BOOK OF ABSTRACTS

BY VIKI PANIC

PHOBIA ANNUAL
NANOPHOTONICS INTERNATIONAL
CONFERENCE

2020

12-14.10.2020

Wrocław University of Science and Technology,
Wrocław, Poland

PANIC 2020

**PhoBiA Annual Nanophotonics International
Conference**

12-14 October 2020, Wrocław, Poland

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Wrocław 2020

Publication co-financed by Wrocław University of Science and Technology.

ISBN 978-83-7493-139-7

DOI: 10.37190/panic2020abstracts

www.oficina.pwr.edu.pl

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Conference programme

12 October (Monday)		
hours	Activity	
9:00-9:30	Opening	
Session I		
9:30-10:10	Prof. Pierre-François Brevet „Coherent and Incoherent Second Harmonic Generation: Seeing at the Nanoscale”	
10:10-10:25	Plenary session I	S. Zelewski „Temperature and high pressure sensing using NaBiF ₄ :Yb, Er upconverting nanoparticles”
10:25-10:40		S. Targońska „Investigation of the fluoride ions content in the Eu ³⁺ -doped apatite on its structure and luminescence properties”
10:40-10:55		K. Sadecka „Ab-initio based tight-binding models for excitons in 2D semiconductor TMD crystals”
10:55-11:20	Short break	
Session II		
11:20-12:00	Prof. Marcin Drąg „Development of tools for selective and parallel detection of proteases important in medicine”	
12:00-12:15	Plenary session II	W. Nawrot „New Technologies for Microfluidic Optical Biosensors”
12:15-12:30		F. Meloni „Electrochemical Detection of Epinephrine with a Poly[(TAT)Ru(TpyCOOH)]- Tyrosinase-based Biosensor”
12:30-12:45		P. Trombik „Effect of chalcone derivatives on PLL-associated DPPC/DPPG/Chol membranes”
12:45-13:45	Long break	
Session III		
13:45-14:00	Plenary session III	A. Paściak „Development and evaluation of experimental methodology for light-to-heat conversion efficiency determination in colloidal nanoheaters”
14:00-14:15		W. Piotrowski „Temperature imaging with Mn ⁴⁺ and Tb ³⁺ codoped ratiometric phosphor”
14:15-14:30		K. Trejgis „Suitability of highly sensitive LaPO ₄ :Nd ³⁺ nanocrystals for SBR approach of luminescent thermometry”
14:30-14:45		P. Falat „Electronic transport properties of topological semimetal candidates HoPtBi and TbPtBi”
14:45-14:50	Technical break	
14:50-16:20	Poster Session I	

13 October (Tuesday)		
hours	Activity	
Session I		
9:00-9:40	Prof. Marti Gich „What have rust and non-reciprocity to do with 5G?”	
9:40-9:55	Plenary session I	K. Nadolski „Counteraction of shape and size in gold nanotriangles”
9:55-10:10		M. Lipok „Game of plasmons - new amyloid detection method”
10:10-10:25		M. Ćwierzona „Polarization-dependent activation of nanocrystals through surface plasmon polaritons propagating in silver nanowires”
10:25-10:40		A. Pniakowska „Tunable hydrophobic-hydrophilic GNCs as a robust probes for protein aggregates”
10:40-11:00	Short break	
Session II		
11:00-11:40	Prof. Anna Pawlik „Divide, adapt and conquer”	
11:40-11:55	Plenary session II	M. Piksa „OLED-based photoinactivation of the bacteria isolated from diabetic foos”
11:55-12:10		M. Grelich-Mucha „Structural and optical properties of fibrils obtained from enantiomers and racemate of transthyretin (105-115) peptide”
12:10-12:25		D. Benkowska-Biernacka „Analysis of lyotropic myelin structures”
12:25-12:40		P. Obstarczyk „Polarization-sensitive microscopy of amyloid superstructures -spherulites”
12:40-13:40	Long break	
Session III		
13:40-13:55	Plenary session III	K. Maciejewska „The 3-in-1 nanosized luminescent thermometer: the synthesis of ultraphosphate nanocrystals with unique paths to non-contact temperature changes sensing”
13:55-14:10		T. H. Q. Vu „Influences of synthesis routes on the optical properties of Ba ₂ MgWO ₆ : Eu ³⁺ and its thermal sensing application”
14:10-14:25		K. Holodnik „Single NaYF ₄ : Er ³⁺ , Yb ³⁺ nanothermometry: Imaging approach”
14:25-14:30	Technical break	
14:30-16:00	Poster Session II	

14 October (Wednesday)		
hours	Activity	
Session I		
8:30-8:45	Plenary session I	K. Nawrot „Multifunctional CdS-Au nanocomposite”
8:45-9:00		R. K. Kosman „The influence of Cd and Hg doping on AgInS ₂ quantum dots”
9:00-9:15		P. Žemojtel „Molecular modeling to validate tribological properties of carbon materials”
9:15-9:30		N. Maldonado Carmona „Encapsulating porphyrins inside acetylated lignin nanoparticles: effect on their UV-vis absorbance and fluorescence profiles.”
9:30-9:45		E. Robbins „Enhancement of Two- and Multi-photon Absorption Photosensitizers”
9:45-10:00	Short break	
Session II		
10:00-11:30	Prof. Richard Hoogenboom „Supramolecular polymer materials”	
11:30-11:45	Plenary session II	S. G. Mucha „Triangular carbon quantum dots: from simple synthesis method to remarkable linear and third-order non-linear optical properties”
11:45-12:00		N. Tarnowicz-Staniak „Anisotropic gold nanoparticles decorated with azobenzene ligands”
12:00-12:40	Long break	
Session III		
12:40-12:55	Plenary session III	M. Wujczyk „Influence of Vanadium(V) Concentration on Up-conversion Luminescence in YV _x P _{1-x} O ₄ Co-Doped with Er ³⁺ -Yb ³⁺ and Tm ³⁺ -Yb ³⁺ Ions ”
12:55-13:10		N. Nowak „Luminescence and biological characterization of new nanosized Eu ³⁺ ions doped vanadate-apatite solid state solution.”
13:10-13:25		J. Drabik „The use of differences in the thermal dependence of ground- and excited state absorption of Tb ³⁺ ions for optical temperature measurement - two possible single band ratiometric approaches”
13:25-13:40		A. Kotulska „Engineering architecture of nanocrystals co-doped with Yb ³⁺ and Er ³⁺ ions for highly efficient Förster Resonance Energy Transfer (FRET) between Er ³⁺ ions and Rose Bengal acceptor”
13:40-13:55		K. Halubek-Gluchowska „Luminescence properties and bioactivity of Yb ³⁺ /Tm ³⁺ ions in SiO ₂ -CaO glass”
13:55-14:10		K. Elzbieciak-Piecka „Cr ³⁺ - based nanocrystalline luminescent lifetime thermometry”
14:10-14.30	Short break	
Session IV		
14:30-15:10	Dr Andrzej Żak „The in-situ TEM imaging interactions occurring in antimicrobial photodynamic therapy”	

Session IV		
14:30-15:10	Dr Andrzej Żak <i>„The in-situ TEM imaging interactions occurring in antimicrobial photodynamic therapy”</i>	
15:10-15:25	Plenary session IV	M. Czajkowski <i>„Early stage studies of oblique helicoidal cholesteric phase for tunable liquid crystal lasers”</i>
15:25-15:40		K. T. Tanko <i>„Novel organic hybrid nanomaterials for organic solar cells”</i>
15:40-15:55		N. Sokolowski <i>„Localization of excitons and influence of a substrate on optical properties in a large-area WS₂ monolayer”</i>
15:55-16:10		D. Hlushchenko <i>„Sol-gel glass photonic microlasers doped with Rhodamine 6G”</i>
16:10-16:25	Closing ceremony	

Poster session I (Monday)

12 October (Monday)		
Poster	Topic	Presenting Author
P1	Exciton and trion emission in hBN encapsulated single monolayer and bi-layer MoTe ₂	Kamil Bruchal
P2	Control of gold nanoparticles morphology by directional synthesis and photothermal modifications.	Alina Chmielowska
P3	Influence of metals on the growth of amyloids of amylin analogues – structural studies	Agata Hajda
P4	Application of cold atmospheric pressure plasma in the continuous synthesis of zinc oxide nanostructures	Małgorzata Policht
P5	Circularly polarized luminescent (CPL) nanomaterials	Marcelina Śmigiel
P6	Temperature and hydrostatic pressure dependence of direct optical transitions in B _x Ga _{1-x} As semiconductor alloys	Nikodem Sokołowski
P7	Fine powdered mixed metal Fe-Mn oxides as solid state oxygen carrier	Magdalena Szkuta
P8	Physicochemical characteristics of multifunctional layered materials	Katarzyna Wal
P9	Examination of fine powdered mixed metal Fe-Mn and Zr oxides as potential solid state oxygen carriers	Borys Winczura
P10	The influence of vanadate groups substitution on structural and spectroscopic properties of fluoroapatite doped with Eu ³⁺ ions	Przemysław Zima
P11	Real-Time Surface-Enhanced Raman Scattering Tracking of Adenine–Gold Charge Transfer Complex Formation on Nanocavity-Shaped Plasmonic Crystals	Remigiusz Trojanowicz

Poster session II (Tuesday)

13 October (Tuesday)		
Poster	Topic	Presenting Author
P12	Studies on intermolecular proton transfer and its influence on liquid crystal and light emission properties	Łukasz Duda
P13	Zn ²⁺ and Cu ²⁺ interactions with antimicrobial peptides and their potential participation in activity enhancement	Dorota Dudek
P14	Generation of myelin structures by thermotropic liquid crystals in CTAB	Karen Garcia Alvarez
P15	Nanofibers for (Bio)Sensing Applications	Kinga Halicka
P16	Iron(II) clathrochelates as ICD-sensitive reporters able to recognize specific elements of albumin surface	Aleksandra Jedynczuk
P17	Blue-emitting folic acid-derived carbon nanodots: remarkable optical properties and control of the binding ability of human serum albumin	Agnieszka Krystyniak
P18	The study of pH influence on ligand exchange reaction for different types of CdS and CdSe/CdS nanoparticles	Anna Lesiak
P19	Clavanins – metal interactions: understanding the relationship between coordination chemistry, structure, thermodynamics and the antimicrobial activity	Adriana Miller
P20	Lyotropic liquid crystals of biological importance: myelin and DNA	Justyna Rojek
P21	Nucleobindin-2 is a Ca ²⁺ ions sensor	Anna Skorupska
P22	Enantioselective hydrolysis of 1-(<i>R,S</i>)-phenylethanol acetate with <i>Synechococcus bigranulatus</i> and <i>Nostoc cf. muscorum</i> cyanobacterial strains	Agnieszka Śliżewska
P23	On the choice of proper average lifetime formula in the case of non-single exponential photoluminescence decay	Michał Klak

Invited lectures

Coherent and Incoherent Second Harmonic Generation: Seeing at the Nanoscale.

Pierre-François Brevet

Institut Lumière Matière, UMR CNRS 5306 Université Claude Bernard Lyon 1, France

E-mail: pfbrevet@univ-lyon1.fr

Second Harmonic Generation (SHG) is the process whereby two photons at a fundamental frequency are converted into a single photon at the harmonic frequency. In non centrosymmetric media, it is an efficient coherent process that has enabled in the past the development of frequency conversion crystals in particular. However, besides coherent SHG, incoherent Second Harmonic Scattering (SHS) also takes place. SHS has been extensively used to study organic molecular compounds with the aim to use them as molecular probes notably. Furthermore, a polarization analysis of the SHS light reveals the symmetry properties of the compounds and has helped tremendously to engineer highly efficient nonlinear optical molecular probes.

Over the last years, SHS has also been used to investigate nanoparticles, and metallic nanoparticles in particular owing to their plasmonic properties, as well as liquids. With nanoparticles, the advantage here lies with the possibility to perform investigations in absence of any substrate, the latter introducing a symmetry breaking bias. In these SHS studies, the competition between size and shape has been explored to unravel a complete picture of the origin of the SHS response. This presentation will discuss this competition using as examples nanoparticles of different shape and size, like spheres, cubes or triangular prisms.

More recently, SHS has been used to probe liquids at the molecular scale. Liquids do not behave as collections of randomly distributed molecules. Short and long range correlation are notably due to dipole-dipole and steric interactions. These correlations introduce a coherent contribution that can be accessed with SHS. The latter case will be discussed in light of recent experiments on aqueous electrolytes.

Development of tools for selective and parallel detection of proteases important in medicine

Marcin Drag

*Department of Chemical Biology and Bioimaging, Wrocław University of Science and Technology,
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland*

Proteolysis is one of the most important and ancient reactions in biology. Enzymes that catalyze this reaction are called proteases. Proteases as “good guys” perform many significant biological processes like cellular quality control, apoptosis, blood coagulation or signal transduction. However, they can be also “bad guys” contributing to pathological events like cancer, diabetes, coagulopathies, inflammation, infectious or degenerative diseases. It is estimated that 5–10% of all pharmaceutical targets being pursued for drug development are proteases.

Despite significant progress in recent years, one of the biggest problems in the investigation of proteases is their similar activity and location. Due to the overlapping substrate specificity (preference in the recognition of natural amino acids) it is very hard to distinguish many major proteolytic enzymes families using chemical tools developed using classic screening technologies. This also very often limits discovery of selective drug or marker for specific activity monitoring. Classic examples here are cysteine proteases from caspase family, which play crucial role in controlling of several major metabolic pathways, especially apoptosis.

Given the fact that more and more proteases are actively involved in many diseases, there is an urgent need for the development of new chemical tools, that relaying on enzymes activity could be used for an accurate monitoring of proteolytic network. In order to detect active form of protease, chemical tools called activity-based probes must be employed. Our group has recently developed technology to obtain new types of ultrasensitive chemical tools (substrates, inhibitors, activity-based probes) for major families of medically important proteases. Using this novel, unique and very efficient technology called Hybrid Combinatorial Substrate Library (HyCoSuL) we have demonstrated that protease substrate specificity can be significantly enlarged by the use of unnatural amino acids in peptide sequence.

References:

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2. Kasperkiewicz et al. *Proc. Natl. Acad. Sci. U S A.* **2014**, 111, 2518
3. Poręba et al. *Cell Chemical Biology* **2016**, 23, 1023
4. Rut et al, *Antiviral Research* **2017**, 139, 88
5. Kasperkiewicz et al., *Journal of the American Chemical Society* **2017**, 139, 10115
6. Poreba et al., *Nature Protocols*, **2017**, 12, 2189

What have rust and non-reciprocity to do with 5G?

Martí Gich

*Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC)
mgich@icmab.es*

To cope with the ever-increasing demand of wireless communications, new generations of mobile and wireless infrastructures will work at significantly higher frequencies, in the range of the so-called millimetre-waves. Those shorter wavelengths, entering the realm of quasioptics, bring about shorter range eye-of-sight transmissions which will require deploying a myriad of antennas and devices. New functional materials supporting low-cost energy efficient mm-wave devices will be needed to back such a paradigm shift. In this talk I will discuss those challenges and the role that magnetic materials could play in this transition. Ongoing research at ICMAB in this direction will also be presented.

Divide, adapt and conquer

Anna Pawlik

*Hirszfeld Institute of Immunology and Experimental Therapy, Polish Academy of Sciences
anna.pawlik@hirszfeld.pl*

Bacteria are abundant in the world (1). There is no natural ecological niche free from bacteria; however, it does not mean that every species can live everywhere. To inhabit an ecological niche bacteria have to reproduce, but this is only the first step to success. Once they replicate, bacteria have to adapt to the environment. However, the environment changes (e.g., pH, temperature, viscosity, nutrients), so bacteria continuously adapt to their niches (2). In fact, bacteria have been designed to be adaptable. They encode many regulatory proteins that help them to sense and to respond to changing, often challenging, conditions. If they cannot respond, they go into dormant forms (e.g., spores, VBNC, persisters) (3). If this is not enough, they mutate (4). Mutation, conjugation, transduction, transformation, and recombination are the genetic approaches that shape bacterial genomes. Only the best-adapted, selected individuals conquer the world.

References:

1. Gibbons, S.M. and Gilbert, J.A. (2015) Microbial diversity-exploration of natural ecosystems and microbiomes. *Curr. Opin. Genet. Dev.*, **35**, 66–72.
2. Chaguza, C. (2020) Bacterial survival: evolve and adapt or perish. *Nat. Rev. Microbiol.*, **18**, 5.
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Supramolecular polymer materials

Richard Hoogenboom

Supramolecular Chemistry Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281-S4, B-9000 Ghent, Belgium
Richard.Hoogenboom@ugent.be

Supramolecular interactions are omnipresent in Nature and are at the basis of all adaptive and responsive processes in natural systems. Prime examples include the formation of double-strand DNA strands as well as the folding of proteins. Importantly, both these examples are based on natural polymer structures that in combination with supramolecular interactions provide a highly sophisticated level of control over the properties of the materials, ranging from information storage and read-out, via self-replication to transport of molecules and materials with high mechanical strength and efficient energy dissipation. Inspired by these natural systems, we aim to develop advanced materials based on the combination of polymer materials with supramolecular interactions which will be discussed in this lecture.

At first the utilization of thermoresponsive polymers as basis for smart polymeric sensors with a memory function will be discussed.² It is demonstrated that thermal phase transitions with large hysteresis (up to 40K) could be obtained based on supramolecular host-guest association,³ which could be exploited as memory function for the thermal history of the solution.⁴ When transferring these host-guest systems to polymeric hydrogels, the supramolecular association of the hydrogel with a tetracationic macrocyclic host was found to induce strong swelling of the hydrogels.⁵ Combining this hydrogel with a thermoresponsive polymer that contains a stronger binding electron rich host in solution allows shuttling of the macrocyclic host between the solution and the hydrogel. As such, this multicomponent supramolecular system revealed heating induced swelling of the hydrogel and cooling induced shrinkage.

Secondly, the preparation of strong and energy dissipating hydrogels will be discussed based on poly(2-isopropenyl-2-oxazoline) that is crosslinked with either a pillar[5]arene as supramolecular crosslinker or with terpyridine metal complexes.^{6,7,8}

The final part of this lecture will be dedicated to the discussion of novel self-healing polymeric elastomers based on the association of triblock copolymers having oppositely charged outer blocks.⁹ Separately these polymers behave as viscous liquids, but when mixed together a supramolecular network is formed through electrostatic interaction between the oppositely charged segments. The charged blocks are phase-separated from the uncharged block in a cylindrical structure with a glass transition temperature (T_g) close to room temperature. Nonetheless, the electrostatic interactions provides elastomeric properties to the materials well beyond this T_g .

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Professor Richard Hoogenboom will come to Wrocław as part of the Visiting Professors program - this is a series of visits of famous scientists, artists, business people from around the world, co-financed by the city through Scientiae Wratislavienses fund.

The in-situ TEM imaging interactions occurring in antimicrobial photodynamic therapy

Andrzej Żak¹, Jakub Grzęda², Marta Piksa³, Krzysztof Pawlik³, Katarzyna Matczyszyn⁴

¹ Electron Microscopy Laboratory, Wrocław University of Science and Technology, Wrocław

² Department of Lightweight Elements Engineering, Foundry and Automation, Wrocław University of Science and Technology, Wrocław

³ Ludwik Hirsztfeld Institute of Immunology and Experimental Therapy, Polish Academy of Science, Wrocław

⁴ Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Technology, Wrocław

E-mail address: andrzej.zak@pwr.edu.pl

The project aimed to dynamically visualize the process of interaction of the photosensitizer with the biofilm of *Staphylococcus aureus* bacteria in a transmission electron microscope (TEM). The observation process has thus become an attempt to depict the phenomena of antimicrobial photodynamic therapy (aPDT) on the nanoscale for the first time.

The project was implemented in a few ways. The first of the project's subtasks was to observe the phenomena of ex-situ antimicrobial photodynamic therapy using methods based on fixation and contrasting of the sample [1]. This confirmed the need for *in situ* observations, with the specimen illuminated directly during the observation.

To bring about the planned observations, the standard TEM had to be rebuilt. First, it has been adapted to the installation of hydrated samples using electron-transparent membranes that separate the liquid from the high vacuum. Then, a special illuminator was brought to the sample, which enabled the activation of the photosensitizer during the observation [2]. Then, a system for generating a phase-contrast was made, which allows us to observe the structure of internal membranes in the whole hydrated cell. The last modification concerned the necessity to strictly control the intensity of the electron beam incident on the specimen. It allows distinguishing between the effects of photosensitizer and electrons that generate large radiation damage [3].

The multifaceted modification of TEM allowed to conduct observations in which the delamination of the peptidoglycan layer in gram-positive bacteria surrounded by an active photosensitizer can be seen. Further observations of this type will allow us to provide answers on the ultrastructural mechanisms of aPDT.

References:

- [1] Maldonado-Carmona N., Marchand G., Villandier N., Ouk T., Pereira M., Calvete M., Calliste C., Zak A., Piksa M., Pawlik K., Matczyszyn K., Lhez S., Porphyrin-loaded lignin nanoparticles against bacteria: a Photodynamic Antimicrobial Chemotherapy and environmentally friendly application, *Frontiers in Microbiology*, pending approval
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Plenary sessions Monday

Temperature and high pressure sensing using NaBiF₄:Yb,Er upconverting nanoparticles

Szymon J. Zelewski,¹ Magda A. Antoniuk,² Robert Oliva,¹ Andrzej Żak,³

Robert Kudrawiec,¹ Marcin Nyk²

¹*Department of Semiconductor Materials Engineering, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, 50-370 Wrocław, Poland*

²*Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, 50-370 Wrocław, Poland*

³*Electron Microscopy Laboratory, Faculty of Mechanical Engineering, Wrocław University of Science and Technology, 50-370 Wrocław, Poland*

E-mail address: szymon.zelewski@pwr.edu.pl

Luminescent sensors based on nanoparticles offer non-contact probing of various physicochemical parameters with high spatial resolution. Biocompatible compounds such as fluoride matrices doped with rare-earth ions offer additional features, such as the ability to excite both Stokes and anti-Stokes emission with near-infrared sources fitting the biological transparency windows.

In this work, we present the application of Yb,Er co-doped fluoride matrix NaBiF₄ for multimodal temperature and pressure sensing. In contrast to the classic NaYF₄ host, yttrium ions are replaced by bismuth ions to reduce the manufacturing cost and make the product more environmentally friendly.

Temperature-dependent luminescence measurements reveal distinct changes of relative emission intensity ratio of chosen thermally coupled Er³⁺ energy bands. The obtained sensitivity ranges from 1.07%/K at 303 K down to 0.27%/K at 523 K. The studied nanoparticles exhibit strong upconversion efficiency in the covered temperature range.

Diamond anvil cells allow for generation of hydrostatic pressures up to several GPa, providing conditions often necessary for crystal formation, as well as studying effects like phase transitions. Emission line shift of ruby (Cr³⁺ ions embedded in Al₂O₃ matrix) is commonly used as a reference for determining the pressure generated inside the cell. Our results show that the infrared (~1.5 μm) emission band of NaBiF₄:Yb,Er exhibits line shift pressure coefficients superior to ruby, while the use of near-infrared excitation laser is desirable for investigations of other luminescent materials potentially mounted in close proximity with the nanocrystals.

The novel NaBiF₄:Yb,Er upconverting nanoparticles have been proven to be promising candidates for multimodal temperature and pressure sensing, with reversible performance up to 15 GPa and over 500 K [1].

References:

- [1] Antoniuk, M. A., Zelewski, S. J., Oliva, R., Żak, A., Kudrawiec, R., Nyk, M. *Combined Temperature and Pressure Sensing Using Luminescent NaBiF₄:Yb,Er Nanoparticles*, ACS Applied Nano Materials 3(5), 4209–4217 (2020); <https://doi.org/10.1021/acsanm.0c00403>

Investigation of the fluoride ions content in the Eu^{3+} -doped apatite on its structure and luminescence properties

Sara Targowska¹, Katarzyna Szyszka¹, Adam Watras¹ and Rafał J. Wiglusz¹

¹ Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okolna 2, 50-422 Wrocław, Poland

E-mail address: s.targowska@intibs.pl; r.wiglusz@intibs.pl

Apatite-structure materials are applied in a wide range of industrial fields as laser hosts, catalysts, luminescent materials, gas sensors, ionic conductors, adsorbents, chemical engineering materials and biomaterials. The apatite is good host lattice for rare earth ions (RE) as luminescence imaging agents. Moreover, it has a wide thermal and chemical stability as well as low toxicity [1–3].

The apatite doped with Eu^{3+} ions $(\text{Ca}_{9.9}\text{Eu}_{0.1}(\text{PO}_4)_2(\text{SiO}_4)_4(\text{OH})_{2-x}\text{F}_x)$, where $x = 0, 0.8, 1.2, 2$, was obtained by microwave-assisted hydrothermal process. The structural and spectroscopic properties were determined by using XRD (X-ray powder diffraction), TEM (Transmission electron microscopy) and SEM (Scanning electron microscopy). Influence of the fluoride ion content was investigated in detail for the purpose of the relationship between the fluorine ion substitution ratio and luminescence intensity of product. In the excitation spectra two bands corresponded to the charge-transfer (CT) between $\text{O}^{2-}\text{Eu}^{3+}$ as well as $\text{F}^{-}\text{Eu}^{3+}$ were detected. The emission spectra provided an information about site-occupied preference of Eu^{3+} ions. It was shown that with increasing of F^{-} ion concentration the peak corresponding to Ca(1) site became more intense suggesting a preference of this site. The ratio between the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition compared to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition indicates the higher asymmetry of the Eu^{3+} ion surrounding with increasing of F^{-} ion amount. Moreover, it was determined the CIE chromaticity coordinates and color temperature based on the emission spectra.

The special attention was paid to investigate changes of luminescence decay profile showing non-exponential character because of two nonequivalent Eu^{3+} ions position in the apatite structure. The average luminescence lifetime strongly depends on of fluorine ion concentration.

Acknowledgements

The authors would like to acknowledge financial support from National Science Centre (NCN) within the projects ‘Preparation and characterisation of biocomposites based on nanoapatites for theranostics’ (No. UMO-2015/19/B/ST5/01330).

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Ab-initio based tight-binding models for excitons in 2D semiconductor TMD crystals

K. Sadecka¹, M. Bieniek^{1,2}, A. Wójs¹, P. Hawrylak²

¹ *Department of Theoretical Physics, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

² *Department of Physics, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5
sadecka27@gmail.com*

Single layers of transition metal dichalcogenides (TMD's) MX_2 ($\text{M} = \text{Mo}, \text{W}, \text{X} = \text{S}, \text{Se}, \text{Te}$) are novel semiconductor research platforms enabling exploration of many fundamental physical phenomena [1]. These include, e. g., low energy bands emulating massive Dirac fermion model, valley degrees of freedom which allow for selective excitation with circularly polarized light, nontrivial topology resulting in valley Zeeman effect [4], and strong electron-electron interactions leading to excitons with binding energy ~ 500 meV [4] and broken symmetry valley- and spin-polarized phases [5-7]. These phenomena vary with metal and chalcogenide atoms. In this work we present the minimal tight-binding models [4] for a single layer of TMD's for every combination of $\text{M} = \text{Mo}, \text{W}$ and $\text{X} = \text{S}, \text{Se}, \text{Te}$ elements. First we fit multidimensional space of Slater - Koster parameters to the electronic dispersion obtained by ab initio density functional theory. Next, our tight-binding models are used for solving the Bethe-Salpeter-like equation and predicting the fine structure of the exciton. We conclude with discussion of the role of orbital composition of electron and hole wave function on the excitonic spectrum and show novel approximation scheme for fast calculations of realistic direct electron - hole interaction.

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New Technologies for Microfluidic Optical Biosensors

Witold Nawrot, Karol Malecha

Department of Microsystems, Wrocław University of Science and Technology

E-mail address: witold.nawrot@pwr.edu.pl

Microfluidics had proven to be a vital tool for high performance optical biosensors development. As they base on microelectronic techniques, the main materials are silicon, glass and ceramic [1]. In recent years, polydimethylsiloxane (PDMS) became very popular due to fast and easy process of manufacturing, optical transparency and low cost of both equipment and materials. A plasma surface modification is commonly used in order to manufacture enclosed channels [2]. It enables bonding with glass with very strong O-Si-O bonds. We have taken this process one step further, developing a method for selective plasma modification, using dielectric barrier discharge [3]. It allows for deposition of a biomaterial before the bonding procedure and embedding it inside the structure. This technology has enabled use of wider variety of biomaterials, some of which cannot be deposited after channel enclosing.

We are also working on introduction of 3D printing to the microelectronic technology. This modern procedure is not only easy to use, but also allows for designing more complex spatial structures. We have two main areas of interest: a ceramic 3D printing [4] and polymer 3D printing on ceramic substrates. The first technology is already being introduced into the industry, with multimaterial processes being the main focus currently. However, the application of this technology in microdevices is still uncharted. The 3D printing on ceramic substrates is a completely new technology developed in our group. It helps to use all the best features from both ceramic technology and polymer additive manufacturing. The ceramic part can incorporate complex electronic systems and provide a good substrate for biomaterial deposition, while 3D printing allows for easy manufacturing of complex structures and use of transparent materials. With the high resolution of current systems, even manufacturing of microfluidic structures and optical waveguides with lenses is possible.

In this talk, both this new technologies will be described with examples, potential applications and insights for the future.

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Electrochemical Detection of Epinephrine with a Poly[(TAT)Ru(TpyCOOH)]- Tyrosinase-based Biosensor

Francesca Meloni, Maria I. Pilo, Gavino Sanna, Nadia Spano, Antonio Zucca
 Department of Chemistry and Pharmacy – University of Sassari, Via Vienna 2 – 07100 Sassari, Italy
 fmeloni1@uniss.it

Epinephrine (EP) belongs to the catecholamines, as well as to biogenic amines group. It exhibits the properties of a chemical neurotransmitter and of a hormone. Epinephrine regulates blood pressure, immune system, heartbeat rate, lipolysis and glycogen metabolism, and is also a potent vasoconstrictor. Moreover, it is released in response to stressful, exciting, dangerous or threatening situation. Abnormalities of EP levels can represent symptoms of several diseases: low levels can be associated with Parkinson disease and orthostatic hypotension, whereas slightly high levels are observed in stress and thyroid hormone deficiency, or can be connected with the presence of tumors. Besides, EP, in combination with dopamine (DOP) and norepinephrine (NOR), is wrongly and illegally used by some athletes as energy stimulators, resulting in an increase in the concentration of DOP and EP in urine. It is, therefore, clearly evident the importance of monitoring changes in the concentration levels of EP in biological fluids, in order to make possible the detection of potential pathologies, but also for the doping control of the athletes. Moreover, when EP is used as a drug, it is also important to control its concentration in pharmaceutical formulations and monitor it in the production process as well as during the therapeutic treatment, in order to avoid side effects of overdosage. Until few years ago, methods for epinephrine detection were commonly based on chromatographic techniques, spectrophotometry etc. which are time consuming and require complex isolation and derivation steps, and expensive instrumentation. Here we report the development of a new electrochemical biosensor for EP detection based on tyrosinase, immobilized on a conducting metallo-polymer film, which is a rapid and low-cost analytical tool. The assembled biosensor consists in a gold disk electrode covered with poly[(TAT)Ru(TpyCOOH)] (TAT = 4'-[(2,2':5,2''-terthien-3'-ethynyl)-2,2':6,2''-terpyridine; TpyCOOH = 4,4',4''-tricarboxylate-2,2':6,2''-terpyridine) [1] on which tyrosinase from *mushroom* has been immobilized. The choice to use poly[(TAT)Ru(TpyCOOH)] as a modifying agent for the electrode surface is due to high conductivity of this type of materials and its electrocatalytic ability. Moreover, this modified electrode surface allows to immobilize the enzyme avoiding denaturing or misfolding processes, as can be proved from voltammetric and chronoamperometric results. The obtained biosensor shows a wide linear range (1 μM - 100 μM) with a LoD value of 0.61 μM , and good selectivity.

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Effect of chalcone derivatives on PLL-associated DPPC/DPPG/Chol membranes

Paulina Trombik, Katarzyna Cieřlik-Boczula

*Faculty of Chemistry, University of Wrocław
F. Joliot Curie 14, 50-383 Wrocław
paulina.trombik@chem.uni.wroc.pl*

Chalcones occur naturally in plants and are precursors of flavonoids. They have attracted vast research attention, as they are known to possess many various biological activities, for example antibacterial, antiviral, antioxidative, immunosuppressive and cytoprotective [1]. Liposomal delivery systems of drugs are also a prominent field of current research. One of the frequently used component for building liposomal lipid membranes is cholesterol (Chol), so it's important to investigate how biologically active compounds (such as chalcones) can modify structures of Chol-mixed liposomal lipid membranes [2].

The model of negatively charged lipid membranes was created by using a mixture of dipalmitoylphosphatidylcholine (DPPC) and dipalmitoylphosphatidylglycerol (DPPG) lipids in the presence of Chol molecules. PLL was used as a model of positively charged basic proteins. In this study two chalcone derivatives were analyzed (4-chloro-trans-chalcone (4CTCh) and 4,4-dichloro-trans-chalcone (4,4CTCh)). The influence of 4CTCh and 4,4CTCh on DPPC/DPPG/Chol/PLL system was evaluated using FT-IR spectroscopy and chemometric analysis – principal component analysis (PCA).

It appeared that both studied chalcone derivatives modified the mutual interactions occurring in the lipid-cholesterol-peptide system, but their impact was varied. They altered the temperature of the membrane main phase transition, affected the trans/gauche ration in hydrocarbon lipid chains and the degree of hydration in the membrane interphase region.

The authors acknowledge the financial support provided by the NCN, Poland, with a decision number of project OPUS 2015/17/B/ST4/03717.

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Development and evaluation of experimental methodology for light-to-heat conversion efficiency determination in colloidal nanoheaters

Agnieszka Paściak, Aleksandra Pilch-Wróbel, Łukasz Marciniak, Artur Bednarkiewicz

*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422
Wrocław, Poland
a.pasciak@intibs.pl*

Cancerous cells are less resistant to increased temperatures than healthy ones [1]. Nevertheless, to localize the hyperthermia (HT) to cancerous tissues only, and avoid excessive heating of delicate healthy tissues, various nanoparticles (NPs) are studied. There are many requirements imposed on these NPs for their versatile characterization. Beside inherent chemical safety and easiness of biofunctionalization, the information how efficiently the external stimulus (e.g. irradiation light or magnetic field) could be transformed into heat is also required. A few methods have been developed to quantify and evaluate the light-to-heat conversion efficiency (LHCE), which however still require careful studies, because they can lead to different results, as an example for ~15 nm gold nanocrystals efficiency, a whole span of values, from <10% [2] up to 100% [3] were obtained. To check the correctness of the literature models, we have used the same gold NPs colloidal batch for a series of experiments. As we discovered, the most commonly used literature model [2] cannot be implemented straightway, because the results strictly depend on such factors as e.g. setup geometry or experimental conditions (stirring of a sample or temperature probe position). We have checked also a less popular model presented by Wang et al. and we have obtained similar results for different combinations. Moreover, we have proposed a simple and very accurate experimental setup based on a droplet, with similar assumptions as in ref. [3], but with an improved dosing system and the measurement procedure. Preliminary results of LHCE obtained with this setup will be presented. Financial support from NanoTBTech-H2020-FETOPEN (801305) “Nanoparticle-based 2D thermal bioimaging technologies,, is greatly acknowledged.

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Temperature imaging with Mn^{4+} and Tb^{3+} codoped ratiometric phosphor

W. Piotrowski¹, K. Trejgis¹, K. Maciejewska¹, K. Ledwa¹, B. Fond², L. Marciniak¹

¹ Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-422 Wrocław, Poland

² Institute of Fluid Mechanics and Thermodynamics, Otto-von-Guericke Universität Magdeburg, 39106 Magdeburg, Germany

E-mail address: w.piotrowski@intibs.pl

The inorganic phosphors co-doped with transition metal (TM) and lanthanide (Ln) ions are particularly attractive for various application as a luminescent thermometers in biomedical[1] and industrial fields[2] due to their high photo- and thermochemical stability. During this lecture spectroscopic properties of a new thermographic phosphor ($\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}, \text{Tb}^{3+}$) which possess emission bands in red and green spectral regions, will be described. The luminescence of Mn^{4+} ions is characterized by strong susceptibility to thermal quenching, when the emission intensity of Tb^{3+} bands is almost temperature independent. Therefore that combination of dopants facilitates the temperature readout and guarantees a high sensitivity of thermographic phosphor to temperature changes. Moreover, the emission bands of the phosphor occur in the non-overlapping spectral regions of the color filter curves of digital cameras. Therefore these two luminescent signals can be almost completely separated between the red and the green channel. To verify the applicative potential of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ powder for thermal imaging, the proof-of-concept experiment was proposed[3].

The quartz tube filled with $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}, \text{Tb}^{3+}$ powder was placed on the heating plate. Our aim was to image the gradual heat diffusion in the tube placed on the heating plate. During the experiment the images from the digital and thermal camera were captured (Fig. 1a-b) and the emission maps for red and green channels (RGB) were extracted (Fig. 1c-d). Their intensities were divided by each other in order to obtain luminescence intensity ratio (LIR) profiles. After the calibration with the use of thermovision camera, temperature profiles were obtained (Figure 1e). The random uncertainty of this technique was calculated to be below 1.6 °C. The high application potential of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ nanocrystals for temperature imaging using a simple digital camera is clearly confirmed by a proposed experiment.

Fig. 1. Photographs from digital (a) and thermovision camera (b), red (c) and green channels of RGB images (d) of quartz tube with $\text{SAO}:0.1\% \text{Mn}^{4+}, 5\% \text{Tb}^{3+}$ powder under UV light; comparison of the calculated thermal profile and thermovision camera measurement recorded at 50 s of heating exposition (e).

Acknowledgments: This work was supported by the National Science Center Poland (NCN) under project no. DEC- UMO-2018/31/G/ST/5/03258 and by the German Research Foundation (DFG) under project 426574030.

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Suitability of highly sensitive $\text{LaPO}_4:\text{Nd}^{3+}$ nanocrystals for SBR approach of luminescent thermometry

Karolina Trejgis, Kamila Maciejewska, Artur Bednarkiewicz, Łukasz Marciniak

*Institute of Low Temperature and Structure Research, Polish Academy of Science, Wrocław, Poland
E-mail address: k.trejgis@intibs.pl*

Luminescence thermometry is a unique technique whereby the temperature of objects is determined in a non-contact mode on the basis of the temperature-dependent luminescence of the phosphor. The phosphors used in thermometry should meet certain requirements, depending on the application environment, and in the case of biomedical applications, it is crucial that such a thermometer reveals biocompatibility; sufficient brightness; high physical, chemical and mechanical stability; real-time luminescence response and high relative sensitivity (S_R) to temperature changes. Moreover, in order to increase the depth of penetration of the beam into the tissues, the phosphor should own both absorption and emission bands in the NIR spectral region, where the optical windows of biological tissues are located, so that the absorption and scattering of light on the tissues are the lowest. The ideal phosphors meeting these requirements are materials doped with Nd^{3+} ions, therefore in this work $\text{LaPO}_4:\text{Nd}^{3+}$ nanoparticles were involved in determining the temperature.

Among the several techniques of luminescence thermometry, luminescence intensity ratio (LIR) based thermometers have been the most widely used so far, however, they encounter some inaccuracies related to the dispersive dependence of the extinction coefficient of the medium surrounding the thermometer and the necessity of spectral separation of analyzed emission bands, which is often difficult and in some cases even impossible. These limitations strongly affect the reliability of the results, therefore the solution to these problems is a new single band ratiometric (SBR) approach of luminescent thermometry. To obtain a single-band ratiometric thermometer, two distinct photo-excitations are used, i.e. 808 nm wavelength adjusted for the ground state absorption (GSA) and 1060 nm beam for the absorption from the excited level (ESA). The temperature dependent luminescent response under those excitation conditions reveals reverse trend, owing to which a high sensitivity of a thermometer based on this approach is obtained. According to the Boltzmann rule, the rise of temperature increases the population of higher levels, therefore the change of temperature from $-150\text{ }^\circ\text{C}$ up to $300\text{ }^\circ\text{C}$ enables firstly, the absorption process from the $^4\text{I}_{1/2}$ level to take place, but also allows the observation of emission bands not only from the $^4\text{F}_{3/2}$ level but also from the higher $^4\text{F}_{5/2}$ and $^4\text{F}_{7/2}$ levels. Accordingly, after exceeding temperatures of $50\text{ }^\circ\text{C}$, $100\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$, the emission bands at 890 nm, 810 nm and 750 nm, which correspond to the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{5/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{9/2}$ electronic transitions of Nd^{3+} , respectively arise under 1060 nm excitation. The relative sensitivity for SBR based thermometer was found to be $S_1=6.62\%/^\circ\text{C}$.

Acknowledgements:

This work was supported by National Science Center Poland (NCN) under project No. DEC-2017/27/B/ST5/02557.

Electronic transport properties of topological semimetal candidates HoPtBi and TbPtBi

Patryk Fałat^{1,2}, Orest Pavlosiuk², Dariusz Kaczorowski², Piotr Wiśniewski²

¹Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland

²Institute of Low Temperature and Structural Research Polish Academy of Sciences, Wrocław, Poland

E-mail address: patryk.falat@pwr.edu.pl

From year to year, there is a growing interest in topological materials, especially among researchers dealing with condensed matter physics and materials science issues [1, 2]. It is caused by their unusual quantum-mechanical properties, which enable them to be utilized either in novel spintronic devices or in state-of-the-art quantum computers [3].

Since some time, the most intensively studied topological materials have been various classes of topological semimetals, like Dirac, Weyl or nodal-line systems. Among other phases, the features typical for topological semimetals have been revealed in half-Heusler Pt-bearing compounds $REPtBi$ ($RE = Gd, Lu, Y$) [4, 5]. Those findings motivated us to study two other rare-earth-based half-Heusler phases, namely HoPtBi and TbPtBi.

Single crystals of both compounds were grown from Bi-flux and investigated with energy-dispersive X-ray spectroscopy and X-ray diffraction to confirm their chemical composition and crystal structure. Then, electronic transport properties were studied by means of electrical resistivity, magnetoresistance, Hall effect and angle-dependent magnetoresistance measurements, performed in wide ranges of temperature and magnetic field. For both materials, large and non-saturating transverse magnetoresistance was found. Besides, at low temperatures, Shubnikov-de Haas oscillations with two principle frequencies were observed in HoPtBi. Analysis of the oscillations yielded small effective masses of charge carriers, viz. $0.18m_e$ and $0.27m_e$. Both compounds exhibit negative longitudinal magnetoresistance, most likely due to chiral magnetic anomaly, which proves topological non-triviality of their electronic structures.

Acknowledgments. This work was supported by the National Science Centre (Poland) under research grant no. 2015/18/A/ST3/00057.

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Plenary sessions Tuesday

Counteraction of shape and size in gold nanotriangles

Krzysztof Nadolski^{1,2}, Emmanuel Benichou¹, Nina Tarnowicz-Staniak², Andrzej Żak³, Christian Jonin¹, Katarzyna Matczyszyn^{2,*}, Pierre-Francois Brevet¹

¹Institut Lumiere Matiere, Universite Claude Bernard Lyon 1, France

²Advanced Materials Engineering and Modelling Group, Wroclaw University of Science and Technology, Poland

³Electron Microscopy Laboratory, Faculty of Mechanical Engineering, Wroclaw University of Science and Technology, Poland

* katarzyna.matczyszyn@pwr.edu.pl; pfbrevet@univ-lyon1.fr

Gold nanoparticles gain an increasing interest in different fields of science due to their unique optical properties, connected with the Localized Surface Plasmon Resonance (LSPR)¹. They have as well been intensively investigated regarding their nonlinear optical properties, including the Hyper Rayleigh Scattering method, based on the Second Harmonic Generation phenomenon^{2,3}. In this method, a critical parameter is the system symmetry. So far the scientists focused on centrosymmetric nanoparticles. This work considers a mixture of centrosymmetric and noncentrosymmetric nanoparticles, namely nanospheres and nanotriangles⁴. It shows that introducing a noncentrosymmetry to the system provokes the signal retardation to vanish; however, triangular nanoparticles exhibit lower first hyperpolarizability values compared to nanospheres.

Figure 1. A question to be answered in this work is whether the noncentrosymmetric nanoparticles will take lead over the centrosymmetric ones.

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Game of plasmons - new amyloid detection method

Maciej Lipok, Patryk Obstarczyk, Joanna Olesiak-Bańska

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology

E-mail address: maciej.lipok@pwr.edu.pl

Amyloid fibrils are protein aggregates recognized due to their connection with the neurodegenerative diseases such as Alzheimer's or Parkinson's. Their detection is a vital step in the curation process. However, commonly used methods such as magnetic resonance imaging and positron emission tomography are expansive and slow [1]. Gold nanostructures are believed to solve that problem due to the incorporation of optical effects such as surface enhanced Raman scattering [2] or chiral plasmon resonance, a fast *ex vivo* amyloid detection method using the change in circular dichroism spectra of anisotropic gold nanostructures upon addition of chiral amyloid structures [3].

We have explored the change in optical properties of gold nanobypiramids in complexes with chiral amyloid aggregates of bovine insulin. We have monitored the changes in both extinction and circular dichroism spectra and confirmed that insulin amyloids can be detected using induced chiral plasmon visible in CD spectra without any functionalization of gold nanobypiramids surface.

The chiral insulin aggregates were incubated using the modified protocol described by Lokszejn [4] and gold nanobypiramids were synthesized following the protocol by Sánchez-Iglesias [5]. Their properties were monitored using spectrophotometer and spectropolarimeter.

Figure 1. TEM image of gold nanobypiramids connected to chiral insulin aggregate.

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Polarization-dependent activation of nanocrystals through surface plasmon polaritons propagating in silver nanowires

M. Cwierzona¹, A. Prymaczek¹, S. Mackowski¹, D. Piatkowski¹

¹ Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University,
Grudziądzka 5, 87-100 Toruń, Poland
dapi@fizyka.umk.pl

In this work we studied polarization-dependent remote activation and detection of photoluminescence coming from submicron nanocrystal droplet deposited locally at one end of single Ag nanowire. By using confocal microscope we observed strong emission coming from free end of the nanowire, illuminated by tightly focused laser beam as presented in Fig. 1. It indicates, that laser launches surface plasmon polaritons (SPPs) which can efficiently propagate through the nanowire and interact with emitters deposited at its opposite end. Eventually, the luminescence is transported by SPPs back to the free end of the nanowire, coupled with microscope objective [1].

Our careful analysis show that intensity and spatial distribution of this emission strongly depends on exact position of the laser spot on the free end of the nanowire. Indeed, spatial distribution of the electric field of tightly focused Gaussian beam is quite complex. It consists of linearly polarized modes, oriented parallel or perpendicular to the nanowire. We show that manipulation of the laser spot with respect to the end of the nanowire can activated different SPPs modes. Furthermore, we demonstrate that the process depends on dimensions of particular nanowire since different diameters can accommodate different SPP modes [2].

Fig. 1. Experiment geometry [1].

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Tunable hydrophobic-hydrophilic GNCs as a robust probes for protein aggregates

Anna Pniakowska, Patryk Obstarczyk, Marcin Grzelczak, Joanna Olesiak-Bańska
*Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology,
 Anna.pniakowska@pwr.edu.pl*

Thiolate-stabilized gold nanoclusters (GNCs) are defined as novel, ultra-small nanomaterials, which present attractive physicochemical and optical properties, associated with their atomically precise structure.[1]

Here we present crown-ether stabilized GNCs as a luminescent markers for amyloid fibrils studies. Amyloids are broadly studied proteins, which tends to misfold and aggregate into complex β -sheet rich polymeric structures. The process of amyloid formation is pathologically associated with neurodegenerative diseases (e.g. Parkinson's disease, Alzheimer's disease). Thus, it is of great importance to identify of amyloids morphology, their polymorphism and its impact on toxicity. [2,3]

In our work we propose an application of gold nanoclusters as a robust probes for quick detection of amyloid fibrils. We present synthesis of gold nanoclusters stabilized with thiol-derivative of crown ether. Obtained GNCs presents efficient transfer from hydrophilic to hydrophobic media within neutral and acidic conditions.[4] Tunable hydrophobic-hydrophilic supramolecular GNCs ensure interaction with defined parts of amyloid fibrils. Strong GNCs self-assembly effect on amyloids fibrils is additionally dictated by crown ether ligands complexation near hydrogen-rich parts of amyloid fibrils. GNCs self-assembly process is confirmed via TEM (fig. 1b) in terms of morphology as well as spectroscopic analysis. Due to highly controlled conditions and selectivity of the process, crown-ether stabilized GNCs serves as promising candidates for amyloids detection.

Figure 1. a) Model of Au NCs functionalized with crown ether 12-Crown-4-CH₂-SH. b) TEM images of amyloid fibrils assembled with Au/12-crown-4 ether NCs

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OLED-based photoinactivation of the bacteria isolated from diabetic foots

M. Piksa¹, C. Lian², S. Persheyev², I. D. W. Samuel², K. Pawlik¹,
K. Matczyszyn³

1. Organic Semiconductor Centre, School of Physics and Astronomy,
University of St Andrews, UK

2. Advanced Materials Engineering and Modelling Group, Faculty of Chemistry,
Wroclaw University of Science and Technology, Poland

3. Ludwik Hirszfeld Institute of Immunology and Experimental Therapy,
Polish Academy of Sciences, Poland

E-mail address: marta.piksa@hirszfeld.pl

Problem: According to the World Health Organization reports growing antimicrobial-resistance (AMR) to pose one of the greatest threats to healthcare, food security, veterinary and agriculture worldwide. AMR infections are especially hazardous for people with the impaired immune system following a chemotherapy, surgery, transplant, HIV infection or diabetes.¹ The last group is our target. Diabetes occurs in 1 in 11 adults in the age of the range 20-79. It causes irreversible damages of nerves and blood vessels often resulting in the development of the diabetic foot diagnosed in around 60 million diabetics worldwide.² This chronic wound placed usually on the limb below the knee creates perfect conditions for bacterial infections obstructing the healing processes and leading to limb amputation which contributes to a significant increase of the mortality.³

Methods: We propose antimicrobial photodynamic therapy (APDT) as an alternative approach to diabetic foot bacteria extermination. APDT bases on three crucial elements: photosensitizer, light and oxygen. The photosensitizer by the absorption of the radiation in the visible range undergoes the excited-states changes resulting in the reactive oxygen species production which are considered to be the main antimicrobial agent.⁴ In order to assess the APDT effectiveness, medical swabs from 9 patients with diabetic foot were obtained and 30 bacteria species were isolated. The photoinactivation of planktonic bacteria was lead on 96-well plates with methylene blue (5 µg/mL) as a photosensitizer (earlier proven effectiveness; approved medical). An organic light-emitting diode (OLED) was used as a light source providing energy dose equal to 54 J/cm² and ensuring a homogeneous area of illumination.

Major results: All isolated bacteria were effectively killed by APDT. However, photosensitizer alone also exhibited bactericidal properties. The highest reductions were observed for the Gram-positive bacteria, especially for *Streptococci*.

Conclusions: Antimicrobial photodynamic therapy is an attractive alternative to bacteria destruction. The sensitivity of APDT is different for each bacteria which might be correlated with specific cell membrane composition and the unique structure of each bacteria species.

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Structural and optical properties of fibrils obtained from enantiomers and racemate of transthyretin (105-115) peptide

Manuela Grelich-Mucha¹, Ana Maria Garcia Fernandez², Vladimir Torbeev², Katarzyna Ożga³, Łukasz Berlicki³, Joanna Olesiak-Bańska¹

¹ Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

² Institut de Science et d'Ingénierie Supramoléculaires (ISIS), International Center for Frontier Research in Chemistry (icFRC), University of Strasbourg, CNRS UMR 7006, Strasbourg, France.

³ Department of Bioorganic Chemistry, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

E-mail address: manuela.grelich@pwr.edu.pl

Amyloid fibrils are elongated peptide aggregates with a β -sheet structure [1] which have shown to possess intrinsic fluorescence: upon excitation at ~ 360 nm, they emit in the visible range, with maximum at 430–450 nm [2, 3]. Another aspect regarding fibrils is their polymorphism, for example twisted or tape-like fibrils can be distinguished [4].

We have synthesized *L*- and *D*-transthyretin (TTR) (105-115) fragment peptide sequences using solid phase peptide synthesis. The peptides were purified using HPLC. Their purity was verified by analytical HPLC and LC-MS. For the aim of experiments, we have incubated both enantiomers *L*- and *D*-TTR(105-115), as well as their racemic mixture. The samples were investigated using different techniques as AFM, TEM, UV-Vis, fluorescence spectroscopy, ATR-FTIR and CD spectroscopy, to get an insight into the structural and optical features of the obtained assemblies. Additionally, molecular dynamics (MD) simulations were performed.

L- and *D*-TTR(105-115) gave rise to twisted morphology, whereas the equimolar mixture to tape-like fibrils. CD spectra confirmed opposite chirality for fibrils obtained from the enantiomers. ATR-FTIR measurements further evidenced secondary β -sheet structure for all of the samples. Moreover, the spectra revealed a parallel arrangement of hydrogen bonds within fibrils formed from enantiomers and antiparallel for the racemic mixture. The antiparallel β -sheet conformation was observed even prior to incubation, which was also evidenced by the presence of protofilaments within racemate. MD simulations confirmed high stability of tape-like fibrils and fluorescence spectra displayed a blue-shift in emission and excitation for fibrils formed by the racemate compared to the single enantiomers. Our results evidence that the peptide fibril structure and arrangement of hydrogen bonding network strongly influence the optical properties of amyloid fibrils, especially regarding the autofluorescence characteristics for amyloids.

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Analysis of lyotropic myelin structures

Dominika Benkowska-Biernacka, Katarzyna Matczyszyn

*Wroclaw University of Science and Technology, Faculty of Chemistry,
Advanced Materials Engineering and Modelling Group
E-mail address: dominika.benkowska@pwr.edu.pl*

There has been a growing interest in the studies of lyotropic liquid crystals (LLC) due to their crucial role in biologically relevant entities. Rod-like molecules such as lipids, DNA or collagen tend to self-organize into mesophases at a certain concentration and temperature. The well-known example of LLC is myelin structures (MS), which is formed by phospholipids multilayers in aqueous environment. Stacked bilayers of amphiphilic molecules show both directional order along the hydrocarbon chains and ability to slide with respect to each other. Therefore, MS might be observed in polarized light as long cylindrical structures with an explicit water core.

In this study, we present analysis of MS composed of zwitterionic phospholipids. The polarized light microscope equipped with a retardation plate was used to detect the existence of mesophases and to provide information about the orientational order of lipids within multilayered tubules. Moreover, we investigated the effect of heating and cooling process on morphology of MS.

Figure 1. The polarized light microscopy image of myelin structures was taken with a retardation plate. White arrows indicate the orientations of crossed polarizers and the blue arrow indicate the full wavelength retardation plate's slow axis. Scale bar 50nm.

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Polarization-sensitive microscopy of amyloid superstructures – spherulites

Patryk Obstarczyk¹, Maciej Lipok¹, Andrzej Żak², Joanna Olesiak-Bańska¹

¹Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wrocław, Poland

²Electron Microscopy Laboratory, Wrocław University of Science and Technology, Wrocław, Poland
E-mail address: patryk.obstarczyk@pwr.edu.pl / joanna.olesiak-banska@pwr.edu.pl

Amyloids are broadly investigated protein misfolding products with characteristic β -sheet assemblies and meaningful role in biology and modern medicine [1]. They're undoubtedly associated with neurodegenerative diseases (i.e. Alzheimer's disease) of poorly understood pathogenic importance. When it is still under debate if commonly studied fibrillar structures are formed in organisms due to self-protection mechanisms from more toxic oligomeric species, amyloidogenic proteins can also further self-assembly into more complex superstructures, known as spherulites [2]. Therefore, taking into account the importance of molecular arrangement in protein bio-functionally it is necessary to conduct structural studies of amyloids.

In our work we present polarization-sensitive two-photon microscopy (ps-2PM) [3, 4] as a versatile tool to resolve the organization of amyloid fibrils in amyloid spherical superstructures - spherulites.

Spherulite-like structures were obtained following to the M. R. Krebs et al. protocol [5] inside of closed cells made of a DPX-mounted cover slip on a microscope slide with a well. Samples were prepared in a manner allowing for observation in hydrated and bio-mimicking conditions. Then, spherulites were investigated under ps-2PM, what resolved the molecular organization of amyloid fibrils in a complex, 3D superstructure.

Figure 1. Image taken under microscope with crossed polarizers, scale bar stands for 10 μ m - maltase cross appears due to the complex birefringent spherulite structure.

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The 3-in-1 nanosized luminescent thermometer: the synthesis of ultraphosphate nanocrystals with unique paths to non-contact temperature changes sensing

Kamila Maciejewska^{1*}, Łukasz Marciniak^{1*}

¹*Institute of Low Temperature and Structure Research,
Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland
k.maciejewska@intibs.pl, l.marciniak@intibs.pl*

Herein, the multimodal noncontact temperature readout approach based on gadolinium ultraphosphate nanocrystals co-doped with Cr³⁺ and Nd³⁺ ions is presented.

The GdP₅O₁₄ doped with Nd³⁺ and Cr³⁺ ions were synthesized using the originally proposed two-step synthesis method: (i) the precipitation of the carbonates, and (ii) the annealing of the carbonates with an excess of (NH₄)₂HPO₄. In order to enhance the reliability of temperature sensing the cross-validation of temperature readout has been provided owing to the complex energy levels diagram of both co-dopants. The following processes have been involved to determine the temperature: i. the Stokes emission of Cr³⁺ and Nd³⁺, ii. the Stokes and anti-Stokes emission of Nd³⁺ and iii. the anti-Stokes emission of Nd³⁺. In the first approach, the luminescence intensity ratio of the broad emission band of Cr³⁺ (⁴T₂ → ⁴A₂) and the narrow emission band of Nd³⁺ (⁴F_{3/2} → ⁴I_{11/2}) was analyzed. The second approach, was based on the intensity ratio of the Stokes ⁴F_{3/2} → ⁴I_{11/2} and anti-Stokes ⁴G_{5/2}, ⁴G_{7/2} → ⁴I_{9/2} emission bands of Nd³⁺ ions. The third approach, took advantage of the two anti-Stokes emission bands of Nd³⁺ ions: ⁴G_{5/2}, ²G_{7/2} → ⁴I_{9/2} and the ⁴F_{9/2} → ⁴I_{9/2} to determine the temperature. All of the established readout approaches exhibit thermally dependent optical responses in the non-overlapping spectral ranges.

In conclusion, via a simple two-stage synthesis method, nanocrystalline ultraphosphates were obtained. The GdP₅O₁₄:Nd³⁺, Cr³⁺ nanocrystals were applied for luminescence thermometry technique with the unconventional optical response. As a consequence, thanks to the different proposed approaches the enhanced temperature readout accuracy was achieved.

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Influences of synthesis routes on the optical properties of $\text{Ba}_2\text{MgWO}_6\text{:Eu}^{3+}$ and its thermal sensing application

T. H. Q. Vu^{1,2}, B. Bondzior¹, D. Stefańska¹, P. J. Dereń^{1*}

¹*Institute of Low Temperature and Structure Research, Polish Academy of Science, Okólna 2, 50-422 Wrocław, Poland*

²*Institute of Chemical Technology, Vietnam Academy of Science and Technology, Ho Chi Minh City 700000, Vietnam*
p.deren@intibs.pl

Recently, Ba_2MgWO_6 has been emerged as a very fascinating host due to its cubic structure and also a very high symmetry sites available for dopants [1–3]. In this study, the influences of synthesis routes on characteristics of this host doped with Eu^{3+} were discussed in detail. $\text{Ba}_2\text{MgWO}_6\text{:Eu}^{3+}$ were synthesized by distinct methods including co-precipitation, high-temperature solid-state, and high energy – milling mechanochemical methods.

The structure of all samples was matched well with the ICSD 024-982 pattern. The average grain sizes were determined at 200 nm, 0.4 – 1 μm , and 2 – 4 μm corresponding to the samples prepared by co-precipitation, solid-state and mechanochemical methods, respectively.

Besides the unique magnetic dipole emission of Eu^{3+} ions, very small emission intensity stemming from two different types of WO_6 groups was also observed. With an increase of grain size, the energy transfer efficiencies from regular WO_6 groups to Eu^{3+} ions were estimated to be 93 %, 99.5 %, and 100%, respectively.

For the thermal sensing application, the relative sensitivities were calculated in the 77 – 350 K temperature range. Two different maximum with relative sensitivities were obtained in the different operating temperature range. The first one was obtained for the sample synthesized by the mechanochemical method with 1.5 % K^{-1} at 120 K and another one is 1.2 % K^{-1} at 248 K for the co-precipitation sample above 175 K.

It was shown that by choosing the synthesis method, it is possible to tune the thermal sensitivity of a novel material $\text{Ba}_2\text{MgWO}_6\text{:Eu}^{3+}$.

Acknowledgments: This study was supported by "The National Science Centre" under Grant No. 2017/25/B/ST5/02670, which is gratefully acknowledged.

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Single NaYF₄: Er³⁺, Yb³⁺ nanothermometry: Imaging approach

K. Hołodnik¹, U. Kostiv², D. Horák², A. Podhorodecki¹, B. Krajnik^{1*}

¹ Department of Experimental Physics, Wrocław University of Science and Technology,
wyb. S. Wyspiańskiego 27, 50-370 Wrocław, Poland

² Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovského nám. 2, 162 06 Prague 6, Czech Republic

E-mail address: bartosz.krajnik@pwr.edu.pl

Upconverting nanoparticles (UCNPs) doped with Er³⁺/Yb³⁺ ions have been recently intensively studied. The green luminescence of Er³⁺ ions occurs at 520 nm (²H_{11/2} → ²I_{15/2}) and 541 nm (⁴S_{3/2} → ²I_{15/2}) [1]. The luminescence intensities ratio of these bands is temperature dependent [2]. Most of the studies are focused on bulk material, where ensemble averaging takes place. Single nanocrystals studies show a huge diversity of the optical properties of the individual nanocrystals, depending on their sizes, ion concentration, and arrangement, surface ligands, etc. [3] Therefore, single nanoparticle studies are necessary for the practical application of lanthanide-based nanothermometers in biochemistry and cell biology.

In this report, the advantages of the imaging methods of lanthanide-based nanothermometers will be presented. All the measurements were performed on the custom-build widefield fluorescence microscope. The emission of both green luminescence bands was extracted with the use of narrow bandpass filters and imaged on the CMOS imaging detector. This method allows for the simultaneous characterization of tens of nanocrystals without the use of time-consuming measurements of luminescence spectra. To image single nanocrystals, we prepared the dilution series with a decreasing concentration of nanoparticles, that allows us for reliable single-nanoparticle studies. Our primary results indicate that the individual properties of the single nanocrystals are very different from nanoparticle to nanoparticle within the same sample batch. Especially the dispersion of green luminescence bands ratio as well as the photoluminescence intensity is significant within one sample.

The imaging approach in studying UCNPs based nanothermometry is an effective alternative for precise characterization of the temperature-dependent properties of nanomaterials. Additional experiments and improved reproducibility of the synthesized nanomaterials are needed for further optimization and practical implementation of lanthanide-based nanothermometers.

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Plenary sessions Wednesday

Multifunctional CdS-Au nanocomposite

Katarzyna C. Nawrot, Dominika Wawrzyńczyk, Marcin Nyk

Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
katarzyna.nawrot@pwr.edu.pl

We present multifunctional penicillamine-stabilized hybrid CdS-Au nanoparticles where Au nanostructures are attached to CdS quantum dots (QD) surface as sphere-like domains. The CdS:Au ratio was precisely designed enabling the nanocomposite to serve in various applications, depending on the conditions. We have previously presented that the material enhances reduction reaction photocatalysis and reactive oxygen species (ROS) generation. This time we performed two-photon excited emission (TPEE) measurements and detected two-photon absorption (TPA) and TPEE comparable to bare CdS QDs, despite metal-driven quenching effect. TPA absorption cross section (σ_2) was up to 15.8×10^3 GM and two-photon brightness (σ_2 -QY) was up to 1.6×10^3 GM [1]. Therefore, the presented material may serve as a theranostic for different applications depending on the conditions: simultaneous bioimaging and inflammation treatment by free radicals neutralization in reduction reaction or cancer cells two-photon imaging with their ROS-driven necrosis.

Figure 1. Processes possible to perform with hybrid CdS-Au nanoparticles.

Acknowledges

We acknowledge support from the National Science Centre Poland under Grant no. UMO-2018/29/B/ST4/02172

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The influence of Cd and Hg doping on AgInS₂ quantum dots

Rafał Krzysztof Kosman, Oleksii Bezkrovnyi, Bartłomiej Cichy
Institute of Low Temperatures and Structure Research, Polish Academy of Sciences
E-mail address: r.kosman@intibs.pl

Semiconductor quantum dots (QDs) are being investigated for application in the fields of photovoltaics, electronics or bioimaging. Probably the most recognizable feature of QDs is the size dependent luminescence. Silver-indium di-sulfide (AIS) is main representative of the I-III-IV group whose optical properties have been extensively studied for the last years. Comparing to the II-VI compounds AIS QDs exhibit several uncommon properties like large Stokes shifts, wide emission bands, long luminescence lifetimes (100–500 ns) and low benign nature of defect states.

One of the greatest advantages of the AIS is its ability to host variety of heterogeneous ions in its structure. This applies to doping with elements such as Mn [1] or Zn [2] as well as large off-stoichiometry in native elements leading to native defects doping [3]. Recent works revealed that low quantum yields and long life times of luminescence are the result of defect mediated transitions and shall be considered separately as surface and structural defects. In the literature one may find interesting reports on positive effect of zinc doping on the improvement of AIS luminescent properties. Along with the increase of the Zn dopant, the following was observed: a blue shift in the absorption and emission spectra, which was the result of broadening the band gap, reduction in luminescence lifetime and an increase in quantum efficiency. It has also been determined that doping with Zn reduces the number of silver defects including vacancies and interstitial atoms that naturally occur in the AIS structure[4][5]. Despite the broad knowledge of the impact of Zn on QD AIS, the impact of other cations in group 12 of the periodic table (Cd and Hg) has not been studied yet. By analogy to Zn, a similar effect on the properties of QD is expected. During this study, AIS QDs were doped with Cd, Hg cations and Zn as a control group. The doping was performed according to the general formula (AgIn)_{1-x}Y_{2x}S₂, where Y is Zn, Cd or Hg cations and X is the amount of dopant. As a result the QDs showed a linear blue shift for the Zn-doped samples, a non-linear shift for Cd and not obvious red-shift for the Hg-doped samples. The luminescence lifetimes decreased significantly for Zn and Cd and did not change for Hg. TEM imaging indicate that the dopant is too small to change the crystal structure.

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Molecular modeling to validate tribological properties of carbon materials

Piotr Żemojtel^a, Łukasz Radosiński^b, Wiesław Stręk^a

^a Polish Academy of Sciences, Institute of Low Temperatures and Structural Research, 50-422 Wrocław, Poland

^b Department of Micro, Nano and Bioprocess Engineering, Faculty of Chemistry, Wrocław University of Science and Technology, +48713202838
p.zemojtel@intibs.pl;

The discovery of variety forms that allotropic carbon structures can get and theoretical identification of the spatial architecture of fullerenes[1] intensified the research activity in the area of nanostructures. Properties of such materials are influenced by the arrangement of atoms. Molecular geometry carbon nanostructures is determined by the electron hybridization. Consistent hybridization along the crystal network is a rule in most naturally occurring forms of carbon like graphite and diamond. However, there is plenty types of carbon allotropes with mixed hybridization – for example diamond like carbon (DLC). Carbon materials in general, have quite unique physical properties being highly durable, with excellent heat conductivity, and low friction coefficient. Molecular dynamics simulations with a bond-order AIREBO[2] potential was utilized to characterize those values. The aim of the work was to check the thermal and tribological properties of carbon nanomaterials with different hybridization through numerical simulations. Then, calculated values will be used in studying the structural changes of photoexcited DLC thin films. First, to model a physical process then – calculate thermal conductivity coefficient itself. Starting from graphene, as a pure sp^2 -hybridized structure, through diaphite[3] – a structure with mixed hybridization, down to diamond which has full sp^3 -hybridization. Above all, calculated values for graphene and diamond are compatible with the literature. Thus, it can be assumed that the non-equilibrium molecular dynamics method can be applied to calculate the thermal properties of such systems.

Figure 1. (a) Model of a diamond substrate with the tip (b) Diamond surface during a sliding motion on a diamond substrate. Color contrast represents distance change in Z axis.

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Encapsulating porphyrins inside acetylated lignin nanoparticles: effect on their UV-vis absorbance and fluorescence profiles

Nidia Maldonado-Carmona, Nicolas Villandier, Tan-Sothea Ouk, Stéphanie Leroy-Lhez

Université de Limoges - Laboratoire PEIRENE
E-mail address: nidia.maldonado@etu.unilim.fr

Porphyrins are tetrapyrrolic compounds with interesting photochemical properties, which makes them suitable for clinical applications, as PhotoDynamic Therapy (PDT) and Photo Antimicrobial ChemoTherapy (PACT). These molecules tend to aggregate in aqueous media, resulting in prolific and intense research to increase the water-availability of these molecules. It has been described that acetylated lignin nanoparticles (@AcLi) are suitable for encapsulating 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine (THPP)^[1] and their photophysical properties had been discussed in another paper^[2]. Nevertheless, it is needed to describe if the results previously found are extensive for other porphyrins.

Methods. Acetylated lignin nanoparticles were prepared as previously described^{[1], [2]}, encapsulating THPP, Zinc(II)-5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine (ZnTHPP) and 5,10,15,20-Tetrakis(4-acetophenyl)-21H,23H-porphine (TAcPP). The nanoparticles were suspended in distilled water or an aqueous buffer, and their UV-vis absorbance profiles and fluorescence emission were analyzed as described elsewhere. Additionally, their susceptibility to light-driven self-degradation was assessed under white-LED light irradiation.

Results. The encapsulation of the porphyrins was achieved, and their photophysical properties were analyzed. In concordance with previous observations, the absorbance profile of porphyrins encapsulated inside acetylated lignin nanoparticles (Por@AcLi) was conserved, being observable the Soret and Q bands. Also, the absorbance profile was more stable under different pH conditions, when compared with the naked compounds. Additionally, their fluorescent properties were measured and their fluorescent quantum yield was calculated [THPP@AcLi, $\phi_F = 0.0031$; ZnTHPP@AcLi $\phi_F = 0.0036$; TAcPP, $\phi_F = 0.0053$]. Moreover, Por@AcLi were resistant to light-driven self-degradation; interestingly, the resistance seems to be due to the aggregation observed inside nanoparticles, as porphyrins under an aggregated state (mixture of phosphate buffer and DMSO 5%) are also resistant.

Conclusions. Acetylated lignin nanoparticles are an easy-to-achieve formulation. Their effectiveness has been demonstrated with three different porphyrins, each one with different pH-stabilities and solubilities.

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Enhancement of Two- and Multi-photon Absorption Photosensitizers¹

Emma Robbins^{ab}, Katarzyna Matczyszyn^a, Stephanie Leroy-Lhez^b

^a Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

^b Université de Limoges - Laboratoire PEIRENE, 123 avenue Albert Thomas, 87060 Limoges, France.
E-mail address: emma.robbsins@pwr.edu.pl

One main issue in the development of photosensitizing dyes is those which can be used in a modular fashion for a variety of biomedical applications. In the case of cancer treatment by photodynamic therapy (PDT), the ideal optical window is between 650 and 850 nm. Classic porphyrin derivatives do not reach this requirement ($\lambda_{\text{max}} \leq 650$ nm). One way to overcome this mismatch is the use of nonlinear optical properties, in particular two-photon absorption (TPA). Here, TPA is very valuable for PDT as it can provide exclusive confinement of the excitation at the focal volume with high 3-dimensional resolution. This reduces thermal photo-damage of surrounding tissue by virtue of the low-energy NIR excitation (700-1100 nm) and possibility for deeper tumour treatments.² However, TPA use for PDT is limited because of low TPA-cross sections, for example, for Foscan® (28 GM).³ To address this problem, several studies have suggested the design of highly conjugated porphyrins. Indeed, the extension of the macrocycle's π -conjugated system leads to major photophysical modifications including an increase of the TPA-cross section.⁴ Recent studies conducted in our laboratory, in collaboration with the Peirene Laboratory (University of Limoges), have underlined the real potential of porphyrin dimers⁵ as well as systems associating pyrimidine with porphyrins.⁶ For these last systems, the meta substitution pattern that was synthesised is not optimal to extend the conjugation and thus the two-photon absorption capacity of the compounds. Therefore, analogous para-substituted compounds are in development. Thus, this presentation will focus on the synthesis and modification of these new porphyrin systems developed for the enhancement of their two (or multiple) photon absorption properties for the generation of singlet oxygen.

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Triangular carbon quantum dots: from simple synthesis method to remarkable linear and third-order non-linear optical properties

Sebastian G. Mucha¹, Lucyna Firlej¹, Katarzyna Matczyszyn², Marek Samoć²

¹ Laboratoire Charles Coulomb, UMR5221, University of Montpellier - CNRS, Montpellier, France,

² Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
sebastian.mucha@umontpellier.fr

In recent years, carbon quantum dots (CQDs) have attracted much attention as an emerging class among carbon-based nanomaterials with superior optical properties and long-term colloidal stability. Due to their biocompatibility, high photostability, and low-cost fabrication, CQDs are extensively explored as promising alternatives for common semiconductor nanostructures.¹⁻² In particular, triangular CQDs have huge potential in several application fields. Although the significant progress was made in synthesis routes and determination of linear properties of various CQDs, their non-linear optical (NLO) responses at various laser wavelengths were only perfunctorily studied.³⁻⁴ Besides, most reported CQDs give a broad emission, resulting in a low color-purity.

We fabricated triangular CQDs of various sizes following the solvothermal method at varying reaction conditions.

Figure 1. Extinction (violet) and normalized 2PA spectra of cyan-emitting CQDs in ethanol dispersion. Inset shows emission under the UV light.

Phloroglucinol molecules were used as carbon sources.⁵ Linear optical characteristics of CQDs' suspensions were studied using steady-state and time-resolved fluorescence spectroscopy. Two-photon absorption (2PA) cross-section values were determined from the two-photon excited fluorescence data (TPEF).⁶ As-obtained blue-, green- and red-emitting CQDs revealed long-living (~4 ns) and efficient (~50%) emission, independent of the excitation wavelength, and with ultra-narrow bandwidth (~30 nm), indicating a

high color-purity. The estimated values of 2PA cross-section normalized by the molar weight (σ_2/M) were in the 0.001-0.004 GM·mol/g range. To the best of our knowledge, this is the first 2PA evaluation of CQDs in the wide wavelength range.

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Anisotropic gold nanoparticles decorated with azobenzene ligands

Nina Tarnowicz-Staniak^{1,2}, Katarzyna Matczyszyn¹

¹Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wrocław, Poland

² Centro de Física de Materiales (CSIC-UPV/EHU), Donostia-San Sebastian, Spain
nina.tarnowicz@pwr.edu.pl

One of the most researched topics in Materials Science are design and preparation of stimuli-responsive materials. [1] Smart materials based on superstructured nanoassemblies [2] are key components of functional materials due to their versatile nature. [3] Hence, precise control of those nanostructured assemblies with external stimuli is an ongoing scientific challenge.

Non-invasive nature, tunability of parameters (such as intensity, wavelength, and exposure time), eco-friendliness, and ability to induce remotely and control spatiotemporally an action with high precision [3, 4] make light an excellent external stimulus for the manipulation of smart materials such as nanoparticles functionalized with photochromic ligands. Such photoresponsive nanoparticles can lead to innovative solutions for energy, health, and environment-related problems. [3]

Although there has been unquestioned progress in the research of azobenzene decorated plasmonic nanoparticles in terms of their physicochemical properties and potential applications [5-7] there are still some remaining challenges in the field. Research interests are currently focused on new types of ligands, functionalization of anisotropic nanoparticles, [8] or transfer of those hybrid nanostructures to water-based systems.

Presented studies focus on the functionalization of gold nanorods with azobenzene derivative with lipoic acid, optimization of functionalization protocol, measurements of the kinetics of photoisomerization, and transfer of those hybrid nanostructures to water.

Fig.1 Fabrication of azobenzene decorated anisotropic plasmonic nanoparticles functional in water poses an interesting scientific challenge in the field of Materials Science.

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Influence of Vanadium(V) Concentration on Up-conversion Luminescence in $YV_xP_{1-x}O_4$ Co-Doped with Er^{3+} - Yb^{3+} and Tm^{3+} - Yb^{3+} Ions

Marta Wujczyk*, Adam Watras, Katarzyna Szyszka and Rafal J. Wiglusz*

*Institute of Low Temperature and Structure Research, PAS, Okolna 2, 50-422 Wroclaw, Poland
m.wujczyk@intibs.pl, r.wiglusz@intibs.pl*

An immense interest in nanosized YXO_4 (where $X = P^{5+}, V^{5+}, As^{5+}$) has been brought in response to the need for novel luminescent materials [1,2]. The YXO_4 materials have been investigated as phosphors for UV, Vis and NIR excitations. Although, the YXO_4 matrices were studied in the case of up- and down-conversions but the $YV_xP_{1-x}O_4$ solid solution has not been investigated for the up-conversion luminescence when doped with Tm^{3+} - Yb^{3+} and Er^{3+} - Yb^{3+} ions.

To determine influence of vanadium(V) ion concentration on up-conversion luminescence, a solid solution of yttrium orthovanadate-phosphate has been obtained. Matrix has been co-doped with two pairs of up-converting Tm^{3+} - Yb^{3+} and Er^{3+} - Yb^{3+} ions. The YVO_4 and YPO_4 compounds composing the solid solution crystalize in the tetragonal space group $I4_1/amd$, with isomorphic crystal zircon- $ZrSiO_4$ structure [3,4]. Therefore, based on the isostructural ties' solid solution of $YV_xP_{1-x}O_4$ can be obtained.

An effort has been devoted to synthesizing series of 0.25 mol% Tm^{3+} , 20 mol% Yb^{3+} : $YV_xP_{1-x}O_4$ and 1 mol% Er^{3+} , 20 mol% Yb^{3+} : $YV_xP_{1-x}O_4$ nanosized materials via coprecipitation method. All samples were heat-treated at 800°C for 3 hours. The morphological and structural properties of obtained materials have been characterized. Additionally, the spectroscopic properties as well as the up-converting mechanism have been studied in detail.

Acknowledgements

The authors would like to acknowledge the National Science Centre in Poland (NCN – Narodowe Centrum Nauki) for the financial support within the Project „Preparation and modulation of spectroscopic properties of $YXZO_4$, where X and Z - P^{5+}, V^{5+}, As^{5+} , doped with ‘s2-like’ ions and co-doped with rare earth ions” (No. UMO-2019/33/B/ST5/02247).

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Luminescence and biological characterization of new nanosized Eu^{3+} ions doped vanadate-apatite solid state solution.

Nicole Nowak¹, Przemysław Zima², Katarzyna Szyszka¹ and Rafał J. Wiglusz¹

1. Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

2. Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland n.nowak@intibs.pl, r.wiglusz@intibs.pl

A success of nanotechnology in field of physical, chemical, and medical sciences, it has now started revolutionizing the bio-detection, drug delivery sciences and bio regeneration techniques. The specific advantages include superior pharmacodynamics, pharmacokinetics, reduced toxicity, and targeting capability. Hydroxyapatites are well known form their biocompatibility and osteoinductivity properties towards living cells especially bone tissue. Synthetic apatites have highly developed specific surface and therefore it can form a strong bond with living tissue such bone and teeth. According to their photostability properties of rare earth ion luminescence they can be used as a biocompatible biosensor [1]. Vanadium as potentially toxic element plays significant role in living organisms [2,3]. Experimentally, it has been proven its role in neuroprotective and neuroregenerative pathway by inhibiting PTP – protein tyrosine phosphatase which is responsible for impair of NGF (nerve growth factor) responsible for regeneration and growth of neurons in central nervous system in mammals. It has been showed that sodium orthovanadate inhibits PTP activity and therefore contributes to rat's hippocampus nerves growth [4, 5].

In this study, it has been obtained nanosized vanadate substituted hydroxyapatite doped with Eu^{3+} ions via precipitation method and post heat-treated at 600°C. The europium (III) ion was established at the concentration of 1 mol % and 2 mol% as well as vanadate (VO_4)_x group was substituted (where x was equal 1, 2, 3, 4, 5 and 6, respectively). Morphology and structure of the obtained materials were characterized by X-ray powder diffraction (XRPD) technique and transmission electron spectroscopy (TEM) technique. Luminescence properties were also investigated on the basis of excitation and emission spectra as well as luminescence decay profiles. The biological properties of the materials were evaluated by hemolysis assay to established whether nanosized vanadate-hydroxyapatite exhibit potential toxic features towards ram's blood red cells.

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The use of differences in the thermal dependence of ground- and excited state absorption of Tb^{3+} ions for optical temperature measurement - two possible single band ratiometric approaches

Joanna Drabik, Łukasz Marciniak

*Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
Okólna 2, 50-422 Wrocław, Poland
E-mail address: j.drabik@intibs.pl*

The use of nanomaterials for non-contact temperature measurement with high spatial resolution and sensitivity is possible due to the dependence of their optical properties on temperature [1]. Ratiometric luminescent thermometry basing on the thermally activated changes in the mutual intensity of the two emission bands, is one of the most widespread approaches. However, due to some measurement limitations, better alternative is to obtain two signals with opposite temperature dependence in the same spectral range. That is why the single band ratiometric (SBR) approach is gaining attention, since it utilizes excitation of the same optically active center with two excitation wavelengths causing emission with opposite thermal characteristics. Lanthanide ions are optimal for SBR [2], [3] due to their unique assets such as well-defined energy level system, high brightness and stability. In our research, we characterized novel $\text{KLaP}_4\text{O}_{12}$ nanomaterials doped with various concentrations of Tb^{3+} ions [4], [5]. It was shown that the emission intensity was thermally quenched upon excitation wavelength matched to the ground state absorption, and the thermally induced increase in the intensity was noted for excited state absorption. By selecting $^5\text{D}_4$ or $^5\text{D}_3$ as level that was being excited, it was possible to control the correlation of the nanothermometer performance with the concentration of Tb^{3+} ions, by activating interionic processes such as $\{^5\text{D}_3, ^7\text{F}_6\} \leftrightarrow \{^5\text{D}_4, ^7\text{F}_0\}$ cross relaxation. In a series of further measurements, the dependence of probabilities of all luminescent processes on temperature were estimated and a system of state equations was formulated. On the basis of further modeling, possible development paths of SBR thermometers were indicated - the beneficial effect of a strong electron-phonon coupling and the importance of high-energy matrix phonons were emphasized. The pros and cons of both proposed solutions were discussed, with particular emphasis on the relative sensitivity of temperature readout, which was as high as $5\%/^{\circ}\text{C}$ at 0°C for the approach using the $^5\text{D}_4$ level excitations and $3\%/^{\circ}\text{C}$ for a wide range of temperatures for the $^5\text{D}_3$ level exciting approach.

Acknowledgements: This work was supported by National Science Center Poland (NCN) under project No. DEC-2017/27/B/ST5/02557.

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Engineering architecture of nanocrystals co-doped with Yb^{3+} and Er^{3+} ions for highly efficient Förster Resonance Energy Transfer (FRET) between Er^{3+} ions and Rose Bengal acceptor

Agata Kotulska¹, Aleksandra Pilch-Wróbel¹, S.Lahtinen², T.Soukka², Artur Bednarkiewicz¹

1 Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okolna 2, 50-422 Wrocław, Poland

2 University of Turku, Department of Biotechnology, Kiinamyllynkatu 10, FI-20520 Turku, Finland
E-mail address: a.kotulska@intibs.pl

Förster Resonance Energy Transfer (FRET) is widely used for studying distance changes between two molecules. Energy transfer between donor (D) and acceptor (A) molecules, can be observed when two conditions are fulfilled simultaneously – both molecules stay within a range of a few nanometers and the spectral overlap occurs between D emission and A absorption. FRET efficiency can be derived based on measured luminescence of D with A and may serve as a spectroscopic ruler. Emission intensity of a donor (I_D) in a presence of acceptor (I_{DA}) is lower ($I_{DA} < I_D$) and additionally luminescence lifetime of the donor (τ_D) gets shorter when FRET mechanism occurs ($\tau_{DA} < \tau_D$). In opposite to conventional fluorescent molecules used so far for FRET, lanthanide doped nanoparticles show anti-Stokes luminescence, excellent photostability of luminescence and long luminescence lifetimes, which enable to reduce background signal, increase observation lifetimes of luminescence and simplify detection systems, and thus enables to improve and simplify FRET measurements. Choosing nanoparticles codoped with Yb^{3+} (as sensitizer) and Er^{3+} (as activator) as a donor and Rose Bengal (RB) dye as acceptor, allows to photoactivate sensitizer ions (Yb^{3+} ions) in NIR spectral region, upconvert the light to visible spectral region (through Yb^{3+} - Er^{3+} upconversion) and observe FRET mechanism between Er^{3+} ions and RB dye. While solving important issues, upconverting NPs bring new challenges to UC-FRET technology, related to the size and architecture of composition of the nanoparticles (such as dopant ions distributions within core and shell). Bringing donor ions closer to the surface has been proposed [1] and recently demonstrated [2, 3] as a way to improve and optimize FRET efficiency. Therefore, here we study the relationship between core-shell NPs design and FRET efficiency, both by modelling and experimentally, by studying luminescence spectra and luminescence kinetics of donor ions in the presence of acceptor.

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Luminescence properties and bioactivity of Yb³⁺/Tm³⁺ ions in SiO₂–CaO glass

Katarzyna Hałubek-Głuchowska, Anna Łukowiak

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

K.Gluchowska@intibs.pl

Materials and devices based on rare earth-doped upconverters are largely employed as bioimaging, laser, photon management, and nanothermometry systems [1–4]. Looking for bioactive upconverting nanoparticles, we have prepared silica–calcia glass powders doped with different concentration of Tm³⁺ and Yb³⁺ ions (Yb³⁺ from 1 mol% up to 4 mol% and Tm³⁺ from 0.15 mol% up to 0.5 mol%) by the sol–gel method and characterized their structure, morphology, and optical properties. XRD pattern indicated amorphous phase of the silica-based glass with partial crystallization of oxides. SEM images showed particles with diameter around 50 nm for lower and around 30 nm for higher concentration of dopants. The upconversion emission spectra and fluorescence lifetimes were registered under near infrared excitation (980 nm) at room temperature to study the energy transfer between Yb³⁺ and Tm³⁺ at various active ions concentrations. We reported the thulium emission bands around 366, 475, 650 nm and 800 nm corresponding to the ¹D₂ → ³H₆, ¹G₄ → ³H₆, ¹G₄ → ³F₄ and ³H₄ → ³H₆ transitions, respectively. To understand the mechanism of Yb³⁺–Tm³⁺ UC energy transfer in the CaO–SiO₂ powders, the energy level diagrams of the Yb³⁺ and Tm³⁺ ions were proposed. Furthermore, we evaluated the ability of doped silica–calcia powders as an induction agent for the formation of apatite layer when soaked in simulated body fluid (SBF). After 3 weeks immersion in SBF, XRD patterns recorded the diffraction peak at 2θ = 26° and 32° which corresponded to the (002) and (211) reflections of hydroxyapatite (HA). The EDX and ICP analysis showed the increase in the concentration of Ca and P elements on the sample surface indicating formation of HA layer.

Acknowledgment

This work was supported by the National Science Centre research grant No. 2016/22/E/ST5/00530.

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Cr³⁺- based nanocrystalline luminescent lifetime thermometry

Karolina Elzbieciak-Piecka¹, Joanna Drabik¹, Daniel Jaque², Łukasz Marciniak¹

¹ Institute of Low Temperature and Structure Research PAS, Wrocław, Poland

² Universidad Autonoma de Madrid, Madrid, Spain

E-mail address: k.elzbieciak@intibs.pl

The most commonly used methods of noncontact temperature readout using luminescent thermometry can be divided into two groups: spectral and temporal. The first one relies on determination of the temperature by the analysis of integral emission intensity of single or the emission intensity ratio of two bands, while the second one involves the analysis of the kinetics of the excited state depopulation for this purpose [1-2].

Despite of the fact that luminescence lifetime measurements require complex detection systems in contrast to ratiometric ones, this technique is more accurate and poses many advantages [3-4]. Luminescence lifetimes do not depend on local concentration of the nanothermometers, surrounding medium or excitation intensity, nevertheless, they are rarely studied [5]. Therefore, in this work, a series of Cr³⁺ doped nanocrystals, namely: Y₃Al₅O₁₂, YAlO₃, Y₃Al₂Ga₃O₁₂, Y₃Ga₅O₁₂, Gd₃Ga₅O₁₂ and La₂LuGa₅O₁₂ were examined as a noncontact temperature sensors in the lifetime-based approach. The influence of the temperature on the shortening of the lifetime of the ²E state of Cr³⁺ was investigated in order to evaluate the role of the host material composition on the thermographic performance of the nanocrystals. Temperature-dependent luminescence decay curves were analyzed according to three different procedures (average lifetime approach, doubleexponential fit and time-gated ratiometric approach), not only the obtained lifetime value but also the thermal sensitivity. It was found that the method involved for the lifetime assessment not only affect the value of obtained decay constant but also, determine the value of the relative sensitivity what is crucial for the reliability estimation of noncontact temperature sensor. Additionally, it was noticed that the relative sensitivities derived from the average lifetime approach and doubleexponential fit revealed a dependence on the crystal field strength. The results included in this work highlighted that much more attention needs to be paid on the analysis procedure and obtained results affected by that and constitute a step into the further optimization.

Acknowledgements

„High sensitive thermal imaging for biomedical and microelectronic application” project is carried out within the First Team programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund

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Early stage studies of oblique helicoidal cholesteric phase for tunable liquid crystal lasers

Stefan Czarnocki¹, Maciej Czajkowski^{1,*}, Bartłomiej Potaniec¹, Joanna Cybińska^{1,2}

¹Lukasiewicz Research Network – PORT Polish Center for Technology Development, Wrocław, Poland

²Faculty of Chemistry, University of Wrocław, Wrocław, Poland

*maciej.czajkowski@port.lukasiewicz.gov.pl

The molecules of liquid crystal dimers composed of two mesogens linked by a flexible aliphatic chain may align in a bent shape and consequently, even non-chiral compounds by their mutual interaction may arrange in helicoidal manner, forming twist-bend nematic (N_{TB}) phase, with helicoid periodicity in order of 10 nm [1,2]. Liquid crystal dimers may be also utilized in liquid crystal mixtures with chiral dopants forming oblique helicoidal cholesteric (CLC_{OH}) phase, with position of the reflection band able to control by the electric field in wide range - from NIR to UV range [3,4]. The periodic structure of the cholesteric phase brings the reflectivity, thus may serve as resonator of the laser and the materials exhibiting CLC_{OH} phase may be utilized for construction of tunable lasers [4].

We synthesized dimeric cyanobiphenyl liquid crystal derivatives, including one new compound exhibiting wide range of the nematic phase. The mixture based on cyanobiphenyl liquid crystals including *E7* mixture was prepared and enclosed in the cell. The sample was investigated under the polarized optical microscope with controlled temperature. The CLC_{OH} alignment was induced above certain threshold and controlled by AC electric field as manifested by the change of the color of the reflection band from red to blue (Fig. 1). It was found that CLC_{OH} alignment in the cell is sensitive also to the temperature.

Fig.1. Change of the color of the reflection of the sample upon change AC electric field amplitude, observed under the microscope.

It will be presented short introduction related to the CLC_{OH} phase, experimental results and structures of synthesized organic dyes studied for their solubility in the liquid crystal host. Usage of the studied materials in liquid crystal lasers is considered.

Acknowledgements

The research was conducted within the framework of research project no 2018/31/B/ST8/02832, cofinanced by National Science Centre, Poland.

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Novel Organic Hybrid Nanomaterials for organic solar cells

Kenedy Tabah Tanko^{1,2}, Yatzil Alejandra Avalos-Quiroz², Riva Alkarsifi², Gilles Quéléver², Olivier Margeat², Jörg Ackermann².

¹Erasmus Mundus Joint Master Chemical Nano-Engineering (CNE),

²Centre Interdisciplinaire de Nanoscience de Marseille (CINaM).

Email: kenedytabah@gmail.com

The challenge of poor light harvesting capabilities of photoactive materials which has been a central focus in organic photovoltaic (OPV) research, is gradually being surmounted with the development of wide bandgap polymer donors and non-fullerene acceptors which can be combined to make excellent photoactive inks for OPVs^[1]. Low cost solution processed interfacial layers are however needed for fully printable OPVs which have the potential to effectively compete with other PV technologies already in the market.^[2] In this work, we successfully prepared stable nanocomposite blends of nickel oxide (NiO_x) nanoparticles with 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (F4-TCNQ) as a molecular dopant. NiO_x nanoparticles were first prepared from nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) by chemical precipitation, then dispersed in absolute ethanol, and F4-TCNQ solution (prepared in ethanol) was added to complete the ink blend. AFM images of spin coated NiO_x:F4-TCNQ composite layers on glass substrates and on top of PM6:ITIC-4F active layers showed complete coverage with sufficient layer morphology to be used as Hole Transport Layer(HTL) in organic solar cells. Doped and undoped NiO_x were applied as HTLs in inverted PM6:ITIC-4F devices. An average Power Conversion Efficiency (PCE) of 0.61% was obtained for devices with undoped NiO_x HTL. This low performance of devices with undoped NiO_x HTL is attributed to the energy level mismatch between the valence band of NiO_x and the HOMO of the PM6 donor. However, molecular doping with F4-TCNQ using a bilayer approach and the nanocomposite (NiO_x:F4-TCNQ) led to PCEs of 4.7% and 1.2% respectively. The improved performance indicates that F4-TCNQ indeed successfully modified the work function of the HTL and further device optimization will lead to much better performances.

(a)

(b)

Device	Voc (V)	Jsc (mA/cm ²)	FF (%)	Best PCE (%)	Parameters
Reference 1	0.88	19.54	58.32	10.03	2nm MoO _x as HTL
Reference 2	0.20	10.70	29.44	0.63	20mg/ml NiO _x Bilayer HTL
OPV1	0.78	15.58	38.57	4.69	30mg/ml NiO _x + 1mg/ml F4TCNQ Blend HTL
OPV2	0.28	12.95	31.81	1.15	20mg/ml NiO _x + 0.15mg/ml F4TCNQ

Fig. 1: (a) Structure of inverted Organic solar cells incorporating nanocomposite NiO_x:F4-TCNQ HTLs. (b) Summary of photovoltaic parameters of PM6:ITIC-4F based OPV devices using MoO_x and NiO_x based HTLs

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Localization of excitons and influence of a substrate on optical properties in a large-area WS₂ monolayer

Nikodem Sokołowski, Jan Kopaczek, Robert Kudrawiec

*Department of Semiconductor Materials Engineering, Wrocław University of Science and Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
E-mail address: 236646@student.pwr.edu.pl*

WS₂ belongs to a transition metal dichalcogenides (TMDs) family. In their bulk forms, compounds are layered materials in which there are strong intralayer bonding and weak, Van der Waals interlayer bonding. That allows us to obtain monolayers of the TMDs (transition metal layer sandwiched by two chalcogen layers). That change of dimensionality from 3D to 2D significantly influences electrical, mechanical and optical properties of materials, e.g. WS₂ changes fundamental bandgap from indirect to direct, absorbs up to 10% of light and has huge exciton binding energy (up to 700 meV), which makes them promising materials for optoelectronic applications. In this work in large-area WS₂ monolayer grown by a CVD method, we determined the influence of 3 substrates (silicon, sapphire, glass) on optical properties by photoreflectance and photoluminescence spectroscopy. Photoreflectance spectroscopy is an absorption-like tool for a very sensitive study of direct optical transitions, which is insensitive to defects and localization of carriers. Photoluminescence spectroscopy relies on detecting light emission from a material. The study revealed different energy of optical transitions depending on the substrates. Temperature-dependence photoreflectance measurement allows us to determine the different temperature coefficient of optical transitions dependence of substrate due to strain associated with different thermal expansion of substrates. Comparing photoluminescence and photoreflectance spectroscopy we noticed giant localization of excitons. The obtained results show that the selection of the substrate and its influence on optical properties is an important element in the study of a monolayer of transition metal dichalcogenides.

Sol-gel glass photonic microlasers doped with Rhodamine 6G

Daria Hlushchenko ^{a), b)}, Katarzyna Komorowska ^{a), b)}

^{a)} *Lukasiewicz Research Network – PORT Polish Center for Technology Development,*

^{b)} *Wroclaw University of Science and Technology*

daria.hlushchenko@pwr.edu.pl

Microlaser is a structure in which the light travels in a closed loop — along a circle, reflecting from the sides creating whispering gallery modes (WGM), that can be interpreted as electromagnetic waves that circulate and are strongly dependent from microlasers dimensions, geometry and dielectric properties (refractive index). Photoluminescence spectrum is determined by the geometry of the resonator and the nature of the active medium [1].

Previously fabricated sol-gel microlasers was impregnated by Rhodamine 6G. For all microlasers was measured emission spectra where photoluminescence observed at 550 nm (fig.1a). An efficient laser emission is observed when the samples pumped at 532 nm. For received microlasers WGM measurement tests was carried out (fig.1b).

Fig. 1. Images of microlasers from photoluminescence microscope

Although regular circular microlasers are able to obtain low threshold lasing, the disadvantage of these highly symmetric designs is their not directional emission. Directionality proposed by introducing a deformation to the regular circular geometry: elliptical cavities, stadium shaped cavities and spiral cavities.

Microresonator circuits was chosen as possible application for such microlasers. One of the most difficult challenges in the design and fabrication of integrated microlaser-based photonic devices and systems is the efficient coupling of light into and out of a microlaser without compromising its narrow resonance linewidth. In our resonator circuit were used planar waveguides for couple microlaser device [1-4].

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Poster session I

Exciton and trion emission in hBN-encapsulated single monolayer and bi-layer MoTe₂

Kamil Andrzej Bruchal¹, Emilia Zięba¹, Joanna Kutrowska-Girzycka¹, Sefaattin Tongay², Christian Schneider³, Marcin Syperek¹

1) Laboratory for Optical Spectroscopy of Nanostructures, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

2) Arizona State University, Tempe, Arizona 85281, USA

3) Technische Physik and Wilhelm Conrad Röntgen Research Center for Complex Material Systems, Physikalisches Institut, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Molybdenum ditelluride (MoTe₂) belongs to a broad family of widely studied transition-metal dichalcogenides with several well recognisable members: MoS₂, MoSe₂, WS₂, and WSe₂. However, the properties of MoTe₂ are still not very well known, and ongoing research continuously uncovers exciting physics of this material. The bulk MoTe₂ can be synthesized in semiconducting 2H as well as semimetallic 1T' phases. In the latter one, MoTe₂ is considered as a type-II Weyls semimetal exhibiting topological quantum effects in transport phenomena. Moreover, it has been demonstrated that application of a relatively small tensile strain can transform the 1T' phase into the 2H due to relatively low transition energy of ~0.9 eV between both phases. From the optical applications point of view 2H-MoTe₂, in its multi-layered form, is an indirect bandgap semiconductor with the gap energy of $E_g \sim 0.93$ eV (~1300 nm). Transition to the direct bandgap material with the $E_g \sim 1.1$ eV (~1130 nm) occurs when MoTe₂ is thinned down to a monolayer (1ML). These peculiar optical properties make the 1ML MoTe₂ and its derivatives interesting candidates for infrared light emitters that can compete with hardly controlled Black Phosphorus in that field.

In this communication, we present the result of comparative studies of exciton and trion emission of exfoliated single monolayer (1ML) and bi-layer (2ML) of MoTe₂ encapsulated in hexagonal Boron Nitride (hBN) and deposited on the Si/SiO₂ substrate. The Raman spectroscopy confirms the presence of 1ML MoTe₂ in the investigating structures by revealing the lack of the B_{1G} mode that exists in the 2ML form of the material. At low temperatures (T=4.2 K), both structures show two inhomogeneously broadened emission bands near 1.1 eV attributed to recombination of fundamental neutral (exciton) and charged exciton (trion) states. The assignment of exciton emission is confirmed by the reflectivity contrast measurement that shows clear spectral feature positioned at the emission peak. The trion binding energy defined as the distance between exciton and trion emission bands is ~22 meV for 1ML and decreases to ~17 meV for 2ML MoTe₂. This change is attributed to modification of the MoTe₂ bandstructure influencing also the exciton banding energy.

The temperature-dependent PL experiment let to examine the stability of exciton and trion complexes in both structures. The exciton emission is observed between T=4.4 K and 300 K, the trion emission tends to vanish around 80 K. At T=300K, the exciton emission for 1ML MoTe₂ is observed near 1.1 eV, however 2ML MoTe₂ is shifting down to ~1.17 eV while the emission intensity is very similar. The 1.17 eV corresponds to the emission wavelength of ~1060 nm which is close to a technologically important spectral window at 1300 nm used for telecom applications. Possibly, with some additional steps including strain or dielectric confinement engineering one can reach the telecom window at 1300 nm that could open new potential applications for dichalcogenide layered crystals.

Control of gold nanoparticles morphology by directional synthesis and photothermal modifications.

Alina Chmielowska, Patryk Obstarczyk, Joanna Olesiak-Bańska

*Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology,
Wybrzeże Wyspiańskiego 27 50-370 Wrocław, Poland
chmielowska.alina@gmail.com, joanna.olesiak@pwr.edu.pl*

Metallic gold nanoparticles exhibit unique optical, electrical and catalytic properties which are both size and shape dependent. [1,2] Localized surface plasmon resonance (LSPR) is an optical phenomenon arising from the collective oscillation of free electrons in metallic nanoparticles in response to the oscillating electric field of the incident light. Under resonance, the incident light can be effectively absorbed and converted into photons or phonons. [1] Since the LSPR depends on the geometric shape and size of the metallic nanoparticles, it can be easily tuned through well controlled synthesis.

Over the past two decades, there has been great progress in the synthesis of gold and silver nanocrystals of various sizes, shapes and with good yield and monodispersity. [2] As when carrying out the synthesis, many factors must be taken into account in order to obtain the desired shape and size of nanoparticles, [3] the greatest possibilities of controlling crystal growth are provided by a two-step method called “seed mediated growth”. Further modification of gold nanoparticles by specifying their surface or changing their shape by acting on them with a femtosecond laser brings many new possibilities of size and shape modification and potential new applications. [4]

The aim of the study was to carry out syntheses to obtain gold nanoparticles in different sizes and shapes. Their LSPR position, sizes and structure was determined based on the absorption spectra and AFM and TEM techniques. Several of the resulting solutions were then subjected to a femtosecond laser beam at a wavelength in the vicinity of the LSPR band of each particular sample. The position of the surface plasmon for each of the samples has been shifted to shorter wavelengths. This most likely indicates that the absorbing structures at higher wavelengths were removed from the solution and melted into nanospheres. Selective removal of specific sizes of nanoparticles may lead to homogeneous distribution of nanorods sizes or a design of materials with specific optical transmittance properties. [5]

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Influence of metals on the growth of amyloids of amylin analogues – structural studies

Agata Hajda,^a Dorota Dudek,^b Magdalena Rowińska-Żyrek,^b Joanna Olesiak-Bańska^a

^a Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27 50-370 Wrocław, Poland

^b Faculty of Chemistry, University of Wrocław, 50383 Wrocław, Poland
hajda19@gmail.com, joanna.olesiak@pwr.edu.pl

Amylin (also called Islet amyloid polypeptide, IAPP) is a specific 37-amino acid peptide hormone. The function of amylin is complementary to that of insulin. Human amylin (hIAPP) has the ability to form amyloid, unlike the rat amylin (rIAPP) that does not. rIAPP differs from hIAPP in its amino acid sequence in six amino acid residues[1]. To prevent unwanted aggregation analog of hIAPP – pramlintide was proposed, which is used as a drug. Pramlintide differs from amylin by three amino acid residues[2] One of hallmarks of type 2 diabetes mellitus (T2DM) is deposition of islet amyloid, but the link between T2DM and amylin is not completely clear.[1] One of the factors influencing the formation of amyloids is the presence and appropriate concentration of certain metal ions. The influence of zinc on amylin has come to be of interest because of its high concentration in the pancreas, where it is stored together with amylin. Zinc deficiency is one of the common symptoms of type 2 diabetes[3]. Another metal associated with diabetes is copper. The metabolism of Cu^{2+} is connected with pathological amyloid formation in diabetes[4]. However, studies with the influence of copper on amylin are not conclusive.

The aim of the study was to determine whether amylin analogues: pramlintide and rat amylin have the ability to aggregate into amyloid forms and to investigate the influence of Zn^{2+} and Cu^{2+} on the aggregation process after different incubation times. The research technique used was AFM, thanks to this technique, it was possible to confirm the presence of amyloid and oligomers. Based on the research, the differences in the morphology (e.g. length, diameter) of fibers and oligomers were detected. The polypeptides without ions were the reference - pramlintide aggregated while rIAPP did not. For pramlintide with Cu^{2+} no fibers were detected. Importantly, in each sample, at different incubation times, spherical aggregates with different morphology were observed, an oligomer fusion process has been observed for pramlintide. For all samples with rIAPP no fibril formation was observed, but for Cu^{2+} spherical aggregates were detected.[5] The differences in oligomer diameters and height profiles along the contour were observed between samples. The results give a greater insight into the processes that may occur in pathological states especially in T2DM in the body and the amyloid formation process itself with the presence of metal ions.

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Application of cold atmospheric pressure plasma in the continuous synthesis of zinc oxide nanostructures

Malgorzata Policht, Piotr Jamroz, Pawel Pohl, Anna Dzimitrowicz

*Wroclaw University of Science and Technology, Department of Analytical Chemistry and Chemical Metallurgy, Wybrzeze St. Wyspianskiego 27, Wroclaw, Poland
malgorzata.policht@onet.pl*

Problem: Currently, an important challenge of the nanotechnology is associated with the development of versatile methods for effective synthesis of nanomaterials of defined properties. Generally, the most desirable nanomaterials are nanostructures due to their further wide range of uses [1]. For that reason, we have developed a novel approach for highly-throughput synthesis of ZnONPs of defined structural properties. **Methods:** In this protocol, we have employed a pulse modulated radio-frequency glow discharge (pm-rf-APGD) as a cold atmospheric pressure plasma source (CAPP) [2]. The pm-rf-APGD was operated in contact between the surface of the flowing liquid electrode, being a ZnO nanostructures precursor solution ($\text{ZnSO}_4 \times 7\text{H}_2\text{O}$, Chempur, Poland) and sharpened metallic electrode. As a stabilizer, the bovine gelatin (Sigma-Aldrich, Germany) was added to the reaction mixture. The resulted ZnO nanostructures were characterized using several experimental techniques including UV/Vis absorption spectrophotometry (UV/Vis), scanning electron microscopy (SEM) supported by an energy dispersive X-ray spectroscopy (EDX). **Results:** As can be seen from SEM photomicrography (Fig.1), the application of pm-rf-APGD as a CAPP source lead to produce spherical, approximately 700 nm in size ZnO nanostructures. Additionally, the EDX spectrum confirmed the synthesis of ZnO. These ZnO nanostructures might be applied as antimicrobial agents towards e.g. *Escherichia coli* (ongoing research project). **Conclusions:** This type of CAPP allows to obtain ZnO nanostructures with sufficient efficiency but in future we plan to adjust the CAPP operating parameters in order to produce smaller in size ZnO nanoparticles.

Fig. 1. Representative SEM photomicrography of ZnO nanostructures.

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Circularly polarized luminescent (CPL) nanomaterials

Marcelina Śmigiel, Anna Pniakowska, Joanna Olesiak-Bañska

*Advanced Materials Engineering and Modeling Group, Wrocław University of Science and Technology,
Wrocław, Poland*

E-mail address: marcelinasmigiel@gmail.com

The use of polarized light gives many new opportunities in the development of technology. Among the many different polarizations, the most interesting seems to be circular polarized light - it is possible that it can be used in 3D displays, chiroptical materials, sensors, photoelectric devices, to control the chirality of nanoparticles.

Circular polarized light can be obtained by use of a linear polarizer and quarter-wave plates (changing the polarization from linear to circular). However, it would be much easier to create materials that would emit circular polarized light, which would prevent energy losses. Such possibilities are provided by chiral luminescent materials. Their uniqueness lies in the ability to circularly polarized luminescence (CPL). This phenomenon is somehow similar to the phenomenon of circular dichroism (CD). While CD is based on different absorption of left and right circularly polarized light by the chiral systems, CPL works on the opposite principle and consists of the emission of left and right circularly polarized light. What is currently most important when it comes to working on CPL materials is to achieve the highest possible luminescence intensity.

One way may be to conduct syntheses from various materials. Traditionally, mainly used organic properties of chiral materials with high quantum efficiency and stable, flexible molecular structures. Currently, many new fluorescent materials are being designed, also from achiral components - both organic and inorganic - you can get CPL-active chiral structures. Constructing this type of nanomaterials requires a combination of chirality and luminescence.

We propose highly luminescent gold nanoclusters as CPL materials. Nanoclusters are ultra-small gold nanoparticles with unique optical properties, often presenting chirality.[3] We show initial experiments on the synthesis of such structures and their optical properties.

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- [3] Joanna Olesiak-Banska, Magdalena Waszkielewicz, Patryk Obstarczyk, Marek Samoc Two-photon absorption and photoluminescence of colloidal gold nanoparticles and nanoclusters *Chem. Soc. Rev.*, 48, 4087-4117, 2019

Temperature and hydrostatic pressure dependence of direct optical transitions in $B_xGa_{1-x}As$ semiconductor alloys

Nikodem Sokołowski¹, Jan Kopaczek¹, Filip Dybała¹, Robert Kudrawiec¹, Kyle M. McNicholas², Seth R. Bank²

¹ Department of Semiconductor Materials Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

² Microelectronics Research Center, University of Texas at Austin, Austin, TX 78758, United States
E-mail address: 236646@student.pwr.edu.pl

The III-V semiconductor alloys diluted by boron are one of the least investigated semiconductor materials. These alloys belong to highly mismatched semiconductor materials, i.e. have large differences of size and electronegativity between mixed atoms from the same group. In this report, 6 samples of $B_xGa_{1-x}As$ alloys with a boron concentration from 4.1% up to 12.1%, which have been grown by molecular beam epitaxy on GaP substrate have been studied by photoreflectance spectroscopy with temperature and hydrostatic pressure. The direct optical transitions between the valence band (a heavy hole, light hole, and spin-orbit split-off band) and the conduction band have been observed in the photoreflectance spectra. The $B_xGa_{1-x}As$ alloys have been measured with temperature from 20 to 300K and the temperature dependence of optical transitions was determined. Investigated alloys have been also measured with hydrostatic pressure up to 18.2kBar and the pressure coefficient of optical transition was determined. The main conclusions of these studies about the incorporation of boron into gallium arsenide alloy are the insignificant change of energy gap (for boron concentration below 8%) and insignificant change of temperature and hydrostatic pressure dependencies in comparison with GaAs but significant change of lattice parameter. Due to the above-mentioned conclusions, the III-V semiconductor materials diluted by boron can be good candidates for i.a. strain compressor layer in heterostructures.

Fine powdered mixed metal Fe-Mn oxides as solid state oxygen carrier

Magdalena Szkuta, Artur Krezlak, Ewelina Ksepko

Wroclaw University of Science and Technology, Poland

E-mail address: ewelina.ksepko@pwr.edu.pl

E-mail address: magdaszkut@wp.pl

Chemical Looping Combustion (CLC) process is belived to be nowadays as one of the most promising fuel combustion methods for both Carbon Capture and also Storage purposes. In this method combustion air and fuel are not mixed up, enabling significant improvement in environment protection since CO₂ and NO_x emissions from gaseous and fossil fuels combustion due to power generation are significantly reduced. After water condensation pure stream of CO₂ is produced which actually storage ready.

An important role is acted by fine powdered materials in this process, often transition metal oxides based. Those metal oxides called oxygen carriers (OCs), transfer oxygen to the fuel. To be used as oxygen carrier synthesized OCs have to transfer oxygen, to have sufficient reactivity with both fuel and oxygen, to be resistant to high process temperatures (ca 1000°C) and show no agglomeration tendency.

The paper shows results on series of the selected bimetallic oxygen carriers. By mechanical mixing and calcination iron and manganese (high concentrations) oxides together with some inert support were obtained. They were characterized by multiply methods such as SEM, EDS, fixed bed and also GC. The morphology of synthesized OCs particles showed fine round particles with a good homogeneity of elements. EDS examinations showed that among of Fe₂O₃ different perovskite and spinel Fe-Mn-Zr structures were formed. Reactivity testing was carried out in microreactor, while GC was used for analysis of both pyrolysis and combustion gasses. For the analysis of oxygen carriers reduction reactions (fuel combustion), particular Polish hard coal was used (low ash content, low sulfur). Theoretical calculations enabled optimal ratio of coal:OC to be selected.

The study proved that obtained novel materials (EU patent granted) showed both CLC and CLOU properties. Which is crucial especially for solid fuels, enabling all fuel to be combusted with rational reaction rates.

This study also confirmed that the synthesized iron-manganese (25_30%) oxides are capable to operate as OCs in coal based CLC power plants.

Physicochemical characteristics of multifunctional layered materials

Katarzyna Wal¹, Piotr Rutkowski², Wojciech Stawiński¹,

¹*Lukasiewicz Research Network – PORT Polish Center For Technology Development
Stalowicka 147, 54-066 Wrocław, Poland*

²*Wrocław University of Science and Technology, Department of Process Engineering and Technology of
Polymer and Carbon Materials, Faculty of Chemistry, Gdańska 7/9, Wrocław 50-344, Poland
E-mail address: katarzyna.wal@port.lukasiewicz.gov.pl*

Layered minerals are large group of layered materials with high ability for modifications. They are known for their application in many industries such as painting, rubber and paper. Furthermore, they are also used in such fields as electrochemistry, photochemistry, adsorption catalysis and cosmetics. [1][2]. Clay minerals stand out from others for their layered structure, high ratio of surface to volume and small grain size [3]. One of their best known representative is vermiculite, which is 2:1 trioctahedral mica-type mineral with growing interest as natural two-dimensional nanomaterial. This type of material can be used as polymer composites and special protection materials component or adsorbent from water and gaseous phase [4].

To achieve increase of the porosity of vermiculite, different acid treatments with variety of concentrations over the clay mineral was evaluated. Acid activated samples were also modified by additional treatment with NaOH, which resulted in obtaining hydrotalcite-like layered double hydroxide (LDH) materials. Novel hybrid material based on modified vermiculite and layered double hydroxide (LDH) were achieved in one-pot synthesis. All the obtained materials and the reference sample were characterized by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, thermogravimetry (TG) analysis and the measurement of the BET specific surface area. The analysis of the results showed that the acid modifications significantly increase of the porosity of vermiculite.

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Examination of fine powdered mixed metal Fe-Mn and Zr oxides as potential solid state oxygen carriers

Borys Winczura, Artur Krezlak, Ewelina Ksepko

Wroclaw University of Science and Technology, Poland

E-mail address: ewelina.ksepko@pwr.edu.pl

borys.winczura@gmail.com

The paper shows results of study of promising mixed metal Fe- Mn and Zr oxides. Those fine powdered structures may have potential application in novel combustion technologies known as Chemical Looping Combustion and Chemical Looping with Oxygen Uncoupling, namely CLC and CLOU respectively. Nowadays, both CLC and CLOU attract attention due to the production of the concentrated pure CO₂ stream which is obtained after water condensation without any energy penalty for its separation. In CLC-CLOU direct contact between fuel (biomass, coal, petcoke, syngas) and air is avoided. To carry out this process an oxygen carrier (OC) must be used. Transitions metal oxides are often used as oxygen carriers to deliver oxygen to fuel.

The objective of this work was to examine novel oxygen carrier materials i.e. mixed Fe-Mn (15-20 wt.%) oxides in terms of their practical applications with selected solid fuel. A series of bimetallic oxygen carriers with selected inert material ZrO₂ were prepared by mechanical mixing method. They were characterized by multiply methods: SEM, EDS, fixed bed and GC. The morphology study of synthesized OCs particles revealed fine round particles as desired with a good homogeneity of elements, and required particle size. EDS examinations by line-scan and mapping of elements showed the presence of Fe₂O₃ (majority) and perovskite and spinel Fe-Mn-Zr (minority) structures were formed. OC's reactivity was tested using energetically applied Polish hard coal. It was mixed with OC with desired ratio. Examinations of semiconducting powders were carried out in quartz microreactor combined with gas chromatograph. In each temperature one OC's reduction reaction was performed. Effect of temperature on combustion efficiency, mechanical stability were determined.

The examinations indicated that combination of iron with manganese oxides (as active part of oxygen carriers) and zirconium oxide (as an inert), improved reactivity and redox stability. Furthermore, they were practically crucial because clearly improved avoiding the agglomeration tendency in CLC-CLOU reaction temperatures. The reactivity of novel OCs' was compared to the reactivity of reference material Fe₂O₃/ZrO₂.

The stable CLC-CLOU performance, and as prognosed decreased agglomeration tendency suggest that these oxygen carriers might be successfully applied in energy generation processes of solid fuels.

The influence of vanadate groups substitution on structural and spectroscopic properties of fluoroapatite doped with Eu^{3+} ions

Przemysław Zima¹, Nicole Nowak², Katarzyna Zawisza² and Rafał J. Wiglusz²

¹Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

²Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

przemyslaw.zima@gmail.com, r.wiglusz@intibs.pl

Fluoroapatite (FAP) is a member of apatite family with a chemical formula of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. It forms tooth enamel and is harder and more structurally and chemically stable than hydroxyapatite [1]. Apart from its biocompatibility and regenerative potential, great advantage of that material is possibility to modulate its properties by ionic substitution. For example, Ca^{2+} ions can be replaced by optically active lanthanide ions what could enable bio-imaging and potential application as theranostic material [2].

Incorporation of vanadium(V) ions into the apatite framework by substitution of VO_4^{3-} for PO_4^{3-} ions can enhance catalytic properties of material. It was reported that vanadium-modified FAP (V-FAP) can act as heterogeneous catalyst in multicomponent organic synthesis [3]. Furthermore, the presence of vanadate groups in FAP lattice can affect dopant luminescence properties what is the main aim of this research.

The vanadate-substituted fluoroapatites doped with 1 mol% Eu^{3+} ions (1 mol%: $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{VO}_4)_x\text{F}_2$ ($x = 1, 2, 3$)) were synthesized by a precipitation method. The structural properties were determined by using an X-ray powder diffraction (XRD). An energy dispersive X-ray spectroscopy (EDS) was used to investigate chemical composition. The emission, excitation spectra and decay times of obtained materials were measured and analyzed in detail. Hemolysis assay was performed to check hemolytic potential of obtained materials.

Acknowledgements

The authors would like to acknowledge financial support from National Science Centre (NCN) within the projects 'Preparation and characterisation of biocomposites based on nanoapatites for theranostics' (No. UMO-2015/19/B/ST5/01330).

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Real-Time Surface-Enhanced Raman Scattering Tracking of Adenine–Gold Charge Transfer Complex Formation on Nanocavity-Shaped Plasmonic Crystals

Remigiusz K. Trojanowicz, Katarzyna Matczyszyn, Riccardo Castagna, Massimo Rippa, Eugenia Bobeico, Jun Zhou, and Lucia Petti

Ecole Normale Supérieure Paris-Saclay

E-mail address: remigiusz.trojanowicz@ens-paris-saclay.fr

Understanding binding of DNA bases with gold surfaces is crucial for designing reliable tools in biosensing technology and organic-based electronics. Herein, we discuss an application of quasi periodic plasmonic nanocavities fabricated by a top-down method to study adenine interactions with gold surfaces. We report plasmon-mediated homogenous catalysis of adenine–gold complex formation, when adenine is deposited onto surfaces in different ways. In particular, we elucidate how additional information can be obtained by adsorbate irradiation with laser far from resonant conditions with a low-localized, high-integral field substrate. A comparative study between mono- and multilayers on gold is proposed, offering a solution to the controversial question of adenine orientation on gold surfaces by revealing charge transfer complex formation during realtime surface enhanced Raman scattering tracking. Additionally, the designed nanocavity-based plasmonic substrates exhibit a high sensitivity with a limit of detection ≈ 25 nM.

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Poster session II

Studies on intermolecular proton transfer and its influence on liquid crystal and light emission properties.

Łukasz Duda^{1, 2, 3}, Bartłomiej Potaniec¹, Maciej Czajkowski¹, Marta Fiedot-Toboła¹, Anna Madej¹, Joanna Cybińska^{1, 3}

¹ Łukasiewicz Research Network – PORT Polish Center for Technology Development, ² Faculty of Chemistry, Wrocław University of Science and Technology, ³ Faculty of Chemistry, University of Wrocław
E-mail address: duda.lukasz96@gmail.com

Extending length of mesogenic cores of liquid crystal molecules may influence their liquid crystal properties like: type of phases, phase transition temperatures, helical twisting power [1]. Moreover, presence of intermolecular hydrogen bond or intermolecular proton transfer may affect the optical properties (absorption and emission of light) of such systems [2]. Mixtures of organic acids and 4-phenylpyridine derivative are one type of them. High affinity of proton of the organic acid to nitrogen atom of pyridine ring promotes its transfer and may lead to creation of ionic assemblies which may further influence the properties of these systems e.g. solubility in nematic matrix. One of the measurement of proton transfer affinity is ΔpK_a defined as difference between pK_a value of acid conjugated with the proper proton acceptor (pyridine derivative) and pK_a value of acid. It may be assumed that type of created bond depends on value of ΔpK_a in acid-base systems. Usually, when ΔpK_a is higher than 3, the proton transfer occurs and the salt is formed, otherwise it is expected that a co-crystal with intermolecular hydrogen bond will be formed [3].

The aim of our studies was to synthesize and characterize properties of hydrogen bond associates/ionic compounds of chiral liquid crystalline phenylpyridine derivative (ZW8565) with various organic acids differs in their pK_a value and to establish the influence of ΔpK_a in these systems on type of the bond being formed. Our studies include: FT-IR measurements, polarizing optical microscopy characterization of liquid crystal phases and phase transitions temperatures of studied systems and their mixtures with nematic liquid crystal matrix, helical twisting power measurements, light emission and absorption properties of *acid-base* binary mixtures.

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Zn²⁺ and Cu²⁺ interactions with antimicrobial peptides and their potential participation in activity enhancement

Dorota Dudek, Magdalena Rowińska-Żyrek

Author affiliations: Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

E-mail address: dorota.dudek@chem.uni.wroc.pl

Antimicrobial peptides (AMPs), are small, polycationic peptides that form part of the innate immune response shared by a variety of living species. Different AMPs are active against fungi, bacteria, viruses, protozoa, and even cancer cells. AMPs can be categorized into a few groups based on: (i) their biological source (bacterial, plant, animal); (ii) peptide properties (charge, hydrophobicity, length); (iii) 3D structure (α , β , $\alpha\beta$ and non- $\alpha\beta$); (iv) covalent bonding pattern (linear one-chain peptides, sidechain–sidechain linked peptides, polypeptide chains with a sidechain to backbone and circular polypeptides with a peptide bond between the N- and C-termini); (v) biosynthesis mechanism (gene coded and non-gene coded); (vi) molecular targets (cell surface, cell penetrating) and (vii) functions (antibacterial, antifungal, antiviral, insecticidal, and spermicidal activities, but also anticancer, wound healing and immune modulation).[1,2] In the last 30 years, a dramatic increase in antimicrobial has been observed. Novel, effective treatments and ways to specifically deliver them to drug resistant bacteria and fungi are being actively sought. Because of the general lack of resistance towards AMPs they are believed to become a novel class of therapeutics.[3] For some AMPs, the presence of divalent metal ions, such as Zn²⁺ and Cu²⁺ has an effect on their activity or mode of action. This is attained either by (i) binding metal ions, so that microbes cannot get enough nutrients essential for their life and virulence (‘nutritional immunity’)[4] or (ii) AMPs need the given metal ion as a booster of their antimicrobial activity, effecting the charge and/or structure of the peptide.[5] The aim of this work is to understand the relationship between the AMP-metal coordination, thermodynamics, structure, stability and their mode of action. Presented data concerns 2 groups of AMPs: (i) calcitermin[6] and its mutants and (ii) non aggregating analogues of amylin. Their complexes with Zn²⁺ and/or Cu²⁺ has been studied with variety of methods. Experiments of mass spectrometry, potentiometry, NMR, UV-Vis and CD spectroscopy, determination of MIC and atomic force microscopy were performed. The results allowed us to determine the stoichiometry, the exact binding site of Zn²⁺ and Cu²⁺ ions, establish geometry of created complexes, compare affinities of metal ions and to move toward explaining possible mode of antimicrobial action.

The work was supported by the National Science Centre (no.UMO-2017/26/E/ST5/00364).

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Generation of myelin structures by thermotropic liquid crystals in CTAB

Karen M. Garcia Alvarez^{ab*}, Dominika Benkowska-Biernacka^b,

Katarzyna Matczyszyn^b

Université de Aix-Marseille^a, Advanced Material Engineering group at Politechnika Wroclawska^b

E-mail address: marlenne.garciaa@gmail.com

Liquid crystals (LC) are a type of material that exhibit a long-range directional order and liquid properties at the same time, which confer them unique properties and allow their application in a wide range of fields [1-3]. What is more, they can also be found in multiple biological structures such as myelin sheath. This structure is a fatty lyotropic LC found in nerve cells which is fundamental for the transmission of electric impulses [4]. Therefore, studying its properties and behaviour, could be essential to improve health conditions or look for new applications.

In the present work, two thermotropic liquid crystals, 4'-n-octyl-4-cyanobiphenyl (8CB) and N-(4-methoxybenzylidene)-4-butylaniline (MBBA) were brought in contact with an aqueous solution of CTAB with different concentrations at distinct temperatures. After the addition of CTAB, the formation of thermotropic myelin figures (MF) by both LCs was observed under polarized light microscope. Additionally, a reduction of the average diameter of MF was detected as the temperature increased. At high temperatures and concentrations, MBBA and 8CB formed MF at the droplets' edges. Nevertheless, we noticed that 8CB exhibit MF mostly inside the droplets at reduced temperature and low concentration.

Figure 1. Micrographs of 8CB in 20 mM CTAB solution at 23 °C observed under polarized light microscope with retardation plate (x20 magnification).

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Nanofibers for (Bio)Sensing Applications

Kinga Halicka, Joanna Cabaj

Department of Organic and Medicinal Chemistry, Wrocław University of Science and Technology, Poland

E-mail address: kinga.halicka@pwr.edu.pl

1. Introduction: Nanofibers (NFs) are one-dimensional nanomaterials characterized by high porosity and high surface area-to-volume ratio. They demonstrate good physical, chemical and mechanical properties. The most important advantages of NFs include ease of functionalization, a variety of used materials and different possible applications [1,2]. The purpose of a sensor device is to obtain an analytically useful signal through a transformation of chemical information. A biosensor involves a biological recognition element and biochemical system for the recognition [3,4].

2. Results: Nanofibers can be applied in different types of sensors, including optical and electrochemical devices. Senthamizhan *et al.* constructed an optical sensor for Hg^{2+} detection using polycaprolactone NFs functionalized with gold nanocluster, obtaining limit of detection (LOD) 1 ppt for a single functionalized nanofiber [5]. In a different study cellulose acetate NFs were functionalized to detect a gene fragment, with LOD reaching 0.08 nM [6]. Asmatulu *et al.* prepared an electrochemical sensor capable of detecting as low concentrations of COX-2 enzyme as 0.01 pg/ml using antibodies and electrochemical impedance spectroscopy [7]. Cyclic and differential pulse voltammetry were applied to develop a sensor for levodopa detection with LOD at 1 μM using graphene/carbon NFs [8].

3. Conclusions: Nanofibers present an emerging technology that has been introduced to our lives, for example in energy storage, clothing or biosciences. Incorporating them into sensing devices may improve their performance, allowing to reach lower detection limit (i.e. 1 ppt) for a variety of substances, including metal ions and biomolecules.

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Iron(II) clathrochelates as ICD-sensitive reporters able to recognize specific elements of albumin surface

Aleksandra Jedynczuk^a, Slawomir Potocki, Vladyslava Kovalska, Serhii Vakarov, Yan Voloshin and Elzbieta Gumienna-Kontecka

^a Faculty of Chemistry, University of Wrocław, Poland
aleksandra.jedynczuk@chem.uni.wroc.pl

Biological macromolecules exhibiting inherent chirality are able to induce asymmetry of achiral organic and coordination compounds, and therefore, may cause an appearance of a signal in their CD spectra. These ICD bands are very sensitive to the arrangement of the binding sites of hosting biomolecules. [1] As a result, the chirality of small molecules gained upon their binding to proteins may reflect both the structural alterations and the conformation transitions of proteins (to be observed *via* changes in the ICD spectra). Clathrochelates are metal-centered compounds because their caging (encapsulating) ligands do not exist in the metal-free form due to thermodynamic reasons. [2] Iron(II) clathrochelates with mono- and dicarboxyphenylsulfide substitution that are inherently CD-silent have been recently reported to give a strong CD output in the visible spectral range upon their binding to BSA. [3] The development in supramolecular compounds area, especially metal complexes for protein surface recognition and application as potential sensors, affinity tags or tool for protein immobilization is important for biochemistry- and medicine-related fields. [4]

The aim of this work was to show that iron(II) clathrochelates during binding to albumin could reflect the transitions of the protein conformation by the changes of the band profile and intensity of their CD spectra. In this study, there were used human and bovine serum albumins and its conformations transitions were triggered by pH variation. The clathrochealte-to-albumin association was monitored by CD spectroscopy and complemented by protein fluorescence quenching. There was also ITC used to established the thermodynamic parameters of this cage metal complexes with BSA. [5]

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Acknowledgements : The project leading to these results has received funding form the European Union's Horizon 2020 Research and Innovation Programme under the Marie Skłodowska-Curie grant agreement No 778245.

Blue-emitting folic acid-derived carbon nanodots: remarkable optical properties and control of the binding ability of human serum albumin

Agnieszka Krystyniak¹, Sebastian G. Mucha², Katarzyna Matczyszyn¹

¹ Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

² Laboratoire Charles Coulomb, UMR5221, University of Montpellier - CNRS, Montpellier, France,
E-mail address: 234210@student.pwr.edu.pl

Carbon is known for its biocompatibility and corresponding nanomaterials are expected to inherit this attractive property. A prime example is a family of luminescent carbon-based dots (CDs), for example, carbon nanodots (CNDs), which offer excellent and tuneable optical properties, long-term colloidal stability, and low-cost fabrication. Therefore, all CDs are in great interest of scientists and can be used in different application domains, including biology (e.g. bioimaging), medicine (e.g. drug delivery systems), photocatalysis and optoelectronics.^[1]

Human serum albumin (HSA) is a globular protein in blood plasma that plays key role in effective distribution of many substances (e.g. drugs) among different body entities.

Here CNDs were synthesized following the solvothermal method with folic acid molecules (FA) as precursors rich in nitrogen and oxygen reactive groups. Optical properties of highly-luminescent nitrogen-doped FA CNDs in aqueous suspensions were described using steady-state and time-resolved spectroscopic techniques. Subsequently, interactions between as-obtained CNDs and HSA were studied in order to control the protein bindings to common drugs, such as digitoxin and ibuprofen.^[2-3]

As the result, our FA CNDs shows intense and long-lived blue emission with high photoluminescence quantum yield (54.1%) and no excitation-dependent tendency. Upon titration with FA CNDs, efficient fluorescence quenching of HSA was observed, suggesting strong interactions which can be affected by proper drugs. FA CNDs thus may be applied as effective nanomaterials in the drug delivery system.^[2-3]

Figure 1. Fluorescence quenching of HSA in the presence of FA CNDs.

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The study of pH influence on ligand exchange reaction for different types of CdS and CdSe/CdS nanoparticles

Anna Lesiak^{1,2*}, Kinga Halicka², Mateusz Bański¹, Maciej Chrzanowski¹, Andrzej Żak³,
Joanna Cabaj², Grzegorz Zatryb¹, Artur Podhorodecki¹

¹Wrocław University of Science and Technology, Faculty of Fundamental Problems of Technology, Wybrzeże
Wyspiańskiego 27, 50-370 Wrocław, Poland

²Wrocław University of Science and Technology, Faculty of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370
Wrocław, Poland

³Wrocław University of Science and Technology, Faculty of Mechanics, Electron Microscopy Laboratory,
50-370 Wrocław, Poland

E-mail address: anna.lesiak@pwr.edu.pl

Semiconducting nanoparticles (NPs) find applications in many fields, with a recent focus on medicine and biology. Functionalization of the surface of NPs is necessary, and one of the most commonly employed techniques is ligand exchange (LE) [1]. Here, the study of pH influence on LE reaction for different types of cadmium-based NPs (quantum dots, nanorods, and nanoplates) is presented. Hydrophobic NPs were transferred to the nonorganic medium by functionalization with D-penicillamine (DPA). The LE procedure was conducted at four different pH levels (4, 7, 9, and 11), and obtained hydrophilic NPs were dispersed in phosphate buffer. Results show that the most effective procedure resulted from a reaction carried at pH = 4; however, NPs with higher photoluminescence intensity were obtained when pH = 11 was used. Comparable emission was achieved from samples at pH = 4 and pH = 9. The least effective transfer, resulting in unstable NPs, occurred when the procedure was conducted at pH = 7 [2].

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Clavanins – metal interactions: understanding the relationship between coordination chemistry, structure, thermodynamics and the antimicrobial activity

Adriana Miller, Magdalena Rowińska - Żyrek, Aleksandra Mikołajczyk,
Agnieszka Matera - Witkiewicz
University of Wrocław, Faculty of Chemistry, F. Joliot-Curie 14, 50-383 Wrocław
adriana.miller@chem.uni.wroc.pl

The growing number of drug-resistant bacterial strains is becoming an increasingly serious problem of current medicine. Therefore, new antibiotics are being sought for more and more intensively.

Antimicrobial peptides (AMPs) are promising candidates to use as new therapeutics. These molecules are active against a broad spectrum of pathogens like fungi, gram-positive and gram-negative bacteria. Naturally, they are present in all multicellular organisms and act as a part of innate immune systems. Despite the fact of presence in those organisms for millions of years, pathogens show almost no resistance for AMPs. [1-3] So far, more than 3000 peptides have been deposited in the AMP databases, which makes them a huge source of potential new antibiotics. [4] Moreover, it has been noticed, that some metal ions, like Zn(II) or Cu(II) can boost peptides' antimicrobial activity. [3]

In this work, we aim to find the relationship between metal coordination ability, structure, mode of action and biological activity of several metal-AMP complexes, focusing on the group of peptides, called clavanins.

Clavanins are histidine-rich cationic peptides, which occur in tunicates (*Styela clava*). There are five types of those peptides, signed as a clavanin A, B, C, D, and E. They consist of 23 amino acids, with four (or in clavanin E - three) histidine residues and show an alpha-helical structure. They are active against both gram-positive and gram-negative bacteria. Their antimicrobial activity relies not only on causing intracellular damage but also on the cell membrane disruption. Interestingly, it has been shown that zinc(II) ions increase bactericidal properties of clavanin A up to 16 times. [5-7]

In this poster, we will show the results of research of clavanin-Zn(II) and clavanin-Cu(II) complexes, which provide information about their stoichiometry, geometry and thermodynamic properties. Results from the membrane disrupting and biological activity experiments will also be presented.

Acknowledgements: Financial support by the National Science Centre (UMO-2017/26/A/ST5/00364) is gratefully acknowledged.

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Lyotropic liquid crystals of biological importance: myelin and DNA

Justyna F. Rojek, Dominika Benkowska-Biernacka, Katarzyna Matczyszyn
Wroclaw University of Science and Technology, Faculty of Chemistry, Advanced Materials Engineering and Modelling Group
Contact: Justyna Rojek, 240436@student.pwr.edu.pl

Liquid crystals (LCs) are structures exhibiting a high degree of order combined with fluidity of liquids. If phase transitions are induced by changes in concentration and temperature, such LCs are called lyotropic. Myelin, a crucial component of the nervous system, and DNA are both lyotropic LCs omnipresent in living organisms. This topic attracts scientific attention, with many conducting research in their formation methods and conditions influencing properties. These studies are a fine base for following studies applicable in medical and optical fields.

To prepare artificial myelin structures a commercially available DLPC was used (Fig. 1a), while liquid-crystalline DNA was prepared from salmon DNA (Fig. 1b). Using a polarized light microscope, methods of formation and phase transition processes were observed. As regards myelin, experiments employing two methods of formation were conducted [1], indicating differences in both size and stability of figures. DNA structures were formed at the edges of the drying droplet and in a closed-cell system, resulting in distinctive figures of different sizes [2].

Figure 1. (a) Myelin structure formed in the contact experiment. (b) DNA structures formed in a closed cell. Photographed with a polarized light microscope.

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Nucleobindin-2 is a Ca^{2+} ions sensor

Anna Skorupska¹, Michał Padjasek², Artur Krężel², Andrzej Ożyhar¹, Dominika Bystranowska¹

¹ Department of Biochemistry, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

² Laboratory of Chemical Biology, University of Wrocław, plac Uniwersytecki 1, 50-137 Wrocław, Poland.
E-mail address: anna.skorupska@pwr.edu.pl, dominika.bystranowska@pwr.edu.pl

Nucleobindin-2 (Nucb2) is a multidomain protein. The tertiary structure of Nucb2 consists of six putative domains i.e. Leu/Ile-rich region, DNA-binding domain, two EF-hand domains (responsible for Ca^{2+} -binding), acidic amino acid rich region and leucine zipper motif [1]. Nucb2 is highly expressed in central nervous system and peripheral tissues: adipose tissue, reproductive system, stomach, heart and pancreas [2,3]. The broad expression pattern of human Nucb2 suggests that this protein might be involved in many biological processes. Nucb2 is implicated in food intake inhibition, carcinogenesis and Ca^{2+} - dependent interactions [4,5] Nucb2 from *Gallus gallus* (ggNucb2), the object of this study, was found to be expressed in eggshell [6]. This suggests that ggNucb2 is linked to the biomineralization process.

Here we demonstrate a four-step protein purification workflow which results in pure ggNucb2 protein free of any affinity purification tags to check the effect of protein interaction with its potential ligand, Ca^{2+} . The procedure consists of the following major steps: immobilized ion metal affinity chromatography (IMAC), removal of His-Tag by HRV3C protease (Sino Biological Inc.), second IMAC and gel filtration. Subsequently, circular dichroism (CD), limited proteolysis and isothermal titration calorimetry (ITC) were utilized to study ggNucb2 interaction with Ca^{2+} ions. We demonstrate that in the presence of Ca^{2+} α -helix content increases. ggNucb2 in the presence of Ca^{2+} is also more resistant to proteolysis than in the presence of EDTA. ITC experiments showed that Nucb2 molecule binds two Ca^{2+} ions and that this process is exothermic. We conclude that the conformational changes affecting protein secondary and tertiary structure suggest that Nucb2s might function as a Ca^{2+} sensor involved, in signal transduction process.

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Enantioselective hydrolysis of 1-(*R,S*)-phenylethanol acetate with *Synechococcus bigranulatus* and *Nostoc cf. muscorum* cyanobacterial strains

Agnieszka Śliżewska, Ewa Żymańczyk-Duda

Department of Biochemistry, Molecular Biology and Biotechnology, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
E-mail address: agnieszka.slizewska@pwr.edu.pl, ewa.zymanczyk-duda@pwr.edu.pl

Biotransformation reactions using cyanobacteria strains, leading to chiral products, may be a promising alternative to chemical synthesis, taking into account economic and environmental considerations. The chiral product obtained in biotransformation reactions can be a valuable building block used in the syntheses of compounds useful in the chemical or pharmaceutical industry and as a model for analysis.

The research was carried out to test the enzymatic apparatus of the *Nostoc cf. muscorum* (CCALA 129) and *Synechococcus bigranulatus* (CCALA 187) cyanobacterial strains using 1-(*R,S*)-phenylethanol acetate as a substrate. It has been shown that the conducted reactions are enantioselective and lead to alcohols and esters with high enantiomeric excess. The biotransformation process was carried out by adding to the 21-day culture of the substrate with various concentrations: 1mM, 2mM, 4mM, 6mM, 8mM, 10mM, 50mM and a time range from 3 hours to 24 hours depending on the strain used. The samples obtained after completion of the biotransformation were analysed by gas chromatography (GC) using a chiral packed column. The scope of the research includes the optimization of the cultivation conditions, selection of substrates to check the biocatalytic properties of cyanobacteria and finally optimization of the biotransformation processes, which will result in an increase in the scale of the process.

On the choice of proper average lifetime formula in the case of non-single exponential photoluminescence decay

M. M. Klak, G. Zatoryb

Department of Experimental Physics, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, 50-370 Wrocław, Poland
micchal.klak@pwr.edu.pl, grzegorz.zatoryb@pwr.edu.pl

In this work, we discuss photoluminescence decays showing non-single exponential behavior in various disordered emitter systems. For such ensembles, there are two formulas describing the average lifetime of emitter's excited state which are commonly used in context of the analysis of experimental data. In many cases, the choice of this formulas has no physical justification. For this reason, the goal of our work was to show that the choice of such mathematical formula describing the average lifetime should depend on the physical properties of discussed system and the interpretation of measured photoluminescence decay curve. It is shown that, after appropriate normalization, photoluminescence decay curve can be interpreted as survival probability function or a probability density function of lifetime and as a result, it is needed to use two different mathematical formulas for calculating the average lifetime. Based on some examples of published experimental data, we analyze different scenarios and discuss which formula allows for correct calculation of the average lifetime of system's excited state. Moreover, it is also shown that values of average lifetime can be underestimated in many cases, depending on the photoluminescence quantum yield due to fact, that some part of information on probability density function of lifetime is lost in the measurement process.

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