

Paris, 4-6 July 2019

FRENCH-POLISH CHEMISTRY CONGRESS BOOK OF ABSTRACTS

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Short history of Assises Franco-Polonaises de Chimie

I^e Assises began with the evening gala – Soiree d'hommage à Jean-Marie Lehn – on July 23, 2015 at the Embassy of the Republic of Poland in Paris, dedicated to **Prof. Jean-Marie Lehn** from the University of Strasbourg, Nobel laureate in chemistry in 1987, the member of the Collège de France. Another important event was a popular science lecture given by Prof. Jean-Marie Lehn "De la Matière à la Vie: Chimie? Chimie" in French, his native language. The audience had no doubts that Prof. Jean-Marie Lehn is a virtuoso of chemistry. July 24, 2015 was the day of the scientific conference Assises Franco-Polonaises de Chimie, where 15 lectures were given. At the end of the conference, young scientists, PhD students at the Faculty of Chemistry, Adam Mickiewicz University, presented the results of their research to Prof. Jean-Marie Lehn. The intimate atmosphere of the meeting in the stylish hall of the Polish Academy of Sciences in Paris made these young people most satisfied with the participation in the meeting, since they had the opportunity to talk to the best French researchers.

On March 14-15, 2018 at the Scientific Center of the Polish Academy of Sciences in Paris second scientific symposium took place – II^e Assises Franco-Polonaises de Chimie. The festive evening on March 14, 2018 at the Embassy of the Republic of Poland in Paris was dedicated to **Prof. Jean-Pierre Sauvage**, University of Strasbourg, Nobel laureate in the field of chemistry in 2016 together with Sir J. Fraser Stoddart and Professor Ben L. Feringa, member of French Académie des Sciences, co-inventor of molecular machines, who gave a popular science lecture entitled "Molecular machines in biology and in chemistry". In addition, on March 15, 2018, 17 lecturers presented their achievements in various fields: from supramolecular chemistry through catalysis, hybrid materials, graphene to applications in sensors and power engineering.

The Assises Franco-Polonaises de Chimie are intended to extend and disseminate the achievements of Polish and French research groups and to promote international cooperation.

FRENCH-POLISH CHEMISTRY CONGRESS CONFERENCE PROGRAM

Thursday 4th - Embassy of the Republic of Poland in Paris

18:30 **OPENING CEREMONY**

18:45 **Prof. KRZYSZTOF MATYJASZEWSKI**, Carnegie Mellon University, Pittsburgh,
Lodz University of Technology
MACROMOLECULAR ENGINEERING BY TAMING FREE RADICALS

Friday 5th - Sorbonne University

SESSION 1

Chairmen: Prof. Łukasz Albrecht, Prof. Florian Monnier

10:00 **Prof. BRUNO AMÉDURI**, Institute Charles Gerhardt, ENSCM, CNRS, Montpellier
*2-TRIFLUOROMETHACRYLIC ACID (MAF) VERSATILE MONOMER FOR
THE INSERTION OF FUNCTIONAL GROUPS IN PVDF*

10:30 **Prof. Teofil Jesionowski**, Poznan University of Technology
FROM HYBRID MATERIALS TO BIOTECHNOLOGY AND NANOMEDICINE

10:45 **Dr. Yvain Nicolet**, Institut de Biologie Structurale, Grenoble
MECHANISM OF THE TRYPTOPHAN LYASE NosL

11:00 **Prof. Bronisław Marciniak**, CAT, Adam Mickiewicz University, Poznań
*PHOTOOXIDATION OF METHIONINE-CONTAINING PEPTIDES: FROM MODEL
COMPOUNDS TO PROTEINS – MECHANISTIC STUDIES*

11:15 **Prof. Will Skene**, Université de Montréal
TOWARDS EXTENDED DUTY CYCLE OF ELECTROCHROMIC MATERIALS

11:30 **Prof. Wojciech Macyk**, Jagiellonian University, Kraków
SELECTED APPROACHES TO PHOTOCATALYTIC CARBON DIOXIDE FIXATION

11:45 **Prof. Anna Chrostowska**, Université de Pau et des Pays de l'Adour
*THE SYNERGY BETWEEN THEORY AND EXPERIMENT IN DEVELOPING THE
BASIC SCIENCE OF NEW BN HETEROAROMATICS*

12:00 **Prof. Miłosz Pawlicki**, University of Wrocław
*ORGANOBORON COMPLEXES IN THE EDGE SHARING MACROCYCLES – THE
TRIPHRYN(2.1.1)-TETRAPHYRIN(1.1.1.1) HYBRID*

12:15 **Prof. Mihail Barboiu**, Institut Europeen des Membranes, ENSCM, CNRS, Montpellier
ARTIFICIAL WATER CHANNELS

12:30 **LUNCH BREAK**

FRENCH-POLISH CHEMISTRY CONGRESS CONFERENCE PROGRAM

SESSION 2

Chairmen: Prof. Regis Gauvin, Prof. Bogdan Marciniec

- 14:30 Prof. ADAM PRONÍ**, Warsaw University of Technology
NONTOXIC SEMICONDUCTOR NANOCRYSTALS FOR ELECTRONICS AND BIOMEDICINE – SYNTHESIS AND FUNCTIONALIZATION
- 15:00 Prof. Katarzyna Matczyszyn**, Wrocław University of Science and Technology
PHOTOACTIVE SYSTEMS BASED ON PHOTOCHROMES AND BIOMOLECULES
- 15:15 Prof. Mathias Destarac**, IMRCP, Université Toulouse 3 Paul Sabatier, CNRS
THIOLACTONE-FUNCTIONAL REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATION AGENTS FOR ADVANCED MACROMOLECULAR ENGINEERING
- 15:30 Prof. Agnieszka Z. Wilczewska**, University of Białystok
COPOLYMERS WITH LIPID MOIETIES AS DRUG CARRIERS
- 15:45 Dr. Till Bousquet**, University of Lille, CNRS
VISIBLE-LIGHT-MEDIATED HYDROXYCARBONYLATION OF DIAZONIUMS SALTS
- 16:00 SHORT BREAK**

SESSION 3

Chairmen: Prof. Anna Chrostowska, Prof. Łukasz John

- 16:15 Prof. Beata Nowicka**, Jagiellonian University, Kraków
THIN FILMS OF SOLVATOMAGNETIC CN-BRIDGED COORDINATION POLYMERS
- 16:30 Dr. Tadeusz M. Muzioł**, Nicolaus Copernicus University in Toruń
STRUCTURAL AND MAGNETIC STUDIES OF COMPLEXES IN SYSTEMS CONTAINING $[Cr/Fe(ox)_3]^3$ AND $[Cu(bpy/phen)_2]^{2+}$ UNITS
- 16:45 Prof. David Virieux**, ICGM, ENSCM, CNRS, Montpellier
WHAT ARE THE FRONTIERS OF ATROPOCHIRALITY?
- 17:00 Dr. Karolina Pułka-Ziach**, University of Warsaw
ELECTRON TRANSPORT THROUGH HELICOMIMETIC OLIGOUREA FOLDAMERS
- 17:15 Dr. Roza Szweda**, ISIS, University of Strasbourg, CNRS
SEQUENCE-DEFINED POLYMERS – A NEXT GENERATION DATA STORAGE MEDIUM
- 17:30 Dr. Justyna Walkowiak-Kulikowska**, Adam Mickiewicz University, Poznań
SYNTHESIS OF FLUORINATED STYRENE DERIVATIVES AND ITS APPLICATION FOR PREPARING AROMATIC FLUOROPOLYMERS

FRENCH-POLISH CHEMISTRY CONGRESS CONFERENCE PROGRAM

Saturday 6th - Polish Academy of Sciences
Scientific Center in Paris

SESSION 4

Chairmen: Prof. Izabela Nowak, Prof. Mihail Barboiu

- 10:00 **Prof. MIR WAIS HOSSEINI**, Institut Le Bel, University of Strasbourg
WELDING CRYSTALS
- 10:30 **Prof. Krzysztof Woźniak**, University of Warsaw
EXPERIMENTAL CHARGE DENSITY DISTRIBUTION IN GROSSULAR UNDER HIGH PRESSURE
- 10:45 **Dr. Yvan Six**, LSO, CNRS, ENSTA, Ecole polytechnique, IP Paris, Palaiseau
BICYCLIC AMINOCYCLOPROPANES AS PRECURSORS OF VARIOUS NITROGEN CONTAINING POLYCYCLIC SYSTEMS
- 11:00 **Dr. Bartosz Szyszko**, University of Wrocław
CHIRAL PHENANTHROPORPHYRINOIDS
- 11:15 **Prof. Richard Daniellou**, Université d'Orléans
CHEMO-ENZYMATIC SYNTHESIS OF A SIMPLE THIOGALACTOLIPIDE FORMING RESPONSIVE HYDROGEL FOR THE LIBERATION OF COSMETIC AGENTS
- 11:30 **Prof. Robert Podgajny**, Jagiellonian University, Kraków
SHAPING PROPERTIES BY PLAYING WITH CYANIDE-BRIDGED COORDINATION BACKBONES
- 11:45 **Dr. Kamila B. Muchowska**, ISIS, Université de Strasbourg, CNRS
SYNTHESIS AND BREAKDOWN OF UNIVERSAL METABOLIC PRECURSORS PROMOTED BY IRON
- 12:00 **COFFEE BREAK**

SESSION 5

Chairmen: Prof. Valerie Marvaud, Prof. Miłosz Pawlicki

- 12:30 **Prof. Marek Samoć**, Wrocław University of Science and Technology, NCN
MULTIPHOTON ABSORPTION IN MOF-BASED NLO PIGMENTS AS A TOOL FOR BETTER REMOTE TEMPERATURE MEASUREMENTS
- 12:45 **Dr. Mickaël Ménand**, Sorbonne Université, CNRS, IPCM, Paris
CHIRAL COMMUNICATIONS IN A THREE-LEVEL CHIRALITY TOTEM. REMOTE CONTROL OF THE MÖBIUS AROMATIC TWISTING IN HEXAPHYRIN CYCLODEXTRIN HYBRIDS

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FRENCH-POLISH CHEMISTRY CONGRESS CONFERENCE PROGRAM

- 13:00 Prof. Łukasz Albrecht**, Łódź University of Technology
VINYLOGY CONCEPT IN THE SYNTHESIS OF SELECTED CARBO- AND HETEROCYCLES
- 13:15 Dr. Paweł Dydio**, ISIS, University of Strasbourg, CNRS
DUAL-CATALYTIC SYSTEMS FOR FUNCTIONALIZATION OF UNREACTIVE SITES OF MOLECULES
- 13:30 Dr. Adam Gorczyński**, Adam Mickiewicz University, Poznań
(METALLO)SUPRAMOLECULAR SYSTEMS FOR TACKLING THE ENVIRONMENTAL ISSUES
- 13:45 Prof. Julien Leclaire**, Université de Lyon
DYNAMIC COVALENT CHEMISTRY AT WORK: SIMULTANEOUS CO₂ CAPTURE AND METAL PURIFICATION FROM WASTE STREAMS
- 14:00 Prof. Artur R. Stefankiewicz**, Adam Mickiewicz University, Poznań
GENERATION OF FUNCTIONAL METALLOSUPRAMOLECULAR ASSEMBLIES BASED ON AMBIDENTATE LIGANDS
- 14:15 LUNCH BREAK**
- 15:30 POSTER SESSION**

SESSION 6

Chairmen: Prof. Janusz Jurczak, Prof. Artur R. Stefankiewicz

- 16:30 Prof. KAROL GRELA**, CNBCH, University of Warsaw
"MISSIONS IMPOSSIBLE" IN RUTHENIUM CATALYZED OLEFIN METATHESIS
- 17:00 Prof. JEAN-MARIE LEHN**, ISIS, Université de Strasbourg
PERSPECTIVES IN CHEMISTRY: TOWARDS ADAPTIVE CHEMISTRY
- 18:00 CLOSING CEREMONY**

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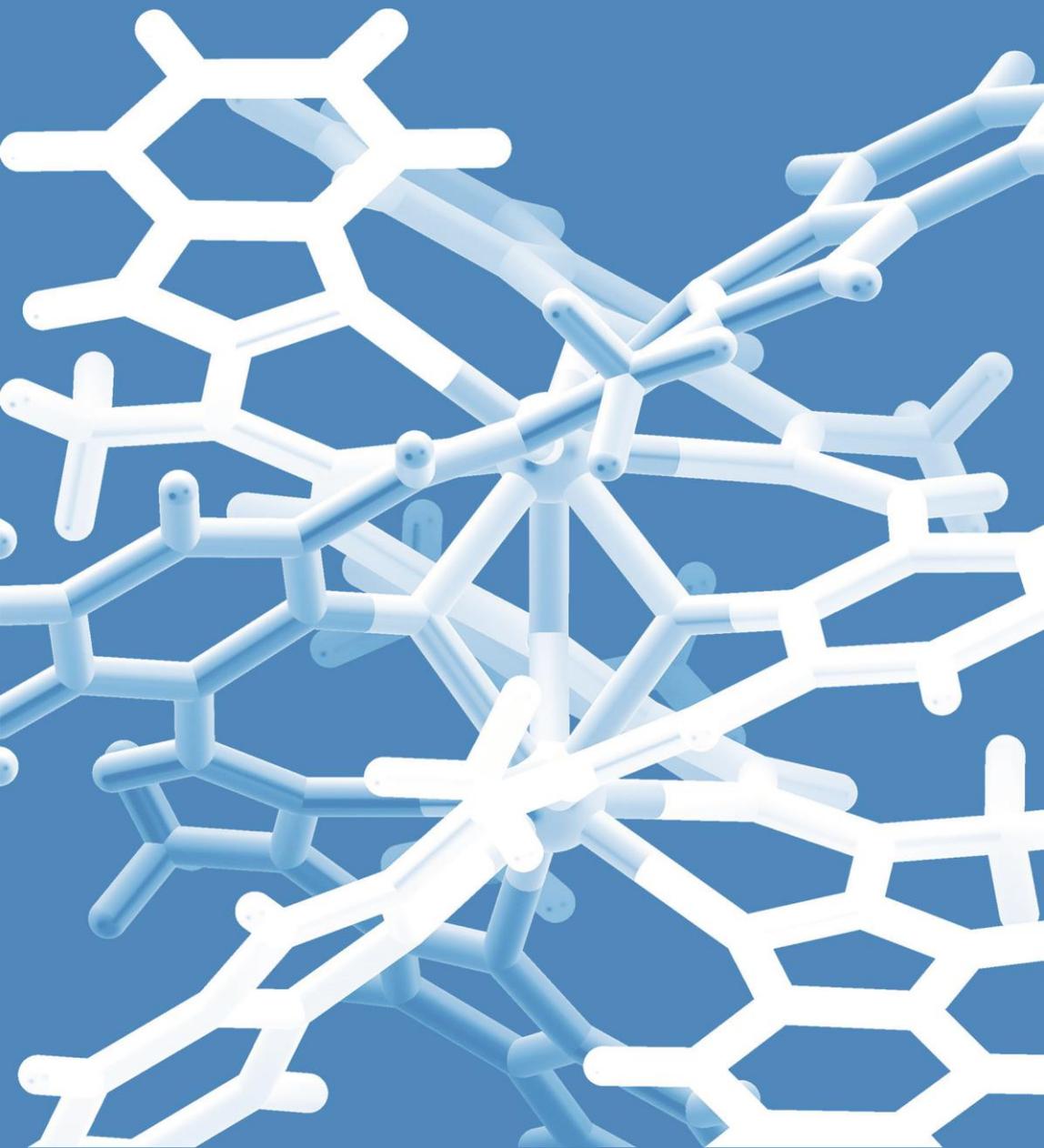
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Centre Scientifique à Paris

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Paris, 4-6 July 2019

FRENCH-POLISH CHEMISTRY CONGRESS
SPECIAL SPEAKERS



MACROMOLECULAR ENGINEERING BY TAMING FREE RADICALS

Krzysztof Matyjaszewski

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Macromolecular Engineering (ME) can be defined as a process comprising rational design of (co)polymers with specific architecture and functionality, followed by precise and efficient polymer synthesis and processing in order to prepare advanced materials with target properties. Preparative ME requires controlled / living polymerization. Radical polymerization could be very well suited for ME due to tolerance to many functionalities. Unfortunately, free radicals are difficult to be controlled, have very short life times (<1 s) and are involved in side reactions. Taming free radicals has been very challenging but was eventually accomplished by living radical polymerization with dynamic equilibria between minute amounts of free radicals and large pool of dormant species. Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen ligands are among most efficient controlled/living radical polymerization systems. ATRP of vinyl monomers was employed for *macromolecular engineering* of polymers with precisely controlled molecular weights, low dispersities, designed shape, composition and functionality. Examples of block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and organic-inorganic hybrid materials and bioconjugates prepared with high precision will be presented. These polymers can be used as components of various advanced materials such as health and beauty products, biomedical and electronic materials, coatings, supersoft elastomers, lubricants, or sealants. Special emphasis will be on nanostructured functional hybrid materials for applications related to biomedicine, environment, energy and catalysis.

References

- [1] K. Matyjaszewski, *Adv. Mat.*, 2018, 30, 1706441.
- [2] T.G. Ribelli, F. Lorandi, M. Fantin, K. Matyjaszewski, *Macromol. Rapid Comm.* 2019, 40, 1800616.
- [3] G. Xie, M.G. Martinez, M. Olszewski, S.S. Sheiko, K. Matyjaszewski, *Biomacromolecules* 2019, 20, 27-54.

PERSPECTIVES IN CHEMISTRY: TOWARDS ADAPTIVE CHEMISTRY

Jean-Marie Lehn

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Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. Similarly, molecular chemistry becomes a dynamic covalent chemistry (DCC) on introduction into the molecular entity of covalent bonds that may form and break reversibly, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. Taken together, these features define a *Constitutional Dynamic Chemistry* (CDC) covering both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. It takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

CDC generates networks of dynamically interconverting constituents, *constitutional dynamic networks*, presenting *agonistic* and *antagonistic* relationships between their constituents that may respond to perturbations by physical stimuli or to chemical effectors. It applies in chemistry as well as in materials science.

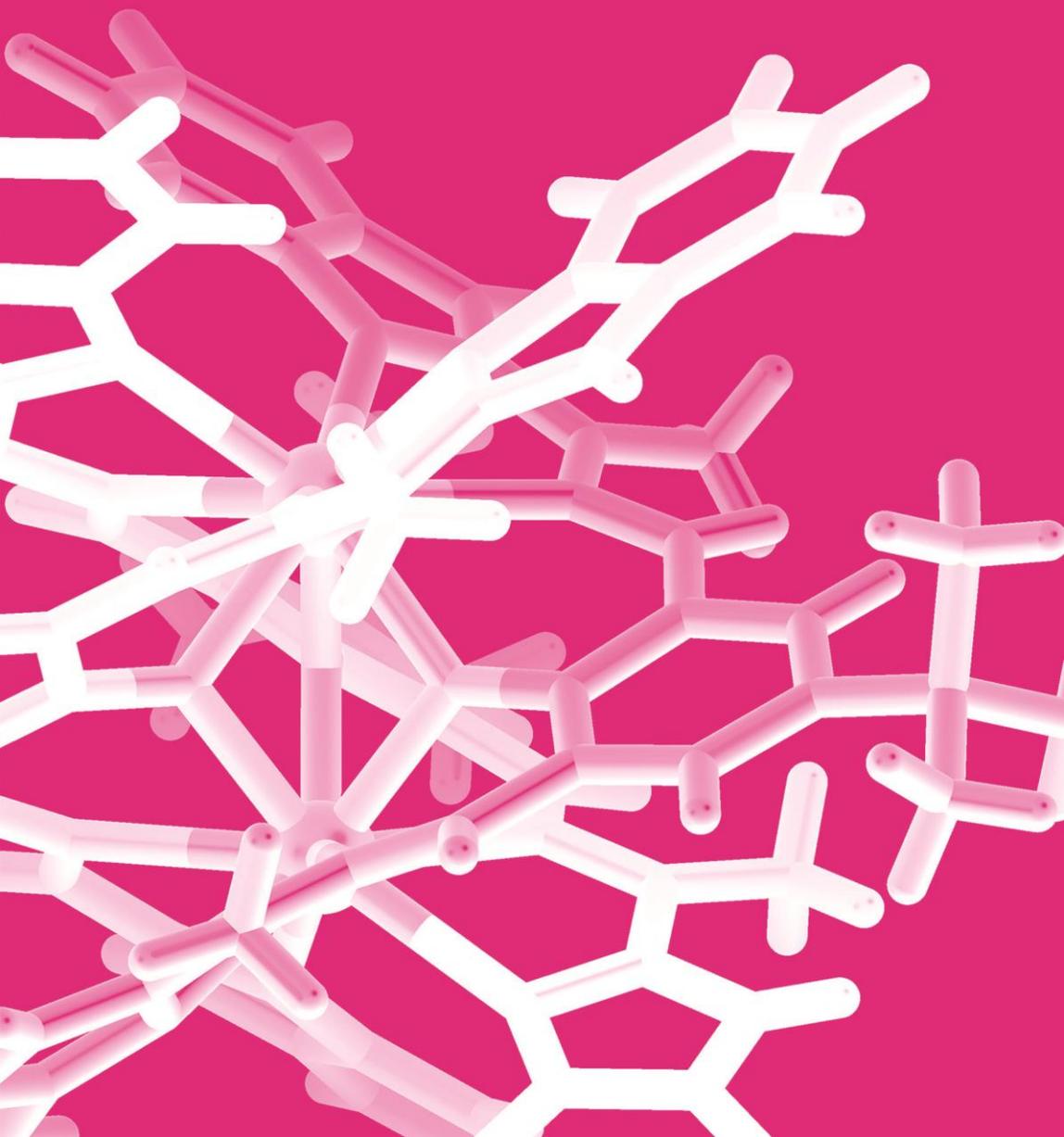
The implementation of these concepts points to the emergence of *adaptive* and *evolutionary chemistry*, towards *systems of increasing complexity*.

References

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FRENCH-POLISH CHEMISTRY CONGRESS PLENARY SPEAKERS



2-TRIFLUOROMETHACRYLIC ACID (MAF) VERSATILE MONOMER FOR THE INSERTION OF FUNCTIONAL GROUPS IN PVDF

Mohammad Wehbi, Sanjib Banerjee, Bruno Améduri

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2-Trifluoromethacrylic acid (MAF) is a versatile building block for the synthesis of new functional monomers [1] It can be homopolymerized by anionic initiation but failed in the presence of any radical systems. However, its radical copolymerization with vinylidene fluoride (VDF) has been successful. This presentation reports overall strategies to synthesize novel functional 2-trifluoromethacrylate monomers and macromonomers as well as their radical copolymerization with VDF, leading to various materials such as higher thermal stable thermoplastics, anticorrosion and adhesive [2] hybrid coatings, membranes, and polymer gel electrolytes for Lithium ion batteries [3] (Fig. 1) [4].

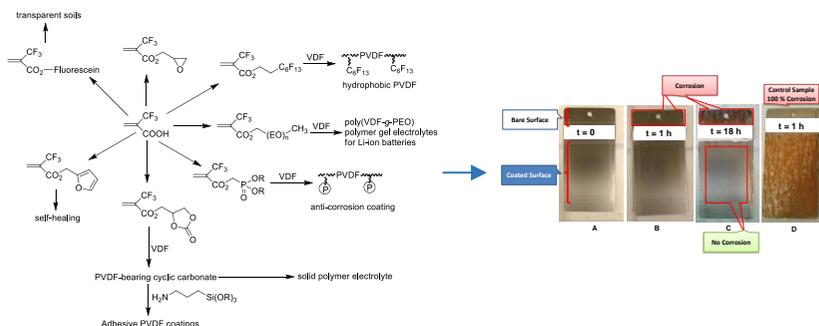


Figure 1. Overall strategies to synthesize novel functional 2-trifluoromethyl monomers from 2-trifluoromethacrylic acid (MAF) and their radical copolymerization with VDF (left). Steel plates coated with poly(VDF-co-MAF Phosphonate) copolymer at the beginning of the experiment (A), after 1 h (B), and after 18 h (C). (D): Uncoated steel plate as reference sample after 1 h (right).

References

- [1] Y. Patil, B. Améduri, *Progr. Polym. Sci.*, 2013, 38, 703–739.
- [2] M. Wehbi, S. Banerjee, *et al. Macromolecules*, 2017, 50, 9329–9339.
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NONTOXIC SEMICONDUCTOR NANOCRYSTALS FOR ELECTRONICS AND BIOMEDICINE – SYNTHESIS AND FUNCTIONALIZATION

Piotr Bujak, Patrycja Kowalik, Adam Pron

Warsaw University of Technology, Noakowskiego 3, 00664 Warszawa, Poland
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Initially prepared semiconductor nanocrystals contained toxic elements (Cd, Pb etc.) which severely limited their technological applications [1]. More recently it turned out that these toxic nanocrystals can be successfully replaced by stoichiometric (Cu (Ag)InS(Se)₂) and alloyed (Cu(Ag)-In-S(Se)) nanocrystals. Ternary (CuFeS(Se)₂) and quaternary (Cu₂ZnSnS(Se)₄) nanocrystals which do not contain indium - one of the most expensive elements used in modern electronics - have also been prepared [2,3].

In the presented lecture different methods of the nanocrystals preparation will be comparatively discussed as well as methods of their surface modification with functionalized ligands [4].

Examples of the use of these organic/inorganic hybrids as components of thermoelectric materials [5,6] or drug carriers capable of recognizing cancer cells [7] will be given.

References

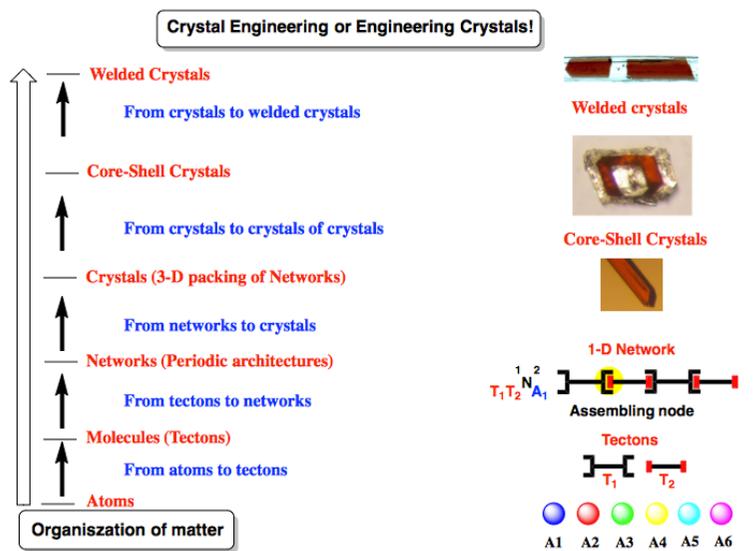
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WELDING CRYSTALS

Mir Wais Hosseini

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Bridging the gap between microscopic (atoms and molecules) and macroscopic (materials) worlds is challenging and requires construction strategies. At the intersection of supramolecular and solid state chemistry and material sciences, we have developed an approach called molecular tectonics. This approach is based on supramolecular synthesis of crystalline materials seen as extended periodic molecular networks. Their construction by selfassembly processes results from repetitive molecular recognition events between programmed tectons or building blocks. The approach is operational and versatile and allows, not only the design and construction of a variety of organic or hybrid complex architectures and core-shell crystals, but also the welding, under mild condition, of crystals into networks of crystals.



"MISSIONS IMPOSSIBLE" IN RUTHENIUM CATALYZED OLEFIN METATHESIS

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Ruthenium-catalyzed olefin metathesis reactions represent an attractive and powerful transformation for the formation of new carbon-carbon double bonds [1]. This area is now quite familiar to most chemists as numerous air and moisture stable ruthenium catalysts are available that enable a plethora of olefin metathesis reactions [1]. However, decreasing the loading and then the trace amount of a catalyst in products, selectivity issues during self-CM and ethenolysis, etc. still remain a challenge, making industrial applications of this methodology difficult. These limitations can be solved by designing new, more selective and stable catalysts and catalysts that can be easier removed or recycled. New catalysts can even make a metathesis based macrocyclisation at high concentration possible for the first time. During the lecture a number of representative examples will be presented.

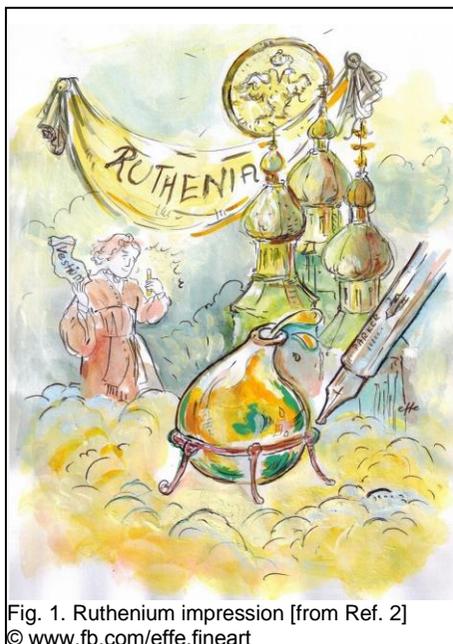


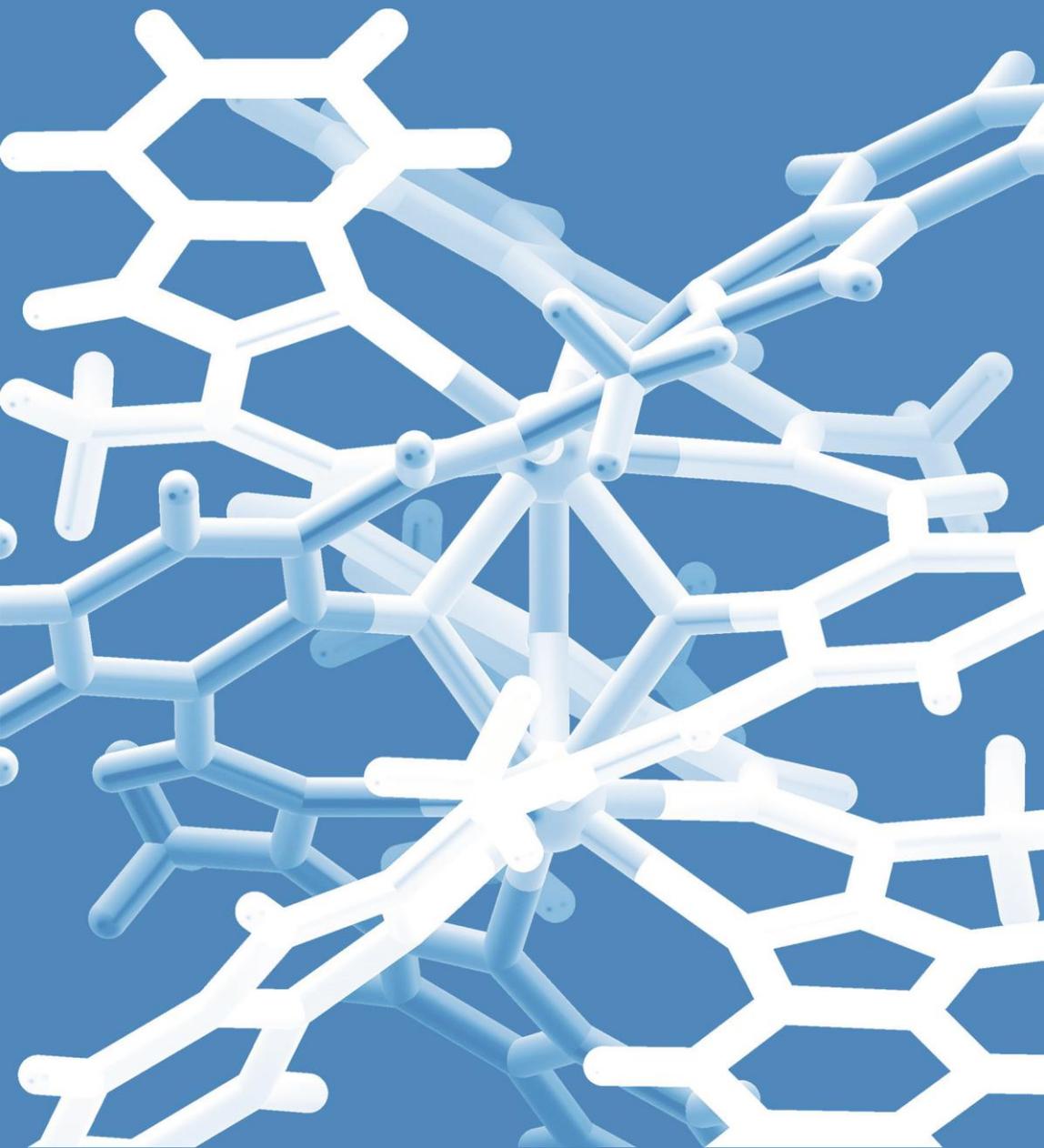
Fig. 1. Ruthenium impression [from Ref. 2]
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References

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Paris, 4-6 July 2019

FRENCH-POLISH CHEMISTRY CONGRESS
INVITED SPEAKERS



FROM HYBRID MATERIALS TO BIOTECHNOLOGY AND NANOMEDICINE

Teofil Jesionowski

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Hybrid materials have currently a great impact on numerous future developments including chemistry, materials science, and environmental protection. Recently, a significant progress has been made in the area of inorganic-organic multifunctional hybrid materials and nanocomposites based on renewable biopolymers (including lignin, chitin, polydopamine, etc.). Considering the variety of combinations of different sources (their individual features and new properties coming from the synergy of components), inorganic-organic hybrids represent an intriguing class of materials with a wide spectrum of applications.

The main aim of this talk is to present recent studies on the development of lignin- and chitin-based hybrid materials as well as the current state of knowledge on marine sponge skeleton uses. Additionally, development on biosensors design strategy based on hybrid materials components as well as selected aspect of nanomedicine in respect to cancer treatment will be emphasized.

First, novel lignin-based hybrid functional materials are presented with special emphasis on their use as electrochemical sensors and/or biosensors, (bio)sorbents for removal of hazardous metal ions, and relatively cheap and pro-ecological polymer fillers. Our recent studies show that chitin-based hybrid materials, obtained accordingly to the Extreme Biomimetic concept, represent a new class of biomaterials with entirely novel physicochemical and structural properties useful for applications in biomedicine and optical devices. Some aspects of dye adsorption on sorbents supported on the skeletons of marine sponges are briefly presented. Finally the role of bio-based supports for enzyme immobilization are also documented. The last topic is dedicated to novel designed materials for cancer treatment.

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MECHANISM OF THE TRYPTOPHAN LYASE NosL

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The radical *S*-adenosyl-L-methionine tryptophan lyase NosL uses radical-based chemistry to convert L-tryptophan into 3-methylindole-2-carboxylic acid (MIA), a fragment in the biosynthesis of the thiopeptide antibiotic nosiheptide. This complex reaction involves several successive steps corresponding to (i) the activation of a specific hydrogen-atom abstraction, (ii) an unprecedented $\cdot\text{CO}_2^-$ radical migration, (iii) a cyanide fragment release, and (iv) the termination of the radical-based reaction. *In vitro* study of this reaction is made more difficult because the enzyme produces a significant amount of a shunt product instead of the natural one. In this presentation, we will discuss further how combining X-ray crystallography, electron paramagnetic resonance spectroscopy and quantum and hybrid quantum mechanical/molecular mechanical calculations, we have made significant progresses in our understanding of the radical-based mechanism of the enzyme, and how the protein matrix controls the reaction. These result pave the way to protein engineering to develop variants of the MIA fragment that could be integrated into the nosiheptide, in order to increase our panel of available molecules to struggle against multidrug-resistant Gram-positive pathogens.

PHOTOOXIDATION OF METHIONINE-CONTAINING PEPTIDES: FROM MODEL COMPOUNDS TO PROTEINS –MECHANISTIC STUDIES

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The oxidation reactions of methionine (Met), its derivatives, and Met-containing peptides have been studied for many years [1-3]. This exciting, and more than twenty-year long, excursion into the mechanisms of photoinduced oxidation of sulfur-containing model compounds, peptides and proteins will be discussed.

To illustrate a complexity of the system studied, some examples will be presented:

- competitive photooxidation of tyrosine and methionine residues in enkephalins, an example of intramolecular secondary electron transfer reactions [4],
- photoinduced C-C-coupling reactions of rigid diastereomeric benzophenone-methionine dyads – intramolecular benzophenone sensitized oxidation [5],
- formation of three-electron sulfur-sulfur bonds as a probe for the interaction between side chains of Met residues - oligoproline peptides containing N- and C-terminal methionine residues [6].

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TOWARDS EXTENDED DUTY CYCLE OF ELECTROCHROMIC MATERIALS

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The reversible spectroscopic changes with applied potential is defined as electrochromism [1]. Electrochromic materials with visible colors that can be detected by the common user are possible with conjugated organic materials [2]. Colors spanning the visible region are possible by incorporating aromatics of varying electron richness into the conjugated framework [3].

Conjugated azomethines are interesting electrochromic materials. They can be considered as environmentally friendly as innocuous water is the by-product formed during their preparation. More interestingly, the intrinsic electron withdrawing character of the azomethine leads to visibly colored materials with relatively short degrees of conjugation [4]. Despite their desired spectroscopic properties, their capacity to sustain multiple redox cycles without degrading lags behind their all carbon polymeric counterparts. It will be demonstrated that extended redox duty cycles of azomethines having repeated color switching capacities are possible with structural modification.

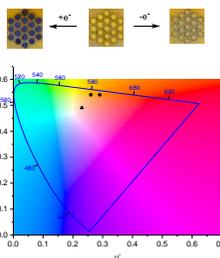


Figure 1. Representative color change possible with oxidation of azomethines occurring at the working gold honeycomb electrode (top) and color coordinate diagram (bottom).

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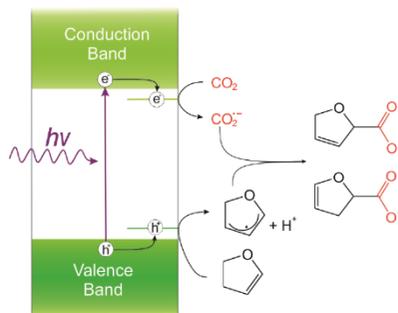
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SELECTED APPROACHES TO PHOTOCATALYTIC
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Carbon dioxide is one of the most thermodynamically stable small molecules, therefore its photocatalytic reduction is complex and difficult. Catalysts designed to facilitate this process should be characterized by sufficiently strong reducing properties. Nowadays, widely studied photocatalysts are mainly *n*-type semiconductors, including TiO₂, WO₃, ZnO, perovskites and many others. They are characterized by strong oxidizing properties, however, usually they do not offer sufficiently strong reducing power, unless the band gap of these materials is very high, which limits light absorption to a deep UV region. The *p*-type semiconductors should offer better reduction abilities than the *n*-type materials. Therefore, one should look for suitable photocatalytic systems, providing electrons for CO₂ reduction, rather among *p*- than *n*-type semiconductors.

Another approach to carbon dioxide reduction is based on its one electron reduction reaction. We have demonstrated, that photogenerated CO₂^{•-} radicals upon coupling with organic radicals may lead to carboxylic acids formation. This reaction, requiring in principle one photon absorption, can be considered as a useful tool in synthesis of fine chemicals based on CO₂ as a reagent (Figure).

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THE SYNERGY BETWEEN THEORY AND EXPERIMENT IN DEVELOPING THE BASIC SCIENCE OF NEW BN HETEROAROMATICS

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The problem that all chemists encounter more and more often concerns the choice of the most promising target molecule for a given set of specifications. The direct application of difficult, time-consuming, and expensive syntheses, without a deep prior analysis, is oftentimes not optimal. The constant back-and-forth dialectic between computations and experiments creates useful connections between theoretical knowledge and practical use of scientific achievements. This synergistic approach between high-level theory and experiment is now being applied more frequently to enhance our comprehension and conceptualization of new systems. We present our recent work on boron(B)-nitrogen(N)-containing heteroaromatics and highlight the synergy between computational electronic structure analysis and experimental physical characterization to develop a fundamental comprehension of physical and chemical properties of this emerging family of compounds [1-4].

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ORGANOBORON COMPLEXES IN THE EDGE SHARING MACROCYCLES – THE TRIPHYPHIN(2.1.1)-TETRAPHYRIN(1.1.1.1) HYBRID

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A formation of specific interaction involving electron deficient elements in particular B(III) is strongly desired because of a specific influence of B-C interaction causing a nontrivial optical response [1-3]. Macrocycles including porphyrinoids form an environment that allows a formation of specific structures by creating a specific coordination core that, depending on the size allows mixing different cations within one structural motif. The triphyrins(2.1.1) have shown a behavior unavailable for tetrapyrins(1.1.1.1) because of a difference in the macrocycle shape but also a size predefined for binding small cations, e.g. boron(III) [4,5].

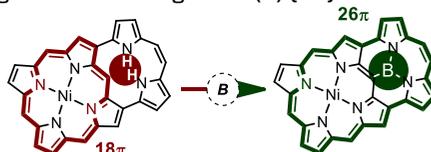


Figure 1. Triphyrin(2.1.1)-Tetrapyrin(1.1.1.1) Hybrid.

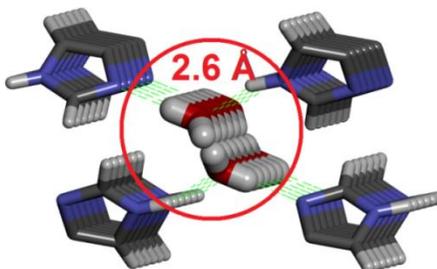
Here we present a rational approach for formation of the edge sharing hybrids merging a tetrapyrin(1.1.1.1) with triphyrin(2.1.1) (Fig. 1). A presence of both components allowed a formation of two centre structure building in a transition metal and metalloid entrapped in a CNN coordination environment. The skeletons merging two structural motifs of tetrapyrin(1.1.1.1) and triphyrin(2.1.1) can be described as an equilibrium of two alternative resonance forms 18π ([18]tetrapyrin(1.1.1.1)) or 26π ([26]Hexaphyrin(2.0.1.1.1.0)) entrapping a B-C interaction. The synthetic approach leading to presented structures with a precisely addressed usable 'defects' drastically modifying crucial parameters of importance for further utilisation along with observed spectroscopic and structural behaviour will be discussed.

ARTIFICIAL WATER CHANNELS

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This lecture discusses the incipient development of the first artificial water channels systems. We include only systems that integrate synthetic elements in their water selective translocation unit. Therefore, we exclude peptide channels because their sequences derive from the proteins in natural channels. We review many of the natural systems involved in water and related proton transport processes. We describe how these systems can fit within our primary goal of maintaining natural function within bio-assisted artificial systems. In the last part, we present several inspiring breakthroughs from the last decade in the field of biomimetic artificial water channels. All these examples demonstrate how the novel interactive water-channels can parallel biomolecular systems. At the same time these simpler artificial water channels offer a means of understanding the molecular-scale hydrodynamics of water for many biological scenarios.

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PHOTOACTIVE SYSTEMS BASED ON PHOTOCROMES AND BIOMOLECULES

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Over last decades, natural systems have gained particular attention as templates to construct well-organized nanostructures. In the last decade, supramolecular scientists have built up a variety of static DNA, HSA nanostructures as well as nanodevices and nanomachines able to move or change conformation [1]. The real challenge achieving practical applications of this biopolymer-based nanosystems is to control their operations by external stimulus [1,2]. Light is the most desired kind of stimulus, because spatiotemporal resolution, excitation tunability or biocompatibility is achieved through remote control. A particularly important group of compounds in this case are azobenzenes, well known photochromic switches. Their relatively easy synthesis and the possibility of modification make these compounds widely used in various applications [3].

A major chiral motif to come across in the nature is helicity, founded at macro- and supramolecular level in numerous structures of biomolecules. This natural chirogenic environment allows to develop complexed hybrid systems with enhanced optical properties due to the fact, that chiral compounds should exhibit rigorous selectivity of binding toward inherently chiral biopolymer matrices. In this context, incorporation of chiral azobenzene derivatives into biopolymer may lead to create smart chiroptical photoresponsive systems with a dramatically improved spatiotemporal control [4,5].

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THIOLACTONE-FUNCTIONAL REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATION AGENTS FOR ADVANCED MACROMOLECULAR ENGINEERING

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There is an increasing need for simple synthetic procedures that allow catalyst-free polymer synthesis and modification under stoichiometric conditions at mild temperatures, without the need for tedious and costly purification steps. In this regard, Du Prez *et al.* have recently shed a new light on the use of γ -thiolactones in the field of polymer chemistry with the so-called amine-thiol-ene conjugation strategy [1]. We recently reported the synthesis of a library of substituted γ thiolactones using a versatile and robust synthetic procedure based on xanthate chemistry, that will be briefly introduced [2,3].

In order to explore the potential of thiolactone chemistry for the field of reversible-deactivation radical polymerization (RDRP), we have developed a toolbox of γ -thiolactone-based RDRP agents including xanthates, bromides, and an alkoxyamine [4]. These RDRP agents were used for the polymerization of more activated and less activated monomers using appropriate RDRP techniques such as RAFT/MADIX, ATRP, and NMP. Well-defined thiolactone-terminated polymers were obtained and characterized for different degrees of polymerizations. An example of thiolactone-telechelic PNIPAM using a thiolactone-based xanthate and an ω -end-chain cyclization strategy was reported. The great reactivity of the thiolactone end-group for postpolymerization modification was proven using primary amines such as benzylamine or propargylamine, which ring-opened the thiolactone with subsequent thiol-thiolsulfonate reaction to scavenge the generated thiol. The original 5-naphthalene ethanethiosulfonate was used to give fluorescence properties to the polymers.

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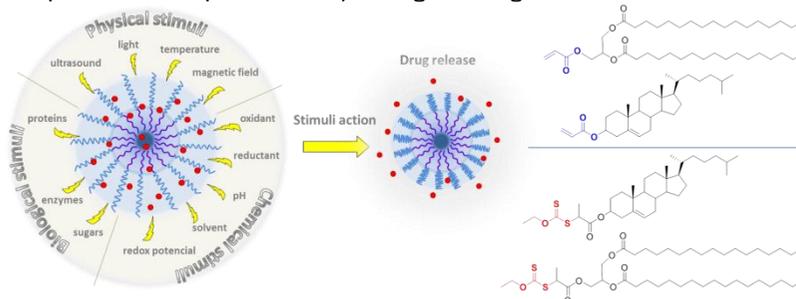
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COPOLYMERS WITH LIPID MOIETIES AS DRUG CARRIERS

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Taking inspiration from nature, scientists have made great efforts to synthesize stimuli-responsive polymers to transport active compounds like small-molecular drugs, peptides or genes. Such nanocarriers not only enhance the properties of already existing drugs in terms of solubility, bioavailability, and prolonged circulation time, but also they can be tailor-made for the selective release of their target at the desired site of action. These smart drug delivery systems (SDDS) are designed to respond to certain stimuli e.g. pH, temperature, redox potential, enzymes, light or magnetic field.



The thermosensitive polymeric carriers with lipid moieties will be presented. Two different approaches of incorporation of lipids such as steroid or glycidic to polymeric chain were used. First was preparation of novel lipid vinyl monomers and its polymerization and copolymerization by Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT). The second was based of new chain transfer agent (CTA) synthesized from natural compounds and polymerization of vinyl monomers (thermosensitive and chelating) in their presence. All the polymers were carefully investigated by various techniques: FT-IR, UV-Vis, DLS, TGA, DSC and others, to confirm the composition, thermosensitivity and self-organization in water.

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VISIBLE-LIGHT-MEDIATED HYDROXYCARBONYLATION OF DIAZONIUMS SALTS

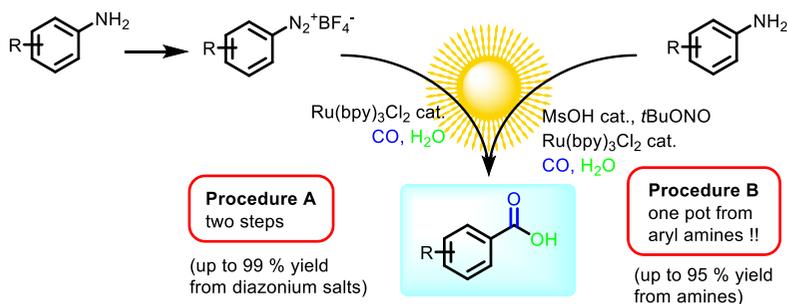
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Over the past decade, visible light photoredox catalysis has continued to generate an impressive interest. In an international context oriented towards the development of sustainable processes, the use of visible light as an inexhaustible source of energy to promote reactions represents a very promising alternative. In 2015, the groups of Jacobi von Wangelin and Xiao reported independently the first alkoxycarbonylation catalyzed by eosin or fluorescein respectively while few months later, Gu described the eosin-catalyzed preparation of diarylketones [1-3].

In this context, we wish to report a visible light-driven photocatalytic hydroxycarbonylation from diazonium salts. The reaction was achieved on aryl diazonium salts whether preformed or generated in situ from the corresponding anilines. This strategy allows a straightforward access to a variety of carboxylic acids under mild conditions [4].



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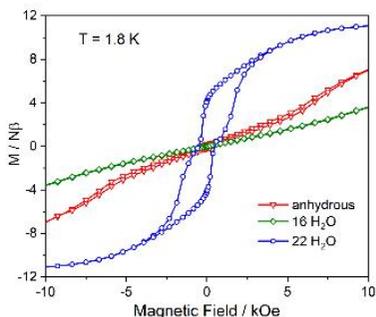
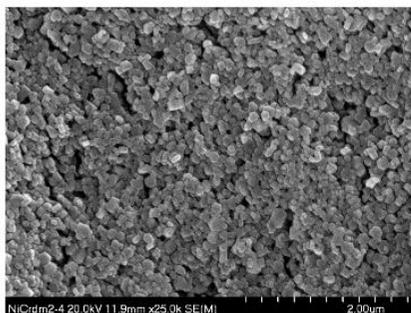
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THIN FILMS OF SOLVATOMAGNETIC CN-BRIDGED
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The possibility of inducing structural and magnetic changes by the sorption of guest molecules is one of the important features of molecular magnetic materials that make them different from classical magnets. Porous magnets and magnetic sponges are potential chemosensitive switches and provide valuable insight into magneto-structural correlations. We have obtained a family of structurally flexible CN-bridged coordination polymers, which show reversible changes in structure and magnetic properties upon dehydration or sorption of small molecules [1,2].

Our recent studies are focused on the development of thin films of solvatomagnetic compounds. For a 2D microporous $\{[\text{Ni}(\text{cyclam})]_3[\text{Cr}(\text{CN})_6]_2\}_n$ (cyclam = 1,4,7,11-tetraazacyclotetradecane) network and its Fe-based congener we have obtained films of $\sim 1 \mu\text{m}$ thickness, which retain the properties of bulk materials [3] and show reversible sorption-driven changes in magnetic properties. The figure below shows SEM image of the film surface and the shape of magnetic hysteresis depending on the degree of hydration.

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STRUCTURAL AND MAGNETIC STUDIES OF COMPLEXES
IN SYSTEMS CONTAINING $[\text{Cr}/\text{Fe}(\text{ox})_3]^3$
AND $[\text{Cu}(\text{bpy}/\text{phen})_n]^{2+}$ UNITS.

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Preparation of magnetic compounds can be achieved by proper selection of ligands acting as bridges between paramagnetic ions [1]. Oxalate anions are widely studied mainly due to (i) a variety of coordination modes and (ii) chirality of trisoxalatometallate unit resulting in a variety of topologies. Dimensionality of these complexes can be modified by proper selection of auxiliary ligands, which can also supply new properties

We prepared three complexes given by the formulae: $[\text{Co}(\text{bpy})_2(\text{ox})][\text{Cu}_2(\text{bpy})_2(\text{ox})\text{Fe}(\text{ox})_3] \cdot 8.5\text{H}_2\text{O}$ 1, $[\text{Cu}_2(\text{bpy})_4\text{Cr}(\text{ox})_3][\text{Cu}(\text{bpy})_2\text{Cr}(\text{ox})_3] \cdot 7\text{H}_2\text{O}$ 2 and $[\text{Cu}_2(\text{phen})_4\text{Cr}(\text{ox})_3][\text{Cu}(\text{phen})_2\text{Cr}(\text{ox})_3] \cdot 19.5\text{H}_2\text{O}$ 3. All these compounds were studied *via* XRD, spectroscopic, magnetic and theoretical methods. In these complexes oxalate bridges between Cu(II) and Cr(III)/Fe(III) were observed and in 1 also between two copper(II) ions. In 1 the interesting topology occurs of 1D chains composed of copper and iron moieties connected by oxalate bridges with significantly different Cu-O bond lengths. The copper(II) ions in the dimer are joined by symmetric oxalate bridge resulting in very strong antiferromagnetic coupling. The isolated Co(III) units separate chains and participates in channel formation. Therefore, this metal-bearing moieties arrangement results in four different oxalate coordination modes and porous structure with large voids filled with water molecules. In 2 and 3 rare unit arrangements composed of complex trimer (cation) and dimer (anion) in the same crystal network were observed. For studied systems with $\text{Cu}_2\text{M}^{\text{III}}$ trimer ($\text{M}^{\text{III}} = \text{Cr}, \text{Fe}$) we observed different orientations of metal ions in the trimer followed by Cu-Fe/Cr-Cu angle ranging from 111.89 to 160.84°. For 2 magnetic model is difficult and complex due to presence of both building blocks in the same structure.

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WHAT ARE THE FRONTIERS OF ATROPOCHIRALITY?

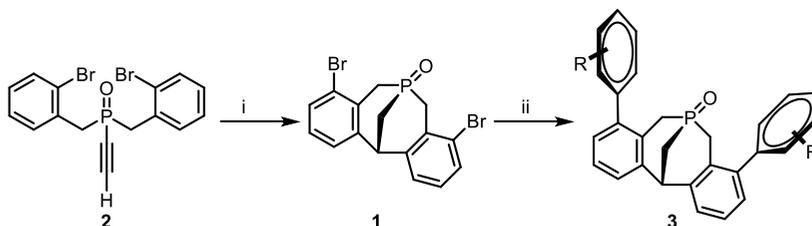
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Conformationally restrained bridgehead phosphine oxide derivatives, such as 1-phospha-bicyclo[3,3,1]-nonanes 1 (also called methanophosphocines) were originally described by Issleib in the late seventies. They were obtained through the radical cyclization of unsaturated and pyrophoric primary alkenylphosphines [1]. We reinvestigated such approach using a double gold-catalyzed cyclization of bis(arylmethyl)ethynylphosphine oxides 2. Mechanistic studies suggest that the reaction proceeded stepwise, forming first the 1H-isophosphinoline 2-oxide as intermediate [2].

We engaged consecutively dibromo derivative 1 in Suzuki-Miyaura coupling. The reaction proceeded smoothly and afforded the expected bis(biaryl) methanophosphocines 3. Ortho-substituted unsymmetrical derivatives presented an original combination of axial and central chirality. Such unusual symmetry and the corresponding chirality will be discussed.



i) 2.5 mol% Ph_3PAuCl , 3 equiv TFOH, 80 °C or O_2 , $\text{ClCH}_2\text{CH}_2\text{Cl}$. ii) 10 mol% Pd_2dba_3 , 20 mol% xantphos, 2 equiv K_2CO_3 , 140 °C, dioxane/ H_2O .

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ELECTRON TRANSPORT THROUGH HELICOMIMETIC OLIGOUREA FOLDAMERS

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Bridge-mediated electron transport is the subject of intense research in many fields of chemistry, physics and biology as it plays an important role in photosynthesis, enzymatic reactions, drug activations and the other key biological processes [1]. Proteins and peptides are known to act as electron transfer mediators. It was demonstrated that the efficiency of this process can be modulated by the secondary structure changes of peptide bridges and α -helices were found to be the most efficient mediators. The influence of the secondary structure on the electron transport process opens a possibility to design artificial folded molecules as bridges. Non-natural, synthetic compounds adopting well-defined, predictable and stable structures are called foldamers [2]. In this presentation we will focus on aliphatic oligoureia foldamers adopting stable

2.5-helical conformation. Oligomers with different chain lengths (2-12 residues) and thiol group attached to *N*- or *C*-terminus were synthesized by solution or solid support methodology. All compounds were studied as electron transfer mediators by current sensing atomic force microscopy (CS-AFM). It was demonstrated that the mechanism of the electron transport process changes depending on the length of the mediator [3]. Moreover, we showed entirely new property of oligoureias that is directional dependence of electron transport [4]. The latter is manifested on current-voltage characteristic as current rectification. The highest rectification ratio observed was around 3 times greater than that observed for helical peptides of similar length. This effect demonstrates that carefully designed oligomers with well-defined secondary structure, e.g. oligoureia foldamers, may be considered as potential candidates for use in nanoelectronics.

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SEQUENCE-DEFINED POLYMERS – A NEXT GENERATION DATA STORAGE MEDIUM

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Since ancient times, people had to store information in order to pass gained knowledge to the next generations. The methodology for storing the information significantly evolved during centuries. However, even though the current technology is very advanced it cannot keep up with growing numbers of bits. Nowadays, the amount of generated data is greater than the storage capacities of conventional media. Due to their limited stability, the hard drives and magnetic tapes are hitting their physical limits.

An interesting data storage medium is natural DNA that carries our genetic code. The DNA sequence contains all instructions necessary for reproduction and proliferation of all known living organisms. It was demonstrated that DNA can be also used to store a binary code [1,2] that can represent text or computer processor instructions using a two-symbol system 0 and 1.

The sequence-defined synthetic polymers are an interesting alternative to DNA [3], the use of synthetic monomers allows to modulate polymer properties e.g. extend the lifetime and use extended monomer alphabet to increase data storage density [4,5]. These synthetic macromolecules can be decrypted by different sequencing techniques, usually tandem mass spectrometry. However, the data capacity in these materials is determined by the macromolecules length. It was recently shown that this limitation can be overcome by the spatial organization of digital polymers using non-covalent synthesis [6]. The proposed synthetic approach might be relevant to the development of archives for long-term data storage.

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SYNTHESIS OF FLUORINATED STYRENE DERIVATIVES AND ITS APPLICATION FOR PREPARING AROMATIC FLUOROPOLYMERS

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Fluorinated aromatic polymers represent an interesting family of fluoropolymers, that may gain a unique combination of high performance properties due to the characteristic effects of the aromatic ring on mechanical strength and thermal properties, as well as fluorine substituent/s on the thermal and surface properties of the resultant polymers. The incorporation of both ie. phenyl ring and fluoro substituent into the polymeric chain can significantly improve physicochemical properties of the material. It is also expected that thermal stabilities higher than that of polystyrene can be achieved by the presence of fluoromethyl groups which should not undergo undesirable β -scission. Furthermore, fluoropolymers with aromatic functional groups in the lateral position to the polymer backbone can be modified by the introduction of functional groups.

The objective of presented work was to develop efficient and cost-effective routes to access various fluorinated styrenic monomers [1,2], to study its reactivity in radical co- and terpolymerizations, the structure of resultant aromatic polymers, as well as influence of fluorinated groups on its physical and chemical properties [3-5].

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EXPERIMENTAL CHARGE DENSITY DISTRIBUTION IN
GROSSULAR UNDER HIGH PRESSURERoman Gajda^a, Marcin Stachowicz^a, Anna Makal^a,
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We have combined high-pressure measurements with the use of a diamond anvil cell with high-resolution experimental X-ray charge density investigations utilising multipole refinement of charge density. The X-ray data collection was conducted on the CRISTAL beamline at the SOLEIL synchrotron (Paris, France). We studied single crystal of a natural garnet mineral called grossular - $\text{Ca}_3\text{Al}_2(\text{SiO}_3)_4$, - which crystallizes in the Ia-3d cubic space group. The beamline parameters such as beam wavelength (0.41 Angstrom) and a special type of Diamond Anvil Cell (DAC) with the opening angle 110° let us collect data with the resolution up to 0.35 Angstrom (with 100% completeness up to 0.45 Angstrom). We have compared our results with experimental charge densities obtained for grossular at ambient conditions. In the case of our measurements for grossular, the calculated properties of the charge density at the (3, -1) BCPs as well as the net atomic charges are comparable. We think that thanks to the new type of DACs with wider opening angle and access to synchrotron radiations quantitative charge density distributions can be determined experimentally for some types of high symmetry compounds. Up to our knowledge this is the first successful determination of quantitative charge density distribution in a crystal under high pressure. We will present details of our investigations including transfer of charge among ions under pressure.

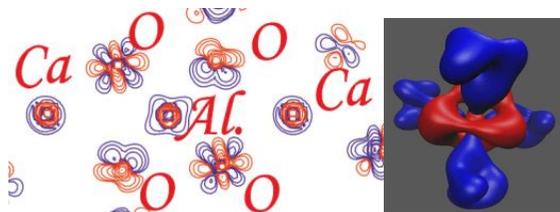


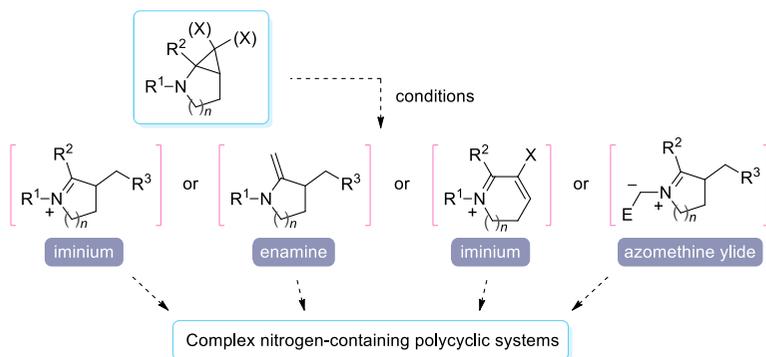
Figure 1. (left) Redistribution of electron density at O and Al ions under high pressure, and (right) the 3D SiO_4 deformation electron density maps at ambient conditions - isosurfaces: blue colour $+0.1 \text{ e}/\text{\AA}^3$, red colour $-0.1 \text{ e}/\text{\AA}^3$.

BICYCLIC AMINOCYCLOPROPANES AS PRECURSORS OF VARIOUS NITROGEN-CONTAINING POLYCYCLIC SYSTEMS

Cheng Chen, Gabriel Doridot, Rafał Karpowicz,
 Pullaiah Kattanguru, Kamila Piotrowska, Gabriela Siemiaszko,
 Olesya A. Tomashenko, Agnieszka Wasilewska, Natalia
 Witkowska, Andrzej Wolan, Justyna A. Kowalska-Six, Bartosz A.
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Bicyclic aminocyclopropane compounds constitute a special class of strained molecules which can undergo cyclopropane-ring opening under a variety of conditions [1,2]. During this talk, several examples will be presented, obtained in our group over the last few years [3-5]. The mechanisms of these reactions involve the generation of iminium, enamine or azomethine ylid species.



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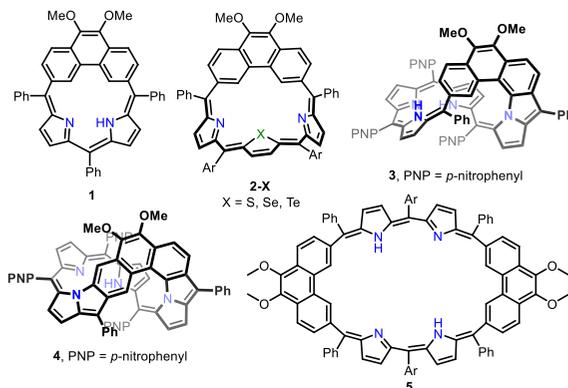
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CHIRAL PHENANTHRIPORPHYRINOIDS

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Redesign of porphyrin molecule realized through a formal replacement of pyrrole unit(s) by other hetero- or carbocycles provided a family of hybrid macrocycles, namely porphyrinoids. Incorporation of phenanthrene moieties into the oligopyrrolic environment yielded phenanthriporphyrin 1, 32-heterophenanthrisapphyrins 2-X, helicenophyrins 3 and 4, and diphenanthriooctaphyrin 5. The latter was formed as two locked, interconvertible conformers that can be easily separated and handled individually. Both stereoisomers were found to have strikingly diverse stereodynamic behavior.



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CHEMO-ENZYMATIC SYNTHESIS OF A SIMPLE THIOGALACTOLIPIDE FORMING RESPONSIVE HYDROGEL FOR THE LIBERATION OF COSMETIC AGENTS

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Hydrogels are formed by specific molecules able to self-assembled thanks to covalent or weak interactions. This creates three dimensional networks that trap a large quantity of water. Covalent bonds lead to irreversible materials while Van der Waals interactions give reversible hydrogels [1]. External parameters' change (pH, temperature) induces disruption of the weak interactions and a network's expansion. It's particularly this property which interests the cosmetic industry. These approaches are currently used for pharmaceutical applications such as diabetes treatment with self-control insulin's liberation for example [2]. Amphiphile and bolaamphiphile compounds are well known for exhibiting hydrogel properties. In our case, these properties are brought by an original thioagalactolipids obtained thanks to biocatalysis. Through directed mutagenesis of the catalytic acid/base residue of the wild type glycosidase from *Dictyoglomus thermophilum*, hydrolysis properties of the enzyme were reduced favouring thioglycosylation reaction [3]. Physico-chemistry studies such as electronic microscopy (TEM, SEM), structural organisation (SAXS), thermal (RMN, DSC) were performed on this material. Active molecules were also trapped in the network to simulate a smart material. Furthermore, the thioagalactolipids could be hydrolysed by skin contact releasing an anti-pigmentation agent. Activity of the resulting thioglycosides was investigated and revealed promising results.

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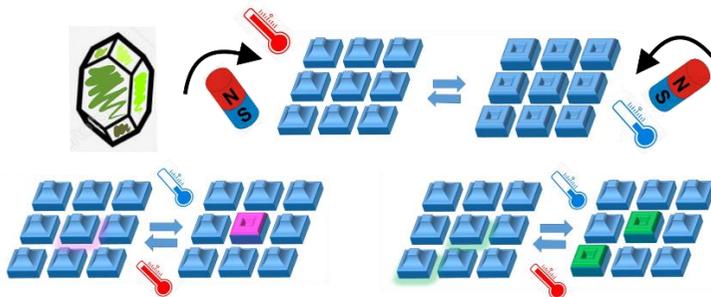
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SHAPING PROPERTIES BY PLAYING WITH CYANIDE-BRIDGED
COORDINATION BACKBONESRobert Podgajny

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The network- and cluster-based compounds with exchange interactions, long range magnetic ordering and magnetic anisotropy can host additional properties, e.g. reversible structural transformations, electron transfer, spin crossover, chirality etc. Considering systematically occurring cyanido-bridged coordination backbones we study various distributions of different spin (or non-spin) carriers and other active units dedicated to the functional properties schemes, *via* embedment of different metal ions and external decoration with molecular species. We also study the construction and crystallization of the related branched or open-cage nanoscale species. In line with the above ideas, this presentation will disclose the selected examples of bi- and trimetallic $[M(CN)_6]^{n-}$ -bridged molecular architectures devoted to the rotational magnetocaloric effect (RMCE) on monocrystals, and single-crystal-to-single-crystal (SCSC) transformations involving electron transfer and spin crossover [1-3].

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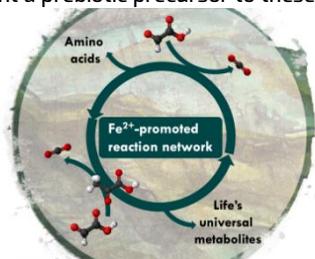
SYNTHESIS AND BREAKDOWN OF UNIVERSAL METABOLIC PRECURSORS PROMOTED BY IRON

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Life builds its molecules from carbon dioxide (CO₂) and breaks them back down again through the intermediacy of just five metabolites, which are the universal hubs of biochemistry [1]. However, it is unclear how core biological metabolism began and why it uses the intermediates, reactions and pathways that it does. Here [2] we describe a purely chemical reaction network promoted by ferrous iron, in which aqueous pyruvate and glyoxylate—two products of abiotic CO₂ reduction [3,4]—build up 9 of the 11 intermediates of the biological Krebs (or TCA) cycle, including all 5 universal metabolic precursors. The intermediates simultaneously break down to CO₂ in a life-like regime that resembles biological anabolism and catabolism [5]. Adding hydroxylamine and metallic iron into the system produces four biological amino acids in a manner that parallels biosynthesis. The observed network overlaps substantially with the Krebs and glyoxylate cycles [6,7], and may represent a prebiotic precursor to these core metabolic pathways.



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MULTIPHOTON ABSORPTION IN MOF-BASED NLO PIGMENTS AS A TOOL FOR BETTER REMOTE TEMPERATURE MEASUREMENTS

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This presentation will include an introduction presenting and advertising the activities of the Polish National Science Centre (Narodowe Centrum Nauki, NCN), the main agency providing grants for fundamental research in Poland, which I represent at this meeting as a member of its Council.

The main scientific topic of the talk will be an excerpt from my activities in an NCN "Maestro" grant, which I received to study, together with my research team, novel effects related to multiphoton absorption and other nonlinear optical (NLO) phenomena in non-standard optical materials. Indeed, we found that the much recently studied materials belonging to the group of metal-organic frameworks (MOFs) can be excellent multiphoton absorbers, which has important consequences for their potential applications in a variety of fields [1], giving us the incentive to coin the term "NLO pigments" to describe materials that are NLO active but are only available as insoluble microcrystals or nanocrystals. As an example, we have demonstrated that, by utilizing three-photon absorption in a lanthanide-ion-doped MOF, we are able to perform near-infrared to visible high-resolution remote luminescence-based temperature sensing [2].

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CHIRAL COMMUNICATIONS IN A THREE-LEVEL CHIRALITY TOTEM. REMOTE-CONTROL OF THE MÖBIUS AROMATIC TWISTING IN HEXAPHYRIN-CYCLODEXTRIN HYBRIDS

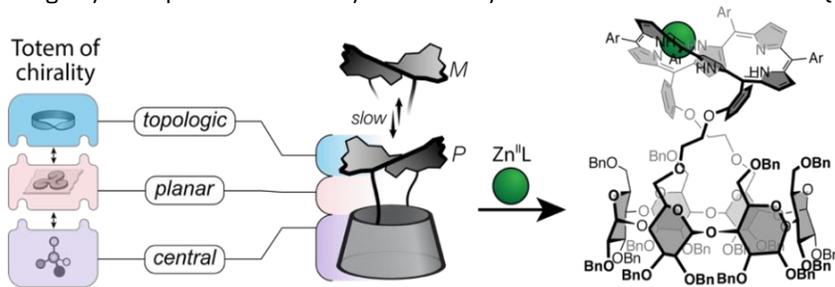
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The inherent chirality of Möbius topology is quasi unexplored making [28]Hexaphyrins, having native Möbius aromaticity, ideal candidates provided that their P/M twisting equilibrium is controlled [1,2]. In this context, we have recently developed hybrid structures combining an hexaphyrin to a cyclodextrin (HCD) [3-5]. Tuning their linking constraints allowed to generate a unique hybrid molecule conjugating a Möbius aromatic macrocycle to a cyclodextrin. The whole edifice embeds a three-level chirality "totem" encompassing central, planar, and topological chiralities. In this communication we will disclose the different types of communication connecting each chirality level through dynamic processes remotely controlled by coordination of achiral effectors [6].



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VINYLOGY CONCEPT IN THE SYNTHESIS OF SELECTED CARBO- AND HETEROCYCLES

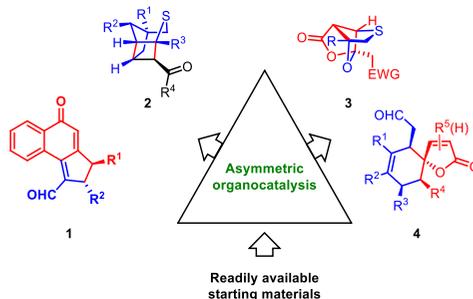
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The development of methods for the preparation of biologically relevant compounds in enantiomerically enriched form is of significance for contemporary organic chemistry. Recently, asymmetric organocatalysis has become a highly useful tool enabling for their enantioselective synthesis based on diverse activation modes [1]. Within this research area, the application of vinylogy concept created new synthetic possibilities.

Herein, we report our studies on organocatalytic, enantioselective vinylogous strategies for the synthesis of biologically relevant molecules such as: carboannulated naphthalen-1(4*H*)-one derivatives **1**, tetrahydrothiopyrans **2**, γ -lactones **3** and **4** [2-6]. The devised approaches utilize readily available chiral organocatalysts to control stereochemical reaction outcomes.



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DUAL-CATALYTIC SYSTEMS FOR FUNCTIONALIZATION OF UNREACTIVE SITES OF MOLECULES

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Catalytic functionalization reactions occur readily at sites of starting materials that are both innately reactive and sterically accessible or that are predisposed by a functional group capable to direct a catalyst [1]. However, selective reactions at unbiased sites of substrates remain challenging and typically require additional pre-activation or directing group installation steps, or the use of highly reactive reagents. Therefore, the synthetic methodologies enabling for direct and selective functionalization of typically unreactive sites are highly desired [1].

Here I will present our studies dedicated to the development of dual-catalytic systems that enable selective functionalization reactions of substrates at their unreactive sites, such as ubiquitous unactivated C-H bonds.[2] Our strategy rests on merging a metal-catalyzed reversible reaction and a metal-catalyzed functionalization reaction (Fig. 1). Due to the mild reagents and conditions of both the reversible reaction and the functionalization reaction, the devised methodologies are general and compatible with a broad scope of substrates, including natural product-like molecules. These studies highlight the potential of the multi-catalytic approach to address challenging transformations to circumvent multi-step procedures and use of highly reactive reagents in organic synthesis.

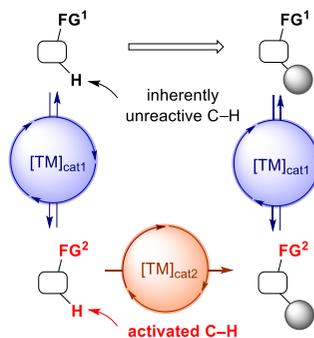


Fig. 1. A dual-catalytic system merges reversible activation and functionalization reactions to enable a direct functionalization of a starting material at an otherwise unreactive site.

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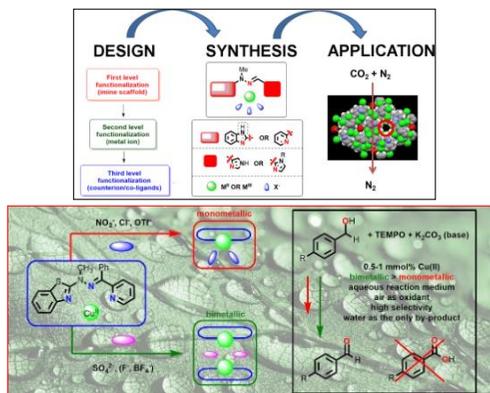
(METALLO)SUPRAMOLECULAR SYSTEMS FOR TACKLING THE ENVIRONMENTAL ISSUES

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"Perhaps the most pressing scientific problem facing humankind is understanding the influence of human activity on the environment, and the most pressing technological problem is understanding what to do about it.". This quote comes from the paper of Prof. G.M. Whitesides [1] that provides a perspective for the emerging/undergoing problems that should be tackled and the role of chemistry to solve them is beyond any dispute.

I would like to show a few of our current scientific endeavors that are related to the therein undertaken environmental issues, specifically regarding CO₂ capture [2], energetic [3] and development of new, environmentally benign catalysts [4]. By appropriate design of molecular scaffolds and utilization of supramolecular interactions, we are able to provide approaches potentially worthy of further evaluation, that could ultimately confer to aiding in solving worldwide problems regarding the environment.

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DYNAMIC COVALENT CHEMISTRY AT WORK: SIMULTANEOUS CO₂ CAPTURE AND METAL PURIFICATION FROM WASTE STREAMS

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CO₂ fixation by amines has been explored as a potential strategy to generate dynamic libraries of ligands for metal separation and recovery of metals. With industrial polyamines such as diethylenetriamine, this simple reaction yields arrays of interconverting species, from which tailored subsets can be selected, yielding organometallic adducts of contrasting solubility. The differences displayed by rare earth and late transition metals in coordinating these adaptive ligands in their first and second coordination spheres can easily be assessed and the resulting knowledge can be used to identify the CO₂ loadings and solvents affording the optimal precipitation of each metal from the dynamic libraries of complexes. The potential added value of this conceptually new supramolecular approach will be illustrated with two early stage prototypes of separation processes. The possibility to integrate utilization to capture was validated during bimetallic separation directly performed with the exhaust gas of an internal combustion engine vehicle. Additionally, the three metal constituents of the La₂Ni₉Co alloys used to manufacture the batteries of electric vehicles can be separated and recovered by successive CO₂-induced selective precipitations. Beyond the concept of CO₂-sourced multi-level dynamic coordination chemistry, this study provides a potential framework to integrate CO₂ capture and utilization and paves the way towards the design of CO₂-sourced sustainable processes.

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GENERATION OF FUNCTIONAL METALLOSUPRAMOLECULAR ASSEMBLIES BASED ON AMBIDENTATE LIGANDS

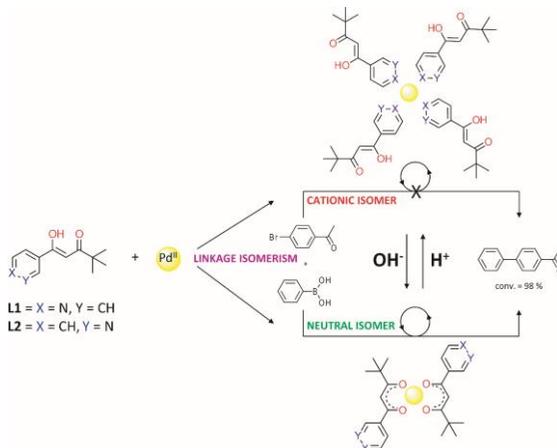
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Application of self-assembly process in the generation of complex supramolecular systems of interesting topology and well-defined function, despite tremendous progress in the field, invariably remains a challenging task. In this context controllable modulation of metallosupramolecular complex topology *via* strategic application of ambidentate ligation and selection of an appropriate metal ion allows for much faster access to a wide "library" of architectures that differ not only in structural properties but also in function. The presentation will encompass several recent examples from our team where assemblies of distinct functions were generated using above mentioned approach [1,2,3].



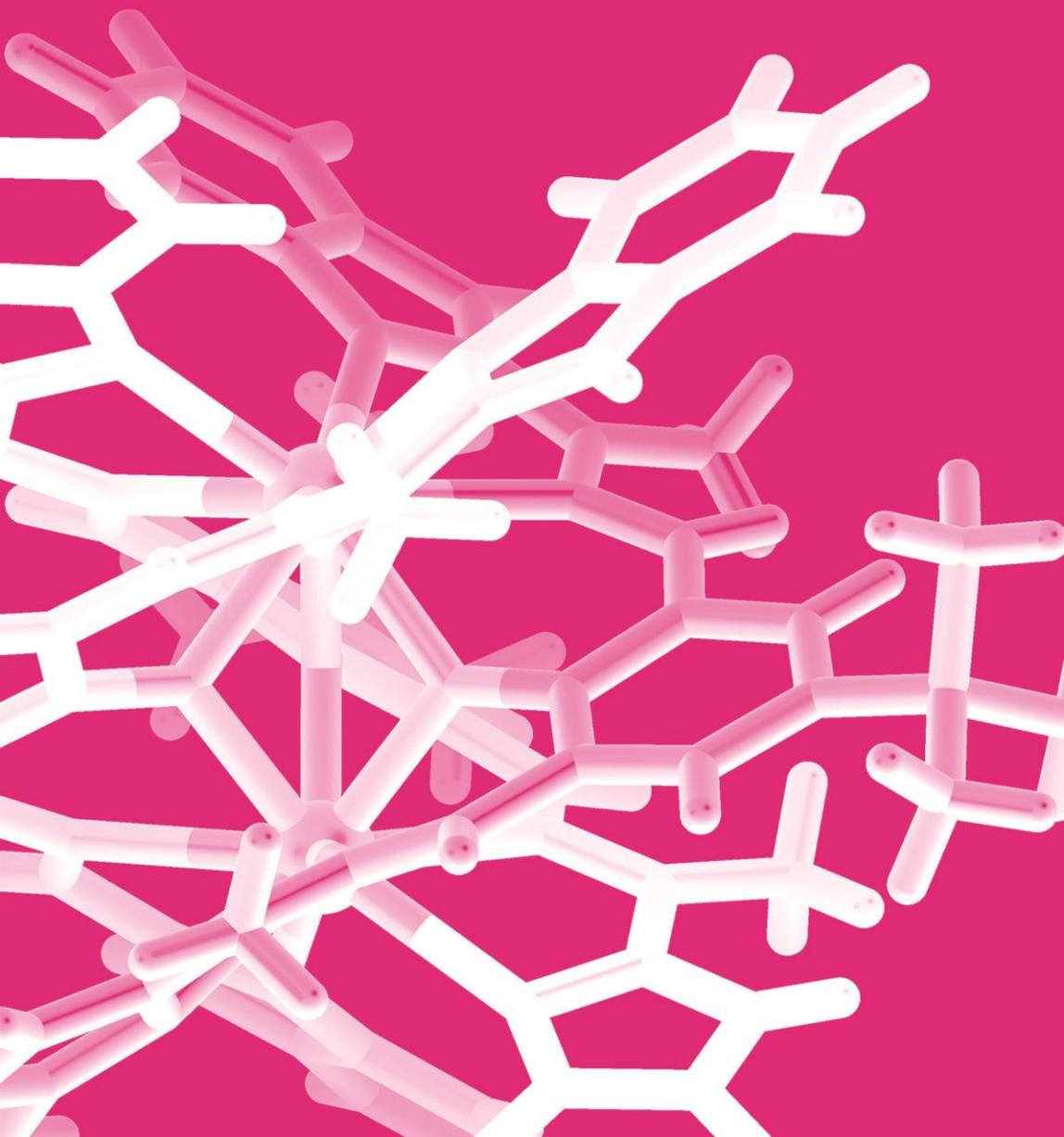
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Paris, 4-6 July 2019

FRENCH-POLISH CHEMISTRY CONGRESS POSTERS



SYNTHESIS AND APPLICATION OF SCHIFF BASE COMPLEXES WITH FIRST-ROW TRANSITION METAL IONS

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Many complexes of the first row transition metals with Schiff bases show catalytic activity in the polymerization of alkenes, oxidation of alkenes and alcohols, hydrogenation of carbonyl compounds or carbon-carbon cross-coupling [1,2]. Preliminary studies performed in our group have shown that the complex of cobalt(II) with tridentate ligand of the Schiff base type, activated with NaHBEt_3 is an effective catalyst of olefin hydrosilylation which selectivity depends on the structure of silane used [3]. In this context, the cobalt(II) complexes with Schiff base ligands can serve as cheaper and environmentally safer alternative to previously tested platinum catalysts [4].

In the communication we present our results of the synthesis and characterization of new supramolecular complexes based on the 3d-electron metal ions e.g. Fe(III), Co(II) and Ni(II) with the tridentate ligands of Schiff bases type as well as their application as precatalysts in the hydrosilylation of alkenes.

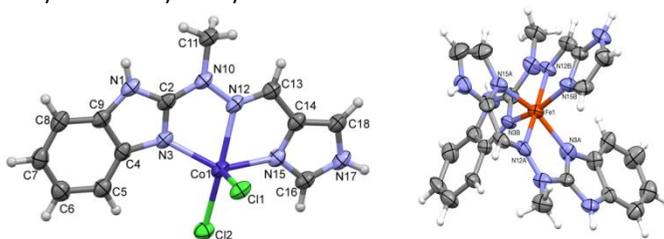


Figure 1. The crystal structures of complexes of Co(II) –left and Fe(III) –right.

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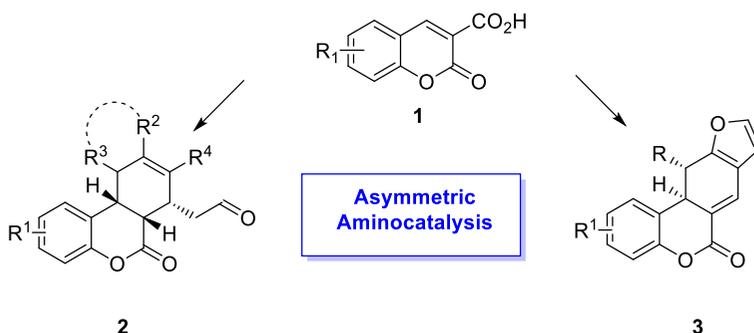
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DECARBOXYLATIVE, AMINOCATALYTIC CASCADES IN THE SYNTHESIS OF 3,4-DIHYDROCOUMARINS

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Development of stereocontrolled strategies leading to molecules of biological interest is of key importance in the contemporary organic chemistry [1,2]. A 3,4-dihydrocoumarin ring system is a constituent of many natural products exhibiting diverse and useful biological properties [3]. Herein, we report our studies on the development of novel and straightforward approaches to 3,4-dihydrocoumarin derivatives **2** and **3** employing aminocatalytic activation modes [4,5].



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SYNTHESIS AND PROPERTIES OF TRIPHENYLAMINE-BASED HYDRAZONE LIGAND AND ITS COMPLEXES WITH TRANSITION METAL IONS

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Metal coordination complexes are promising electrochromic materials because of their intense coloration and redox reactivity [1]. These compounds show a capability to change an optical properties in response to an external electric impulse. Intensive coloration of the complexes of transition metal ions may be caused by d-d transition, metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge transfers [2,3].

We present the synthesis of ligand L containing terpyridine moiety, which is known to undergo an oxidative electropolymerization, and its complexes with transition metal ions (Fe^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Ag^+). Compounds were characterized by spectroscopic methods and their electrochemical properties were investigated.

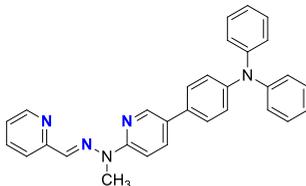


Figure. Structure of the ligand L.

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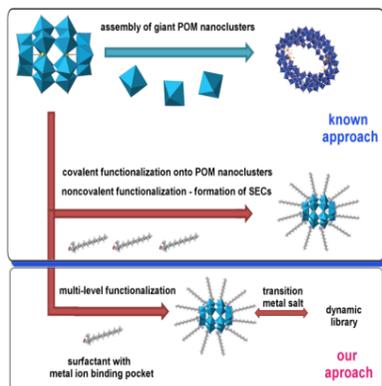
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NEW APPROACH FOR GENETATION OF HYBRID MATERIALS: COMPLEX-DECORATED SURFACTANT-ENCAPSULATED CLUSTERS (CD-SEC)

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Generation of well-defined organic-inorganic hybrid materials with controllable size and morphology is challenging and active area of modern research in view of their unique properties and thus multifunctional applications. Specifically polyoxometalates (POMs) were recognized as a very promising group for the construction of those, nonetheless there are domains where the profound understanding of hierarchical mutual interactions and assembly are lacking, as in bioassays for instance. We therefore



present an efficient approach towards the synthesis of a novel group of POM-based nanocomposites that we name Complex-Decorated Surfactant Encapsulated-Clusters (CD-SECs). Obtained materials are unique in the sense that the organic surfactant may simultaneously behave as a metal-coordinating agent, thus allowing for a multi-level derivatization of the synthesized SECs via utilization of the non-covalent interactions. We demonstrate possibilities and limitations for generation of three families of hybrids H1-H3 with the total of seven different constructing approaches.

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FUNCTIONAL SILSESQUIOXANES AS MOLECULAR BUILDING
BLOCKS FOR NOVEL HYBRID SYSTEMS

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Silsesquioxanes are a large family of specific organosilicon compounds with diverse spatial structures, described by the general formula $[RSiO_{1.5}]_n$ [1]. Due to the application reasons and for the well-defined 3D architecture, the most interesting subgroup are cage silsesquioxanes. It has been recently updated with a new type of Si-O-Si framework, i.e. double-decker silsesquioxane derivatives (DDSQ) [2]. Within this group of compounds, di- and tetrafunctional DDSQ-based systems may be found where the same siloxane core may be distinguished. Nowadays, the silsesquioxane-based materials have gained much attention and the decisive role for their design is to specify the proper reactive group to be anchored on the DDSQ core that can be modified *via* respective, e.g. catalytic process [3,4].

In this communication recent achievements in the field of synthesis of new functionalized molecular di- and tetrafunctional double – decker silsesquioxanes and their application in the formation of molecular DDSQ-based systems are presented.

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FROM POLYESTERS TO BEAUTY OF COORDINATION CHEMISTRY. CASE STUDY ON AMINOPHENOLATE ZINC COMPLEXES

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The commercial potential of biodegradable polymers, including aliphatic polyesters and copolyesters is tremendous in the sphere of short lifetime ecological products and bioapplications, such as bioresorbable surgical sutures, bioimplants, vascular stents, tissue scaffolds, controlled drug release matrices, and nanomaterials. Therefore, the subject of synthesis and chemistry of biodegradable polymers, modification and programming of targeted properties is a constant challenge, in the sphere of both academic and industrial research. The most attractive method for the synthesis of polyesters is the living ring-opening polymerization (ROP) of cyclic esters in the presence of suitable catalysts, making it possible to modify polymer properties already at the stage of their synthesis.

Among a variety of initiators, metal complexes are the most effective ones in the context of biomedical applications, especially the biometal complexes of Ca, Mg, and Zn. Here, we have presented how the L-M-OR structural motif determined as the most effective in the polymerization of ROP cyclic esters influences the synthesis strategies of heteroleptic zinc complexes. Next, how researches in the field of coordination chemistry has been directly transferred to the design of catalytic systems active in ROP and the theoretical studies of reaction mechanisms [1-4].

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- The authors would like to express their gratitude to the National Science Centre in Poland (Grant 2017/25/B/ST5/00597).
-

SYNTHESIS OF NEW PERFLUOROPHENYL PHOSPHONATE ANALOGUES OF PHENYLGLYCINE

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Chemistry of α -aminophosphonates played a significant role in the development of organophosphorus compounds [1]. As structural analogues of α -amino acids, α -aminophosphonates found application in organic and medicinal chemistry due to their various biological activities [2,3]. Among α -aminophosphonates, the fluorinated ones constitute particularly important group of compounds. [4].

Recently we reported a convenient synthetic method for the preparation of a series of perfluorinated phosphonate analogues of phenylglycine and homophenylalanine [5]. In the frame of this work new perfluorophenyl phosphonate analogues of phenylglycine were synthesised. Our synthetic protocol involves a two-step sequence consisting of preparation of aldimine followed by a hydrophosphonylation (Fig. 1).

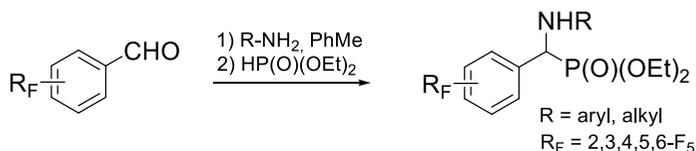


Figure 1. Synthetic approach to perfluorinated phosphono-phenylglycine analogues.

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CHIRAL Cu(I) HELICATES WITH 1,2-DIAMINOCYCLOHEXANE MOIETY AND THEIR DNA/ENZYME RECOGNITION

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Chiral recognition is a vital process in a vast number of natural systems. Enantiopure 1,2-diaminocyclohexane (DACH) can be easily derivatized to obtain a range of stereodirecting reagents and ligands. Moreover, DACH based ligands occurred to be a great core for helicates construction, preferentially formed in the presence of d-electron metal ions [1]. Such complexes may exhibit versatile properties due to differences in central ion surroundings, therefore they might be considered as potential probes/sensors of bio-molecules with specific hybridization.

Herein, we would like to present the influence of the coordination environment of the Cu(I) complexes on the nucleic acids binding behaviour. For this purpose three Cu(I) complexes of general formula $[Cu_2L_2](PF_6)_2$, where L is the ligand being the product of condensation of DACH (*trans*-1R,2R-, *trans*-1S,2S- and *cis*-1R,2S-diaminocyclohexane) with quinolone-2-carbaldehyde, were synthesized, crystallized and tested for their affinity toward several biomolecules.

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STRATEGIES TO LABEL PAMAM DENDRIMERS WITH METAL CARBONYL INFRARED PROBES FOR THEIR SITE-SELECTIVE CONJUGATION TO BIOMACROMOLECULES

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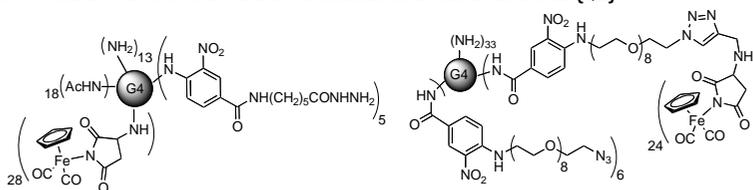
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Biomolecules labelling is an important area of research with applications in the understanding of biological processes, the development of diagnostic tools and new approaches in the treatment of diseases. Recent developments in bioconjugation are directed towards strategies exploiting chemoselective ligations between functional groups that are not naturally occurring in biomacromolecules and only react with each other to ensure high selectivity and site-specificity.

Metal carbonyl complexes show specific and intense absorption bands in the mid-infrared spectral range (2200-1800 cm^{-1}) owing to the carbonyl ligands, where few other vibrators absorb. These features make them detectable at very low concentrations by infrared (IR) spectroscopic techniques.

We present here different strategies explored to label poly(amidoamine) (PAMAM) dendrimers with multiple copies of metal carbonyl infrared tags in view of their site-selective attachment to biomacromolecules such as antibodies [1,2].



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NOVEL, EFFICIENT CATALYTIC METHODS FOR FUNCTIONALIZATION OF SILSESQUIOXANES

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Silsesquioxanes have attracted considerable attention due to their nano-sized, hybrid structure and versatile applications in material chemistry.

The aim of the poster is to demonstrate our highly efficient and selective catalytic approach to functionalized silsesquioxanes via the coupling reaction of silsesquioxanes containing silanol (Si-OH) groups with various types of reagents (e.g., allyl-substituted organometallic compounds or commercially available hydrosilanes) (Fig. 1) [1-5].

Our methodology undergoes under mild reaction conditions with evolution of no corrosive or reactive by-products. This approach also opens up a possibility to introduce a variety of functional groups into silsesquioxanes with excellent yields and selectivity. Other advantages of this approach include the simplicity of experimental and isolation techniques.

This methodology can be of great importance and practical use for the functionalization of silsesquioxanes, which have the potential for wide applications in many fields of material science.

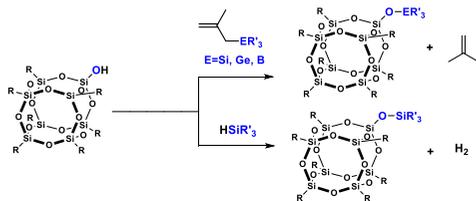


Figure 1. Novel approach to the functionalization of POSS silanols.

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ELECTROSPUN NANOMATERIALS FOR ENZYME IMMOBILIZATION AND BIODEGRADATION OF ENVIRONMENTAL POLLUTION

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Electrospinning is the method of nanofibers obtaining from molten polymers or their solutions [1]. Among various available methods of fibers production only electrospinning appears to be a technique commercially applied for the mass production of single nanofibers, due to the relatively low price and speed of production as compared to other methods [2]. The electrospun nanofibers obtained find application in the fields of medicine, chemistry, biology, biochemistry, textile, cosmetics and even photovoltaics [3]. Nevertheless, one of the most interesting applications of electrospun nanofibers is their use as carriers for enzyme immobilization. Among others, the wide range of oxidoreductase enzymes such as tyrosinases, peroxidases and laccases, which possess environmental application, might be immobilized using the above-mentioned materials. Produced biocatalytic systems may degrade various water pollutants such as phenols, dyes and pharmaceuticals. Immobilization of enzymes using electrospun materials increases their stability, and reusability that results in possible practical applications of the immobilized biocatalysts in biodegradation processes [4]. It should be emphasized that presented solutions are environmentally friendly and in accordance with the rules of green chemistry.

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MACROPOROUS ORGANIC-INORGANIC HYBRIDS BASED ON FUNCTIONALIZED SILICON COMPOUNDS

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The aim of this work was to develop an efficient approach to prepare a macroporous scaffold for sophisticated bone replacement, avoiding a long-lasting and complex methodology. For instance, such a scaffold can be based on the 3-(trimethoxysilyl)propyl methacrylate-POSS hybrid was synthesized via the reaction of 3-(trimethoxysilyl)propyl methacrylate and the trifluoromethanesulfonate-POSS salt. The results show that the chemical composition, structural dimensions, topography, and microstructural properties of the scaffold fulfill the potential requirements for hard-tissue engineering. The microstructural properties were evaluated with the use of X-ray microcomputed tomography (micro-CT) and nanoindentation tests. The former makes it possible to estimate the geometrical measures of the microstructure (porosity, thickness distribution, etc.), whereas the latter makes it possible to estimate the mechanical properties of the constituents of the material (hardness, stiffness modulus, creep, etc.). The aforementioned laboratory testing methods are modern techniques, currently being developed for materials science, making it possible to determine the microstructural/measures of the analyzed system [1-6].

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PHARMACEUTICALS AS EMERGING ENVIRONMENTAL CONTAMINANTS - PERSPECTIVES OF BIOLOGICAL REMOVAL

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The growing production, consumption and disposal of pharmaceuticals create the risk of their increased migration to the environment. Pharmaceutical residues appearing in soil and water may affect the hormonal balance of living organisms, cell proliferation or interactions with macro and microorganisms present in the ecosystem. In addition, some of these biologically active compounds can also accumulate in animal and plant tissues.

An important group of pharmaceuticals, which are among the most commonly used antimicrobial agents, are nitrofurans derivatives. They have a wide spectrum of antibacterial activity against selected Gram-negative bacteria as well as bacteria from genera *Streptococcus* and *Staphylococcus*. Moreover, they are known for their antifungal and antiprotozoal properties. Hence, they are used in both human and veterinary medicine as well as feed additives to promote growth in animal husbandry. The most common nitrofurans are furazolidone, nitrofurantoin, nitrofurazone and furaltadone.

Therefore, a deep understanding of their biological removal from the environment as well as cellular adaptation processes which include modifications of the external cell structure, enzymatic activity or changes in genetic material is extremely important.

The objective of the studies presented was to investigate the ability of selected environmental microbial strains to decompose nitrofurans derivatives and examine the impact of those compounds on bacterial adaptation to use nitrofurans as a carbon and energy source.

The results of the study indicate how isolated bacteria strains adapt to use of selected nitrofurans derivatives as a carbon and energy source and what mechanisms are in this process involved. Importantly, an exposure of bacteria to selected nitrofurans-derived compound provokes significant changes in microbial cell morphology, cell properties and their metabolic activity.

The research was conducted with financial support of the National Science Centre (Poland) grant No. 2017/27/B/NZ9/D1603.

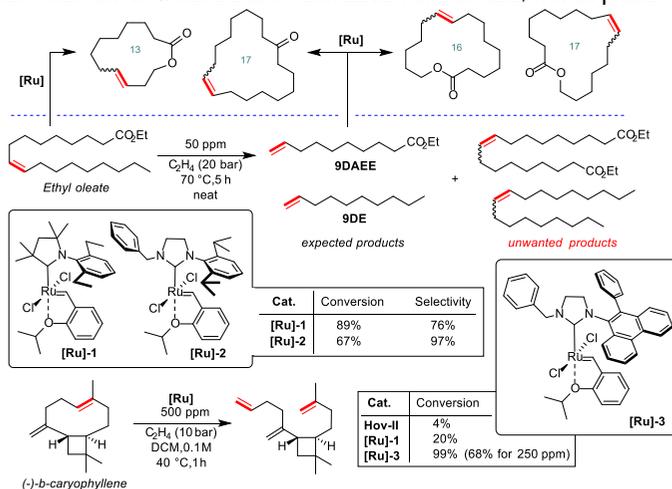
CATALYTIC OLEFIN METATHESIS FOR PREPARATION OF MACROCYCLIC MUSKS AND FINE CHEMICALS FROM BIOMASS

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Ruthenium-catalyzed olefin metathesis reaction represent an attractive and powerful transformation for the formation of carbon-carbon double bonds [1]. Herein we report successful utilization of sequential ethenolysis and ring-closing metathesis of dec-9-enoic acid based dienes in synthesis of macrocyclic lactones that possess a strong scent of musk. Alternatively, oleic ester can be utilized in musk production, using tailored catalysts and techniques developed in our group [2]. In addition, application of metathesis in self-CM of α -olefins and valorization of biomass, will be presented.



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PREDICTION OF HEAVYATOM BINDING SITE

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Drug design is a process of development of new live-saving molecules based on the prediction of the interactions between small molecules and macromolecules (usually proteins). To obtain the most accurate results we need to know the molecular structure of targeted protein. One of the most common way to do that is to measure the diffraction of X-rays on the protein crystals. In the method of reassembling the molecular structure of the protein from its diffracted patterns we need very detailed information about the phase of the primary X-ray beam. This lead us to the biggest bottle-neck of the method called phase problem. As there are physical limitation regarding the light beam measurements, we have to use various semi-empirical methods of which the Multi-wavelength or Single-wavelength Anomalous Dispersion are the most common. This method involve making the heavy atom derivative of the protein studied and then try to observe the diffraction which shows the deviation from the Bragg Law.

Despite decades of effort, the preparation of heavy atom derivatives is still mostly achieved by trial-and-error rather than any empirical search for a perfect derivative. We want to solve this problem by investigating the nature of protein - heavy atom interaction and thereby develop a method for more rational design of heavy-atom derivative screening. We have used the gold-dependent protein family as a starting point. Currently we would like to present a database consisting of the information about the protein-heavy atom interactions with calculated binding energy or other congruent factors portraying the nature of those interactions.

The work was supported by grant no. POWR.03.02.00-00-1026/16 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development

THE USE OF IONIC LIQUIDS IN THE PREPARATION OF FUNCTIONAL MATERIALS WHICH INCLUDE LIGNIN

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The carried out activities associated with the lignin study topic resulted in the development of a research path – an attempt to use environmentally friendly ionic liquids as "green", designable compounds which enable the modification of the biopolymer structure [1–3]. For this purpose, commonly known, relatively cheap and friendly ionic liquids were used, but also a group of novel ILs was designed which modified the lignin structure by increasing the content of carbonyl groups when used under mild air oxidation conditions. This was important in terms of using the products in various fields of science.

In the framework of the conducted research work, a single extremely important goal of the undertaken actions emerges. It concerns the utilization of lignin, which is post-production waste in the pulp and paper industry. The utilization of this biopolymer to date has been focused on obtaining energy/heat. The conducted studies aimed to broaden the possibilities of using lignin in applications with the so-called high added value. This, in consequence, may contribute to a more efficient utilization of the product, but also to the intensification of the development of low-waste technologies. The presented research is mainly based on experimental studies carried out at a laboratory scale, primarily in the aspect of the development of basic research, however there will certainly be the possibility of their practical application in the near future and implementation of selected products in industry.

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ZnO/LIGNIN HYBRID MATERIALS WITH POTENTIAL ANTIMICROBIAL ACTIVITY AS FUNCTIONAL FILLERS OF HIGH-DENSITY POLYETHYLENE CONTAINER

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In recent years, hybrid materials based on lignin and its derivatives have attracted great interest in both science and industry. The addition of an inorganic component to hybrid materials serves mainly to improve the mechanical properties and the thermal stability of the final product.

In the present study, dual ZnO/lignin hybrid fillers were obtained and subjected to detailed physicochemical and morphological-microstructural analysis [1]. The effectiveness of combination of the components was assessed using Fourier transform infrared spectroscopy. It was shown that the addition of zinc oxide improves the thermal stability of the final hybrid filler. A hybrid material consisting of ZnO and lignin in a weight ratio of 1:5 exhibited very good antimicrobial activity, especially against Gram-positive bacteria. In all cases, the action of this material was stronger than that of the positive control, the antibiotic tetracycline. Blow-molded containers made of polyethylene containing 5 wt% of ZnO/lignin with different lignin contents were prepared with a single-screw extruder. The effect of ZnO/lignin hybrid fillers on the properties of a high-density polyethylene container was investigated by means of a uniaxial compression test. Mechanical tests demonstrated a significant twofold increase in the compression force for blends with a ZnO:lignin ratio of 1:5. Additionally, DSC analysis was performed to study the influence of the dual fillers on the microstructure of the blended polyethylene.

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HIGHLY EFFICIENT CU(I) CATALYST SYSTEM BASED ON AMBIDENTATE LIGANDS IN AMINATION REACTION OF ARYL HALIDES

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Ambidentate pyridyl- β -diketones ligands containing two distinct coordination sites of different nature (*i.e.* anionic β -diketonate and neutral pyridine) despite their wide use for the construction of coordination compounds and complexed metallosupramolecular architectures, have so far been rarely employed in catalysis [1,2]. The catalytic system based on copper(I) and such ligands allowed efficient coupling of aryl bromides and iodides with aqueous ammonia under mild temperature conditions (25 – 80°C) and synthesis of a large scope of aniline derivatives [3]. Hence, a number of factors, such as industrial applications of amination, one of the smoothest conditions ever reported in literature and low cost of catalyst made this methodology convenient to use.

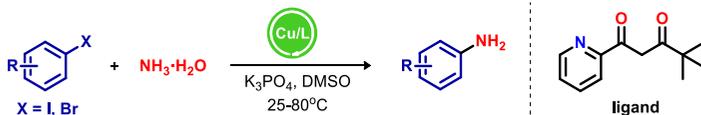


Figure 1. Reaction scheme for amination catalyzed by Cu/L systems.

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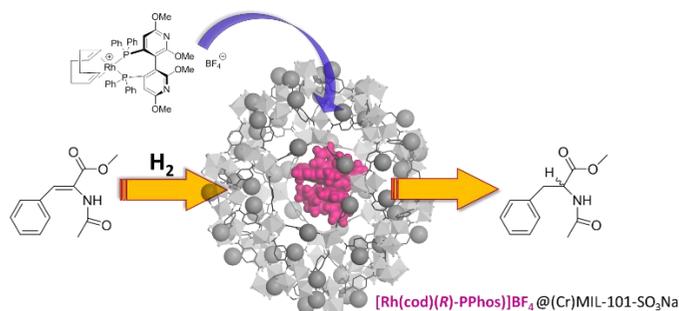
SIMPLE NON-COVALENT IMMOBILIZATION OF ENANTIOSELECTIVE HYDROGENATION CATALYSTS INSIDE MOFs BY ION EXCHANGE

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Metal-organic frameworks (MOFs) are dream materials for heterogeneous catalysis owing to their very high porosity, well-defined crystalline structure and easy tuneability. Indeed, tailoring the MOFs' nodes and linkers for improved catalytic activity and selectivity have attracted tremendous recent interest. Although this approach is scientifically very appealing, we have chosen to investigate an alternative strategy, i.e. simple non-covalent immobilisation of homogeneous catalysts inside MOFs [1,2]. This approach benefits from decades of catalysts' structure development and fine-tuning in solution and also opens up the prospects of high throughput screening of myriads of commercially available catalysts without the need for their tedious synthetic modification.



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ELECTROCHEMISTRY AND ELECTROCHROMIC PROPERTIES OF IRON(II) COMPLEXES

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Transition metal complexes combines the electrochromic properties of transition metal ions with organic molecules and polymers, and due to they are interesting materials for electrochromic uses[1]. The color changes of materials based on transition metal ions may be caused by the redox reaction of metal ion or the ligand molecule [2].

Of particular interest are complexes of Fe(II) ions with which exhibit a specific colors due to the strong MLCT absorption from the metal ions to the ligand moieties and undergo metal-based redox reactions in the cyclic voltammetry measurements exhibiting visible color changes [2-4]. Complexes of Fe(II) ions with different ligands have been obtained and characterized and their properties will be presented [3,4].

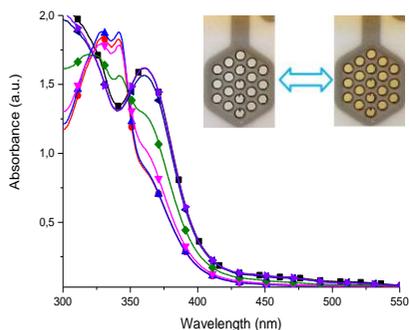


Figure. The spectroelectrochemical properties of Fe(II) complex with terpyridine ligand.

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QUANTUM-CHEMICAL STUDY OF THE MECHANISMS OF SELECTED SODIUM TRIETHYLBOROHYDRIDE-CATALYSED STYRENE HYDROSILYLATION REACTIONS

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Hydrosilylation, which involves the addition of Si-H bond to an unsaturated bond, is one of the key methods of preparation of organosilicon compounds. Conventional catalysts of the reaction are based on complexes of precious metals or other transition elements, yet unremitting effort is made in search of simpler and cheaper substances to catalyse the process of hydrosilylation with organoboron compounds awaking an increasing interest [1-2].

Within this research a study of the mechanism of styrene reactions with phenylsilane, 1,1,3,3-tetramethylsiloxane (TMD5O) and hexamethyldisiloxane (HMDSO), in the presence of sodium triethylborohydride, was performed with the application of quantum chemical methods within density functional theory – namely M06-2X hybrid functional and 6-31++G(d,p) basis set. The proposed mechanism encompasses a series of complete and coherent steps, which remain in full accordance with experimental data on the observed reactions [3]. Their regioselectivity and the formation of an unusual product of styrene reaction with TMD5O were elucidated, explanations were also given for the dependence of styrene conversion on the content of NaBEt₃H and sodium hydride in the reaction system as well as for the failure of styrene reaction with HMDSO.

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FUNCTIONALIZED GRAPHENE OXIDE AS A NEW, HIGH PERFORMANCE ADSORBENT OF HEAVY METAL IONS AND ORGANIC DYES

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During the last decade, two-dimensional materials (2DMs) have gathered a great attention due to their unique chemical and physical properties which make them attractive platforms for diverse applications in sensing and uptake wide range of contaminants [1]. Metal ions and organic dyes in the aqueous environment have caused various diseases and seriously threaten ecosystem and public health with the rapid development of the industry in recent years [2]. Many efforts have been made to develop portable sensors for monitoring heavy metals and dyes in the environment. The obtained results show a new generation of adsorbents based on two-dimensional materials (2DMs) along with their full spectroscopic and morphological characterization. By mastering supramolecular and (dynamic) covalent chemistry approaches, we functionalized 2DMs sheets with functional molecular units exhibiting high affinity towards various heavy metal ions and cationic dyes. In particular, the growth of 2D covalently functionalized architectures were attained by exploring the functionalization of GO through the ring-opening reaction of epoxy groups. Such an approach will make it possible to control the affinity of GO towards specific metal ions and fabricate robust and highly functionalized 2D architectures, which were used in preliminary studies as adsorbents for removal of heavy metal ions and organic dyes.

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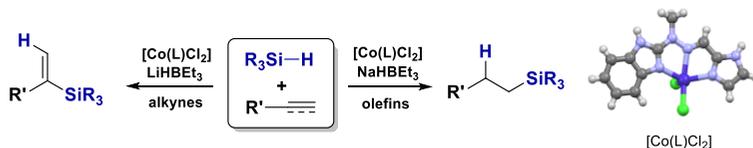
COBALT(II) COMPLEX WITH TRIDENTATE SCHIFF BASE LIGAND - NEW PRECATALYST FOR HYDROSILYLATION OF ALKENES AND ALKYNES

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Hydrosilylation is one of the most important catalytic reactions used in a large industrial scale for the synthesis and modification of silicon compounds.¹ The commonly used catalysts in this process are platinum compounds, in particular Karstedt and Speier catalysts. However, high price of platinum and impossibility of its reuse in technological processes, have prompted scientists to search for alternative solutions, based on much cheaper catalysts containing *3d* transition metal complexes.²

In the communication we present our results on the catalytic activity of new system based on Co(II) complex with the tridentate Schiff base ligand and alkali metal trialkylborohydrides in highly selective hydrosilylation of alkenes and alkynes.



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The research was financially supported by the National Science Center (Poland) within project No. UMO-2016/23/B/ST5/00177.

GENERATION AND POST-SYNTHETIC MODIFICATION OF Co-COMPLEX VIA MICROWAVE-ACCELERATED SONOGASHIRA-GLASER CASCADE REACTION

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We report the first example of application of a metallosupramolecular imine-type cobalt complex obtained via sub-component self-assembly in a Sonogashira-Glaser cascade reaction. Unexpectedly, we found that the (triisopropyl)alkynyl reagent introduced for the Sonogashira reaction with the bromo-functionalized $[\text{Co}^{\text{III}}(\text{L}1)_2]\text{ClO}_4$ complex plays a "Trojan horse" role, inducing a subsequent Sonogashira-Glaser tandem, where the alkynyl substituents 'activated' the diamagnetic Co^{III} species for its Pd-mediated Glaser reduction to the paramagnetic Co^{II} structure.

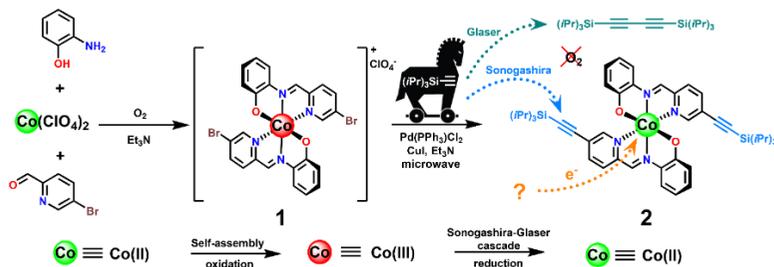


Figure 1. Subcomponent self-assembly of $[\text{Co}^{\text{III}}(\text{L}1)_2]\text{ClO}_4$ (1) and its subsequent functionalization via Sonogashira-Glaser tandem.

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SYNTHESIS, STRUCTURAL STUDIES AND ANTIGLIOMA
POTENTIAL OF SOME PHOSPHONO-
PERFLUOROPHENYLALANINE DERIVATIVES FORMED
BY S_NAr REACTIONS

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Regioselective nucleophilic addition-elimination (S_NAr) reactions found application for fluorinated amino acids syntheses [1,2]. A series of novel phosphono-perfluorophenylalanine derivatives were synthesized by subjecting diethyl (2-(perfluorophenyl)-1-(phenylamino)ethyl)-phosphonate to S_NAr reactions with different type of nucleophiles (thiols, amines, and phenols). The structures of the products were confirmed on the basis of spectroscopic and spectrometric studies. For two representatives, X-ray single crystal diffraction analysis and DFT investigations were performed providing information concerning to the conformational preferences in the solid and isolated states, as well as, in chloroform solution in which NMR data were recorded and was approximated via the usual polarisable continuum model (PCM). Some of the phosphono-perfluorophenylalanine derivatives obtained as well as representatives of previously synthesized perfluorophenyl phosphonate analogues of phenylalanine [3], were subjected to biological studies aimed at evaluation of the compounds antiproliferative potency on selected glioma cell lines.

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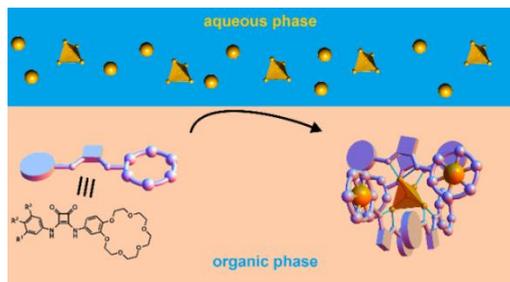
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ION-PAIR INDUCED SUPRAMOLECULAR ASSEMBLY FORMATION FOR SELECTIVE EXTRACTION AND SENSING OF POTASSIUM SULFATE

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Selective extraction of sulfates in the form of alkali metal salts using charge-neutral molecular receptors is one of the holy grails of supramolecular chemistry. Herein, we present a squaramide-based ion pair receptor equipped with a crown ether site that is able to extract potassium sulfate from aqueous to organic phase. This is not the case for the monotopic anion receptor lacking the crown ether unit. ¹H NMR, UV-vis, DOSY-NMR, DLS, MS experiments and solid-state single crystal structure provided evidence of the formation of a supramolecular core-shell like assembly upon interaction of the receptor with potassium sulfate. The presence of monovalent potassium salts, in contrast, promoted formation of simple 1:1 complexes. This feature was utilized to overcome the Hofmeister series and allow for selective extractions of extremely hydrophilic sulfates over lipophilic nitrate anions, which was unambiguously proved by quantitative AES and ion chromatography measurements. A simple modification of the receptor structure led to a "naked eye" optical sensor able to selectively detect sulfates under both SLE and LLE conditions.



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INVERSE ELECTRON-DEMAND DIELS-ALDER (IEDDA)
CONJUGATION OF HALF-SANDWICH METALLOCARBONYL
ENTITIES TO A MODEL PROTEIN

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Bioorthogonal reactions refer to chemical reactions that can be carried out in complex biological settings without interfering with native biochemical processes. Bioorthogonal methods are now widely applied to protein modification / labeling via reaction of non-natural amino acids [1]. In the past decade, a variety of reactions has been identified as suitable for the conjugation of biomolecules using different ligation concepts. One of them is the inverse electron demand Diels-Alder (IEDDA) reaction between 1,2,4,5-tetrazines and strained olefins or alkynes [2]. The aim of this study was to synthesize half-sandwich metallocarbonyl complexes containing a norbornene handle [3]. These complexes display unique spectroscopic properties since they absorb in the mid-IR spectral region allowing them to be detected by IR spectroscopy. IEDDA reactions between metallocarbonyl norbornenes and model 3,6-dipyridyl tetrazine as well as tetrazine groups chemically incorporated into Bovine Serum Albumin were extensively investigated.

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STRUCTURAL ANALYSIS OF A SERIES OF NHC ALTERED NITRO OLEFIN METATHESIS CATALYSTS

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Presented study shows a structural analysis of a series of NHC altered nitro olefin metathesis catalysts.

Using the data obtained from diffraction studies, we have calculated buried volume (Vbur%) for the series of NHC ligands in SambVca 2 software developed by Cavallo group [1]. The same software allowed us to prepare steric maps based on Vbur% calculations (Fig. 1).

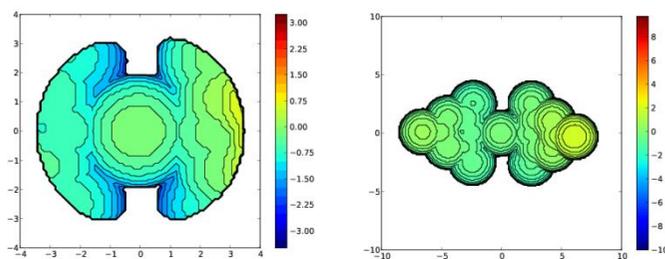


Figure 1. Steric maps calculated in SambVca software [1] for SIMes bearing catalyst for standard 3.5 Å (left) an enlarged 10 Å (right) sphere radius.

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MULTIPLE PROPERTY MODIFICATION BY COMPONENT EXCHANGE

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Imines have a wide range of uses in chemistry, including metal coordination and as protecting groups [1]. Their reversible formation is suitable for self-healing applications [2,3]. The reversible behavior further allows component exchange either by imine metathesis or aldehyde/amine exchange [4,5]. This provides the means for property tailoring. It will be shown that multiple properties can be modified by component exchange, especially for functional materials. It will be shown that color, fluorescence, and electrochemical properties can be reversibly tuned by reversible imine formation and component exchange. Ultimately, component exchange can be incorporated into plastic electronics for adjusting the properties of working devices.

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HIGHLY EMISSIVE MATERIALS FOR USE IN ELECTROFLUORESCENT DEVICES

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Electrofluorescence is the modulation of emission with applied potential [1]. Electrofluorescent materials therefore undergo electrochemically mediated fluorescence turn-off and turn-on. Incorporating electrochemical response in traditional fluorophores is possible by covalently attaching an electroactive moiety to the emissive core. While this approach leads to efficient electrochemically mediated fluorescence response in solution, the otherwise strong emission is quenched in devices. This is a result of intrinsic quenching in the solid state from aggregation caused quenching [2]. Ideal fluorophores for use as the emission layer in electrofluorescent devices therefore must be highly emissive in the solid state. The preparation of fluorophores that are highly emissive in the solid state will be presented. Their use as the electrochemically responsive layer in working electrofluorescent devices will also be examined.

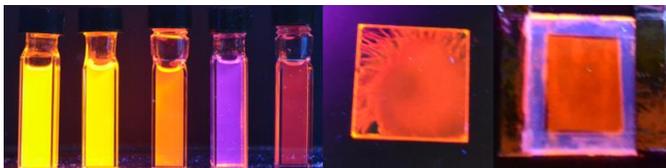


Figure 1. Photographs showing the solvatochromic properties of an intrinsic fluorophore in different solvents (left), as thin film on glass (middle), and in a functioning electrofluorescent device.

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MICROORGANISMS ADAPTATION TO XENOBOTICS ASSIMILATION

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For many years, there is still growing pollution of the environment with chemical compounds with high biological activity. Xenobiotics, such as pesticides and pharmaceuticals, already adversely affect the functioning of organisms at relatively low concentrations. The main factor limiting contamination of the environment with xenobiotics is the process of their biodegradation by environmental microorganisms. The assimilation of xenobiotics by bacteria present in waters and soils is strongly dependent on their bioavailability for cells. That is why it is so important to know and understand the mechanisms of adaptation of environmental bacterial cells to the degradation of toxic pollutants [1,2].

In order to fully and multifaceted assessment of the adaptation mechanisms of bacterial cells, analyzes of changes in the cell wall structure, its chemical composition and permeability were performed. In addition, cell shape and size studies were carried out, which were combined with the analysis of their adhesive properties.

All studies were carried out using bacterial strains isolated from the environment and subjected to short-term and long-term contact with pharmaceuticals, such as nitrofurantoin, and related aromatic compounds.

The results of the study indicate the diversity of cell strategies for survival in the presence of xenobiotics. The changes in cell surface properties, including total cell membrane permeability, varied. An important novelty of the study was the application of advanced spectroscopic methods to the study. They allowed to get to know how the surface of cells exposed to xenobiotics changed.

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NOVEL SUPRAMOLECULAR ARCHITECTURES WITH Cu(I), Ag(I) AND Ni(II) METAL IONS AND THEIR BIOLOGICAL PROPERTIES

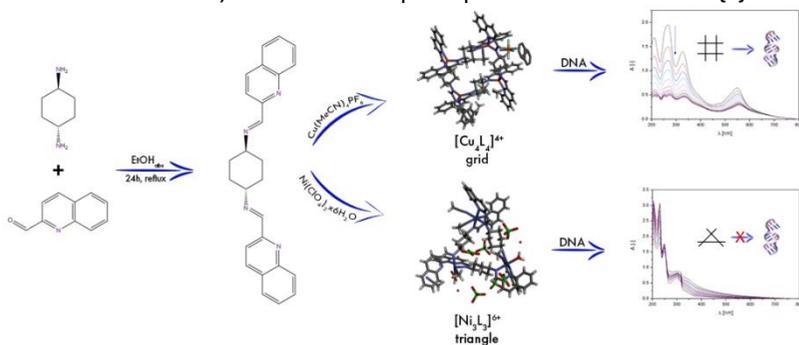
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The fascination with supramolecular chemistry over the past few years has led to the synthesis of an increasing number of complex functional structures. (N₂)₂-donor ligand was synthesized by condensation reaction of 1,4-diaminocyclohexane with 2-quinolinecarboxaldehyde. As a result of the complexation reaction, a molecular triangle with Ni(II) ions and a grid with Cu(I) ions were obtained [1]. They exhibit different affinity to B-DNA: grid interacts with it, while triangle does not. Using spectroscopic methods such as: electronic absorption titration, fluorescence competitive binding with ethidium bromide (EB) and circular dichroism (CD) the ability of complexes to bind to DNA, BSA (Bovine Serum Albumin) and induction G-quadruplex have been examined [2].



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MFJ: The work was supported by the National Science Centre, Poland (SONATINA grant, no. 2017/24/C/ST5/00181).

ELECTROPOLYMERIZED THIN FILMS – STRUCTURE
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Electrochemically controlled formation of thin films of polymers at electrode surfaces is one of the routes to design new functional materials [1]. Electropolymerization is the technique of surface modification in which a polymeric film is electrodeposited onto the electrode surface by utilizing an applied potential to initiate the polymerization of substrates and it requires a good solubility of monomers in the solution of electrolyte. The preparation and electrochemical as well as spectroelectrochemical properties of organic polymers and metallopolymers will be demonstrated [2,3].

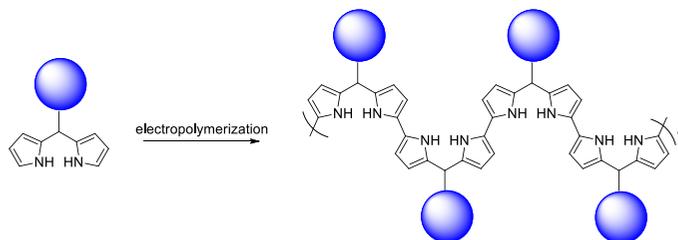


Figure. Schematic representation of electropolymerization of dipyrromethane-functionalized monomers.

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SPECTROELECTROCHEMISTRY OF DITHIENOPYRROLE BASED
POLYMERS

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Two new dithienopyrrole derivatives were synthesized, namely dithieno[3,2-b:2',3'-d]pyrrole *N*-functionalized with 4-(2-heptylthiazol-4-yl)phenyl (DTP1) and 4-(5-octylthiophen-2-yl)phenyl (DTP2) groups. Both monomers readily electropolymerize to yield the corresponding polyDTP1 and polyDTP2.

Thin polymeric films deposited on platinum or ITO electrodes exhibit electrochromic behavior. As evidenced by UV-vis-NIR spectroelectrochemistry, both polymers undergo classical (for conjugated polymers) oxidation, involving the formation of polarons in the first step and bipolarons in the second one. An interesting feature of the oxidation of polyDTP2 is the highly delocalized nature of bipolarons, indicative of the metallic state (featureless absorption tail extending towards NIR part of the spectrum). In order to elucidate the exact nature of the electrochemical oxidation process detailed Raman spectroelectrochemical investigations of polyDTP2 were carried out, supported by the vibrational model calculations using two methods: DFT and General Valence Force Field (GVFF). The results show that the polarons (radical cations) are formed in the pyrrole ring whereas bipolarons (dications) exhibit classical configuration with charges located in C₂ positions of the thiophene rings [1].

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ADVANCEMENTS OF THE MULTICOMPONENT CATALYTIC SYSTEM FOR ALKYNE METATHESIS

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Alkyne metathesis, a reaction discovered in mid-70s, although put away for decades, is gaining increasing interest in organic synthesis [1]. It offers a way to obtain stereodefined macrocyclic alkenes selectively in a sequence of ring-closing alkyne metathesis (RCAM) and hydrogenation reactions, which is not always possible with olefin metathesis. The first homogeneous, multicomponent catalyst consisted of molybdenum hexacarbonyl activated by 1,3-dihydroxybenzene at elevated temperature [2].

In a classical multicomponent catalytic system, phenolic co-catalyst is used in equimolar amount relative to the alkyne. On the other hand, molecular catalysts are also known, however, their preparation is laborious and they require rigorously inert atmosphere to operate [3]. Up until now, silanols of various types have not been thoroughly investigated as alkyne metathesis activators, although there are examples of their successful use [4]. This kind of co-catalysts is also a more environmentally friendly and harmless substitute for phenols. Another improvement of the system is to use more labile Mo(0) complexes as precatalyst. This presentation is going to summarize advancements in the catalysis of alkyne metathesis contributed by both these factors.

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SALT RECOGNITION BY DITOPIC RECEPTORS UTYLIZING AMINO BENZOIC ACIDS SCAFFOLDS

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Design of ion pair receptors, compounds capable of simultaneous recognizing cations and anions, has recently emerged as a promising area of supramolecular chemistry. Due to electrostatic or/and allosteric effects heteroditopic receptors may serve as hosts recognizing ion pairs in a cooperative manner what can eliminate the drawbacks of homotopic receptors which, in order to interact with the ion, must compete with the counterion. Simultaneous binding of cation and anions improves the salt lipophilicity, thus facilitating its solubilization, extraction and membrane transport and makes such systems extremely important in context of biology, environmental protection and medicine. Effective cooperativity requires proper embedding of distinct recognition motifs for both cations and anions on a single molecular scaffold. In this project, we present *o,m,p*-aminobenzoic acids as scaffolds for ion-pair receptors, utilizing azacrown ether cation recognition site and substituted urea as a tunable anion recognition site (Fig. 1). The proposed architecture is highly modular, and allow for easy alteration of building blocks so as to tune the binding properties and to allow further functionalization, e.g. immobilization on a solid support [1,2].

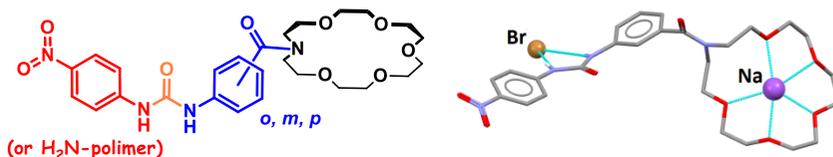
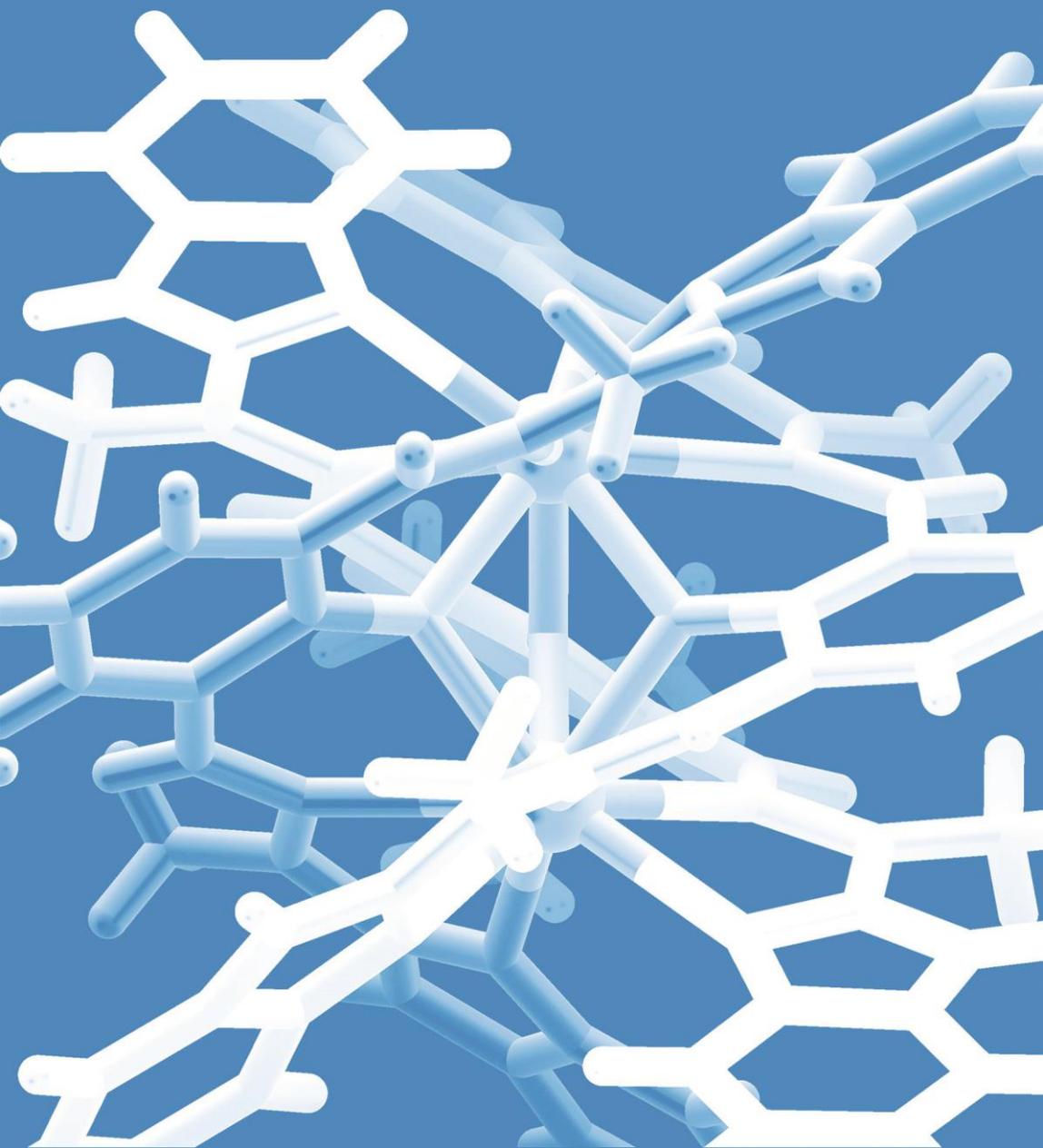


Figure 1. (left) General architecture of aminobenzoic acid derived receptors. (right) example of a solid state structure of a NaBr@receptor complex.

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