*The **CREA**tion of the Department of Physical Chemistry of Biological Sys**TE**ms [CREATE]*

666295 — CREATE — H2020-WIDESPREAD-2014-2015/H2020-WIDESPREAD-2014-2

2nd annual update of IPC research programme

[Deliverable D 3.3]

Level of dissemination: Public

Warsaw, June 2019

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I. Overview

According to the CREATE proposal, deliverables 3.2 – 3.4 should consist of an upgrade of IPC research plan which, subsequently, is reported to the Polish Ministry of Science and Higher Education. However, as reported under Deliverable 3.1, in the meantime this procedure of reporting research plans to the Ministry of Science and Higher Education was changed. At present, only research tasks which are to be financed directly from the funds of the Ministry should be reported. For this reason a different approach was adopted to the deliverables 3.2 – 3.4. Currently, the abovementioned deliverables are composed of 2 parts:

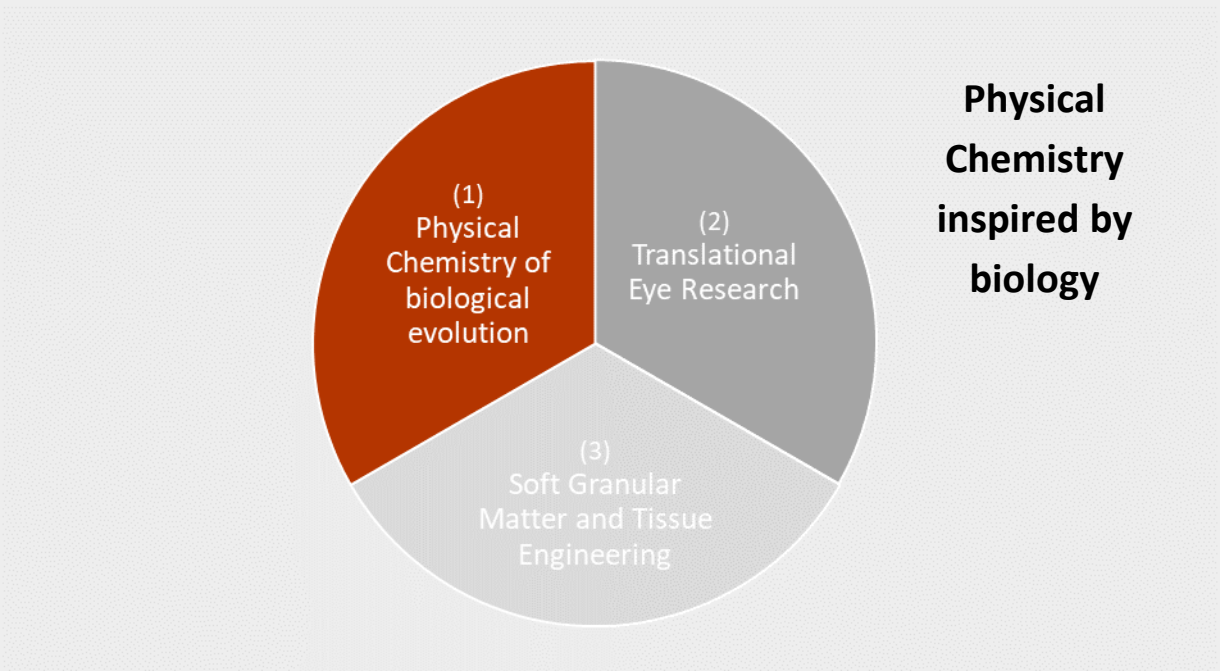
- description of strategic projects of huge impact to be implemented by the ERA Chair holder, possibly with collaboration of other research groups from IPC PAS (main part of the document)
- specification of research tasks reported to the Polish Ministry of Science and Higher Education to be financed from governmental subvention (annex no. 1).

Previously, **three strategic projects of huge impact on IPC PAS,** which were set by the ERA Chair holder, were described in detail under Deliverable 3.2, i.e.:

(1) Physical Chemistry of biological evolution

(2) Research Agenda of Translational Eye Research

(3) Soft Granular Matter and Tissue Engineering



Current status of their implementation will be described under the Deliverable 4.3.

Due to the fact that proposed research plan is very complex, ambitious and long-term, will be continued in the current year. For this reason, no other new topics can be added to this research agenda.

ANNEX

IPC research programme reported to the Ministry of Science and Higher Education

This project has received funding from the *European Union's Horizon 2020 research and innovation programme* under grant agreement No 666295

Research group 1 – Plasmonic nanostructures for bio-spectroscopic analysis

dr hab. Agnieszka Kamińska

1. Team research tasks

1) Analysis of the stage of pancreatic cancer using the methods of Raman spectroscopy and surface-enhanced Raman spectroscopy coupled with microfluidics.

2) Development of a method for the separation of cancer cells from the blood by means of the dielectrophoresis method coupled with SERS measurements.

2. Aim of the research

The aim of the research will be the quantitative and qualitative analysis of the obtained results of examined pancreatic cancer (in the form of tissues and homogenates) samples, in terms of the stage, using standard Raman and SERS spectroscopy) and the development of an innovative method of isolation, concentration and simultaneous spectral analysis of circulating cells cancer.

3. Research methodology

The research will include the analysis of postoperative cancer tissues with different stages of pancreatic cancer and the detection of circulating tumor cells (CTCs) of pancreatic tumors from the patient's blood. Research will be carried out according to two schemes: direct and indirect analysis. In the direct studies (tumor tissue analysis), Raman spectra will be collected in mapping mode. In the indirect tests the SERS signal of the analyzed samples will be obtained after homogenization of available tumor tissues (analysis of tumor homogenates). In indirect detection, we intend to use three further methods: (i) analysis of SERS homogenates "directly", (ii) detection of cancer cells based on the so-called spectra of the 'Raman reporters', i.e. molecules, mainly dyes that give very strong Raman signals, in an antigen-antibody interaction system using specific affinity for antibodies to tumor cell proteins ('immunoRaman' test) and (iii) using 'Raman reporters' study for the presence of CTCs in blood from patients with pancreatic cancer using microfluidic techniques.

Intermediate detection will increase the sensitivity and selectivity of the assays within the planned studies of the same cancer.

Research group 3 – Physical Optics and Biophotonics Group

Professor Maciej Wojtkowski

Research task: An enhancement of cerebrovascular imaging with contrast agents using 800nm and 1300nm OCT systems.

Aim of the research: To develop alternative methods of the contrast improvement in Optical Coherence Microangiography reconstructions of growing brain tumor using Intralipid.

Methods: This is continuation of work done in 2018. Recently our group has demonstrated new OCM instrument dedicated to animal brain imaging enabling to characterize the cytoarchitecture of mouse brain at cellular level and the blood circulation system dynamics in three dimensions [2, 3]. OCM enables also to contrast Intrinsically micro-vessels by analyzing temporal phase variations of the interferometric signals - so called Optical Coherence Microangiography (OCMA). In order to improve imaging contrast in OCMA we propose using intralipid to visualize the glioblastoma tumor up to late phases of its growth. Intralipid is the polydisperse aqueous suspension of fat emulsions and they are more symmetrical in shape compared to red blood cells (RBCs). The main principle beyond the increase in contrast with intralipid injection is that they acts as strong backscatters and fill the gap between adjacent RBCs as they flow with similar speed as RBC's. The set-up is currently installed at Nencki Institute of Experimental Biology.

Literature:

[1] R. K. Wang, S. L. Jacques, Z. Ma, S. Hurst, S. R. Hanson, and A. Gruber, "*Three dimensional optical angiography"* Opt. Express 15, 4083–4097 (2007).

[2] O. Liba, E.D. SoRelle, D. Sen, and A. de la Zerda *"Contrast-enhanced optical coherence tomography with picomolar sensitivity for functional in vivo imaging"* Sci. Rep. 6, 23337 (2016).

Research group 4 – Surface Nanoengineering group

Dr. hab. inż. Joanna Niedziółka-Jönsson

SYNERGETIC GROUP

Surface modification for (bio)sernsors.

The aim of the research is to modify the surface of an optical fiber probes to be used as a transducer for detection of (bio)molecules. In our research, we will use an interferometry method [1] to determine the rate constants of association and dissociation reactions.
Moreover, we would like to continue studies of the influence of the presence both native and additional oxide layer on resonance, propagation and sensitivity of the optical system based on long-period fiber gratings [2,3], as well as developing methods for modification of these layers.

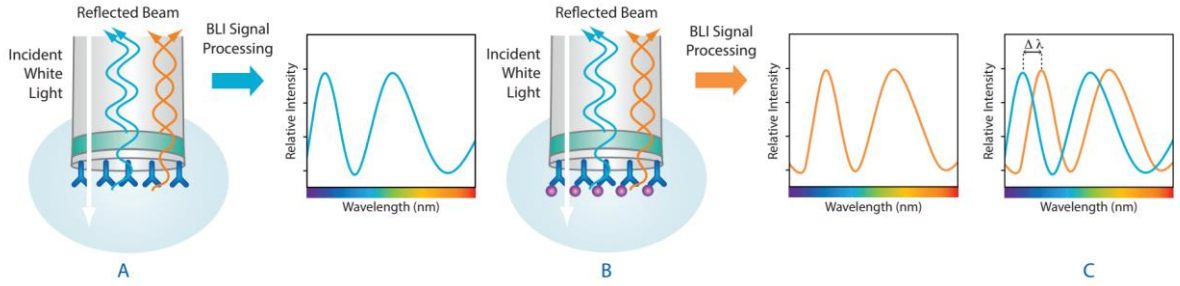


Figure. Schematic representation of the measurement system by interferometry (www.moleculardevices.com).

We would like to use the surface plasmon resonance of metallic nanostructure to study molecular interaction between peptide – protein, bacteriophage adhesin – lipopolysaccharides with a help of UV-vis spectrometry in suspensions [4,5].

Literature:

[1] R. Różycki-Bakon, M. Koba, P. Firek, E. Roźniecka, J. Niedziółka-Jönsson, M. Śmietana, "Stack of nano-films on optical fiber end-face for label-free biosensing applications", Journal of Lightwave Technology, 34 (2016) 5357-5363.

[2] M. Janczuk-Richter, M. Piestrzyńska, D. Burnat, P. Sezemsky, V. Stranak, W. J Bock, R. Bogdanowicz, J. Niedziólka-Jönsson, M. Śmietana, "Optical investigations of electrochemical processes using a long-period fiber grating functionalized by indium tin oxide", Sensors & Actuators: B., 279 (2019) 223–229.

[3] M. Piestrzyńska, M. Dominik, K. Kosiel, M. Janczuk-Richter, K. Szot-Karpińska, E. Brzozowska, L. Shao, J. Niedziółka-Jonsson, W.J. Bock, Mateusz J. Smietana, „Ultrasensitive tantalum oxide nano-coated long-period gratings for detection of various biological targets", Biosensors & Bioelectronics 133 (2019) 8-15.

[4] A. Lesniewski; M. Los, M. Jonsson-Niedziółka, A. Krajewska, K. Szot, J.M. Los, J. Niedziolka-Jonsson; Biocon. Chem., 25 (2014) 644-648.

[5] P. Kannan, M. Los, J. M. Los, J.oanna Niedziolka-Jonsson; Analyst, 2014, 139 (14), 3563 - 3571.

Research group 5 – Phase behaviour and dynamics in polymer solutions

Professor Jacek Gregorowicz

Ionic liquids as solvents in polymer technology – continuation.

Within the project in 2020 we plan to continue investigations of surfactants aggregation, mainly ionic surfactants, in dilute solutions (micellization) and investigations of lyotropic liquid crystalline phases form by these surfactants in hydrophilic ionic liquids. We aim at understanding how structure of a surfactant, structure of an ionic liquid and water present in a system influence the aggregation process. The investigations of the aggregation processes will obey measurements of surface tension, ^{1}H NMR chemical shifts and diffusion coefficients. Investigations of liquid crystalline phase will be performed with use of optical microscopy, DSC and X-ray diffractometry. In addition investigations of micellization processes with confocal microscopy is planned.

Research group 6 – Nanoelectrochemistry group

Dr. hab. Wojciech Nogala

1. Research tasks

a) Scanning electrochemical microscopy (SECM) mapping of topography and redox activity of immobilized E. coli bacteria
b) Imaging of protective activity of red blood cells against extracellular hydrogen peroxide

2. Aim of the research

a) Determination of spatial position of enhanced redox activity loci in individual bacteria
b) Detection of water channels on the cell membrane

3. Description and methodology

Although cell membranes are hardly permeable to charged hydrophilic species, such as $Fe(CN)_6^{3-}$ or $Ru(NH_3)_6^{2+}$,[1] the ability of *E. coli* bacteria to reduce or oxidize ionic mediators is a known fenomenon.[2] This suggest the existence of channels permeable to these ions or redox active proteins at the bacteria surface. Nothing is known about the location of such an activity on the cell surface. A similar problem to solve is a question about location of aquaporin protein molecules in the membrane of red blood cells. Aquaporins facilitate transport of hydrogen peroxide into the cell,[3] where is disproportionated by catalase to water and molecular oxygen.[4] To find location of aforementioned activities we are going to perform recently proposed nanoscale resolution hopping mode SECM mapping of activity and topography[5] of immobilized *E. coli* bacteria and human red blood cells. $Fe(CN)_6^{3-}$ or $Ru(NH_3)_6^{2+}$ will be generated at the SECM nanotip by oxidation of $Fe(CN)_6^{4-}$ or reduction of $Ru(NH_3)_6^{3+}$, respectively. Hydrogen peroxide will be generated at the mercury nanoelectrode by 2-electron oxygen reduction.

Literature:

[1] Lin, TE.; Rapino, S.; Girault, HH.; Lesch A. Chem. Sci. 2018, 9, 4546–4554.
[2] Gao, G.; Wang, D.; Brocenschi, R.; Zhi, J.; Mirkin, MV. Anal. Chem. 2018, 90, 12123−12130.
[3] Martinotti, S.; Laforenza, U; Patrone, M.; Moccia, F.; Ranzato, E. Int. J. Mol. Sci. 2019, 20, 764.
[4] Sepunaru, L.; Sokolov SV.; Holter, J.; Young, NP.; Compton, RG. Angew. Chem. Int. Ed. 2016, 55, 9768–9771.
[5] Jedraszko, J.; Michalak, M.; Jonsson-Niedziolka, M.; Nogala, W. J Electroanal. Chem. 2018, 815, 231-237.

Research group 7 – Chemistry in Confined Spaces

Dr. Volodymyr Sashuk

1. Research task

Photoswitching under confinement

2. Aim of research

The aim of the work is the reversible isomerization of photoswitches in supramolecular systems of varying complexity.

3. Description and methodology, literature

The reversible binding of photoswitches with macrocyclic compounds is a very promising but poorly researched method of creating dynamic complex systems. Preliminary studies have shown that the structural and electronic changes of a photoswitch do not always cause 'tangible' changes in its binding properties.[1] As part of the proposed project, we intend to identify "guest-host" couples capable of reversible self-assembly under the influence of light. The model photoswitch will be azobenzene, and tested macrocycles–cucurbiturils, pillarpyridiniums and pillararenes. Research will include interactions between both individual molecules and the molecules deposited on the surface of nanoparticles. We predict that limiting the degrees of freedom on the surface of nanoparticles will favor the reversibility of supramolecular systems.
The synthesis of organic molecules, nanoparticles and their functionalization will take place according to literature protocols and own ones based on classical retrosynthetic algorithms. Binding and self-assembly of nanoparticles will be investigated using ITC, NMR, UV-Vis and SEM

[1] Samanta et al. Reversible photoswitching of encapsulated azobenzenes in water, *PNAS*, **2018**, 115, 9379-9384.

Research group 8 – Dynamics of light-induced bimolecular reactions

Dr. hab. Angulo Gonzalo

SYNERGETIC GROUP

1. The Team's research task

Experimental studies of the kinetics and dynamics of electron, proton and energy transfer reactions in solution and other disordered media with one and two excitation pulses.

Experimental and theoretical study of intramolecular reactions with the help of the generalized Langevin equation: expansion to more than one reaction coordinate.

Novelty: we want to expand to the study of chemical reactions in gels.

2. Aim of research

Improve the physical description and therefore the prediction capabilities of the studied reactions.

3. Description and research methods, literature.

Fluorescence up-conversion and transient absorption in short time scales. Stationary electronic spectroscopy. Now also: fluorescence microscopy. Another novelty: we are going to deeply improve the experimental set-up for transient fluorescence and expand its capabilities.

[1] Influence of the excitation light intensity on the rate of fluorescence quenching reactions: pulsed experiments. Gonzalo Angulo et al, Phys. Chem. Chem. Phys., **2017**, 19, 6274—6285.

[2] How good is the generalized Langevin equation to describe the dynamics of photo-induced electron transfer in fluid solution? Gonzalo Angulo et al *Journal Of Chemical Physics* **2017**, *146*, 244505.

[3] Salt Effect in Ion-Pair Dynamics after Bimolecular Photoinduced Electron Transfer in a Room-Temperature Ionic Liquid. A. Rosspeintner, M. Koch, G. Angulo, E. Vauthey *J. Phys. Chem. Lett.* **2018**, *9*, 7015−7020

[4] Optical transient absorption experiments reveal the failure of formal kinetics in diffusion assisted electron transfer reactions. Gonzalo Angulo et al. *Physical Chemistry Chemical Physics*, **2018**, *20*, 25531- 25546.

4. Figure illustrating the research task

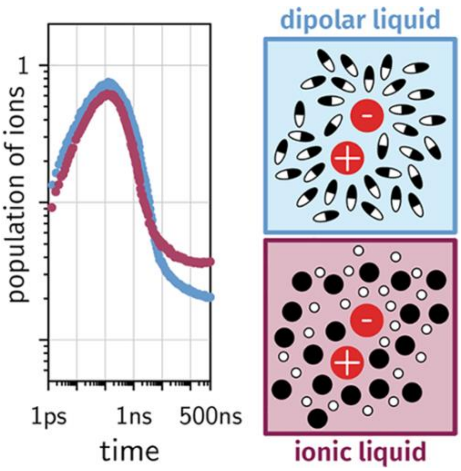


Fig. Kinetics of the products of photo-induced electron transfer reaction between perylene and N,N-dimethylaniline in dipolar and ionic liquid solutions of the same viscosity. We found that in the ionic liquid the only difference with respect to the dipolar liquid is the final yield of the ions produced, all the rest of the kinetics are very similar. Surprisingly, this can be very well explained by the Encounter Theory with addition of the simple Debye-Hueckel treatment of the ionic liquid.

RESEARCH GROUP 9 – Coordination metal complexes and functional materials

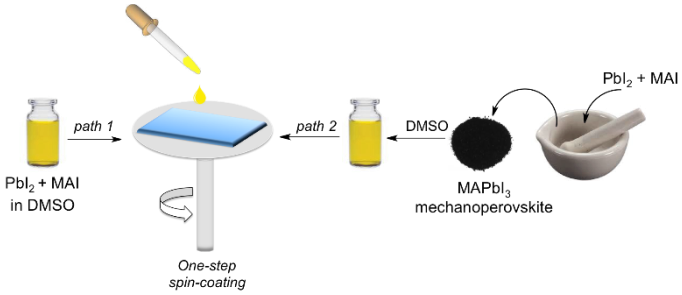
Professor dr. hab. inż. Janusz Lewiński

PROSPECTIVE GROUP

Scientific activity of our group has multidisciplinary character and encompasses the fundamental inorganic and organometallic chemistry as well as materials science and nanoscience. In 2020 our research program will focus on the development of two the most important classes of inorganic-organic hybrid materials nowadays: (I) hybrid inorganic-organic halide perovskites for photovoltaic applications and (II) porous metal-organic frameworks (MOFs).

I. Development and photovoltaic applications of hybrid inorganic-organic halide perovskites

The field of lead halide perovskites is thriving in the last few years and represents emerging materials for delivery of the next generation of solar cells. Perovskite solar cells have enabled power conversion efficiency comparable with established technologies, such as silicon and cadmium telluride.



We aim to rise the challenge of further development of original inorganic-organic hybrid lead halide perovskites and investigations on their physicochemical properties of the bulk crystals and perovskite thin films. As lead toxicity is one of the key challenges facing with lead halide perovskites, our research effort will be also devoted to developing low toxic metal halide perovskites and their derivatives for photovoltaic applications. Particularly, we will focus on the synthesis of hybrid perovskites using the mechanochemical process developed in our group recently.[1,2,3] Next, perovskite thin films for characterization will be fabricated through one-step spin-coating procedure using a precursors solution as well as solution prepared after dissolution of mechanochemically synthesized polycrystalline perovskite powder (Scheme 1). Integral part of this research will be the utilization of resulted materials as an absorbing layer for solar energy conversion and optoelectronic applications in a close cooperation with the reputable international expert across in the photovoltaic area (Prof. M. Graetzel, *EPFL Lausanne*).

[1] D. Prochowicz, M. Franckevičius, A. M. Cieślak, S. M. Zakeeruddin, M. Grätzel, J. Lewiński *Journal of Materials Chemistry A*, **2015**, 3, 20772.

[2] D. Kubicki, D. Prochowicz, A. Hofstetter, M. Saski, P. Yadav, D Bi, N. Pellet, J. Lewiński, S.M. Zakeeruddin, M. Grätzel, L. Emsley, *J. Am. Chem. Soc.*, **2018**, 140, 3345.

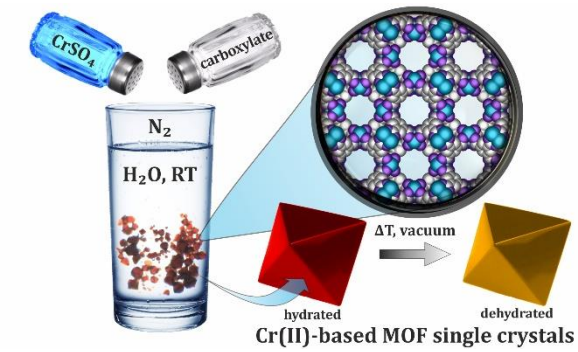
[3] D. Prochowicz, P. Yadav, M. Saliba, D.J. Kubicki, M.M. Tavakoli, S.M. Zakeeruddin, J. Lewiński, L. Emsley, M. Grätzel*, Nano Energy*, **2018**, 49, 523.

II. Development and applications of porous metal-organic frameworks (MOFs)

MOFs have been one of the fastest growing fields in chemistry during the past decade due to their remarkable properties *e.g.* large surface area, high thermal stability, adjustable pore size as well as customisable chemical properties. Along with the increasing chemical and structural variety of MOF materials the more and more sophisticated areas of application have emerged, which often require

tailoring the properties of MOFs by post-synthetic modifications. One of the promising strategies to achieve that goal is to utilise the redox-activity of MOFs, which could afford new materials of enhanced catalytic, selective gas sorption and electron transfer properties.

Based on our expertise in the field of functional porous materials[1,2] we are planning to develop new synthetic strategies for the preparations of various MOFs, including novel redox-active MOFs.



We have already demonstrated the straightforward synthetic strategy of single-crystalline redox-active chromium (II)-based MOFs, which were prepared in water at room temperature.[3] We are going to further develop this strategy by introduction of a greater variety of organic linkers and transition metal centres (e.g. Fe, Co, Ni) to prepare more complex MOF networks with high application potential in gas separation as or catalysis. We also plan to utilize alternative solvent-free synthetic strategies i.e., mechanochemistry, which has already been identified as a powerful tool for preparation of complex porous materials in a relatively simple and environmentally-friendly way.

[1] D. Prochowicz, K. Sokołowski, I. Justyniak, A. Kornowicz, D. Fairen-Jimenez, T. Friščić, J. Lewiński, *Chem. Commun*., **2015**, 51, 4032.

[2] D. Prochowicz, J. Nawrocki, M. Terlecki, W. Marynowski, J. Lewiński, *Inorg. Chem*., **2018**, 57, 13437.

[3] M. Leszczyński, A. Kornowicz, D. Prochowicz, I. Justyniak, K. Noworyta, J. Lewiński, *Inorg. Chem.*, **2018**, 57, 4803.

Research group 10 – Soft Condensed Matter

Professor Robert Hołyst

SYNERGETIC GROUP

1. Physical chemistry inspired by biology.
2. We will test new experimental method for determination of equilibrium constant for molecular complex formation in vitro and in vivo.
3. In our method, we use the laser to photo-bleach fluorescently labeled molecules. From the change of fluorescent intensity and known molecular brightness we calculate a number of photo-bleached molecules. For example we can use immobilized DNA in gels and anticancer drugs (some of them, like doxorubicin are fluorescent). Photobleaching would affect most strongly only those drugs which were attached to immobilized DNA. In this way we would get a number of drug-DNA complexes formed and the equilibrium constant. This method was proposed by Jorg Langowski from the Cancer Institute in Heidelberg . we will test this method in our lab and introduce it as a new method in our toolbox which we use for the study of biochemical reactions.

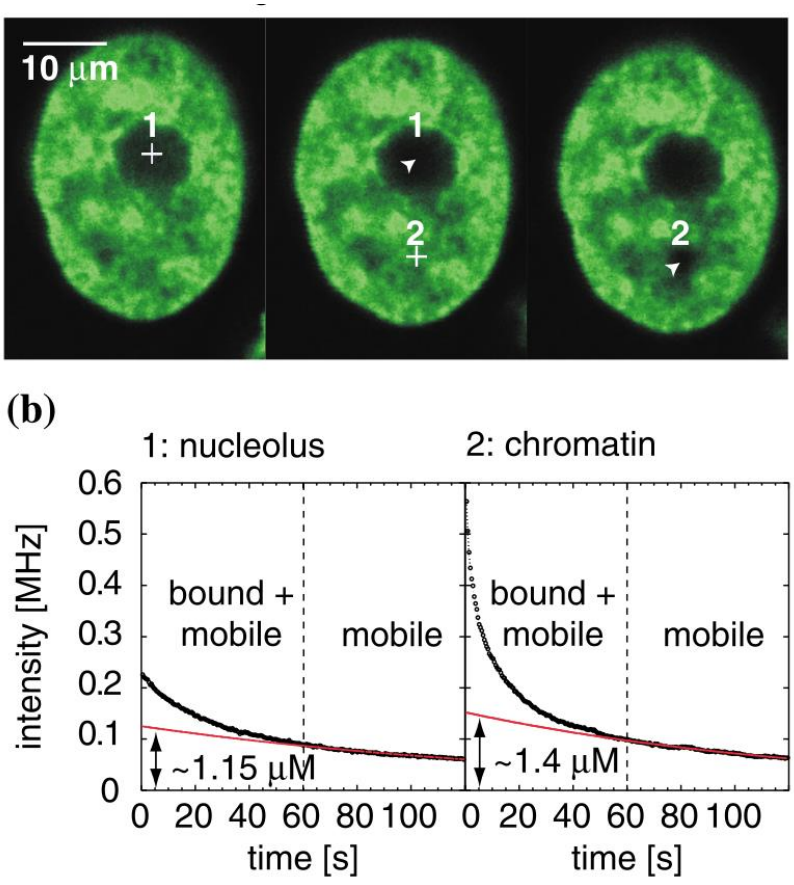


Fig.1 This figures shows photobleaching of GFP molecule attached to histones in nucleolus and chromatin. After Langowski in J. Mol. Biol. (2003) 334, 229–240.

Research group 11 - Microfluidics and Complex Fluids Research Group
Professor dr. hab. Piotr Garstecki

SYNERGETIC GROUP

In 2020 the Microfluidics and Complex Fluids Research Group, besides realization of two large research programs within grants from the National Science Center and from the Foundation for Polish Science, will conduct research activities in three directions:

i) development of microfabrication and surface modification strategies for fabrication of microfluidic devices,

ii) development of systems and methods using microfluidic solutions for analytical and synthetic chemistry, and

iii) development of concepts for new amphiphilic molecules for minimization of spontaneous generation of micelles and nanodroplets in water emulsions in fluorinated oils.

Research group 12 – Organization and synthesis of nanoparticles

Dr. hab. Marcin Fiałkowski

1. **Team research task**

    a) Photo-responsive fabrication of water/oil Pickering emulsions

    b) Characterization of the properties of the obtained emulsions.

2. **Aim of the research**

    Our goal is to develop a fcile method of synthesis of water-in-oil or/and oil-in-water Pickering emulsion that is created in response to external photostimulation. Such system will enable encapsulation of water- or oil-soluble compounds in response to visible light as an extarnal stimuli. Also, we plan to find a method to bind together chemically the particles located at the water-oil interface.

3. **Description and methodology of research**

    We plan to employ gold nanoparticles coated with a mixture of hydrophobic ligands and ligands functionalized with donor-acceptor Stenhouse adduct (DASA). Upon illimination with visible light, DASA izomerizes to a zwitterionic form which is accompanied by substantial increase in its hydrophility. The nanoparticles become amphiphilic and can form Pickering emulsion. In our research we will adapt the oil-water interfacial syntesis protocol developed recently in our group [T. Andryszewski, M. Iwan, M. Hołdyński, M. Fiałkowski, Chemistry of Materials 28, 5304 (2016)] to photo-responsive gold nanoparticles.

Research group 13 – Physical chemistry of complex systems

Dr. hab. Wojciech Góźdź

In 2020 we are planning to perform the following research tasks:

We are going to investigate the effects on confinement on the fluid composed of particles with competing interactions. The particles attract themselves at short distances and repel at large distances. They form many different liquid crystal phases like cluster crystals, hexagonal, gyroid, or lamellar phase [1]. We are going to investigate stability and deformation of these phases under different types of confinement. We will study the influence of the geometry, symmetry, and topology of the confining media on the structure of different crystalline phases. We will perform Monte Carlo simulations in Grand Canonical ensemble to investigate the stability and structure of the confined fluid [2].

Important publications:

[1] Zhuang, Y.; Zhang, K.; Charbonneau, P. *Equilibrium Phase Behavior of a Continuous-Space Microphase Former*. Physical Review Letters **2016**, 116, 098301

[2] Serna, H.; Noya, E. G.; Góźdź, W. *Assembly of helical structures in systems with competing interactions under cylindrical confinement*. Langmuir **2018**, 35, 702–708.

Research group 14 – Charge transfer processes in hydrodynamic systems

Dr. hab. Martin Jonsson Niedziółka

PROSPECTIVE GROUP

Task 1: Using flow injection microfluidics to investigate the inhibition and regenereation of enzymes.

Goal: The goal of the task to investigate the timescale of inhibtion and recovery of enzyme function using a microfluidic system where the concentration of inhibitor can be changed rapidly. This can give us clues to the mechanism of the inhibition and eventually be of help to better understand and protect enzymes from deactivation.

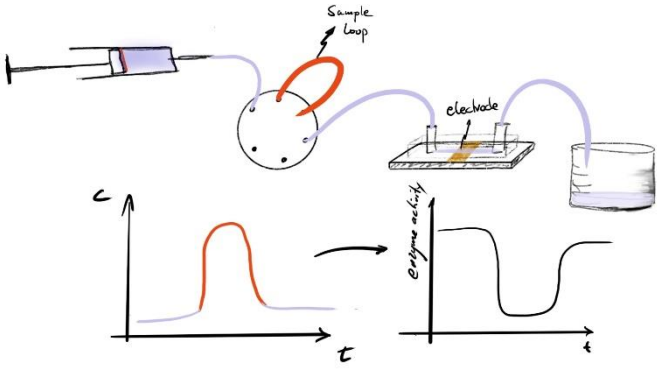


Fig 1 Schematic illustration of the flow injection system for investigation of enzyme inhibition.

Task 2: Measuring endogenous levels of glutamate in vitro in neuron cell cultures

Goal: The goal is to develop a biosensor that makes it possible to perform long-term measurements of glutamate using electrochemical methods at low overpotential in cell-cultures. In further studies the effect of glutamate on dendritic spine head protrusions will be investigated.

Literature:

[1] *Trends in Neurosciences*, **33:**121, 2010

[2] *Nature*, **420:** 812, (2002)

Research group 16 – Dynamics of nanocrystal structure induced by surface chemistry

Dr. hab. Zbigniew Kaszkur

[1] Team research task

a) Ex-situ and in-situ powder diffraction studies of the structure of nanocrystalline catalytic materials

b) Atomistic simulations of metal and binary alloy clusters – fragments of fcc lattice and systems containing 5-fold symmetry axis (icosahedron, decahedron). Structure dynamics and diffraction pattern.

[2] Aim of the research

The studies target measurement and interpretation of a subtle peak evolution of metal nanocrystals during catalytic reaction at their surface. This evolution reflects structural atomistic mechanism of chemical reaction in heterogenous catalysis and is interpreted using atomistic simulations.

[3] Description and methodology of research

Methodology of this research is based on the diffraction method developed in our group. It enables measurement and interpretation of a metal nanocrystal surface process in-situ [1-5].

Literature:

[1] J. Appl. Cryst. (2017), 50, 585.

[2] PhysChemChemPhys. (2015), 17, 28250.

[3] J. Appl. Cryst., (2014), 47, 2069.

[4] RSC Adv., (2014),4 (28), 14758.

[5] Phys.Chem.Chem.Phys. (2009), 11, 5416.

Research group 17 – Environmental Chemistry Group

Dr. hab. Rafał Szmigielski

Environmental Chemistry Group plans to conduct the following research task in 2020:

Chemical characterization of buta-1,3-diene fine aerosol

Buta-1,3-diene an organic compound massively employed in chemical industry, including petroleum and polymer manufacturing. During the industrial processes/distribution a substantial mass of buta-1,3-diene is uncontrollably released into the atmosphere to pollute the ambient air. Once emitted, buta-1,3-diene undergoes a complex set of chemical processes, mainly triggered by hydroxyl radicals and/or ozone, leading to fine particles of an unknown chemical profile and toxicity. These processes contribute to the smog phenomena observed in in the urban sites, such as big cities or urban agglomerations with an industrial sites.

buta-1,3-diene

Objectives of the research planned are:

- ✓ generation of buta1,3-diene fine aerosol under various temperature and relative humidity conditions in the EPA smog chamber. These will be pursued in collaboration with the American Environmental Agency (EPA US)
- ✓ aerosol fractioning in terms of its particle size distribution and sampling onto filter surfaces
- ✓ transferred the buta-1,3-diene aerosol into the methanol solutions to make the aerosol extracts
- ✓ conducting GC/MS and LC/MS analyses to determine the chemical composition of the buta-1,3-diene aerosol and quantification of its major components (markers)

The planned research task fulfils the scientific interest of the research group on the understanding of atmospheric processes leading to smog phenomena.

Literature:

[1] Nestorowicz, G., *et al*., *Atmos. Chem. Phys*, 2018.

[2] Lewandowski M., *et al., Atmos. Chem. Phys*, 2015.

[3] Noziere, B. *et all*., *Chem. Rev*., 2015.

Research group 18 – Functional Polymers

Dr. Piyush Sindhu Sharma

1. Fabrication of the thin films of ZnO nanoparticles and their application as signal transducers in chemosensors (continuation).

The proposed work is focused on fabrication of thin films of ZnO nanoparticles surface-modified with various ligands, their characterization and application of the devised surfaces as signal transducers in chemosensors. Two methods of surface preparation will be tested. Langmuir-Blodgett technique will be used for preparation of well-ordered films, while electrophoresis will be used as a tool for development of surfaces with enhanced roughness. Main focus of the work will be on application of such surfaces for surface enhanced Raman spectroscopy (SERS) and electrochemical signal transduction.

ZnO nanoparticles modified with selected ligands will be synthesized in research group ZT09. Structure and morphology of the devised films will be studied with use of IR spectroscopy, as well as AFM and SEM microscopy. Subsequently, the devised films will be studied as platforms for SERS by using model molecules. Furthermore, possible application of the devised films as signal transduction elements in electrochemical sensors of proteins will be studied.

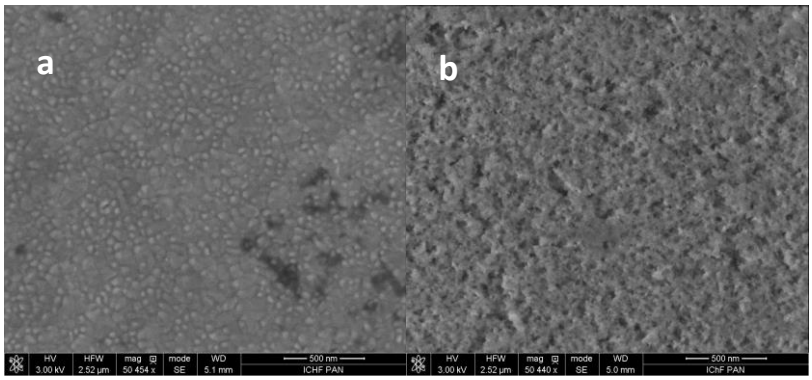


Fig. 1. SEM images of films of ZnO nanoparticles coated with butylamine prepared on Au-coated glass slides by (a) Langmuir-Blodgett technique and (b) by electrophoresis at 30 kV/m.

2. Electric field-driven orientation and immobilization of proteins (new)

Effectiveness of molecularly imprinted polymer films in analyte rebinding strongly depends on uniformity of the devised binding cavities. This is especially important in case of protein imprinting due to the analyte flexibility. In order to create uniform binding sites it is important to uniformly orient template molecule on the surface of signal transducing unit.

For that purpose, an electric-field assisted protein immobilization technique will be devised and tested. The method will be based on chemical immobilization of selected proteins on the electrode surface placed in an external electric field. The chemical binding of the protein to the surface leads to formation of film of randomly oriented protein molecules. Application of the external electric field shall lead to orientation of protein molecules along the field coupled with their migration to the electrode. This effect, coupled with chemical binding step shall lead to formation of films of uniformly oriented proteins on the surface. Prepared films will be studied primarily by PM-IRRAS technique in order to elucidate protein orientation. Furthermore, uniformity of the films will be studied by AFM and electrochemical techniques. The effect of protein shape, ionic strength of the solution, as well as electric field strength on the protein film uniformity and orientation will be studied.

3. Determination of peroxide explosives with use of molecularly imprinted polymers and surface enhanced Raman spectroscopy (continuation).

Goal of the present project is fabrication of polymer molecularly imprinted with triacetone triperoxide (TATP). This compound is explosive and it is easy to synthesize at home. For that reason it is often used as explosive by terrorists. Therefore, there is a need for development of selective chemosensors for detection and determination of this compound.

During work performed to date, quantum-chemical calculations of the pre-polymerization complexes of the TATAP with selected functional monomers have been performed. Monomers forming strongest complexes with TATP have been selected. The necessary monomers have been synthesized. Furthermore, preliminary electrochemical studies of selected organic peroxides have been performed (Fig. 1) and work on electrochemical deposition of thin films of TATP-imprinted polymers has been started.

Planned continuation of the work includes optimization of the procedure of thin film deposition as well as the template extraction. In the subsequent step devised films will be deposited on the supports for surface enhanced Raman spectroscopy (SERS). This technique will be used for studies of the peroxide binding in the MIP films.

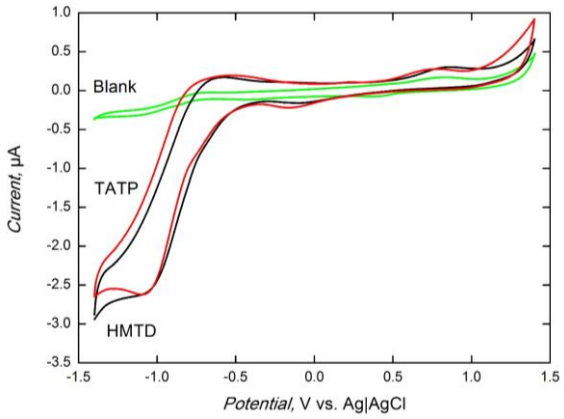


Fig. 1. Cyclic voltammetry of 1 mM organic peroxides on GC electrode in deaerated 0.1 M (TBA)ClO4 in acetonitrile. Scan rate: 50 mV/s.

Research group 19 – Soft Granular Matter and Tissue Engineering

Dr. Jan Guzowski

In year 2020 our research will focus on physics of soft granular matter (close-packed emulsions, suspensions, foams) and on tissue engineering employing microfluidics as a tool.

Task 1: development of new 3D culture methods; microfluidic droplets [1] will serve as templates for formation of hydrogel capsules [2] for application as cell carriers; we will investigate:

- ***formation of 'topological' capsules made of several close-packed segments*** achievable via re-encapsulation; we will study flow of close-packed hydrogel microbead suspension via microfluidic channel (collaboration: prof. H. Stone, Princeton University);
- ***angiogenesis*** based on using such capsules to control spatial distribution of cells, e.g., endothelial, fibroblasts, pericytes (collaboration Dr. Cesare Gargioli, University of Rome Tor Vergata);
- ***anti-cancer drug efficiency*** in 3D culture and co-culture studies based on the capsules as cell culture scaffolds (collaboration Dr. Kinga Macjhrzak, SGGW; prof. M. Massimi, University L'Aquila)

Task 2: development of new bio-printing techniques based on microfluidics; monodisperse emulsions and foams generated in microchannels will be used as printable materials (bioinks) for tissue engineering; we will study:

- ***synthesis of porous materials*** in particular by using continuous phase (biopolymer such as gelatin [3]) of enchanced mechanical properties (collaboration: Prof. C Stubenrauch, University of Stuttgart)

References:

[1] J. Guzowski, P. Garstecki, Phys. Rev. Lett. 2015, 114, 188302.
[2] L. Bray, C. Werner, ACS Biomater. Sci. Eng. 2018, 4, 337-346.
[3] M. Costantini, J. Jaroszewicz, Ł. Kozoń, K. Szlązak, W. Święszkowski, P. Garstecki, C. Stubenrauch, A. Barbetta, J. Guzowski, Angew. Chem., 2019, 131, 1-7.

Research group 21 – Spectroscopic and microscopic (STM/AFM) studies of intermolecular interactions

Dr. hab. Robert Nowakowski

PROSPECTIVE GROUP

1. **Nanomechanical properties of the phospholipid bilayer in the so-called ripple phase**

A phospholipid bilayer deposited on a solid substrate shows different physicochemical properties depending on the physical state. Below the so-called transition temperature, the bilayer is in the gel phase while above this temperature, in the liquid-crystalline phase. There is also an intermediate phase, which is called a ripple phase, that differs from the gel and liquid-crystalline phases in that the phospholipid molecules form periodic structures on the surface of the bilayer. The aim of our research will be to study the nanomechanical properties of supported bilayers in the ripple phase.

2. **Catalytic effects of bimetallic alloys supported on porous media**

Research is planned to investigate the catalytic effects of bimetallic alloys nanoparticles, such as Ni-Cu, Ni-Co. For this purpose, several techniques, like: AFM, TPR, TPO, BET, as well as an electrochemical oxidation of C2-C4 hydrocarbons will be used. The mechanism of poisoning using the probes molecules (i.e. CO) will be examined using DRIFT (Diffussion Reflectance Fourier Transform Spectroscopy). For this purpose, model catalytic layers containing Pt, Ni and Cu will be prepared.

3. **Aggregation of selected organic electroactive compounds of complex molecular and electronic structures – microscopic investigations**

This is a continuation of our microscopic studies (STM/AFM) of low and high molecular weight organic semiconductors of potential applications in organic electronics. Our aim is to extend our research to new organic semiconductors of complex molecular and electronic structures and to new research techniques which enable to obtain correlated information about topology and electronic properties of organic layers (for examples: AFM with conductive probe or Kelvin Probe Microscopy). We expect that obtained results will broaden our knowledge concerning mechanism of electric conductivity occurred in thin layers of the investigated semiconductors.

Research group 22 – Charge transfer in biological systems and at the interfaces

Dr. Piotr Zarzycki

1. Research task

Role of charge-assisted hydrogen bonding in the self-assembly and structure of the supramolecular architectures.

2. Aim of research

Design, synthesis and characterization of the supramolecular architectures formed with hydrogen bonding in which donor and/or acceptor of hydrogen atom bear permanent charge.

3. Description and methodology

We plan theoretical and experimental research on the role of strong charge-assisted hydrogen bonding in the self-assembly, structure and properties of the supramolecular architectures consisting of macrocyclic building blocks.

Research group 23 – Modified electrodes for potential application in sensors and cells

Professor Marcin Opałło

1. **Electrochemical detection of nanoparticles**

We will continue research on electrochemical detection of nanoparticles and other nanoobjects in forced convection conditions on rotating disc electrode and in flow systems made by #D printing technique. We will attempt electrochemical detection of nanoparticles at liquid-liquid interface with help of scanning electrochemical microscopy. For this purpose electrocatalytic reduction of dioxygen and electrodissolution reaction will be employed.

2. **Research on electrocatalytic properties TiO_2 nanotubes** on the examples of oxidation of simple organic molecules and water.

In this research scanning electrochemical microscopy will be employed.

3. **Selective molecular recognition with help of imprinting into conductive polymers**

Thin films of polymers will be directly electrodeposited on chemical recognition to analytical signals transducers. These devices will be employed for detection of selected analytes important in healthcare, environmental protection and food control.

Research group 24 – Complex Systems and Chemical Processing of Information

Professor Jerzy Górecki

The research activity of the Group 24 will be concerned with complex phenomena in physico-chemical systems. The subjects of the planned research are:

1. Identification of stationary structures and phase transitions in systems with SALR type interactions (Short range Attraction and Long range Repulsion), that are confined within a small volume. The research will be based on theoretical methods of statistical physics and microscopic computer simulations using molecular dynamics. In particular, we plan to consider mixtures of ionic liquids and an inert liquid in the presence of an electrode. The solution of this problem can be important for optimization of conditions for energy storage in supercapacitors. The problem of structures arising in a limited volume is fundamental for understanding the origins of life.

2. Performing experiments on complex phenomena and self-organization in systems with surface interactions and developing theoretical models describing such systems. We plan to investigate novel materials that show spontaneous motion on the water surface. The new theoretical models, we are going to develop, will take into account the hydrodynamic flows induced by gradients of surface tension. The development of such models is an important for generalization of the methods presently used.

3. Demonstration of new applications illustrating information processing with interacting chemical oscillators. Development of new algorithms and optimization of information processing structures for selected, far from equilibrium chemical media. Experimental verification of information processing devices predicted by the theory. Within this project we are going to develop simple systems that can solve selected problems with a high accuracy.

Research group 25 – Laboratory astrochemistry

Professor Robert Kołos

1. The goal

Photochemistry of the simplest phosphaalkynes of astrochemical importance

2. Target

Elucidation of phosphapropyne and phosphabutyne photolysis pathways, identification of certain exotic, unsaturated phosphorus-carbon chain molecules, e.g. HCCP or HCCCP.

3. Description

Phosphapropyne and phosphabutyne, obtained by preparative organic synthesis (ca. 100 mg scale) in cooperation with Ecole Normale Supérieure de Chimie de Rennes (France) will serve as the starting material for low-temperature photochemical investigations. The precursor molecules, isolated in solidified noble gases (Ne, Ar, Kr or Xe), are to be irradiated with excimer laser (193 nm or 248 nm) or discharge-lamp photons (121.6 nm or 254 nm). Infrared absorption, Raman scattering, as well as UV/Vis absorption and luminescence measurements shall provide the photoproduct detection. Identification of the newly formed species will be assisted with (i) isotopic labelling and (ii) quantum chemical calculations (carried out mainly at the density functional theory level) pertinent to molecular structures, energetics and spectroscopy, as well as to the prediction of photoreaction paths.

Research group 27 – Laser Centre

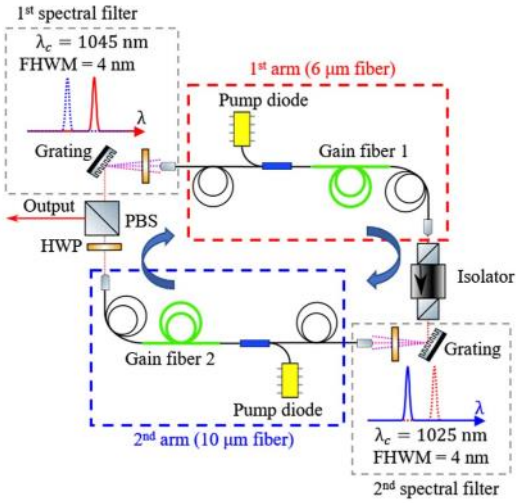
Dr hab. Yuriy Stepanenko

Taks 1:

The design of Mamyshev oscillator based on LMA fibers

Aim of the task:

The main goal of the task is to design and build an ultrafast laser oscillator based on Mamyshev regeneration scheme.



Methods:

The Mamyshev oscillator [1] is a type of laser oscillator made of two optical amplifiers connected by spectral filters with shifted spectral characteristics.
In order to lower nonlinear effects in this type of laser oscillator we will use fibers with enlarged mode field area. This change will help to increase laser pulse energy circulating inside the laser cavity.

[1] P. Sidorenko et al. Optics Letters **43**, 2672 (2018).

Task 2:

Investigations of vibrational relaxation pathways in liquids and forcing ultrafast chemical reactions with resonant infrared pulses.

Aim of a task:

Understanding mechanisms of relaxations of vibrational energy provided to a molecule in liquid state through modes of lower energies.

Methodology:

Studies will be conducted with use of a recently built in Laser Center setup for infrared pump – stimulated Raman probe spectroscopy. The setup facilitates excitation of a selected molecular vibration with femtosecond infrared pulse tunable in the range 1300 nm – 4500 nm and subsequent probing redistribution of vibrational energy with broadband stimulated Raman probe.

[1] M. Pastorczak, et.al., *EPJ Web Conf.*, 2019, **205**, 09026.

[2] J. Y. Shin, et.al., *The Journal of Physical Chemistry B*, 2017, **121**, 2486-2494.

Research group 28 – Catalysis for sustainable energy production and environmental protection

Dr. hab. J. C. Colmenares

PROSPECTIVE GROUP

Research task for 2020:

Research on the synthesis of new composite photocatalysts based on semiconductors (e.g. Mn_xO_y, TiO_2) and carbonaceous materials (e.g. composite carbon from chitosan and lignin). Study on the phenomenon of thermo-photocatalysis in the selective oxidation of organic compounds.

Research goals:

The aim of our research will be to use simple methods for the synthesis of composite materials based on carbon carriers (e.g. lignin-chitosan type). An additional research goal will be to test these materials in the frame of thermo-photocatalysis concept for the selective oxidation of model compounds representing lignocellulose structure (e.g. glucose, benzyl alcohol) to aldehydes and hydrogen.

Description and methodology:

The methodology includes: a. The use of, for example, a hydrothermal and sol-gel methods for preparing innovative nanocomposite photocatalysts based on semiconductors (e.g. MnxOy, TiO2) and carbon support (e.g. biochar from wastes: seaweed or/and lignin/chitosan), b. characterization of the obtained materials by techniques such as: XRD, FTIR, XPS, UV-vis, c. basic kinetic studies (selective photocatalytic oxidation of model compounds of lignocellulose structure in liquid phase), and photocatalysts' stability studies that will be carried out using stationary photoreactors, liquid and gas chromatograph.

Literature:

[1] K. Cerdan, W. Ouyang, J.C. Colmenares, M.J. Muñoz-Batista, R. Luque, and A.M. Balu. *Chemical Engineering Science,* 194 (2019) 78–84.

[2] V. Nair, M.J. Muñoz-Batista, M. Fernández-García, R. Luque and J.C. Colmenares. *ChemSusChem*, (2019). DOI: 10.1002/cssc.201900175.

Research group 29 – Photophysics and spectroscopy of photoactive systems

Professor Jacek Waluk

PROSPECTIVE GROUP

Photoinduced conversion of molecules with hydrogen bonds

We plan to investigate several series of organic compounds which possess intramolecular hydrogen bonds. Upon irradiation, these molecules reveal spectral changes. The goal is to determine the structure of the photoproducts, to elucidate the mechanisms of photoinduced transformations and, finally, to gain control over the reaction kinetics.

The research methodology will include measurements of stationary and time-resolved electronic and vibrational spectra, combined with quantum-chemical calculations.

Research group 30 – Nuclear Hyperpolarization of Molecular Systems and Nanomaterials

Dr. Tomasz Ratajczyk

Comprehensive real-time monitoring of photoprocesses via simultaneous 1D and 2D UV-vis-NMR spectroscopy.

Photochemical reactions are one of the essential processes in nature. Comprehensive knowledge of these processes is critical for a better understanding of nature, and for the utilization of this knowledge in material science. Therefore, the comprehensive characterization of photochemical processes is of central interest to the scientific community. Nuclear Magnetic Resonance (NMR) offers insight into different chemical processes at the molecular-level. However, comprehensive real-time monitoring of the chemical reactions which are crucial for photoproceesses, is a demanding task.1,2 In the research plan for 2020, the NMR real-time monitoring of photoprocesses is addressed. In particular, this research focuses on the monitoring of the photodecomposition of photoactive molecules which are important for biological and material science - for example, porphycene (which can be used in a phototherapy), which is a basic framework for very functional biomolecules.3 For this monitoring, the photoreactor will be integrated with an NMR spectrometer via a continuous flow system. Photochemical reactions will be monitored by 1D and 2D NMR spectra simultaneously, thanks to the Non-Uniform Sampling (NUS) approach which will be employed for this purpose. Finally, dual UV-vis-NUS-NMR monitoring will be implemented. The described method could provide much insight into the photochemical decomposition processes of porphycene. This methodology may be useful for the characterization of different photochemical processes. The approach that is presented here could be useful as a potential analytical method.

Literature:

[1] M. Pietrzak, J. Dobkowski, A. Gorski, S. Gawinkowski, M. Kijak, R. Luboradzki, P.E. Hansen, J. Waluk, Phys Chem Chem Phys. 2014, 16, 9128-9137.

[2] D. Golowicz, K. Kazimierczuk, M. Urbańczyk, T. Ratajczyk, ChemistryOpen 2019, 8, 196-200.

[3] J.Ostapko, K. Nawara, M. Kijak, J. Buczynska, B. Lesniewska, M. Pietrzak, G. Orzanowska, J. Waluk, Chem. Eur. J. 2016, 22, 17311-17320.

Research group 31 –
Dr. Anna Ochab – Marcinek

1. Team research tasks

Modeling stochastic gene expression in a cell population taking into account cell growth and cell division.

2. Aim of the research

To estimate what contribution to the coefficient of variation of the protein molecule number distribution in a population in bacterial cells is caused by random variability of cell cycle length, discreteness of protein molecule numbers, dependence of gene expression on cell age and age structure of the population.

3. Description and methodology of research, literature

Our research is theoretical. The gene expression models we use are based on a time-dependent Master equation, supplemented with a description of the protein distribution between daughter cells during cell division, the probability distribution of the cell cycle length and the age structure of the population. In certain cases it is possible to obtain analytical or approximate solutions for the equations that describe the evolution of the first and second moments of the protein molecule number probability distribution or concentration probability distribution. It is also possible to simulate biochemical reactions and cell divisions using the modified Gillespie algorithm.