal birefringence $B$. We also measured the spectral dependence of the group modal birefringence $G$ using the spectral interferometry method [12,13]. The phase and the group modal birefringence is weakly dependent upon wavelength, which is a characteristic feature of fibers with stress-induced birefringence. The relative change of $B$ and $G$ in the spectral range 600-1050 nm estimated by polynomial fitting of the measurement data does not exceed 25%.

References:


(WCB/11/VI/2011 "Polimerowe światłowody mikrostrukturalne" – zlecenie zewnętrzne z EIT+)
BIOCHIAR PRODUCTION INCREASES THE POLYCYCLIC AROMATIC HYDROCARBONS CONTENT IN SURROUNDING SOILS AND POTENTIAL CANCER RISK

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Biochar produced with the traditional method is characterised by very low mechanical strength and high brittleness, therefore during the emptying of kilns, shifting, reloading and transport it undergoes considerable fragmentation. As a consequence, in the vicinity of kilns fine coal gets into the soil, and the silt fractions of biochar are carried with the wind over longer distances. In the immediate vicinity of the kilns soil may also be contaminated with the liquid products of pyrolysis [1]. PAHs migrating into the soil together with biochar are very hard-biodegradable [2], which contributes to their increased stability in the soils and extends the time over which they may pose a threat to organisms and to the environment.

The objective of the study was the identification of the source of contamination of soils and estimation of potential cancer risk that may be caused by contact with soils situated in the vicinity of biochar production sites. Samples of soils collected in the immediate vicinity of traditional biochar producing plants, located within the area of the Bieszczady National Park (Poland) were analysed for the content of polycyclic aromatic hydrocarbons (PAHs). Assessing the threat to human health, the incremental lifetime cancer risk (ILCRS) was estimated [3].

The content of the sum of 16 PAHs varied within the range from 1.80 to 101.3 μg/g (Table 1), exceeding the norms permitted in many European countries. The calculated coefficients on the basis of which one can determine the origin of PAHs (molecular diagnostic ratios) demonstrated that the potential source of PAHs in the soils may be processes related with the production of biochar (Fig. 1) [4].

![Fig. 1. Molecular diagnostic ratios for identification of PAH pollution sources](image)

Estimated on the basis of results of incremental lifetime cancer risks (ILCRS) within the range from $2.33 \times 10^{-4}$ to $1.05 \times 10^{-1}$ indicated that the soils studied may constitute a significant cancer risk for persons who have contact with them. The
values of ILCRS should be considered as at least high, which permits the conclusion that sites of that type may create a hazard to human health.

Table 1. The concentration of PAHs in examined samples, BaP_{eq} benzo(a)pyrene equivalent concentrations, and incremental lifetime cancer risks (ILCRS).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>PAH16 (µg/g)</th>
<th>BaP_{eq} (µg/g)</th>
<th>ILCRS (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1a</td>
<td>9.89</td>
<td>0.99</td>
<td>1.34 \cdot 10^{-3}</td>
</tr>
<tr>
<td>W1b</td>
<td>8.23</td>
<td>0.76</td>
<td>1.03 \cdot 10^{-3}</td>
</tr>
<tr>
<td>W1c</td>
<td>4.29</td>
<td>0.32</td>
<td>4.33 \cdot 10^{-4}</td>
</tr>
<tr>
<td>W2a</td>
<td>1.80</td>
<td>0.17</td>
<td>2.33 \cdot 10^{-4}</td>
</tr>
<tr>
<td>W2b</td>
<td>45.42</td>
<td>1.92</td>
<td>2.60 \cdot 10^{-3}</td>
</tr>
<tr>
<td>W3a</td>
<td>68.34</td>
<td>2.12</td>
<td>2.87 \cdot 10^{-3}</td>
</tr>
<tr>
<td>W3b</td>
<td>101.28</td>
<td>77.89</td>
<td>1.05 \cdot 10^{-1}</td>
</tr>
<tr>
<td>W4a</td>
<td>16.54</td>
<td>0.27</td>
<td>3.59 \cdot 10^{-4}</td>
</tr>
<tr>
<td>W4b</td>
<td>16.58</td>
<td>0.74</td>
<td>1.00 \cdot 10^{-3}</td>
</tr>
<tr>
<td>W5a</td>
<td>28.15</td>
<td>2.88</td>
<td>3.89 \cdot 10^{-3}</td>
</tr>
<tr>
<td>W5b</td>
<td>87.41</td>
<td>7.08</td>
<td>9.58 \cdot 10^{-3}</td>
</tr>
</tbody>
</table>

The study demonstrated that soils in the immediate vicinity of kilns are strongly contaminated with PAHs. The concentrations of PAHs are considerably higher than the permissible limits laid down in the regulations in force in many countries. Both the analysed MDRs and the features of the situation of the sampling sites indicate potentially that the source of those contaminants is the production of biochar in that area. In accordance with the estimated values of ILCRS, the cancer risk resulting from contact with the contaminated soils should be considered as at least high. It should be strongly emphasised that the level of the risk may be underestimated. It should also be noted that apart from the cancer risk to humans there is a great hazard to animals occurring in that region. The fauna of the region includes many protected species that should be granted special protection. Those sites may, therefore, create serious hazard to the ecosystems and to human health.

References:

(Grant PSPB-135/2010)
THE CONVERSION OF SEWAGE SLUDGE TO BIOCHAR REDUCES PAHs CONTENT AND ECOTOXICITY BUT INCREASES HEAVY METALS CONTENT

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Industrialisation and urbanisation increase the volume of sewage sludge produced by wastewater treatment plants [1]. Sewage sludge is a valuable source of phosphorus, nitrogen, microelements and organic matter which have a favourable effect on the properties of soil and thus also on the level of yields [2]. However, the presence of contaminants in sewage sludge, such as highly toxic organic compounds (polycyclic aromatic hydrocarbons - PAHs), potentially toxic elements (trace metals) and pathogenic microorganisms, significantly restricts its application for soil fertilisation or for the reclamation of degraded soils [3,4]. Sewage sludge conversion to biochar may be a chance for minimisation of negative effects related with the agricultural utilisation of sewage sludges.

The objective of the study was the estimation of the effect of pyrolysis of sewage sludge on the content of contaminants (PAHs and trace metals) and on toxicity towards plants (Lepidium sativum), bacteria (Vibrio fischeri) and crustaceans (Daphnia magna). Biochars (BC) were prepared at 500, 600 and 700°C. The pyrolysis heating rate was employed at 25°C/min and nitrogen gas was injected at a rate 630 ml N2/min to ensure an oxygen-free atmosphere. The temperature was held for 5 h (slow pyrolysis). The properties of sewage sludges and sewage sludge-derived biochars are presented elsewhere [5].

Sewage sludges conversion to biochar significantly reduced the PAHs content (from 8- to 25-fold depending on pyrolysis temperature and kind of sludge) (Fig. 1).

![Fig. 1. The PAHs content (sum of 16 US EPA) in sewage sludges (SS) and sewage sludge-derived biochars (BC). Values are given as averages with standard deviations (n = 3).](attachment:image.png)
The pyrolysis of sewage sludges caused also a significant reduction of their toxicity towards the test organisms (Fig. 2). Whereas, after pyrolysis an increase was noted in the content of trace metals (Pb, Cd, Zn, Cu, Ni and Cr).

![Graph of root growth inhibition](image)

Fig. 2. Effect of 1% dose of sewage sludges (SS) or sewage sludge-derived biochars (BC) on root growth inhibition of *L. sativum*. Values are given as averages with standard deviations (n = 3).

The results indicate that for sewage sludges which exceed the norms concerning the content of PAHs, limiting their agricultural utilisation, their conversion to biochars may be the solution. A decrease was also noted in the toxicity of the biochars relative to the initial raw sewage sludge, with certain exceptions. All the biochars caused an improvement of germination of seeds of *L. sativum*, and root growth stimulation was observed relative to the initial sludges. Most of the biochars created also favourable conditions for the bacteria *V. fischeri* compared to the sewage sludges. The test organism that showed to be the most sensitive to the contaminants present in the biochars was *D. magna*. Only for leachates from biochars obtained at the lowest temperature a reduction of mortality of the test organisms was noted relative to the initial sewage sludge.

References:
DESYMMETRIZATION-CYCLIZATION OF
DIMETHYLPHENYLPHOSPHINE DERIVATIVES

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The synthesis of cyclic organophosphorus compounds possessing phosphaindane core is usually accomplished by several methods including intramolecular nucleophilic substitution at phosphorus,[1] intramolecular electrophilic substitution[2] or RCM methodology.[1] Another possible method of the synthesis of this unit is an intramolecular carbon-carbon bond formation through electrophilic aromatic substitution. This transformation could be achieved starting from vinyl or allyl-substituted arylphosphine oxides or from the specifically designed alcohols.[3]

During the course of our current research project concerning the desymmetrization of symmetrically substituted tertiary phosphine derivatives we were interested in the synthesis of phosphine derivatives possessing phosphaindane skeleton through intermolecular aromatic electrophilic substitution reaction using β-hydroxyalkylphosphine oxides 2 as substrates (Scheme 1).

\[
\begin{align*}
\text{O} & \quad \text{Me} \\
& \quad \text{Me} \\
\text{1} & \quad \text{RC(O)R', base} & \quad \text{2} & \quad \text{cyclization} & \quad \text{3}
\end{align*}
\]

**Scheme 1. Synthetic pathway to 3**

In the first step, the synthesis of β-hydroxyalkylphosphine oxides 2 was accomplished (Scheme 2).

\[
\begin{align*}
\text{O} & \quad \text{Me} \\
& \quad \text{Me} \\
\text{1} & \quad \text{1. n-BuLi, (1.0), 50 min} \\
& \quad \text{2. RC(O)R' or RC(O)H, 1 h} & \quad \text{THF, -78 °C} & \quad \text{2} & \quad \text{68-97%} & \quad \text{21 examples}
\end{align*}
\]

**Scheme 2. Synthesis of 2**

The developed method of the synthesis of phosphine oxides 2 allowed the synthesis of these compounds in good to excellent yields using both aldehydes and ketones as carbonyl compounds.

In the next step, optimization of cationic intramolecular cyclization has been performed. Among the tested acids phosphoric acid (85% or 100%) appeared to give the best conversions of substrate into product (Scheme 3).
The developed reaction conditions were applied for other β-hydroxyalkylphosphine oxides 2 (Scheme 4).

Surprisingly, under the developed reaction conditions only 2a underwent cyclization into phosphaindane, whereas the other compounds underwent predominant cyclization into benzophosphorinane core. The formation of such products could be explained by rearrangement of primary cation prior to cyclization step.

References:

(National Research Centre grant SONATA-BIS 2 Nr 2012/07/E/ST5/00544)
A NEW CLASS OF P-STEREOGENIC CYCLOHEXANE-BASED DIPHOSPHINE LIGANDS - EFFECTIVE APPLICATION OF BIRCH REDUCTION IN ORGANOPHOSPHORUS CHEMISTRY

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The design and synthesis of chiral phosphine ligands have played significant role in the development of efficient transition metal-catalyzed asymmetric reactions. Large variety of structurally diverse organophosphorus compounds have already been tested in these reactions. Among them, P-stereogenic tertiary phosphines appear to be quite important and promising ligands.[1] Since P-chiral organophosphorus compounds cannot be found in enantiomerically pure form in the natural chiral pool, the development of the efficient methodologies of the synthesis of P-stereogenic phosphines is still an active area of research. Although numerous chiral diphosphine ligands containing acyclic linker have been reported so far, cyclohexane-based diphosphines received relatively little attention.[2] More rigid structure of this class of ligands should have a beneficial effect on the stereoselectivity of the catalytic asymmetric reactions. Therefore, a development of a new and efficient methodology of the synthesis of P-stereogenic diphosphines with cyclohexane linkers appears as a quite interesting target.

The aim of the presented research project is the development of a new methodology of the synthesis of bis(phosphinoyl)cyclohexanes starting from Birch reduction products. At this moment, few different tasks are under development. At first, we examined the reaction of t-buty[1,4-cyclohexadien-3-yl]methylphosphine oxide and its corresponding isomerized and hydrogenated analogs with >PH-type compounds in the presence of a strong base (Scheme 1).

Scheme 1. Synthesis of 1,2-bis(phosphinoyl)cyclohexenes
In case when \( \text{Ph}_2\text{PH} \) was used, we observed the formation of mixture of Michael-type addition products in good overall yield and high degree of diastereoselectivity, however reaction with other secondary phosphines failed to occur.

We have also conducted preliminary P=O bonds reduction reactions present in bis(phosphinoyl)cyclohexanes (Scheme 2).

\[
\begin{align*}
\text{P(O)(tBu)Me} & \quad \text{P(O)R}_2 \\
1. \text{MeOTf} & \quad 2. \text{LiAlH}_4 & \quad 3. \text{BH}_3\text{-SMe}_2
\end{align*}
\]

**Scheme 2.** Reduction of P=O bounds in diphosphine dioxides.

Finally the stereoselective synthesis of optically pure Birch reduction product and its corresponding isomerized and hydrogenated analogs was examined. As predicted, all steps proceeded with retention of configuration at phosphorus atom (Scheme 3).

\[
\begin{align*}
\text{Birch reduction} & \quad \text{isomerization} & \quad \text{H}_2
\end{align*}
\]

**Scheme 3.** Synthesis of optically pure Birch reduction product and its corresponding isomerized and hydrogenated analogs

Further efforts will be put towards the synthesis of optically pure diphosphine dioxides, reduction of P=O bounds and finally catalytic tests of synthesized diphosphine ligands in model catalytic transformations.

References:


*(National Research Centre research grant Nr 2012/05/N/ST5/01154)*
STUDY ON REACTIVITY OF STERICALLY HINDERED ORTHOMETHOXY SUBSTITUTED BIARYL PHOSPHINES

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Electron rich sterically hindered phosphines constitute an important class of phosphorus ligands widely used in homogeneous catalysis as complexes with transition metals.[1] The careful analysis of the literature shows that only in very rare cases such ligands were prepared starting from corresponding phosphine oxides. Especially in the cases of ortho-methoxyaryldicycloalkylphosphines the reduction of phosphate oxides to phosphines is extremely difficult, so the examples of such reduction are very unusual.

The present studies are concentrated on the explanation and overcoming observed phenomenon of unusual reactivity of ortho-methoxyaryldicycloalkyl phosphate oxides. As we had reported previously, naphthyl-dicyclohexylphosphine oxides bearing methoxy substituent ortho to phosphorus underwent deprotection of the methoxy oxygen atom under all tested reduction conditions.[2] Since the direct reduction of phosphine oxides of desirable structures was not possible, the alternative procedure based on conversion of phosphoryl group to chlorophosphonium chloride was realised.[3] Obtained in situ salts were converted to corresponding phosphines, phosphine sulfides, phosphine selenides and phosphine boranes in good to excellent yields.

References:

(Grant DEC-2012/05/B/ST5/00362)
Our research project aimed at the synthesis and application of new phosphine ligands containing six-membered ring phosphines in their structure has been based on 1-phenylphosphorin-2-en-4-one (2) as a single, suitably functionalized and versatile precursor. Its synthesis in the required non racemic form either via asymmetric process involving enantioselective deprotonation and oxidation of achiral 1-phenylphosphorinan-3-one (1) or by resolution of racemic 2 were already developed in the past years. In the latter case, synthesis of 2 in the required gram scale was accomplished by means of oxidation of 1 with a small excess of IBX or a small excess of HIO₃/DMSO. We wish to report now that our continued efforts to improve the synthesis of 2 have led to the development of a procedure enabling direct conversion of saturated phenylphosphorinanone 1 to unsaturated phosphorinanone 2 under catalytic conditions utilizing for the first time a substoichiometric amounts of HIO₃-DMSO. A possibility for this development emerged from the screening of different oxidants listed in Table 1.

Table 1. Synthesis of unsaturated 2 from the saturated 1 under various conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent</th>
<th>Solvent</th>
<th>Reaction conditions</th>
<th>% a</th>
<th>% b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5 equiv. DDQ</td>
<td>Dioxane</td>
<td>95 °C, 24 h</td>
<td>50</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>10 equiv. MnO₂</td>
<td>CHCl₃</td>
<td>100 °C, 72 h</td>
<td>61</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>4 equiv. IBX</td>
<td>DMSO</td>
<td>60 °C, 12 h</td>
<td>52</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>1.2 equiv. HIO₃*DMSO</td>
<td>DMSO</td>
<td>75 °C, 3 h</td>
<td>62</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>0.25 equiv. HIO₃*DMSO</td>
<td>DMSO</td>
<td>75 °C, 2 h</td>
<td>44</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>0.1 equiv. HIO₃*DMSO</td>
<td>CHCl₃</td>
<td>135 °C (MW), 1.5 h</td>
<td>70</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>2 equiv. NBS + Et₃N</td>
<td>CH₂Cl₂</td>
<td>r.t., 12 h</td>
<td>70</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>1.5 equiv. CuBr₂</td>
<td>CHCl₃/EtOAc</td>
<td>75 °C, 8 h</td>
<td>55</td>
<td>42</td>
</tr>
<tr>
<td>9</td>
<td>2.2 equiv. NH₄Br + 2 equiv. Oxone®</td>
<td>MeOH</td>
<td>75 °C, 72 h</td>
<td>60</td>
<td>19</td>
</tr>
</tbody>
</table>

a: isolated yield
b: from GC analysis
Under the optimized conditions 1-phenyl-phosphorin-2-en-4-one 1-oxide (1) was smoothly oxidized to 2 in 61% isolated yield upon exposure to 0.1 equiv. of HIO₃·DMSO in chloroform-DMSO (ca. 40:1) at 135 °C for 1.5 h. The optimized protocol enabled also a convenient preparation of phosphorinenone 2 in a 2.5 gram scale with similar efficiency. It should be also underscored, that in contrast to other HIO₃ α,β-dehydrogenations of ketones reported previously, our procedure required use of only small amounts of DMSO to secure successful oxidation. Minimizing the amount of used DMSO greatly facilitated isolation and purification of the product.

Monitoring of the oxidation process by ¹H NMR revealed that formation of the oxidation product 2 was accompanied by simultaneous formation of dimethyl sulfide (DMS) resulting from reduction of DMSO. This led to the conclusion that DMSO serves not only as the activator for HIO₃ but also as an oxidant securing conversion of HIO₂·DMSO to HIO₃·DMSO prerequisite for the catalytic cycle to occur.

**Scheme 1.** Proposed catalytic cycle for oxidation of 1-phenyl-phosphorinan-3-one 1-oxide (1) by HIO₃·DMSO

Use of HIO₃ as oxidant in organic synthesis has been so far very limited due to hazardous properties of HIO₃. Some reported explosions are already on record. The developed possibility of using this oxidant in only catalytic amounts is thus of great practical advantage and of general synthetic importance. As a good example of its practical utility can serve synthesis of a unique phosphacridinone system 3 from saturated 1-phenylphosphorin-4-one 1-oxide (1) and 1,3-butadiene which entails two [4+2]-cycloadditions and six oxidation steps occurring in a one-pot sequence under the influence of HIO₃·DMSO catalytic system.

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STATISTICAL THERMODYNAMICS AND COMPUTER SIMULATIONS OF COMPLEX MOLECULES IN BULK AND AT SURFACES

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The following problems have been studied: (1) the structure and properties of a mixture of amphiphilic molecules and ions at a solid surface [1]; (2) re-entrant phase transitions in confined two-patch colloidal particles [2]; (3) the structure and thermodynamic properties of systems consisting of terminally grafted oligomers immersed in fluids [3]; (4) the behavior of solvent primitive model of an electric double layer in slit-like pores: microscopic structure, adsorption and capacitance [4]; (5) adsorption of block copolymers on solid surfaces by Monte Carlo simulations [5]. We have also published a review article [6] that summarizes all our findings of the behavior, thermodynamic properties, microscopic structure and phase transitions in the systems involving tethered layers in contact with one- and multicomponent fluids.

References:

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