POSTER SESSION

WEDNESDAY, JUNE 11th, 2014

CHAIRPERSONS:

Agnes Móricz and Łukasz Cieśla

1.

Co-clustering of chromatographic data

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Separation and determination of individual components in a complex mixture is a necessary and important step in chemical and biological sciences. In everyday laboratory practice, chromatographic methods are frequently applied to accomplish these fundamental goals. They are well suited for the compositional analysis of drugs, biological fluids, food samples, cosmetics, etc. However, with the increasing number of samples and parameters being analyzed, useful chemical information can be hidden in analytical data. Recently, there is a trend to uncover groups of samples by means of clustering with respect to their specific chemical features. It can be done with the so-called co-clustering or biclustering techniques [1]. Co-clustering is a useful tool when a particular subset of samples should be related with meaningful subset of parameters. The main advantage of such a methodology is that samples and parameters are clustered simultaneously. As a result, individual samples can belong to several clusters, and detected clusters can overlap to each other [2].

In this study, theoretical aspects of co-clustering are discussed, and as an example a real data set of 572 samples of olive oil is used. For each sample concentrations of eight fatty acids (palmitic, palmitoleic, stearic, oleic, linoleic, eicosanoic, linolenic, and eicosenoic) were determined by gas chromatography [3]. Olive oil samples have been collected in nine different regions in Italy (North Apulia, Calabria, South Apulia, Sicily, Inland Sardinia, Coast Sardinia, East Liguria, West Liguria, and Umbria).

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2.

Identification of geographical origin of Indian opium on the basis of amino acid profiles

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The Opium poppy *(Papaver somniferum)* is cultivated mainly in Turkey, Indian subcontinent, China, Spain, France and Australia. Dried latex from this plant is called opium. Due to its narcotic properties, illicit cultivation of Opium poppy, its further processing and distribution is strictly prohibited. Attempts have been made to develop an analytical tools facilitating identification of geographical origin of opium.

It is well known that the mineral nutrition of plants can be related with place of their cultivation. On the other hand, link between the mineral nutrition of plants and their amino acid composition was reported [1]. Thus, the possibility to assess geographical origin of opium samples on the basis of their amino acid profiles was evaluated.

A total of 124 samples of opium collected from three states of India were examined according to their amino acid composition. 14 amino acids (i.e. aspartic acid, threonine, serine, glutamic acid, glycine, alanine, valine, isoleucine, leucine, tyrosine, phenylalanine, histidine, lysine, and arginine) were quantitated using liquid chromatography coupled with fluorescence detection [2]. On the basis of obtained profiles chemometric models discriminating samples according to their origin were constructed. In order to build models, discriminant variant of partial least squares algorithm, D-PLS [3], was used.

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3.

Detection of counterfeit medicines based on chromatographic impurity profiles

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Quality control of drugs is of great importance in the protection of human health. Counterfeit medicines are a global concern because they are not subjected to quality control, and thus their safety and effectiveness cannot be guaranteed. Safety assessment of drugs is not based solely on the identification and quantification of the active substances but also on the analysis of secondary components which might exhibit toxic effects (e.g. residual solvents, impurities). In this work the samples of counterfeit and authentic Viagra medicine were analyzed by means of High-Performance Liquid Chromatography with Diode-Array Detection (HPLC-DAD). The obtained impurity profiles were used as fingerprints and analyzed using chemometric methods. In order to distinguish between counterfeit and authentic samples of medicine the discriminant variant of partial least squares, PLS-DA method was used [1]. Whereas to uncover differences in chemical composition variable importance in projection criterion VIP, was applied [2]. By means of this discriminant approach 90% of samples was correct assigned to the appropriate classes.

Literatura

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4.

Probing a chemical space for fragmental topology-activity landscapes (FRAGTAL): Application for diketo acid and catechol HIV integrase inhibitor offspring fragments

Andrzej Bak[1] , Tomasz Magdziarz[1], Violetta Kozik[1], Krystyna Jarzembek[1], Marcin Rojkiewicz[1], Agata Kurczyk[1], Katarzyna Serafin and Jaroslaw Polanski[1]

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The nature of the drug-target interactions ruled by inter- and/or intra-molecular forces is a tremendously complex and divergent process that still lacks a universal approach. Hence, several approaches to drug discovery have been developed in the quest to identify the differences between drug- and non-drug molecules (chemicals). Most often, these methods are related to the drug-likeness concept originating from the idea that drug compounds differ from other molecules in their physicochemical properties.

In reality, molecular descriptors quantifying drug-like properties (DP) are easily available from molecular formulae, e.g. the number of hydrogen bond donors (HBD) or acceptors (HBA). The emergence of the quantitative property-based Lipinski Ro5 ‘sieve’ is focused on the importance of restricting the chosen *in silico* molecular parameters of preclinical drug candidates in the pharmacokinetic-friendly property space. The discrimination Ro5 model restrains the ‘drug-like property space’ through a set of threshold values which are necessary but are not sufficient boundary guidelines of the preferred ‘drug architecture’ that is especially useful in the computer-driven process of filtering chemical libraries; however, this concept is still elusive and ambiguous. Fragment-based drug design or fragonomics, which has recently been getting more and more widespread appeared to offer an alternative way for identifying advantageous drug structures. This methodology assumes the existence of a preferred molecular ‘core’, namely a framework that works as an ‘anchor’ for the ‘ornamenting’ blocks – privileged motifs. Generally, the problem of identifying relevant molecular fragments is a complex issue that is related to the so-called frequent subgraph mining (FSM). More practical FSM approaches to drug design are still a matter of future developments that need some sophisticated algorithms for massive *in-silico* database mining and data processing.

Fragmental topology-activity landscapes (FRAGTAL), a new concept for encoding molecular descriptors for fragonomics into the framework of the molecular database records is presented. Thus, a structural repository containing biological activity data was searched in a substructure mode by a series of molecular fragments constructed in an incremental or decremental manner. The resulted series of database hits annotated with their activities construct FRAGTAL descriptors encoding a frequency of the certain fragments among active compounds and/or their activities. Actually, this method might be interpreted as a simplified adaptation of the frequent subgraph mining (FSM) method. The FRAGTAL method reconstructs the way in which medicinal chemists are used to designing a prospective drug structure intuitively. A representative example of the practical application of FRAGTAL within the ChemDB Anti-HIV/OI/TB database for disclosing new fragments for HIV-1 integrase inhibition is discussed. In particular, FRAGTAL method identifies ethyl malonate amide (EMA) as the diketo acid (DKA) related arrangement. Since new molecular constructs

based on the EMA fragment are still a matter of future investigations we referred to this as an the DKA offspring.

5.

Chemometric analysis of TLC spots and adsorbents by NIR and ATR spectrophotometry

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The TLC infrared detection is very rarely presented in literature, however it is easy to handle. The spot can be measured by NIR-reflectance spectrophotometry without destroying adsorbent layer and by ATR-FTIR spectroscopy after grinding small fragment of adsorbent from the centre of the spot.

The infrared spectra of pure TLC plates and caffeine/theophylline spots in 14 various concentrations (2 – 56 ug per spot, total 15 distinct conentrations) were collected from silica, alumina, DIOL, NH2, CN, RP8, RP18, RP2 and cellulose plates. Thermo Nicolet 67000 with diamond ATR or integrating NIR sphere units were used to collect spectra. The wavenumber ranges were: 650 – 4000 (6950 data points) and 4000 – 10000 (1557 data points). The whole dataset consisted of 555 NIR spectra and 135 ATR-FTIR spectra.

The explorative analysis (scaled PCA) of the NIR dataset led to conclusion, that the adsorbents form very distinct clusters and there is an easy ability to identify adsorbent from NIR spectra of the spot, regardless of caffeine concentration. Only slight dependence of caffeine concentration in spot was observed, which was surely not enough to build quantitative supervised chemometric models. Over 80% of variance was included in two first PCs. There is a clustering tendency between caffeine and theophylline NIR spots on silica, however this tendency is also related to variability between plates, therefore trying to find discriminative model would be overoptimistic.

In the case of ATR-FTIR, the spectra of cellulose and alumina were outliers in multivariate space, and first two PCs (95% of variance) is related to differences between them and other adsorbents. Clustering of other adsorbents can be seen in PC3 and PC4 space (about 2% of variability). Removing of outliers changes only slightly clustering of other adsorbents.

The final conclusion from this preliminary study is that quantitative detection in TLC by infrared method cannot be easily applied. However, the NIR spectrum of the plate is quite constant regardless of presence/absence of any substance in measured place. Taking into the

account the distinction of spectra of various adsorbents, NIR can be useful tool to identify the adsorbent of the plate, even in the case of used/developed plates.

6.

"Quantitative structure-metabolism relationship modeling of new aryl-piperazine derivatives metabolism rates."

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Low metabolic stability of drug derivatives is a factor, that often excludes them from further clinical trials. Therefore, a way to predict this stability in a cheap, fast and efficient manner is valuably considered. In this experiment a half time of 30 potent anti-depressive drugs was evaluated. Several molecular descriptors using Gaussian and Dragon software were also computed. Using Statistica software a transformation and auto-scaling was applied to the whole dataset. Applying multiple linear regression, a model was proposed that quantitatively shows which molecular descriptors possess the most significant effect on metabolic stability of the studied compounds. Metabolic stability test was performed with the use of microsome preparations obtained from rat liver in *in vitro* conditions in the presence of NADPH. The study of the possible first phase metabolic biotransformation catalyzed mostly by cytochrome P450 enzymes was conducted. Separation and quantification of compounds was performed using a Single Quadrupole LC-MS system with C18 column. A relationship between structure of arylpiperazines and their half-time were straight-forward discussed.

7.

THE INFLUENCE OF CHAOTROPIC EFFECT ON RETENTION OF FLUOROQUINOLONES IN RP-HPLC, RP-OPLC AND RP-TLC SYSTEMS

Małgorzata Kamińska[1], Marek Studziński[1], Patrycja Cieśla[1], Anna Czajkowska-Żelazko[1/2], Mateusz Jasikowski[1/3], Karol Pilorz [1] and Irena Choma[1]

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Chaotropic ions are small inorganic compounds causing disruption of the water structure. They are arranged in the so-called Hofmeister series according to ability to cause "chaos" in water structure, what is connected with their polarizability, charge delocalization and symmetry [1]. Chaotropic ions, oppositely to surfactants, show weak interactions with alkyl chains of bonded phase in RP chromatographic systems. However, they influence interaction of basic compounds with alkyl chains increasing their retention. According to Kazakevich and LoBrutto theory, chaotropic anions, as perchlorate or hexafluorophosphate, disrupt hydrogen bridges in water shell surrounding the solute, in this way increasing hydrophobicity of the solute [2,3]. The influence of chaotropic anions on retention of cationic solutes can be also interpreted by ion-pair or dynamic ion-exchange mechanism. Probably the mechanism of retention is complex and related to contribution of all above mentioned models.

Five amphoteric piperazynyl fluoroquinolones, which are bases in acidic conditions, and flumequine, which is neutral at a low pH, were analyzed in HPLC, OPLC and TLC RP systems [4]. The influence of chaotropic ions on retention of these drugs was compared and discussed.

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8.

Solubility parameter used to predict the effectiveness of monolithic in-needle extraction (MINE) device for the direct analysis of liquid samples

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Combination of extraction and chromatographic techniques opens NEW possibilities in sample preparation area. Macroporous poly(styrene-divinylbenzene) (PS-DVB) monoliths with different proportion of monomers were prepared by in situ polymerization in stainless steel needles [1]. MINE devices were used in the preparation of a series of test water samples for chromatographic analysis. Taking into account possible large flow resistance of monolithic sorbent layer it was necessary to examine the permeability of the in-needle device.

So far in-needle technique was relatively seldom used for direct separation of analytes from liquid samples and most often was combined with head-space (HS) or purge and trap (P&T) techniques. This limited application is associated with a high flow resistance produced by a sorbent layer. New proposal - the application of monolithic filling in the in-needle device should prevent changes occurring in the sorbent layer and increase the efficiency of this sample preparation tool.

The magnitude of interactions between three components: monolithic sorbents, eluents and analytes were estimated by using solubility parameters [2]. The expected calculated results were compared with experimental ones. Therefore, it can be concluded, that based on the solubility parameter concept, it is possible to select a suitable sorbent and solvent for the proper isolation of the examined analytes.

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[2] Pietrzyńska M., Adamska K., Szubert M., Voelkel A. Solubility parameter used to predict the effectiveness of monolithic in-needle extraction (MINE) device for the direct analysis of liquid samples, Analytica Chimica Acta 805 (2013) 54–59

9.

Chromatographic analysis of defense sprays for forensic purposes

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Defence sprays are pressurised metal cans equipped with a nozzle and containing liquid solution of active ingredient. The active ingredients are having irritant effect on humans, causing burning sensation, troubled breathing and temporary blindness. Natural and synthetic capsaicinoids (CAP's) as well as chlorobenzylidene malononitryle (CS) are most often encountered on Polish market. Sometimes formulations containing obsolete 2-chloroacetophenone (CN) still can be found. Defence sprays which are freely accessible on polish market are, despite of their name, often used by perpetrators. Items connected with such cases are subjects of chemical analysis in forensic laboratories. Samples are analysed using gas chromatography with mass spectrometry (GC-MS).

If original can is send to be analysed, preparation is limited to taking a sample of liquid content and diluting it with polar organic solvent e.g. methanol. Even for seemingly empty cans some amount of the original content can be recovered after cutting it. If some other materials are to be analysed, like clothes of victim or suspect, the first step of analysis is to separate and concentrate the traces of active component. CS and CN are volatile enough to be separated using passive adsorption from the headspace of the sample. To separate capsaicinoids (active ingredients of "pepper sprays") liquid extraction with methanol must be conducted.

Details of the isolation procedures and parameters of chromatographic analysis will be presented on the example of two real cases: one with PAVA (colourless synthetic capsaicinoid) and one with the traces of CS gas.

10.

Chromatographic methods of identification and purification of styrylquinoline derivatives

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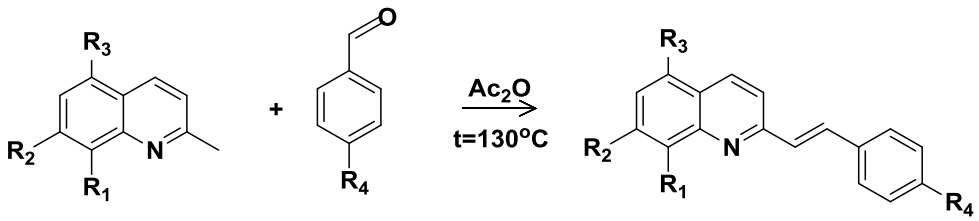
The fungal infections become serious problem of modern medicine. Especially after, the growth of systemic mycoses and the emergence of drug resistance that have been noticed recently. Some simple derivative of quinaldine are effectively applied in the modern pharmacotherapy as 5,7-dichloro-quinolin-8-ol. In this study we are searching for new styrylquinoline derivatives which potentially show antifungal properties. Four synthesis was carried out following the scheme:



1) $\mathbf{R_1}$= -H, $\mathbf{R_2}$= -H, $\mathbf{R_3}$= -H, $\mathbf{R_4}$= $-C_4H_{9;}$
2) $\mathbf{R_1}$= -H, $\mathbf{R_2}$= -H, $\mathbf{R_3}$= -H, $\mathbf{R_4}$= $-OC_4H_7$
3) $\mathbf{R_1}$= -H, $\mathbf{R_2}$= -H, $\mathbf{R_3}$= -H, $\mathbf{R_4}$= $-OC_6H_{13;}$
4) $\mathbf{R_1}$= -OH, $\mathbf{R_2}$= -Cl, $\mathbf{R_3}$= -Cl, $\mathbf{R_4}$= $-C_4H_9$

Post- reaction mixtures were analyzed by thin layer chromatography (TLC) in the following conditions of separation- stationary phase: aluminium sheets coated with silica gel 60 F_{254} (DC Kieselgel 60 F_{254}, Merck), mobile phase: ethyl acetate/ hexane (1:8, v/v). Visualization was carried out at a wavelength of 254 nm. The TLC chromatograms were the basis for the design of column chromatography separation for each product. The detailed procedure are provided in the table:

Synthesis	**Stationary phase**	**Mobile phase**
1	Silica gel 0,035-0,070mm, 60A (Poch S.A.)	ethyl acetate/ hexane (1:8, v/v)
2	Silica gel 0,035-0,070mm, 60A (Poch S.A.)	ethyl acetate/cyclohexane(1:10,v/v)
3	Silica gel 0,035-0,070mm, 60A (Poch S.A.)	ethyl acetate/ hexane (1:8, v/v)
4	Silica gel 0,035-0,070mm, 60A (Poch S.A.)	ethyl acetate/ hexane (1:10, v/v)

11.

Investigation of glycerol oxidation mechanism over nanogold catalyst using NMR and MALDI techniques.

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Abstract

Glycerol constitutes a potential starting material for various industrially valuable products, such as glyceric acid, tartronic acid, acetic acid and acrolein. Heterogeneous catalysts based on nanoparticulate gold supported by a variety of carriers such as: copper, nickel, silica play a key role in the promotion and control of oxidation reactions. The selectivity of oxidation to specific products is determined by numerous parameters, among others: the metal particles size, the pore size of the support and the pH of the reaction medium [1,2].

Understanding the way of the glycerol oxidation and modification of reaction conditions allows to control of the process towards the required products with high selectivity. The reaction mechanism research were performed by spectroscopic techniques ^{1}H, ^{13}C NMR spectra, in the alternative the two-dimensional correlation COSY, HMQC and MALDI.

References

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Acknowledgements

This study was supported by the grant ORGANOMET No: PBS2/A5/40/2014 from the Polish National Research and Development Center

[c] Author received a grant for the project *DoktoRIS - Scholarship program for innovative Silesia* co-financed by the European Union in the framework of the ESF

12.

„Synthesis of thioterephtalamides obtained from methyl esters of chosen aminoacids and thioterephthaloyl chloride”

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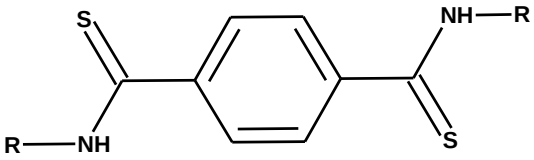
Keywords: thioamides, diamides, terephtalic acid, carrier compound, column chromatography, NMR Spectra

Abstract:

The aim of this study are to synthesizing new thioterephtalic acid diamides (thioterephtalamides) from thioterephthaloyl chloride, phosphorus pentasulfide with carrier compound and methyl esters of chosen aminoacids, investigating the physicochemical properties of the new compounds and trying to find their crystallographic structure. Chemical structure obtained intermediates products and thioterephtalamides was determined by ^{1}H NMR, ^{13}C NMR spectra. Solubility and melting point were determined for new molecules.



R = methyl ester aminoacid

References:

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13.

[4 +2] Cycloaddition reactions - new hexasubstituted benzene derivative.

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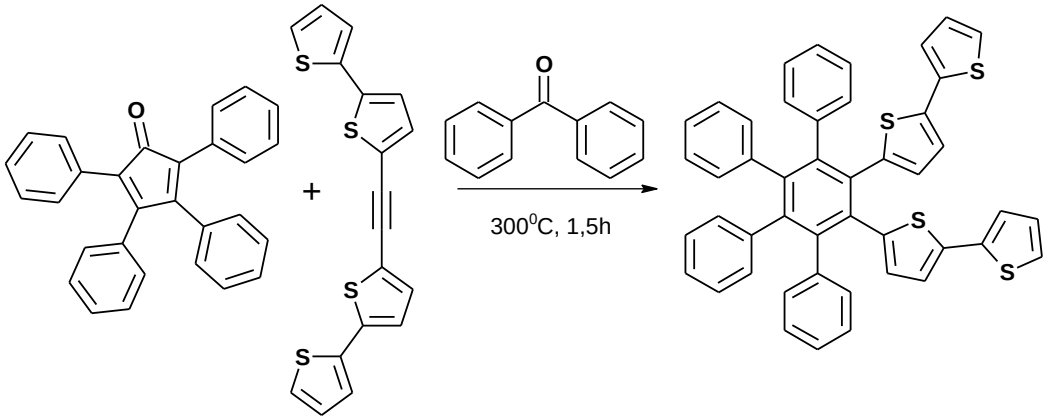
[4 +2] Cycloaddition reaction (with CO-extrusion) of disubstituted alkynes to selected cyclopentadienones creates the new opportunities in the synthesis of organic compounds [1], [2]. This reaction opens up the possibility to obtain compounds with potential uses in the organic electronics: donor-acceptor systems, π- conjugated derivatives or monomers for conductive polymers, to name a few. In the first step of our research bis(2,2'-bithiophene-5-yl)acetylene (in the Sonogashira coupling) was obtained. This alkyne, enables to obtain a various hexasubstituted benzene derivative containing 2,2'-bithiophene substituents (Scheme 1).



Scheme 1. The synthesis of hexasubstituted benzene derivative (example).

The aim of the study was to obtain 1,2-bis(2,2'-bithiophene-5-yl)acetylene by Sonogashira coupling, followed by [4 +2] cycloaddition reaction (with CO-extrusion) to selected cyclopentadienones leading to the formation of hexasubstituted benzene derivative. The structure of all the obtained compounds was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.

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Agata Szłapa acknowledge a scholarships from the DoktoRis project co-financed by the European Social.

14.

SYNTHESIS OF FLUORENE AND CARBAZOLE DERIVATIVES AS FLUORESCENT MATERIALS FOR ORGANIC ELECTRONICS

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Keywords: carbazole, fluorene, Sonogashira coupling, TMSA, TBAF, diacetylene.

Abstract: Nowadays, organic fluorescent compounds are very attractive due to their versatile applications in the fields of organic electronics (e. g.: OLEDs - *Organic Light-Emitting Diodes*, OFETs - *Organic Field-Effect Transistors*, OPVs - *Organic Photovoltaics*) [1], biochemistry, supramolecular chemistry and many others. The large number of organic molecules have been designed and synthesized as potential candidates for optoelectronic materials, such as 9,9-disubstituted fluorene [2] or N-substituted carbazole derivatives [3].

Herein, we present the synthesis of fluorene and carbazole derivatives substituted by terminal alkynes in second or third position, respectively. These compounds were prepared *via* Sonogashira coupling using TMSA (trimethylsilylacetylene), and typical catalytic system CuI/[$PdCl_2(PPh_3)_2$] or [$Pd(PPh_3)_4$]. Furthermore, the novel conjugated dimers of fluorene and carbazole derivatives (connected by 1,3-butadiynes) were obtained *via* Sonogashira coupling. Conjugated fluorene and carbazole dimers have been obtained in reaction between corresponding iodoarens and a gaseous diacetylene (which has been generated from 1,4-dichloro-2-butyne). Additionally, we report an alternative synthetic route for the preparation of above mentioned new compounds from 1,4-bis(trimethylsilyl)butadiyne in the presence of TBAF (tetrabutylammonium fluoride) and standard catalytic system CuI/[$Pd(PPh_3)_4$]. It was found that the second route allowed to obtained the novel compounds in much higher yield.

The new obtained molecules are well soluble in common organic solvents. Besides, all the new compound in the present study are fluorescent. The optical and electrochemical properties of new derivatives were investigated using UV-Vis and luminescence spectroscopy. Chemical structure of all products were characterized using HRMS, ^{1}H NMR and ^{13}C NMR spectroscopy.

These compounds will be further used as ligands for transition-metal complexes. The novel compounds are very promising and interesting materials which can be applied in organic electronics.

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Marek Matussek acknowledge a scholarships from the DoktoRis project co-financed by the European Social.

15.

[4 +2] Cycloaddition reactions - new hexasubstituted benzene derivative.

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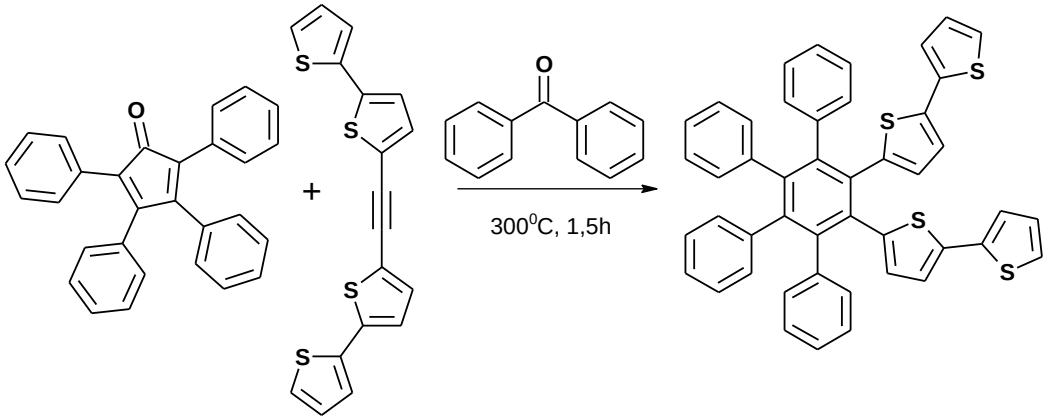
[4 +2] Cycloaddition reaction (with CO-extrusion) of disubstituted alkynes to selected cyclopentadienones creates the new opportunities in the synthesis of organic compounds [1], [2]. This reaction opens up the possibility to obtain compounds with potential uses in the organic electronics: donor-acceptor systems, π- conjugated derivatives or monomers for conductive polymers, to name a few. In the first step of our research bis(2,2'-bithiophene-5-yl)acetylene (in the Sonogashira coupling) was obtained. This alkyne, enables to obtain a various hexasubstituted benzene derivative containing 2,2'-bithiophene substituents (Scheme 1).



Scheme 1. The synthesis of hexasubstituted benzene derivative (example).

The aim of the study was to obtain 1,2-bis(2,2'-bithiophene-5-yl)acetylene by Sonogashira coupling, followed by [4 +2] cycloaddition reaction (with CO-extrusion) to selected cyclopentadienones leading to the formation of hexasubstituted benzene derivative. The structure of all the obtained compounds was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.

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Agata Szłapa acknowledge a scholarships from the DoktoRis project co-financed by the European Social.

15.

New tetrasubstituted benzene derivative - [2+2+2]cycloaddition reactions

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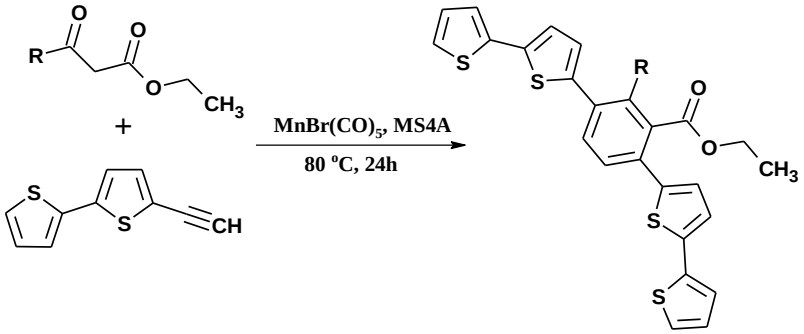
Thiophene derivatives are very important group of organic materials used in electronics. Therefore, there are continously ongoing developments in the new methods of obtaining both molecules and macromolecules with thiophene motif. A completely new perspective for the synthesis of thiophene derivatives is the [2+2+2] cycloaddition reactions of terminal alkynes to β-keto esters catalyzed by manganese complex i.e. [$MnBr(CO)_5$] [1], [2]. It make possible to obtain a dericatives with potential usage in the organic electronics, that contains heteroaromatic substituents in position 1 and 4, respectively.

The aim of the study was to obtain 5-ethynyl-2,2'-bithiophene by Sonogashira coupling [3], followed by the [2 +2 +2] cycloaddition to selected β-keto esters , leading to the formation of tetrasubstituted benzene derivatives (Scheme 1). The structure of all the compounds obtained was confirmed by ^{1}H NMR, ^{13}C NMR, HRMS.



Scheme 1. [2+2+2] cycloaddition reactions of 5-ethynyl-2,2'-bithiophene to β-keto esters.

References:

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*Sławomir Kula is supported by the Forszt project co-financed by EU from the European Social Fund.

16.

Separation **isomers bromoderivatives by a new synthesis aminolevulinic acid.**

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17.

Sorption of heavy metal ions on graphene oxide modified with (3-mercaptopropyl)-trimethoxysilane

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Graphene oxide (GO) is a novel two-dimensional carbon nanomaterial which is considered one of the most interesting materials in recent years. GO can be synthesized through the strong oxidation of graphite with the use of potassium permanganate or potassium dichromate. Properties of the GO such as presence of reactive functional groups, hydrophilic nature and large surface area are very important from the standpoint of the sorption process [1].

The aim of present work was to perform a synthesis of GO by Hummer method [2] and functional modification of its surface by (3-mercaptopropyl)trimethoxysilane (GO-SH) [3]. The sorption of selected metal ions (Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II)) on GO-SH was investigated. The results of experiment indicate that maximum adsorption can be achieved in broad pH ranges: 5-10 for Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II). The maximum adsorption capacities of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) on GO-SH at pH = 5 are 20.9, 20.8, 40.9, 22.2, 36.4, 108.0 mg g^{-1}, respectively. Adsorption isotherms suggest that sorption of metal ions on GO-SH nanosheets is monolayer coverage and adsorption is controlled by chemical adsorption involving the strong surface complexation of metal ions with the sulfur-containing groups on the surface of GO-SH.

18.

Sulfonic-modified graphene oxide in adsorption of metal ions.

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Graphene and graphene oxide (GO) have received much attention for their many potential application in analytical chemistry mainly due to high adsorptive properties. Unmodified and modified GO can be applied as a sorbent in solid-phase extraction (SPE) in preconcentration and further determination of trace metal ions in water samples [1,2]. The oxidation process introduces large quantities of oxygen atoms on the GO surface in the form of hydroxyl, epoxy, carboxyl or ester groups. Introduced groups can efficiently bind the metal ions by sharing an electron pair.

The aim of this study was to investigate the sorption capacities of sulfonic acid functionalized graphene oxide (GO-SO_3H) towards heavy metal ions, such as Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II). GO-SO_3H was prepared as follows. First step of GO-SO_3H preparation was synthesis of GO by the oxidation of graphite powder according to Hummers method [3]. Subsequently, the functional groups introduced onto the GO surface reacted with (3-mercaptopropyl)trimethoxysilane (3-MPTMS) in order to obtain GO-SH [4]. In the last step thiol groups were oxidized to the sulfonic acid groups using H_2O_2 [5]. Langmuir and Freundlich models were applied to calculate the maximum adsorption capacities of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) ions on the GO-SO_3H surface. The concentration of metals ions after experiments were determination using inductively coupled plasma emission spectrometry (ICP-OES). The study shows that GO-SO_3H can be very attractive as sorbent in analytical chemistry due to its unique adsorption capacities. Obtained results revealed that GO-SO_3H is an attractive and efficient sorbent in developed methodology.

19.

Dispersive micro solid phase extraction for preconcentration of selected metal ions of graphene.

Klaudyna Czech, Damian Stefański, Katarzyna Pytlakowska, Violetta Kozik

20.

“Sila”-Sonogashira coupling in a heterogeneous system - investigations using chromatographic techniques.

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Numerous reports describe the coupling of trimethylsilylacetylene with aryl halides in Sonogashira-type reactions. The C(sp)–Si bond is generally not affected by these reaction conditions. The silyl group can, therefore, if desired, subsequently be removed to furnish a structurally modified terminal alkyne. The trimethylsilyl group is thereby used as a protective group. This process avoids totally the formation of the alkyne homocoupling Glaser-type product. In "Sila"-Sonogashira reaction, aryl halides can be coupled directly with alkynylsilanes via the Si–C bond activation by using the Pd/Cu catalyst system In our study, we wanted to check the possibility of the “sila”-Sonogashira reaction in a heterogenous systems using Pd/Cu catalysts. Various chromatographic methods were used for the purpose of this study. This includes: TLC, HPLC and HPLC-ESI MS, MALDI TOF. These techniques provide qualitative and quantitative specification of the reaction products.

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Acknowledgements

This study was supported by the Grant ORGANOMET No: PBS2/A5/40/2014 from the Polish National Research and Development Center.

[3] Author received a grant for the project *DoktoRIS - Scholarship program for innovative Silesia* co-financed by the European Union in the framework of the ESF