

# BOOK OF ABSTRACTS

# PANIC

PhoBiA Annual Nanophotonics International Conference

## 2022



30.05-03.06

Wroclaw University  
of Science and Technology





# PANIC Summer School 2022

**PhoBiA Annual Nanophotonics  
International Conference**

30 May–3 June 2022, Wrocław, Poland



Oficyna Wydawnicza Politechniki Wrocławskiej  
Wrocław 2022



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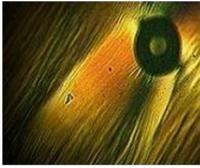
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# Summer School programme

Monday – 30.05.2022	
Hours	Activity
9:00–9:30	Registration
9:30–9:45	Opening ceremony
Session I	
9.45–11:15	Invited lecture – Prof. Rafał Klajn <b>Colloidal synthesis of nanoparticles</b>
11:15–12:30	Poster session with a coffee break
12:30–14:00	Invited lecture – Prof. Rafał Klajn <b>Optical, magnetic, and catalytic properties of nanoparticles</b>
14:00–15:00	Lunch break
Session II	
15:00–16:30	Invited lecture – Prof. Stephane Parola <b>Nanosciences and metallic particles – synthesis, properties, applications</b>
19:00– ...	Welcome dinner
Tuesday – 31.05.2022	
Hours	Activity
Session I	
8.45–10:15	Invited lecture – Prof. Wiktor Szymański <b>Molecular basis for the application of light in medicine</b>
10:15–10:45	Coffee break
10:45–12:15	Invited lecture – Prof. Rafał Klajn <b>Self-assembly and chemical transformation of nanoparticles</b>
12:15–13:15	Lunch break
Session II	
13:15–14:45	Invited lecture – Prof. Stephane Parola <b>Solvothermal synthesis of metallic particles self-assembly, 3D printing and applications</b>
16:30	Visit to Hydropolis



Wednesday – 01.06.2022	
Hours	Activity
<b>Session I</b>	
8.45–10:15	Invited lecture – Prof. Stephane Parola <b>Synthesis of monolithic xerogels and aerogels</b>
10:15–10:45	Coffee break
10:45–12:15	Invited lecture – Prof. Wiktor Szymański <b>Reversible photopharmacology: Towards light-controlled therapy</b>
12:15–13:15	Lunch break
<b>Session II</b>	
13:15–14:45	Invited lecture – Leading and mentoring session Prof. Wiktor Szymański
14:45–15:00	Technical break
15:00–16:15	Flash Presentation Session
Thursday – 02.06.2022	
Hours	Activity
<b>Session I</b>	
8.45–10:15	Invited lecture – Prof. Luis Carlos <b>Luminescence spectroscopy and luminescent materials. Some basic concepts.</b>
10:15–10:45	Coffee break
10:45–12:15	Invited lecture – Prof. Luis Carlos <b>Using light to measure the temperature. Starting with the basics.</b>
12:15–13:15	Lunch break
<b>Session II</b>	
13:15–14:45	Invited lecture – Prof. Raffaele Mezzenga <b>Lipidic Mesophases: fundamentals and applications</b>
15:00–17:00	<b>PhoBiA Student Photonics Symposium (PS)<sup>2</sup></b>



Friday – 03.06.2022	
Hours	Activity
<b>Session I</b>	
8.45–10:15	Invited lecture – Prof. Luis Carlos <b>Applications in nanomedicine: Heater-thermometer platforms and intracellular thermometers.</b>
10:15–10:45	Coffee break
10:45–12:15	Invited lecture – Leading and mentoring session Prof. Raffaele Mezzenga
12:15–13:15	Lunch break
<b>Session II</b>	
13:15–15:45	Invited lecture – Prof. Raffaele Mezzenga <b>Liquid-Liquid Phase Separation (LLPS) vs. Liquid-Liquid Crystalline Phase Separation (LLCPS) in Filamentous Colloids</b>
15:45–16.15	Closing Ceremony



# Detailed list of PhD students' presentations

Wednesday – 01.06.2022	
Hours	Activity
<b>Session II</b>	
13:15–14:45	<b>Invited lecture – Leading and mentoring session Prof. Wiktor Szymański</b>
13:15–13:30	<b>K. Sulowska</b> <i>“Real-time fluorescence biosensing with plasmonic silver nanowires”</i>
13:30–13:45	<b>S. Mucha</b> <i>“Folic acid-derived carbon nanodots: how to convert the non-fluorescent molecule into the effective two-photon absorption biomarker”</i>
13:45–14:00	<b>M. Grelich-Mucha</b> <i>“Autofluorescence properties of lysozyme amyloids”</i>
14:00–14:15	<b>P. Obstarczyk</b> <i>“Noncovalent intramolecular forces – gold nanoparticles ligand chemistry and amyloid fibrils interfaces”</i>
14:15–14:30	<b>M. Lipok</b> <i>“On the creation and properties of gold nanoclusters helical assemblies”</i>
14:30–14:45	<b>S. Sirimatayanant</b> <i>“OPA/TPA Spectra of the wt-Rhodopsin Calculated using TD-DFT/MM with Polarizable Embedding”</i>
14:45–15:00	Technical break
15:00–15:15	<b>K. Nadolski</b> <i>“Gold nanoparticles for copper (II) ion sensing by Second Harmonic Scattering”</i>
15:15–15:30	<b>A. Pniakowska</b> <i>“Two-photon investigation of chiroptical properties of gold nanoclusters”</i>
15:30–16:15	<b>Flash Presentation Session</b>
15:30–15:35	<b>P. Falat</b> <i>“Improved germicidal performance of Visible-to-UVA/UVC upconversion process in lanthanide doped oxyorthosilicates”</i>



15:35–15:40	<b>E. Waglewska</b> <i>“Self-assembled bilosomes with stimuli-responsive properties as bioinspired nanoplatform for support photodynamic treatment of skin cancer cells”</i>
15:40–15:45	<b>M. Piksa</b> <i>“Photoinactivation of clinical bacterial strains with the use of OLED”</i>
15:45–15:50	<b>M. Zdończyk</b> <i>“Xanthene derived dyes as potential activators for photonics applications”</i>
15:50–15:55	<b>A. Szarwaryn</b> <i>“Solvatochromic properties of selected dyes solubilized in different micellar systems”</i>
15:55–16:00	<b>K. Halicka</b> <i>“Nanomaterials-based detection of dopamine”</i>
16:00–16:05	<b>J. Warachim</b> <i>“Study of Singlet and Triplet Channels of [2+2] Photocycloaddition of Nitrostyrene to Indene”</i>
16:05–16:10	<b>N. Tyszkiewicz</b> <i>“Application of microbial fuel cells for contaminants degradation and current generation”</i>
16:10–16:15	<b>M. Policht</b> <i>“Prolonged stability of silver nanoparticles in the presence of protic ionic liquids”</i>
<b>Friday – 03.06.2022</b>	
<b>Hours</b>	<b>Activity</b>
<b>Session I</b>	
<b>10:45–12:15</b>	<b>Invited lecture - Leading and mentoring session Prof. Raffaele Mezzenga</b>
10:45–11:00	<b>O. Kaczmarczyk</b> <i>“In-situ transmission electron microscopy imaging of liquid crystals – challenges and perspectives”</i>
11:00–11:15	<b>D. Benkowska-Biernacka</b> <i>“Characterization of lyotropic myelin figures using linear and nonlinear optical studies”</i>
11:15–11:30	<b>L. Duda</b> <i>“Fabrication of formable sol-gel and polymer films for planar photonic systems”</i>
11:30–11:45	<b>A. Hajda</b> <i>“New dyes based on BODIPY and benzothiazoles motif for amyloid detection”</i>



<b>11:45–12:00</b>	<b>A. Kabański</b> <i>“The influence of temperature and <math>Cr^{3+}</math> ions concentration on spectroscopic properties of <math>[EA]_2NaCr_xAl_{1-x}(HCOO)_6</math>”</i>
<b>12:00–12:15</b>	<b>N. Tarnowicz-Staniak</b> <i>“Indirect Excitation of Azobenzene Molecules – Plasmon-Assisted Approach”</i>



## List of PhD students' posters

Poster no.	Presenter	Title
P01	Maja Szymczak	Spectroscopic properties of $\text{Li}_2\text{Mg}_3\text{TiO}_6:\text{Cr}^{3+}$ for noncontact temperature sensing
P02	Magdalena Kulpa-Greszta	Contactless energy conversion on multimodal $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-Au}$ nanoparticles
P03	Mateusz Pieprz	Spectroscopic properties of $\text{Cr}^{3+}$ , $\text{Nd}^{3+}$ co-doped $\text{La}_3\text{Ga}_5\text{GeO}_{14}$ for NIR luminescence thermometry
P04	Magda A. Antoniak	Transferring hydrophobic quantum dots into water dispersion and how it influences their optical properties
P05	Weronika Bodylska	Eu-Cu heterometallic-organic framework for selective ascorbic acid detection
P06	Zainab Majid Salim Allami	G-DNA interactions with new ruthenium compounds
P07	Sunday Ocholi Samson	Biological synthesis of high added value compounds (using selected Cyanobacteria strains)
P08	Weronika Forysiak	Sequence and stereo-defined polyurethanes – synthesis and thermal characteristic
P09	Pawel Cwynar	Large scale synthesis of sequence-defined polyurethanes
P10	Przemyslaw Pietrusiak	Nanoparticles as carriers for volatile monoterpenes in modern agriculture
P11	Monika Sapeta	Investigation of oxidative stress under external stimuli on cell culture
P12	Aleksander de Rosset	Long-term characterization of three different carbon cathodes in microbial fuel cell



# Invited lecturers



**Prof. Luís Carlos** is a Full Professor at the Department of Physics, University of Aveiro, Portugal, and a correspondent member of the Lisbon Academy of Sciences (Physics) and Brazilian Academy of Sciences (Chemistry). In 2000, he established the photonic hybrids and nanomaterials group (Phantom-G), which was a pioneer in the study of luminescent nanothermometers and organic-inorganic light-emitting hybrids. Prof. Carlos has an h-index of 76 (Scopus). He has published more than 535 documents in peer-reviewed international journals with ca. 26898 citations (Google Scholar) (ca. 23114, Scopus). His current scientific interests include luminescent nanothermometry, physicochemical properties of lanthanide-based compounds, applications of organic-inorganic hybrids in luminescent solar concentrators, integrated optics, and solid-state lighting, and luminescent/magnetic nanocrystals as new hybrid probes for multimodal imaging.

Prof. Luis Carlos, affiliated at University of Aveiro (Portugal), is going to deliver a series of lectures concerning the applications of **lanthanide doped nanomaterials in temperature sensing**.



# Luminescence spectroscopy and luminescent materials. Some basic concepts

L. D. Carlos

*Phantom-g, CICECO-Aveiro Institute of Materials, Physics Department, University of Aveiro, Campus  
Universitário de Santiago, 3810-193 Aveiro, Portugal  
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Luminescence is a general term that describes any non-thermal processes in which energy is emitted in the ultraviolet, visible or infrared spectral regions from an electronically excited species. The term broadly includes the commonly-used categories of fluorescence and phosphorescence. Fluorescence occurs where emission ceases almost immediately after withdrawal of the exciting source, whereas in phosphorescence the emission persists for some time after removal of that excitation.

The lecture will discuss the fundamental aspects behind photoluminescence discussing in particular trivalent lanthanide emitting centers and their applications in light-emitting diodes and luminescent solar concentrators.

## Using light to measure the temperature. Starting with the basics.

L. D. Carlos

*Phantom-g, CICECO-Aveiro Institute of Materials, Physics Department, University of Aveiro, Campus  
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The emergence of luminescent nanothermometry during the last decade opened up the possibility of measure thermal flows at spatial scales below 10  $\mu\text{m}$ , unreachable by conventional electrical methods. Diverse phosphors capable of providing a contactless thermal reading through their light emission properties have been examined, e.g., polymers, DNA or protein conjugated systems, organic dyes, quantum dots, and trivalent lanthanide ( $\text{Ln}^{3+}$ ) ions incorporated in organic-inorganic hybrids, multifunctional heater-thermometer nanoplatfoms, upconverting, downconverting and downshifting nanoparticles. The implementation of these  $\text{Ln}^{3+}$ -based phosphors (with an emphasis in upconverting nanoparticles) as ratiometric thermometers was extensively reviewed in the past five years<sup>1</sup>.

The lecture will describe the basic concepts behind this fascinating application of luminescence that exploded in the last decade.

### References:

- [1] Brites C.D.S., Balabhadra S., Carlos L.D., *Lanthanide-Based Thermometers: At the Cutting-Edge of Luminescence Thermometry*, Adv. Opt. Mater. 7, 1801239, 2019.



# Applications in nanomedicine: Heater-thermometer platforms and intracellular thermometers

L. D. Carlos

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Present technological demands in disparate areas, such as micro and nanofluidics, micro- and nanoelectronics, photonics and biomedicine, among others, have reached to a development such that conventional contact thermal probes are not accomplished to perform accurate measurements with submicrometric spatial resolution. The development of novel non-contact thermal probes is, then, mandatory, contributing for an expansionary epoch of luminescence thermometry. Luminescence thermometry based on trivalent lanthanide ions becomes very popular since 2010 due to the unique versatility, stability and narrow emission band profiles of the ions that cover the entire electromagnetic spectrum with relatively high emission quantum yields. [1]

Here we give a perspective overview of the current movement towards the technique usage in nanomedicine as a new tool for thermal imaging and intracellular temperature determination.

## References:

- [1] Brites C.D.S., Balabhadra S., Carlos L.D., *Lanthanide-Based Thermometers: At the Cutting-Edge of Luminescence Thermometry*, Adv. Opt. Mater. 7, 1801239, 2019.



**Prof. Rafał Klajn** completed his PhD in Chemical and Biological Engineering at Northwestern University in 2009, where he worked under the supervision of Prof. Bartosz A. Grzybowski. He then joined the Weizmann Institute of Science (Israel), where he is currently a full professor and the Head of the Helen and Martin Kimmel Center for Molecular Design. The interests of his research group revolve around nanoscale self-assembly and reactivity, and the development of new stimuli-responsive nanomaterials. He has served on the advisory boards of several journals, including Chem, Chemical Society Reviews, ChemPhotoChem, and ACS Nano. He is the founding chair of the Gordon Research Conference (GRC) series on Artificial Molecular Switches & Motors and has been elected chair of the GRCs Self-Assembly & Supramolecular Chemistry (2023) and Systems Chemistry (2024). He is the recipient of several awards, including the 2010 IUPAC Prize for Young Chemists, the 2013 ACS Victor K. LaMer Award, the 2016 Netherlands Scholar Award for Supramolecular Chemistry, and the 2019 Sigma-Aldrich Lectureship in Materials Science.

Prof. Rafał Klajn from Weizmann Institute of Science in Rehovot (Israel) will provide PhD students attending PANIC Summer School 2022 with the latest advances in the field of **nanoplasmonics**.



## Colloidal synthesis of nanoparticles

Rafał Klajn

*Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, 76100, Israel  
rafal.klajn@weizmann.ac.il*

In the first lecture, nanoparticles will be introduced as hybrid organic–inorganic entities comprising an inorganic core and a thin organic coating. In most cases, the inorganic core is crystalline, and the formation of nanoparticles follows the nucleation-and-growth model. We will discuss the various synthetic methods developed over the years to make nanoparticles, with particular emphasis on controlling their dispersity and size. We will appreciate that the organic ligands are essential to keep the particles stable in solution, and as such, they are crucial components of the syntheses. Moreover, different ligands can preferentially bind to different crystallographic faces of a nanoparticle, decreasing their surface energies and facilitating the formation of these faces, thus controlling the shape of the resulting nanoparticle. We will see that, similar to many reactions in organic chemistry, the synthesis of nanoparticles can proceed under kinetic or thermodynamic control, giving rise to nanoparticles of drastically different shapes. We will also discuss the applicability of the seeded-growth method for the synthesis of bicomponent nanoparticles and cover other synthetic methods, such as digestive ripening.

## Optical, magnetic, and catalytic properties of nanoparticles

Rafał Klajn

*Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, 76100, Israel  
rafal.klajn@weizmann.ac.il*

The properties of inorganic matter on the nanoscale heavily depend on particle size and shape. For example, reducing the size of gold crystals results in a gradual transition from a metal to a semiconductor to an insulator. In the nanometer size regime, the localized surface plasmon resonance emerges – a phenomenon that gives noble metal nanoparticles their brilliant colors and other unique optical properties. We will discuss how these properties depend on the nanoparticles' size, shape, chemical composition, and degree of aggregation. With this knowledge, we will cover the design principles of nanoparticle-based sensors for various analytes, whereby the analyte of interest can either trigger the aggregation of gold nanoparticles or induce the disassembly of nanoparticle aggregates, both of which result in pronounced color changes. Emerging applications in photothermal therapy will also be discussed. The second part of this lecture will focus on the nanoparticles of magnetic materials and catalytically active nanoparticles – peculiar species that stand at the interface between homogeneous and heterogeneous catalysis.



# Self-assembly and chemical transformation of nanoparticles

Rafał Klajn

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Many practical applications of nanoparticles depend on the ability to assemble them into higher-order structures. The first part of this lecture will focus on the various types of interactions that can be employed to induce self-assembly of nanoparticles, including van der Waals forces, magnetic and electric dipole-dipole interactions, hydrogen bonding, and Coulombic interactions. In the nano regime, the magnitudes of the different kinds of interactions are often similar; hence, they can compete with one another to afford exotic nanoparticle assemblies. The unique optical, electronic, catalytic, and magnetic properties of the resulting materials will be discussed. We will also note that the structures of these nanoparticle assemblies often mimic those of simple inorganic salts, such as CsCl – a thought-provoking analogy between nanoparticles and atomic-scale species. In the second part of the lecture, this analogy will be extended to chemical reactions: similar to small molecules, nanoparticles can be subjected to chemical reactions and converted to nanoparticles of a different shape and/or composition. Here, we learn how reactions such as the galvanic replacement and processes such as the Kirkendall effect can give rise to nanoparticles with unique shapes (such as nanocages, nanorattles, and nanodendrites) tailored for desired applications.



**Prof. Raffaele Mezzenga** received his PhD from EPFL Lausanne in 2001 and spent 2001–2002 as a postdoctoral scientist at University of California, Santa Barbara, working on the self-assembly of polymer colloids. In 2003 he moved to the Nestlé Research Center in Lausanne as research scientist, working on the self-assembly of surfactants, natural amphiphiles and lyotropic liquid crystals. In 2005 he was hired as Associate Professor in the Physics Department of the University of Fribourg, and he then joined ETH Zurich on 2009 as Full Professor. His research focuses on the fundamental understanding of self-assembly processes in polymers, lyotropic liquid crystals, food and biological colloidal systems. Prof. Mezzenga has been recipient of several national and international distinctions such as the 2011 AOCS Young Scientist Research Award, the 2013 Dillon Medal and the 2017 Fellowship of the American Physical Society, the Biomacromolecules/Macromolecules 2013 Young Investigator Award of the American Chemical Society, the 2004 Swiss Science National Foundation Professorship Award and the 2018 Spark Award.

Prof. Raffaele Mezzenga is going to deliver lectures on **lyotropic liquid crystals**.



# Lipidic Mesophases: fundamentals and applications

Raffaele Mezzenga<sup>1,2</sup>

<sup>1</sup>Department of Health Sciences and Technology, ETH Zürich, 8092 Zürich, Switzerland

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Amphiphilic lipids aggregate in aqueous solution into a variety of structural arrangements. Among the plethora of ordered structures that have been reported, many have also been observed in nature. In addition, due to their unique morphologies, the hydrophilic and hydrophobic domains, very high internal interfacial surface area, and the multitude of possible order–order transitions depending on environmental changes, very promising applications have been developed for these systems in recent years. These include crystallization in inverse bicontinuous cubic phases for membrane protein structure determination, generation of advanced materials, sustained release of bioactive molecules, and control of chemical reactions. The outstanding diverse functionalities of lyotropic liquid crystalline phases found in nature and industry are closely related to the topology, including how their nanoscopic domains are organized. This leads to notable examples of correlation between structure and macroscopic properties, which is itself central to the performance of materials in general. The physical origin of the formation of the known classes of lipidic lyotropic liquid crystalline phases, their structure, and their occurrence in nature are described, and their application in materials science and engineering, biology, medical, and pharmaceutical products, and food science and technology are exemplified.

In this lecture I will illustrate the fundamentals of lipid self-assembly into mesophases, their analogies and differences with block copolymers, their physical properties and their range of applications from food to water crystallization nanoconfinement and cryo-enzymatic reactions.

## References

- [1] R. Mezzenga, J.M. Seddon, C.J. Drummond, B.J. Boyd, G.E. Schröder-Turk, L. Sagalowicz, *Nature-Inspired Design and Application of Lipidic Lyotropic Liquid Crystals*, Adv. Mater. 2019, 31, 1900818.



# Liquid-Liquid Phase Separation (LLPS) vs. Liquid-Liquid Crystalline Phase Separation (LLCPS) in Filamentous Colloids

Raffaele Mezzenga<sup>1,2</sup>

<sup>1</sup>Department of Health Sciences and Technology, ETH Zürich, 8092 Zürich, Switzerland

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Liquid-Liquid phase separation (LLPS) of macromolecules is ubiquitous in nature and implies, in the most common form, the demixing of a macromolecule rich-phase (often as droplets) from a macromolecules-depleted continuous phase. Liquid-liquid phase separation in the context of biomacromolecules has been shown to be at the center of important cellular processes and is involved in the formation of the so-called membraneless organelles. In the case of filamentous colloids, the process is similar in the outcome, but fundamentally different in the ruling physics since the interactions among the biomacromolecules are essentially of liquid crystalline nature. This is referred to Liquid-Liquid Crystalline Phase Separation (LLCPS). In this talk I will discuss analogies and differences between LLPS and LLCPS and illustrate this with specific examples, in particular digging from our recent work on amyloid liquid-liquid crystalline phase separation, and the new implications that this brings to the fields of liquid crystals and liquid-liquid phase separation in general.

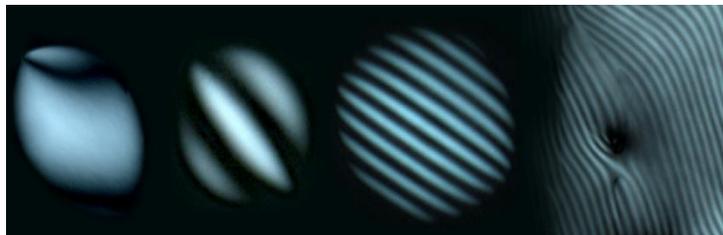


Fig. 1. Amyloid tactoid evolution during liquid-liquid crystalline phase separation

## References

- [1] G. Nyström, M. Arcari, R. Mezzenga, *Nature Nanotechnology* 13, 330 (2018).
- [2] M. Bagnani, G. Nyström, C. De Michele, R. Mezzenga, *ACS Nano* 13, 591 (2019).
- [3] M. Bagnani, P. Azzari, S. Assenza, R. Mezzenga, *Scientific Reports* 9, 1–9 (2019).
- [4] H. Almohammadi, M. Bagnani & R. Mezzenga, *Nature Communications* 11, 5416 (2020).
- [5] P. Azzari, M. Bagnani, R. Mezzenga, *Soft Matter*, 17, 6627 (2021).



**Prof. Stephane Parola** is Professor at the University of Lyon and Director of the Chemistry Laboratory of the Ecole Normale Supérieure (ENS) of Lyon, France. He received a PhD European Label from the University of Nice-Sophia Antipolis (France) and Chalmers University of Technology (Sweden) in 1996, and the habilitation to supervise research from University Lyon 1 in 2004. His research achievements are in the fields of molecular precursors of materials, chemistry of inorganic and hybrid materials, colloidal chemistry, powders, thin films and monoliths, synthesis and surface modification of nanomaterials, properties of materials. He is interested in applications related to photonics, environment or medicine. In particular, he designed original solid-state non-linear optical filters, explored the chemistry and properties of plasmonic nanomaterials, photocatalytic materials, or investigated processes towards colloids synthesis and particles assemblies. He published 120 scientific articles and holds 18 patents with several transfers to industry and one start-up company.

Prof. Stephane Parola from École Normale Supérieure de Lyon (France) will acquaint the Summer School attendees with the newest trends in **nanomaterials for various photonics applications**.



# Nanosciences and metallic particles – synthesis, properties, applications

S. Parola

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The field of nanoscience have experienced huge developments and breakthroughs within the past 20 years. An introduction to nanoscience will emphasize the importance of this field in materials innovation, the challenges as well as economical and societal impacts. Among the most investigated materials, metallic and in particular gold nanoparticles possess unique optoelectronic properties that can be used in many processes and products, related to electronics, solar cells, biology and medicine and catalysis.

The synthesis aspects will be discussed. Most of the synthesis methods proposed allow limited concentration and purity of the colloidal suspensions, preventing from any large-scale development. Procedures for the synthesis of gold pentatwinned nanostructures based on a seed mediated growth process overcoming the concentration limitations of other available methods and offering quantitative yields together with a fine control of the shape and monodisperse size, as well as flexible plasmonic properties will be presented. It will be shown recent developments on the industrialization route to produce large amounts of nanostructures, with minimal waste and postprocessing, making possible their use various applications and industrial developments. Examples of applications in biosensing, photocatalysis, and optics will be given as illustration. The possibility to introduce chirality on nanostructures is also an interesting feature of such process and recent developments in this field will be discussed.



# Solvothermal synthesis of nanoparticles self-assembly, 3D printing and applications

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Hybrid materials are intensively investigated for optical applications (bioimaging, sensors, filters, photocatalysis...) [1].

The solvothermal synthesis of metal fluorides or oxides nanoparticles will be discussed. They can be further self-assembled to build 2D or 3D structures and heterostructures [2, 3]. Controlled destabilization of stable colloidal suspension was used to prepare for instance oxides (YAG), fluorides crystalline xerogels and aerogels and mixed-composite with controlled porosity, mechanical resistance and optical properties [4]. Combination of ultra-small nanoparticles with soft-chemistry process opens also possibilities to use high resolution 2-photon 3D printing to design hybrid or ceramic nanostructures with optical properties [5]. This offers a wide possibility of compositions of materials for applications in energy storage, catalysis, photocatalysis, optics, sensors.

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# Synthesis of monolithic xerogels and aerogels

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Hybrid materials and in particular transparent monolithic materials (xerogels, aerogels) are intensively investigated for optical applications (sensors, filters, imaging, photocatalysis...). The preparation of 3D composite structures incorporating either molecular entities and/or functional nanoparticles represents a challenge on the way to optical devices. Two methodologies will be discussed, (i) the preparation of monolithic transparent silica-based material using the sol-gel process and incorporation of functional nanostructures (plasmonic, luminescent) and (ii) the preparation of monolithic composites from destabilization process of colloidal suspension.

The first strategy operates through the sol-gel process, which allows the design of transparent hybrid monolithic xerogels or aerogels. Plasmonic or luminescent nanostructures can be introduced during the process. Plasmonic nanostructures are functionalized in order to allow their homogeneous incorporation in the transparent hybrid silica matrices. Co-dispersion of the metallic structures with dyes can be achieved. The role of the concentration, shape and size of the metal nanoparticles on the nonlinear optical response is crucial. Similarly, luminescent nanoprobles can be introduced in transparent aerogels and used as liquid or gas phase sensors.

The use of small building blocks nanoparticles suspension to prepare micro-structured materials by self-assembly represents another convenient route towards 3D structuration and monolithic crystalline functional materials. Controlled destabilization of stable colloidal suspension leads to gelation of assembled nanoparticles and preparation of 3D monolithic structures. This approach was used to prepare oxides (YAG), fluorides (Rare Earth) crystalline aerogels and mixed-composite aerogels with high controlled porosity, mechanical resistance and optical properties. This offers a wide possibility of compositions of porous materials for applications in catalysis, photocatalysis, optics, sensors.



**Prof. Wiktor Szymanski** ([www.szymanski-lab.nl](http://www.szymanski-lab.nl)) received his PhD degree from The Warsaw University of Technology, Poland, in 2008, working under the supervision of Prof. Ryszard Ostaszewski. He spent two years working on the use of biotransformations in organic chemistry with Prof. Ben L. Feringa and Prof. Dick B. Janssen at the University of Groningen. Since 2010 he has been working on the construction of photoactive protein- peptide- and DNA-bioconjugates and photopharmacology in the Feringa Labs. In 2014, he joined the Medical Imaging Center, University Medical Center Groningen, where he was appointed in 2015 as tenure track assistant professor and in 2019 as associate professor (adjunct hoogleraar).

Prof. Wiktor Szymański will present his knowledge and experience in **photopharmacology**.



## Molecular Basis for the Application of Light in Medicine

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Light has the potential to enter the clinic as a unique control element for the processes happening in the human body. It acts as a biorthogonal, safe and precise trigger that can be fully controlled in terms of intensity, wavelength spatiotemporal precision. However, human tissues do not usually react to light in the visible range. To enable this interaction, we need to build bridges between light and life. Those bridges are molecules that are both bioactive a photoactive.[1,2]

In this lecture, I will analyze the processes that a molecule can undergo once it enters the excited state upon absorbing a photon (Jablonski diagram, Figure A) and I will highlights how those processes are being used in medicine. I will focus on clinically established (optical imaging, [3] photodynamic therapy [4]), emerging (optoacoustic imaging [5]) and experimental (photo-pharmacology [6]) approaches that translate light into a diagnostic or therapeutic effect (Figure B).

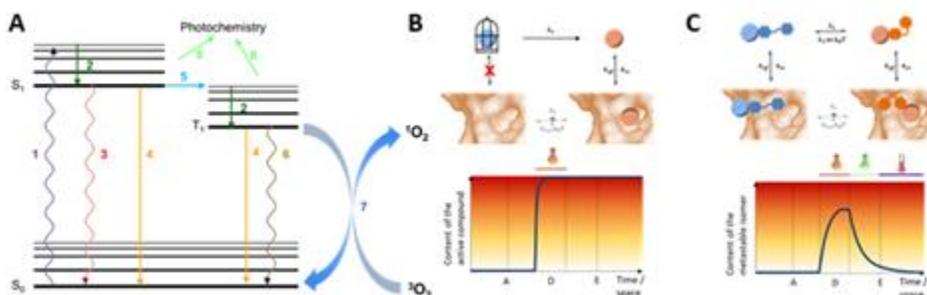


Fig. 1. Jablonski Diagram (A) and the photochemical processes used in irreversible (B) and reversible (C) activation of therapeutics

Next, I will highlight the synergies between medical imaging and therapy, offered by light, through photo-responsive optical [7] and magnetic resonance [8, 9] imaging agents. I will focus on the therapeutic scenarios enabled by the use of photocleavable protecting groups (PPGs), explaining their design [10–12] and applications [13, 14].

**Acknowledgements:** The financial support of the Dutch Scientific Organization (NWO VIDI grant 723.014.001 and ECHO grant 711.017.012) is gratefully acknowledged.

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# Reversible Photopharmacology: Towards Light-Controlled Therapy

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Current pharmacological treatments rely on using bioactive compounds that evoke a response by interacting with molecular targets in the human body. The selectivity of this interaction is crucial and the lack of it leads to the emergence of severe side-effects in the body and toxicity in the environment.

To solve this problem, drugs could be introduced whose activity could be reversibly or irreversibly turned on with light. The aim of this presentation is to describe the emerging concept of photopharmacology (Figure A) [1], which is currently being developed and applied to precisely control the activity of drugs using light. Light offers unparalleled advantages in regulation of bioactivity and as an input/output signal in medical (mostly optical/optoacoustic) imaging. Combination of those two paradigms along the principles of theranostics requires light-responsive tools that empower both therapy and imaging.

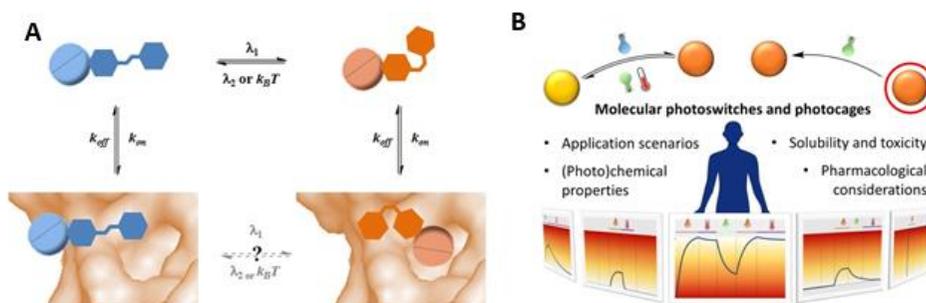


Fig. 1. The principle of photopharmacology (A) and its key molecular tools (B)

The presentation will focus on our efforts towards bridging light and medicine, focusing first on new light-operated tools [2]: molecular photoswitches [3–6] (Figure B). The examples of light-controlled bioactive molecules presented will include small molecules [7–10] and proteins [11]. Finally, using those examples, I will discuss the structural aspects [12] and design principles [13, 14] in photopharmacology.

**Acknowledgements:** The financial support of the Dutch Scientific Organization (NWO VIDI grant 723.014.001 and ECHO grant 711.017.012) is gratefully acknowledged.

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# Plenary sessions



## Real-time fluorescence biosensing with plasmonic silver nanowires

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For efficient biosensing there are several key requirements that must be met in a device, such as specificity and selectivity combined with simple and cost-effective technology, and straightforward operation. Majority of available technologies suffer from some disadvantages, which can be mitigated by application of metallic nanoparticles featuring plasmon resonance. We will show how metallic nanoparticles with elongated shapes – silver nanowires – can be applied for biosensing photoactive proteins.

In our approach, we apply silver nanowires (AgNWs) as a functional platform for biosensing. These structures benefit from simple synthesis, visibility under an optical microscope, modification of the surface, and plasmonic activity. For demonstration we used photoactive proteins equipped with a streptavidin linker. Fluorescence of the proteins was detected with wide-field fluorescence microscopy, which enables to acquire fluorescence kinetics in real-time including observation of emission of single proteins. Figure 1 shows a snapshot fluorescence image of proteins conjugated to AgNWs with a corresponding transmission image of AgNWs prior deposition of the protein solution.

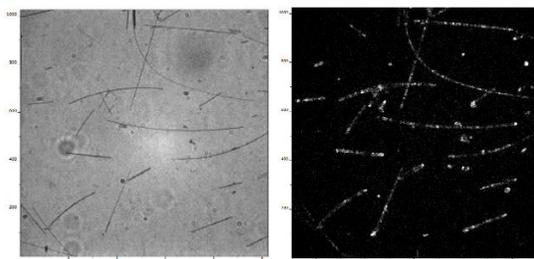


Fig. 1. Transmission picture of AgNWs positions (left). Fluorescence map of single proteins conjugated with AgNWs after 30 seconds of deposition of protein solution (right).

The results of comprehensive experiments indicate that plasmonic enhancement of protein fluorescence yields substantial improvement of the signal-to-noise ratio, enabling faster and more specific detection. By controlling the spatial orientation of AgNWs the sensitivity of single proteins can be achieved. This approach has been implemented in detecting other analytes, such as molecules, viruses, and alike.

This work was supported by the National Science Centre within the OPUS grants 2016/21/B/ST3/02276, 2017/27/B/ST3/02457, and 2017/26/E/ST3/00209, and project nr POWR.03.05.00-00-Z302/17.

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# Folic acid-derived carbon nanodots: how to convert the non-fluorescent molecule into the effective two-photon absorption biomarker

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Carbon dots (CDs), a novel class of carbon nanomaterials that can be fabricated using cost-effective methods, have recently attracted enormous attention [1, 2]. They seem to be promising agents to use in biochemical assays (e.g., bioimaging) as they show, *inter alia*, biocompatibility and excellent linear optical properties (i.e., efficient one-photon excited emission, OPE) [3]. However, to enhance their applicative potential, the non-linear optical activity of CDs (e.g., two-photon excited emission, TPE) should also be explored.

Here we present a new, facile, and low-cost route of carbon nanodots synthesis from folic acid (FA CNDs), and analyze their structural properties and the fluorescence activity in the OPE and TPE regimes. Combining the ultrasounds and hydrothermal treatments, we converted molecules of FA (poorly soluble in water) into the FA CNDs, largely dispersible in aqueous media. As-prepared FA CNDs are composed of the graphitic domains embedded in the polymer matrix and decorated with various polar moieties. An aqueous dispersion of FA CNDs provides bright blue emission upon the OPE and TPE processes, with the fluorescence quantum yield and the averaged lifetime estimated to be 54.1% and 7.5 ns, respectively. The two-photon absorption spectrum (TPA) is strong, and fully covers the red and near-infrared regions that correspond to the first biological window. The molar-mass scaled TPA cross-sections reach 0.31 GM·mol/g at 710 nm, being comparable with the most representative nanoprobes in this spectral range. We also report on the FA CNDs' application as one- and two-photon biomarkers for the fluorescence-based monitoring of myelin figures resembling the multilamellar membrane that covers nerve fibers [4].

In conclusion, FA CNDs with excellent OPE and TPE fluorescence properties in aqueous dispersion were prepared using a simple, low-cost strategy. These new CNDs satisfy all application requirements from the biochemical fields, and they can be considered as superior fluorescent alternatives for inorganic nanomaterials and organic dyes.

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# Autofluorescence properties of lysozyme amyloids

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Amyloids are peptide or protein aggregates associated with some neurodegenerative disorders, including, e.g., Alzheimer's disease. These aggregates are characterized by the presence of the secondary  $\beta$ -sheet structure.[1] Despite several hypotheses about the origin of their one-photon (1P) excited autofluorescence properties, their two-photon (2P) excited autofluorescence still remains elusive.[2-4]

We investigated autofluorescence properties of hen egg-white lysozyme (HEWL) monomers and fibrils. The samples were dissolved at the varying NaCl content. We analyzed their morphology and the secondary structure. Additionally, we performed 1P and 2P excited fluorescence lifetime measurements of amyloid fibrils.

The outcomes evidence that not only HEWL fibrils, but also monomers exhibit 1P and 2P autofluorescence properties. However, the fluorescence intensity is markedly enhanced upon formation of HEWL fibrils. The results demonstrate that not only transition into higher-order fibrillar aggregates leads to the increased fluorescence intensity. Increasing NaCl concentration influences the morphology and the secondary structure content, which finally contribute to the increased intensity of 1P and 2P autofluorescence. Moreover, we observed that the 2P excited emission spectrum is red-shifted compared to the 1P one. We confirmed the existence of diverse relaxation pathways, as the 2P excited fluorescence lifetime is shorter than that for the 1P case.

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# Noncovalent intramolecular forces – gold nanoparticles ligand chemistry and amyloid fibrils interfaces

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Amyloids as the hallmark of neurodegenerative disorders (i.e., dementia, Parkinson's or Alzheimer's disease) are structurally characterized by cross- $\beta$  organization and exhibit high morphological heterogeneity [1, 2]. Distinct polymorphs are also of distinct toxicity and pathology spreading rate [3]. Therefore, design of novel and functional probes of amyloids structural features is of great importance and lay the groundwork for more successful therapeutic approaches in the future [4, 5]. Moreover, their external and internal structure including solvent-exposed interfaces are differing in terms of hydrophobicity, as entire aggregate is composed of amino acids of distinct solubility [6]. Beside  $\pi$ -conjugated systems based on simple organic molecules, gold nanoclusters are promising materials to apply in bio-imaging, as they have unique optical properties (i.e., large Stokes shifts and tailored luminescence) and high electron density due to the gold atoms presence. Thus, they are attractive for both light and electron microscopy staining – i.e., multimodal [7, 8].

Herein, we present a discussion regarding amyloids staining with gold nanoclusters supported by preliminary research on near infra-red fluorescent and functional gold nanoclusters capped with 2-(mercaptomethyl)-12-crown-4 ether being designed to interact with amyloid hydrophobic interfaces.

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# On the creation and properties of gold nanoclusters helical assemblies

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Gold nanoclusters are getting more attention every year due to their molecular-like properties – discrete energy levels and strong photoluminescence - making them promising candidates for next generation optical markers [1, 2]. Moreover, their optical properties could be further tuned due to assembly. Although self-assembly ligand mediated methods are thoroughly investigated in the literature of the subject, there are only a few reports on template-assisted methods, which are far more reproducible and offer tunable periodicity of the assembled particles as well as formation of hierarchical structures [3].

We discovered a new way to assemble Au<sub>25</sub>(PET)<sub>18</sub> gold nanoclusters in a helical manner adopting liquid crystal template (P-9-OPIMB) used previously to assemble plasmonic nanoparticles [4]. This material upon cooling slowly from isotropic phase forms liquid crystal B4 phase consisting of helical nanofilaments[5] Gold nanoclusters helical assemblies were prepared by mixing with template molecules before the heating-cooling cycles. Moreover, nanoclusters were functionalized with two ligands, 1-dodecanethiol (DDT) and liquid crystalline ligand (LC) derived from the template material, what enhanced the mutual affinity of gold nanoclusters to template molecules. Functionalization and stability of nanocluster during the whole process was confirmed by MALDI-MS spectra and the morphology of gold nanoclusters decorated helical nanofilaments was proven by TEM and AFM imaging. Collected data showed that only double functionalization of gold nanocluster surface using both DDT and LC results in effective nanocluster coating of helical template filaments. Finally, we observed that both functionalization and assembly flattened the absorption spectra and red-shifted their fluorescence emission spectra maximum.

In conclusion, we have successfully adapted liquid-crystal mediated nanoparticle assemble method to arrange gold nanocluster in a helical manner, showing that it might be a universal method to create helical heterostructures with different types of gold nanoparticles. Moreover, both functionalization and assembly modified nanocluster emission, what show their potential as gold nanocluster optical properties tuning factor.

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# OPA/TPA Spectra of the wt-Rhodopsin Calculated using TD-DFT/MM with Polarizable Embedding

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We investigate one- and two-photon absorption spectra of wt-Rhodopsin using QM/MM methodology with polarizable embedding. Our calculations reveal that the lowest-lying TPA absorption band (S0-S1) at ca. 1000 nm has one order of magnitude lower cross-section than the two absorption bands within 500-700 nm region, corresponding to the S0-S2 and S0-S3 electronic excitations. The intensity trend is reversed in the OPA spectrum. The calculated TPA spectrum displays a qualitatively similar intensity pattern as the spectrum by Olivucci and co-workers [1] who used a very sophisticated XMCQDPT2/MM methodology with electrostatic embedding to obtain it. It seems that quite different TPA spectrum of the wt-Rhodopsin calculated by Palczewska et al. [2] may suffer from the usage of a small QM size of the system combined with an electrostatic embedding. One of us [3] has shown that to converge TPA properties using electrostatic embedding, the QM subsystem of the protein needs to contain over 300 atoms.

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## Gold nanoparticles for copper(II) ion sensing by Second Harmonic Scattering

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Detection of copper ions is essential for various fields, such as medicine [1] or food safety [2]. Gold nanoparticles, exhibiting Localized Surface Plasmon Resonance, have been shown to be an appropriate means for copper (II) ions colorimetric detection [3]. Second Harmonic Scattering (SHS), namely simultaneous annihilation of two photons at the fundamental frequency and creation of a single photon at harmonic frequency, is promising for sensing purposes due to its sensitivity to the surface of nanoparticles [4]. Current work concerns Second Harmonic Scattering for copper (II) ion sensing. Samples containing various concentrations from 1 to 25 000  $\mu\text{M}$   $\text{CuBr}_2$  were studied. Their UV-Vis spectra, Zeta potential and DLS measurements showed domination of weak interactions between citrate and copper for low copper content, meanwhile from  $\sim 1$  mM copper(II) bromide concentration, the gold aggregation dominates. SHS of the samples has been investigated, along with polarization-resolved measurements, further confirming the nature of interactions. A sensing detection limit below  $1\mu\text{M}$  was reported.

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# Two-photon investigation of chiroptical properties of gold nanoclusters

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The term chirality refers to the molecules with non-superimposable mirror image. For decades chirality found in common organic biomolecules has inspired scientists to mimic the chiral response in newly developed nanoobjects. One class of them are gold nanoclusters (AuNCs) in which the chirality originates from chiral arrangement of the structure, inherently chiral inner metal core or the chiral ligands [1]. Apart from chirality the AuNCs possess unique linear and nonlinear optical properties arising from their composition and discrete electronic structure. The increasing interest in gold nanoclusters as efficient luminescent markers in two-photon microscopy has also unveiled their relevance in a new domain of two-photon chirality-based applications, such as multiphoton imaging or detection with chiral discrimination of the desired species. In this context, the determination of two-photon chiroptical properties of AuNCs is particularly interesting due to their strong nonlinear response in the near infrared region, favorable for potential application in the first and second spectral biological window.

In nonlinear optics domain one can define chirality using parameters:  $\Theta_{\text{TPCD}}$ ,  $\Theta_{\text{TPLCD}}$ , that quantify the strength of the two-photon chiroptical effects as a relative difference between the values of two-photon absorption cross-sections ( $\sigma_2$ ) for the left-handed and right-handed circularly polarized illumination [2]. Our recent study of two-photon circular dichroism of AuNCs was pioneering in terms of characterization of  $\Theta_{\text{TPCD}}$ ,  $\Theta_{\text{TPLCD}}$  and  $\sigma_2$  using the Z-scan technique [3]. Here we propose two-photon fluorescence detected circular dichroism (TP-FDCD) as a complementary technique of quantitative description of two-photon chiroptical properties of nanoclusters determined via luminescence. We optimised the protocol of TP-FDCD measurements on a custom-modified two-photon excited luminescence (TPEL) optical set-up. We present for the first time an extensive characterization of TP-FDCD of strongly luminescent gold nanoclusters in a broad NIR range of excitation. Significant results, compared to conventional CD characterization of gold nanoclusters, showed around 320-times enhanced two-photon dissymmetry factor ( $g_{2\text{P-FDCD}}$ ) vs one-photon dissymmetry factor ( $g_{1\text{P-CD}}$ ).

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# In-situ transmission electron microscopy imaging of liquid crystals – challenges and perspectives

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Liquid crystals may sound mysterious to people who are not related to the subject, but they are an inseparable part of our lives. Liquid crystals possess unique anisotropic optical properties and thanks to their combined fluidity and partially ordered structure they can be easily manipulated by external signals, which is the reason why they are widely applied in technology. The main methods used for their characterization are polarized light microscopy, DSC, SAXS and nonlinear optical imaging techniques[1].

Transmission Electron Microscopy (TEM) is a powerful imaging technique known for its incomparable resolution and capabilities. For years TEM has allowed scientists to look into the smallest parts of the materials and discover the world on the nanoscale and the improvements in sample preparation, as well as the microscope itself, made in-situ imaging of subtle materials and phenomena possible. Even though liquid crystals have been known to scientists for over 100 years, there is no more but only one report about TEM imaging of liquid crystals in the native state [2]. One of the reasons for this is the microscope environment, which is a high vacuum. As observations of many dynamic processes require a liquid environment, there is a need to isolate the sample from the surrounding vacuum inside the microscope. Nanocrystals formation, growth of complex structures, nanoparticle and biological interactions are examples of processes, that cannot be observed in a phase other than liquid. Imaging in vacuum-free conditions around the sample may cause many problems and cannot be performed using conventional TEM method [3]. The second issue that regards hydrated samples, as well as liquid crystals imaging, is the damaging effect of the electron beam [4]. For this reason, the electron dose has to be strictly controlled to obtain reliable results.

This talk will be focused on the challenges of TEM imaging of liquid crystals, especially in-situ phase transitions, and perspectives of correlative microscopy. The methods for liquid sample preparation, the possible solutions for the problems and the promising multiphoton-electron correlative microscopy of liquid crystals doped with nanomaterials will be widely discussed.

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## Characterization of lyotropic myelin figures using linear and nonlinear optical studies

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A well-known example of a biologically derived lyotropic mesophase attracting a considerable body of experimental and theoretical efforts is the myelin sheath, which plays a crucial role in action potential propagation [1, 2]. The study of this structure still gains attention due to unsolved questions about the causes of its degradation processes [3].

In this work, we investigated artificial myelin figures (MFs) composed of bilayer-forming phosphocholines [4, 5]. Due to the cylindrical shape and amphiphilic nature of those zwitterionic phospholipids, they tend to self-assembly into elongated multilamellar structures in the presence of excess water (Fig. 1).

The combination of polarized light microscopy and fluorescence microscopy provided us with deep insight into lipid arrangement within MFs. Two-photon excited fluorescence microscopy was applied to examine different structural morphologies of phospholipid-based lamellar mesophases, using folic acid-derived carbon nanodots (FA CNDs) as effective markers. These results show a promising approach to labeling the core and the multilayered walls of MFs [6].

In conclusion, we evidenced that one- and two-photon fluorescence microscopies can be successfully incorporated into research on multilayered microstructures.

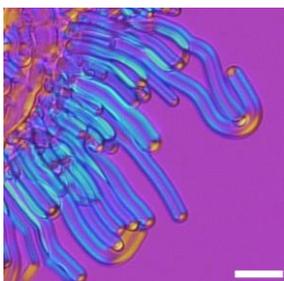


Fig. 1. The polarized optical microscopy image of myelin figures taken with a retardation plate. The scale bar is 30  $\mu\text{m}$

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# Fabrication of formable sol-gel and polymer films for planar photonic systems

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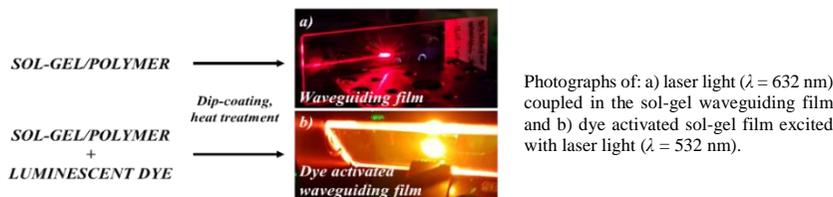
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Thin sol-gel and polymeric films with controllable refractive index and thickness may be achieved by dip-coating method by means of proper selection of materials and preparation protocol. An important advantage is their low cost, facile fabrication and easy processing. They may find application as planar waveguides [1,2] or, when activated with organic luminescent dyes, as light amplification media [3].

We report fabrication of thin films based on SiO<sub>2</sub> or organically modified SiO<sub>2</sub> (ORMOSIL) and TiO<sub>2</sub>. Some of them were activated with Rhodamine B. Preparation of polymeric films is discussed as well. Influence of different preparation conditions on optical properties of films was studied. The refractive index and thickness were evaluated using ellipsometry or/and profilometry. It was found that they can be controlled by adjusting the relative amount of SiO<sub>2</sub> and TiO<sub>2</sub> precursors, heat treatment conditions and withdrawal speed. Sol-gel films activated with Rhodamine B were characterized using absorption and emission spectroscopy. The optical transmission losses of selected planar waveguides were determined using scattered-light method. Moreover, simple approach of fabrication of the periodic structures in ORMOSIL based and polymeric thin films using nanoimprint technique was implemented.



We showed, that formable materials such as ORMOSIL-based and polymeric films may be further processed to obtain planar photonic components of desired shape by facile mechanical imprint method.

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## New dyes based on BODIPY and benzothiazoles motif for amyloid detection

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Increasing numbers of patients that develop Alzheimer's disease, Parkinson's disease or Type 2 Diabetes cause the need for new therapies that are still beyond the reach of modern medicine. Mentioned pathologies have two things in common, they are incurable and their development is associated with protein aggregates called amyloids [1]. Therapies targeted at eliminating toxic aggregates do not show as good results as predicted [2]. This creates the need for new methods of detecting amyloids at various stages of aggregation, which would provide new information on these complex structures.

New dyes that combine BODIPY core and benzothiazoles with different end functional groups were designed and synthesized to act as amyloid-binding probes with favourable one-photon and two-photon (TP) optical properties. Dyes containing difluoroborylene (BF<sub>2</sub>) group have potential TP properties that depends on structural variations like changes in electro-active functional groups, also compounds based on this motif were already successfully used on mice [3, 4]. Two-photon excitation gives deeper optical penetration, lower scattering which is in advanced to on-photon techniques [5].



Fig. 1. The structure of investigated compounds

One-photon optical properties – fluorescence, Uv-Vis Absorption, fluorescence lifetime were compared without and in the presence of amyloids. Two dyes with opposite terminal functional groups were investigated (Fig. 1) – (OMe/CF<sub>3</sub>) and (CF<sub>3</sub>/OMe). Depending on the electronic motif of the dye (DAA or AAD), different changes in fluorescence spectrum and intensity were observed in the presence of amyloids. Concentrations below 10 μM were sufficient to observe several times increase in fluorescence intensity. The obtained results confirm that the newly synthesized dyes can serve as potential markers of amyloid.

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# The influence of temperature and Cr<sup>3+</sup> ions concentration on spectroscopic properties of [EA]<sub>2</sub>NaCr<sub>x</sub>Al<sub>1-x</sub>(HCOO)<sub>6</sub>

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Hybrid organic-inorganic compounds with perovskite-type structure ABX<sub>3</sub> attract a lot of attention due to their outstanding properties, i.e., magnetic, ferroelectric, optical, and temperature-dependent effects [1, 2]. The characteristics of these materials can be significantly tuned by changing the type of components and dopant concentrations [2].

Among various materials, the double perovskite structures A<sub>2</sub>M<sup>I</sup>M<sup>III</sup>X<sub>6</sub>, herein, the series of [EA]<sub>2</sub>NaCr<sub>x</sub>Al<sub>1-x</sub>(HCOO)<sub>6</sub>, where  $x = 1, 0.78, 0.57, 0.30, 0.21,$  and 0, exhibit particular structural and luminescent properties. The change of the Cr<sup>3+</sup> ions concentration affects the luminescence, especially the intensity of the broad spin-allowed <sup>4</sup>T<sub>2g</sub> → <sup>4</sup>A<sub>2g</sub> transition observed around 750 nm. Moreover, the changes in temperature have significant impact on the intensity of the emission, resulting from the spin-forbidden <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> transition near 700 nm (Fig. 1). The investigation of temperature-dependent emission gives important insights into the relationship between crystal structure and luminescence characteristics.

The presentation will be focused on the preparation of investigated single crystals, structural analysis, and detailed optical studies. Particular attention will be paid to temperature-dependent emission measurements, which provide the basis for classifying this group of materials as non-contact luminescence thermometers.

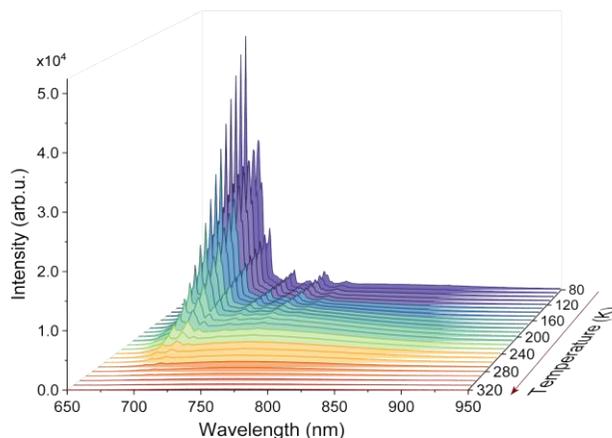


Fig. 1. Temperature-dependent emission spectra of [EA]<sub>2</sub>NaCr<sub>0.78</sub>Al<sub>0.22</sub>(HCOO)<sub>6</sub>

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# Indirect Excitation of Azobenzene Molecules – Plasmon-Assisted Approach

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Many light-responsive systems rely on organic photoswitches, such as azobenzenes. Azobenzenes are presumably, the most common type of photochromic molecules and can undergo isomerization from their more thermodynamically stable *trans* (E) state to *cis* (Z) form upon UV irradiation [1]. However, to facilitate their use for applications in molecular devices, electronics, energy storage, photopharmacology or optogenetics, their overall optical properties, such as the Z-isomer lifetime or the position of excitation wavelengths, often need to be modified [2].

Many chemical or physical factors can influence the Z-E photoswitching of azobenzenes (Azo), including gold nanoparticles (AuNPs) [4–6]. However, their catalytical impact was investigated only for small, spherical nanostructures. Hence our objective was to study the influence of bigger, anisotropic AuNPs of a rod-like shape. We hypothesized that due to their optical properties, the indirect control over the Azo photoswitching properties would be possible, particularly the expansion of the Z-isomer excitation wavelength into the red or near-infrared range.

Our novel approach was possible because of the proper stabilization of AuNPs using cellulose fibers, as proposed before by us for photocatalytic applications [7]. We also show the method for preparing the three-component hybrid material consisting of azobenzene, cellulose, and gold nanorods.

The Z-E relaxation of Azo was monitored using a UV-Vis-NIR absorption fiber spectrophotometer in the dark and under illumination with the red light. The influence of the plasmonic composite or the photoswitching behaviour of the hybrid material were compared with the control samples without gold. The results indicate that gold nanorods can indirectly control the Z-E relaxation of azobenzenes and that hybrid three-component material is sensitive toward red light illumination. This research illustrates that the excitation wavelengths of the Azo Z-isomer can be tuned by tailoring the optical properties of AuNPs.

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# Flash presentation session



# Improved germicidal performance of Visible-to-UVA/UVC upconversion process in lanthanide doped oxyorthosilicates

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Within ultraviolet (UV) radiation it is possible to distinguish three main spectral regions: UVA (320–400 nm), UVB (280–320 nm), and UVC (200–280 nm). When utilized for disinfection purposes, they influence on pathogens in a different way [1]. For instance, UVC radiation is the most effective to be absorbed by DNA and RNA and, as a result, the photoproduct that prevents the irradiated microbes from further replication is formed [2]. On the other hand, UVA provides sanitizing effect *via* reactive oxygen species (ROS) generation, leading to the death of microorganisms under oxidative stress [3].

The main goal of this research is to investigate the influence of co-doping Pr<sup>3+</sup>-based oxyorthosilicates Y<sub>2</sub>SiO<sub>5</sub> with Tm<sup>3+</sup> and Yb<sup>3+</sup> ions on its germicidal performance against the biofilm cultures of *A. baumannii*, *S. aureus* and *C. albicans* via spectroscopic properties alteration in UV spectral region. Due to abundant ladder like energy level structure of Pr<sup>3+</sup> ions it is possible to realize the anti-Stokes process of photon upconversion upon 447 nm laser excitation. As a consequence, broad emission band ranging between 250–350 nm with the maximum intensity in UVC region at ca. 270 nm occurs, which could be utilized against microbial species. However, UV sterilization effect can be considerably enhanced by UVA radiation emission at ca. 370 nm, occurring simultaneously under visible light irradiation from incorporated into oxyorthosilicates host matrix Tm<sup>3+</sup> ions. Moreover, co-doping with Li<sup>+</sup> ions increases the energy transfer probability from Pr<sup>3+</sup> to Tm<sup>3+</sup> ions, which results in significant UVA emission intensity enhancement of Tm<sup>3+</sup> ions. The results gathered in this study are profoundly meaningful for the improvement of materials emitting upconverted UV radiation for germicidal purposes.

**Acknowledgments:** This work was supported by the National Science Centre Poland under SHENG research grant (no. 2018/30/Q/ST5/00634).

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# Self-assembled bilosomes with stimuli-responsive properties as bioinspired nanoplatform for support photodynamic treatment of skin cancer cells

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Melanoma, which usually occurs in the lower epidermal layer, is one of the most aggressive skin cancers due to its multiple metastases and high mortality rate. In an advanced stage, it is highly resistant to conventional treatments (including chemotherapy and radiotherapy), so the search for novel and effective therapeutic strategies, such as phyto-photodynamic therapy (phyto-PDT), to combat this cancer becomes crucial [1].

Herein, we present self-assembling colloidal nanostructures stabilized by bile salts (so-called bilosomes), co-encapsulating a hydrophilic photosensitizer (Methylene Blue, MB) and a hydrophobic phytochemical compound (curcumin, CUR), as bioinspired nanoplatform in potential phyto-PDT. The applied nanoplatform was assessed by physicochemical analysis (size, zeta potential, shape, morphology) by using dynamic and electrophoretic light scattering (DLS, ELS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Then we accomplished its cytotoxicity and photo-cytotoxicity studies on human epithelial skin melanoma cell line (A375) using an MTT reduction assay. Internalization and bioimaging of empty and co-loaded bilosomes in A375 cells was also a crucial focus of our study.

Our research has shown that the proposed nanoplatform is internalized by the A375 cell line being simultaneously nontoxic to these cells without irradiation over a wide range of concentrations. Importantly, antitumor activity (irradiation within the therapeutic window at  $\lambda = 630$  nm) showed that double-loaded bilosomes (MB+CUR) have higher efficacy against melanoma cells compared to MB alone. In conclusion, the results demonstrate that the developed multifunctional bilosomes can be efficient hybrid cargo delivery systems useful for induction of phyto-photodynamic effects on melanoma cells.

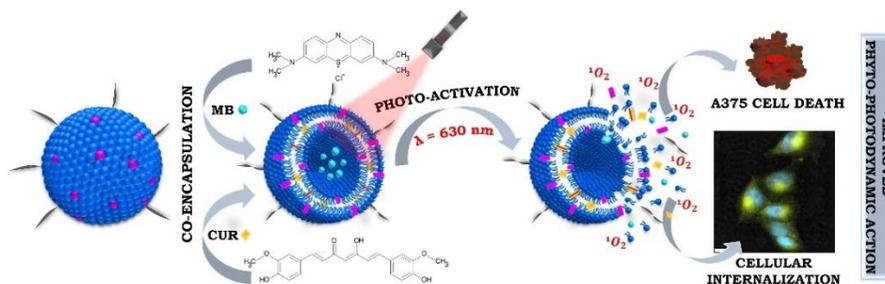


Fig. 1. Schematic representation of the action of the developed nanoplatform in phyto-photodynamic therapy of human melanoma cells

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## Photoinactivation of clinical bacterial strains with the use of OLED

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Photoinactivation is a process of pathogens or cancer cells destruction by reactive oxygen species generated with the use of light at a specific wavelength and a chemical compound sensitive to this particular light in a presence of molecular oxygen. A target could be either viruses, fungus, parasites, or bacteria. In the last case, the importance of photoinactivation gathers strength due to the growing global problem of antibiotic resistance among bacteria [1, 2]. Finding new methods to fight bacterial infections is a great challenge as regards health care of hospitalized patients, people with immunity disorders, and chronic wound healing. Photoinactivation poses here attractive alternative and great research area [3].

The aim of this study was to investigate the efficiency of photoinactivation of bacterial strains isolated directly from hospitalized patients. People diagnosed with diabetic foot, defined as an unhealing wound appearing usually in the down limb area, are at high-risk for bacterial infections leading to limb amputation or death thus they were chosen for sample collections.

As a result, we have collected 30 bacterial strains and 23 bacterial species. All bacteria showed sensitivity to photoinactivation, however, the final effect was dependent on bacterial species. For some strains, we have obtained a reduction level greater than 99.9% which proved the high potential of this antimicrobial approach.

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# Xanthene derived dyes as potential activators for photonics applications

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Today's technology and photonics are based on newer and newer organic dyes with high luminescent properties. Together with good optical properties, these dyes must also be chemically and thermally stable, especially as they often are incorporated into sol-gel matrices during the preparation of hybrid platforms. One possible answer to modern requirements could be xanthene dyes and their derivatives [1].

In this study, we demonstrate novel long chain substituted xanthene derivatives and their spectroscopic and chemical properties [2, 3]. Functionalized by O-alkylation compounds were simultaneously prepared using different methods (conventional or microwave heating, ball milling as new, eco-friendly method). The presented synthesis examination allowed us to obtain two different compounds during one step, with open and closed lactone rings substituted with different length alkyl chains. Increasing the reaction efficiency to 77% was obtained using the microwave-assisted method. We also demonstrate that fluorescein can be effectively functionalized by O-alkylation carried out under ball-milling conditions, saving time and energy and affording the desired products with good yields and minimal byproduct formation.

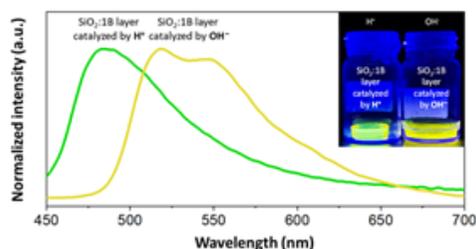


Fig. 1. Emission spectra for SiO<sub>2</sub> gel layers doped with derivative 1B ( $\lambda_{\text{ex}}$  for H<sup>+</sup> catalyzed material = 320 nm, while for OH<sup>-</sup> catalyzed = 360 nm); inset: photograph of dried gels under UV light ( $\lambda_{\text{ex}}$  = 365 nm) [2]

When considering potential applications and, consequently, designing materials with well-defined emission spectral range, tautomerization and prototropism of fluorescein and its derivatives are particularly problematic phenomena. We show the possibility of doping SiO<sub>2</sub>-based layers with methylated derivative. To obtain such layers, various pH catalysts in a sol-gel silica network synthesis were used, resulting in different emission colors under a UV lamp after gelation, which most likely resulted from the various forms trapped in the matrix.

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# Solvatochromic properties of selected dyes solubilized in different micellar systems

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Solvatochromic probes have been used successfully for some time, which allowed for the assessment of the solvation capacity of the solvent. One of the molecules commonly used for this purpose is Reichardt's dye. On the basis of spectrophotometric data obtained with its use, one of the most commonly applied polarity scales was constructed, called the  $E_T(30)$  scale [1]. Currently, attempts are being made to expand this dye with newer solvents, such as, for example, ionic liquids, and even in recent times with micellar systems of different nature.

In the proposed studies, in addition to the assessment of the used solvent effect, it was also shown that the shift of the UV-Vis absorption bands also takes place in the case of an attempt to the dye solubilized in a micelle molecule. Consequently, various types of ionic and non-ionic surfactants with different CMC (critical micelle concentration) were applied for the micelles' self-assembly, and then samples with the solubilized dye were subjected to spectrophotometric analysis. In the case of the analyzed systems, significant shifts in the UV-Vis bands and changes in intensity were observed. Also, betaine dyes and other organic chromophores were tested for use as molecular probes, and shifts in the UV-Vis absorption bands were also present, leading to the conclusion that the tested compounds could potentially be used in the future to create new polar scales. Molecular probes (solvatochromic dyes) along with solubilized/co-encapsulated other the active compounds (e.g. drugs), due to the possibility of using them for evaluation of the micelle's internal environment, could act as indicators to assess micellar carrier stability in the context of controlled drug release, being a promising prospect for biomedical applications.

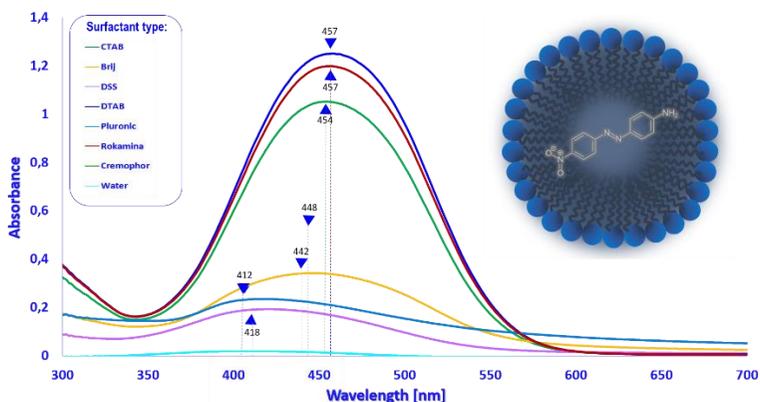


Fig. 1. An example of the UV-Vis spectrum for one of the analyzed chromophores

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# Nanomaterials-based detection of dopamine

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- 1. Introduction:** A biosensor transforms chemical information into an interpretable signal with the involvement of biomolecules in the recognition process. Biosensors have found applications in many areas, including medicine and clinical diagnostics. Nanotechnology has allowed further expansion of the research in this field [1, 2]. Nanomaterials due to their unique properties, reasonable costs, and controllable shape have become an interesting group of materials in the electroanalytical measurements and sensing technologies, and their use improves the performance of biosensors [3].
- 2. Methods:** Carbon dots were synthesized from citric acid and urea in dimethylformamide. The mixture was heated for 12 h to obtain nanomaterials. These CDs, along with an enzyme – laccase – were then used to modify a glassy carbon electrode. A differential pulse voltammetry technique was employed to test the ability of the system to detect the presence of dopamine in the sample.
- 3. Results:** Electrochemical measurements showed that obtained platform exhibited good linearity in a wide range of concentrations with the limit of detection within a micromolar range.
- 4. Conclusions:** It is important to develop methods that will allow the detection of biomolecules, such as neurotransmitters, with high selectivity and specificity, in order to prevent or diagnose diseases, improve quality of life, and minimize health risks. Performed experiment resulted in a sensing platform based on nanomaterials, which allowed for the detection of dopamine at a micromolar level.

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# Study of Singlet and Triplet Channels of [2 + 2] Photocycloaddition of Nitrostyrene to Indene

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The presented results demonstrate the mechanism of the stereoselective [2 + 2] photocycloaddition reaction of nitrostyrene to indene using *ab initio* quantum chemistry methods. Although this reaction has been analyzed and described based on experimental research, its exact mechanism is unknown and has not been studied by computational quantum chemistry methods. It has only been hypothesized that it occurs on the potential energy surface of a low-lying triplet state [1, 2].

The mechanism of the title reaction was investigated employing the Kohn-Sham density functional theory (KS-DFT), assuming the  $\omega$ B97XD long-range corrected hybrid density functional with dispersion corrections, as well as using the Møller-Plesset perturbation theory to the second order (MP2) and algebraic diagrammatic construction to the second order and [ADC(2)]. The MP2 and ADC(2) calculations were carried out using the spin-components-scaling (SCS) variants. The def2-TZVPP or aug-cc-pVDZ basis sets were used in ground and excited-state calculations, respectively [3].

Based on the reaction course of photocycloaddition postulated in the experimental work, the molecular mechanism of the reaction was investigated on the excited-state potential energy surface of the singlet and triplet states. The latter could be observed after a singlet-triplet intersystem transition. Preliminary analysis of the potential energy surface topology for singlet and triplet channels indicates that the photocycloaddition reaction should mainly occur through the singlet channel in the  $^1\pi\pi^*$  excited state, having an intermolecular charge-transfer character. This conclusion arises from the fact that the alternative route via the triplet potential energy surface has a significant energy barrier to overcome compared to the barrier-free singlet channel.

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## Application of microbial fuel cells for contaminants degradation and current generation

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Microbial fuel cells (MFCs) are unique systems that can convert the chemical energy of organic pollutants into electrical energy. As a catalyst, these systems use electroactive bacteria capable of oxidizing compounds and transferring electrons. The objective of this study was to use MFCs for simultaneous degradation of crude oil and electricity production.

In this study single-chamber MFCs made from poly(methyl methacrylate) were used. The anode chambers were inoculated with a mixture of mineral salt medium and anyolite from MFCs enriched initially with contaminated areas such as: 1) a sewer and 2) an oil separator at the petrol station, as well as contaminated soil from Sri Lanka. Crude oil and acetate were used as an energy source. The growth dynamics of the microorganisms was observed by real-time voltage monitoring and electrochemical tests of MFC. The highest power density of 26 W/m<sup>3</sup> was recorded after 127 days of operation, a level comparable to that of acetate as the only fuel in the same type of MFC. Power production was accompanied by a significant drop in surface tension, which may indicate the production of biosurfactants.

The results indicate that it is possible to use microbial fuel cells for the simultaneous degradation of waste compounds and production of electricity. However, further research should focus on investigating the products formed during bioelectrochemical crude oil degradation.

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# Prolonged stability of silver nanoparticles in the presence of protic ionic liquids

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The stability of nanostructures is a key element in their applications, as uncontrolled aggregation leads to changes in their properties and increased toxicity [1, 2]. Finding the right stabilizer remains a big challenge for nanotechnology. We have used 3-alkoxymethyl-1-*H*-imidazol-1-ium salicylates ([H-Im-C<sub>1</sub>OC<sub>n</sub>][Sal]), a group of protic ionic liquids (PILs) with broad and diverse functions [3, 4], as silver nanoparticles (AgNPs) stabilizers for the first time. We have synthesized AgNPs using an aqueous extract of green tea *Camellia sinensis*. Optical characterization revealed that we have obtained small (40–75 nm) and stable for over 20 days AgNPs with the addition of [H-Im-C<sub>1</sub>OC<sub>n</sub>][Sal] compared to the unstabilized sample. This research indicates high potential of using [H-Im-C<sub>1</sub>OC<sub>n</sub>][Sal] to maintain stable AgNPs dispersion – crucial in biological and biotechnological applications.

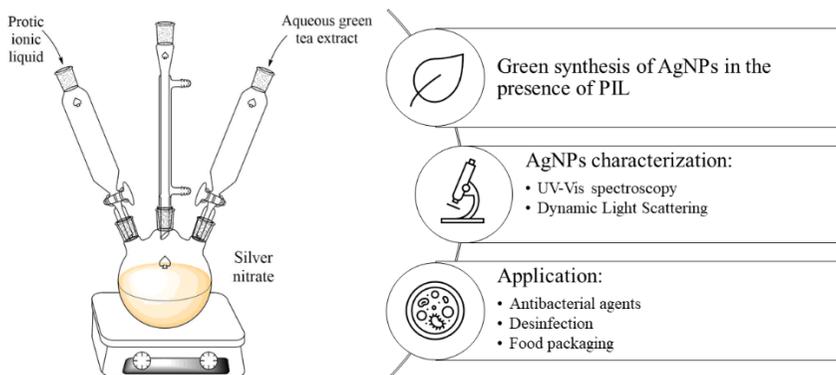


Fig. 1. Scheme of a reaction system for AgNPs synthesis along with their characterization techniques and potential application

The research was supported by the European project Horizon 2020 „Open innovation test bed for developing safe nano-enabled bio-based materials and polymer bionanocomposites for multifunctional and new advanced application” no. 953206.

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# Poster session



P01

# Spectroscopic properties of $\text{Li}_2\text{Mg}_3\text{TiO}_6:\text{Cr}^{3+}$ for noncontact temperature sensing

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Luminescence thermometry (LT) is a technique that has recently been gaining more and more research interest, due to its advantages such as noncontact temperature readout and its applicability in a wide temperature range, from cryogenic[1] to extremely high-temperature conditions[2]. LT is particularly attractive for biological applications, where the main challenge is to design a sensor that emits radiation in the biological transparency window (900–1350 nm) and has high sensitivity in the biologically relevant temperature range.

Accordingly, this study presents a  $\text{Li}_2\text{Mg}_3\text{TiO}_6$  doped with  $\text{Cr}^{3+}$  ions for thermometric application. The proposed temperature sensor is based on the intensity ratio of bands originating from the  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  and  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transitions of the chromium(III) ion substituting simultaneously titanium(IV) and magnesium(II) crystallographic sites.

The effect of the dopant concentration (0.1–10%  $\text{Cr}^{3+}$ ) on the morphology and luminescence properties of the materials was investigated. Basing on the thermal dependence of the emission spectra of obtained phosphors measured in a wide temperature range (123–563 K) the luminescence intensity ratio and relative sensitivities were determined.

The study showed that by the optimization of the dopant concentration, which in turn affects the strength of the crystal field, it is possible to obtain a luminescent thermometer with the relative sensitivity of 0.7%/K at 303K, which makes it potential to be adapted for biological applications.

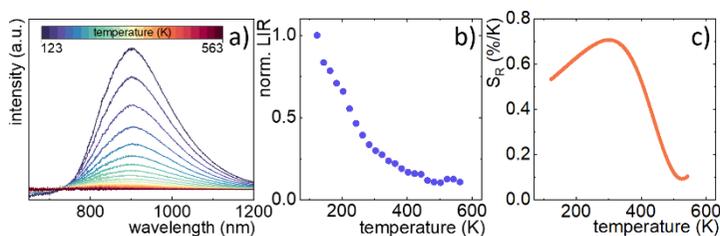


Fig. 1. Emission spectra of  $\text{Li}_2\text{Mg}_3\text{TiO}_6:10\% \text{Cr}^{3+}$  as a function of temperature (123–563 K) upon  $\lambda_{\text{exc}} = 445 \text{ nm}$ ; and corresponding thermal dependencies of luminescence intensity ratio (LIR) (b); and relative sensitivity (c).

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P02

## Contactless energy conversion on multimodal $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-Au}$ nanoparticles

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Size and morphology controlled magnetite nanoparticles were synthesized using thermal decomposition protocol. Cubic  $\text{Fe}_3\text{O}_4$  nanoparticles with a mean size of around 70 nm were obtained with strict regulation of the substrate (iron acetylacetonate), solvent (dibenzyl ether) and additive (oleic acid) ratio as well as reaction temperature and time. The magnetic nanoparticles were modified with a porous silica shell and next Au nanoparticles were deposited on the surface of a core-shell structure. Particle size and morphology were characterized using TEM imaging (Tecnai Osiris X-FEG transmission electron microscope), and nanocomposites composition by STEM EDX mapping. The crystal structure of the  $\text{Fe}_3\text{O}_4$  nanoparticles was confirmed by the X-ray powder diffraction technique (XRD) (Bruker D8 Advance diffractometer equipped with Cu lamp as the X-ray source (1.54 Å) and  $\text{K}\alpha_2$  nickel filter) and compared with the ICDD diffraction database. The energy conversion under the action of external stimulants (alternating magnetic field and NIR laser radiation within 1<sup>st</sup> and 2<sup>nd</sup> optical biological window) working separately and in synergy shows high effectiveness of multimodal nanocomposites in contactless temperature stimulated processes.



# Spectroscopic properties of Cr<sup>3+</sup>, Nd<sup>3+</sup> co-doped La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub> for NIR luminescence thermometry

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Near-infrared (NIR) emitting materials have recently become more and more popular due to their wide application possibilities in night vision and noninvasive monitoring of human physiological state. NIR emission is particularly important for biological applications since it is characterized by a larger penetration depth in biological tissues [1]. One of the interesting potential applications of NIR luminescence is its use in luminescence thermometry. This technique offers a large number of advantages over conventional thermometers, e.g., non-contact, non-invasive and self-referential temperature response [2].

The material dealt with in this work is La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>. It is characterized by a weak crystal field strength, hence when doping with Cr<sup>3+</sup> ions the emission spectra of this phosphor is characterized by the broad emission band associated with the <sup>4</sup>T<sub>2</sub>→<sup>4</sup>A<sub>2</sub> electronic transition. The emission intensity of this band is highly susceptible to thermal quenching. On the other hand emission intensity of Nd<sup>3+</sup> ions is barely affected by the temperature. Thus their emission intensities ratio can be exploited as a remote temperature sensor.

In this work both the influence of the concentration of dopants (0.1–10% Cr<sup>3+</sup> and 0.1–5% Nd<sup>3+</sup>) and the synthesis temperature on the luminescent and thermometric properties of the obtained materials were investigated. The beneficial influence of the co-doping with Nd<sup>3+</sup> ions on the relative sensitivity of the Cr<sup>3+</sup> based ratiometric luminescence thermometry is discussed.

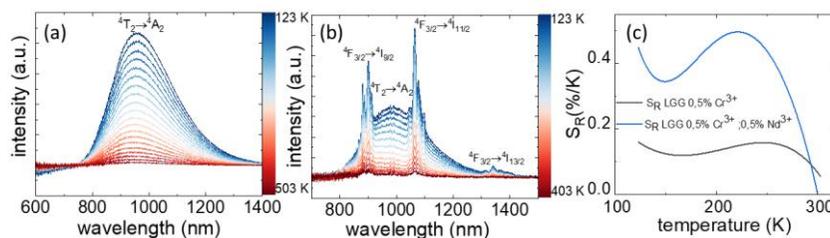


Fig. 1. Emission spectra of La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>:0.5%Cr<sup>3+</sup> (a) and La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>: 0.5% Cr<sup>3+</sup>, 0.5%Nd<sup>3+</sup> (b) as a function of temperature (123–300 K) upon  $\lambda_{\text{exc}} = 445$  nm, and corresponding relative sensitivities of ratiometric luminescent thermometers (c)

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P04

## Transferring hydrophobic quantum dots into water dispersion and how it influences their optical properties

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The main aim of this work is to study the influence of transferring hydrophobic trioctylphosphine oxide-capped CdSe quantum dots (QDs) into water dispersion on their one- and two-photon induced optical properties. In the first novel strategy, the transition of semiconductor nanostructures from hydrophobic to hydrophilic was enabled by covering the as-synthesized CdSe QDs with Pumilio homology domain-based proteins (PUF).[1] As a result, stable and colloidal QD:PUF assemblies were formed. This study reveals that the functionalizing the surface of QDs only by long peptide chains allows of designing an efficient two-photon induced bioimaging nanoprobe for nonlinear optical microscopy. In the second approach, an emulsification/solvent-evaporation method was used to encapsulate CdSe QDs along with the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> upconverting nanoparticles (NPs).[2] Thus, colloidal core-shell nanocapsules (NCs) loaded with both nanostructures and dispersed in an aqueous environment were obtained. We have evidenced that not only the encapsulation process allows of dispersing hydrophobic nanocrystals into nontoxic aqueous solution, but also it can be promising technique for intentional merging two different kinds of nanomaterials into a single hybrid nanostructure.

For both methods, the linear optical properties of CdSe QDs before and after functionalization were carefully compared. Furthermore, nonlinear optical features of all samples were investigated using a tunable femtosecond laser system and the two-photon excited emission method (TPEE) that allows us to estimate the two-photon absorption (TPA) cross-sections  $\sigma_2$ . The results indicate that both strategies provide manufacturing of hydrophilic QDs with excellent optical properties despite the change of the solvent in which QDs were dispersed.

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## Eu-Cu heterometallic-organic framework for selective ascorbic acid detection

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Metal–organic frameworks (MOFs) are a type of hybrid inorganic/organic materials with diverse structural properties, which may be adjusted by unlimited metal cluster/ligand variations. Their exceptional physicochemical properties are being constantly and actively exploited for various applications such as energy harvesting, gas storage, separation, catalysis, and drug delivery [1]. MOFs based on rare earth elements also provide great application possibilities in the detection of ions, explosives, temperature, volatile organic compounds and biomolecules due to the possible high accuracy, sensitivity and selectivity [2].

Ascorbic acid is one of the biological cofactors that plays a vital role in the body's general physiological functioning. The lack of ascorbic acid may be associated with many diseases, thus it is important to track the level of the acid in biological fluids [3].

Following this topic, the aim of our research was to obtain a new material based on Cu-MOF doped with  $\text{Eu}^{3+}$  for selective ascorbic acid detection. It was characterized using different techniques such as XRD, IR, EDS, TGA and SEM. The luminescence properties were analyzed using a fluorescence spectrometer. The results showed that obtained Eu-Cu MOF could selectively detect ascorbic acid starting from the concentration of  $3.55 \cdot 10^{-4}$  M and after only 5 min (Fig. 1).

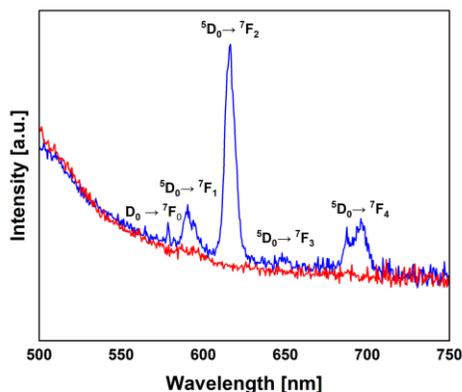


Fig. 1 Emission spectra for Eu-Cu MOF before (–) and after (–) treatment with ascorbic acid (5 min,  $3.55 \cdot 10^{-4}$  M)

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## G-DNA interactions with new ruthenium compounds

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G-quadruplexes (G4s), non-canonical DNA and RNA structures are built up from  $\pi$ - $\pi$  stacked G-quartets stabilized by Hoogsteen hydrogen bonds and centrally coordinated metal ions, e.g., Na<sup>+</sup>, K<sup>+</sup> [1]. Some of these sequences have been identified as potential anticancer drug targets. As the formation of G4s in human telomeric DNA plays an important role in cancer cell immortalization by inhibiting telomerase expressed in more than 85% in cancer cells [2], [3]. Currently there is an interest in exploring chemical probes as new anticancer drugs that can disrupt telomere maintenance by stabilizing the telomere G4s by inhibiting telomerase activity and inducing the growth arrest or apoptosis of the cancer cells. Most G4 DNA stabilisers are based on planar polyaromatic compounds that interact with guanine quartets via  $\pi$ - $\pi$  stacking. These molecules are often replaced with positively charged groups to increase their solubility and also the electrostatic interactions with the DNA [5]. Ideal G-quadruplex binder should show a high level of selectivity between quadruplex and duplex DNA when attempting to develop a powerful anticancer drug. Square-based pyramidal metal complexes have been recently reported as quadruplex DNA stabilisers [6]. Since many years a lot of scientific groups have developed a number of Ru(II) and Ru(III) complexes which were shown to possess good antitumor activity. Ruthenium complexes have a selective antimetastatic properties and low systemic toxicity which appear to penetrate reasonably well the tumor cells and bind effectively to DNA.

In this context, we decided to study the interactions between the DNA and ruthenium complexes based on biophysical methods. A series of spectroscopic studies have been carried out in order to evaluate the quadruplex binding affinity, selectivity and structure-activity relationships of new ruthenium complexes with different DNA structures. In order to evaluate the ability of complexes to interact with quadruplex and duplex DNA, spectroscopic titration's experiments as well as fluorescence intercalation displacement (FID) assays were carried out. The structures and relative stabilities of these duplexes and G4 in the absence and presence of organometallic complexes were evaluated by circular dichroism (CD) studies.

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P07

## Biological synthesis of high added value compounds (using selected Cyanobacteria strains)

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This research is aimed at generating high added value compounds from cyanobacteria strain photobiocatalysts. Although several microorganisms have been used for the generation of valuable metabolites [1], but the productive potential of cyanobacteria species to transform unsaturated fatty acids as well as chiral phosphonic compounds (under investigation) has remained largely unexplored. Here we are investigating the potential of cyanobacteria as photobiocatalyst in producing different bio-based products like alkanol or saturated fatty acids from unsaturated fatty acids such as 7-Octenoic acid (142.2 g/mol). This preliminary research method will then be applied to biocatalyze phosphonic compounds with vinyl and epoxy phosphonates as target substrates for biotransformation with cyanobacteria. In this preliminary research, *Synechococcus bigranulatus* and *Nostoc cf-muscorum* were selected for the purpose of biotransformation. *Synechococcus bigranulatus* was cultured in BG-11 medium and *Nostoc cf-muscorum* was cultured in BG-10 medium. The unsaturated fatty acid was treated in five steps using the cyanobacterial cultures to produce desired compounds: the biotransformation under special conditions of temperature (~29°C), continuous illumination (7–12 μm photons/m<sup>2</sup>, provided by fluorescent SunGlo 8 W (Hagen) lamp)[2], and time (24 h); centrifugation for biomass removal; cell viability assay to examine the live and dead cells; extraction using suitable solvent such as ethyl acetate or methanol; and the analysis of results using Liquid Chromatography with Mass Spectrometry detector (LC/MS). The following were the obtained results on the LC/MS analysis: hydroxycaprylic acid (160.2 g/mol) was suspected in a biotransformed sample containing *Nostoc cf-muscorum*. while Oxiraneoctanoic acid (186.2g/mol) was suspected in *Synechococcus bigranulatus* sample. However, the results are yet to be concluded as the identification of the products is still ongoing! The current results of the investigation demonstrated the useful potential of the selected cyanobacteria strains to transform the unsaturated fatty acid to saturated compound with the same functional moiety (i.e., cyanobacteria have the potential of reducing the double bonds in the substrates-unsaturated to single bonds – saturated [3]) or a compound with the introduced oxygens functionality (hydroxy- or epoxy group).

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## Sequence and stereo-defined polyurethanes – synthesis and thermal characteristic

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Natural biopolymers, eg. proteins, can self-organize into complex structures and fold into different motifs, which is influenced by their primary structure. What's more, the sequence of amino acid monomers has a great impact on proteins properties and functions. The regulation of the properties of synthetic polymers by controlling monomer composition and order in macromolecule chains is a very intriguing approach that has not been thoroughly investigated, so far. Recently, scientists from the field of polymer chemistry have developed methods to synthesize uniform polymers with a well-defined sequence of monomers. These are mainly methods based on iterative synthesis on a solid support [1] or in solution [2]. Unfortunately, both methods have their limitations. Solution synthesis requires purification after each step, which is facilitated in the case of solid phase synthesis. The drawback of the second approach is the need to use excess reagents and solvents [3]. However, it is not known to what extent we can control the properties of synthetic macromolecules by altering their sequence and stereochemistry.

Here, we investigated oligourethane models to learn about a sequence-property relationship and how stereocontrol can influence their characteristics. The solution synthesis protocol has been simplified by limiting purification steps, therefore, the oligourethanes with good yield and high purity can be obtained on a large scale. We have synthesized stereocontrolled sequence-defined oligourethanes, and studied their degradation pathway and the thermal properties.

We found that the regulation of melting and glass transition temperature is possible by inducing chirality or aromaticity into macromolecules. Chiral unit insertion provided greater changes for  $T_m$ , whereas  $T_g$  was more significantly influenced by aromatic monomers. Furthermore monomer composition and order within macromolecules also has an influence on thermal degradation and dictates resulting degradation products. Monomer sequence and stereochemistry are also the tools for programming hydrodynamic volume and optical activity [4].

**Acknowledgments:** The authors are highly grateful to the Polish National Science Centre, grant number 2018/31/D/ST5/01365 for financial support.

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## Large scale synthesis of sequence – defined polyurethanes

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Sequence-defined polymers (SDPs) are discrete macromolecules with controlled monomer order. These novel materials open a new field for polymer chemistry and possibility of tuning the properties by changing monomer positions. Precisely designed sequence may lead to self-assembly structure and folding similar to natural proteins [1]. Polyurethanes are wide-spread polymers that have many applications, so the sequence-defined polyurethanes as the advanced version may also be use in lots of fields where precision is matter. As for now, SDP materials are used only in laboratory but in order to spread them to an industry there is a need of scalable, high yield strategy that will be able to get automatized further [2].

In this work we study the one-pot approach for the synthesis of sequence-defined polyurethanes. The idea of this method is to carry on all reactions in one vessel. The whole synthesis protocol is based on repetitive circle of alternating reactions – activation and coupling that are driven by reagents adding. So far, it has been successful in performing 8 chemoselective reactions that result in pentamers. Full conversion of the monomers can be monitored by the HPLC chromatography. As a key advantage of our method is a lack of purification between steps. It is necessary only at the end of reaction to extract the product. Reducing a number of purification cause also a significant decrease of solvents used that is in line with a green chemistry trend in the world. We also proved that the one-pot approach may be scalable up to 500 times that are one of the main limitation in other methods of synthesis SDPs [3]. Easy protocol and possibility of monitoring the reaction conversion by the HPLC open a possibility of automatization what may makes this method interesting for an industry for larger manufacturing.

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## Nanoparticles as carriers for volatile monoterpenes in modern agriculture

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Monoterpenes constitute a large group of natural origin compounds, including secondary metabolites. They can be found in many plant species and essential oils acquired from them. Due to the wide range of different structures, they exhibit high and diverse biological properties [1]. Monoterpenes are used as antifungal, antimicrobial, antioxidant or anticancer agents [2]. Due to such extensive properties, they are used in various industrial sectors. Modern agriculture is looking for new plant protection products due to growing issues with insects, diseases and continuous increasing in the demand for food. To follow the rules of *Sustainable Development Goals* it is required that new plant protection means have to be harmless and should have lower influence on humans and nontargeted organisms than synthetic ones. In the past years, the development of monoterpenes and their derivatives usage in agrochemistry applications is observed and promoted. However, monoterpenes, as a natural occurring compounds are being exposed to environmental factors, e.g., moisture, temperature or degradation by light. For example, eugenol, carvacrol, and thymol are susceptible to oxidation and can be evaporated or decomposed under light, air or heat conditions. To prevent this limitations nanoparticles have been investigated as a carrier to improve monoterpenes stability and effectiveness in the natural environment [3, 4].

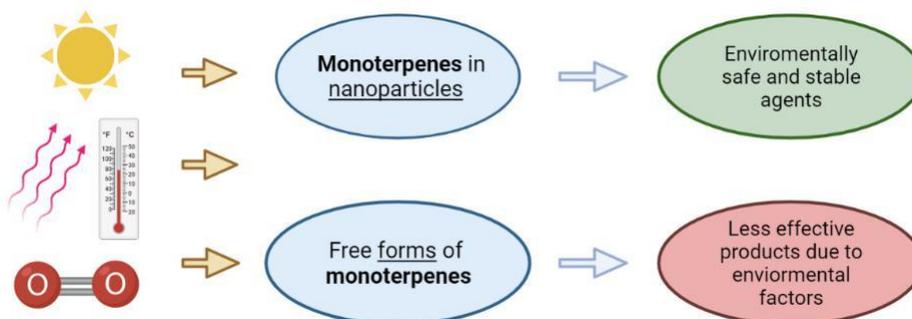


Fig. 1. Strategy of creating more stable monoterpenes' agents. Created by BioRender.com

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## Investigation of oxidative stress under external stimuli on cell culture

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Chronic inflammation is a consequence of long-term acute inflammation in the body and may lead to the induction of chronic diseases, i.e., obesity, diabetes, neurodegenerative diseases. One of the reasons for this condition may be the accumulation of excessive amounts of free radicals. Under physiological conditions, this state is favourable because it accelerates many positive for human body processes, e.g., wound healing and bone fusion. Unfortunately, free radicals also have a negative role in the body that can be generated in situ and/or come from the environment external [1]. The performed studies have shown that curcumin and metformin possessed antioxidant properties. Through the use of metabolomics, it is possible to monitor changes in metabolism: (i) after the administration of therapeutics and (ii) the induction of oxidative stress.

The purpose of this study was to explore the antioxidative role of curcumin and metformin with a description of their antioxidative potential. The obtained results confirmed the main hypothesis for both substances. Metformin and curcumin decreased the number of free radicals generated in cells under oxidative stress and contributed to an increase in cell viability. For this purpose, cell viability tests (MTT) and the amount of generated free radicals (DCF-DA) were performed. The <sup>1</sup>HNMR method was used to analyse the metabolome of cells in the state of oxidative stress in cells. Referring to the <sup>1</sup>HNMR spectra of extracellular metabolites of the controls, it was observed during the oxidative stress, the appearance of additional metabolites such as sarcosine, isobutyrate, pyroglutamine, methylguanidine, 2-hydroxyvalerate and isovalerate, which are the external metabolites – oxidative stress biomarkers.

Thanks to the methods of biological activity and metabolomics studies, it is also possible to check the influence of various nanostructures on the viability of cells, their anti-inflammatory effects, and to monitor changes in cell metabolism. Viability tests and the amount of free radicals tests can be used to test the activity of drugs enclosed in nanoparticles.

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## Long-term characterization of three different carbon cathodes in microbial fuel cell

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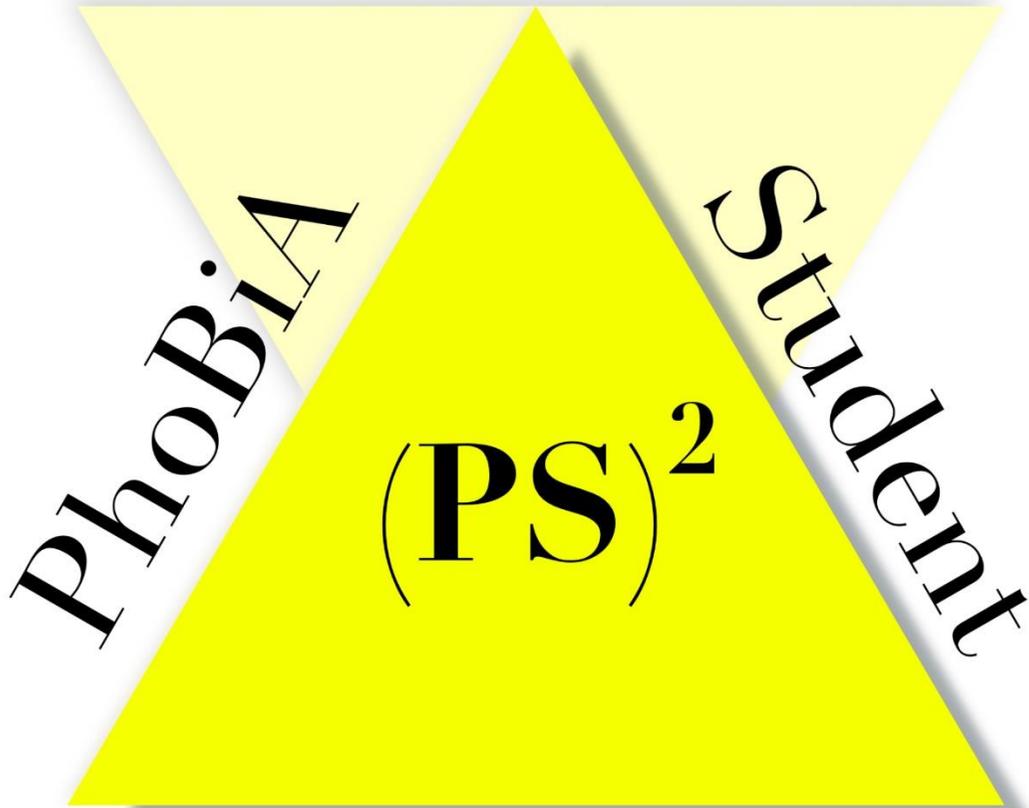
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The overall performance of the microbial fuel cell (MFC) depends on the selection of appropriate electrode materials, the design of the MFC, microorganisms, and optimization of the operating parameter [1]. In this study, two available commercial activated carbons, CWZ-22 and CWZ-35 were used as cathode materials in air-cathode microbial fuel cell. Additionally, the influence of modification of CWZ-22 activated carbon with silicone particles on the performance of a single-chamber microbial fuel cell was researched. The performance of MFCs were investigated through real time temporal analysis, linear sweep voltammetry and electrochemical impedance spectroscopy measurements. The MFC equipped with the activated carbon cathode CWZ-22 with an internal resistance of 162  $\Omega$ , revealed a maximum power density of 23.3 W m<sup>-3</sup>. Modification of CWZ-22 with silicone particles resulted in a reduction in maximum power generation of 10% and increasing the internal resistance of the MFC by 10%. On the other hand, the use of CWZ-35 as a cathode material led to a slight decrease in power generation by 4%. However, the electrochemical impedance spectroscopy measurements indicated a poor long-term performance of activated carbon CWZ-35 as a cathode. The obtained results demonstrated the possibility of using cheap and easily available commercial activated carbons as high-performance cathode materials and indicate unfeasibility of silicone as a binder.

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# Photonics Symposium

**Poster session for students**

02.06.2022 - 15:00 - D-20 building

Registration deadline - 12.05.2022



# PhoBiA Student Photonics Symposium

## Poster session

Poster no.	Presenter	Title
P1	Piotr Kuich	Near infrared emission of NaYF <sub>4</sub> : 2% Nd <sup>3+</sup> nanoparticles and microcrystals
P2	Joanna Halama	Protein nanoparticles – structure and fluorescent properties
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P5	Karolina Sączuk	Antimicrobial Photodynamic Therapy in the treatment of <i>Staphylococcus aureus</i> infections
P6	Michalina Ślemp	Marangoni bursting – a method of nano- and micro-crystals fabrication
P7	Weronika Zając	Luminescent synthetic opals for angle-dependent emissive colour



## Near infrared emission of NaYF<sub>4</sub> : 2% Nd<sup>3+</sup> nanoparticles and microcrystals

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Lanthanides are elements with extraordinary rich energy level structure. Their  $4f^n$  subshell is partially filled, and shielded by  $5s$  and  $5p$  outer subshells, which results in a relatively large number of atomic-like energy levels. Emission from excited states occurs due to intra-configuration electron transitions within  $4f^n$  subshell [1]. In particular, luminescent nano- (NPs) and micro-particles (MPs) doped with lanthanide ions exhibiting absorption and emission in the near infrared range (NIR), have several potential features that allow for their non-invasive application in bioimaging, most importantly deep penetration depth and auto-fluorescence suppression, but also long luminescence lifetime, good photostability, narrow emission peaks and large Stoke's shifts [2].

In this work, NaYF<sub>4</sub> : 2% Nd<sup>3+</sup> NPs and MPs were obtained. Four different syntheses strategies have been used for optimization - one of which involved thermal decomposition for NPs synthesis with oleic acid (OA) as a capping agent, and the others involved obtaining MPs using a microwave reactor, with various organic compounds as capping agents, such as oleic acid (OA), citric acid (CA) and EDTA.

The MPs morphology was examined using scanning electron microscopy (SEM), whereas the NPs – with transmission electron microscopy (TEM). Emission measurements were performed under  $\lambda = 808$  nm laser beam excitation.

The best NIR emission measurements results from the synthesized materials were obtained for MPs with EDTA used as ligand. For the other products the emission was correspondingly of lower intensity. The MPs with CA require further optimization of the synthesis process to obtain a more homogeneous distribution of their morphology.

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## Protein nanoparticles – structure and fluorescent properties

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Nowadays, markers such as inorganic semiconductor quantum dots, carbon nanodots, organic molecular dyes are widely used in fluorescent bioimaging. However, some of them are characterized by low quantum yield or lack of photostability and biocompatibility [1]. Therefore, researchers are looking for alternative labels that combine appropriate optical properties with features necessary for *in vivo* imaging. Recently, a new generation of bioorganic markers were discovered – fluorescent peptide nanodots [2]. As self-assembling peptides usually do not possess any visible fluorescence, they can be converted into strongly fluorescent ones by thermal treatment [2]. It is commonly believed that the source of the observed fluorescence effect is electron delocalization due to formation of an extensive network of hydrogen bonds at the moment of refolding the structure. The  $\alpha$ -helices present in the peptide are transformed into metastable  $\beta$ -sheets [3].

The aim of master's thesis was to investigate the possibility of synthesizing fluorescent nanodots from proteins, to optimize the synthesis of insulin nanoparticles, to verify of their fluorescent properties using spectroscopic methods and to compare the results with the properties of insulin amyloid fibers, which are known for their structure containing numerous  $\beta$ -sheets. The conducted research shows that the applied procedure leads to the formation of a material characterized by strong fluorescence and initial studies over its morphology, performed by atomic force microscopy (AFM), revealed the formation of nanoparticles. Our novel material, upon excitation at 370 nm demonstrate fluorescence emission with the maximum at 420 nm. Interestingly, this property is similar to autofluorescence obtained for amyloid fibrils [4]. However, imaging performed with the AFM shows a completely distinct morphology. Therefore, our studies present an important information about the relation between optical properties and morphology of protein aggregates.

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## Derivatives of diphenylamine in optoelectronic applications

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Diphenylamine (DPA) is an organic compound with the formula  $(C_6H_5)_2NH$ . It has a rigid structure and is thermally stable. DPA has been the subject of much research aimed at using it and its derivatives in optoelectronic devices. Previous reports confirm many properties of DPA derivatives that support their use in optoelectronics, such as two-photon absorption, hole conduction properties and high electron mobility [1]. The synthesis of one of the DPA derivatives (Fig. 1) based on Stille, Buchwald-Hartwig reactions will be presented at the conference. The best approach developed to create new promising compounds for use in optoelectronics is to reduce the band gap of the conjugated molecules. It is important to transfer the charge from the donor side to the acceptor side [2]. DPA works well as an electron donor in the most commonly used donor-acceptor (D-A) system [3]. The electron-donor units of DPA provide fluorescence and nonlinear optical properties. The color of the emitted light is influenced by functional groups that manipulate the HOMO-LUMO (HOMO – Highest Occupied Molecular Orbital; LUMO – Lowest Unoccupied Molecular Orbital) energy level. The donor part of the molecule raises the HOMO energy, while the electron acceptors lower it. Electron transport in chemistry is extremely important, so DPA is an ideal candidate for the synthesis of optoelectronic materials [1].

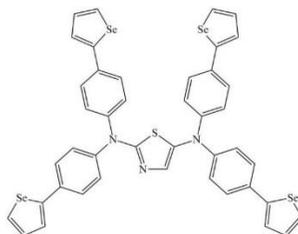


Fig. 1. Chemical structure of N,N',N'',N'''-tetrakis(4-(selenophen-2-yl)phenyl)-4,5-dihydrothiazole-2,5-diamine

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## Second Harmonic Generation of DNA base pairs

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Engineered organic compounds have sparked a lot of interest in the development of innovative photonic devices for a wide variety of applications, from sensing to communication [1], [2]. Biomaterials have a lot of promise in this area, notably in terms of cost, availability, and waste. Determining the nonlinear optical characteristics of compounds like proteins and DNA largely remains in this respect a pending issue [3]. Hyper-Rayleigh Scattering (HRS) technique is an effective approach to measure the first hyperpolarizability of molecules in solution [4], [5].

HRS in the liquid phase is based on the incoherent scattering of the second harmonic light generated by the instantaneous molecular orientational fluctuations. The conventional strategy for this method is to determine the second harmonic intensity as a function of power with comparison with a known compound (the external reference method) or of solute molecule concentration with comparison to the neat solvent intensity (the internal reference method) [6].

In this work, we report the HRS response of DNA bases as nucleotide sodium salts dispersed in water. Similar experiments have been previously reported, whereas the biggest issue was the low solubility of the corresponding nucleosides in neat water [7]. In the present study, they all exhibit a much higher solubility.

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## Antimicrobial Photodynamic Therapy in the treatment of *Staphylococcus aureus* infections

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Over the years, an emergence of antibiotic-resistant strains of bacteria has been observed. *Staphylococcus aureus*, despite being a part of human microbiome, causes a significant number of difficult to treat healthcare-associated infections, due to the worldwide spread of strains resistant to multiple drugs, such as penicillin, methicillin or vancomycin [1].

The antibiotic overuse in both human and animal health led to a decrease in the effectiveness of conventional infection treatments [2]. Antimicrobial Photodynamic Therapy (aPDT) is one of the most promising, novel ways of infection treatment, ingenious in its simplicity. It is a non-invasive treatment, utilizing three major components: light, a photosensitizer and oxygen. The photosensitizer is applied onto the infected region. When irradiated with light of a specific wavelength it reacts with oxygen, forming reactive oxygen species (ROS) – antimicrobial agents [3].

In our work, the efficiency of aPDT on *S. aureus* strains was investigated. The experiments were conducted with the use of methylene blue as a photosensitizer and a femtosecond laser light source. Additionally, experiments without methylene blue were performed, to validate the impact of laser light itself on the survivability of *S. aureus*. Different laser powers and sample irradiation times were examined.

Obtained results evidence a significant decrease of bacteria survivability after conducted aPDT with methylene blue. Moreover, with the increase of laser power and time of irradiation, the impact of aPDT was more pronounced.

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## Marangoni bursting – a method of nano- and micro-crystals fabrication

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Marangoni bursting – is a phenomenon that leads to a spontaneous emulsification of binary mixture of volatile alcohol and water deposited as a small drop over immiscible liquid substrate [1, 2]. Fingering instability arising due to fast alcohol evaporation at room temperature results in the segmentation of the original drop into millions of droplets. Both the thermocapillary Marangoni effect and the wetting force have their impact on the size, velocity, and range of wandering drops. Here, Marangoni bursting, performed on a solid substrate, is used for fabrication of nano- and micro-crystals of organic substance added to the alcohol/water mixture prior its deposition. This phenomenon leaves on the substrate a wide distribution of crystals sizes (from 10 nm up to several mm). As an example, we used organic 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (DCNP) substance and dissolved it in isopropanol/water solution. DCNP is insoluble in water, while it dissolves in isopropanol (IPA). We noticed that during Marangoni bursting with the decreasing amount of IPA due to evaporation, and movement of the liquid, interesting dendritic-like structures were obtained. The choice of DCNP was dictated by the fact that its crystals are interesting for probing size-dependent light-matter interaction changes. DCNP is nonlinear optical material of second order as it produces second harmonic generation (SHG) excited with 1064 nm 10 ns laser pulses which is then partially reabsorbed resulting in broad fluorescence with maximum around 600 nm [3, 4]. In this study we used 100 fs laser working at 790 nm for DCNP excitation. Depending on the size and shape of the crystals, SHG:luminescence ratio changes. This may indicate that the structure of the crystals differs. In some measurements, 2-photon absorption (TPA) has led to appearance of fluorescence at around 430 nm. This short wavelength fluorescence was never observed in the bulk DCNP crystals, but it was predicted by the quantum chemical calculations of electronic state energies for molecular assemblies as H- and J-aggregates [4]. We postulate that TPA at 395 nm by nano-size DCNP aggregates is responsible for this fluorescence. As such, the method provides astonishing possibilities for modification of crystal sizes and/or structures for probing their size-dependent properties what is important in nanophotonics and other fields.

This work was supported by the National Science Centre, Poland [grant number UMO-2018/29/B/ST3/00829].

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## Luminescent synthetic opals for angle-dependent emissive colour

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The history of photonic crystals known to today's scientists began in 1987 with the works of Yablonovitch [1] and John [2]. Photonic crystals are remarkably interesting and deeply-studied group of modern optical materials, because of their periodical arrangement of the forming elements, which gives such effects as chromatic dispersion of diffracted light (easy to notice on 2D crystals) or Bragg reflection (3D crystals) [3].

Nowadays, artificial opals consisted of monodisperse polymeric and silica nanospheres are relatively easy to synthesize. And what's more, a possibility of doping photonic crystals with various types of materials makes it possible to obtain compounds with unique optical properties [4]. Use of these materials allows to design completely new and difficult to counterfeit security features.

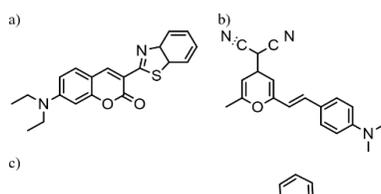


Fig.1 Chemical formula of selected dyes:  
a) Coumarin 6, b) DCM, c) POPOP.

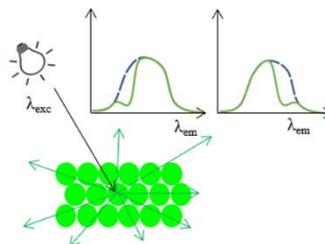


Fig.2 Schematic representation of emission measurement from different angles.

We synthesized a series of colloidal photonic crystals, based on poly(methyl methacrylate) (PMMA) – undoped and doped with organic dyes. We have chosen the dyes with respect to high quantum efficiency and different spectral range of the emission. Structures of the selected dyes are presented in Figure 1. The size of the nanospheres forming the synthesized 3D opals was optimized in order to cover the emission range of the dye by the reflection band of the photonic crystal. We performed full spectroscopic characterization of the fabricated luminescent opals, including angle-dependent emission of light at the output of the photonic crystal.

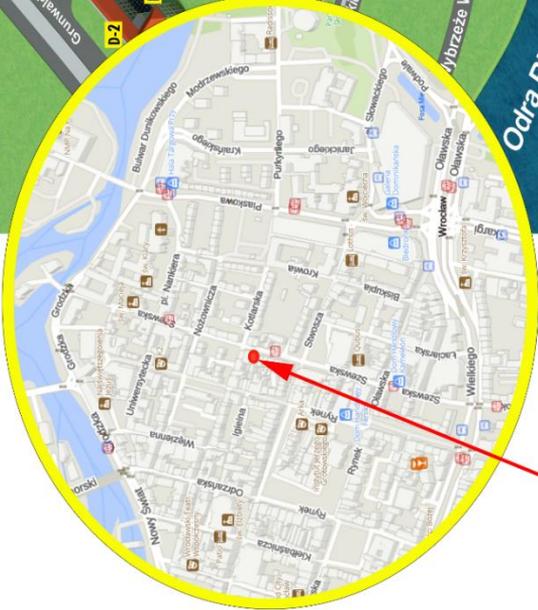
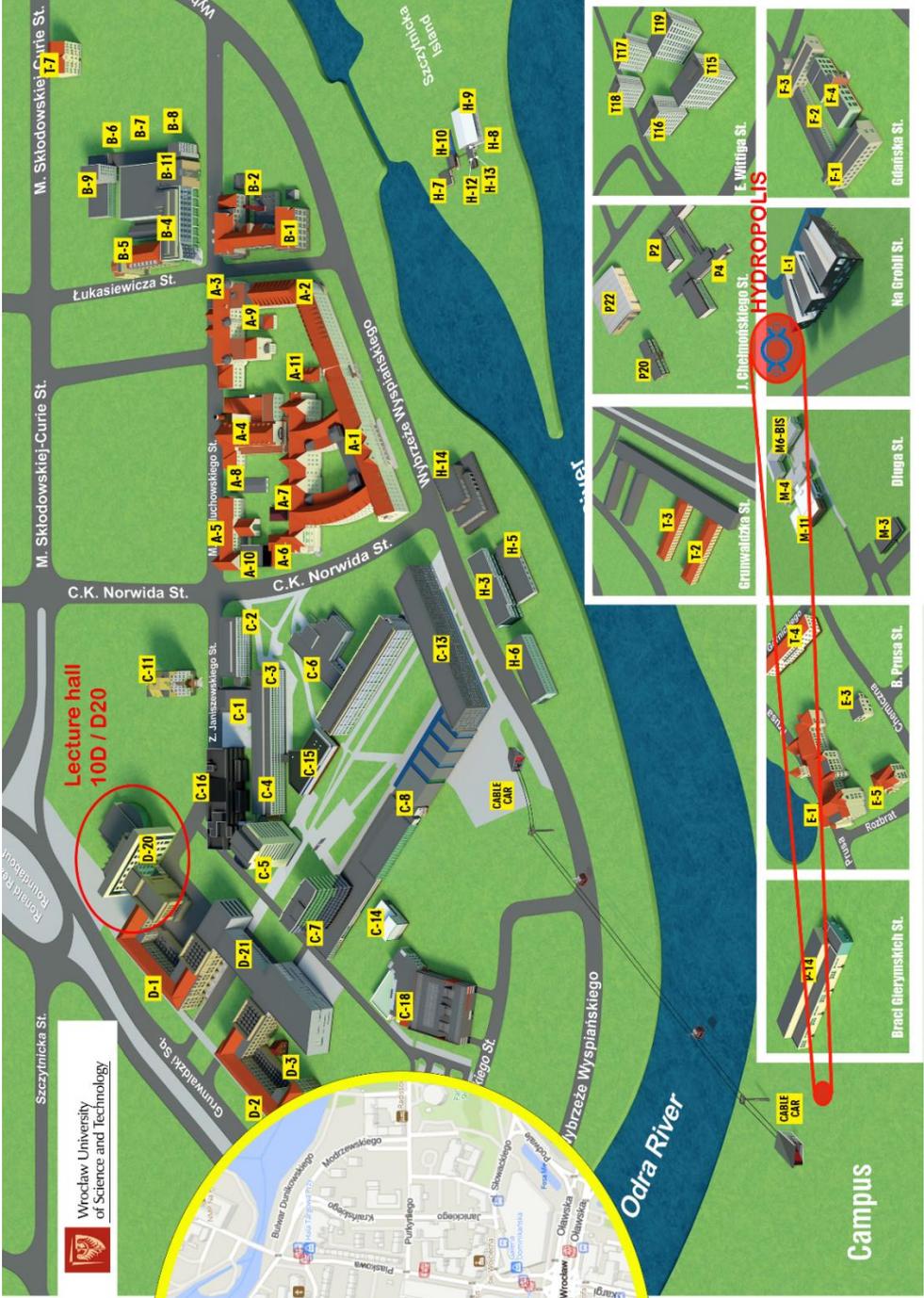
The fabricated luminescent opals showed unusual angle-dependent emission spectrum, covering three different spectral ranges.

These studies were supported by the National Centre for Research and Development (Poland) within the framework of the 12th edition of the LIDER programme – project contract no.LIDER/39/0203/L-12/20/NCBR/2021.

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